

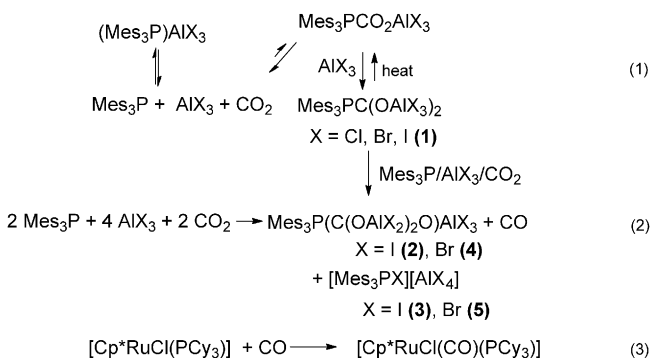
Stoichiometric Reduction of CO₂ to CO by Aluminum-Based Frustrated Lewis Pairs**

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The dramatic rise in the consumption of fossil fuels since the industrial revolution has resulted in rapid increases in atmospheric CO₂ levels, exacerbating global climate change.^[1] While mitigating emissions through reduced consumption and improved efficiency will most likely offer the best solutions, technologies such as carbon capture and storage continue to be developed in the hopes of eliminating some industrial emissions.^[2] In addition to the environmental motivation, the rising costs and dwindling supplies of fossil fuels have prompted efforts to develop alternative energy sources. While this has generated a number of clever innovations in energy technology,^[3–8] one approach that has garnered attention and addresses both the environmental and alternative energy issues is based on the concept of utilizing CO₂ as a C₁ source for fuels. Indeed, one perturbation of this idea is the “methanol economy” espoused by Olah some 10 years ago.^[9,10] To avoid further environmental issues and deal with thermodynamic realities, this vision requires the reduction of CO₂ by photochemically generated H₂.^[11,12] While intense efforts are targeting the photocatalytic splitting of water,^[13,14] recent efforts have targeted fundamentally new main-group-mediated routes to the reduction chemistry of CO₂.^[15–18]

Recently, we have been exploiting the concept of “frustrated Lewis pairs” (FLPs) for the activation of a variety of small molecules.^[19–22] In particular, we have shown that systems derived from sterically demanding phosphines and boranes are capable of reversibly binding CO₂.^[23] Subsequently, we showed that FLPs derived from aluminum halides (X = Cl or Br) and PMes₃ (Mes = 2,4,6-C₆H₂Me₃) react with CO₂ to give the species Mes₃PC(OAlX₃)₂ (X = Cl, Br).^[16] Treatment of these products with ammonia–borane (H₃NBH₃) and subsequent hydrolysis resulted in the stoichiometric reduction of CO₂ to methanol. Herein, we report that these P/Al/CO₂ compounds also provide a pathway for the reduction of CO₂ to CO. Initial information regarding the mechanism of this remarkably facile and metal-free reduction are presented.

The species Mes₃P(C(OAlI₃)₂) (**1**) was readily synthesized in a similar fashion to chloride and bromide analogues [Eq. (1)].^[16] The compound is isolated by precipitation after



5 minutes following the combination of the reagents. The ²⁷Al NMR resonance for **1** is observed at 20 ppm and is markedly upfield from those of Mes₃PC(OAlX₃)₂ (X = Cl, Br), which is consistent with literature values of ²⁷Al shifts for aluminum halides.^[24] Allowing the initial reaction mixture of PMes₃ and AlI₃ to stir under CO₂ for 16 h afforded two new compounds **2** and **3** in a 1:1 ratio, as evidenced by ³¹P NMR spectroscopy. The ³¹P NMR resonance for **2** was observed at 20 ppm, exhibiting P–C coupling of 118 Hz. ²⁷Al NMR spectroscopy showed a broad peak at 31 ppm (ν_{1/2} = ca. 170 Hz), which is slightly downfield from the starting material **1** at 20 ppm. Crystals of the product **2** were also obtained and were shown to be Mes₃P(C(OAlI₂)₂O)(AlI₃) (Figure 1). This

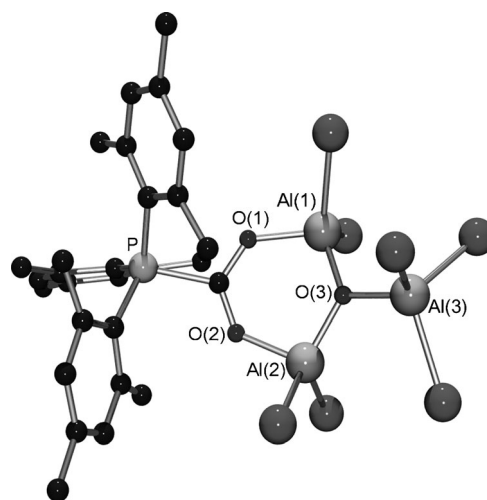


Figure 1. POV-ray depiction of **2**. H atoms are omitted for clarity.

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product contains a six-membered ring comprised of a CO₂ fragment linked to an I₂AlOAlI₂ fragment. PMes₃ is carbon-bound in an exocyclic position, while an additional equivalent of AlI₃ is bound to the transannular oxygen atom. The P–C distance of 1.906(5) Å is similar to that previously reported in Mes₃P(C(OAlX₃)₂) (X = Cl, Br).^[16] The C–O and related Al–O distances were found to be 1.241(5) Å and 1.261(4) Å and 1.847(3) Å and 1.860(3) Å, respectively. The Al–O distances in the I₂AlOAlI₂ fragment were 1.806(3) and 1.811(3) Å while the O–AlI₃ distance is longer (1.831(3) Å) consistent with the nature of this dative bond. It is noteworthy that while the X-ray data confirm the presence of two distinct Al environments in **2**, ²⁷Al NMR data showed only a single broad resonance. As dissymmetric aluminum centers often give broad resonances, this could arise from overlapping signals. Alternatively, a fluxional process could account for this observation. However, the poor solubility of **2** precluded acquisition of ²⁷Al NMR spectral data at low temperature.

The additional product **3** gives rise to a ³¹P NMR resonance at –15 ppm and a sharp ²⁷Al NMR singlet at –25 ppm. These data are consistent with the formulation of the product **3** as the salt [Mes₃PI][AlI₄]. This was confirmed by a crystallographic study of crystals obtained from the reaction mixture (see the Supporting Information), while **3** was also prepared independently from the reaction of PMes₃, AlI₃, and I₂.

The capture of oxide and consequent formation of the Al–O–Al fragment in **2**, infer the reduction of CO₂ to CO. Infrared spectroscopy of the headspace gas revealed an absorption centered at 2143 cm^{–1},^[25] confirming CO is produced in this reaction. Employing ¹³CO₂ the reaction was shown to generate a new peak at 184.5 ppm in the ¹³C NMR spectrum while the corresponding headspace gas gave rise to an absorption centered at 2096 cm^{–1}. These data are the spectroscopic signatures of ¹³CO and this was confirmed by comparison to those of an authentic sample. The liberated CO was captured by exposure of the head gas to a solution of [Cp*RuCl(PCy₃)],^[26] prompting the formation of [Cp*Ru(CO)Cl(PCy₃)] in 80 % yield based on the stoichiometry in which one equivalent of CO arises from reaction of two equivalents of phosphine [Eq. (3)]. Collectively, these data imply that the reaction of two equivalents of phosphine and CO₂ react with four equivalents of AlI₃ to produce one equivalent of **2**, **3**, and CO [Eq. (2)]. The reduction of CO₂ to CO and the oxide that is incorporated in **2** is concurrent with formal oxidation of phosphine to iodophosphonium, generating the salt **3**.

The analogous reaction of PMes₃ and AlBr₃ was also performed. In a similar fashion exposure of the solution to CO₂ for 2 days at 25 °C afforded a mixture of two products **4** and **5** in a 1:1 ratio. Vapor diffusion of cyclohexane into the bromobenzene solution afforded crystals of Mes₃P(C(OAlBr₂)₂O)(AlBr₃) **4**. This product exhibited a ³¹P{¹H} NMR signal at 19.5 ppm while a broad ²⁷Al NMR resonance was observed at 88 ppm. Employing ¹³CO₂ the species [C-**4**] was prepared and a resonance at 176.8 ppm with a P–C coupling constant of 123 Hz was seen in the ¹³C NMR spectrum. The second product **5** was confirmed to be the salt [Mes₃PBr][AlBr₄] by independent synthesis from PMes₃,

AlBr₃, and Br₂. This latter species gave rise to a ³¹P{¹H} NMR shift at 38.5 ppm and an ²⁷Al NMR signal at 81 ppm. Compounds **4** and **5** were also characterized crystallographically (see the Supporting Information). In the case of **4**, the geometry was almost identical to that described above for **2**, with the Al–O bond lengths to the PCO₂ fragment being 1.837(3) Å and 1.840(3) Å, while the Al–O bond lengths in the Br₂AlOAlBr₂ fragment are 1.792(3) Å and 1.795(3) Å. While spectroscopic data suggested the formation of the chloride analogue may occur, the prolonged heating of PMes₃ and AlCl₃ under CO₂ led to a mixture of products that were not separable.

Efforts to garner some insight into the mechanism of this reduction were undertaken. Monitoring solutions of PMes₃ and AlX₃ (X = Br, I) by ³¹P{¹H} NMR spectroscopy showed only a broad resonance attributable to the formation of weak donor–acceptor adducts in rapid exchange with excess AlX₃. Upon exposure to CO₂, there is rapid and near quantitative generation of the initial species Mes₃PC(OAlX₃)₂ as the only observable product. Subsequent monitoring of these reactions over time showed the decline of the resonances from Mes₃PC(OAlX₃)₂ and the appearance of the peaks resulting from the corresponding products **2/3** and **4/5** as the exclusive products (Figure 2).

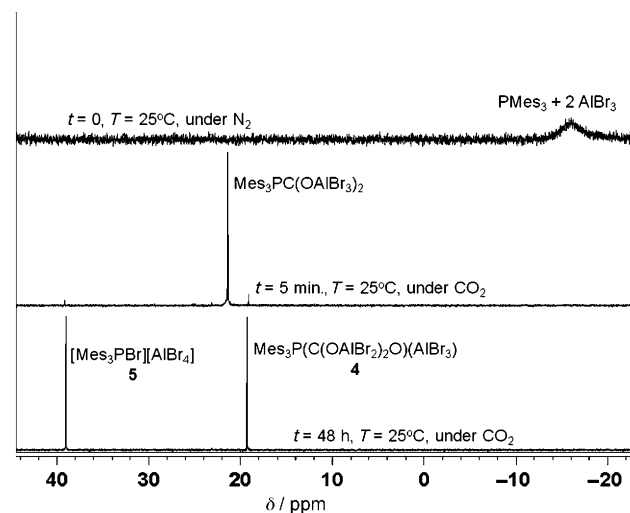


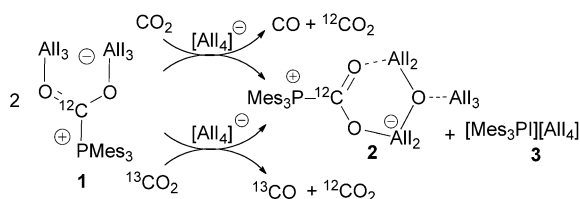
Figure 2. ³¹P{¹H} NMR spectra of PMes₃ and two equivalents of AlBr₃.

These spectral data seem to imply that the species **1** and Mes₃PC(OAlBr₃)₂ are intermediates en route to **2** and **3** and **4** and **5**, respectively. However, it is noteworthy that when **1** is isolated, this species is found to be stable at room temperature under atmospheres of N₂ or CO₂. Only at elevated temperature under CO₂ was the conversion of isolated **1** into **2** and **3** observed. Similarly, exposure of a solution of [C-**1**] to a ¹³CO₂ atmosphere showed no evidence of CO₂ exchange into **1** at room temperature. It is proposed that the reaction is initiated by thermal dissociation of AlX₃ from **1** or Mes₃PC(OAlBr₃)₂ to generate the species Mes₃PCO₂AlX₃. Such a species would be analogous to the previously reported and thermally unstable species *t*Bu₃PCO₂B(C₆F₅)₃.^[23] The inability

ity to observe or isolate this transient species is consistent with a recent computational report that shows $\text{Mes}_3\text{PCO}_2\text{AlCl}_3$ is about 35 kcal mol^{-1} less stable than $\text{Mes}_3\text{PC}(\text{OAlCl}_3)_2$.^[27] Further support for this postulate was derived from treatment of $[\text{C}^{13}]\text{-1}$ with excess PMes_3 under N_2 . This resulted in the appearance of a broad ^{31}P NMR resonance attributable to the adduct $\text{Mes}_3\text{P}(\text{AlI}_3)$ in rapid exchange. Furthermore, a new albeit weak resonance at 7 ppm was observed. The observation of a $\text{P}-^{13}\text{C}$ coupling of 120 MHz is consistent with the retention of the Mes_3PCO_2 fragment. While it is tempting to suggest that this transient species is $\text{Mes}_3\text{PCO}_2\text{AlI}_3$, all efforts to prepare or isolate this minor product were unsuccessful.

The experimentally observed reaction rates of formation of $\text{Mes}_3\text{P}(\text{C}(\text{OAlX}_2)_2\text{O})(\text{AlX}_3)$ qualitatively follow the trend $\text{I} > \text{Br} > \text{Cl}$. This suggests the barrier to reaction of $\text{Mes}_3\text{PC}(\text{OAlX}_3)_2$ increases with increasing Lewis acidity of AlX_3 . In stark contrast to the rapid formation of $\text{Mes}_3\text{P}(\text{C}(\text{OAlX}_3)_2(\text{X} = \text{Cl, Br, I}),$ the analogous chemistry with $\text{P}(o\text{-tol})_3$, AlI_3 , and CO_2 led to the very slow generation of the species $(o\text{-tol})_3\text{PC}(\text{OAlI}_3)_2$ (**6**). Furthermore, only on heating to 90°C under CO_2 was **6** seen to begin to react further. The slow formation of **6** and subsequent reaction with additional CO_2 are attributed to the greater stability of the Lewis acid-base adduct $(o\text{-tol})_3\text{P}(\text{AlI}_3)$ (**7**).

The solubility of **1** in $\text{C}_6\text{H}_5\text{Br}$ was found to be dramatically improved in the presence of the salt $[\text{Mes}_3\text{PMe}][\text{AlI}_4]$ (**8**). NMR data for a 1:1 mixture of **1** and **8** showed unchanged ^{31}P signals but broadened ^{27}Al resonances for the two species, suggesting rapid iodide exchange may account for the improved solubility. Exposing this combination of **1** and **8** to $^{13}\text{CO}_2$ prompts the formation of **2** and **3** at room temperature in approximately 5 h. The liberation of ^{13}CO was evidenced by ^{13}C NMR and FT-IR analysis however no appreciable ^{13}C incorporation into the CO_2 fragment of the product **2** was observed. This experiment was also confirmed in the reverse sense as employing $[\text{C}^{13}]\text{-1}$ gave $[\text{C}^{13}]\text{-2}$ and no evidence of liberated ^{13}CO (Scheme 1). This demonstrates that the PCO_2



Scheme 1. Labeling experiments for the formation of **2** and **3**.

fragment in **2** is derived from that in **1** and further that it is exogenous CO_2 that is reduced to CO and the oxygen atom in **2**.

Preliminary kinetic data were consistent with first-order dependence of the formation of **2** and **3** on both **1** and **8**. Kinetic data were obtained over a 30 K range (288–318 K) allowing the determination of the activation parameters: $\Delta H^\ddagger = 82(2) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -21(6) \text{ J mol}^{-1} \text{ K}^{-1}$. While these data infer an associative mechanism, suggesting that $[\text{AlI}_4]^-$ prompts degradation of **1** to generate free phosphine

and AlI_3 for conversion of **1** into **2**, the precise details of the conversion of **1** to **2** and **3** continue to be the subject of investigation.

In summary, we have described the room-temperature conversion of CO_2 into CO mediated by Al/P -based FLPs. The precise mechanistic details of the concurrent capture of the oxide in $\text{Mes}_3\text{P}(\text{C}(\text{OAlX}_2)_2\text{O})(\text{AlX}_3)$ continues to be the subject of study. Furthermore, we are targeting new systems for the catalytic reduction of CO_2 .

Experimental Section

All manipulations were performed under an atmosphere of dry, oxygen-free N_2 by means of standard Schlenk or glovebox techniques (Innovative Technology glovebox equipped with a -35°C freezer). NMR spectra were obtained on a Bruker Avance 400 MHz or a Varian NMR system 400 MHz spectrometer and spectra were referenced to residual solvent or an external reference. Chemical shifts (δ) are given in ppm and absolute values of the coupling constants are in Hz. IR spectra were collected on a Perkin-Elmer Spectrum One FT-IR instrument using a G-2 gas cell (10 cm long). Elemental analyses (C, H) were performed in house. The compound $[\text{Cp}^*\text{RuCl}(\text{PCy}_3)]$ was synthesized from $[(\text{Cp}^*\text{RuCl})_2]$ and PCy_3 by a literature procedure.^[28]

$\text{Mes}_3\text{PC}(\text{OAlI}_3)_2$ (**1**): The compound was synthesized in an analogous manner to the previously reported $\text{Mes}_3\text{P}(\text{CO}_2)(\text{AlX}_3)_2$ ($\text{X} = \text{Cl, Br}$).^[16] however, the compound was worked up 5 min. after addition of CO_2 to the FLP solution. The compound could be synthesized by combining PMes_3 (0.500 g, 1.29 mmol) and AlI_3 (1.05 g, 2.58 mmol) in bromobenzene (20 mL). Precipitation using hexanes (ca. 20 mL) afforded a white solid, which was filtered and dried on a frit. Yield of isolated product: 1.4 g (87%). ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 6.83$ (d, $^4J_{\text{H-H}} = 4.4 \text{ Hz}$, 3H, *m*-Mes), 6.70 (d, $^4J_{\text{H-H}} = 4.4 \text{ Hz}$, 3H, *m*-Mes), 2.48 (s, 9H, *o*- CH_3^{Mes}), 2.06 (s, 9H, *p*- CH_3^{Mes}), 1.90 ppm (s, 9H, *o*- CH_3^{Mes}). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 22.0$ ppm. ^{27}Al NMR (104 MHz, $\text{C}_6\text{D}_5\text{Br}$): $\delta = 20$ ppm (bs, $\nu_{1/2} = \text{ca. } 1500 \text{ Hz}$). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 167.8$ (d, $^1J_{\text{C-P}} = 119 \text{ Hz}$, CO_2), 146.5 (d, $^4J_{\text{C-P}} = 3.0 \text{ Hz}$, *p*- C_6H_2), 144.9 (d, $^2J_{\text{C-P}} = 11.6 \text{ Hz}$, *o*- C_6H_2), 144.4 (d, $^2J_{\text{C-P}} = 10.3 \text{ Hz}$, *o*- C_6H_2), 134.5 (d, $^3J_{\text{C-P}} = 12.2 \text{ Hz}$, *m*- C_6H_2), 133.7 (d, $^3J_{\text{C-P}} = 12.5 \text{ Hz}$, *m*- C_6H_2), 115.0 (d, $^1J_{\text{C-P}} = 74.5 \text{ Hz}$, *i*- C_6H_2), 25.5 (d, $^3J_{\text{C-P}} = 5.7 \text{ Hz}$, *o*- CH_3^{Mes}), 23.9 (d, $^3J_{\text{C-P}} = 5.2 \text{ Hz}$, *o*- CH_3^{Mes}), 21.2 ppm (d, $^2J_{\text{C-P}} = 1.5 \text{ Hz}$, *p*- CH_3^{Mes}). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 22.0$ ppm (d, $^1J_{\text{P-C}} = 119 \text{ Hz}$).

$[\text{Mes}_3\text{PX}][\text{AlX}_4]$, $\text{X} = \text{I}$ (**3**), $\text{X} = \text{Br}$ (**5**): These species were obtained in similar fashions and thus only one is detailed (see Supporting Information for further details). A 50 mL round-bottom Schlenk flask equipped with a magnetic stir bar was charged with PMes_3 (300 mg, 0.77 mmol) and AlI_3 (315 mg, 0.77 mmol). Toluene (20 mL) was added to this all at once. A solution of I_2 (196 mg, 0.77 mmol) in toluene (ca. 5 mL) was then added dropwise to this mixture. The mixture turned to a pale yellow oily solution and was allowed to stir for 30 min. The solvent was removed in vacuo to obtain a pale orange solid. The solid was stirred in hexanes (ca. 10 mL) for 10 min. and the mixture was filtered on a glass frit and washed with hexanes (ca. 5 mL) and dried (720 mg, 89%). **3**: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 6.82$ (d, $^4J_{\text{H-P}} = 4.4 \text{ Hz}$, 3H, *m*-Mes), 6.63 (d, $^4J_{\text{H-P}} = 6.0 \text{ Hz}$, 3H, *m*-Mes), 2.17 (s, 9H, *o*- CH_3^{Mes}), 2.12 (s, 9H, *p*- CH_3^{Mes}), 1.73 ppm (s, 9H, *o*- CH_3^{Mes}). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = -14.5$ ppm. ^{27}Al NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = -25$ ppm (s). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 146.4$ (d, $^4J_{\text{C-P}} = 3.4 \text{ Hz}$, *p*- C_6H_2), 145.4 (d, $^2J_{\text{C-P}} = 11.8 \text{ Hz}$, *o*- C_6H_2), 143.4 (d, $^2J_{\text{C-P}} = 12.1 \text{ Hz}$, *o*- C_6H_2), 133.4 (d, $^3J_{\text{C-P}} = 12.3 \text{ Hz}$, *m*- C_6H_2), 132.9 (d, $^3J_{\text{C-P}} = 12.3 \text{ Hz}$, *m*- C_6H_2), 119.3 (d, $^1J_{\text{C-P}} = 65.5 \text{ Hz}$, *i*- C_6H_2), 26.3 (d, $^3J_{\text{C-P}} = 6.4 \text{ Hz}$, *o*- CH_3^{Mes}), 24.4 (d, $^3J_{\text{C-P}} = 4.3 \text{ Hz}$, *o*- CH_3^{Mes}), 21.4 ppm (d, $^5J_{\text{C-P}} = 1.8 \text{ Hz}$, *p*- CH_3^{Mes}). **5**: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 6.87$ (d, $^4J_{\text{H-P}} = 4.4 \text{ Hz}$, 3H, *m*-Mes), 6.71 (d, $^4J_{\text{H-P}} = 6.4 \text{ Hz}$, 3H, *m*-Mes), 2.14 (s, 9H, *p*- CH_3^{Mes}), 2.13 (s, 9H, *o*- CH_3^{Mes}), 1.76 ppm (s, 9H, *o*- CH_3^{Mes}).

$^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 38.5$ ppm. ^{27}Al NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 81$ ppm (s). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 147.2$ (d, $^4J_{\text{C-P}} = 3.0$ Hz, $p\text{-C}_6\text{H}_5$), 145.4 (d, $^2J_{\text{C-P}} = 10.3$ Hz, $o\text{-C}_6\text{H}_5$), 143.7 (d, $^2J_{\text{C-P}} = 15.4$ Hz, $o\text{-C}_6\text{H}_5$), 133.7 (d, $^3J_{\text{C-P}} = 12.1$ Hz, $m\text{-C}_6\text{H}_5$), 133.2 (d, $^3J_{\text{C-P}} = 13.5$ Hz, $m\text{-C}_6\text{H}_5$), 119.0 (d, $^1J_{\text{C-P}} = 74.4$ Hz, $i\text{-C}_6\text{H}_5$), 24.9 (d, $^3J_{\text{C-P}} = 6.2$ Hz, $o\text{-CH}_3^{\text{Mes}}$), 24.4 (d, $^3J_{\text{C-P}} = 5.5$ Hz, $o\text{-CH}_3^{\text{Mes}}$), 21.5 ppm (d, $^5J_{\text{C-P}} = 1.5$ Hz, $p\text{-CH}_3^{\text{Mes}}$).

Generation of $\text{Mes}_3\text{P}(\text{C}(\text{OAlEt}_2)_2\text{O})(\text{AlEt}_3)$ (**2**) and $[\text{Mes}_3\text{P}][\text{AlEt}_4]$ (**3**) with reduction of CO_2 : A 100 mL Schlenk bomb equipped with a Teflon cap and a magnetic stirbar in the glovebox was charged with PMes_3 (0.5 g, 1.29 mmol) and AlEt_3 (1.0 g, 2.45 mmol). Bromobenzene (20 mL) or fluorobenzene (20 mL) was added to this all at once. (NOTE: Product isolation was greatly facilitated by using fluorobenzene owing to its lower boiling point; however, the reaction was faster in bromobenzene). The bomb was transferred to the Schlenk line equipped with a CO_2 outlet. The bomb was degassed at room temperature, filled with CO_2 (ca. 2 atm.), and sealed. The solution was stirred rapidly overnight (ca. 16 h for bromobenzene) or for 4 days (for fluorobenzene) in the glovebox, resulting in a change in color from purple to dark yellow. The solvent was then removed in vacuo, and hexanes (ca. 10 mL) was added to the residue. The precipitate was rapidly stirred for about 10 min. and then filtered on a glass frit. A 1:1 mixture of **2** and **3** was obtained (1.35 g).

Isolation of **2** and **4**: These species were obtained in a similar manner and thus only one is detailed (see Supporting Information for further details). Small portions of **2** could be separated from a 1:1 mixture of **2**:**3** (above) by slow cooling a fluorobenzene solution to -38°C . Crystals obtained were suitable for X-ray crystallography. The crystals were partly soluble in deuterated bromobenzene. **2**: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 7.09\text{--}6.83$ (m, 7–8H, $1.5\text{-C}_6\text{H}_5\text{F}$), 6.82 (bs, 3H, $m\text{-Mes}$), 6.70 (bs, 3H, $m\text{-Mes}$), 2.33 (bs, 9H, $o\text{-CH}_3^{\text{Mes}}$), 2.06 (s, 9H, $p\text{-CH}_3^{\text{Mes}}$), 1.83 ppm (bs, 9H, $o\text{-CH}_3^{\text{Mes}}$). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 19.5$ ppm. ^{27}Al NMR (104 MHz, $\text{C}_6\text{D}_5\text{Br}$): $\delta = 31$ ppm (bs, $\nu_{1/2} = \text{ca. } 170$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = 173.9$ (d, $^1J_{\text{C-P}} = 118$ Hz, CO_2), 162.8 (d, $^1J_{\text{C-F}} = 244$ Hz, $i\text{-C}_6\text{H}_5\text{F}$), 147.0 (d, $^4J_{\text{C-P}} = 3.0$ Hz, $p\text{-C}_6\text{H}_5$), 144.7 (bs, 2C, $o\text{-C}_6\text{H}_5$), 133.5 (bs, 2C, $m\text{-C}_6\text{H}_5$), 130.0 (d, $^3J_{\text{C-F}} = 7.7$ Hz, $m\text{-C}_6\text{H}_5\text{F}$), 124.1 (d, $^4J_{\text{C-F}} = 3.1$ Hz, $p\text{-C}_6\text{H}_5\text{F}$), 115.3 (d, $^2J_{\text{C-F}} = 20.6$ Hz, $o\text{-C}_6\text{H}_5\text{F}$), 113.6 (d, $^1J_{\text{C-P}} = 76.2$ Hz, $i\text{-C}_6\text{H}_5$), 26.0 (bs, $o\text{-CH}_3^{\text{Mes}}$), 23.8 (bs, $o\text{-CH}_3^{\text{Mes}}$), 21.3 ppm (s, $p\text{-CH}_3^{\text{Mes}}$). ^{19}F NMR ($\text{C}_6\text{D}_5\text{Br}$): $\delta = -112.4$ ppm. **4**: ^1H NMR (CD_2Cl_2): $\delta = 7.52\text{--}7.24$ (m, 5H, $\text{C}_6\text{H}_5\text{Br}$), 7.17 (bs, 6H, $m\text{-Mes}$), 2.41 (s, 9H, $p\text{-CH}_3^{\text{Mes}}$), 2.32 (bs, 9H, $o\text{-CH}_3^{\text{Mes}}$), 2.11 ppm (bs, 9H, $o\text{-CH}_3^{\text{Mes}}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 19.5$ ppm. ^{27}Al NMR (104 MHz, CD_2Cl_2): $\delta = 88$ ppm (bs). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 176.8$ (d, $^1J_{\text{C-P}} = 123$ Hz, CO_2), 147.9 (d, $^4J_{\text{C-P}} = 3.0$ Hz, $p\text{-C}_6\text{H}_5$), 145.5 (bd, $^2J_{\text{C-P}} = 11$ Hz, $o\text{-C}_6\text{H}_5$), 134.0 (bd, $^3J_{\text{C-P}} = 12.4$ Hz, $m\text{-C}_6\text{H}_5$), 131.9 (s, $\text{C}_6\text{H}_5\text{Br}$), 130.5 (s, $\text{C}_6\text{H}_5\text{Br}$), 127.4 (s, $\text{C}_6\text{H}_5\text{Br}$), 122.7 (s, $\text{C}_6\text{H}_5\text{Br}$), 113.7 (d, $^1J_{\text{C-P}} = 76.6$ Hz, $i\text{-C}_6\text{H}_5$), 25.1 (bs, $o\text{-CH}_3^{\text{Mes}}$), 24.3 (bs, $o\text{-CH}_3^{\text{Mes}}$), 21.5 ppm (d, $^5J_{\text{C-P}} = 1.6$ Hz, $p\text{-CH}_3^{\text{Mes}}$).

Quantification of CO: A 50 mL Schlenk bomb equipped with a Teflon cap and a magnetic stirbar in the glovebox was charged with PMes_3 (50 mg, 0.13 mmol) and AlEt_3 (100 mg, 0.24 mmol). Bromobenzene (2 mL) was added to this all at once. The bomb was transferred to the Schlenk line equipped with a CO_2 outlet. The bomb was degassed at room temperature, filled with CO_2 (ca. 2 atm.) and sealed. The solution was stirred rapidly for ca. 16 h in the glovebox, and the solution color changed from purple to dark yellow. A second 50 mL Schlenk bomb equipped with a Teflon cap and a magnetic stirbar was charged with $[\text{Cp}^*\text{RuCl}(\text{PCy}_3)]$ (71 mg, 0.13 mmol) in $[\text{D}_8]\text{toluene}$ (1 mL) and was attached to the outlet of the first Schlenk bomb by a short piece of Tygon tubing (see the Supporting Information,

Figure S3). Both flasks were open to each other and allowed to stir for ca. 3 h. The solution containing the ruthenium complex was then analyzed by ^{31}P NMR spectroscopy and the ratios integrated (see the Supporting Information), which indicated a 61:39 mixture of $[\text{Cp}^*\text{RuCl}(\text{PCy}_3)]$: $[\text{Cp}^*\text{RuCl}(\text{PCy}_3)(\text{CO})]$.

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