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Conversion of Carbon Dioxide to Methanol Using a C–H Activated Bis(imino)pyridine Molybdenum Hydroboration Catalyst

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Supporting Information



ABSTRACT: Using a multistep synthetic pathway, a bis(imino)pyridine (or pyridine diimine, PDI) molybdenum catalyst for the selective conversion of carbon dioxide into methanol has been developed. Starting from (^{Ph2PPr}PDI)Mo(CO), I₂ addition afforded [(^{Ph2PPr}PDI)MoI(CO)][I], which features a seven-coordinate Mo(II) center. Heating this complex to 100 °C under vacuum resulted in CO loss and the formation of [(^{Ph2PPr}PDI)MoI][I]. Reduction of [(^{Ph2PPr}PDI)MoI][I] in the presence of excess K/Hg yielded (κ^{6} -*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)MoH following methylene group C–H activation at the α -position of one PDI imine substituent. The addition of CO₂ to (κ^{6} -*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)MoH resulted in facile insertion to generate the respective η^{1} -formate complex, (κ^{6} -*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)Mo(OCOH). When low pressures of CO₂ were added to solutions of (κ^{6} -*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)MoH containing pinacolborane, the selective formation of H₃COBPin and O(BPin)₂ was observed along with precatalyst regeneration. When HBPin was limited, H₂C(OBPin)₂ was observed as an intermediate and (κ^{6} -*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)Mo(OCOH) remained present throughout CO₂ reduction. The hydroboration of CO₂ to H₃COBPin was optimized and 97% HBPin utilization by 0.1 mol % (κ^{6} -*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)MoH was demonstrated over 8 h at 90 °C, resulting in a methoxide formation turnover frequency (TOF) of 40.4 h⁻¹ (B–H utilization TOF = 121.2 h⁻¹). Hydrolysis of the products and distillation at 65 °C allowed for MeOH isolation. The mechanism of (κ^{6} -*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)MoH mediated CO₂ hydroboration is presented in the context of these experimental observations. Notably, (κ^{6} -*P*,*N*,*N*,*N*,*C*,*P*-^{Ph2PPr}PDI)MoH is the first Mo hydroboration catalyst capable of converting CO₂ to MeOH, and the importance of this study as it relates to previously described catalysts is discussed.

INTRODUCTION

For more than a century, developed nations have relied on fossil fuel combustion to satisfy a large fraction of their energy demands.¹ As a result, atmospheric CO₂ concentrations have climbed by 36% over 250 years² and an additional 30 Gt of CO₂ is released into the atmosphere annually.³ Moreover, increasing atmospheric CO₂ concentrations have been linked to higher global temperatures,⁴ rising sea levels,⁵ and ocean acidification.⁶ Diverse and complementary approaches to mitigate these effects by reducing CO₂ emissions are being considered,^{7,8} and the conversion of CO₂ into value-added products has become an increasingly relevant area of chemical research.⁹⁻¹¹ Syntheses that rely on CO₂ as a carbon-based feedstock are industrially desirable since this molecule is abundant, inexpensive, and renewable.¹² These characteristics have led to CO₂ utilization for the production of urea, inorganic carbonates, and salicylic acid;¹³ however, the efficient and selective reduction of CO₂ into suitable fossil fuel alternatives is an unresolved challenge that continues to draw interest from the scientific community.14

Efficient homogeneous catalysts for the conversion of CO₂ into CO,¹⁵ formic acid,¹⁶ formaldehyde (or formaldehyde-derived oligomers and derivatives),¹⁷ methanol,¹⁸⁻²⁷ and methane²⁸ have only recently been developed. Of these products, methanol is the most appropriate transportation fuel for our existing energy infrastructure since it is a liquid under ambient conditions with an energy density of 22.7 MJ/kg.²⁹ Although H₂ is an ideal reductant in terms of cost and atom efficiency, the hydrogenation of CO₂ to MeOH using homogeneous frustrated Lewis pair or Ru catalysts has been hindered by a lack of selectivity¹⁸ and modest activity at elevated temperatures (140-160 °C).¹⁹ Silanes have been used to achieve Ir-20 and Ru-catalyzed²¹ conversion of CO₂ into methoxysilanes; however, a limited turnover number (TON) for selective methoxide group formation was reported in each case $(TON = 3 \text{ for } Ir;^{20} 32 \text{ for } Ru^{21})$. Free *N*-heterocyclic carbenes have also been found to mediate the reduction of CO2 into

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Figure 1. Previously described transition metal catalysts for the hydroboration of CO₂ to methoxyborane.^{17a,e,26,27}

 $Ph_2Si(OMe)_2$ and $Ph_2HSiOSiHPh_2$ at ambient temperature (methoxide formation TON of 6 over 24 h).²²

While reducing CO₂ to the methoxide level using H₂ and silanes has been met with limited success,³⁰ borane reagents have proven to be highly effective for this transformation. Depending on the nature of the borane, frustrated Lewis pairs,² alkali metal²⁴ and alkaline earth metal²⁵ reagents have all been found to catalyze the hydroboration of CO_2 to the respective methoxyborane. To date, only three well-defined transition metal catalyst systems have been found to selectively mediate this transformation: $(^{R}POCOP)NiH^{26} [R = ^{t}Bu^{26} (Figure 1, A),$ ¹Pr,^{26b,c} or ^cPe^{26b,c}], $[(\kappa^5 - P, P, N, N, O - ({}^{i}Pr_2PNH(CH_2)_2)_2N - 27]$ $((CH_2)_2NP^iPr_2CO_2)Ru][BPh_4]^{27}$ (Figure 1, B), and $(R_3P)_2RuH(L)(XL')^{17}$ [R = Cyp, L = CO, XL' = O₂CH, O₂COMe, or H₂BPin (Figure 1, C);^{17a} R = Cy, L = H₂, XL' = H and H_2^{17e}]. Using 0.2 mol % A relative to catecholborane under 1 atm CO₂, complete conversion to H_3 COBCat and O(BCat)₂ was observed within 1 h at ambient temperature (methoxide formation TON = 165, B–H utilization $TOF = 495 h^{-1}$).^{26a} Complexes B and C have been shown to catalyze the selective hydroboration of CO₂ to methoxyborane using HBPin with limited methoxide formation TONs of 927 and 3,17a,e respectively.

In 2014, we reported that ($^{Ph2PPr}PDI$)Mo(CO) (1) (where PDI is pyridine diimine) catalyzes C=O bond hydrosilylation with TOFs of up to 330 h⁻¹ at 90 °C.³¹ Having determined that this transformation occurs by way of phosphine substituent dissociation, we hypothesized that (κ^5 -P,N,N,N,P-Ph2PPrPDI)-Mo-L (L = weakly coordinating neutral ligand) complexes may exhibit superior carbonyl reduction activity relative to 1.³¹ Continuing our investigation of ($^{Ph2PPr}PDI$)Mo chemistry, this contribution describes the preparation of a 7-coordinate Mo hydride complex following chelate C–H activation, in addition to its utility as a CO₂ reduction catalyst.

RESULTS AND DISCUSSION

Synthesis and Characterization. Having recently reported the preparation of 1^{31} (eq 1) from ^{Ph2PPr}PDI³² and Mo(CO)₆, a synthetic pathway for CO-free analogues was sought. Refluxing toluene solutions of 1 under vacuum for days failed to result in CO loss.³¹ Therefore, we hypothesized that oxidizing 1 would diminish Mo-CO backbonding and render this ligand susceptible to dissociation. Addition of stoichiometric I₂ to a toluene solution of 1 resulted in precipitation of a purple solid within hours of stirring at ambient temperature. Isolation of the product and analysis by ³¹P NMR spectroscopy revealed two doublets centered at 39.62 and 39.22 ppm, indicating that both phosphine arms remain coordinated to the Mo center. The ¹H and ¹³C NMR spectra collected for this complex were



also indicative of left-to-right ^{Ph2PPr}PDI inequivalence. Importantly, a pseudo triplet was observed at 238.4 ppm (J_{PC} = 20.5 Hz) in the ¹³C NMR spectrum and infrared spectroscopy revealed one CO stretch at 1826 cm⁻¹. Taken together, this data suggests that I₂ addition to 1 results in formation of the seven-coordinate Mo(II) complex, [(^{Ph2PPr}PDI)MoI(CO)][I] (2, eq 1).³³

Relative to 1 ($\nu_{CO} = 1740 \text{ cm}^{-1}$),³¹ complex 2 exhibits significantly weakened Mo-CO backbonding and heating a THF solution of the latter to 100 °C for 24 h resulted in CO dissociation and formation of an amber-colored complex identified as $[(^{Ph2PPr}PDI)MoI][I]$ (3, eq 1). Analysis by IR and ^{13}C NMR spectroscopy revealed no evidence of CO coordination, and the ³¹P NMR spectrum of **3** was found to feature a single resonance at 6.18 ppm, indicating equivalent phosphine environments. Furthermore, complexes 1 (bright pink), 2 (purple), and 3 (amber) are readily distinguishable by UV-visible spectroscopy (see Figures S33-35 and Table S4 of the Supporting Information). The spectrum of 1 is dominated by charge transfer bands with maxima at 299, 345, 399, and 537 nm; all of which have molar absorptivity values of greater than 9000 M⁻¹cm⁻¹. Two-electron oxidized 2 features comparatively weak charge transfer bands at 328 (ε = 6350 M^{-1} cm⁻¹), 410 (ε = 2330 $M^{-1}cm^{-1}$), and 541 nm ($\varepsilon = 5040 M^{-1}cm^{-1}$). Finally, complex 3 exhibits a predominant charge transfer band at 452 nm (ε = 2300 M⁻¹cm⁻¹) with a shoulder at 527 nm (ε = $1030 \text{ M}^{-1} \text{cm}^{-1}$).

The solid state structure of 3 (Figure 2) was determined by single crystal X-ray diffraction, and noteworthy metrical parameters are provided in Table 1. The geometry about Mo can best be described as distorted octahedral with N(1)-Mo(1)-N(3) and P(1)-Mo(1)-P(2) angles of 141.6(4)° and 169.30(7)°, respectively. Inspection of the PDI chelate imine N=C distances reveals considerable elongation [1.324(15) and



Figure 2. Solid state structure of **3** shown at 30% probability ellipsoids. Hydrogen atoms and I⁻ counterion are omitted for clarity. For complete atom labeling and metrical parameters, see Figure S1 and Table S2 of the Supporting Information.

Table 1. Notable Bond	Lengths	(Å)	and	Angles	(deg)
Determined for 3					

	3
Mo(1)-N(1)	2.036(11)
Mo(1)-N(2)	2.112(10)
Mo(1)-N(3)	2.077(10)
Mo(1)-P(1)	2.472(3)
Mo(1)-P(2)	2.453(3)
Mo(1)-I(1)	2.7810(17)
N(1)-C(2)	1.332(16)
N(3)-C(8)	1.324(15)
C(2) - C(3)	1.442(17)
C(7)–C(8)	1.401(18)
N(1)-Mo(1)-N(3)	141.6(4)
P(1)-Mo(1)-P(2)	169.30(7)
N(2)-Mo(1)-I(1)	178.2(3)

1.332(16) Å] relative to unreduced PDI ligands (1.28 Å).³⁴ The C(2)–C(3) and C(7)–C(8) distances determined for 3 of 1.442(17) and 1.401(18) Å, respectively, are also significantly contracted from the C_{imine}–C_{pyridine} bond lengths found for unreduced chelates (1.50 Å).³⁴ Comparable C_{imine}–C_{pyridine} distances reported for $[({}^{\rm IPr2Ar}BPDI)Mo(N_2)]_2(\mu_2\eta^1,\eta^1-N_2)$ of 1.421(5) and 1.437(5) Å have recently been assigned to two-electron reduction of the chelate;³⁵ however, this complex features a geometry in which Mo does not lie in the idealized PDI chelate plane. As previously described, d-orbital radial expansion enhances second-row metal backbonding such that redox noninnocent ligand LUMOs are greatly destabilized, rendering their population unlikely.^{31,32,36} For this reason, we refrain from assigning the ^{Ph2PPr}PDI chelate of 3 as redox-active (i.e., reduced by one or more electrons), even though ^{Ph2PPr}PDI is known to accept electrons when bound to formally zerovalent Mn.^{37,38}

Having isolated and characterized **3**, its reduction to an appropriate catalyst precursor was explored. Adding an excess

of K/Hg to 3 in THF afforded a green solution after 3 d at ambient temperature. Upon workup, the resulting product was analyzed by multinuclear NMR spectroscopy. The ¹H NMR spectrum of this complex was found to feature two unique backbone methyl resonances at 2.88 and 2.50 ppm, indicative of left-to-right ^{Ph2PPr}PDI inequivalence. A set of methylene-derived resonances was also shifted downfield to 4.85 and 4.77 ppm. Further inspection by gHSQCAD revealed that the ¹H resonance at 4.77 ppm was correlated to a newly formed C-H environment (54.9 ppm, suggesting concomitant Mo-H formation) while ¹H resonances at 5.44 and 4.85 ppm were associated with a ¹³C NMR resonance at 57.8 ppm (Figure S13 of the Supporting Information). Collecting ¹H-coupled ¹³C data confirmed that the resonance centered at 54.9 ppm is a doublet $(J_{\rm CH} = 171.12 \text{ Hz})$, indicating it is bound to a single hydrogen atom (see Figure S14 of the Supporting Information).³⁹ Attempts to locate a Mo-H resonance by COSY or NOESY NMR spectroscopy were unsuccessful. The ³¹P NMR spectrum of this product featured two sets of doublets at 46.93 and 57.94 ppm (J_{PP} = 97.2 Hz), further supporting static left-to-right Ph2PPrPDI inequivalence. Taken together, NMR spectroscopic data indicates that reduction of 3 using K/Hg affords the C-H activated Mo(II) product, $(\kappa^6-P, N, N, N, C, P-Ph2PPrPDI)$ -MoH (4, eq 2).



To confirm the unusual coordination environment proposed for 4, the solid state structure of this complex was determined by single crystal X-ray diffraction. As shown in Figure 3, the geometry about Mo can best be described as distorted pentagonal bipyramidal. Due to the rigidity of the C–H activated propylene



Figure 3. Solid state structure of 4 shown at 30% probability ellipsoids. Hydrogen atoms other than H1M and a partially occupied toluene molecule are omitted for clarity. For complete atom labeling and metrical parameters, see Figure S2 and Table S3 of the Supporting Information.

arm of ^{Ph2PPr}PDI, the phosphine donors are restricted from linearity with a P(1)-Mo(1)-P(2) angle of 152.91(7)°. The N(1)-Mo(1)-N(3) angle of 144.3(2)° is similar to the one observed for 3; however, the angle defined by N(1)-Mo(1)-C(10) is only 38.0(2)° (Table 2). Interestingly, C-H activation

Table 2. Notable Bond Lengths (Å) and Angles (deg) Determined for 4

4
1.940(7)
2.072(5)
2.121(6)
2.448(2)
2.433(2)
1.75(8)
2.259(8)
1.399(9)
1.324(9)
1.374(9)
1.406(10)
1.408(11)
38.0(2)
144.3(2)
152.91(7)
176.8(3)

affords a Mo(1)–C(10) bond distance of 2.259(8) Å and the *trans*-influence of this alkyl is responsible for a comparatively long Mo(1)–N(3) contact of 2.121(6) Å. The C(10)–N(1) distance of 1.399(9) Å is indicative of a single bond, and the proximity of C(10) to Mo(1) forces a fairly short Mo(1)–N(1) contact of 1.940(7) Å. Although the in-plane PDI bond precision determined for 4 is poorer than desired for electronic structure discussion, the C(2)–C(3) and C(7)–C(8) distances of 1.406(10) and 1.408(11) Å, respectively, indicate that a significant amount of electron density is being transferred from Mo to the ligand framework.

CO₂ Functionalization. Considering that CO₂ insertion into Mo–H bonds has been well-documented,⁴⁰ its addition to 4 was investigated. When 0.2 atm of CO₂ was admitted to a J. Young tube containing a frozen benzene- d_6 solution of 4 (0 °C), complete conversion to a new complex was observed by multinuclear NMR spectroscopy after 10 min at 25 °C (eq 3).



The ¹H NMR spectrum of the product featured resonances consistent with left-to-right chelate inequivalence in addition to a sharp singlet at 9.14 ppm. This resonance, along with a newly observed ¹³C NMR resonance at 169.7 ppm,^{40a} is consistent with formation of the respective formate complex, $(\kappa^6-P,N,N,N,C,P^{-Ph2PP}rPDI)Mo(OCOH)$ (5, eq 3). Complex 5 is believed to possess an η^1 -formate ligand since this binding mode renders it an 18-electron complex. Infrared spectroscopy revealed a formate C=O stretch at 1625 cm⁻¹ (KBr),

providing further support for η^1 -coordination. In the absence of reducing agent, the addition of more than 0.2 atm CO₂ to 4 at 0 °C has been found to result in decomposition by way of chelate loss.

Having determined that CO₂ insertion into the Mo-H bond of 4 is facile, the stoichiometric reduction of CO₂ was attempted in the presence of excess HBPin. Upon adding 20 equiv of HBPin relative to 4 in benzene- d_6 and exposing the solution to 1 equiv of CO₂, reaction progress was monitored by NMR spectroscopy. After 3 d at 25 °C, small quantities of H₃COBPin and $O(BPin)_2$ were identified (Figure S21 of the Supporting Information). Realizing that reduction beyond the formate level was slow under these conditions (5 remained observable by ³¹P NMR spectroscopy, Figure S22 of the Supporting Information), the reaction was heated to 60 °C and continued monitoring over 2 d revealed near quantitative conversion of CO₂ to H₃COBPin and O(BPin)₂ by ¹H NMR spectroscopy (Figure S23 of the Supporting Information). The collection of ³¹P NMR spectroscopic data confirmed that 4 is regenerated in the absence of CO_2 (Figure S24 of the Supporting Information).

Attempts to optimize this transformation were then made to enable catalytic CO₂ reduction. Upon adding 1 atm CO₂ to a J. Young tube containing a benzene- d_6 solution of 100 equiv HBPin relative to 4 at -70 °C, the reaction was heated to 90 °C and monitored. After 2 h, most of the HBPin had been consumed and a mixture of H₂C(OBPin)₂, H₃COBPin, and $O(BPin)_2$ was observed in a 2:1:2 ratio by ¹H NMR spectroscopy (Figure 4). After 5 h at 90 °C, the product mixture consisted only of H₃COBPin and O(BPin)₂ as judged by ¹H and ¹¹B NMR spectroscopy (Figure S26 of the Supporting Information). Complex 5 was observed throughout the reaction by ³¹P NMR spectroscopy (Figure S27 of the Supporting Information). Repeating the reaction in the absence of catalyst did not result in CO₂ reduction. Since phosphine-promoted CO₂ hydroboration has been reported in the presence of 9-BBN,^{23c,d} a control experiment employing 1 mol % ^{Ph2PPr}PDI was conducted. This experiment did not afford H₃COBPin; however, a minimal amount (3%) of HCO₂BPin was detected by ¹H and ¹¹B NMR spectroscopy after 4 h at 90 °C (Figures S28 and S29 of the Supporting Information). Employing 1 mol % 4 under these conditions affords a methoxide formation TON of 33 (99 based on B–H) and TOF of 6.6 h^{-1} (B–H utilization TOF = 19.8 h^{-1}). The observation of $H_2C(OBPin)_2$ under CO_2 at low HBPin concentrations is also important from a mechanistic standpoint (see following section).

To explore the full synthetic utility of this transformation, a 100 mL thick-walled glass bomb was charged with 0.1 mol % 4 in neat HBPin and 1 atm of CO_2 was added at -70 °C (eq 4).

$$1 \operatorname{atm} \operatorname{CO}_{2} + 1000 \operatorname{HBPin} \xrightarrow{4 (0.1 \operatorname{mol}\%)}{90 \, {}^{\circ}\mathrm{C}, 8 \operatorname{h}} H_{3} \operatorname{COBPin} + O(\operatorname{BPin})_{2}$$

$$1) H_{2}O, 24 \operatorname{h}$$

$$2) \operatorname{Distillation} \qquad (4)$$

$$H_{3} \operatorname{COH} (58\%)$$

After heating to 90 °C for 8 h, analysis by ¹H NMR spectroscopy revealed 97% B–H bond utilization to selectively generate H₃COBPin and O(BPin)₂, equating a 4-mediated CO₂ to methoxide TOF of 40.4 h⁻¹ (TON = 323; TOF = 121.2 h⁻¹ relative to B–H). The product mixture was then treated with deionized H₂O, and upon stirring for 24 h, distillation at 65 °C yielded MeOH (0.022 g, 58% isolated yield





Figure 4. ¹H NMR spectra of 4-mediated CO₂ hydroboration over the course of 5 h at 90 °C.



Figure 5. Proposed mechanism of 4-mediated CO₂ hydroboration.

relative to HBPin; see Figures S31 and S32 of the Supporting Information). Although boranes are nonideal reductants, the low catalyst loading and solvent-free conditions used to achieve this transformation are advantageous from a green chemistry perspective.⁴¹

Mechanism of Hydroboration. Upon investigating the 4-mediated hydroboration of CO_2 to methoxyborane under a

range of conditions, a mechanistic pathway consistent with our experimental observations is proposed (Figure 5). Starting from 4, the insertion of CO₂ generates catalyst resting state 5. Incoming HBPin undergoes σ -bond metathesis with the Mo–O bond of 5 to regenerate 4 and yield the respective borylformate, HCO₂BPin. The carbonyl functionality of this intermediate may competitively coordinate since it remains in solution, and its

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insertion into the Mo–H bond of 4 results in the respective alkoxide intermediate, (κ^6 -P,N,N,N,C,P-^{Ph2PPr}PDI)Mo-(OCH₂OBPin) (Figure 5, bottom right). This complex has not been observed while monitoring CO₂ hydroboration in the presence of low HBPin concentrations, suggesting that σ -bond metathesis with HBPin to generate H₂C(OBPin)₂ is facile. The methoxyborane product, H₃COBPin, may then be formed by way of σ -bond metathesis between the Mo–H bond of 4 and a C–O bond of H₂C(OBPin)₂. This pathway would also result in the formation of (κ^6 -P,N,N,N,C,P-^{Ph2PP}PDI)Mo(OBPin) (Figure 5, bottom left); however, this complex is not observed and is proposed to react with HBPin to liberate O(BPin)₂ and reform 4.

Although the mechanism presented in Figure 5 is similar to those proposed for alkaline earth metal²⁵ and Ni^{26,42} catalyzed CO₂ hydroboration, our observations suggest that H₃COBPin might be generated through a different reaction pathway. Hill and co-workers suggested that heating H₂C(OBPin)₂ to 60 °C might result in its conversion to formaldehyde and O(BPin), by way of 1,2-elimination.²⁵ Alternatively, computational efforts by Huang et al. have indicated that β -boroxide elimination from (PCP)Ni(OCH₂OBCat) is responsible for the formation of formaldehyde and (PCP)Ni(OBCat).42 It must also be mentioned that OCH₂ has been observed during Ru-catalyzed CO₂ hydroboration, allowing for the isolation of formalin.^{17a} The possibility that formaldehyde is formed during 4-mediated CO₂ reduction cannot be discounted; however, spectroscopic evidence of its formation has not been observed under a range of conditions. When 4-catalyzed hydroboration was conducted at low HBPin concentration, a buildup of $H_2C(OBPin)_2$ was noted (Figure 5), suggesting that alkoxide intermediate $(\kappa^{6}$ -P,N,N,N,C,P-^{Ph2PPr}PDI)Mo(OCH₂OBPin) does not undergo β -boroxide elimination to give formaldehyde and $(\kappa^6-P,N,N,N,C,P^{-Ph2PPr}PDI)Mo(OBPin)$. Since accumulation of $H_2C(OBPin)_2$ occurs at 90 °C, the breakdown of this intermediate to yield formaldehyde is either slow or not occurring under these conditions. Rather, it is proposed that σ -bond metathesis between free $H_2C(OBPin)_2$ and the Mo-H bond of 4 to yield H_3 COBPin is slow in the presence of excess CO_2 since 5 is observed spectroscopically.

Catalyst Comparison and Intricacies. To put the synthetic utility of 4 as a CO₂ to MeOH conversion catalyst into context, a comparison to previously reported hydroboration catalysts is warranted. Considering well-defined transition metal catalysts, (tBuPOCOP)NiH26 (Figure 1, A) remains the most efficient for the conversion of CO₂ to H₃COBCat, exhibiting a methoxide formation TOF of 165 h⁻¹ at ambient temperature.²⁶ Comparatively, 4 was found to mediate slow methoxide formation at ambient temperature and heating to 90 °C was required to reach an appreciable methoxide formation TOF $(40.4 h^{-1})$. The methoxide formation TON of 323 achieved using 0.1 mol % 4 relative to borane is greater than the TON of 9 achieved using the tris(aminophosphine)Ru hydroboration catalyst reported by Sgro and Stephan (Figure 1, B);²⁷ however, the efficacy of the latter catalyst was not assayed at 90 °C. Finally, Sabo-Etienne and co-workers have demonstrated that complexes of type $(Cyp_3P)_2RuH(CO)(XL')$ (XL' = O_2CH , O_2COMe , or H_2BPin) (Figure 1, C) are capable of producing approximately 3 equiv of H_3COBP in after 0.5 h at room temperature.^{17a}

Surprisingly, $^{Ph2PPr}PDI$ chelate C–H activation was found to result in the formation of an alkyl ligand that possesses a β -methylene group. The H atoms of this group do not participate

in β -hydride elimination, even at temperatures up to 90 °C. We believe that the Mo center is simply unable to access these atoms due to the rigidity of the metallacyclopentane ring which they are a part of.⁴³ It is also notable that the Mo–C bond of 4 is inert toward carbonyl insertion pathways and B–H σ -bond metathesis throughout the course of CO₂ hydroboration. It should be mentioned that the synthesis and reactivity of 4 are made possible by the diphenylphosphinopropyl arms of ^{Ph2PPr}PDI, as these substituents enable distinct reduction chemistry from that reported for aryl-substituted (PDI)Mo complexes.³⁵ As inferred from this study, the high degree of modularity achievable for donor-substituted PDI chelates should continue to provide unusual catalyst structures and reactivity.

CONCLUSION

The synthesis, characterization, and catalytic properties of the first well-defined Mo catalyst for the reduction of CO₂ to MeOH have been established. The oxidative addition of I_2 to 1 was found to weaken metal-to-ligand backbonding, enabling CO dissociation and concomitant preparation of the respective diiodide complex, 3. The reduction of 3 using K/Hg resulted in intramolecular C-H activation of the chelate to yield 4. By single crystal X-ray diffraction, this precatalyst was found to possess a distorted pentagonal bipyramidal geometry due to the formation of a persistent metallacyclopentane. The addition of CO_2 to 4 revealed facile insertion to yield 5, which possesses an η^1 -formate ligand. The utilization of **4** as a CO₂ reduction catalyst in the presence of HBPin resulted in the selective formation of H₃COBPin and O(BPin)₂ over a range of temperatures. This reaction was optimized such that 0.1 mol % 4 was employed in the absence of solvent at 90 °C, allowing a methoxide formation turnover frequency (TOF) of 40.4 \tilde{h}^{-1} (B-H utilization TOF = 121.2 h^{-1}) and the isolation of MeOH following hydrolysis. Finally, the mechanism of 4-mediated CO₂ hydroboration has been proposed to proceed through a series of insertion and σ -bond metathesis events.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all synthetic manipulations were performed in an MBraun glovebox under an atmosphere of purified nitrogen. Pentane, toluene, diethyl ether, and tetrahydrofuran were purchased from Sigma-Aldrich, dried using a Pure Process Technology solvent system, and stored in the glovebox over activated 4 Å molecular sieves and metallic sodium (Alfa Aesar) before use. Benzene- d_{6i} acetone- d_{6i} and acetonitrile- d_3 were obtained from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves and metallic potassium (purchased from Sigma-Aldrich) prior to use. 2,6-Diacetylpyridine and Celite were purchased from TCI America and Acros, respectively. Mo(CO)₆ and 3-(diphenylphosphino)propylamine were purchased from Strem Chemicals, and 4,4,5,5tetramethyl-1,3,2-dioxaborolane (HBPin) was used as received from Sigma-Aldrich. Carbon dioxide was used as received from Praxair. $^{Ph2PPr}_{PDI^{32}}$ and $(^{Ph2PPr}_{PDI})Mo(CO)$ (1)³¹ were prepared according to literature procedures. Solution phase ¹H, ¹³C, ¹¹B, and ³¹P nuclear magnetic resonance (NMR) spectra were recorded at room temperature on either a 400 or 500 MHz Varian NMR Spectrometer. All ¹H and ${}^{13}C$ NMR chemical shifts are reported in ppm relative to Si(CH₃)₄ using ¹H (residual) and ¹³C chemical shifts of the solvent as secondary standards. ³¹P and ¹¹B NMR data are reported in ppm relative to H₃PO₄ and 0.1 M boric acid in water, respectively. IR spectroscopy was conducted on Bruker VERTEX 70 spectrometer with an MCT detector. Elemental analyses were performed at Robertson Microlit Laboratories Inc. (Ledgewood, NJ). UV-visible spectra were collected on an Agilent 8453 spectrophotometer.

X-ray Crystallography. Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in the glovebox and transferred to glass fiber with Apiezon N grease before mounting on the goniometer head of a Bruker APEX Diffractometer (Arizona State University) equipped with Mo K α radiation. A hemisphere routine was used for data collection and determination of the lattice constants. The space group was identified, and the data was processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix, least-squares procedures on [F²] (SHELXS). Attempts to refine an inversion twin for 3 resulted in a twin fraction of 0.00166, which was therefore removed from the final refinement. The solid state structure of 4 features A-level alerts due to a disordered phenyl ring that has been modeled as two partially occupied rings with restrictions placed on thermal parameters and bond distances. For 4, two large electron density peaks were located within 1.2 Å of Mo but were not modeled as H atoms due to their proximity to existing Mo-N bonds. Crystallographic parameters for 3 and 4 are located in Table S1 of the

Supporting Information. Preparation of [(^{Ph2PPr}PDI)MoI(CO)][I] (2). In a nitrogen filled glovebox, a 20 mL reaction vial was charged with 0.10 g (0.135 mmol) of 1 and 10 mL of toluene. To the pink solution, 0.034 g (0.135 mmol) of iodine dissolved in 5 mL of toluene was slowly added while stirring. A purple solid precipitated within 5 min of stirring. After 5 h, the reaction mixture was filtered through a sintered frit to remove the purple solid. After washing with toluene and ether and drying under vacuum, 0.127 g (0.128 mmol, 95%) of a purple solid identified as 2 was isolated. This complex was recrystallized from a concentrated acetone/THF solution at -35 °C prior to analysis. Anal. Calcd for C40H41N3I2OM0P2·C4H8O: C, 49.68; H, 4.64; N, 3.95. Found: C, 49.81; H, 4.38; N, 4.30. ¹H NMR (acetone-d₆, 400 MHz): 8.46 (d, 8.0 Hz, 1H, Py), 8.33 (d, 8.0 Hz, 1H, Py), 8.01 (t, 8.0 Hz, 1H, Py), 7.77 (t, 6.8 Hz, 2H, Ph), 7.57 (m, 2H, Ph), 7.48 (t, 8.4 Hz, 2H, Ph), 7.36 (m, 2H, Ph), 7.20 (m, 6H, Ph), 6.99 (t, 8.0 Hz, 2H, Ph), 6.92 (t, 8.4 Hz, 2H, Ph), 6.31 (t, 8.8 Hz, 2H, Ph), 4.48 (d, 12.0 Hz, 1H, CH₂), 4.24 (d, 12.0 Hz, 1H, CH₂), 4.03 (t, 12.0 Hz, 1H, CH₂), 3.41 (t, 12.0 Hz, 1H, CH₂), 2.98 (m, 3H, CH₂), 2.64 (d, 2.4 Hz, 3H, CH₃), 2.57 (m, 1H, CH₂), 2.34 (m, 2H, CH₂), 2.31 (s, 3H, CH₃), 2.19 (m, 2H, CH₂). ¹³C NMR (acetone- d_{6} , 100.49 MHz): 238.4 (pseudo t, J_{CP} = 20.5 Hz, CO), 176.6 (*Py*), 175.8 (*Py*), 155.4 (C=N), 153.8 (C=N), 142.8 (d, J_{CP} = 161.0, *Ph*), 135.4 (d, J_{CP} = 15.0 Hz, *Ph*), 133.7 (d, J_{CP} = 13.8 Hz, *Ph*), 133.5 (d, J_{CP} = 10.8 Hz, *Ph*), 133.2 (*Py*), 132.3 (d, J_{CP} = 26.2 Hz, *Ph*), 130.8 (d, J_{CP} = 13.3 Hz, Ph), 130.5 (d, J_{CP} = 15.2 Hz, Ph), 130.5 (d, $J_{\rm CP} = 30.3$ Hz, Ph), 129.1 (d, $J_{\rm CP} = 14.7$ Hz, Ph), 128.2 (Py), 128.1 (d, $J_{CP} = 7.9$ Hz, Ph), 127.2 (Py), 61.4 (NCH₂), 59.3 (NCH₂), 28.2 (d, $J_{CP} = 46.6$ Hz, CH_2CH_2P), 26.9 (d, $J_{CP} = 3.9$ Hz, CH_2CH_2P), 26.1 (d, $J_{\rm CP}$ = 5.2 Hz, CH₂CH₂P), 25.9 (d, $J_{\rm CP}$ = 36.7 Hz, CH₂CH₂P), 17.3 (CH₃), 17.1 (t, $J_{\rm CP}$ = 4.0 Hz, CH₃). ³¹P NMR (acetone- d_6 , 161.78 MHz): 39.62 (d, $J_{\rm PP}$ = 13.7 Hz), 39.22 (d, $J_{\rm PP}$ = 13.7 Hz). IR (KBr pellet): $\nu_{\rm CO} = 1826 \text{ cm}^{-1}$

Preparation of [(^{Ph2PPr}PDI)Mol][I] (3). In a nitrogen filled glovebox, a 100 mL thick-walled reaction bomb was charged with 0.080 g (0.080 mmol) of 2 dissolved in 20 mL of THF and a magnetic stir bar. The sealed bomb was frozen in liquid nitrogen and degassed on a Schlenk line before being refluxed at 100 °C in a preheated oil bath. A brownish-amber solid began to precipitate within 2 h of stirring. After 12 h, the reaction mixture was allowed to cool at room temperature and degassed on the Schlenk line. Once the liberated CO gas was removed, the reaction was allowed to reflux for 24 h at 100 °C to ensure reaction completion. After another CO removal step, the bomb was brought inside the glovebox and an amber solid was isolated on top of a sintered frit. The product was washed with THF, ether, and pentane and dried under vacuum to yield 0.053 g (0.055 mmol, 68%) of an amber solid identified as 3. Single crystals suitable for X-ray diffraction were grown from a concentrated solution in acetone/THF at -35 °C. Anal. Calcd for C39H41N3I2MoP2: C, 48.61; H, 4.29; N, 4.36. Found: C, 48.35; H, 4.13; N, 4.13. ¹H NMR (acetonitrile-d₃, 400 MHz): 7.46 (t, 8.0 Hz, 1H, Py), 7.30 (m, 7H, Ph), 6.92 (t, 7.2 Hz, 2H, Ph), 6.72 (t, 7.6 Hz, 4H, Ph), 6.45 (d, 8.0 Hz, 2H, Py), 6.01 (d,

7.2 Hz, 3H, *Ph*), 5.55 (t, 14.4 Hz, 2H, *Ph*), 5.01 (d, 14.4 Hz, 2H, *Ph*), 3.98 (s, 6H, CH₃), 3.51 (m, 1H, CH₂), 3.28 (t, 7.2 Hz, 1H, CH₂), 3.14 (m, 2H, CH₂), 2.93 (m, 2H, CH₂), 2.81 (m, 2H, CH₂), 2.62 (m, 2H, CH₂), 1.88 (m, 2H, CH₂). ¹³C NMR (acetonitrile- d_3 , 100.49 MHz): 156.9 (C=N), 138.4 (*Py*), 133.6 (*Ph*), 131.4 (*Py*), 130.3 (*Ph*), 129.6 (*Ph*), 128.7 (*Py*), 127.2 (*Ph*), 118.8 (*Py*), 57.2 (NCH₂CH₂), 28.1 (PCH₂CH₂), 26.4 (PCH₂CH₂), 15.4 (CH₃). ³¹P NMR (acetonitrile- d_3 , 161.78 MHz): 6.18 (s).

Preparation of (κ^{6} -P,N,N,N,C,P-^{Ph2PPr}PDI)MoH (4). In a nitrogen filled glovebox, a 20 mL reaction vial was charged with 4.2 g of mercury and 3 mL of THF. To it, 0.016 g of freshly cut metallic potassium was added and stirred for 30 min to form clear potassium amalgam solution. To the solution, 0.078 g (0.081 mmol) of 3 in 10 mL of THF was slowly added and the mixture was allowed to stir at ambient temperature for 3 d. The resulting green solution was filtered through Celite, and the solvent was removed in vacuo to yield a green solid. After washing with pentane and drying, 0.051 g (87%) of a dark green solid identified as 4 was isolated. Single crystals suitable for X-ray diffraction were grown from a concentrated toluene solution at -35 °C. Anal. Calcd for C39H41N3MoP2: Calcd C, 66.00%; H, 5.82%; N, 5.92%. Found: C, 65.88%; H, 5.57%; N, 5.64%. ¹H NMR (benzene-d₆, 400 MHz): 7.83 (t, 8.4 Hz, 2H, Ar), 7.56 (m, 3H, Ar), 7.49 (t, 8.0 Hz, 2H, Ar), 7.07 (m, 3H, Ar), 7.02 (m, 1H, Ar), 6.62 (m, 1H, Ar), 6.51 (m, 5H, Ar), 5.60 (t, 8.4 Hz, 2H, Ar), 5.49 (m, 2H, Ar), 5.44 (t, 11.9 Hz, 1H, NCH₂), 4.85 (d, 10.8 Hz, 1H, NCH₂), 4.77 (b, 1H, HCMo), 2.88 (s, 3H, CH₃), 2.82 (m, 1H,CH₂), 2.62 (m, 2H, CH₂), 2.50 (s, 3H, CH₃), 2.27 (m, 1H, CH₂), 2.06 (m, 2H, CH₂), 1.39 (m, 1H, CH₂), 1.18 (m, 1H, CH₂), Mo-H peak not located. ¹³C NMR (benzene-d₆, 100.49 MHz): 147.3 (C=N), 145.5 (C=N), 139.3 (Ar), 138.7 (d, J_{CP} = 57 Hz, Ar), 134.3 (d, J_{CP} = 33.5 Hz, Ar), 134.0 (d, J_{CP} = 34 Hz, Ar), 132.7 (d, J_{CP} = 2.5 Hz, Ar), 132.6 (d, J_{CP} = 9.2 Hz, Ar), 132.2 (Ar), 131.9 (d, J_{CP} = 16.2 Hz, Ar), 131.0 (d, J_{CP} = 19.9 Hz, Ar), 129.1 (d, J_{CP} = 30.6 Hz, Ar), 117.1 (Ar), 106.5 (Ar), 104.2 (Ar), 57.8 (NCH₂), 54.9 (d, J_{CP} = 7.5 Hz, NCHMo), 33.8 (d, $J_{\rm CP}$ = 47.9 Hz, CH₂CH₂P), 31.4 (d, $J_{\rm CP}$ = 33.4 Hz, CH₂), 30.5 (d, $J_{\rm CP}$ = 55.7 Hz, CH₂), 29.6 (d, J_{CP} = 42.1 Hz, CH₂), 17.1 (CH₃), 13.2 (CH₃). ³¹P NMR (benzene-*d*₆, 161.78 MHz): 57.94 (d, 97.2 Hz, PPh₂), 46.93 (d, 97.2 Hz, PPh₂).

Preparation of (κ^6 -P,N,N,N,C,P-^{Ph2PPr}PDI)Mo(OCOH) (5). In a nitrogen filled glovebox, a J. Young NMR tube was charged with 0.010 g (0.014 mmol) of 4 dissolved in 0.7 mL of C₆D₆. The tube was frozen at 0 °C and degassed, and 0.2 atm of CO₂ was added. Within 10 min, formation of a new compound identified as 5 was observed by multinuclear NMR spectroscopy. Upon removal of excess CO2 and solvent, 0.009 g (0.012 mmol, 85%) of a green solid identified as 5 was isolated. Anal. Calcd for C40H41N3M0O2P2: Calcd C, 63.74%; H, 5.48%; N, 5.57%. Found: C, 63.51%, H, 5.42%, N, 5.28%. ¹H NMR (benzene-d₆, 400 MHz): 9.14 (s, 1H, CHO), 7.25 (m, 4H, Ar), 7.12 (m, 5H, Ar), 7.02 (t, 7.2 Hz, 3H, Ar), 6.90 (t, 7.6 Hz, 1H, Ar), 6.59 (t, 7.6 Hz, 2H, Ar), 6.43 (t, 7.6 Hz, 4H, Ar), 6.26 (t, 12.0 Hz, 1H, NCH₂), 5.62 (s, 1H, NCHMo), 5.56 (t, 7.8 Hz, 2H, Ar), 5.25 (t, 8.4 Hz, 2H, Ar), 4.55 (d, 12.0 Hz, 1H, NCH₂), 3.34 (m, 2H, CH₂), 2.80 (m, 1H, CH₂), 2.73 (s, 3H, CH₃), 2.47 (s, 3H, CH₃), 2.04 (m, 1H, CH₂), 1.87 (m, 1H, CH₂), 1.76 (t, 14.4 Hz, 1H, CH₂), 1.39 (m, 3H, CH₂), 0.74 (m, 1H, CH_2). ¹³C NMR (benzene- d_6 , 100.49 MHz): 169.7 (MoOCOH), 148.1 (C=N), 148.1 (C=N), 144.6 (Ar), 132.8 (d, $J_{CP} = 17.8$ Hz, Ar), 132.2 (d, $J_{CP} = 20.0$ Hz, Ar), 131.3 (d, $J_{CP} = 17.2$ Hz, Ar), 130.9 (d, J_{CP} = 18.9 Hz, Ar), 129.4 (Ar), 128.6 (d, J_{CP} = 7.6 Hz, Ar), 128.5 (d, J_{CP} = 10.0 Hz, Ar), 127.6 (d, J_{CP} = 10.0 Hz, Ar), 117.5 (Ar), 106.8 (Ar), 106.1 (Ar), 57.4 (NHCMo), 50.2 (NCH₂), 30.5 (d, J_{CP} = 14.9 Hz, CH₂), 28.8 (CH₂), 23.9 (d, J_{CP} = 30.6 Hz, CH₂), 20.9 (d, J_{CP} = 34.2 Hz, CH₂), 16.6 (CH₃), 13.5 (CH₃). ³¹P NMR (benzene-*d*₆, 161.78 MHz): 43.80 (d, 186.2 Hz, *PPh*₂), 28.10 (d, 186.2 Hz, PPh₂). IR (KBr pellet): $\nu_{\text{OCOH}} = 1625 \text{ cm}^{-1}$.

Stoichiometric Reduction of CO₂ Using 4. In the glovebox, a 20 mL scintillation vial containing 0.014 mmol of 4 was charged with pinacolborane (0.28 mmol) in 0.7 mL of benzene- d_6 . The mixture was transferred into a J. Young NMR tube and sealed under nitrogen. After degassing the tube, 0.2 atm of CO₂ gas was added to the frozen

solution at 0 $^{\circ}$ C. The reaction was first monitored at 25 $^{\circ}$ C and then upon heating to 60 $^{\circ}$ C by multinuclear NMR spectroscopy.

Hydroboration of CO₂ Using 1 mol % 4. In the glovebox, a 20 mL scintillation vial containing 0.0011 mmol of 4 was charged with pinacolborane (0.11 mmol) in 0.7 mL of benzene- d_6 . The mixture was transferred into a J. Young NMR tube and sealed under nitrogen. After degassing the tube, an atmosphere of CO₂ gas was added to the frozen solution at -70 °C, and the tube was allowed to heat in an oil bath preheated at 90 °C for 5 h. The reaction was monitored over time by multinuclear NMR spectroscopy.

Hydroboration of CO₂ **Using 0.1 mol % 4.** In the glovebox, a 20 mL scintillation vial containing 0.0035 mmol of 4 was charged with pinacolborane (3.5 mmol) in 0.7 mL of benzene- d_6 . The mixture was transferred into a 100 mL reaction bomb and sealed under nitrogen. After degassing the bomb, an atmosphere of CO₂ gas was added at -70 °C. Upon thawing, the tube was placed in a 90 °C oil bath for 8 h. A few drops of the reaction mixture were dissolved in C_6D_6 and complete consumption of starting borane was observed by ¹H, ¹³C, and ¹¹B NMR spectroscopy. After recombining fractions and removing the NMR solvent *in vacuo*, the borylated products were hydrolyzed with water (2 mL) while stirring at ambient temperature for 24 h. The volatile components were separated by short path distillation, and methanol was recovered (58% isolated yield, relative to HBPin).

Control Reaction between Pinacolborane and CO₂. In the glovebox, a 20 mL scintillation was charged with 0.016 mL of pinacolborane and 0.7 mL of benzene- d_6 . The mixture was transferred into a J. Young NMR tube and sealed under nitrogen. After degassing the tube, an atmosphere of CO₂ gas was added at -70 °C, and the tube was allowed to heat in an oil bath preheated at 90 °C for 4 h. The reaction was analyzed by ¹H NMR spectroscopy and transformation of the reactants was not observed.

Control Reaction Employing ^{Ph2PPr}**PDI as a Catalyst.** In the glovebox, a 20 mL scintillation vial containing 0.0045 mmol of ^{Ph2PPr}PDI was charged with pinacolborane (0.45 mmol) in 0.7 mL of benzene- d_6 . The mixture was transferred into a J. Young NMR tube and was sealed under nitrogen. After degassing the tube, an atmosphere of CO₂ gas was purged into the frozen solution at -70 °C, and the tube was allowed to heat in a 90 °C oil bath for 4 h. The reaction was analyzed by multinuclear NMR spectroscopy. No trace of methoxide was observed; however, 3% of pinacolboryl formate was identified by ¹H and ¹¹B NMR spectroscopy (see Figures S28 and S29 of the Supporting Information).

ASSOCIATED CONTENT

Supporting Information

Crystallographic information for **3** (CCDC-1052031) and **4** (CCDC-1052032) and multinuclear NMR, infrared, and UV–visible spectroscopic data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01102.

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Notes

The authors declare no competing financial interest.

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