Aluminum Hydride-Catalyzed Hydroboration of Carbon Dioxide

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ABSTRACT: This study describes the first use of a bis(phosphoranyl)methanido aluminum hydride, [ClC($PPh_2NMes)_2AlH_2$] (**2**, Mes = $Me_3C_6H_2$) for the catalytic hydroboration of CO_2. Complex **2** was synthesized by the reaction of a lithium carbenoid [Li(Cl)C($PPh_2NMes)_2$] with two equivalents of AlH_3•$NEtMe_2$ in toluene at -78 °C. 10 mol% of **2** was able to catalyze the reduction of CO_2 with HBpin in C_6D_6 at 110 °C for 2 days to afford a mixture of methoxyborane [MeOBpin] (**3a**; yield: 78%, TOF: 0.16 h^{-1}) and bis(boryl)oxide [pinBOBpin] (**3b**). When more potent [BH_3•SMe_2] was used instead of HBpin, the catalytic reaction was extremely pure, resulting in the formation of trimethyl borate [$B(OMe)_3$] (**3e**) [catalytic loading: 1 mol% (10 mol%); reaction time: 60 min (5 min); yield: 97.6% (>99%); TOF: 292.8 h^{-1} (356.4 h^{-1})] and B_2O_3 (**3f**). Mechanistic studies show that the Al-H bond in complex **2** activated CO_2 to form [ClC($PPh_2NMes)_2$Al(H){OC(O)H}] (**4**), which was subsequently reacted with BH_3•SMe_2 to form **3e** and **3f**, along with the regeneration of complex **2**. Complex **2** also shows good catalytic activity towards hydroboration of carbonyl, nitrile and alkyne derivatives.

Introduction

Main-group elements are considered as sustainable alternatives to precious transition-metal species in chemical catalysis due to their high abundancy and relatively low toxicity.[1] In particular, aluminum is the most abundant main-group element and its Lewis acidic compounds have shown to catalyze a wide range of classic organic reactions, such as the Meerwein-Ponndorf-Verley reduction of carbonyls,[2] Friedel-Crafts acylation of aromatics[3] and the ring-opening polymerization of lactams.[4] However, aluminum does not possess donor and acceptor valence orbitals with small energy gaps, which classically prevents aluminum compounds to mimic transition-metal complexes in catalysis. In the past few years, this limitation has been overcome by designing novel aluminum hydride compounds with highly polarized Al-H bonds. The hydridic H atoms are able to display reactivity similar to transition metal hydride complexes.[5] For example, Berben et al. showed that bis(imino)pyridine complex of aluminum catalyzed the dehydrogenative coupling of benzylamine,[6] dehydrogenation of formic acid,[7] and electrocatalytic production of hydrogen via a metal-ligand cooperative mechanism.[8] Roesky et al. illustrated that the β-diketiminato aluminum hydride complexes mediated the catalytic hydroboration of carbonyl compounds and alkynes.[9,10] Thomas and Cowley et al. reported that commercially available aluminum hydrides such as DIBAL-H and $LiAlH_4$ catalyzed the hydroboration of alkenes, alkynes, and nitriles via σ-bond metathesis.[11,12] Research groups of Harder and Mulvey reported that lithium aluminates catalyzed hydrophosphination of alkynes and hydrogenation of imines through a Li-Al cooperation mechanism.[13,14] Nikonov et al. also demonstrated that the β-diketiminato aluminum hydride complex catalyzed the hydrosilylation of alkenes via the activation of silane by the Lewis acidic aluminum center in the first step of the catalysis.[15] Rueping et al. reported the first asymmetric hydroboration of ketones using aluminum complexes bearing chiral biphenol-type ligands.[16] These results serve as evidence that tailor-made aluminum hydride complexes exhibit transition-metal like reactivity in mediating catalytic reduction of unsaturated polar bonds (C=O, C=N) and C-C multiple bonds. Despite these pertinent recent developments, the implementation of aluminum hydride complexes for catalytic CO_2 transformation into value-added chemicals has not been reported.[17] In fact, Aldridge et al. showed that β-diketiminato aluminum hydride complexes are not efficient catalysts for the hydroboration of CO_2 with boranes because of unfavorable kinetics of the σ-bond metathesis mechanism.[18] Inoue et al. reported that N-heterocyclic imido aluminum hydride complexes promoted CO_2 reduction through a non-aluminum-containing intermediate to form ill-defined product mixtures.[19]

Recently, a series of bis(phosphoranyl)methanediide and methanide complexes of main-group elements have been shown, whereby the ylidic PN bonds (P=N ↔ P^+–N^-; Figure 1) of the ligands promote strong electron transfer from the N atoms to main-group elements.[20] In particular, we have shown that the boron derivatives of bis(phosphoranyl)methanediide and methanide, [H_5B_2-C($PPh_2S)_2$Li(OEt_2)][21] and [ClC($PPh_2NMes)_2BH_2$][22] were among the most efficient catalysts for CO_2 reduction to methanol derivatives. We anticipated that such electronic properties could also enhance the hydridic character of an Al-H bond, resulting in the kinetically and thermodynamically favorable addition to CO_2. Herein, we report the synthesis of a bis(phosphoranyl)methanido aluminum hydride and its use in the catalytic hydroboration of CO_2 coupled with DFT calculations that rationalize our experimental findings. We also report that this complex is an efficient catalyst for the hydroboration of a wide variety of substrates, such as aldehydes, ketones, nitriles and alkynes.

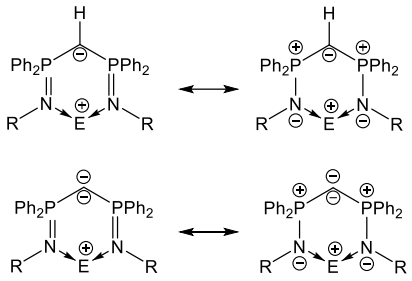
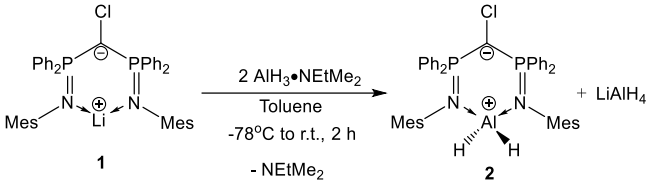


Figure 1. Ylidic structure of bis(phosphoranyl)methanediide and methanide complexes of main-group elements (E)

Results and Discussion

Our starting point was the lithium carbenoid [Li(Cl)C($PPh_2NMes)_2$] (**1**, Mes = $C_6H_2Me_3$) species which we reported in 2015.[22] Upon treatment with two equivalents of AlH_3•$NEtMe_2$ in toluene at -78 °C followed by warming to room temperature and stirring for 1 hour (Scheme 1), a white suspension was observed. After filtering the white precipitate, which was identified as $LiAlH_4$, [$ClC(PPh_2NMes)_2AlH_2$] (**2**) was obtained as a colorless crystalline solid (92 % yield) in the concentrated filtrate. The results show that AlH_3•$NEtMe_2$ undergoes a disproportionation reaction to form "AlH_2^+", stabilized by the carbenoid backbone, and an AlH_4^- species in the presence of compound **1**. Complex **2** was analyzed and characterized by NMR spectroscopy and X-ray crystallography. The ^{1}H NMR spectrum shows a set of signals for the ligand backbone while featuring a broad signal at 5.0 ppm with an integration of 2 H representing the AlH_2^+ moiety. The ^{31}P NMR spectroscopy shows a new singlet at 39.0 ppm, more than 10 ppm downfield from **1** (27.2 ppm).[22] X-ray crystal structure of **2** (Figure 2) features a six-membered CPNAlNP ring in a half chair conformation due to the presence of an AlH_2^+ moiety (Al-N: 1.886(3), 1.900(3) Å). The C1 atom is planar, which agrees with the absence of a CH bond reflected in the NMR data. The P–N bond lengths in **2** are elongated (1.623(3), 1.625(3) Å) in comparison with those in **1** (1.596(3), 1.593(2) Å),[22] which indicates that the negative charge on the C1 atom in **2** is more delocalized into the P-N σ* orbitals by negative hyperconjugation. Complex **2** is air- and moisture-sensitive, as well as being soluble and stable in non-polar solvents like benzene and toluene up to 120 °C. Decomposition into the protonated ligand [$Cl(H)C(PPh_2NMes)_2$] in hot toluene was not observed.

Next, the catalytic ability of the bis(phosphoranyl)methanido aluminum hydride complex **2** towards the hydroboration of CO_2 with boranes was then examined. To begin with, we verified that there was no reaction between CO_2 and boranes (HBpin, BH_3•SMe_2 and HBcat) in C_6D_6 at 110 °C. In addition, there was no reaction between complex **2** and HBpin at 110 °C for 48 h.[29] In the presence of **2** (10 mol %), the reduction of CO_2 with HBpin in C_6D_6 at 110 °C afforded a mixture of methoxyborane [MeOBpin] (**3a**, Scheme 2) (55.8 % in 24 h; 78 % in 48 h, TOF: 0.16 h^{-1}) and bis(boryl)oxide [pinBOBpin] (**3b**). The catalytic activity in terms of TOF is in the range of other main-group metal-catalyzed CO_2 hydroboration with pinacolborane (HBpin) (TOF = 0.07 – 14.5 h^{-1}).[23] A similar reduction of CO_2 with catecholborane (HBcat) using **2** as a catalyst proceeded with less efficiency (24 h, 28.8 % conversion) to afford a mixture of methoxyborane [catBOMe] (**3c**) and $B_2(cat)_3$ (**3d**). In the catalysis, most of HBcat was unreacted, while a mixture of $B_2(cat)_3$, (^{11}B NMR: 22.5 ppm) and undientified four-coordinate borane compounds (^{11}B NMR: -14.5 ppm) was observed, in addtion to **3c** and **3d**. This suggests that intermediates in the catalysis could react with HBcat to form $B_2(cat)_3$ and catalytically inactive complexes, leading to low conversion of the catalysis.



Scheme 1. Synthesis of the bis(phosphoranyl)methanido aluminum hydride **2**

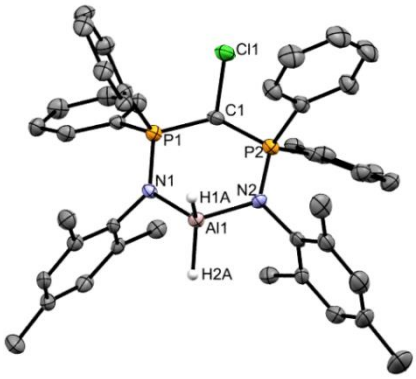
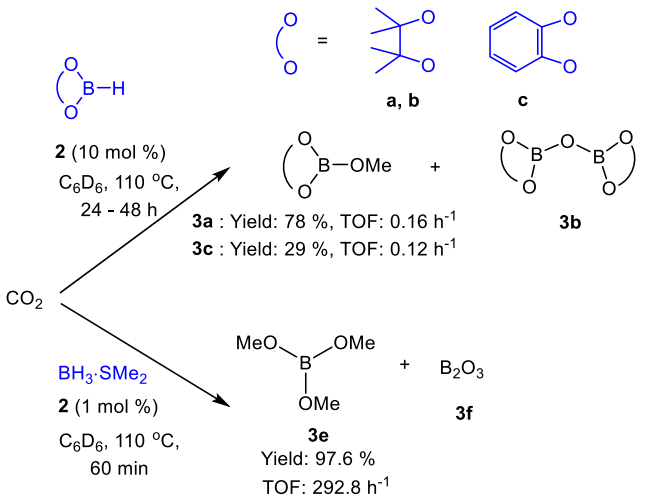


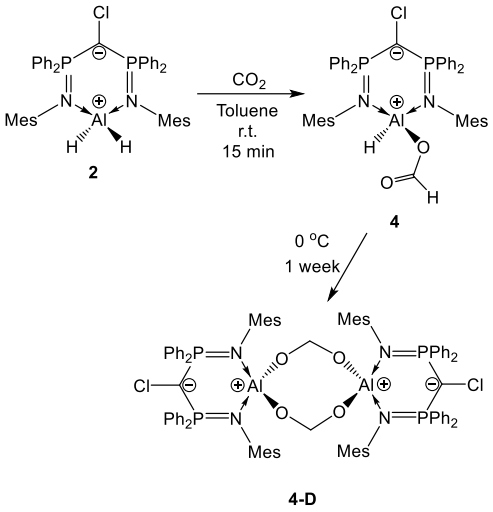
Figure 2. X-ray crystal structure of **2** with thermal ellipsoids at 50 % probability. All H atoms except on the Al1 atom are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cl1-C1 1.785(3), C1-P2 1.725(4), P2-N2 1.623(3), N2-Al1 1.886(3), Al1-N1 1.900(3), N1-P1 1.625(3), P1-C1 1.719(4), P2-C1-P1 133.3(2), N2-Al1-N1 103.6(1).

When more potent and $NaBH_4$-free[24] [BH_3•SMe_2] was used instead of HBpin, the catalytic reaction was much more efficient (1 mol % of **2**), forming trimethyl borate [$B(OMe)_3$] (**3e**) in only 1 h (Yield: 97.6 %, TOF: 292.8 h^{-1}, Scheme 2) together with white precipitates. Hydrolysis of the latter in D_2O quantitatively formed boric acid (by ^{11}B NMR) which is indicative that the white precipitate formed during the catalysis is B_2O_3. When the amount of complex **2** was increased to 10 mol %, the catalytic activity increased significantly (5 min, 110 °C, Yield: >99 %, TOF: 356.4 h^{-1}). Complex **2** is one of the very few main-group element compounds that can catalyze the reduction of CO_2 with BH_3, including the ambiphilic phosphine-borane compound [1-$B(OR)_2$-2-PR'_2-C_6H_4] (TOF: 43 - 257 h^{-1}; R′ = Ph, *i*Pr; $(OR)_2$ = $(OMe)_2$, catechol, pinacol),[25] bis(thiophosphinoyl)methanide-supported lithium borohydride [$H_5B_2C(PPh_2S)_2Li(OEt_2)$] (TOF: 150 h^{-1}),[21] bis(iminophosphoranyl)methanido boron hydride [$ClC(PPh_2NMes)_2BH_2$] (TOF: 157 h^{-1}),[22] ring expansion product arising from phosphine-derived carbenes with 9-borabicyclo[3.3.1]nonane (9-BBN)[26] and NHC-silyliumylidene complex [$(I_{Me})_2SiH$]I (TOF: 19.8 h^{-1}, I_{Me} = :C{N(Me)C(Me)}$_2$).[27] It is noteworthy that the catalytic activity of complex **2** is more efficient than these examples in terms of both reaction time and TOF.



Scheme 2. 2-catalyzed hydroboration of CO_2. Yields were calculated based on conversion of H.

The catalytic mechanism was studied by performing stoichiometric step-wise reactions with the aim of isolating reactive intermediates. Complex **2** was reacted with CO_2 in toluene at room temperature for 15 min (Scheme 3), whereby complex **2** was fully consumed. The ^{31}P NMR spectrum of the reaction mixture showed a single new signal at 40.5 ppm, while the ^{1}H NMR spectrum showed a new singlet at 8.5 ppm (1 H) suggesting the formation of a formate moiety coupled with a set of signals representative of the bis(iminophosphoranyl)methanido ligand. The spectroscopic data indicates that CO_2 inserts into one Al-H bond in complex **2** to form $[ClC(PPh_2NMes)_2Al(H)\{OC(O)H\}]$ (**4**). It was isolated as a white precipitate by simply removing volatiles of the reaction mixture *in vacuo*. Complex **4** is stable in the solid state, but slowly decomposes in C_6D_6, toluene and CH_2Cl_2. Efforts were made to crystallize this compound in CH_2Cl_2, which was unsuccessful due to its slow evolution in solution. However, a single new species formed after a week in attempts to crystallize **4**, indicative by the appearance of a new signal at 42.5 ppm in the ^{31}P NMR spectrum. The ^{1}H NMR spectrum showed a singlet at 8.24 ppm with an integration of 4 indicating the formation of two OCH_2O moieties. In addition, the ^{1}H NMR spectrum showed a set of signals for the bis(iminophosphoranyl)methanido ligand. Colorless crystals were obtained from the initial CH_2Cl_2 solution of **4**, crystallized at 0 °C for one week. The X-ray crystallographic analysis proved the formation of the acetal derivative $[LAl(OCH_2O)_2AlL]$ (**4-D**, L = $ClC(PPh_2NMes)_2$). Thus, in the absence of any additional substrate, the second Al-H is sufficiently hydridic to reduce the formate moiety to an acetal moiety. Complex **4-D** is stable in solution (toluene, CH_2Cl_2) and in the solid state. The X-ray crystal structure of complex **4-D** comprises of an $Al(OCH_2O)_2Al$ eight membered ring (Figure 3). The ring structure (Al-O: 1.731(4), 1.710(8) Å) is comparable with the one supported by β-diketiminate ligand $[RAl(OCH_2O)_2AlR]$ (Al-O: 1.7123(11), 1.7239(11) Å; R = $HC\{C(Me)NDipp\}_2$, Dipp = 2,6-*i*$Pr_2C_6H_3$), which was isolated from the reaction of the germanium(II) formate [RGeOC(O)H] and aluminum hydride $[RAlH_2]$.[28]



Scheme 3. Formation of complex **4-D**

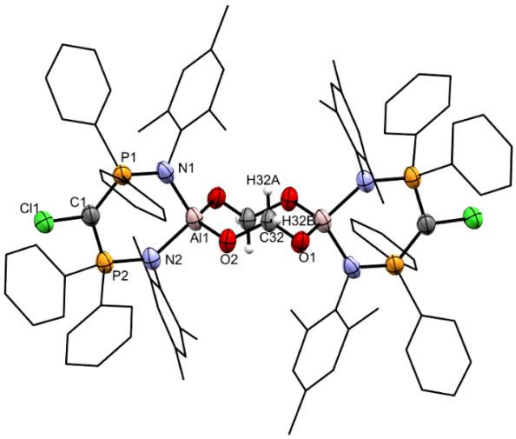
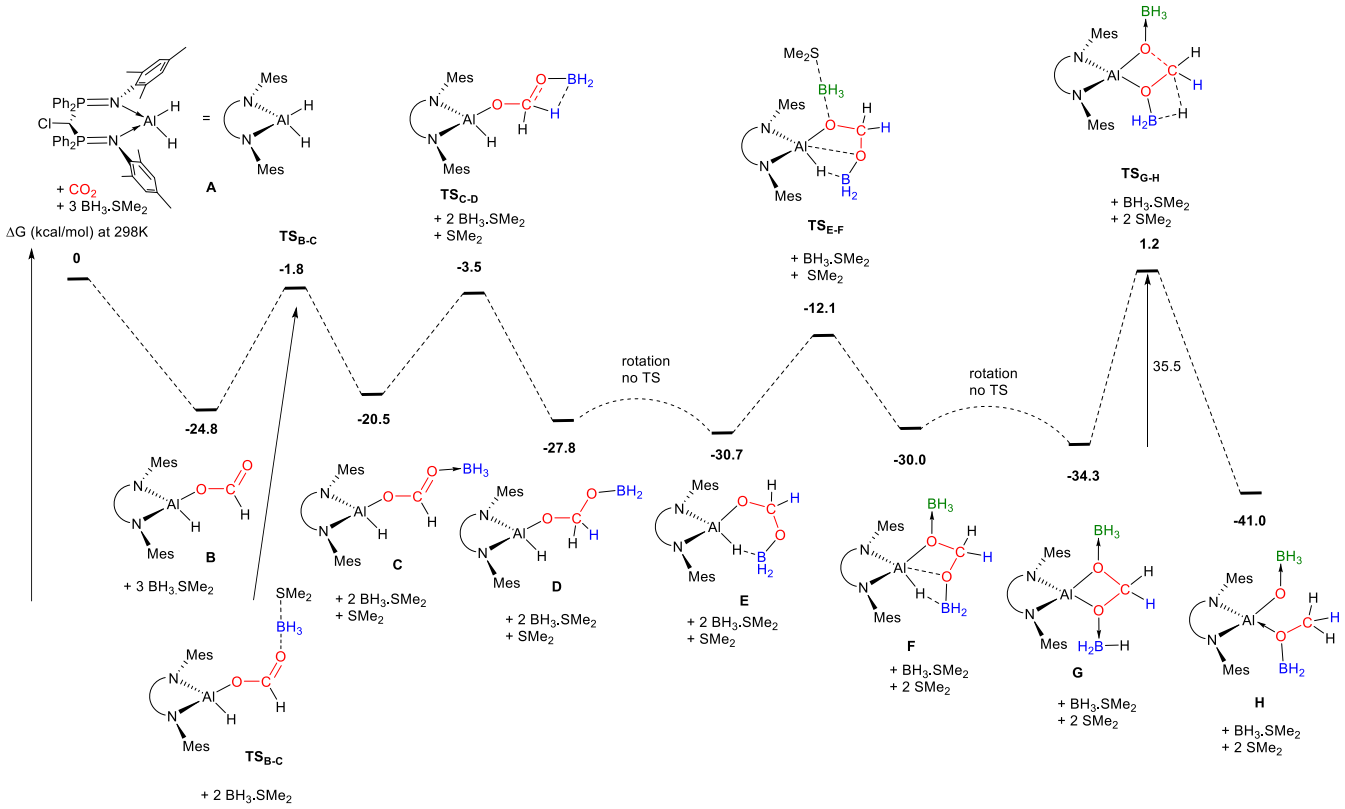
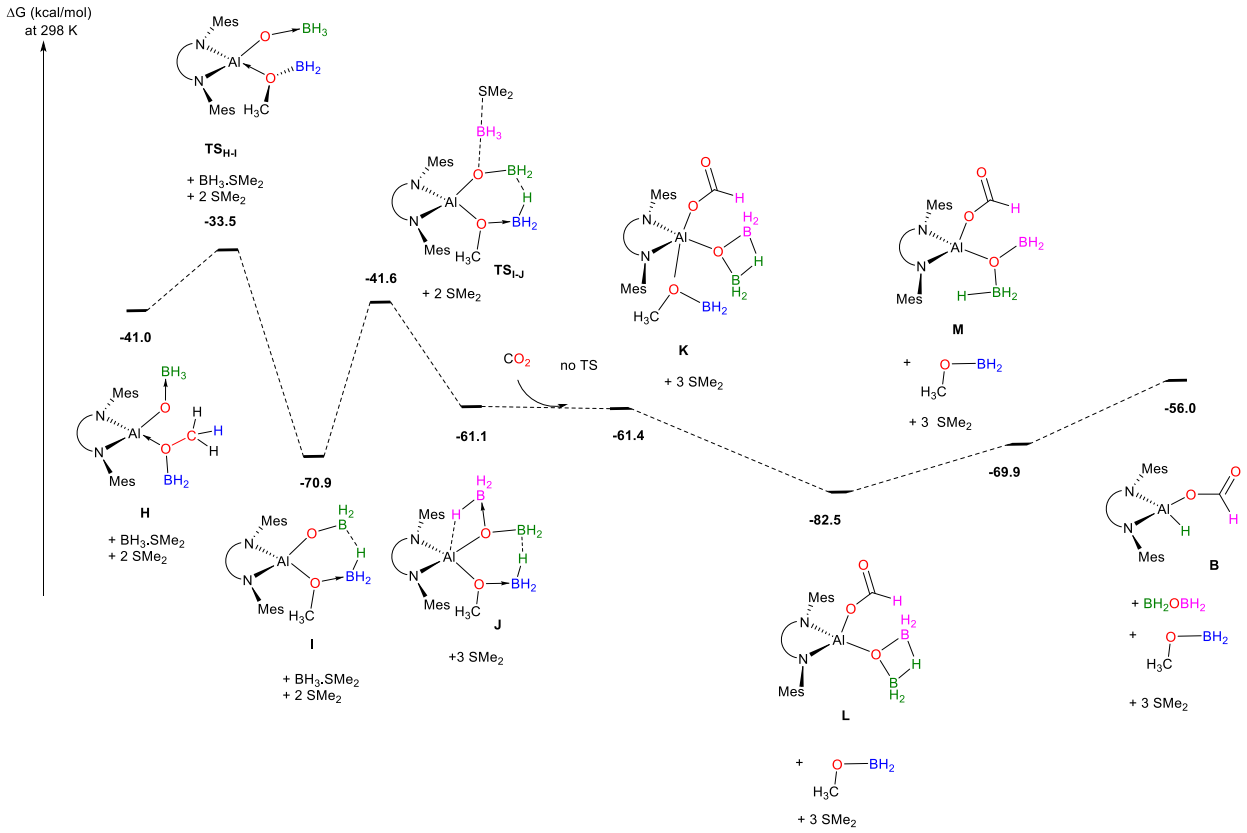


Figure 3. X-ray crystal structure of **4-D** with thermal ellipsoids at the 50 % probability level. Selected hydrogen atoms are elided for clarity. Selected bond lengths (Å) and angles (deg): Cl1-C1 1.797(5), C1-P1 1.747(6), C1-P2 1.704(6), P2-N2 1.632(4), P1-N1 1.624(4), N1-Al1 1.881(5), N2-Al1 1.891(4), Al1-O2 1.731(4), Al1-O1 1.710(8), O1-C32 1.392(11), O2-C32 1.476(8), N1-Al1-N2 104.64(19), O1A-Al1-O2 109.2(5), N1-Al1-O1A 119.5(4), N2-Al1-O2 108.80(19), Al1-O2-C32 116.6(4) , O2-C32-O1 111.2(8).



Scheme 4. DFT studies of catalytic CO_2 hydroboration with BH_3•SMe_2 from Complex **A** to **H**, showing the three C-H bond formations from CO_2. ΔG in kcal/mol, calculated at 298K



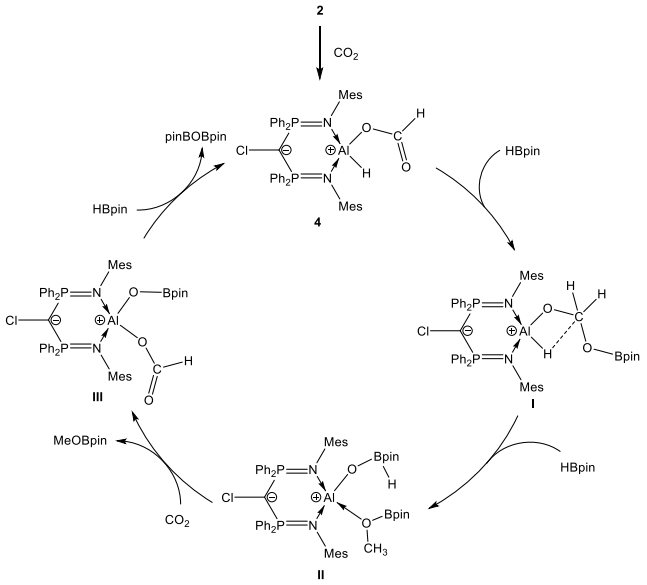
Scheme **5**. DFT studies of catalytic CO_2 hydroboration with BH_3•SMe_2 from **H** to the formation of **3e** and regeneration of **B**. ΔG in kcal/mol, calculated at 298K

To prove that complex **4** is an intermediate in the catalysis, 10 mol % of **4** was used to catalyze the reaction of CO_2 with HBpin in C_6D_6 at 110 °C for 48 h to afford a mixture of methoxyborane **3a** (Yield: 78 %) and bis(boryl)oxide **3b**. Similarly, **4**-catalyzed hydroboration of CO_2 with BH_3•SMe_2 in C_6D_6 at 110 °C formed [$B(OMe)_3$] (**3e**, Yield: 98 %) in 60 mins. The yields of the products are comparable with those in the catalytic CO_2 hydroboration using **2** as a catalyst. In particular, complex **2** was regenerated after these catalytic runs. On the other hand, 10 mol % of complex **4-D** was unable to catalyze the hydroboration of CO_2 with HBpin or BH_3•SMe_2 in C_6D_6 at 110°C. In summary, these results show that complex **2** is an active catalyst and complex **4** is an intermediate in the catalytic reduction of CO_2, while **4-D** is an off-cycle product.

Moreover, complex **4** was reacted with 3 equivalents of BH_3•SMe_2 in C_6D_6 to form a mixture of bis(iminophosphoranyl)methanido compounds, confirmed by ^{31}P NMR spectroscopy (7 signals: 41.1 – 42.5 ppm). The reaction mixture was then heated at 110 °C overnight. ^{31}P NMR spectroscopy showed that complex **2** was regenerated, along with the formation of $B(OMe)_3$ represented by ^{11}B NMR spectroscopy. This indicates that the **2**-catalyzed CO_2 hydroboration with BH_3•SMe_2 proceeds via several intermediates and complex **2** is the active catalyst in the mechanism. To further support our claim that the reaction proceeds via several intermediates, HRMS was performed and we were able to detect the presence of such intermediates (Scheme 4 and 5; **C**-**E**: HRMS (ESI): *m*/*z* calcd for $C_{44}H_{48}BN_2O_2AlP_2Cl$: 771.2788 $[(M + H)]^+$; found: 771.2774. **F**-**I**: HRMS (ESI): *m*/*z* calcd for $C_{44}H_{51}B_2N_2O_2AlP_2Cl$: 785.3116 $[(M + H)]^+$; found: 785.3167. **J**: HRMS (ESI): *m*/*z* calcd for $C_{44}H_{54}B_3N_2O_2AlP_2Cl$: 799.3444 $[(M + H)]^+$; found: 799.3474. **K**: HRMS (ESI): *m*/*z* calcd for $C_{44}H_{49}B_2N_2O_3AlP_2Cl$: 799.2908 $[(M + H)]^+$; found: 799.2938. **L**-**M**: HRMS (ESI): *m*/*z* calcd for $C_{44}H_{49}B_2N_2O_3AlP_2Cl$: 771.2908 $[(M + H)]^+$; found: 771.2978.).

On the basis of these experimental studies, a catalytic cycle for the hydroboration of CO_2 with BH_3•SMe_2 is proposed (Scheme 4 and 5) and studied by DFT calculations (see the Supporting Information for details). Complex **B** results from insertion of CO_2 into an Al-H bond of complex **A** (model of compound **2**) in a strongly exergonic step (ΔG = -24.8 kcal/mol). A transition state for this process was not found, despite several attempts. BH_3•SMe_2 then coordinates with the C=O double bond through $\mathbf{TS_{B\text{-}C}}$ (ΔG = -1.8 kcal/mol) to form compound **C** (ΔG = -20.5 kcal/mol). The transition state for SMe_2 substitution by the CO moiety at BH_3 is accessible, requiring 23.0 kcal/mol. Subsequently, the B-H bond in compound **C** adds to the >C=O bond via $\mathbf{TS_{C\text{-}D}}$ (ΔG = -3.5 kcal/mol) to form complex **D** (ΔG = -27.8 kcal/mol). At this point, it is obvious that the first two C-H bond formations are accessible. The acetal group in complex **D** then undergoes rotation around the C-O bond to form complex **E** (ΔG = -30.7 kcal/mol), concurrently allowing the borane to interact with the aluminum hydride. A second BH_3•SMe_2 is then added to allow for the third C-H bond to be formed. It coordinates to the oxygen atom of the acetal group in complex **E**, to result in complex **F**, which is almost iso-energetic (ΔG = -30.0 kcal/mol) via $\mathbf{TS_{E\text{-}F}}$ (ΔG = -12.1 kcal/mol). Notably, in complex **F**, the oxygen atom and BH_2 moieties are adequately positioned to favor Al-O bond and BH bond formations leading to complex **G** (ΔG = -34.3 kcal/mol), in a facile process (without TS). Complex **G** is a symmetrical complex featuring two Al-O bonds and two O-BH_3 moieties. Subsequently, the B-H bond is added to the acetal group via $\mathbf{TS_{G\text{-}H}}$ (ΔG = -5.3 kcal/mol) resulting in the cleavage of the O-C bond and the formation of $MeOBH_2$ coordinated to the Al center in complex **H** (ΔG = -41.0 kcal/mol). The formation of the third C-H bond is the rate determining step of the whole process. The computed barrier of 35.5 kcal/mol is rather high, but consistent with a reaction requiring 110 °C to occur. At this point, the "CH_3O" moiety has been generated from CO_2, and the second part of the process is dedicated to its elimination as "CH_3OBH_2" from the Al center and reformation of Al-H moieties to initiate a second cycle as depicted in Scheme 5. A facile rotation around the Al-O axes of the $MeOBH_2$ and OBH_3 moieties leads to a very strong stabilization (complex **I** , ΔG = -70.9 kcal/mol). The associated $\mathbf{TS_{H\text{-}I}}$ is found at ΔG = -33.5 kcal/mol, just 7.5 kcal/mol higher than complex **H**. In complex **I**, the BH_3 moiety forms an unsymmetrical 3c-2e interaction with the BH_2 group of $MeOBH_2$. Coordination of a third BH_3•SMe_2 molecule occurs via $\mathbf{TS_{I\text{-}J}}$ (ΔG = -41.6 kcal/mol), requires *ca.* 29 kcal/mol, due to increased steric crowding. Upon coordination, a B-H bond interacts with the Al center in complex **J** (ΔG = -61.1 kcal/mol). A pathway regenerating complex **B** rather than the higher energy complex **A** was found from **J** involving a second CO_2 molecule. In fact, the insertion of CO_2 into the B-H bond in **J** occurs barrierless to form complex **K** which is isoelectronic (ΔG = -61.1 kcal/mol). In this complex, a formate OC(O)H, a methoxyborane $MeOBH_2$ and BH_3-coordinated OBH_2 moieties are bound to Al which is thus, pentacoordinated. De-coordination of the $MeOBH_2$ moiety is thus quite exergonic to form complex **L** (ΔG = -82.5 kcal/mol). The σ-bond metathesis reaction between the Al-O and B-H bonds occurs by cleaving the 3c-2e interaction between borane moieties through complex **M**, which results in forming $O(BH_2)_2$ and regenerating complex **B**. Finally, as is well known in boron chemistry, three $MeOBH_2$ molecules undergo substituent rearrangements to form $B(OMe)_3$ and BH_3, while three $O(BH_2)_2$ molecules lead to B_2O_3 and BH_3. In summary, the highest kinetic barrier in the proposed mechanism is 35.5 kcal/mol, related to the third CH bond formation (complex $\mathbf{TS_{G\text{-}H}}$) between complexes **G** and **H**. The other CH bond formations are much more facile. The calculation results are thus in accordance with the experimental conditions and observations (formation of formyl complex **4** and acetal complex **4D** at room temperature).

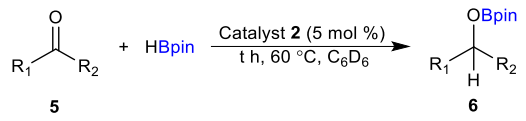
Based on the above calculations, the catalytic cycle for the hydroboration of CO_2 with HBpin is proposed (Scheme 6). Firstly, CO_2 inserts into the Al-H bond of complex **2** to give complex **4**. Subsequently, HBpin adds across the C=O bond in **4** to form **IntI**. The Al-H bond then undergoes σ-bond metathesis with the O-C bond to form MeOBpin coordinating with the Al center. In addition, the resulting Al-O bond coordinates with the second HBpin to form **IntII**. CO_2 then displaces MeOBpin and reacts with HBpin to form a formate moiety bonded to the aluminum in **IntIII**. The third HBpin undergoes σ-bond metathesis with the Al-O bond in **IntIII** to form complex **4** and pinBOBpin.



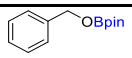
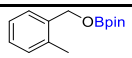
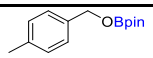
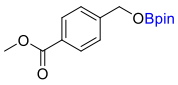
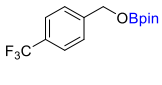
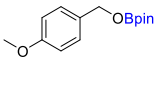
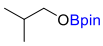
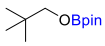
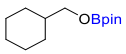
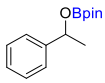
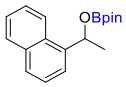
Scheme 6. Catalytic cycle for the hydroboration of CO_2 with HBpin

Following the hydroboration of CO_2, the catalytic ability of complex **2** towards the hydroboration of carbonyl, alkyne and nitrile derivatives were further examined. Firstly, we verified that there were no reactions between substrates with HBpin in C_6D_6 at room temperature or 110 °C without catalyst. On the other hand, catalyzed hydroboration of aromatic aldehyde ArC(O)H (Ar = Ph **5a**, Table 1) with HBpin as well as its derivatives with electron donating (Ar = MeC_6H_4 **5b** & **5c**, $MeOC_6H_4$ **5f**) and withdrawing substituents ($MeCO_2C_6H_4$ **5d**, $F_3CC_6H_4$ **5e**) were completed in 1 h using 5 mol % of **2** at 60°C. The corresponding borate esters were obtained in high yield. Secondly, moderate yield was achieved for the hydroboration of non-aromatic aldehydes **5g** – **5k**. Thirdly, a higher catalytic loading and temperature were required for the hydroboration of ketones **5m** – **5p** when compared to aldehydes in line with their reduced electrophilic character. Fourthly, 10 mol % of **2** catalyzed the hydroboration of aromatic nitriles ArC≡N (Table 2) in high yields. As shown in Table 2, a large scope of electron donating substituent (Ar = $MeOC_6H_4$ **7b**), electron withdrawing substituents (Ar = $F_3CC_6H_4$ **7d**, $F_2C_6H_3$ **7e**) and sterically hindered substituents (Ar = $(CH_3)_3C_6H_2$ **7c**) were hydroborated twice to form the corresponding diboryl amine products [$ArCH_2N(Bpin)_2$]. Replacing the aromatic substituents with alkyl groups (**7f** – **7h**) resulted in both slower reaction rates and lower product yields. Finally, complex **2** was also able to catalyze the hydroboration of aromatic alkynes (ArC≡CH, **9a** – **9d**) with electron donating or withdrawing substituents to form the corresponding trans-boryl alkenes *trans*-[Ar(H)C=CH(Bpin)]. Based on the previous experiments to reduce CO_2, it is suggested that the Al-H bond in complex **2** activates the carbonyl, alkyne or nitrile compounds, which are then reacted with HBpin to form the corresponding hydroborated products, along with the regeneration of complex **2**.

Table 1. Catalytic hydroboration of aldehydes and ketones

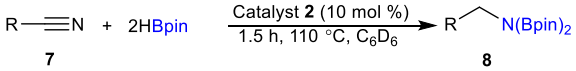


5 **6**

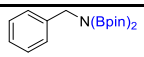
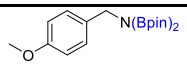
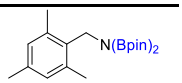
 **6a** t = 1, 93 %, 18.6 h^{-1}	 **6b** t = 2, 97 (94) %, 9.7 h^{-1}	 **6c** t = 2, >99 %, 10.0 h^{-1}
 **6d** t = 2, >99 %, 10.0 h^{-1}	 **6e** t = 3, >99 (95) %, 6.7 h^{-1}	 **6f** t = 1, 93 %, 18.6 h^{-1}
 **6g** t = 1, 92 %, 18.4 h^{-1}	 **6h** t = 1, 93 (88) %, 18.6 h^{-1}	 **6k**[b] t = 1, >99 (92) %, 20.0 h^{-1}
 **6m**[b,c] t = 6, 88 (68) %, 2.9 h^{-1}	 **6n**[b,c] t = 6, 70 (54) %, 2.3 h^{-1}	 6p[b,c] t = 6, 89 (73) %, 3.0 h^{-1}

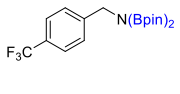
[a]Reaction conditions: Substrate (0.5 mmol), 1 equiv. of HBpin (0.5 mmol), 5 mol% of **2** in C_6D_6 (0.5 mL). Yields are determined by ^1H NMR spectroscopy on the basis of the integration of consumed carbonyl compound and R(R')C(H)OBpin resonances. Isolated yields are reported in parentheses. [b]Reaction temperature: 110 °C [c]Catalytic loading of **2**: 10 mol %. All the catalytic trials were repeated in triplicate.

Table 2. Catalytic hydroboration of nitriles



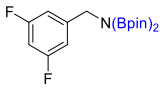
7 **8**

 **8a** 99 (73) %, 6.6 h^{-1}	 **8b** 88 %, 5.9 h^{-1}	 **8c** 38 %, 2.5 h^{-1}



8d

92 (87) %, 6.1 h^{-1}

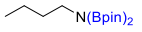


8e

91 (89) %, 6.1 h^{-1}

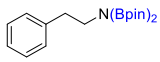
8f

58 %, 3.9 h^{-1}



8g

38 %, 2.5 h^{-1}

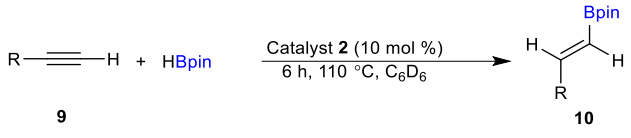


8h

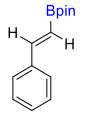
23 %, 1.5 h^{-1}

[a]Reaction conditions: Nitrile compounds (0.2 mmol), 2 equiv. of HBpin (0.4 mmol), C_6D_6 (0.5 mL). Catalyst loading is relative to the nitrile compounds. Yields are determined by ^{1}H NMR spectroscopy on the basis of the integration of consumed nitrile compound and $RCH_2N(Bpin)_2$ resonances. Isolated yields are reported in parentheses. All the catalytic trials were repeated in triplicate.

Table 3. Catalytic hydroboration of alkynes

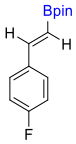


9 **10**



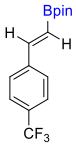
10a

97 %, 1.6 h^{-1}



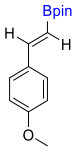
10b

78 %, 1.3 h^{-1}



10c

88 %, 1.5 h^{-1}



10d

88 %, 1.5 h^{-1}

[a]Reaction conditions: Alkyne compounds (0.5 mmol), 1 equiv. of HBpin (0.5 mmol), C_6D_6 (0.5 mL). Catalyst loading is relative to the alkyne compounds. Yields are determined by ^{1}H NMR spectroscopy on the basis of the integration of consumed alkyne compound and *trans*-RCH=CBpin resonances. Isolated yields are reported in parentheses. All the catalytic trials were repeated in triplicate.

Conclusion

In conclusion, the bis(iminophosphoranyl)methanide aluminum complex **2** is a versatile catalyst for the hydroboration of carbon dioxide, carbonyl compounds, alkyne and nitrile derivatives with HBpin to form methoxyborane, borate esters, diboryl amines and *trans*-boryl alkenes, respectively. In particular, complex **2** efficiently reduces CO_2 with BH_3•SMe_2 to form $B(OMe)_3$. Its activity is higher than that of known base-metal catalysts used for such reaction. We have observed that the additions to form the formate AlOCHO and the acetal $AlOCH_2OAl$ derivatives are facile. DFT calculations rationalized that further reduction to the methanol derivative is rather demanding. In light of its catalytic reactivity, we believe that complex **2** or its analogues, will find uses in other catalytic applications. Such endeavors are currently pursued in our laboratories and results will be reported in due course.

Experimental Section

General procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Compound **1** was prepared according to the literature procedure.[22] Toluene was dried over Na/K alloy and distilled prior to use. C_6D_6 was dried over K metal and distilled prior to use. $CDCl_3$ was dried over CaH_2 and distilled prior to use. Chemicals were purchased from Sigma-Aldrich. They were degassed when received and then stored in a glove box. They used directly without further purification. When chemicals were stored under air, they were dried, distilled and degassed by standard Schlenk technique before use. The ^{1}H, ^{11}B{^{1}H}, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a JEOL ECA 400 spectrometer. The NMR spectra were recorded in C_6D_6 and the chemical shifts are relative to $SiMe_4$ for ^{1}H, ^{13}C and ^{29}Si; BF_3·Et_2O for ^{11}B, H_3PO_4 for ^{31}P respectively. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Control experiments are written in the Supporting Information.

Synthesis of **2**: AlH_3•$EtNMe_2$ (2.0 mmol) was added dropwise to a solution of **1** (1.0 mmol) in toluene at -78 °C in a Schlenk flask. The reaction mixture was raised to room temperature and a white suspension was observed. The mixture was stirred for 1 hour and was subsequently dried under vacuum to remove excess AlH_3•$EtNMe_2$. The residue was extracted with 10 ml of toluene to yield a white precipitate. Yield: 0.65 g, 0.92 mmol (92 %, based on **1**). Colorless crystals were grown from concentrated toluene solution of **2**. ^{1}H NMR (395.9 MHz, C_6D_6, ppm): δ 8.02 (m, 8H, *m*-Ph-*H*), 7.04 (m, 12H, *o*,*p*-Ph-*H*), 6.55 (s, 4H, *m*-Mes-*H*), 5.00 (br, 2H, AlH_2), 2.23 (s, 12H, *o*-CH_3), 2.01 (s, 6H, *p*-CH_3). ^{13}C{^{1}H} NMR (99.5 MHz, C_6D_6, ppm): δ 138.30 (t, Ph *m*-*C*), 137.81 (s, Mes *m*-*C*), 134.26 (t, Ph *o*-*C*), 133.96 (s, Mes *o*-*C*), 131.14 (s, Ph *p*-*C*), 130.75 (d, $J_{P\text{-}C}$ = 102.95 Hz, Ph *ipso*-*C*), 130.60 (t, P_2C), 129.71 (s, Mes *p*-*C*), 127.29 (t, $J_{P\text{-}C}$ = 5.72 Hz, Mes ips*o*-*C*), 20.83 (s, Mes *o*-CH_3), 20.42 (s, Mes *p*-CH_3). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6) δ 38.98 (s). HRMS (ESI): *m*/*z* calcd for $C_{43}H_{45}N_2AlP_2Cl$: 713.2562 [(M + H)]$^+$; found: 713.2573.

Synthesis of **4**: Complex **2** (1.43 g, 2.0 mmol) was dissolved in 40 ml of toluene in a Schlenk flask. The reaction mixture was freeze-pump-thaw degassed thrice. CO_2 gas (1 bar) was streamed into the flask using a Schlenk line along with vigorous stirring. After 15 minutes, the reaction mixture was dried under vacuum to yield a white precipitate. Yield: 1.51 g (100%). ^{1}H NMR (395.9 MHz, C_6D_6, ppm): δ 8.52 (s, 1H, OC(=O)*H*), 8.12 (m, 4H, *m*-Ph-*H*), 7.88 (m, 4H, *m*-Ph-*H*), 7.10 (m, 4H, *p*-Ph-*H*), 7.02 (m, 8H, *o*-Ph-*H*), 6.57 (s, 2H, *m*-Mes-*H*), 6.50 (s, 2H, *m*-Mes-*H*), 2.26 (s, 6H, *o*-CH_3), 2.12 (s, 6H, *o*-CH_3), 1.99 (s, 6H, *p*-CH_3). ^{13}C{^{1}H} NMR (99.5 MHz, C_6D_6, ppm): δ 161.6 (s, *C*(O)H), 138.1 (d, $J_{P\text{-}C}$ = 53.2 Hz, Mes, ips*o*-C), 136.4 (s, Mes *o*-C), 134.8 (s, Ph *m*-C), 134.3 (s, Ph *o*-C), 131.5 (s, Mes *p*-C), 131.3 (s, Ph *m*-C), 129.8 (d, $J_{P\text{-}C}$ = 53.2 Hz, Ph *ipso*-C), 124.4 (s, Ph *p*-C), 20.8 (s, Mes *p*-CH_3), 20.6 (s, Mes *p*-CH_3), not observable (P*C*P). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, ppm): δ 40.55 (s). HRMS (ESI): *m*/*z* calcd for $C_{44}H_{45}N_2O_2AlP_2Cl$: 757.2460 [(M + H)]$^+$; found: 757.2467.

Synthesis of **4-D**: Complex **2** (1.43 g, 2.0 mmol) was dissolved in 40 ml of toluene in a Schlenk flask. The reaction mixture was freeze-pump-thaw degassed thrice. CO_2 gas (1 bar) was

streamed into the flask using a Schlenk line along with vigorous stirring. Upon stirring for 16 hours, white precipitates were observed in the flask. The reaction mixture was dried under vacuum and extracted with DCM (10 ml) and hexane (1 ml) mixture. The resulting filtrate was left to stand at 0˚C to yield colourless crystals of **4-D**. Yield: 0.08g (5.3%). ^{1}H NMR (395.9 MHz, C_6D_6, ppm): δ 8.24 (s, 4H, OCH_2O), 8.02 (m, 16H, *m*-Ph-*H*), 7.08 (m, 24H, *o*,*p*-Ph-*H*), 6.52 (s, 8H, *m*-Mes-*H*), 2.13 (s, 24H, *o*-CH_3), 1.98 (s, 12H, *p*-CH_3). ^{13}C{^{1}H} NMR (99.5 MHz, C_6D_6, ppm): δ 161.3 (s, O-*C*H_2-O), 138.1 (s, Mes *o*-C), 135.5 (s, Ph *m*-C), 135.1 (s, Ph *o*-C), 134.4 (t, Mes, *ipso*-C), 131.7 (s, Mes *p*-C), 129.8 (s, Ph *m*-C), overlapped with solvent (Ph *ipso*-C), 124.4 (s, Ph *p*-C), 20.5 (s, Mes *p*-CH_3), 20.3 (s, Mes *o*-CH_3), not observable (P*C*P). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, ppm): δ 40.55 (s). HRMS (ESI): *m*/*z* calcd for $C_{88}H_{89}N_4O_4Al_2P_4Cl_2$: 1513.4842 $[(M + H)]^+$; found: 1513.4854.

Complex **2** Catalyzed Hydroboration of CO_2 with HBPin: In a J-Young NMR tube, complex **2** (0.035 g, 0.05 mmol) and 1,3,5-tri-tert-butylbenzene (0.0245 g, 0.10 mmol, internal standard) were dissolved in toluene (0.5 ml). HBpin (0.064g, 0.5 mmol) was then added into the tube. The reaction mixture was freeze-pump-thaw degassed thrice. CO_2 gas (1 bar) was streamed into the tube using a Schlenk line. The tube was subsequently heated under 110˚C for 48 hrs. Yield was calculated based on total number of protons converted into methoxy product with reference to the integral of internal standard. Yield = 78.4%.

Complex **2** Catalyzed Hydroboration of CO_2 with BH_3•SMe_2: In a J-Young NMR tube, complex **2** (0.0035 g, 0.005 mmol) was dissolved in toluene (0.5 ml). BH_3•SMe_2 (0.038 g, 0.5 mmol) was then added into the tube. The reaction mixture was freeze-pump-thaw degassed thrice. CO_2 gas (1 bar) was streamed into the tube using a Schlenk line. The tube was subsequently heated under 110˚C for 1 hr. CH_3 protons of SMe_2 were used as the internal standard for calculating yield. Yield was calculated based on total number of protons converted into methoxy product. Yield = 97.6%.

Complex **2** Catalyzed Hydroboration of CO_2 with HBCat: In a J-Young NMR tube, complex **2** (0.035 g, 0.05 mmol) and 1,3,5-tri-tert-butylbenzene (0.0182 g, 0.074 mmol, internal standard) were dissolved in toluene (0.5 ml). HBCat (0.064g, 0.5 mmol) was then added into the tube. The reaction mixture was freeze-pump-thaw degassed thrice. CO_2 gas (1 bar) was streamed into the tube using a Schlenk line. The tube was subsequently heated under 110˚C for 24 hrs. Yield was calculated based on total number of protons converted into methoxy product with reference to the integral of internal standard. Yield = 28.8%.

General procedures for the complex **2** catalyzed hydroboration of carbonyl compounds, nitriles and alkynes: Hydroboration (Tables 1-3) were performed in J-Young NMR tube under Ar gas. Complex **2** was dissolved into 0.5 ml of C_6D_6. HBPin was then added into the solution and followed by addition of the respective substrates. The tube was subsequently heated in an oil bath in respective temperatures. The conversion of the substrates were obtained based on total number of protons converted into their hydroborated products. The products were isolated by drying the reaction mixture under vacuum, followed by extraction with n-hexane. The resulting solution were dried under vacuum and characterized by NMR spectroscopy. Isolated yields of selected products were subsequently obtained by weight.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures (PDF), theoretical studies (XYZ) X-ray crystallographic data (CIF)

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Author Contributions

The manuscript was contributed equally by C.-C. Chia and Y.-C. Teo. All authors have given approval to the final version of the manuscript.

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(29) In Bage, A. D.; Hunt, T. A.; Thomas, S. P. *Org. Let.* **2020,** *22*, 4107-4112, BH_3 was found as hidden catalyst. To verify whether BH_3 could be formed in the catalysis (Scheme 2), HBpin reacted with 10 mol % of complex **2** in C_6D_6 at 110 °C for 48 h and no reduction of HBpin was observed. To conform that there was no BH_3, TMEDA was then added to the mixture at room temperature and no TMEDA-$(BH_3)_n$ (n = 1, 2) complexes were formed. The results suggest that no BH_3 or adducts thereof, or BH_4^- or other borate species were formed in the catalysis. Complex **2** is the only active catalyst in the hydroboration of CO_2. Even if BH_3 was formed in catalysis, it could be reacted with compound **2** in the hydroboration. To support this, 10 mol % of complex **2**, 10 mol% of $BH_3.SMe_2$, HBpin and 4-(trifluoromethyl)benzaldehyde [OC(H)(4-CF_3-C_6H_4)] (**5e**) were reacted in C_6D_6 at 60 °C, a mixture of **6e** and borate ester [B{OCH2(4-CF_3-C_6H_4)}$_3$] (^{11}B = 17.52 ppm) was formed. The latter is the product of **5e** with $BH_3.SMe_2$.

SYNOPSIS TOC. The bis(phosphoranyl)methanido aluminum hydride catalyzed the reduction of CO_2 with BH_3•SMe_2 to afford trimethyl borate [$B(OMe)_3$] and B_2O_3.