A Tris(triphenylphosphine)aluminum Ambiphilic Precatalyst for the Reduction of Carbon Dioxide with Catecholborane

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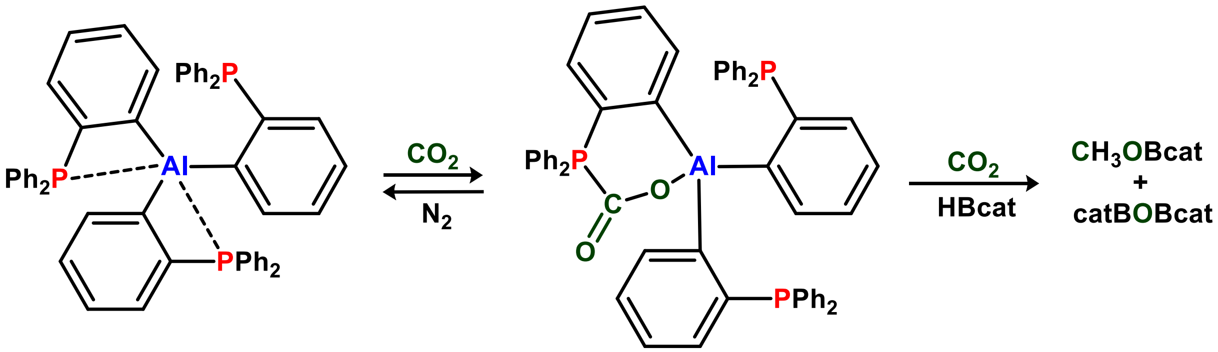
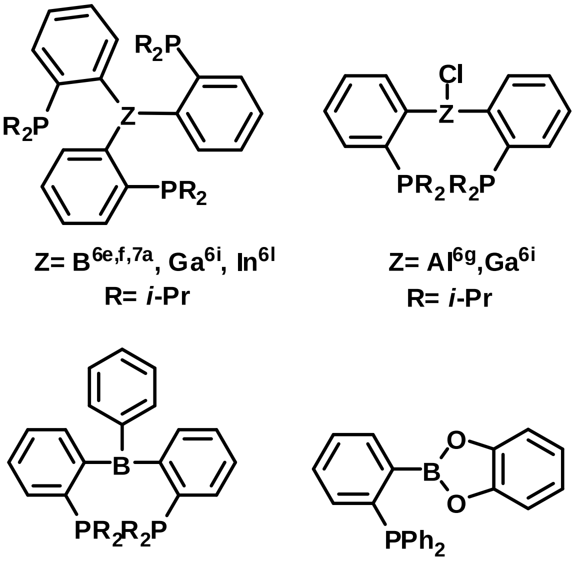


Abstract

Ambiphilic species $Al(C_6H_4(o\text{-}PPh_2))_3$ (**2**) was synthesized and fully characterized, notably using X-ray diffraction. Species **2** exhibits pseudo-bipyramid trigonal geometry caused by the two Al-P interactions. **2** reacts with CO_2 to generate a CO_2 adduct commonly observed in the activation of CO_2 using Frustrated Lewis Pairs (FLPs). This ambiphilic species serves as a precatalyst for the reduction of CO_2 in presence of catecholborane (HBcat) to generate CH_3OBcat, which can be readily hydrolyzed in methanol. The reaction mixture confirms that in presence of HBcat, **2** generates known CO_2 reduction catalyst 1-Bcat-2-PPh_2-C_6H_4 (**1**) and intractable catecholate aluminum species. It was however possible to isolate a single-crystal of $Al(\kappa^2_{O,O}\text{-}(MeO)_2Bcat)_3$ (**5**) supporting this hypothesis. Also, the borane protected analogue of **2**, $Al(C_6H_4(o\text{-}PPh_2.BH_3))_3$ (**4**), does not react with catecholborane, suggesting the influence of the pending phosphines in the transformation of **2** into **1**.

Introduction

Ambiphilic compounds containing both Lewis acid and Lewis base moieties in the same molecular framework, most notably containing group XIII and XV elements, have generated growing interest in the past decade for a myriad of applications. These molecules, including the well-known “Frustrated Lewis Pairs (FLPs)”,[1] have been used as multi-center catalysts,[2] as precursors for nonlinear optical materials and sensors,[3] for activating small molecules,[4] and as ligands for transition metals.[5,6] A particularly interesting design of ambiphilic molecule is the phosphine borane derivatives that have been developed over the past few years mostly by Bourissou *et al.*[6,7] These mono-, bis-, and tris-phosphine species demonstrated versatile coordination modes to transition metal centers, notably as Z-type ligands for transition metals (Figure 1).[8] More recently, monophosphine boranes have shown impressive reactivity in singlet dioxygen activation,[7d] in the catalytic Michael addition reaction,[7e] and in trapping reactive intermediates of organic transformations.[7b] Whereas borane ambiphilic molecules have been extensively studied over the past decade, the reactivity of aluminum-containing ambiphilic molecules has not garnered much attention, notably because of the synthetic challenges associated with their synthesis and their kinetic instability.[4f-h;5d,j,t; 9] Nevertheless, such compounds have demonstrated interesting potential in the activation of small molecules and in catalysis.



Z= B^{6e,f,7a}, Ga^{6i}, In^{6l}
R= *i*-Pr

Z= Al^{6g},Ga^{6i}
R= *i*-Pr

R= Ph$^{6c.6m}$, *i*-Pr$^{6a,c,d,5x-y}$

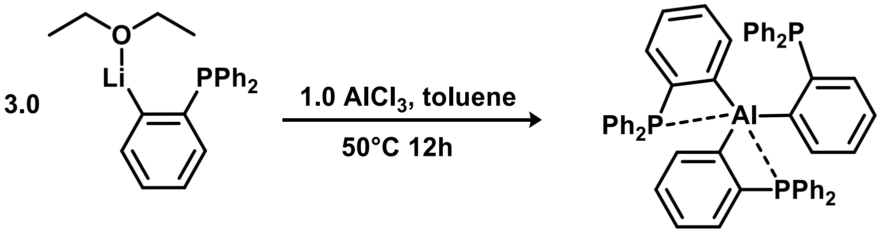
1^{15}

Figure 1. Some previously reported aryl bridged ambiphilic compounds

One area where ambiphilic molecules could have a significant impact is in the activation and functionalization of carbon dioxide. The latter molecule possesses both an electrophilic carbon atom and nucleophilic oxygen atoms, thereby acting as an ambiphilic substrate. In a seminal report, Stephan and Erker have demonstrated that ambiphilic FLPs are efficient in the activation of carbon dioxide.[10] Since then, a large variety of ambiphilic and FLP systems have been shown to be active in carbon dioxide capture.[4f-g;11] However, there are only a handful of ambiphilic systems able to functionalize carbon dioxide into value added chemicals. It has been shown that the FLP system consisting of $PMes_3/AlX_3$, (Mes = mesityl, X=Cl, Br) can reduce CO_2 to methanol using $BH_3.NH_3$ as hydrogen source.[12] It was also shown that that CO_2 could be hydrogenated using $TMP/B(C_6F_5)_3$ (TMP = 2,2,6,6-tetramethylpiperidine).[13] However, these two systems have limited use since they require stoichiometric amounts of FLPs. Using TMP and $B(C_6F_5)_3$, Piers has demonstrated the catalytic reduction of carbon dioxide using Et_3SiH, but with low turnovers.[14] In a recent breakthrough, our research group demonstrated that molecule 1-

Bcat-2-PPh_2-C_6H_4 (**1**) (cat = catechol), with modest Lewis acid and basic ambiphilicity, acts as a catalyst for CO_2 reduction in presence of hydroboranes to generate methoxyboranes which can be readily hydrolyzed into methanol.[15] In order to broaden the scope of such systems, we were curious to see the effect of using an aluminum center enclosed in a tris-arylphosphine scaffold. Herein, we report the preparation of a novel tri-phosphine organoalane $Al(C_6H_4(o\text{-}PPh_2))_3$ (**2**) which can reversibly bind carbon dioxide under ambient conditions. Species **2** can be used as a precatalyst for the reduction of CO_2 in presence of cathecolborane (HBcat), generating catalyst **1** and aluminum catecholate species, including $Al(\kappa^2{}_{O,O}\text{-}(MeO)_2Bcat)_3$ (**5**) which was structurally characterized.

Results and discussion



2

Scheme 1. Synthesis of $Al(C_6H_4(o\text{-}PPh_2))_3$ (**2**)

By using the reaction pathway illustrated in Scheme 1, the ambiphilic species $Al(C_6H_4(o\text{-}PPh_2))_3$ (**2**) was synthesized in 76% yield from previously reported o-lithiated triphenylphosphine.[16] Colorless crystals of **2** suitable for X-ray diffraction studies were obtained from toluene at -40°C. According to the results of single-crystal X-ray diffraction analysis, **2** crystallized in the $\boldsymbol{P}_{-1}$ space group with two crystallographic independent molecules in the asymmetric unit (one of the two independent molecules is shown in Figure 2). **2** adopts a distorted trigonal bipyramid geometry in the solid state with two Al-C-C-P four-membered rings. The trigonal bipyramid of AlC_3P_2 in the first molecule (Al1) is more distorted than that of the second one (Al2). The Al-C bond lengths in the first molecule range from 1.976(2) to 2.005(3) Å, which are comparable to those observed in similar structures, and the two Al-P bond lengths are significantly different from each other (2.630(1) and 2.820(1) Å). The P1-Al1-P3 angle of 155.56 (3)° is far from the ideal value of 180°. The distance between Al1 and the third phosphorous atom (3.408(1) Å) is too important to exhibit significant bonding interaction. The most important difference between the two independent molecules is that the longer of the two bonding Al-P interactions is significantly shorter in the second molecule (2.726(1) Å) than in the first one (2.820(1) Å). As a consequence, the coordination environment around Al2 is more crowded than in the first molecule which leads to the third phosphine moiety being pushed away from the metal centre (Al2-P5 distance of 3.438(1) Å). The other bond lengths in the second molecule are quite similar to the first one.

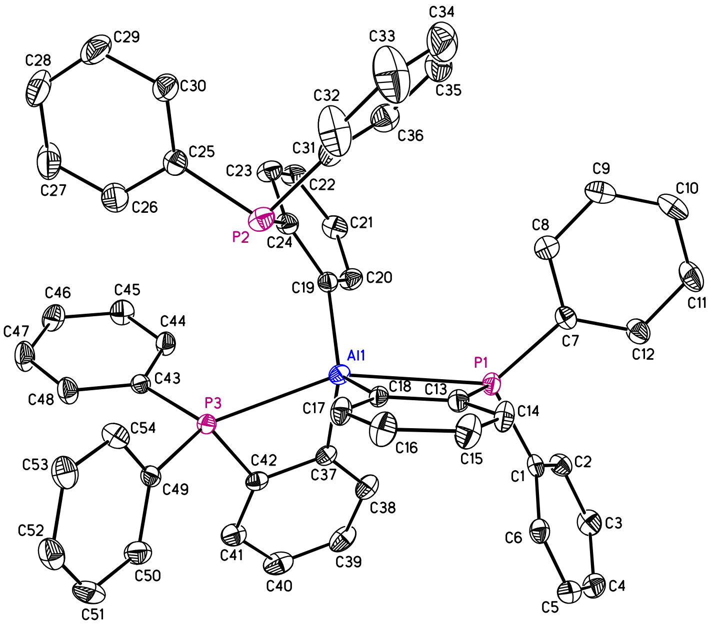


Figure 2 - ORTEP drawing of the first molecule of **2** in the asymmetric unit cell, with anisotropic atomic displacement ellipsoids shown at the 50% probability level. The other molecule is illustrated in Figure S3. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1-P1 = 2.8197(9); Al1-P3 = 2.6305(9); Al1-C19 = 1.976(2); Al1-C18 = 1.992(2); Al1-C37 = 2.005(2) Å; C19-Al1-C18 = 128.11(10); C19-Al1-C37 = 113.71(9); C18-Al1-C37 = 117.52(9); C19-Al1-P3 = 102.05(7); C18-Al1-P3 = 104.27(7); C37-Al1-P3 = 67.52(7); C19-Al1-P1 = 101.61(7); C18-Al1-P1 = 64.82(6); C37-Al1-P1 = 97.20(7); P3-Al1-P1 = 155.56(3).

Müller and colleagues published one similar structure, $Al\{C_6H_4[o\text{-}CH_2P(Ph)_2]\}_3$, in which the trigonal bipyramid of AlC_3P_2 was less distorted, with a P1-Al1-P2 bond angle of 164.78(8)^o.[17] Such discrepancy can be attributed to the flexibility of the five-membered rings around the central aluminum atom in $Al\{C_6H_4[o\text{-}CH_2P(Ph)_2]\}_3$ compared to the four-membered rings in **2**.

The P1-Al and P2-Al bond distances of respectively 2.676(3) Å and 2.782(2) Å in the complex reported by Müller are quite comparable to that of **2**, but the P3-Al distance (4.440(6) Å) is much longer. Similar bond distances of 2.66 and 2.78 Å have also been reported by Bourissou.[6g] Only a handful of structures with two or three four-membered rings containing aluminum and non-metal elements have been reported.[18]

The $^{31}P\{^{1}H\}$ NMR spectrum of **2** in a benzene-d_6 solution shows one sharp singlet at -1.5 ppm indicating a fast exchange process between all the phosphines. In order to assess this fluxional process, variable temperature NMR experiments were performed using a 0.07 M solution of **2** in toluene-d_8 down to – 100° C. It was observed that the single peak for **2** started to broaden at -90°C, indicative of the slowing of the exchange process. However, it was not possible to go at lower temperature because of the freezing temperature of toluene. Nevertheless, it is possible to compare this data with the report by Müller on $Al\{C_6H_4[o\text{-}CH_2P(Ph)_2]\}_3$.[17] Indeed, in the latter complex, the broadening appears at -80°C suggesting that the tension in the four-membered rings in **2** induce a more dynamic behaviour than in the species with five-membered rings. In order to explore the bonding feature in **2**, DFT calculations at the B3PW91, 6-31G** level of theory were performed. As shown in Figure 3, the shortest P-Al bond is of 2.73 Å in the optimized structure, while the distance between the *trans* P atom and Al is slightly longer (2.82 Å). The non-interacting P atom is 3.47 Å away from the aluminum centre. These values are strikingly similar to those found in the solid state and reflect the accuracy of the model. According to the NBO calculations, the bond orders were of 0.3293, 0.2536, and 0.0639 for the shortest to the longest Al-P bond lengths, respectively. It indicates that the two shorter Al-P distances have partial bonding, whereas no bond is observed with the last phosphine.

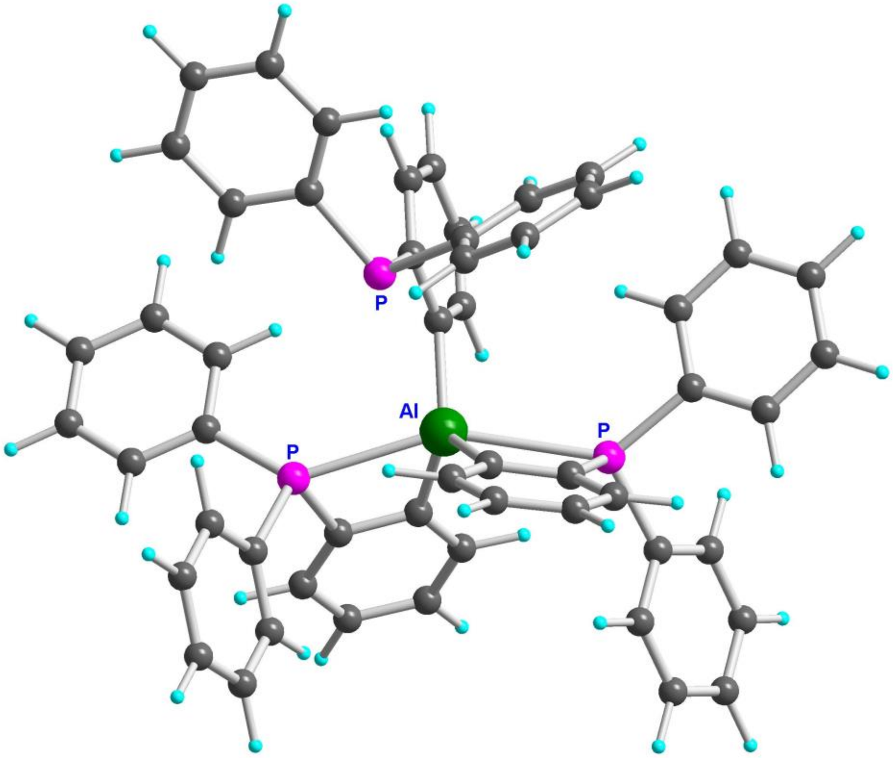
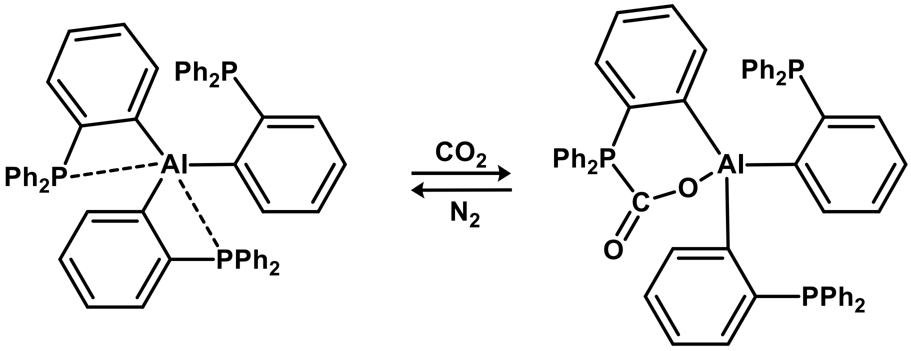


Figure 3. Optimized structure of **2** using DFT calculations at the B3PW91, 6-31G** level of theory. Selected bond lengths [Å] and angles [°]: Al1-P1 = 2.85; Al1-P3 = 2.69; Al1-C19 = 2.00; Al1-C18 = 2.00; Al1-C37 = 2.01 Å; C19-Al1-C18 = 123.6; C19-Al1-C37 = 114.9; C18-Al1-C37 = 120.6; C19-Al1-P3 = 104.0; C18-Al1-P3 = 105.5; C37-Al1-P3 = 67.0; C19-Al1-P1 = 101.0; C18-Al1-P1 = 64.6; C37-Al1-P1 = 96.7; P3-Al1-P1 = 154.2.

This interesting fluxional behavior prompted us to study the reactivity with carbon dioxide since the phosphine centers could still be available for CO_2 coordination. When a 0.03 M solution of **2** in benzene-d_6 was exposed to 1 atmosphere of CO_2 at room temperature, a reaction took place immediately leading to two new signals in the $^{31}P\{^1H\}$ NMR spectrum, a doublet at -5.1 ppm and a triplet at -6.2 ppm integrating for two and one phosphorous atoms, respectively, both with a small $J_{P\text{-}P}$ of 3.2 Hz. To our knowledge, this species represents the first report of an aryl bridged *o*-aryl ambiphilic CO_2 adduct.



2 **3**

Scheme 2. Generation of **3** upon exposure of **2** to CO_2

In order to find out if one or two CO_2 molecules could coordinate to **2**, the synthesis of **3** was carried out in presence of $^{13}CO_2$, generating **3-^{13}C**. The resulting $^{31}P\{^1H\}$ NMR spectrum showed splitting of the triplet signal to a doublet of triplets with $^1J_{C\text{-}P}$= 102 Hz while the doublet remained unchanged, thus suggesting that only one CO_2 molecule can interact with the aluminum species. The $^{13}C\{^1H\}$ NMR spectrum exhibited a new signal at 159.5 ppm, reminiscent of activated CO_2, also with a $^1J_{P\text{-}C}$ of 102 Hz, confirming that the new product arises from a single CO_2 coordination.[4g] However, as no additional coupling with the other two phosphorous atoms were observed for the ^{13}C atom, we were curious to see what caused the additional 3.2 Hz $J_{P\text{-}P}$ coupling in **3**. Since the isolation at the solid state of **3** was not possible, the structure of the CO_2 adduct was determined using DFT. The enthalpy profile determined by DFT calculations showed that the formation of **3** is favorable by 4.1 kcal/mol with respect to free **2** and CO_2, which is in accordance with the experimental results (Figure 4). The NBO analysis did not show any significant bonding interaction to be present between the phosphine centres and the aluminum core (values of 0.0372, 0.0131, and 0.0874). Therefore, the origin of the coupling is not arising from $^3J_{P\text{-}P}$ or $^5J_{P\text{-}P}$ scalar couplings through Al-P interactions, but presumably from a

$^{6}J_{P\text{-}P}$ scalar interaction through the *P*-C=C-Al-C=C-*P* backbone, although through-space interactions cannot be excluded.[19]

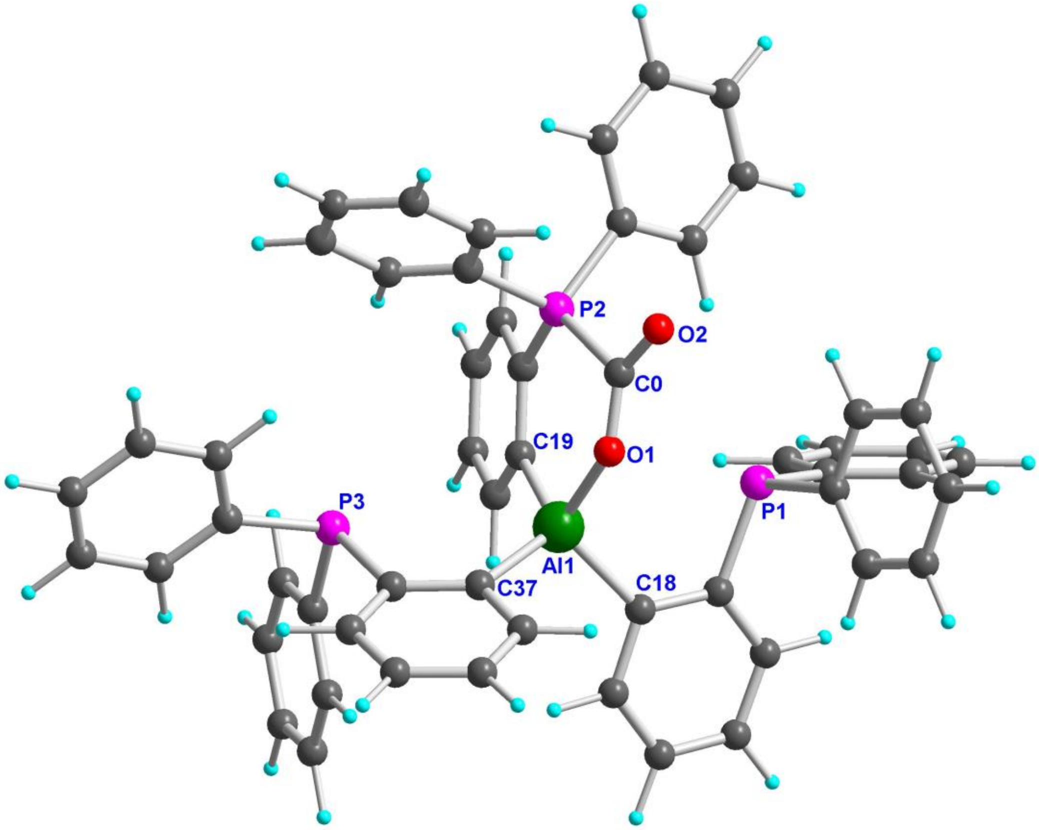


Figure 4. Optimized structure of **3** using DFT calculations at the B3PW91, 6-31G** level of theory. Selected bond lengths [Å] and angles [°]: Al1-P1 = 3.48; Al1-P3 = 3.64; Al1-C19 = 2.01; Al1-C18 = 2.00; Al1-C37 = 2.00; Al1-O1 = 1.86; P2-C0 = 1.94; C0-O1 = 1.27; C0-O2 = 1.21 Å; C19-Al1-C18 = 107.7; C19-Al1-C37 = 122.9; C18-Al1-C37 = 109.6; O1-C0-O2 = 130.9; O1-C0-P2 = 116.3; O2-C0-P2 = 112.6; O1-Al1-C18 = 111.6; O1-Al1-C19 = 103.2; O1-Al1-C37 = 101.4.

After removing the volatiles from the J-Young NMR tube under vacuum for 1 hour and dissolving in *ca.* 0.6 mL of benzene-d_6, multinuclear NMR spectroscopy revealed complete conversion of **3** back to **2**. Alternately, leaving a solution of **3** under nitrogen for 12 hours resulted in a mixture of **2** and **3** in approximately 5:1 ratio (according to the values of NMR integration). These results demonstrate that the CO_2 adduct is reversible, and suggest a fluxional behavior between the CO_2 adduct and free **3**, a well-known behavior in the ambiphilic activation of carbon dioxide.[10] More interestingly, none of the previously reported aluminum based ambiphilic molecules are known to give-up CO_2 at room temperature in solution at room temperature.[4g,f,12] Leaving the solution under nitrogen for another 12 hours resulted in complete conversion back to **2**.

Because the calculations indicate that this CO_2 adduct is much more favorable than in the case of the previously reported organocatalyst 1-Bcat-2-PPh_2-C_6H_4 (**1**), (-4.1 kcal.mol^{-1} vs +9.9 kcal.mol^{-1}), we were curious to see if catalytic reduction of carbon dioxide could be achieved through this novel CO_2 adduct. The $^{31}P\{^1H\}$ and ^1H NMR monitoring of the reaction between a 5 mM solution of **2** containing 49 equivalents of HBcat under one atmosphere of CO_2 at 60°C did show the presence of catalytic activity. In the first 30 minutes after the addition of CO_2, the ^1H NMR spectrum did not show any significant change (Figure 5). However, after 30 minutes, the ^1H NMR did show a signal corresponding to CH_3OBcat at 3.37 ppm. As observed in Figure 5, the concentration of CH_3OBcat increased rapidly once the induction period was over and then started slowing down with diminishing concentration of HBcat. The addition of 1000 equiv of HBcat to a 1.5 mM solution of **2** in benzene-d_6 under 2 atmosphere of CO_2 yielded quantitative formation of CH_3OBcat over a 72 hour period at 70° C.

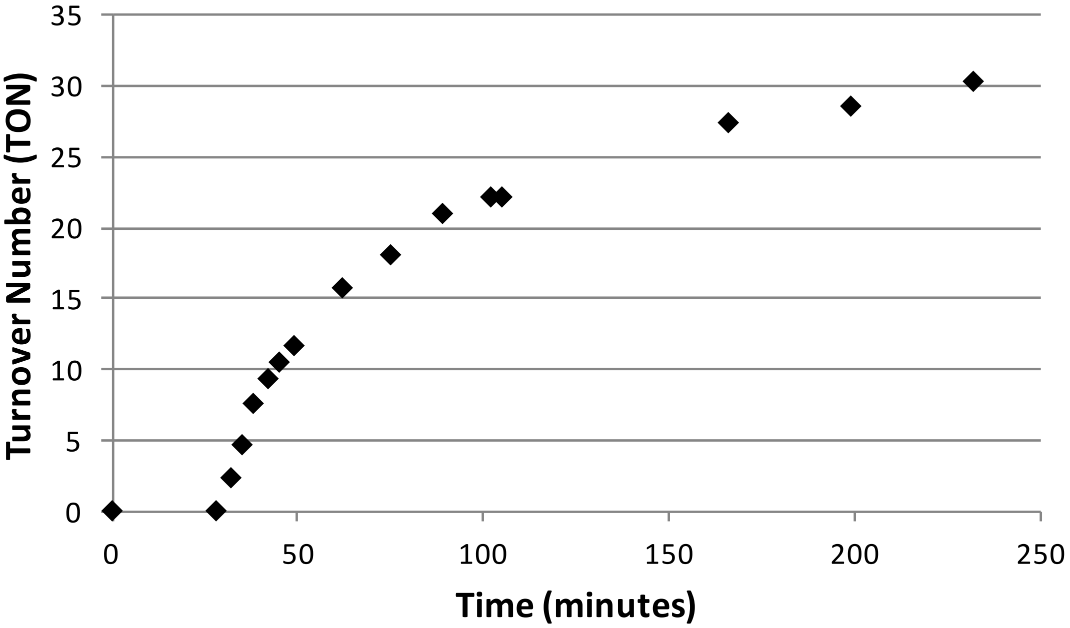
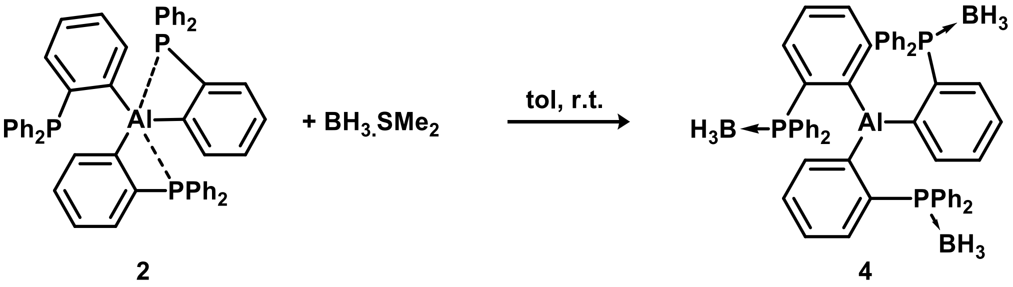


Figure 5. Turnover number (TON) for the formation of CH_3OBcat from a 5 mM solution of **2** in benzene-d_6 in the presence of 49 eq of HBcat under 1 atm of CO_2 at 60°C. The TONs are based on the number of hydrogen atoms transferred to CO_2.

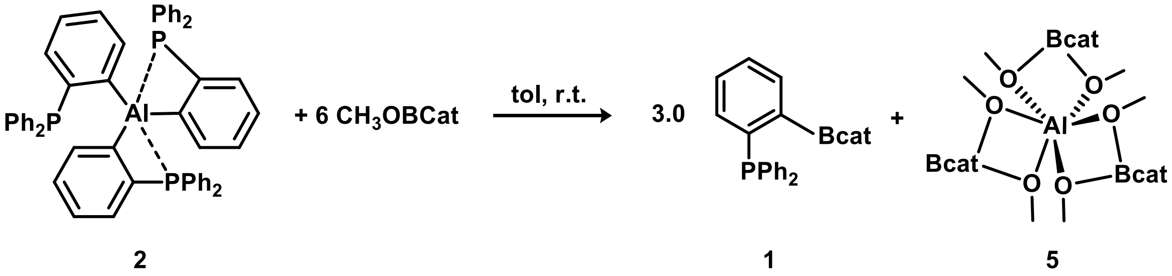
In order to assess possible rearrangements of the precatalyst during catalysis, the reaction of **2** with 4 equiv of catecholborane at room temperature was monitored using multinuclear NMR spectroscopy. A complex set of signals in the ^{31}P NMR spectrum suggested that several rearrangements were occurring, but none of the signals corresponded to **2**. However, heating the solution at 70°C for 3 hours did reduce the number of observable species with a predominant signal at -4.6 ppm reminiscent of species **1**. The aromatic signals observed in the ^{1}H NMR of the reaction mixture were also consistent with the formation of organocatalyst 1-Bcat-2-PPh_2-C_6H_4 (**1**). Most notable was the apparition of a downfield doublet at 8.08 ppm that is assigned to the resonance of the proton *ortho* to the borane moiety of **1**. However, a large amount of refractory white precipitate appeared in the solution, which could be attributed to the presence of catecholate aluminum species. Species **1** was successfully isolated in measurable amounts (40% yield) by reacting **2** with 4 equivalents of HBcat in toluene at 70 °C for 3 hours. The crystallization from the reaction mixture afforded quality crystals of **1**.

Although the isolation of the aluminum-containing products formed under large excess of HBcat was not possible, it is possible to speculate that the degradation of HBcat in the presence of the Lewis basic moieties of **2** can be at the origin of the formation of **1**. Indeed, Westcott *et al.* demonstrated that in presence of phosphine moieties, HBcat can degrade into several boron-containing products, including notably B_2cat_3, BH_3 and $[(PR_3)_2BH_2][Bcat_2]$.[20] Therefore, one possible pathway would be for nucleophilic boron containing species such as the $[Bcat_2]$ anion to attack the oxophilic aluminum centre, thus generating a highly nucleophilic phenoxide anion, that would in turn attack the boron of another cathecolborane to form species **1**. In order to support such assumption, the synthesis of the BH_3 protected adduct of **2** was carried out. Reacting **2** with an excess of $BH_3.SMe_2$ followed by removal of the volatiles *in vacuo* generated derivative **4**, as demonstrated by the single broad peak at 22.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum (See Scheme 3).[21] $^{11}B\{^1H\}$NMR also showed a broad signal at -33 ppm, confirming the interaction with phosphorous. Interestingly, the addition of 30 equiv of HBcat to a solution of **4** in benzene-d_6 did not yield any new compound nor catalytic activity when exposed to CO_2 even after heating at 70 °C for 12 hours.



Scheme 3. Proposed protection of the phosphine moieties of **2** in presence of excess $BH_3.SMe_2$.

It was also possible to observe that **1** was also generated when six equivalents of MeOBcat were added to **2**. As it was observed in the presence of HBcat, the only other species observed were refractory materials. Fortunately, it was possible to fish out of solution a single crystal that was identified as species $Al(\kappa^2{}_{O,O}\text{-}(MeO)_2Bcat)_3$ (**5**) (Scheme 4). Unfortunately, all attempts to purify and isolate this compound in a significant quantity failed. However, the presence of such species in solution supports our hypothesis that rearrangements caused by nucleophilic anionic borate species can be at the origin of the generation of species **1** and consequently of the catalytic activity. The ORTEP representation of **5** is shown in Figure 7.



Scheme 4. Synthesis of species **5**

According to the result of the X-ray diffraction analysis, the structure of **5** is refined to the ***P***-1 space group. Two crystallographic independent molecules and one solvent molecule of toluene, disordered in two different orientations in a 50:50 ratio, are present in the asymmetry unit. As shown in Figure 6, the central Al atom in each molecule of **5** is coordinated by six o-CH_3 groups forming a slightly distorted octahedron. In complex **5**, the Al-O bond lengths range from 1.859(1) to 1.884(1) Å in the first molecule, and from 1.862(1) to 1.874(1) Å in the second molecule, distances that are comparable with those in the closest structures reported, which consist of the aluminum species $[Al(\kappa^2{}_{O,O}\text{-}\mu\text{-}OR)_2Al(OR)_2)_3]$ (R = alkyl).[22] Because of the presence of the four-membered rings, the octahedron is distorted with O-Al-O angles ranging from 158.76(6)° to 161.82(6)°. While the pseudo-D_3 geometry is commonly found in aluminum chemistry, aluminum containing products having three four-membered rings with non-metal elements is quite rare. The molecules of **5** are packed together to form single-layered sheet in the ***a*-*c*** plane. The different sheets are arranged alternatively along the ***b*** axis to form a 3D framework of **5**, as shown in Figures S19 and S20.

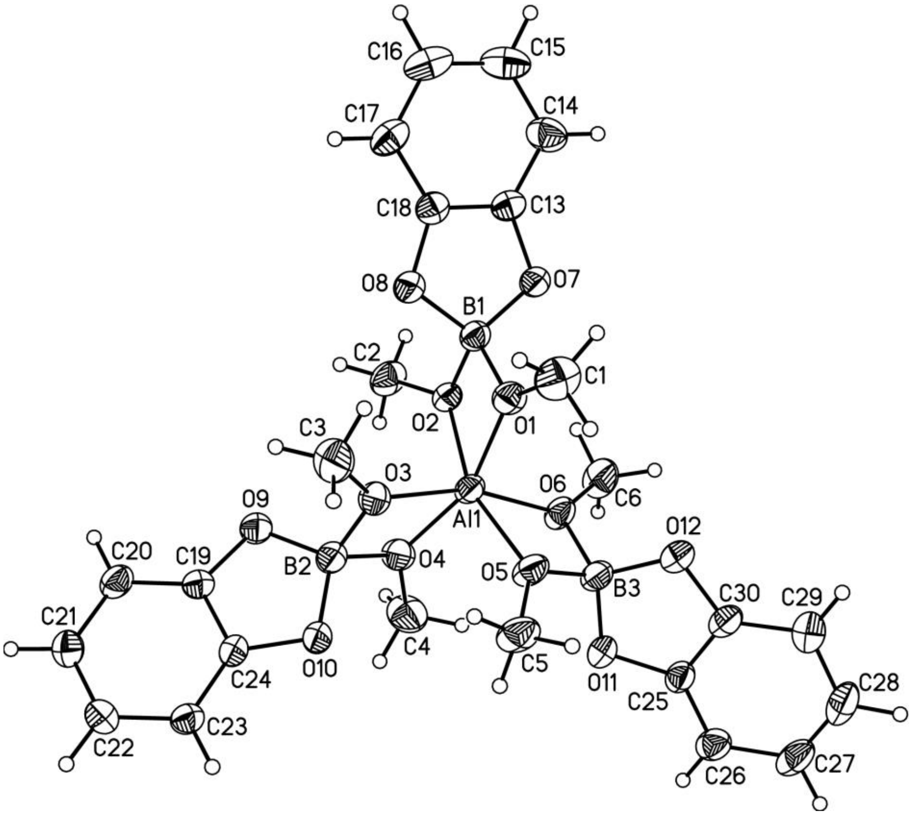


Figure 6 - ORTEP drawing of one independent molecule of **5**. The other molecule is illustrated in Figure S18. Anisotropic atomic displacement ellipsoids are shown at the 50% probability level. The hydrogen atoms are drawn using an arbitrary sphere size for clarity. The hydrogen atoms are drawn using an arbitrary sphere size for clarity. Selected bond lengths [Å] and angles [°] : Al1-O1 = 1.8593(14); Al1-O3 = 1.8606(13); Al1-O4 = 1.8691(15); Al1-O5 = 1.8737(14);

Al1-O6 = 1.8747(13); Al1-O2 = 1.8842(13); O1-Al1-O3 = 94.66(6); O1-Al1-O4 = 159.10(7); O3-Al1-O4 = 70.65(6); O1-Al1-O5 = 98.34(6); O3-Al1-O5 = 96.92(6); O4-Al1-O5 = 98.16(7); O1-Al1-O6 = 98.84(6); O3-Al1-O6 = 162.51(7); O4-Al1-O6 = 98.77(6); O5-Al1-O6 = 70.22(6); O1-Al1-O2 = 70.38(6); O3-Al1-O2 = 100.59(6); O4-Al1-O2 = 97.08(6); O5-Al1-O2 = 159.80(6); O6-Al1-O2 = 94.42(6).

Generation of **5** provides significant thermodynamic stability to the system by generating strong Al-O and B-O bonds. This reaction is a good example of the relative kinetic instability of arylaluminum species in the presence of oxygen sources. Although such aluminum compounds are efficient in the activation of carbon dioxide, it is necessary to account for their reactivity with potential reduction products in order to avoid catalyst decomposition. As such, aryl bridged alanes are probably not suitable catalysts for the carbon dioxide reduction into methoxyboranes using hydroboranes.

Conclusion

A novel triphosphine alane ambiphilic molecule with interesting coordination geometry has been synthesized and characterized by X-ray diffraction. Its fluxional behavior in solution indicates a rapid process where phosphine moieties dissociate from the metallic center, leaving the aluminum open for further coordination. Remarkably, **2** is able to bind CO_2 at room temperature in a reversible way to form a new CO_2 coordination complex. Decomposition of **2** into an interesting hexavalent aluminum species and reported active catalyst **1** by reaction with HBcat and CO_2 reduction product CH_3OBcat suggests that even though phosphine-alane compounds seem like promising alternatives for the activation/reduction of carbon dioxide, their sensitivity limits the scope of their application in catalysis. In fact, reduction with borane reagents will ultimately lead to decomposition of the catalyst. Studies to stabilize the system and broaden the scope of reducing agents to alkylsilanes are currently underway.

Experimental Section

General procedures: Unless otherwise specified, manipulations were carried out under an atmosphere of dinitrogen, using standard glovebox and Schlenk techniques. Reactions were carried either in a sealed J-Young NMR tube, in which case NMR conversions are indicated, or in standard flame dried Schlenk glassware. All solvents were distilled from Na/benzophenone, benzene-d_6 and toluene-d_8 were purified by vacuum distillation from Na/K alloy. Toluene was stored on Na/K alloy. Bone dry CO_2 was purchased from Praxair and used as received. $^{13}CO_2$ (99% isotope label) was purchased from Cambridge Isotope Laboratories and also used as received. Lithiated *o*-bromophenyldiphenylphosphine[166] and CH_3OBcat[23] were synthesized in good yields by following literature procedures. The full characterization of species **1** was already reported elsewhere.[15]

NMR spectra were recorded on a Agilent Technologies NMR spectrometer at 500 MHz (^1H), 125.758 MHz (^{13}C), 202.456 MHz (^{31}P) 160.46 MHz (^{11}B), on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^1H), 100.580 MHz (^{13}C), 161.923 MHz (^{31}P), or on a Bruker NMR AC-300 at 300MHz (^1H), 75.435 MHz (^{13}C), 121.442 MHz (^{31}P). ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are referenced to residual protons or carbons in deuterated solvent. The temperatures of the VT NMR experiments were measured using a thermocouple inside the probe, which was calibrated with methanol prior to use. Multiplicities are reported as singlet (s), broad singlet (s, br) doublet (d), triplet (t), multiplet (m), or virtual triplets (vt). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. gHMQC, gHSQC, NOESY 2D, COSY and $^{1}H\{^{31}P\}$ NMR experiments were performed in order to properly assign spectra.

Al(C_6H_4(*o*-PPh_2))$_3$ (2) : 2-(diphenylphosphino) phenyllithium diethyletherate (1.035g, 3.00 mmol) was placed in a Schlenk vessel with 0.134g of $AlCl_3$ (0.134g, 1.00 mmol). Toluene (c.a. 20ml) was then added directly on the solid reactants resulting in a sudden rise of temperature indicating an exothermic reaction. The mixture was then heated at 50°C for 12 hours. The solution was collected by cannula filtration and the filtrate was concentrated *in vacuo* yielding 0.64 g of **2** as a colorless solid (76% yield). The material was further purified by dissolving in toluene, filtering and storing at -40 °C for 3 days after which the product precipitated as colorless crystals suitable for X-ray diffraction (0.33g, 39% yield). .

^{1}H NMR (500 MHz, benzene-*d*$_6$): δ 8.11 (d, 3H, $^{3}J_{H\text{-}H} = 7.2$ Hz), 7.36-7.51 (bm, 1H), 7.30-7.33 (m, 3H), 7.26 (m, 12H), 7.17-7.18 (m, 2H), 7.06-7.09 (m, 3H), 6.88-6.95 (m, 18H). $^{13}C\{^{1}H\}$ (126MHz, benzene-*d*$_6$): 144.6 (d, $^{3}J_{P\text{-}C} = 2.4$ Hz), 144.6 (dd, $^{2}J_{P\text{-}C} = 18.6$Hz, $^{3}J_{P\text{-}C} = 1.0$ Hz), 144.6 (s), 138.9 (ddd, $^{2}J_{P\text{-}C} = 21.6$ Hz, $^{2}J_{P\text{-}C} = 12.4$ Hz, $^{3}J_{P\text{-}C} = 2.4$ Hz), 136.7 (s), 134.2 (d, $^{2}J_{P\text{-}C} = 19.6$ Hz), 133.6 (dd, $^{2}J_{P\text{-}C} = 10.4$ Hz, $^{2}J_{P\text{-}C} = 5.2$ Hz), 132.0 (s), 129.3 (s), 128.9 (s), 128.8 (d, $^{2}J_{P\text{-}C} = 6.7$ Hz), 128.7 (bs, width = 8.5 Hz), 128.6 (s), 128.5 (dd, $^{3}J_{P\text{-}C} = 4.8$ Hz, $^{3}J_{P\text{-}C} = 2.4$ Hz), 128.4 (bs, width = 6.6 Hz). $^{31}P\{^{1}H\}$ (203 MHz, benzene-d_6): δ -1.5.

Al(C_6H_4(*o*-PPh_2))$_3$(CO_2) (3): A solution of **2** in benzene-*d*$_6$ (2.8 mg in *c.a.* 0.6ml, 5.7 mmol/L) was placed in a J-young NMR tube. This tube was frozen in liquid nitrogen on the schlenk line and put under vacuum for 30 minutes. An atmosphere of CO_2 was then allowed to flow in the tube for 5 to 10 seconds, and the tube was closed. The liquid nitrogen bath was then gradually removed to let the solution slowly thaw. 96% yield based on NMR integration.

^{1}H NMR (500 MHz, benzene-d$_{6}$,): δ 8.48 (bs, 1H), 8.01 (d, 2H, $^{3}J_{\text{H-H}}$= 7.0 Hz), 7.41-7.32 (m, 12H), 7.26 (bs, 1H) 7.11-6.92 (m, 18H), 6.90-6.85 (m, 2H), 6.80-6.62 (m, 6H). ^{13}C {^{1}H} (126MHz, benzene-d$_{6}$) δ145.3 (s), 141.7 (dt, $^{2}J_{\text{P-C}}$ = 19.7 Hz, $^{3}J_{\text{P-C}}$ = 7.7Hz), 140.7 (d, $^{2}J_{\text{P-C}}$ = 13.1 Hz), 139.9 (d, $^{2}J_{\text{P-C}}$ = 12.2 Hz), 139.7 (d, $^{2}J_{\text{P-C}}$ = 25.9 Hz), 134.4 (d, $^{2}J_{\text{P-C}}$ = 9.9 Hz), 134.0 (d, $^{2}J_{\text{P-C}}$ = 17.5 Hz), 133.8 (s), 133.7 (s), 133.6 (d, $^{3}J_{\text{P-C}}$ = 2.7 Hz), 132.6 (d, $^{2}J_{\text{P-C}}$ = 13.3 Hz), 131.1 (d, $^{3}J_{\text{P-C}}$ = 3.8 Hz), 129.4 (s), 127.8 (d, $^{2}J_{\text{P-C}}$ = 11.0 Hz), 127.0 (d, $^{2}J_{\text{P-C}}$ = 12.6 Hz), 120.9 ($^{1}J_{\text{P-C}}$ = 78 Hz).^{31}P{^{1}H} (203 MHz, benzene-d$_{6}$): -5.1 (d, 2P, $^{6}J_{\text{P-P}}$=3.2 Hz); -6.2 (t, 1P, $^{6}J_{\text{P-P}}$=3.2 Hz).

Al(C$_{6}$H$_{4}$(*o*-PPh$_{2}$.BH$_{3}$))$_{3}$ (4) : 110 mg (110mg, 0.13mmol) of **2** were introduced into a small schlenk. Toluene was then directly added to this product and the resulting mixture was stirred until a clear solution was obtained. An excess of BH$_{3}$.SMe$_{2}$ (0.1 ml, 1.1 mmol, 8.1 equiv) was added to the solution and the reaction was left stirring for an hour. The solvent and excess reagents were then removed *in vacuo*. The product was obtained without further purification as a very static white powder. Reaction is quantitative. ^{1}H NMR (500 MHz, benzene-d$_{6}$): δ 8.07 (bs, 3H), 7.62 (t, 3H, $^{3}J_{\text{P-H}}$ = 8.6 Hz), 7.53 (t, 9H, $^{3}J_{\text{H-H}}$ = 8.6 Hz), 7.06 (t, 3H, $^{3}J_{\text{H-H}}$ = 8.2 Hz), 7.02-6.89 (m, 18H), 6.77 (bs, 6H, width = 40.7 Hz), 2.15 (bs, 9H, width = 380.7 Hz). ^{13}C{^{1}H} (126MHz, benzene-d$_{6}$) δ 141.4 (d, $^{2}J_{\text{P-C}}$ = 18.6 Hz), 134.0 (d, $^{2}J_{\text{P-C}}$ = 9.5 Hz), 134.0 (d, $^{1}J_{\text{P-C}}$ = 65.3Hz), 133.6 (d, $^{2}J_{\text{P-C}}$ = 9.5 Hz), 133.6 (s), 131.1 (d, $^{3}J_{\text{P-C}}$ = 2.4 Hz), 130.7 (d, $^{1}J_{\text{P-C}}$ = 57.7 Hz), 130.7 (d, $^{3}J_{\text{P-C}}$ = 2.4 Hz), 129.3 (d, $^{3}J_{\text{P-C}}$ = 2.4 Hz), 128.9 (d, $^{2}J_{\text{P-C}}$ = 10.5 Hz), 128.6 (d, $^{2}J_{\text{P-C}}$ = 10.0 Hz), 128.3 (s), 126.6 (d, $^{2}J_{\text{P-C}}$ = 9.1 Hz). ^{11}B (161 MHz, benzene-d$_{6}$) δ -33.0 (s). ^{31}P (202 MHz, benzene-d$_{6}$) δ 22.3 (s).

[Al($\kappa^2_{O,O}$-μ-OMe)$_2$Bcat)$_3$] (5): A solution of CH_3OBcat in toluene was added to a solution of (1) in toluene via cannula. A white precipitate was instantly formed. This mixture was left stirring under a flow of nitrogen for an hour at room temperature. The reaction was filtered and washed thoroughly with toluene. Few crystals of **5** were isolated, enough for one crystallographic study.

CO_2 reduction catalytic tests: $Al(C_6H_4(o\text{-}PPh_2))_3$ (**2**) (2.0 mg 2.5 X 10^{-3} mmol) was dissolved in *ca.* 0.6 mL of benzene-d_6. HBcat (14.7 mg, 0.12 mmol, 49equiv) was added to the solution and the mixture was introduced in a J-young NMR tube. The J-young NMR tube was frozen in a liquid nitrogen bath after which the headspace of the J-young was filled with 1atm. of CO_2. The reaction was then followed by NMR spectroscopy. Yields are reported by ^1H NMR integration using hexamethylbenzene (1.35 mg, 8.3 X 10^{-3} mmol) as an internal standard.

Crystallographic studies: Nice single crystals with suitable size for all three compounds (**2** and **5**) were mounted on CryoLoops with Paratone-N and optically aligned on a Bruker SMART APEX-II X-ray diffractometer with 1K CCD detector with the aid of a digital camera. Initial intensity measurements were performed using a fine-focused sealed tube, graphite-monochromated, X-ray source (Mo Kα, $\lambda = 0.71073$ Å) at 50 kV and 30 mA. Standard APEX-II[24] software package was used for determining the unit cells, generating the data collection strategy, and controlling data collection. SAINT[25] was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using SCALE (SADABS[26]). The structures of all compounds were solved by direct methods and refined by full-matrix least-squares methods with SHELX-97[27] in the SHELXTL6.14 package. As the solvent molecules in **2** are highly disordered, the SQUEEZE subroutine in PLATON[28] software suit was used to remove the scattering contributions from the highly disordered guest molecules. The resulting new HKL file was adopted to further refine the structural model. All of the H atoms (on C atoms) were generated geometrically and refined in riding mode. Crystallographic information for all obtained phases is summarized in Table S1. Atomic coordinates and additional structural information are provided in the CIF file of the Supporting Information.

Supporting Information Available: Cartesian coordinates for compounds **2** and **3** and additional crystallographic figure for **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have been deposited with CCDC (CCDC No. 947976 for **2** and CCDC No. 947978 for **5**). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk, or via the internet at www.ccdc.cam.ac.uk.

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[19] One reviewer raises the point that such coupling could arise from long-range through space coupling rather than scalar coupling. This possibility was considered and cannot be excluded, but several observations go against it. First, the low symmetry of **3** in the optimized structure (P1-P2 and P2-P3 bond lengths of 4.39 and 5.03Å, respectively) would suggest a different coupling

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constant between the phosphorous atoms. Also, long-range coupling would be possible if electronic communication between the nuclei is present, but we did not observe any orbital suggesting that the three phosphorous atoms are able to communicate through space. See Hierso, J.-C.; Fihri, A.; Ivanov, V. V.; Hanquet, B.; Pirio, N.; Donnadieu, B.; Rebière, B.; Amardeil, R.; Meunier, P. *J. Am. Chem. Soc.* **2004**, *126*, 11077-11087.

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