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# Ancillary Ligand Effects on Carbon Dioxide-Ethylene Coupling at Zerovalent Molybdenum

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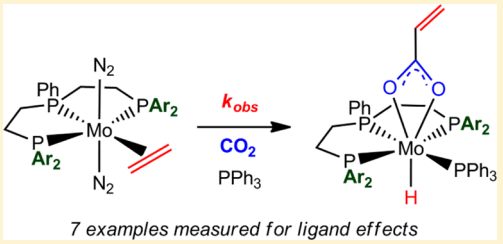
Supporting Information

**ABSTRACT:** A series of zerovalent molybdenum complexes bearing triphosphine ligands, $[Ar_2PCH_2CH_2]_2PPh$, have been synthesized and evaluated for reductive functionalization of $CO_2$ with ethylene. The ability to form dimeric triphosphine molybdenum(II) acrylate hydride species from $CO_2$-ethylene coupling was found to be highly sensitive to steric encumbrance on the phosphine aryl substituents. Trapping of triphosphine molybdenum(II) acrylate hydride species using triphenylphosphine afforded isolable monomeric $CO_2$ functionalization products with all ancillary ligands studied. Kinetic analysis of the acrylate formation reaction revealed a first-order dependence on molybdenum, but no influence from $CO_2$ pressure or the triphenylphosphine trap. Systematic attenuation of steric and electronic features of the triphosphine ligands showed a strong $CO_2$ functionalization rate influence for ligand size with $[(3,5\text{-}^t\text{Bu-}C_6H_3)_2PCH_2CH_2]_2PPh$ coupling nearly four times slower than with $[(3,5\text{-Me-}C_6H_3)_2PCH_2CH_2]_2PPh$. A considerably milder electronic effect was observed with complexes bearing $[(4\text{-F-}C_6H_4)_2PCH_2CH_2]_2PPh$ reducing $CO_2$ at approximately half the rate as with $[Ph_2PCH_2CH_2]_2PPh$.



7 examples measured for ligand effects

## INTRODUCTION

Expanding evidence for the deleterious effects of anthropogenic carbon dioxide production has brought $CO_2$ capture, utilization, and storage (CCUS) efforts to the forefront of chemical and engineering research. The challenge of mitigating greenhouse gas emissions while satisfying society's energy demand is immense and will most certainly require technological advances across many scientific fields. One area in which homogeneous transition-metal-mediated processes are poised to contribute is the utilization of carbon dioxide for commodity chemical production.[1] Although the chemical fixation of $CO_2$ to value added chemicals alone *will not* meaningfully impact carbon emissions, it is one of the few CCUS endeavors that offer to both create an intrinsic economic gain and safely sequester $CO_2$ for an extensive lifetime.[2] Chemical $CO_2$ utilization thus presents an attractive complement to larger scale carbon capture activities where high costs, safety, and storage permanence remain evolving challenges.[3]

Current utilization of $CO_2$ as a feedstock for commodity chemicals remains quite limited. Carbonates, salicylic acid, urea, and (to a limited extent) methanol are the only direct $CO_2$ fixation products now manufactured on significant industrial scale, leaving $CO_2$ as one of the world's largest unharnessed carbon resources.[4] The production of acrylates from the coupling of $CO_2$ with ethylene is a potential utilization process that could substantially expand the role of carbon dioxide as a renewable synthon. Acrylates, which are currently manufactured from propylene oxidation, are utilized on a more than 4 million ton annual scale for a variety of applications including fabrics and superabsorbent polymers.[5] The conversion of carbon dioxide and ethylene to acrylate at transition metals has garnered the attention of numerous researchers[6] since the first reported example from Carmona and co-workers.[7] More recently, our laboratory has followed this seminal work with the discovery of a $CO_2$-ethylene coupling reaction mediated by *trans*-$(Triphos)Mo(N_2)_2(C_2H_4)$ (**1-$C_2H_4$**) (Triphos = $(Ph_2PCH_2CH_2)_2PPh$) (Figure 1).[8] NMR and IR spectroscopic studies of the $CO_2$-ethylene coupling reaction indicate that **1-$C_2H_4$** generates acrylate through an intermediate species in which carbon dioxide and ethylene are co-localized on the metal (**1-INT**). Additional kinetic and isotopic labeling analysis of the conversion of **1-INT** to the dimeric molybdenum(II) acrylate hydride species (**1-dimer**) suggests that the reaction proceeds with a rate-limiting oxidative coupling to form a C−C bond, followed by a relatively swift $\beta$-hydride elimination (Figure 1).

Isolation of an acrylate product from molybdenum-mediated $CO_2$-ethylene coupling augurs well for its ability to utilize $CO_2$; however, the poor lability of the metal-acrylate interaction and the sluggish pace of the coupling reaction (half-life of ~8 h) will require advancements in order to make significant contributions to chemical synthesis. Given the implication that metalalactone formation from **1-INT** limits the rate of acrylate formation, the most obvious target is to attenuate the ligands to optimize this reaction. Unfortunately, the structural or electronic environments that may facilitate the oxidative coupling reaction were not self-evident. While this trans-

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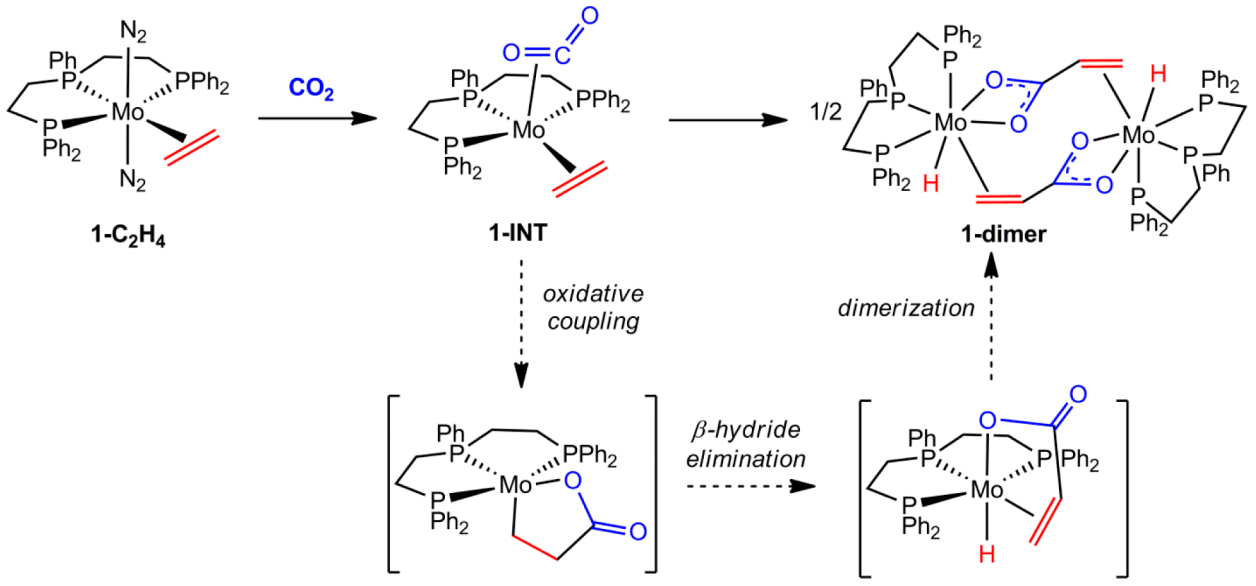


**Figure 1.** Probable pathway for acrylate formation from **1-$C_2H_4$**.

formation is formally oxidative, the effective metal valence of **1-INT** and the metalalactone are probably quite similar due to Dewar–Chatt–Duncanson resonance forms.[9] Likewise, the role of steric constraint in an intramolecular bond formation such as this was not entirely obvious. These questions, as well as the desire to accelerate acrylate formation, have motivated a systematic investigation of the influence of ancillary ligand substituents on the rate of $CO_2$-ethylene coupling.

## RESULTS AND DISCUSSION

Examination into the role of the ancillary Triphos ligand on $CO_2$ functionalization began with preparation of a family of related tridenate ligands described in Figure 2. For synthetic

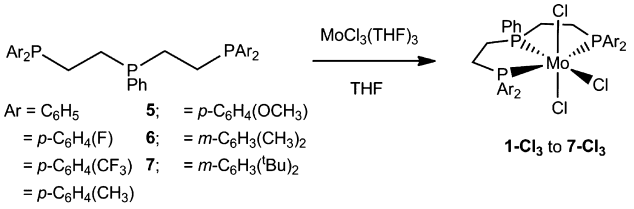


**Figure 2.** Synthesis of $[(Ar_2PCH_2CH_2)_2PPh]MoCl_3$ complexes.

convenience the aryl substituents on the terminal phosphines were selected for attenuation, and the ligands were prepared via radical or base-catalyzed coupling of divinylphenylphosphine and the corresponding diarylphosphine.[10] Coordination of the tridentate ligands was accomplished by treatment with $MoCl_3(THF)_3$ to afford the $[(Ar_2PCH_2CH_2)_2PPh]MoCl_3$ (**2-** to **7-$Cl_3$**) complexes in good yields, analogous to the procedure previously employed for (Triphos)$MoCl_3$ (**1-$Cl_3$**).[11] These paramagnetic species were characterized by combustion analysis, $^1$H NMR spectroscopy, and cyclic voltammetry. In some cases it was possible to discern the presence of both *mer* and *fac* isomers by NMR spectroscopy. This geometric flexibility has been observed in previous studies with (Triphos)$MoCl_3$ complexes.[12] Electrochemical analyses of **2-** to **7-$Cl_3$** indicated strong similarities to those reported by George and co-workers for **1-$Cl_3$**.[13] A key feature conserved throughout **1-** to **7-$Cl_3$** is a partially reversible feature at ca. −1.5 V relative to ferrocene, which has previously been assigned as the reduction of molybdenum(III) trichoride to the molybdenum(II) trichoride anion.[13] The potential of this reduction was used to establish a spectrum for relative metal electrophilicity engendered by each ligand (Table 1). As

**Table 1. $Mo^{III}/Mo^{II}$ Reduction Potentials of $[(Ar_2PCH_2CH_2)_2PPh]MoCl_3$**

| complex | $E^\circ$ (V)[a] |
|---|---|
| **1-$Cl_3$** | −1.49 |
| **2-$Cl_3$** | −1.42 |
| **3-$Cl_3$** | −1.30 |
| **4-$Cl_3$** | −1.51 |
| **5-$Cl_3$** | −1.53 |
| **6-$Cl_3$** | −1.56 |
| **7-$Cl_3$** | −1.55 |

[a]Cyclic voltammetry recorded at ambient temperature using 2 mM compound THF solution with 0.2 M $^n$Bu$_4$NPF$_6$ under $N_2$ atmosphere at 20 mV/s. All potentials are referenced to ferrocene/ferrocenium.

expected, compounds **6-$Cl_3$** and **7-$Cl_3$** bearing 3,5-dialkylaryl substituents were found to be most electron-donating, while fluoro- and trifluoromethyl-substituted **2-$Cl_3$** and **3-$Cl_3$** displayed the greatest electrophilicity.

Following the synthesis of an array of molybdenum(III) trichoride compounds, the preparation of corresponding molybdenum(0) species suitable for $CO_2$-ethylene coupling was targeted. For comparison to our previous studies of acrylate formation, the *trans*-$[(Ar_2PCH_2CH_2)_2PPh]Mo(C_2H_4)(N_2)_2$ (**2-$C_2H_4$**–**7-$C_2H_4$**) complexes were selected and prepared either by sodium amalgam or sodium triethylborohydride reduction of the molybdenum trichloride species (Figure 3).[8] Complexes **2-$C_2H_4$**–**7-$C_2H_4$** were typically isolated in moderate yields as yellow powders from chilled diethyl ether solutions layered with pentane. Application of this isolation method to the previously reported **1-$C_2H_4$** occasionally afforded small crystalline samples, which permitted confirmation of its structure by X-ray diffraction (Figure 4).[8a] The solid state structure of **1-$C_2H_4$** exhibits an idealized $C_s$ symmetry with *trans* positioned dinitrogen ligands and ethylene carbons (C(1)


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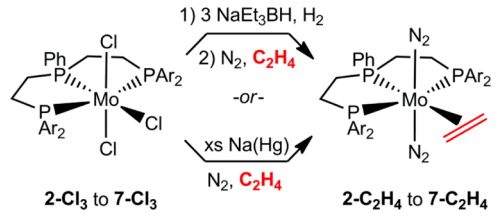


**Figure 3.** Synthetic routes to the *trans*-$[(Ar_2PCH_2CH_2)_2PPh]Mo(C_2H_4)(N_2)_2$ species.

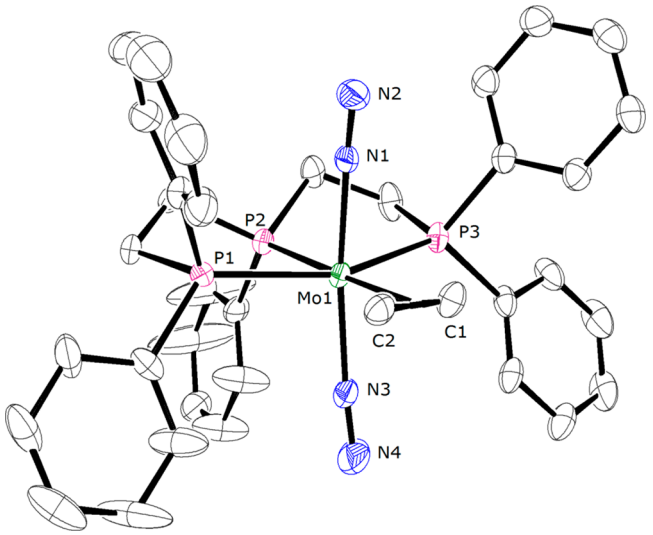


**Figure 4.** Molecular structure of **1-$C_2H_4$** with ellipsoids at 30% probability. All hydrogen atoms and a co-crystallized toluene molecule are omitted for clarity.

and C(2)) lying nearly coplanar with the Triphos phosphorus atoms (P(1)−P(3)). The metrical parameters exhibit modest elongation of the bound ethylene C(1)−C(2) bond length, 1.41(1) Å, along with minimal activation of the dinitrogen N−N bond lengths (1.09(1) and 1.11(1) Å). Such bond distances are quite similar to those observed for related ethylene and *trans*-bis(dinitrogen) molybdenum(0) complexes that have been structurally characterized.[14,15] The NMR and IR spectra for **2-$C_2H_4$**−**7-$C_2H_4$** were also comparable to those observed for **1-$C_2H_4$**.[8a] Each species exhibited a doublet and triplet resonance in the $^{31}P$ NMR spectrum at ca. 75 and 95 ppm, respectively, with resonances for the bound ethylene observed between 1.42 and 2.42 ppm in the $^{1}H$ NMR spectra. The most notable features in the solid-state infrared spectra were two strong bands with an approximate 2:1 intensity assigned to the N≡N stretching frequencies. The frequency of these bands (Supplementary Table S1) offer further assessment of the electronic character engendered by the chelating ligands and are generally consistent with the trend observed from the cyclic voltammetry of the molybdenum(III) trichloride species.

With a collection of *trans*-$[(Ar_2PCH_2CH_2)_2PPh]Mo(C_2H_4)(N_2)_2$ complexes in hand, measurement of the relative rates of $CO_2$-ethylene coupling to acrylate became the focus of investigation. Initial experiments to measure these rates employed a technique our laboratory has previously used successfully in studies with **1-$C_2H_4$**. This involved treatment of benzene-$d_6$ solutions of **2-$C_2H_4$**−**7-$C_2H_4$** with 4 atm of carbon dioxide to rapidly generate a molybdenum(0) ethylene carbon dioxide intermediate (**2-INT**−**7-INT**) and then monitoring the relatively slow conversion of the intermediate species into a dimeric molybdenum(II) acrylate hydride complex. Interestingly, though addition of $CO_2$ to **2-$C_2H_4$**−**7-$C_2H_4$** did produce facile formation of **2-INT**−**7-INT**, only the *p*-fluorophenyl-substituted species converted to an observable molybdenum acrylate hydride complex (**2-dimer**) (Figure 5). The other molybdenum(0) ethylene carbon dioxide intermediates, **3-INT**−**7-INT**, proved stable under carbon dioxide for greater than 2 days at ambient temperature and slowly degraded upon heating at 45 °C without any acrylate formation detectable by NMR spectroscopy.

Noting that the two systems with the smallest ancillary ligand substituents (**1-INT** and **2-INT**) successfully formed isolable acrylate hydride species, it was hypothesized that steric repulsions may destabilize or kinetically block access to the dimeric molybdenum complex for the larger ligands. In order to circumvent this barrier, complexes **2-INT**−**7-INT** were generated in the presence an exogenous trapping agent, triphenylphosphine, which has been employed to stabilize

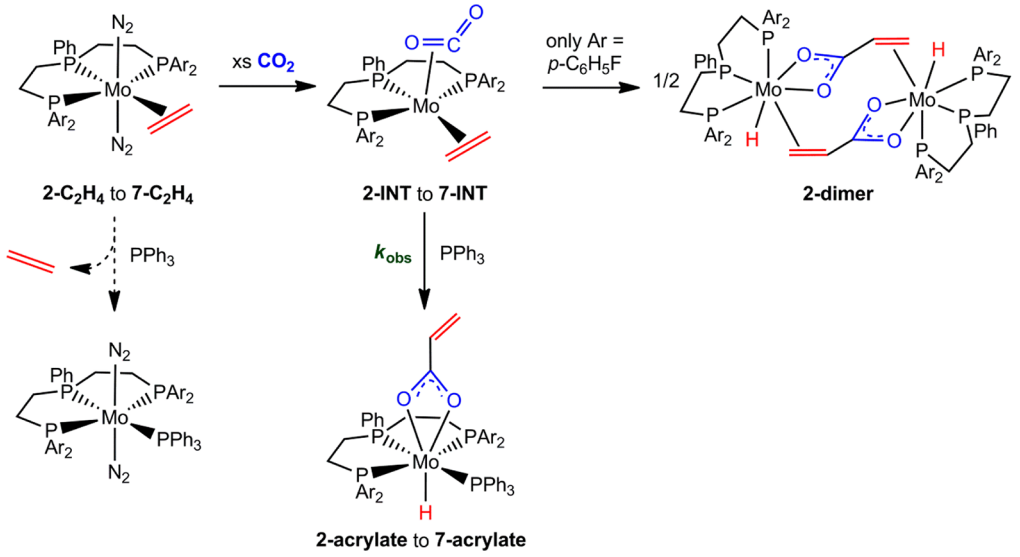


**Figure 5.** $CO_2$-ethylene coupling reactions for the *trans*-$[(Ar_2PCH_2CH_2)_2PPh]Mo(C_2H_4)(N_2)_2$ complexes.


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other monomeric Triphos molybdenum carboxylate hydride species.[8] Gratifyingly, the addition of $PPh_3$ afforded isolable $[(Ar_2PCH_2CH_2)_2PPh]Mo(H)PPh_3(CO_2CH{=}CH_2)$ (**2-acrylate−7-acrylate**) for all the Triphos variants studied. Complexes **2-acrylate−7-acrylate** were characterized by a combination of combustion analysis and NMR and IR spectroscopy, as well as by comparison to the previous characterized **1-acrylate** congener. These species were typically isolated as red-orange powders, exhibiting modest solubility in arene or ethereal solvents. The $^1$H NMR spectra of each complex displayed three diagnostic resonances between 4.5 and 5.5 ppm for the acrylic olefin protons and a 12-line resonance at ca. −5 ppm originating from the metal-hydride. The corresponding $^{31}$P NMR spectra exhibited three resonances, a doublet of doublets at ca. 110 ppm, and two doublet of triplets at ca. 100 and 50 ppm.

The ability to prepare molybdenum(II) acrylate hydride triphenylphosphine compounds with all ligands **1−7** made this species the preferred target for assessing the ancillary ligand influence on $CO_2$-ethylene coupling. Kinetic analysis of the conversion of each molybdenum(0) ethylene carbon dioxide intermediate (**1-INT−7-INT**) to the corresponding molybdenum(II) acrylate hydride triphenylphosphine species (**1-acrylate−7-acrylate**) was performed using $^{31}$P NMR spectroscopy. In a typical experiment, 1 equiv of $PPh_3$ was added to a frozen benzene-$d_6$ solution of **2-$C_2H_4$**, followed addition of 4 atm of carbon dioxide. Upon thawing, the sample quick conversion of **2-$C_2H_4$** to **2-INT** (<30 min) was observed. Following complete consumption of **2-$C_2H_4$**, the conversion of **2-INT** to **2-acrylate** was monitored over 2−3 half-lives to obtain a rate constant for $CO_2$-ethylene coupling (Figure 5). Control experiments using **1-$C_2H_4$**, **6-$C_2H_4$**, and **7-$C_2H_4$** showed no observed rate constant influence for varied additions of $PPh_3$ (1−10 equiv) or carbon dioxide (1−4 atm). For experiments using electron-withdrawing ligand variants (e.g., **2-$C_2H_4$** and **3-$C_2H_4$**), it was critical to keep the reaction mixture frozen until the excess carbon dioxide was added to avoid competing formation of an alternate species tentatively identified as *trans*-$[(Ar_2PCH_2CH_2)_2PPh]Mo(N_2)_2PPh_3$, the product of ethylene substitution with $PPh_3$ (Figure 5). This side reaction is likely more prevalent for electron-poor species due to a weaker metal-ethylene $\pi$-bonding interaction.[16] Repeating these kinetic measurements at least three times for each analogue afforded the set of rate constants listed in Table 2.

Surprisingly, the data do not indicate a strong correlation between the rate of coupling and the reduction potential of the metal center. While the range of observed rate constants spans only a factor of 5, the steric impetus of the ancillary ligand does attenuate the reaction with the smallest complex (**1-$C_2H_4$**) achieving the fastest rate and the largest (**7-$C_2H_4$**) the slowest rate. Perhaps a better separation of the steric and electronic influences comes from pairwise comparison of **6-$C_2H_4$** and **7-$C_2H_4$**. These two 3,5-dialkyl aryl-substituted Triphos complexes exhibit reduction potentials within a scant 9 mV of each other, but the $^t$Bu-substituted congener couples $CO_2$ and ethylene roughly four times more slowly than the Me analogue. The precise origin of this steric influence remains speculative since no dependence on incoming $PPh_3$ ligand was observed. It is possible that the crowded environment slows bond rotations about the $CO_2$ and ethylene that may be required to achieve lactone formation, or that larger substituents influence the flexibility of the Triphos ligand backbone. However, the data in hand relegate these possible sources to hypotheses.

Most likely an electronic preference exists for the acrylate formation reaction, but this influence is largely obscured by steric or other factors. One comparison that provides some limited insight in this area is the relative rate of phenyl- and *p*-fluorophenyl-substituted **1-$C_2H_4$** and **2-$C_2H_4$**. Since these two species were the only studied variants capable of forming the sterically hindered dimeric molybdenum acrylate hydride complexes, their steric impetus is likely minimized. Notably, reduction potential of the faster **1-$C_2H_4$** is 66 mV more negative than **2-$C_2H_4$**, suggesting a mild preference for electron-donating groups in the $CO_2$-ethylene coupling reaction. Together, this study of ancillary ligand effects suggests optimized rates for coupling $CO_2$ and ethylene to acrylate may be obtained using related ligand platforms bearing smaller and, to a lesser degree, more electron-donating substituents. Our laboratory is currently investigating ligands of this type, as well as methods to induce reductive acrylate extrusion to enable catalytic turnover of the $CO_2$ functionalization process.

**Table 2. Observed Rate Constants for Acrylate Formation from $[(Ar_2PCH_2CH_2)_2PPh\ Mo](C_2H_4)(CO_2)$[a]**

| complex | $k_{obs} \times 10^5$ ($s^{-1}$) |
|---|---|
| **1-$C_2H_4$** | 5.2(1) |
| **2-$C_2H_4$** | 3.2(1) |
| **3-$C_2H_4$** | 4.05(4) |
| **4-$C_2H_4$** | 3.26(4) |
| **5-$C_2H_4$** | 2.3(1) |
| **6-$C_2H_4$** | 4.15(8) |
| **7-$C_2H_4$** | 0.8(1) |

[a]Rate constants measured by NMR spectroscopy at 24 °C in benzene.

## CONCLUDING REMARKS

The rare ability of molybdenum(0) to couple $CO_2$ and ethylene into acrylate appears to be general across a wide range of tridentate phosphine ligands of the class $(Ar_2PCH_2CH_2)_2PPh$. Surprisingly, the formation of dimeric molybdenum(II) acrylate hydride species can be disfavored by even modest changes in the steric impetus of the phosphine aryl substituents. However, the use of triphenylphosphine as an intermolecular trap serves to access monomeric acrylate hydride complexes in each case. Kinetic examination of the acrylate formation reaction indicates that neither the pressure of $CO_2$ nor the concentration of $PPh_3$ plays a direct role in the rate of reaction, suggesting that the C−C bond formation between $CO_2$ and ethylene is likely still the rate-limiting step in the presence of added phosphine. Alteration of aryl substituents on the tridentate phosphine shows a strong steric influence on the rate of acrylate formation despite observation that $CO_2$ and ethylene are already bound at the metal. This, along with the absence of $[PPh_3]$ dependence, hints that flexibility of the chelate ligand or rotation of the unsaturates at the metal may be important factors in C−C bond formation. The influence of ligand electron donation on the rate of coupling is more difficult to detect, but comparisons of the phenyl- and *p*-fluorophenyl-substituted species indicates a mild enhancement for more electron-rich metals. These observations suggest the examination of smaller, more election-donating ligands on zerovalent molybdenum could substantially accelerate the rate of $CO_2$ reduction, and that issues such as the freedom of motion for any chelating forms of these ligands ought to be closely examined.


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## EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out using standard vacuum, Schlenk, cannula, or glovebox techniques. Under standard glove conditions, purging was not performed between uses of pentane, diethyl ether, benzene, toluene, and THF; thus, traces of all of these solvents were in the atmosphere and could be found intermixed in the solvent bottles while reactions were conducted. Ethylene and carbon dioxide were purchased from Corp Brothers and stored over 4 Å molecular sieves in heavy-walled glass vessels prior to use. $MoCl_3(THF)_3$ was obtained as previously described.[17] $[(4\text{-}F\text{-}C_6H_4)_2PCH_2CH_2]_2PPh$ (**2**), $[(4\text{-}CH_3C_6H_4)_2PCH_2CH_2]_2PPh$ (**4**), $[(4\text{-}OMe\text{-}C_6H_4)_2PCH_2CH_2]_2PPh$ (**5**), $[(3,5\text{-}Me\text{-}C_6H_3)_2PCH_2CH_2]_2PPh$ (**6**), $(3,5\text{-}^t\text{Bu-}C_6H_3)_2PH$, and $(4\text{-}CF_3C_6H_5)_2PH$ were also prepared according to literature procedures.[18] All other chemicals were purchased from Aldrich, Fisher, VWR, Strem, or Cambridge Isotope Laboratories. Tetrabutylammonium hexafluorophosphate ($^n Bu_4NPF_6$, electrochemical grade) was dried at 60 °C under vacuum for 24 h and stored in the glovebox. Solvents were dried and deoxygenated using literature procedures.[19] $^1H$, $^{13}C$, $^{19}F$, and $^{31}P$ NMR spectra were recorded on Bruker DRX 400 MHz and Avance 300 and 600 MHz spectrometers. $^1H$ and $^{13}C$ chemical shifts are referenced to residual solvent signals; $^{19}F$ and $^{31}P$ chemical shifts are referenced to the external standards $C_6H_5CF_3$ and $H_3PO_4$, respectively. Probe temperatures were calibrated using ethylene glycol and methanol as previously described.[20] IR spectra were recorded on Jasco 4100 FTIR and Mettler Toledo React IR spectrometers. Cyclic voltammetry was performed on a Pine Research AFCBP1 bipotentiostat. The three-electrode system consisted of a platinum disk working electrode (BASi, 1.6 mm diameter), a platinum wire counter electrode, and a $Ag/AgNO_3$ reference electrode (BASi). The reference was filled with 0.01 M $AgNO_3$ and 0.2 M $^n Bu_4NPF_6$ in THF, +0.09 V vs the ferrocene/ferrocenium couple. Prior to each cyclic voltammetry experiment, the platinum disc was successively polished with 1-, 0.3-, and 0.05-$\mu$m alumina slurry to obtain a mirror surface and then sonicated in and rinsed with Milli-Q water and acetone. Ferrocene was added at the end of experiments, and the potential was converted from $Ag/Ag^+$. X-ray crystallographic data were collected on a Bruker D8 QUEST diffractometer. Samples were collected in inert oil and quickly transferred to a cold gas stream. The structures were solved from direct methods and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Crystallographic calculations were carried out using SHELXTL. Irradiated reactions were performed in a Rayonet Photochemical Reactor using an array of 350 nm wavelength bulbs or a Biotage Microwave Initiator apparatus. Elemental analyses for select compounds in each series were performed at Atlantic Microlab, Inc., in Norcross, GA or Robertson Microlit Laboratory in Ledgewood, NJ. Several of the $[(Ar_2PCH_2CH_2)_2PPh]Mo(C_2H_4)(N_2)_2$ complexes repeatedly afford elemental analyses that were well matched for carbon and hydrogen, but drastically low in nitrogen. This suggests a loss of $N_2$ ligand during shipping. Those $[(Ar_2PCH_2CH_2)_2PPh]Mo(H)\text{-}PPh_3(CO_2CH{=}CH_2)$ complexes prepared via Method A were not subjected to elemental analysis. Evidence for the purity of these complexes has been provided by NMR spectroscopy, which is detailed in the Supporting Information.

**Preparation of $[(4\text{-}CF_3C_6H_5)_2PCH_2CH_2]_2PPh$ (3).** A microwave vial was charged with 1.50 g (4.66 mmol) of $(4\text{-}CF_3C_6H_5)_2PH$, 0.27 g (1.66 mmol) of divinylphenylphosphine, and 0.032 g (0.19 mmol) of azobis(isobutyronitrile) in approximately 1 mL of benzene. The reaction mixture was placed in a microwave reactor and irradiated at 88 °C for 24 h. The resulting oil was purified by silica gel chromatography with 95:5 hexane to ethyl acetate eluent to give 1.08 g of **3** (81%) as a white solid. $^1H$ NMR (23 °C, $CDCl_3$): $\delta$ 1.71 (m, 4H, $PCH_2$), 1.88−1.98 (m, 2H, $PCH_2$), 2.05−2.13 (m, 2H, $PCH_2$), 7.34 (m, 11H, aryl), 7.52 (m, 10H, aryl). $^{13}C$ $\{^1H\}$ NMR (23 °C, $CDCl_3$): 23.46 ($PCH_2$), 23.77 ($PCH_2$), 123.44, 123.50, 128.92, 130.07, 131.04, 131.37, 132.86, 133.23 (aryl), 142.32 ($CF_3$). $^{31}P$ $\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ −17.6 (t, 30.8 Hz, 1P, PPh), −12.8 (d, 30.8 Hz, 2P, $PAr_2$). $^{19}F$ NMR (23 °C, $C_6D_6$): $\delta$ −62.60 (s). (ESI) $m/z$ calcd for $C_{38}H_{29}F_{12}P_3$ $[M + H]^+$: 807.132, found 807.136.

**Preparation of $[(3,5\text{-}^t\text{Bu-}C_6H_3)_2PCH_2CH_2]_2PPh$ (7).** A high pressure Schlenk vessel was charged with 0.300 g (0.73 mmol) of $(3,5\text{-}^t\text{Bu-}C_6H_3)_2PH$, 0.053 g (0.33 mmol) of divinylphenylphosphine, 0.014 g (0.15 mmol) of $NaO^tBu$, and approximately 5 mL of THF. The reaction was heated at 60 °C for 4 h, after which the volatiles were removed in vacuo, and the resulting oil was purified by silica gel chromatography with 90:10 hexane to ethyl acetate elutent to give 0.200 g of **7** (57%) as colorless oil. $^1H$ NMR (23 °C, $C_6D_6$): $\delta$ 1.23 (d, 3 Hz, 72H, $C(CH_3)_3$), 1.97 (m, 4H, $PCH_2$) 2.25−2.39 (m, 4H, $PCH_2$), 7.02−7.06 (m 3H, aryl) 7.32−7.35 (m, 2H, aryl), 7.47−7.49 (m, 4H, aryl), 7.47−7.59 (m, 8H, aryl). $^{13}C$ $\{^1H\}$ NMR (23 °C, C6D$_6$): $\delta$ 23.91, ($PCH_2$) 24.12, ($PCH_2$) 30.91, ($ArC(CH_3)_3$) 34.63, ($ArC(CH_3)_3$) 120.92, 126.02, 128.39, 128.79, 132.66, 132.85, 138.75, 139.07. $^{31}P$ $\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ 16.16 (t, 30 Hz, 1P, PPh), 10.18 (d, 30 Hz, 2P, $PAr_2$).

**General Procedure for the Preparation of $[(Ar_2PCH_2CH_2)_2PPh]MoCl_3$ (2-Cl$_3$−7-Cl$_3$).** Complexes **2-Cl$_3$**−**7-Cl$_3$** were prepared in a manner analogous to that reported for **1-Cl$_3$**. In a typical synthesis 1 equiv each of $[(Ar)_2PCH_2CH_2]_2PPh$ and $MoCl_3(THF)_3$ were stirred in tetrahydrofuran for 16 h at ambient temperature, over which time the reaction mixture turned from orange to yellow-green. Pentane was added to the reaction mixture to precipitate the product from solution. The suspension was then filtered, washed with additional pentane, and dried to afford desired product as yellow powders.

**$\{[(4\text{-}F\text{-}C_6H_4)_2PCH_2CH_2]_2PPh\}MoCl_3$ (2-Cl$_3$).** Yield 83%. Anal. Calcd for $C_{34}H_{29}Cl_3F_4MoP_3$: C, 50.49; H, 3.61. Found: C, 50.78; H, 3.61. $^1H$ NMR (23 °C, $CD_2Cl_2$): two isomers $\delta$ 73.67 ($w_{1/2}$ = 762 Hz), −40.60 ($w_{1/2}$ = 706 Hz), −35.5 ($w_{1/2}$ = 1273 Hz), −23.9 ($w_{1/2}$ = 856 Hz), −16.9, −14.6, −13.0 7.4, 8.8, 9.9, 10.1, 10.8, 11.4, 14.4, 14.7, 15.3 ($w_{1/2}$ = 104 Hz), 17.2, 17.9, 20.3, 22.9, 23.8. $^{19}F\{^1H\}$ (23 °C, $CH_2Cl_2$): two isomers $\delta$ −111.22, −106.10, −105.37, −103.17.

**$\{[(4\text{-}CF_3\text{-}C_6H_5)_2PCH_2CH_2]_2PPh\}MoCl_3$ (3-Cl$_3$).** Yield 75%. Anal. Calcd for $C_{38}H_{29}F_{12}P_3MoCl_3$: C, 45.24; H, 2.90. Found: C, 44.90; H, 2.66. $^1H$ NMR (23 °C, $CD_2Cl_2$): two isomers $\delta$ −73.98 ($w_{1/2}$ = 137 Hz), −42.94 ($w_{1/2}$ = 81 Hz), −41.03, −35.23, −23.56, −14.51, −13.32 ($w_{1/2}$ = 483 Hz), 8.68, 10.12, 10.77, 12.06, 14.58, 15.38, 16.30, 17.63, 18.34 21.35 ($w_{1/2}$ = 1230 Hz), 22.57, 26.76. $^{19}F\{^1H\}$ NMR (23 °C, $CH_2Cl_2$): two isomers $\delta$ −65.48, −63.25, −61.53, −60.25.

**$\{[(4\text{-}CH_3\text{-}C_6H_5)_2PCH_2CH_2]_2PPh\}MoCl_3$ (4-Cl$_3$).** Yield 90%. Anal. Calcd for $C_{38}H_{41}P_3MoCl_3$: C, 57.12; H, 4.92. Found: C, 57.33; H, 5.20. $^1H$ NMR (23 °C, $CD_2Cl_2$): two isomers $\delta$ −75.59, −42.85, −41.70, −35.81, −23.83, −17.73, 0.20, 1.31, 1.83, 2.84, 3.18, 3.45, 4.74, 8.38, 9.61, 10.23, 11.42, 13.32, 14.69, 15.29, 15.99, 16.86, 19.59, 22.14, 23.95.

**$\{[(4\text{-}OCH_3\text{-}C_6H_4)_2PCH_2CH_2]_2PPh\}MoCl_3$ (5-Cl$_3$).** Yield 72%. Anal. Calcd for $C_{38}H_{41}Cl_3O_4MoP_3$: C, 53.26; H, 4.82. Found: C, 52.73; H, 5.43. $^1H$ NMR (23 °C, $C_6D_6$): two isomers $\delta$ −73.9, −39.5, −41.8, −22.6, −17.0, 3.71, 4.0, 4.2, 4.3, 9.3, 9.7, 10.3, 10.8, 15.4, 17.4, 22.5.

**$\{[(3,5\text{-}CH_3\text{-}C_6H_3)_2PCH_2CH_2]_2PPh\}MoCl_3$ (6-Cl$_3$).** Yield 87%. Anal. Calcd for $C_{42}H_{49}Cl_3MoP_3$: C, 59.41; H, 5.82. Found: C, 59.63; H, 5.98. $^1H$ NMR (23 °C, $C_6D_6$): two isomers $\delta$ −66.3, −41.8, −37.2, −19.6, −19.6, −12.1, 3.0, 3.2, 3.6, 3.9, 8.0−8.9, 9.9, 11.1, 17.4, 21.3, 23.4.

**$\{[(3,5\text{-}t\text{Bu-}C_6H_3)_2PCH_2CH_2]_2PPh\}MoCl_3$ (7-Cl$_3$).** Yield 89%. Anal. Calcd for $C_{66}H_{97}Cl_3MoP_3$: C, 66.85; H, 8.25. Found: C, 66.57; H, 7.99. $^1H$ NMR (23 °C, $C_6D_6$): two isomers $\delta$ −79.7, −43.3 ($w_{1/2}$ = 664.2), 1.3 ($w_{1/2}$ = 121.84), 1.8 ($w_{1/2}$ = 57.82), 7.2, 7.5, 8.1, 9.9 ($w_{1/2}$ = 45.32), 10.9 ($w_{1/2}$ = 81.11), 16.7 ($w_{1/2}$ = 1516), 22.7, 32.3 ($w_{1/2}$ = 1283).

**General Procedure for the Preparation of *trans*-$[(Ar_2PCH_2CH_2)_2PPh]Mo(C_2H_4)(N_2)_2$ (2-$C_2H_4$−7-$C_2H_4$).** Complexes **2-$C_2H_4$**−**7-$C_2H_4$** were prepared by procedures analogous to those previously reported for **1-$C_2H_4$** using either sodium amalgam (Method A) or sodium triethylborohydride (Method B) as a reducing agent. *Method A*: A heavy-walled glass reaction vessel was charged with $[\{(Ar)_2PCH_2CH_2\}PPh]MoCl_3$, 10 equiv of 0.5% sodium amalgam, and approximately 10 mL of tetrahydrofuran. On a vacuum line,


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approximately 0.5 atm of ethylene and 1 atm of dinitrogen were added at −196 °C. The resulting reaction mixture was stirred at ambient temperature for 16 h, the volatiles were removed in vacuo, and the residue was extracted through Celite with diethyl ether. The product solution was concentrated, layered with pentane, and chilled to −35 °C to afford the desired product as a yellow powder. *Method B*: A heavy-walled glass reaction vessel was charged with [{(Ar)$_2$PCH$_2$CH$_2$}PPh]MoCl$_3$, 3 equiv of NaEt$_3$BH solution (1 M in THF), and approximately 10 mL of tetrahydrofuran. The red-orange reaction mixture was then treated with of 1 atm of dihydrogen gas and stirred at ambient temperature for 14 h. The reaction mixture was then frozen at −196 °C. the excess dihydrogen removed in vacuo and replaced with approximately 0.5 atm of ethylene. The vessel was allowed to warm to ambient temperature and stirred a further 3 h. The volume of the reaction mixture was reduced by half, and the vessel was placed under an atmosphere of dinitrogen. After standing under dinitrogen for 1 h, the remaining solvent was removed, and the desired product obtained by the purification procedure described above.

***trans*-{[(4-F-C$_6$H$_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(N$_2$)$_2$ (2-C$_2$H$_4$).** Yield 66% (from Method A) or 64% (from Method B). $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 1.70 (m, 2H, PC*H*$_2$), 2.03 (m, 2H, PC*H*$_2$), 2.15 (br s, 4H, C$_2$*H*$_4$), 2.61 (m, 2H, PC*H*$_2$), 2.84−2.99 (m, 2H, PC*H*$_2$), 6.97−7.01 (m, 11H, aryl), 7.37 (m, 4H, aryl), 7.65 (m, 2H, aryl), 7.72 (m, 4H, aryl). $^{13}$C{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 25.83 (*C*$_2$H$_4$), 26.6 (PCH$_2$), 34.0 (PCH$_2$), 114.3, 114.5, 115.12, 115.4, 128.8, 129.6, 132.9, 133.2, 134.9, 138.3 (aryl) two aryl resonances not located. $^{31}$P{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 73.59 (d, 16.8 Hz, 2P, PAr$_2$), 96.85 (t, 16.8 Hz 1P, PPh,). $^{19}$F{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ −112.72 (s), −110.87 (s). IR (KBr) $\nu_{N\equiv N}$ = 1982, 2052 cm$^{-1}$ (approximately 1:2 relative intensity).

***trans*-{[(4-CF$_3$-C$_6$H$_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(N$_2$)$_2$ (3-C$_2$H$_4$).** Yield 62% (from Method A). $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 1.55 (m, 2H, PC*H*$_2$), 1.85 (m, 2H, PC*H*$_2$), 2.42 (br s, 4H, C$_2$*H*$_4$), 2.68 (m, 4H, PC*H*$_2$), 6.91 (m, 1H, aryl), 7.02 (m, 6H, aryl), 7.34 (m, 14H, aryl). $^{13}$C{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 30.11 (PCH$_2$), 33.97 (PCH$_2$), 39.35 (*C*$_2$H$_4$), 124.01, 125.19, 125.76, 125.88, 129.20, 130.65, 131.73, 133.67 (aryl), 142.19 (*C*F$_3$), 143.99 (*C*F$_3$). $^{31}$P{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 76.0 (d, 16.2 Hz, 2P, PAr$_2$), 98.6 (t, 16.2 Hz, 1P, PPh). $^{19}$F{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ −62.6 (s), −62.5 (s). IR (KBr): $\nu_{N\equiv N}$ = 2062, 1992 cm$^{-1}$ (approximately 1:2 relative intensity).

***trans*-{[(4-CH$_3$-C$_6$H$_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(N$_2$)$_2$ (4-C$_2$H$_4$).** Yield 82% (from Method A). Anal. Calcd for C$_{40}$H$_{45}$P$_3$MoN$_4$·C$_7$H$_8$: C, 65.42; H, 6.19; N, 6.49. Found: C, 64.53; H, 5.69; N, 6.21. $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 1.51 (br s, 4H, C$_2$*H*$_4$), 1.78 (m, 2H, PC*H*$_2$), 1.98 (s, 6H, C*H*$_3$), 2.01 (s, 6H, C*H*$_3$), 2.66 (m, 4H, PC*H*$_2$), 2.92−3.07 (m, 2H, PC*H*$_2$), 6.92−7.04 (m, 11H, aryl), 7.33 (m, 4H, aryl), 7.53 (m, 2H, aryl), 7.64 (m, 4H, aryl). $^{13}$C{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 20.88 (*C*H$_3$), 29.58 (PCH$_2$), 33.74 (PCH$_2$), 37.94 (*C*$_2$H$_4$), 128.34, 129.03, 131.27, 131.31, 131.59, 133.09, 137.42, 138.91 (aryl). $^{31}$P{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 73.2 (d, 17.0 Hz, 2P, PAr$_2$), 97.9 (t, 17.0 Hz, 1P, PPh). IR (KBr): $\nu_{N\equiv N}$ = 2048, 1982 cm$^{-1}$ (approximately 1:2 relative intensity).

***trans*-{[(4-OCH$_3$-C$_6$H$_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(N$_2$)$_2$ (5-C$_2$H$_4$).** Yield 35% (from Method A). $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 1.41 (br s, 4H, C$_2$*H*$_4$), 1.88 (m, 4H, PC*H*$_2$), 2.08 (m, 2H, PC*H*$_2$), 2.15 (m, 2H, PC*H*$_2$), 3.23 (s, 6H, Ar-OCH$_3$) 3.24 (s, 6H, Ar-OCH*H*$_3$) 6.69 (m, 8H, *Ar*-OCH$_3$) 7.05 (m, 3H, aryl), 7.29−7.35 (m, 8H, *Ar*-OCH$_3$), 7.37 (m, 2H, aryl). $^{13}$C{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 21.20 (PCH$_2$), 31.24 (PCH$_2$), 36.61 (*C*$_2$H$_4$), 48.21 (OCH$_3$), 49.15(OCH$_3$), 125.46, 128.32, 128.88, 129.09, 132.78, 133.11, 134.23, 137.86, 148.91, 149.27 (aryl). $^{31}$P{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 72.5 (d, 16.4 Hz, 2P, PAr$_2$), 96.7 (t, 16.4 Hz, 1P, PPh). IR (KBr) $\nu_{N\equiv N}$ = 2049, 1982 cm$^{-1}$ (approximately 1:2 relative intensity).

***trans*-{[(3,5-CH$_3$-C$_6$H$_3$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(N$_2$)$_2$ (6-C$_2$H$_4$).** Yield 72% (from Method A). $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 1.60 (s, 4H, C$_2$*H*$_4$), 1.91 (m, 2H, PC*H*$_2$), 2.07 (s, 6H, C*H*$_3$), 2.08 (s, 6H, C*H*$_3$), 2.21 (m, 2H, PC*H*$_2$), 2.68 (m, 2H, PC*H*$_2$), 2.98−3.13 (m, 2H, PC*H*$_2$), 6.70 (d, 11 Hz, 2H, aryl), 6.84−7.12 (m, 5H, aryl), 7.22 (m, 1H, aryl), 7.47 (m, 1H, aryl), 7.52 (t, 8.9 Hz, 2H, aryl). $^{13}$C{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 21.22 (*C*H$_3$), 21.36 (*C*H$_3$), 30.07 (PCH$_2$), 34.05 (PCH$_2$), 39.41 (*C*$_2$H$_4$), 129.12, 129.97, 130.16, 130.91, 130.98, 131.71, 131.83, 132.31, 136.18, 136.95, 137.63, 138.25 (aryl). $^{31}$P {$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 74.36 (d, 16.0 Hz, 2P, PAr$_2$), 97.16 (t, 16.0 Hz, 1P, PPh). IR (KBr): $\nu_{N\equiv N}$ = 1982, 2048 cm$^{-1}$ (approximately 1:2 relative intensity).

***trans*-{[(3,5-*t*Bu-C$_6$H$_3$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(N$_2$)$_2$ (7-C$_2$H$_4$).** Yield 71% (from Method A). $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 1.23 (s, 72H, ArC(C*H*$_3$)$_3$), 2.00 (s, 4H, C$_2$*H*$_4$), 2.37 (m, 2H, PC*H*$_2$) 2.51 (m, 2H, PC*H*$_2$), 2.74 (m, 2H, PC*H*$_2$), 3.16 (m, 2H, PC*H*$_2$), 7.02 (m, 1H, aryl) 7.11 (m, 2H, aryl), 7.48 (m, 8H, aryl), 7.66 (m, 2H, aryl), 7.74 (m, 4H, aryl). $^{13}$C{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 30.18 (PCH$_2$), 31.90 (C(*C*H$_3$)$_3$), 31.99 (C(*C*H$_3$)$_3$), 35.45 (PCH$_2$), 39.75 (*C*$_2$H$_4$), 128.98, 129.81, 130.84, 131.49, 131.63, 132.26, 136.83, 137.52, 138.13, 139.58 (aryl), 2 aryl and *C*(CH$_3$)$_3$ resonances not located. $^{31}$P{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 80.18 (d, 15.0 Hz, 2P, PAr$_2$), 97.99 (t, 15.0 Hz, 1P, PPh). IR (KBr) $\nu_{N\equiv N}$ = 1981, 2046 cm$^{-1}$.

**General Procedure for the Determination of Kinetics of Acrylate Formation.** In a typical experiment a J. Young tube was charged with 0.5 mL of a ca. 0.03 M benzene-$d_6$ solution of **1-C$_2$H$_4$** and a capillary of triethyl phopshite in benzene-$d_6$ for use as an integration standard. The sample was frozen at −35 °C, and 1 equiv of PPh$_3$ (0.1 M solution in benzene-$d_6$) was added. Immediately following PPh$_3$ addition, the sample was further cooled to −196 °C, and on a high vacuum line 4 atm of carbon dioxide was added via a calibrated gas bulb. The tube was then thawed, shaken, and inserted into a temperature-controlled NMR probe. The reaction progress was monitored by $^{31}$P NMR spectroscopy over greater than 2 half-lives following complete conversion of **1-C$_2$H$_4$** to **1-INT** (approximately 30 min). $^{31}$P {$^1$H} NMR spectroscopy was performed by taking 128 scans with a delay time of 2 s at each time interval of 15 min. The decay of the resonances of **1-INT** was converted to concentration and fitted to a first-order plot of ln [**1-INT**] versus time, which gave the observed rate constants as the slope. Sample graphs may be found in the Supporting Information. The kinetic measurements were repeated no fewer than three times, using at least two independent synthetic batches for each complex. Spectral features for (**2-INT** - **7-INT**) are listed below.

**{[(4-F-C$_6$H$_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(CO$_2$) (2-INT).** $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 0.70 (m, 4H, C$_2$*H*$_4$), 2.02 (m, 4H, PC*H*$_2$), 2.21−2.69 (m, 4H, PC*H*$_2$), 6.85 (m, 9H, aryl), 7.02 (m, 5H, aryl), 7.45 (m, 7H, aryl). $^{31}$P{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 65.1 (d, 3.7 Hz 2P, PAr$_2$), 94.3 (t, 3.7 Hz, 1P, PPh). $^{19}$F{$^1$H} (23 °C, C$_6$D$_6$): $\delta$ −111.53 (s), −112.21 (s).

**{[(4-CF$_3$-C$_6$H$_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(CO$_2$) (3-INT).** $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 0.52 (m, 4H, C$_2$*H*$_4$), 2.21 (m, 2H, PC*H*$_2$), 2.43 (m, 4H, PC*H*$_2$), 3.05 (m, 2H, PC*H*$_2$), 6.85 (m, 2H, aryl), 6.90 (m, 3H, aryl), 6.94 (m, 1H, aryl), 7.06 (d, 7.7 Hz, 2H, aryl), 7.09 (m, 2H, aryl), 7.12 (d, 7.7 Hz, 2H, aryl), 7.21 (d, 7.7 Hz, 2H, aryl), 7.25 (d, 7.7 Hz, 2H, aryl), 7.43 (m, 5H, aryl). $^{31}$P{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ 68.96 (d, 7.3 Hz, 2P, PAr$_2$), 96.80 (t, 7.3 Hz, 1P, PPh). $^{19}$F{$^1$H} NMR (23 °C, C$_6$D$_6$): $\delta$ −62.7 (s), −62.6 (s).

**{[(4-CH$_3$-C$_6$H$_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(CO$_2$) (4-INT).** $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 0.30 (m, 4H, C$_2$*H*$_4$), 1.84 (m, 2H, PC*H*$_2$), 1.94 (s, 6H, C*H*$_3$), 2.02 (s, 6H, C*H*$_3$), 2.21 (m, 2H, PC*H*$_2$), 2.69 (m, 2H, PC*H*$_2$), 2.95 (m, 2H, PC*H*$_2$), 6.90 (m, 9H, aryl), 7.06 (m, 5H, aryl), 7.66 (m, 7H, aryl). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 64.9 (d, 5.2 Hz, 2P, PAr$_2$), 96.1 (t, 5.2 Hz, 1P, PPh).

**{[(4-OCH$_3$-C$_6$H$_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(CO$_2$) (5-INT).** $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 0.97 (m, 4H, C$_2$*H*$_4$), 2.18 (m, 4H, PC*H*$_2$), 2.55 (s, 6H, OC*H*$_3$), 3.29 (s, 6H, OC*H*$_3$), 3.09 (m, 4H, PC*H*$_2$). $^{31}$P{$^1$H} NMR (23 °C C$_6$D$_6$): $\delta$ 67.7 (d, 3.1 Hz, 2P, PAr$_2$) 99.5 (t, 3.1 Hz, 1P, PAr).

**{[(3,5-Me-C$_6$H$_3$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(C$_2$H$_4$)(CO$_2$) (6-INT).** $^1$H NMR (23 °C, C$_6$D$_6$): $\delta$ 1.00 (m, 4H, C$_2$*H*$_4$), 2.01 (s, 12H, C*H*$_3$), 2.06 (s, 12H, C*H*$_3$), 3.23 (m, 4H, PC*H*$_2$), 3.58 (t, 6 Hz, 4H, PC*H*$_2$), 6.62 (d, 5 Hz, 4H, aryl), 6.75 (s, 2H, aryl), 6.98 (d, 5 Hz, 4H, aryl), 7.04 (d, 5 Hz, 2H, aryl), 7.39 (m, 1H, aryl), 7.66 (m, 2H, aryl), 8.05 (t, 8 Hz, 2H, aryl). $^{13}$C {$^1$H} NMR (23 °C, C$_6$D$_6$): 21.8 (*C*H$_3$), 22.0 (*C*H$_3$), 29.3 (*C*$_2$H$_4$), 66.3 (PCH$_2$), 68.1 (PCH$_2$), 123.1, 127.8, 129.6, 129.8, 130.0, 130.1, 131.0, 131.1, 136.7, 138.2 (aryl) one aryl resonance and carbonyl not located. $^{31}$P{$^1$H} NMR (23 °C, C$_6$D$_6$):


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65.84 (d, 18 Hz, 2P, $PAr_2$), 96.83(t, 18 Hz, 1P, PPh) IR (KBr): $\nu_{C=O}$ 1699 $cm^{-1}$.

**{[(3,5-*t*Bu-$C_6H_3$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo($C_2H_4$)($CO_2$) (7-INT).** $^1H$ NMR (23 °C, $C_6D_6$): $\delta$ 0.45 (m, 4H, $C_2H_4$), 1.27 (s, 36H, CC$H_3$), 1.29 (s, 36H, CC$H_3$), 3.12 (m, 4H, PC$H_2$), 3.47 (m, 4H, PC$H_2$), 6.60−6.72 (m, 4H, aryl), 6.77 (s, 2H, aryl), 6.98−7.07 (m, 6H, aryl), 7.70 (m, 3H, aryl), 8.07 (m, 2H, aryl). $^{31}P\{^1H\}$ NMR (23 °C, $C_6D_6$): 67.70 (d, 2.7 Hz, 2P, $PAr_2$), 98.76 (d, 2.7 Hz, 2P, PPh).

**General Procedure for the Preparation of [($Ar_2PCH_2CH_2$)$_2$PPh]Mo(H)$PPh_3$($CO_2$CH=$CH_2$) (2-acrylate−7-acrylate).** Complexes **2-$C_2H_4$−7-$C_2H_4$** were prepared by procedures analogous to those previously reported for **1-acrylate** either by carbon dioxide addition to *trans*-[$(Ar)_2PCH_2CH_2\}_2$PPh]Mo($C_2H_4$)$(N_2)_2$ in the presence of triphenylphosphine (Method A) or transmetalation of silver acrylate with in situ generated [$(Ar)_2PCH_2CH_2\}_2$PPh]Mo(H)-$PPh_3$(Cl) (Method B). In a typical synthesis using Method A, a J. Young tube was charged with [$(Ar)_2PCH_2CH_2\}_2$PPh]Mo($C_2H_4$)-$(N_2)_2$, 1 equiv of $PPh_3$, and approximately 0.5 mL of benzene-$d_6$. On a vacuum line, 4 atm of carbon dioxide was admitted to the sample via calibrated gas bulb at −196 °C. The tube was warmed to ambient temperature, shaken thoroughly, and left to stand overnight. $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopy revealed complete conversion along with a small quantity of free $PPh_3$. In a typical synthesis using Method B, a 20 mL scintillation vial was charged with [$(Ar)_2PCH_2CH_2\}_2$PPh]-$MoCl_3$ and 1 equiv of $PPh_3$ in approximately 5 mL of THF. Then 2 equiv of $NaHBEt_3$ (1 M in tetrahydrofuran) was added via syringe, and the reaction stirred at ambient temperature for 2 h, changing rapidly from yellow to dark green. The volatiles were removed in vacuo, affording a dark residue that was washed with pentane, extracted with toluene, and dried to afford a dark green solid. The solid was then treated with 1 equiv of silver acrylate in a cosolvent of toluene/diethyl ether and stirred for 1 h at ambient temperature. The solution was then filtered, concentrated to ca. 1 mL, and crystallized from toluene/diethyl ether at −35 °C to afford the desire product as reddish solids.

**{[(4-F-$C_6H_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(H)$PPh_3$($CO_2$CH=$CH_2$) (2-acrylate).** Yield 56% (Method B). Anal. Calcd for $C_{34}H_{29}MoO_2P_4$: C, 63.71; H, 4.67. Found: C, 63.49; H, 4.40. $^1H$ NMR (23 °C, $C_6D_6$): $\delta$ −4.93 (tdd, 1H, 13.6, 42.3, 73.4 Hz Mo-*H*), 1.28 (m, 2H, PC$H_2$), 1.84, (m, 2H, PC$H_2$), 2.35−2.47 (m, 4H, PC$H_2$) 4.70 (dd, 1H, 2.1, 10.3 Hz, C*H*=$CH_2$), 5.13 (dd, 10.3, 17.2 Hz, 1H, C*H*=$CH_2$), 5.44 (dd, 2.1, 17.2 Hz, 1H, CH=C$H_2$), 6.70−6.83 (m, 16 H, aryl), 6.90 (t 8.1 Hz, 3H, aryl), 7.03 (m, 6H, aryl), 7.29, (m, 2H, aryl), 7.38 (m, 6H, aryl) 7.71 (t, 7.5 Hz, 3H aryl). $^{13}C\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ 26.26 ($PCH_2$), 34.77 ($PCH_2$), 124.03, 131.41, ($CH=CH_2$)) 114.87, 127.81, 127.94, 129.14, 129.20, 134.54, 135.08, 135.08, 135.08, 135,20, 135.72, 137.29 (aryl), three aryl signals not located. $^{31}P\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ 47.2 (dt, 12 Hz, 154 Hz, 1P, $PPh_3$), 99.7 (dt, 20 Hz, 154 Hz, 1P, PPh), 107.2 (dd, 12 Hz, 20 Hz, 2P, $PAr_2$). $^{19}F\{^1H\}$ (23 °C, $C_6D_6$): $\delta$ −112.84 (s), −113.41 (s). IR (KBr): $\nu_{C=O}$ = 1587 $cm^{-1}$.

**{[(4-$CF_3$-$C_6H_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(H)$PPh_3$($CO_2$CH=$CH_2$) (3-acrylate).** Yield 51% (Method A). $^1H$ NMR (23 °C, $C_6D_6$): $\delta$ −4.79 (tdd, 1H, 14.2, 44.0, 72.0 Hz, Mo-*H*), 1.78 (m, 4H, PC$H_2$), 2.29−2.45 (m, 4H, PC$H_2$), 4.70 (dd, 1H, 2.0, 10.3 Hz, CH=C$H_2$), 5.09 (dd, 1H, 10.3, 17.3 Hz, C*H*=$CH_2$), 5.40 (dd, 1H, 2.1, 17.2 Hz, CH=C$H_2$), 6.67 (m, 4H, aryl), 6.81 (m, 6H, aryl), 7.04 (m, 12H, aryl), 7.32 (m, 2H, aryl), 7.29 (m, 9H, aryl), 7.46 (m, 3H, aryl). $^{13}C\{^1H\}$ NMR (23 °C, $C_6D_6$): 26.15 ($PCH_2$), 34.78 ($PCH_2$), 125.11 ($CH=CH_2$), 131.09 ($CH=CH_2$), 133.28 ($CF_3$), 133.93 ($CF_3$), 127.83, 127.92, 129.20, 129.49, 131.34, 131.43, 134.44, 134.63, 134.84, 134.95, 136.35, 138.32, 138.44 (aryl). $^{31}P\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ 46.5 (dt, 12.5, 151.8 Hz, 1P, $PPh_3$), 102.3 (dt, 18.5, 152.3 Hz, 1P, PPh), 112.0 (dd, 12.5, 18.1 Hz, 2P, $PAr_2$). $^{19}F\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ −62.5 (s), −62.3 (s). IR (KBr): $\nu_{C=O}$ = 1606 $cm^{-1}$

**{[(4-$CH_3$-$C_6H_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(H)$PPh_3$($CO_2$CH=$CH_2$) (4-acrylate).** Yield 68% (Method B). Anal. Calcd for $C_{59}H_{48}F_{12}P_4MoO_2$: C, 69.41; H, 5.92. Found: C, 69.13; H, 6.14. $^1H$ NMR (23 °C, $C_6D_6$): $\delta$ −4.71 (tdd, 73.9, 41.5, 13.4 Hz, 1H, Mo-*H*), 1.59 (m, 2H, PC$H_2$), 2.00 (m, 4H, PC$H_2$), 2.15 (s, 6H, C$H_3$), 2.20 (s, 6H, C$H_3$), 2.59−2.67 (m, 2H, PC$H_2$), 4.41 (dd, 1.9, 9.7, 1H, CH=C$H_2$), 5.23 (dd, 9.7, 17.2 Hz, 1H, C*H*=$CH_2$), 5.56 (dd, 1.9, 17.2 Hz, 1H, C*H*=$CH_2$), 6.83 (m, 7H, aryl), 6.90 (m, 5H, aryl), 7.03 (m, 9H, aryl), 7.33 (m, 7H, aryl), 7.58 (m, 5H, aryl), 7.85 (m, 3H, aryl). $^{13}C\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ 21.61 (*C*$H_3$), 21.65 (*C*$H_3$), 26.33 (*P*$CH_2$), 34.70 (*P*$CH_2$), 123.30 (CH=$CH_2$), 131.81 (CH=$CH_2$), 127.60, 127.68, 129.13, 129.20, 131.5, 131.64, 133.68, 134.04, 134.44, 134.64, 135.45, 135.57, 137.78, 138.24 (aryl) two aryl signals not located. $^{31}P\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ 49.3 (dt, 11.9, 156.8 Hz, 1P, $PPh_3$), 99.4 (dt, 18.5, 156.9 Hz, 1P, PPh), 108.6 (dd, 12.0, 20.0 Hz, 2P, $PAr_2$). IR (KBr): $\nu_{C=O}$ = 1515 $cm^{-1}$.

**{[(4-$OCH_3$-$C_6H_4$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(H)$PPh_3$($CO_2$CH=$CH_2$) (5-acrylate).** Yield 79% (Method B). Anal. Calcd for $C_{34}H_{29}MoO_6P_4$: C, 65.31; H, 5.57. Found: C, 65.59; H 5.43. $^1H$ NMR (23 °C, $C_6D_6$): $\delta$ −4.73 (tdd, 73.7, 42.3, 12.5 Hz, 1H, Mo-*H*), 1.16−1.22 (m, 2H, PC$H_2$), 2.56−2.68 (m, 4H, PC$H_2$), 3.33 (s, 6H, C$H_3$), 3.35 (s, 6H, C$H_3$), 4.74 (dd, 2.3, 10.6, 1H, CH=C$H_2$), 5.26 (dd, 10.6, 17.4 Hz, 1H, C*H*=$CH_2$), 5.55 (dd, 2.3, 17.4 Hz, 1H, C*H*=$CH_2$), 6.74 (m, 7H, aryl), 6.91 (m, 5H, aryl), 7.04 (m, 9H, aryl), 7.40 (m, 7H, aryl), 7.64 (m, 5H, aryl), 7.89 (m, 3H, aryl). $^{13}C\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ 49.35 (*C*O*C*$H_3$), 51.34 (*C*O*C*$H_3$), 27.52 (*P*$CH_2$), 35.41 (*P*$CH_2$), 122.20 (CH=$CH_2$), 131.92 (CH=$CH_2$), 128.11, 128.68, 130.72, 130.92, 131.20, 132.44, 133.86, 134.24, 134.64, 134.64, 134.78, 135.27, 137.58, 137.64 (aryl) three aryl resonances not located. $^{31}P\{^1H\}$ NMR (23 °C, $C_6D_6$) $\delta$ 49.31 (dt, 10.1, 155.3 Hz, 1P, $PPh_3$) 98.93 (dt, 19.1, 155.3 Hz, 1P, $PAr_2$) 106.41 (dd, 10.1, 19.1 Hz, 2P, PPh). IR (KBr): $\nu_{C=O}$ = 1518 $cm^{-1}$

**{[(3,5-$CH_3$-$C_6H_3$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(H)$PPh_3$($CO_2$CH=$CH_2$) (6-acrylate).** Yield 60% (Method A). $^1H$ NMR (23 °C, $C_6D_6$): $\delta$ −4.37 (ddt, 74.3, 38.1, 13.4 z, 1H, Mo-*H*), 1.20 (m, 2H, PC$H_2$), 1.52 (m, 2H, PC$H_2$), 2.03 (s, 12H, Ar−C$H_3$), 2.15 (s, 12H, Ar−C$H_3$), 2.76−2.89 (m, 4H, PC$H_2$), 4.71, (dd, 10.3, 2.3 Hz, 1H, CH=C$H_2$), 5.28 (dd, 17.3, 10.3 Hz, 1H, C*H*=$CH_2$), 5.56 (dd, 17.3, 2.3 Hz, 1H, CH=C$H_2$), 6.80−6.94 (m, 11H, aryl), 7.02−7.07 (m, 6H, aryl), 7.20−7.42 (m, 12H, aryl) 7.86 (t, 7.8 Hz, 3H, aryl). $^{13}C\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ 20.03 (Ar$CH_3$), 20.63 (Ar$CH_3$), 26.20 ($PCH_2$), 34.20, ($PCH_2$), 121.95, ($CH=CH_2$) 127.07, 127.31, 128.44, 128.61, 130.37, 130.48, 130.90, 130.98, 133.01, 133.27, 134.80, 137.12, 137.34, 141.16, 141.69 (aryl) two aryl resonances not located. $^{31}P\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ 52.09 (dt, 11.5, 156 Hz, 1P, $PPh_3$) 102.96 (dt, 17, 156 Hz, 1P, $PAr_2$) 109.60 (dd, 11.5, 17 Hz, 2P, PPh). IR (KBr): $\nu_{C=O}$ = 1518 $cm^{-1}$

**{[(3,5-*t*Bu-$C_6H_3$)$_2$PCH$_2$CH$_2$]$_2$PPh}Mo(H)$PPh_3$($CO_2$CH=$CH_2$) (7-acrylate).** Yield 16% (Method A). $^1H$ NMR (23 °C, $C_6D_6$): $\delta$ −4.74 (ddt, 72.9, 41.0, 15.2 z, 1H, Mo-*H*), 1.56 (m, 2H, PC$H_2$), 1.99 (m, 2H, PC$H_2$), 1.56 (s, 36H, Ar−CC$H_3$), 1.63 (s, 36H, Ar−CC$H_3$), 2.62 (m, 4H, PC$H_2$), 4.73, (dd, 9.9, 2.4 Hz, 1H, CH=C$H_2$), 5.26 (dd, 17.5, 9.9 Hz, 1H, C*H*=$CH_2$) 5.55 (dd, 17.5, 2.4 Hz, 1H, CH=C$H_2$), 6.80−6.94 (m, 11H, aryl), 7.02−7.07 (m, 6H, aryl), 7.20−7.42 (m, 12H, aryl) 7.86 (t, 7.8 Hz, 3H, aryl). $^{13}C$ NMR (23 °C, $C_6D_6$): $\delta$ 15.90, (Ar*C*$CH_3$) 16.21 (Ar*C*$CH_3$), 26.14, (*P*$CH_2$) 34.39 (*P*$CH_2$), 35.28, (Ar*C*$CH_3$) 121.57, 123.45, 126.45, 127.69, 127.87, 129.18 129.65, 131.55, 133.59, 133.85, 134.46, 135.34, 137.83, 138.38, 153.71 (aryl), 177.42 ($O_2CC_2H_3$) three aryl signals not located. $^{31}P\{^1H\}$ NMR (23 °C, $C_6D_6$): $\delta$ 56.03 (dt, 12, 157 Hz, 1P, $PPh_3$), 99.14 (dt, 20, 157 Hz, 1P, $PAr_2$), 108.42 (dd, 12, 20 Hz, 2P, PPh). IR (KBr): $\nu_{C=O}$ = 1513 $cm^{-1}$

**Spectroscopic Characterization of {[[(4-F-$C_6H_4$)$_2$PCH$_2$CH$_2$]$_2$PPh]Mo(H)($CO_2$CH=$CH_2$)}$_2$ (2-dimer).** A reaction vessel was charged with 200 mg of [{(4-$CF_3$-$C_6H_4$)$_2$PCH$_2$CH$_2$}-PPh]Mo($N_2$)$_2$($C_2H_4$) in toluene. The reaction vessel was then filled with 2 atm of $CO_2$, left to stir at room temperature for 24 h, and then dried in vacuo. The resultant brownish-red mixture that resulted was extracted with pentane followed by diethyl ether and toluene. The diethyl ether fraction was then reduced in volume and layered with pentane, which precipitated 115 mg of an orange-red solid as a crude reaction product, which we were unable to purity further from residual free ligand. Two isomers: $^1H$ NMR (23 °C, $C_6D_6$) $\delta$ −7.09 (ddd, 13.9, 55.9, 94.3 Hz, Mo-*H*), −6.70 (ddd, 12.5, 66.4, 97.8 Hz, Mo-*H*), 1.7−2.2, 2.18, 3.65, (m, $PCH_2$ and CH=$CH_2$) 6.91−7.14 (m, aryl) 7.56 (m aryl), 8.15, (m aryl) 8.23 (m aryl). $^{31}P$ $\{^1H\}$ NMR NMR (23 °C, $C_6D_6$): $\delta$ 80.3 (dd, 14.5, 27.6 Hz), 79.5 (dd 14.5, 27.6 Hz), 86.7 (m),


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87.9 (m), 99.9 (m), 105.8 (m), 110.8 (m), 118.7 (m). $^{19}F\{^{1}H\}$ NMR (23 °C, $C_6H_6$): $\delta$ −111.22(s), −106.10(s), −105.37(s), −103.17(s).

## ■ ASSOCIATED CONTENT

### Supporting Information

Crystallographic information file for **1-$C_2H_4$** in cif format and selected spectral and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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