

Room Temperature Reduction of CO₂ to Methanol by Al-Based Frustrated Lewis Pairs and Ammonia Borane

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In the past several decades, increasing levels of carbon dioxide in the atmosphere have been a major contributing factor to recent global warming and climate change. With the current global concentration likely surpassing those of the past 2.1 million years,¹ the rapid rise in CO₂ levels since the industrial revolution prompts efforts to limit CO₂ emissions to avoid potentially devastating impacts on the climate.² The sequestration of CO₂³ or its direct use as a C₁ feedstock⁴ are both possible means of reducing the release of this greenhouse gas. However, a more general statement of the problem from a chemical perspective is the limited known reactivity of CO₂.

Recently, we have reported the concept of “frustrated Lewis pairs” (FLPs) where steric congestion precludes combinations of Lewis acids and Lewis bases from forming classical Lewis acid–base adducts.⁵ Such FLPs have been shown to undergo remarkable reactivity, including the reversible activation of H₂,⁶ B–H⁷ and N–H⁸ bond activation, THF ring-opening,⁹ addition to olefins¹⁰ or alkynes,¹¹ and metal-free hydrogenation of functional groups such as imines,¹² nitriles,^{12a,b} aziridines,^{12a,b} enamines,¹³ and silylenoethers.¹⁴ Most recently, we have also discovered the reactivity of FLPs with CO₂¹⁵ and N₂O.¹⁶ While the capture of N₂O results in quite robust products, the capture of CO₂ by these phosphine–borane systems is easily reversible. As part of our ongoing program in FLP chemistry, we have explored related reactivity of more commonly available Lewis acids. Aluminum halides (X = Cl or Br) are indeed readily available and inexpensive.¹⁷ Herein, we report the irreversible capture of CO₂ using AlX₃ (X = Cl or Br) with PMes₃ (Mes = 2,4,6-C₆H₂Me₃). This combination of a Lewis acid and base exhibits both classical and FLP characteristics.¹⁸ Moreover these combinations react with CO₂ irreversibly in an acid–base ratio of 2:1. Remarkably, these species also react rapidly with excess ammonia borane at room temperature to give CH₃OH upon quenching with water.

A 1:1 solution of PMes₃/AlX₃ (X = Cl **1**, Br **2**)¹⁹ in bromobenzene reacts to form weak Lewis adducts. This is evidenced by the very broad multiplet in the ³¹P{¹H} NMR spectrum in the –10 to –20 ppm region, which is significantly downfield of the resonance derived from PMes₃ (–35 ppm). In addition, these adducts give rise to broad doublets in the ²⁷Al NMR spectra (**1**: 110 ppm, *J*_{Al–P} = 258 Hz; **2**: 100 ppm, *J*_{Al–P} 222 Hz). The broadness in these resonances is attributable to an equilibrium involving free phosphine and AlX₃. Attempts to acquire temperature dependent NMR data were precluded by the poor solubility in most solvents and the limited temperature range accessible in bromobenzene. Nonetheless, these classical Lewis adducts could be isolated in 81 and 84% yields, respectively. These species were fully characterized spectroscopically. In both cases, the ¹H NMR spectra show resonances indicating that the *ortho*-methyl groups and *meta*-H atoms of the mesityl groups are inequivalent, consistent with a significant barrier to rotation of the mesityl rings. This notion is further supported by the solid state structures of **1** and **2** in which the mesityl rings are

shown to adopt propeller-like orientations (Figure 1). The P–Al bond distances in **1** and **2** were found to be 2.5239(11) and 2.5360(10) Å, respectively. This compares to the literature values of 2.58(2) Å predicted on the basis of a solid state NMR study.²⁰

The inference of equilibria involving the formation of **1** and **2** suggests these classical Lewis pairs can dissociate and exhibit FLP-type reactivity. To probe this postulate, these solutions were exposed to 1 atm of CO₂ in C₆D₅Br in sealed J-Young NMR tubes. In both cases, monitoring of the reactions by NMR spectroscopy showed the liberation of PMes₃ and the formation of new products in approximate 1:1 ratios. The new species gave rise to ³¹P{¹H} NMR signals at 20 and 22 ppm for the reactions of **1** and **2**, respectively. ¹H NMR spectra also showed broad peaks in the methyl and aromatic regions suggesting the possibility of exchange of free PMes₃ and the newly formed compounds **3** and **4**, respectively. The generation of free phosphine further suggests that the stoichiometry of reaction of CO₂ with the adducts **1** and **2** is not 1:1. Thus, 1:2 mixtures of PMes₃/AlX₃ were prepared and reacted with CO₂. These reactions yielded the immediate formation of the previously observed **3** and **4**, with no evidence of free PMes₃. These compounds were subsequently isolated in 82 and 83% yields.¹⁹ While the spectroscopic data were consistent with the inclusion of the constituents, the structures of these products were ultimately identified by X-ray crystallographic studies. These products, formulated as Mes₃P(CO₂)(AlX₃)₂ (X = Cl **3**; Br **4**) (Figure 1) were comprised of phosphine bound to the C-atom of CO₂ while AlX₃ units are bonded to each of the O-atoms. The resulting P–C bond lengths in **3** and **4** were found to be 1.927(8) and 1.918(5) Å, respectively, while the O–Al distances were 1.807(5) and 1.808(6) Å in **3** and 1.829(4) and 1.803(3) Å in **4**. The C–O bond lengths were determined to be 1.233(8) and 1.251(8) Å in **3** and equivalent at 1.248(6) Å in **4**. The C–O bond lengths are significantly longer than terminal C=O bonds in *t*Bu₃PCO₂(B(C₆F₅)₃) (1.2081(15) Å) and Mes₂PCH₂CH₂B(C₆F₅)₂(CO₂) (1.209(4) Å).¹⁵ Nonetheless, the C–O in **3** and **4** are shorter than the 1.2988(15) and 1.284(4) Å of C–O–B linkages seen in these phosphine borane derivatives.¹⁵ This is consistent with the greater Lewis acidity of the borane fragments in these species in comparison to the aluminum halides in **3** and **4**. The similarity of the two C–O bond distances is consistent with delocalization of the formal negative charge over the C(OAlX₃)₂ fragments. The O–C–O angles are 126.6(7)° and 125.8(4)° in **3** and **4**, respectively, while the C–O–Al angles differed substantially from each other being 141.3(5)° and 165.2(6)° and 140.0(3)° and 178.7(4)° in **3** and **4**, respectively.

The binding of both O-atoms to Al in **3** and **4** clearly has an impact on the C–O bond strength. IR spectra do not reveal a clear or typical C=O stretch, and the vibration could not be assigned. This is consistent with the remarkable stability of **3** and **4** to CO₂ loss even on heating to 80 °C under a vacuum. These results are at first glance surprising since these systems employ markedly less Lewis acidic and basic components than the phosphine/borane

adducts $t\text{Bu}_3\text{PCO}_2\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2(\text{CO}_2)$ which rapidly lose CO_2 at 80 and -20 °C, respectively.¹⁵ The formation of two Al–O in **3** and **4**, as opposed to one B–O bond in the latter cases, could explain this enhanced stability. This is a rare example of double activation of CO_2 , although similar systems have been proposed.²¹

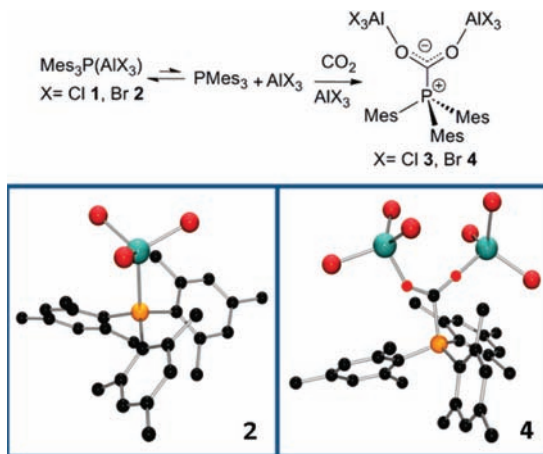
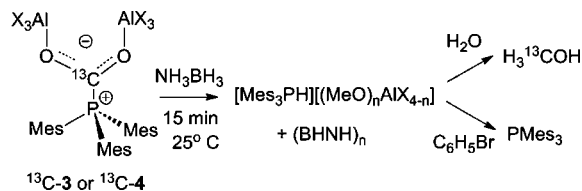


Figure 1. Synthesis of **1–4** and POV-ray depictions of **2** and **4**; H atoms are omitted. C, black; P, orange; F, pink; Al, teal; Br, scarlet.

The reaction of **3** or **4** with excess ammonia borane (H_3NBH_3) (3 equiv) was initially monitored by ^{31}P NMR spectroscopy. In less than 15 min, the resonance arising from the starting material was replaced with a new signal at -26 ppm with a P–H coupling constant of 475 Hz. This was attributable to generation of the cation $[\text{Mes}_3\text{PH}]^+$. To garner further information on the nature of this reaction, the isotopologues ^{13}C -**3** and ^{13}C -**4** were prepared. The ^{13}C resonances for these species are observed at 172 and 173 ppm, each with a $J_{\text{P}-\text{C}}$ of 123 and 119 Hz, respectively. Upon reaction of ^{13}C -**3** or ^{13}C -**4** with H_3NBH_3 , ^{11}B NMR spectral data indicate dehydrogenation of H_3NBH_3 to borazine and other products²² while the ^{31}P NMR spectra indicate the formation of $[\text{Mes}_3\text{PH}]^+$. The ^{13}C NMR spectra showed the loss of the CO_2 signal derived from **3/4** and the appearance of approximately 4 quartet resonances between 50–65 ppm with a $J_{\text{C}-\text{H}}$ of 146–149 Hz.¹⁹ Integration of these signals shows they account for approximately 60 and 64% of the ^{13}C in the precursor. These data infer the formation of Al-methoxy species which are unstable with respect to ligand redistribution (Scheme 1). This view is supported by the isolation of crystals of $[\text{Mes}_3\text{PH}][\text{AlBr}_4]^{19}$ from a reaction mixture, albeit in low yield.

Following quenching of the reaction with D_2O , the organic phase was shown to contain free PMes_3 by ^{31}P NMR spectroscopy while the aqueous phase exhibited a ^{13}C resonance as a quartet at 49 ppm ($J_{\text{C}-\text{H}} = 142$ Hz), identical to an authentic sample of CH_3OH in D_2O .¹⁹ The yield of CH_3OH , quantified by integration relative to an internal standard, 1,4-dioxane, showed average extracted yields of 37–51%.¹⁹ While the second O-atom is thought to be incorporated into Al byproducts, its precise fate remains unknown at this time. Nonetheless these data demonstrate the reduction of the FLP-activated CO_2 to CH_3OH . In a very recent report, Ashley et al.²³ showed the tetramethylpiperidine/ $\text{B}(\text{C}_6\text{F}_5)_3$ FLP effected conversion of CO_2/H_2 to CH_3OH in 24% yield in 6 days at 160 °C.

Scheme 1. Stoichiometric Reduction of **3** or **4** to CH_3OH



In summary, we have described the rapid, room temperature conversion of FLP-activated CO_2 to CH_3OH using ammonia borane as the hydrogen source. The mechanism of this reduction and the development of new catalytic FLP systems are the subject of current efforts.

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Supporting Information Available: Experimental, NMR, analytical, and X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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