Aluminum-Hydride-Catalyzed Hydroboration of Carbon Dioxide

Cher-Chiek Chia, Yeow-Chuan Teo, Ning Cham, Samuel Ying-Fu Ho,
Zhe-Hua Ng, Hui-Min Toh, Nicolas Mézailles, Cheuk-Wai So

► To cite this version:

Cher-Chiek Chia, Yeow-Chuan Teo, Ning Cham, Samuel Ying-Fu Ho, Zhe-Hua Ng, et al.. Aluminum-Hydride-Catalyzed Hydroboration of Carbon Dioxide. *Inorganic Chemistry*, 2021, 60 (7), pp.4569-4577. 10.1021/acs.inorgchem.0c03507 . hal-03405902

HAL Id: hal-03405902

<https://hal.science/hal-03405902>

Submitted on 27 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Aluminum Hydride-Catalyzed Hydroboration of Carbon Dioxide

Cher-Chiek Chia,^a Yeow-Chuan Teo,^a Ning Cham,^a Samuel Ying-Fu Ho,^{a,b} Zhe-Hua Ng,^a Hui-Min Toh,^a Nicolas Mézailles,^{b*} Cheuk-Wai So^{a*}

^aDivision of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371. ^bLaboratoire Hétérochimie Fondamentale et Appliquée, CNRS, Université Paul Sabatier, 31062 Toulouse, France.

ABSTRACT: This study describes the first use of a bis(phosphoranyl)methanido aluminum hydride, [ClC(PPh₂NMes)₂AlH₂] (**2**, Mes = Me₃C₆H₂) for the catalytic hydroboration of CO₂. Complex **2** was synthesized by the reaction of a lithium carbenoid [Li(Cl)C(PPh₂NMes)₂] with two equivalents of AlH₃•NEtMe₂ in toluene at -78 °C. 10 mol % of **2** was able to catalyze the reduction of CO₂ with HBpin in C₆D₆ 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 [BH₃•SMe₂] 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 B₂O₃ (**3f**). Mechanistic studies show that the Al-H bond in complex **2** activated CO₂ to form [ClC(PPh₂NMes)₂Al(H){OC(O)H}] (**4**), which was subsequently reacted with BH₃•SMe₂ 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 abundance 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 aromatics³ 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 LiAlH₄ 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 CO₂ 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 CO₂ 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 CO₂ 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, [H₃B₂-C(PPh₂S)₂Li(OEt₂)]²¹ and [ClC(PPh₂NMes)₂BH₂]²² were among the most efficient catalysts for CO₂ 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 CO₂. Herein, we report the synthesis of a bis(phosphoranyl)methanido aluminum hydride and its use in the catalytic hydroboration of CO₂ 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(PPh₂NMes)₂] (**1**, Mes = C₆H₂Me₃) species which we reported in 2015.²² Upon treatment with two equivalents of AlH₃•NEtMe₂ 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 LiAlH₄, [ClC(PPh₂NMes)₂AlH₂] (**2**) was obtained as a colorless crystalline solid (92 % yield) in the concentrated filtrate. The results show that AlH₃•NEtMe₂ undergoes a disproportionation reaction to form “AlH₂⁺”, stabilized by the carbenoid backbone, and an AlH₄⁻ species in the presence of compound **1**. Complex **2** was analyzed and characterized by NMR spectroscopy and X-ray crystallography. The ¹H 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 AlH₂⁺ moiety. The ³¹P NMR spectroscopy shows a new singlet at 39.0 ppm, more than 10 ppm downfield from **1** (δ 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 AlH₂⁺ 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(PPh₂NMes)₂] in hot toluene was not observed.

Next, the catalytic ability of the bis(phosphoranyl)methanido aluminum hydride complex **2** towards the hydroboration of CO₂ with boranes was

then examined. To begin with, we verified that there was no reaction between CO₂ and boranes (HBpin, BH₃•SMe₂ and HBcat) in C₆D₆ 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 CO₂ with HBpin in C₆D₆ 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 CO₂ hydroboration with pinacolborane (HBpin) (TOF = 0.07 – 14.5 h⁻¹).²³ A similar reduction of CO₂ 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 bis(boryl)oxide [(catB)₂O] (**3d**). In the catalysis, most of HBcat was unreacted, while a mixture of B₂(cat)₃ (“B NMR: 22.5 ppm) and four-coordinate borane compounds (“B NMR: -14.5 ppm) was observed. This suggests that intermediates in the catalysis could react with HBcat to form B₂(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 NaBH₄-free²⁴ [BH₃•SMe₂] 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 D₂O quantitatively formed boric acid (by ¹¹B NMR) which is indicative that the white precipitate formed during the catalysis is B₂O₃. 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 CO₂ with BH₃, including the ambiphilic phosphine-borane compound [1-B(OR)₂-2-PR'₂-C₆H₄] (TOF: 43 - 257 h⁻¹; R' = Ph, *i*Pr; (OR)₂ = (OMe)₂, catechol, pinacol),²⁵ bis(thiophosphinoyl)methanide-supported lithium borohydride [H₃B₂-C(PPh₂S)₂Li(OEt₂)] (TOF: 150 h⁻¹),²¹ bis(iminophosphoranyl)methanido boron hydride [ClC(PPh₂NMes)₂BH₂] (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 CO₂. 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 CO₂ in toluene at room temperature for 15 min (Scheme 3), whereby complex **2** was fully consumed. The ³¹P NMR spectrum of the reaction mixture showed a single new signal at 40.5 ppm, while the ¹H 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 CO₂ inserts into one Al-H bond in complex **2** to form [ClC(PPh₂NMes)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 C₆D₆, toluene and CH₂Cl₂. Efforts were made to crystallize this compound in CH₂Cl₂, 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 ³¹P NMR spectrum. The ¹H NMR spectrum showed a singlet at 8.24 ppm with an integration of 4 indicating the for-

mation of two OCH₂O moieties. In addition, the ¹H NMR spectrum showed a set of signals for the bis(iminophosphoranyl)methanido ligand. Colorless crystals were obtained from the initial CH₂Cl₂ solution of **4**, crystallized at 0 °C for one week. The X-ray crystallographic analysis proved the formation of the acetal derivative [LAl(OCH₂O)₂AlL] (**4-D**, L = ClC(PPh₂NMes)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, CH₂Cl₂) and in solid state. The X-ray crystal structure of complex **4-D** comprises of an Al(OCH₂O)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-diketiminato ligand [RAl(OCH₂O)₂AlR] (Al-O: 1.7123(11), 1.7239(11) Å; R = HC{C(Me)NDipp}₂, Dipp = 2,6-*i*Pr₂C₆H₃), which was isolated from the reaction of the germanium(II) formate [RGeOC(O)H] and aluminum hydride [RAIH₂].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).

To prove that complex **4** is an intermediate in the catalysis, 10 mol % of **4** was used to catalyze the reaction of CO₂ with HBpin in C₆D₆ 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 CO₂ with BH₃•SMe₂ in C₆D₆ 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 CO₂ 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 CO₂ with HBpin or BH₃•SMe₂ in C₆D₆ 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 CO₂, while **4-D** is an off-cycle product.

Moreover, complex **4** was reacted with 3 equivalents of BH₃•SMe₂ in C₆D₆ to form a mixture of bis(iminophosphoranyl)methanido compounds, confirmed by ³¹P NMR spectroscopy (7 signals: 41.1 – 42.5 ppm). The reaction mixture was then heated at 110 °C overnight. ³¹P NMR spectroscopy showed that complex **2** was regenerated, along with the formation of B(OMe)₃, represented by ¹¹B NMR spectroscopy. This indicates that the **2**-catalyzed CO₂ hydroboration with BH₃•SMe₂ 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 C₄₄H₄₈BN₂O₂AlP₂Cl: 771.2788 [(M + H)]⁺; found: 771.2774. F-I: HRMS (ESI): *m/z* calcd for C₄₄H₅₁B₂N₂O₂AlP₂Cl: 785.3116 [(M + H)]⁺; found: 785.3167. J: HRMS (ESI): *m/z* calcd for C₄₄H₅₄B₃N₂O₂AlP₂Cl: 799.3444 [(M + H)]⁺; found: 799.3474. K: HRMS (ESI): *m/z* calcd for C₄₄H₄₉B₂N₂O₃AlP₂Cl: 799.2908 [(M + H)]⁺; found: 799.2938. L-M: HRMS (ESI): *m/z* calcd for C₄₄H₄₉B₂N₂O₃AlP₂Cl: 771.2908 [(M + H)]⁺; found: 771.2978.).

On the basis of these experimental studies, a catalytic cycle for the hydroboration of CO₂ with BH₃•SMe₂ is proposed (Scheme 4 and 5) and studied by DFT calculations (see the Supporting Information for details). Complex **B** results from insertion of CO₂ 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. BH₃•SMe₂ then coordinates with the C=O double bond through TS_{B-C} (ΔG = -1.8 kcal/mol) to form compound **C** (ΔG = -20.5 kcal/mol). The transition state for SMe₂ substitution by the CO moiety at BH₃ is accessible, requiring 23.0 kcal/mol. Subsequently, the B-H bond in compound **C** adds to the >C=O bond via TS_{C-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 kinetically facile processes. The acetal group in compound **D** then undergoes rotation around the C-O bond to form compound **E** (ΔG = -30.7 kcal/mol), concurrently

allowing the borane to interact with the aluminum hydride. A second BH₃•SMe₂ has then to be added to allow for the third C-H bond to be formed. It coordinates to the oxygen atom of the acetal group in compound **E**, to result in complex **F**, which is almost iso-energetic (ΔG = -30.0 kcal/mol) via TS_{E-F} (ΔG = -12.1 kcal/mol). Notably, in complex **F**, the oxygen atom and BH₂ 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-BH₃ moieties. Subsequently, the B-H bond is added to the acetal group via TS_{G-H} (ΔG = -5.3 kcal/mol) resulting in the cleavage of the O-C bond and the formation of MeOBH₂ 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 “CH₃O” moiety has been generated from CO₂, and the second part of the process is dedicated to its elimination as “CH₃OBH₂” 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 MeOBH₂ and OBH₃ moieties leads to a very strong stabilization (complex **I**, ΔG = -70.9 kcal/mol). The associated TS_{H-I} is found at ΔG = -33.5 kcal/mol, just 7.5 kcal/mol higher than complex **H**. In complex **I**, the BH₃ moiety forms an unsymmetrical 3c-2e interaction with the BH₂ group of MeOBH₂. Coordination of a third BH₃•SMe₂ molecule occurs via TS_{I-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 CO₂ molecule. In fact, the insertion of CO₂ 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 MeOBH₂ and BH₃-coordinated OBH₂ moieties are bound to Al which is thus, pentacoordinated. De-coordination of the MeOBH₂ 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(BH₂)₂ and regenerating complex **B**. Finally, as is well known in boron chemistry, three MeOBH₂ molecules undergo substituent rearrangements to form B(OMe)₃ and BH₃, while three O(BH₂)₂ molecules lead to B₂O₃ and BH₃. In summary, the highest kinetic barrier in the proposed mechanism is 35.5 kcal/mol, related to the third CH bond formation (complex TS_{G-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 CO₂ with HBpin is pro-

posed (Scheme 6). Firstly, CO₂ inserts into the Al-H bond of complex **2** to give to form 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**. CO₂ 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 CO₂ with HBpin

Following the hydroboration of CO₂, 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 C₆D₆ 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 = MeC₆H₄ **5b** & **5c**, MeOC₆H₄ **5f**) and withdrawing substituents (MeCO₂C₆H₄ **5d**, F₃CC₆H₄ **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 = MeOC₆H₄ **7b**), electron withdrawing substituents (Ar = F₃CC₆H₄ **7d**, F₂C₆H₃ **7e**) and sterically hindered substituents (Ar = (CH₃)₃C₆H₂ **7c**) were hydroborated twice to form the corresponding diboryl amine products [ArCH₂N(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 CO₂, 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

$\text{R}_1-\text{C}(=\text{O})-\text{R}_2 + \text{HBpin} \xrightarrow[\text{t h, 60 } ^\circ\text{C, C}_6\text{D}_6]{\text{Catalyst } \mathbf{2} \text{ (5 mol \%)}} \text{R}_1-\text{CH}(\text{H})-\text{CH}(\text{OBpin})-\text{R}_2$		
5	6	
6a	6b	6c
t = 1, 93 %, 18.6 h ⁻¹	t = 2, 97 (94) %, 9.7 h ⁻¹	t = 2, >99 %, 10.0 h ⁻¹
6d	6e	6f
t = 2, >99 %, 10.0 h ⁻¹	t = 3, >99 (95) %, 6.7 h ⁻¹	t = 1, 93 %, 18.6 h ⁻¹
6g	6h	6k^b
t = 1, 92 %, 18.4 h ⁻¹	t = 1, 93 (88) %, 18.6 h ⁻¹	t = 1, >99 (92) %, 20.0 h ⁻¹
6m^{b,c}	6n^{b,c}	6p^{b,c}
t = 6, 88 (68) %, 2.9 h ⁻¹	t = 6, 70 (54) %, 2.3 h ⁻¹	t = 6, 89 (73) %, 3.0 h ⁻¹

^aReaction conditions: Substrate (0.5 mmol), 1 equiv. of HBpin (0.5 mmol), 5 mol% of **2** in C₆D₆ (0.5 mL). Yields are determined by ¹H NMR spectroscopy on the basis of the consumption of the carbonyl compounds and the identity of the R(R')C(H)OBpin resonances. Isolated yields are reported in parentheses. ^bReaction temperature: 110 °C. Catalytic loading of **2**: 10 mol %. All the catalytic trials were repeated in triplicate.

Table 2. Catalytic hydroboration of nitriles

^aReaction conditions: Nitrile compounds (0.2 mmol), 2 equiv. of HBpin (0.4 mmol), C₆D₆ (0.5 mL). Catalyst loading is relative to the nitrile compounds. Yields are determined by ¹H NMR spectroscopy on the basis of the consumption of the nitrile compounds and the identity of the RCH₂N(Bpin)₂ resonances. Isolated yields are reported in parentheses. All the catalytic trials were repeated in triplicate.

Table 3. Catalytic hydroboration of alkynes

^aReaction conditions: Alkyne compounds (0.5 mmol), 1 equiv. of HBpin (0.5 mmol), C₆D₆ (0.5 mL). Catalyst loading is relative to the alkyne compounds. Yields are determined by ¹H NMR spectroscopy on the basis of the consumption of the alkyne compounds and the identity of the *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 CO₂ with BH₃•SMe₂ 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 AIOCHO and the acetal AIOCH₂OAl derivatives are facile. DFT calculations rationalized that further reduction to the methanol derivative is rather demanding. In light of its transition-metal-like 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. C₆D₆ was dried over K metal and distilled prior to use. CDCl₃ was dried over CaH₂ 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. The ¹H, ¹³B{¹H}, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a JEOL ECA 400 spectrometer. The NMR spectra were recorded in C₆D₆ and the chemical shifts are relative to SiMe₄ for ¹H, ¹³C and ²⁹Si; BF₃•Et₂O for ¹¹B, H₃PO₄ for ³¹P respectively. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University.

Synthesis of 2: AlH₃•EtNMe₂ (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 AlH₃•EtNMe₂. The residue was extracted with 10 ml of toluene to yield a white precipitate. Yield: 0.65 g, 0.92 mmol (91 %, based on **1**). Colorless crystals were grown from concentrated toluene solution of **2**. ¹H NMR (395.9 MHz, C₆D₆, 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, AlH₂), 2.23 (s, 12H, *o*-CH₃), 2.01 (s, 6H, *p*-CH₃). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 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-C} = 102.95 Hz, Ph *ipso*-C), 130.60 (t, P₂C), 129.71 (s, Mes *p*-C), 127.29 (t, J_{P-C} = 5.72 Hz, Mes *ipso*-C), 20.83 (s, Mes *o*-CH₃), 20.42 (s,

Mes *p*-CH₃). ³¹P{¹H} NMR (121.5 MHz, C₆D₆) δ 38.98 (s). HRMS (ESI): *m/z* calcd for C₄₃H₄₅N₂AlP₂Cl: 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. CO₂ 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 %). ¹H NMR (395.9 MHz, C₆D₆, 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*-CH₃), 2.12 (s, 6H, *o*-CH₃), 1.99 (s, 6H, *p*-CH₃). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, ppm): δ 161.6 (s, C(O)H), 138.1 (d, *J*_{P-C} = 53.2 Hz, Mes, *ipso*-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-C} = 53.2 Hz, Ph *ipso*-C), 124.4 (s, Ph *p*-C), 20.8 (s, Mes *p*-CH₃), 20.6 (s, Mes *p*-CH₃), not observable (PCP). ³¹P{¹H} NMR (121.5 MHz, C₆D₆, ppm): δ 40.55 (s). HRMS (ESI): *m/z* calcd for C₄₄H₄₅N₂O₂AlP₂Cl: 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. CO₂ 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 %). ¹H NMR (395.9 MHz, C₆D₆, ppm): δ 8.24 (s, 4H, OCH₂O), 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*-CH₃), 1.98 (s, 12H, *p*-CH₃). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, ppm): δ 161.3 (s, O-CH₂-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*-CH₃), 20.3 (s, Mes *o*-CH₃), not observable (PCP). ³¹P{¹H} NMR (121.5 MHz, C₆D₆, ppm): δ 40.55 (s). HRMS (ESI): *m/z* calcd for C₈₈H₈₉N₄O₄Al₂P₄Cl₂: 1513.4842 [(M + H)]⁺; found: 1513.4854.

Complex 2 Catalyzed Hydroboration 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. CO₂ 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 based on the integral of internal standard. Yield = 78.4 %.

Complex 2 Catalyzed Hydroboration with BH₃•SMe₂: In a J-Young NMR tube, complex **2** (0.0035 g, 0.005 mmol) were dissolved in toluene (0.5 ml). BH₃•SMe₂ (0.038 g, 0.5 mmol) was then added into the tube. The reaction mixture was freeze-pump-thaw degassed thrice. CO₂ gas (1 bar) was streamed into the tube using a Schlenk line. The tube was subsequently heated under 110°C for 1 hr. CH₃ protons of SMe₂ 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 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. CO₂ 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 based on 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 C₆D₆. 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)

AUTHOR INFORMATION

Corresponding Author

*C.-W. So: CWSO@ntu.edu.sg

*N. Mézailles: mezailles@chimie.ups-tlse.fr.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

This work is supported by the National Research Foundation Singapore, NRF-ANR (NRF2018-NRF-ANR026 Si-POP) and Ministry of Education Singapore, AcRF Tier 2 (MOE2019-T2-2-129) (C.-W. So). We thank CalMip (CNRS, Toulouse, France) for access to calculation facilities

REFERENCES

- (1) (a) Harder, S. Early Main Group Metal Catalysis: Concepts and Reactions; Wiley-VCH: Weinheim, Germany, 2019. (b) Power, P. P. Main-group Elements as Transition metals. *Nature* **2010**, *463*, 171-177. (c) Weetman, C.; Inoue, S. The Road Travelled: After Main-Group Elements as Transition Metals. *ChemCatChem* **2018**, *10*, 4213-4228 and references therein.
- (2) (a) Meerwein, H.; Schmidt, R. Ein neues Verfahren zur Reduktion von Aldehyden und Ketonen. *Justus Liebigs Ann. Chem.* **1925**, *444*, 221-238. (b) Verley, A. Exchange of Functional Groups between Two Molecules. Exchange of Alcohol and Aldehyde Groups. *Bull. Soc. Chim. Fr.* **1925**, *37*, 537-542. (c) Ponndorf, W. Der reversible Austausch der Oxydationsstufen zwischen Aldehyden oder Ketonen einerseits und primären oder sekundären Alkoholen andererseits. *Angew. Chem.* **1926**, *39*, 138 - 143.
- (3) Friedel, C.; Crafts, J. M. Sur une nouvelle méthode générale de synthèse d'hydrocarbures, d'acétones, etc.. *Compt. Rend.* **1877**, *84*, 1392-1450.
- (4) Wei, Y.; Wang, S.; Zhou, S. Aluminum Alkyl Complexes: Synthesis, Structure, and Application in ROP of Cyclic Esters. *Dalton Trans.* **2016**, *45*, 4471-4485.
- (5) (a) Nikonov, G. I. New Tricks for an Old Dog: Aluminum Compounds as Catalysts in Reduction Chemistry. *ACS Catalysis* **2017**, *7*, 7257-7266. (b) Less, R. J.; Simmonds, H. R.; Wright, D. S. Reactivity and Catalytic Activity of tert-Butoxy-aluminum Hydride Reagents. *Dalton Trans.* **2014**, *43*, 5785-5792. (c) Jakhar, V. K.; Barman, M. K.; Nembenna, S. Aluminum Monohydride Catalyzed Selective Hydroboration of Carbonyl Compounds. *Org. Lett.* **2016**, *18*, 4710-4713. (d) Zhang, G.; Wu, J.; Zeng, H.; Neary, M. C.; Devany, M.; Zheng, S.; Dub, P. A. Dearomatization and Functionalization of Terpyridine Ligands Leading to Unprecedented Zwitterionic Meisenheimer Aluminum Complexes and Their Use in Catalytic Hydroboration. *ACS Catalysis* **2019**, *9*, 874-884. (e) Mukherjee, D.; Osseili, H.; Truong, K.-N.; Spaniol, T. P.; Okuda, J. Ring-opening of Cyclic Ethers by Aluminum Hydridotriphenylborate. *Chem. Commun.* **2017**, *53*, 3493-3496. (f) Franz, D.; Sirtl, L.; Poethig, A.; Inoue, S. Aluminum Hydrides Stabilized by N-Heterocyclic Imines as Catalysts for Hydroborations with Pinacolborane. *Z. Anorg. Allg. Chem.* **2016**, *642*, 1245-1250. (g) Prashanth, B.; Bhandari, M.; Ravi, S.; Shamasundar, K. R.; Singh, S. Electronically Unsaturated Three-Coordinate Aluminum Hydride and Organoaluminum Cations. *Chem. - Eur. J.* **2018**, *24*, 4794-4799.
- (6) Myers, T. W.; Berben, L. A. Aluminum-Ligand Cooperative N-H Bond Activation and an Example of Dehydrogenative Coupling. *J. Am. Chem. Soc.* **2013**, *135*, 9988-9990.
- (7) Myers, T. W.; Berben, L. A. Aluminum-Ligand Cooperation Promotes Selective Dehydrogenation of Formic Acid to H₂ and CO₂. *Chem. Sci.* **2014**, *5*, 2771-2777.
- (8) Thompson, E. J.; Berben, L. A. Electrocatalytic Hydrogen Production by an Aluminum(III) Complex: Ligand-Based Proton and Electron Transfer. *Angew. Chem., Int. Ed.* **2015**, *54*, 11642-11646.
- (9) Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. An Aluminum Hydride That Functions like a Transition-Metal Catalyst. *Angew. Chem., Int. Ed.* **2015**, *54*, 10225-10229.
- (10) Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W. An Aluminum Dihydride Working as a Catalyst in Hydroboration and Dehydrocoupling. *J. Am. Chem. Soc.* **2016**, *138*, 2548-2551.
- (11) Bismuto, A.; Thomas, S. P.; Cowley, M. J. Aluminum Hydride Catalyzed Hydroboration of Alkynes. *Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 15356-15359.
- (12) Bismuto, A.; Cowley, M. J.; Thomas, S. P. Aluminum-Catalyzed Hydroboration of Alkenes. *ACS Catalysis* **2018**, *8*, 2001-2005.
- (13) Elsen, H.; Färber, C.; Ballmann, G.; Harder, S. LiAlH₄: From Stoichiometric Reduction to Imine Hydrogenation Catalysis. *Angew. Chem., Int. Ed.* **2018**, *57*, 7156-7160.
- (14) (a) Pollard, V. A.; Fuentes, M. A.; Kennedy, A. R.; McLellan, R.; Mulvey, R. E. Comparing Neutral (Monometallic) and Anionic (Bimetallic) Aluminum Complexes in Hydroboration Catalysis: Influences of Lithium Cooperation and Ligand Set. *Angew. Chem., Int. Ed.* **2018**, *57*, 10651-10655. (b) Pollard, V. A.; Young, A.; McLellan, R.; Kennedy, A. R.; Tuttle, T.; Mulvey, R. E. Lithium-Aluminate-Catalyzed Hydrophosphination Applications. *Angew. Chem., Int. Ed.* **2019**, *58*, 12291-12296.
- (15) Jakobsson, K.; Chu, T.; Nikonov, G. I. Hydrosilylation of Olefins Catalyzed by Well-Defined Cationic Aluminum Complexes: Lewis Acid versus Insertion Mechanisms. *ACS Catalysis* **2016**, *6*, 7350-7356.
- (16) Lebedev, Y.; Polishchuk, I.; Maity, B.; Dinis Veloso Guerreiro, M.; Cavallo, L.; Rueping, M. Asymmetric Hydroboration of Heteroaryl Ketones by Aluminum Catalysis. *J. Am. Chem. Soc.* **2019**, *141*, 19415-19423.
- (17) Strongly Lewis acidic aluminum complexes such as AlBr₃, Al(C₆F₅)₃, [Et₂Al][CH₆B₁₁I₆] have been used in catalytic CO₂ reduction processes: (a) Ménard, G.; Stephan, D. W. Room Temperature Reduction of CO₂ to Methanol by Al-Based Frustrated Lewis Pairs and Ammonia Borane. *J. Am. Chem. Soc.* **2010**, *132*, 1796-1797. (b) Chen, J.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y. X. Selective Reduction of CO₂ to CH₄ by Tandem Hydrosilylation with Mixed Al/B Catalysts. *J. Am. Chem. Soc.* **2016**, *138*, 5321-5333.
- (18) Caise, A.; Jones, D.; Kolychev, E. L.; Hicks, J.; Goicoechea, J. M.; Aldridge, S. On the Viability of Catalytic Turnover via Al-O/B-H Metathesis: The Reactivity of β -Diketiminato Aluminum Hydrides towards CO₂ and Boranes. *Chem. - Eur. J.* **2018**, *24*, 13624-13635.
- (19) Franz, D.; Jandl, C.; Stark, C.; Inoue, S. Catalytic CO₂ Reduction with Boron- and Aluminum Hydrides. *ChemCatChem* **2019**, *11*, 5275-5281.
- (20) (a) Panda, T. K.; Roesky, P. W. Main-group and Transition-metal Complexes of Bis(phosphinimino)methanides. *Chem Soc Rev* **2009**, *38*, 2782-2804. (b) Fustier-Boutignon, M.; Nebra, N.; Mézailles, N. Geminal Dianions Stabilized by Main Group Elements. *Chem. Rev.* **2019**, *119*, 8555-8700.
- (21) Lafage, M.; Pujol, A.; Saffon-Merceron, N.; Mézailles, N. BH₃ Activation by Phosphorus-Stabilized Geminal Dianions: Synthesis of Ambiphilic Organoborane, DFT Studies, and Catalytic CO₂ Reduction into Methanol Derivatives. *ACS Catalysis* **2016**, *6*, 3030-3035.
- (22) Ho, S. Y. F.; So, C.-W.; Saffon-Merceron, N.; Mézailles, N. Formation of a Zwitterionic Boronium Species from the Reaction of a Stable Carbenoid with Borane: CO₂ Reduction. *Chem. Commun.* **2015**, *51*, 2107-2110.
- (23) (a) Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Aldridge, S. Cooperative Bond Activation and Catalytic Reduction of Carbon Dioxide at a Group 13 Metal Center. *Angew. Chem., Int. Ed.* **2015**, *54*, 5098-5102. (b) Anker, M. D.; Arrowsmith, M.; Bellham, P.; Hill, M. S.; Kociok-Koehn, G.; Liptrot, D. J.; Mahon, M. F.; Weetman, C. Selective Reduction of CO₂ to a

- Methanol Equivalent by $\text{B}(\text{C}_6\text{F}_5)_3$ -Activated Alkaline Earth Catalysis. *Chem. Sci.* **2014**, 5, 2826-2830. (c) Chong, C. C.; Kinjo, R. Catalytic Hydroboration of Carbonyl Derivatives, Imines, and Carbon Dioxide. *ACS Catal.* **2015**, 5, 3238-3259. (d) Hadlington, T. J.; Kefalidis, C. E.; Maron, L.; Jones, C. Efficient Reduction of Carbon Dioxide to Methanol Equivalents Catalyzed by Two-Coordinate Amido-Germanium(II) and -Tin(II) Hydride Complexes. *ACS Catal.* **2017**, 7, 1853-1859.
- (24) Fujiwara, K.; Yasuda, S.; Mizuta, T. Reduction of CO_2 to Trimethoxyboroxine with BH_3 in THF. *Organometallics* **2014**, 33, 6692-6695.
- (25) (a) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. A Highly Active Phosphine-Borane Organocatalyst for the Reduction of CO_2 to Methanol Using Hydroboranes. *J. Am. Chem. Soc.* **2013**, 135, 9326-9329. (b) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. Reducing CO_2 to Methanol Using Frustrated Lewis Pairs: On the Mechanism of Phosphine-Borane-Mediated Hydroboration of CO_2 . *J. Am. Chem. Soc.* **2014**, 136, 10708-10717. (c) Declercq, R.; Bouhadir, G.; Bourissou, D.; Légaré, M.-A.; Courtemanche, M.-A.; Nahi, K. S.; Bouchard, N.; Fontaine, F.-G.; Maron, L. Hydroboration of Carbon Dioxide Using Ambiphilic Phosphine-Borane Catalysts: On the Role of the Formaldehyde Adduct. *ACS Catalysis* **2015**, 5, 2513-2520.
- (26) Wang, T.; Stephan, D. W. Carbene-9-BBN Ring Expansions as a Route to Intramolecular Frustrated Lewis Pairs for CO_2 Reduction. *Chem. - Eur. J.* **2014**, 20, 3036-3039.
- (27) Leong, B.-X.; Lee, J.; Li, Y.; Yang, M.-C.; Siu, C.-K.; Su, M.-D.; So, C.-W. A Versatile NHC-Parent Silyliumylidene Cation for Catalytic Chemo- and Regioselective Hydroboration. *J. Am. Chem. Soc.* **2019**, 141, 17629-17636.
- (28) Tan, G.; Wang, W.; Blom, B.; Driess, M. Mechanistic Studies of CO_2 Reduction to Methanol Mediated by an N-Heterocyclic Germylene Hydride. *Dalton Trans.* **2014**, 43, 6006-6011.
- (29) In Thomas, S. P. et al. *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- $(\text{BH}_3)_n$ ($n = 1, 2$) 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 $\text{BH}_3\cdot\text{SMe}_2$, HBpin and 4-(trifluoromethyl)benzaldehyde [$\text{OC}(\text{H})(4\text{-CF}_3\text{-C}_6\text{H}_4)$] (**5e**) were reacted in C_6D_6 at 60 °C, a mixture of **6e** and borate ester [$\text{B}\{\text{OCH}_2(4\text{-CF}_3\text{-C}_6\text{H}_4)\}_3$] ($^1\text{B} = 17.52$ ppm) was formed

SYNOPSIS TOC. The bis(phosphoranyl)methanido aluminum hydride catalyzed the reduction of CO_2 with $\text{BH}_3 \cdot \text{SMe}_2$ to afford trimethyl borate $[\text{B}(\text{OMe})_3]$ and B_2O_3 .