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Aluminum-Hydride-Catalyzed Hydroboration of Carbon Dioxide

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 $(PPh_2NMes)_2AlH_2$] (2, Mes = Me₃C₆H₂), for the catalytic hydroboration of CO₂. Complex 2 was synthesized by the reaction of a lithium carbenoid $[Li(Cl)C(PPh_2NMes)_2]$ with 2 equiv of AlH₃·NEtMe₂ in toluene at -78 °C. 2 (10 mol %) 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 toward the 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 been 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 from mimicking 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 a 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. 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 the 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 CO_2 with boranes because of unfavorable kinetics of the σ bond metathesis mechanism.¹⁸ Inoue et al. reported that Nheterocyclic 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 ($P = N \leftrightarrow P^+ - N^-$; Figure

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1) of the ligands promote strong electron transfer from the N atoms to main-group elements.²⁰ In particular, we have shown



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

that the boron derivatives of bis(phosphoranyl)methanediide and methanide, $[H_5B_2-C(PPh_2S)_2Li(OEt_2)]^{21}$ and $[ClC-(PPh_2NMes)_2BH_2]$,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.

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 2 equiv of AlH₃· NEtMe₂ in toluene at -78 °C followed by warming to room temperature and stirring for 1 h (Scheme 1), a white

Scheme 1. Synthesis of the Bis(phosphoranyl)methanido Aluminum Hydride 2



suspension was observed. After the white precipitate was filtered, which was identified as $LiAlH_4$, [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** (27.2 ppm).²² The X-ray crystal structure of **2** (Figure 2) features a six-membered CPNAlNP ring in a half chair conformation due to the



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-Cl 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).

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 nonpolar 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** toward 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





^aYields were calculated based on conversion of H.

[pinBOBpin] (3b). The catalytic activity in terms of TOF is in the range of other main-group metal-catalyzed CO₂ hydroborated products 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 B₂(cat)₃ (**3d**). In the catalysis, most of HBcat was unreacted, while a mixture of B₂(cat)₃ (¹¹B NMR: 22.5 ppm) and unidentified four-coordinate borane compounds (¹¹B NMR: -14.5 ppm) was observed, in addition to **3c** and **3d**. 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.

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 ^{'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 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 [H₅B₂-C(PPh₂S)₂Li(OEt₂)] (TOF: 150 h⁻¹),²¹ bis(iminophosphoranyl)methanido boron hydride [ClC-(PPh₂NMes)₂BH₂] (TOF: 157 h⁻¹),²² the ring expansion product arising from phosphine-derived carbenes with 9borabicyclo[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.

The catalytic mechanism was studied by performing stoichiometric stepwise 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 ³¹P NMR spectrum of the

Scheme 3. Formation of Complex 4-D



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 $[ClC(PPh_2NMes)_2Al(H){OC(O)H}]$ (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_{61} toluene, and CH_2Cl_2 . 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 formation 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 1 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 an Al $(OCH_2O)_2$ Al eight-membered ring (Figure 3). The ring structure (Al-O: 1.731(4), 1.710(8) Å) is



Figure 3. X-ray crystal structure of **4-D** with thermal ellipsoids at the 50% probability level. Selected hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cl1–Cl 1.797(5), Cl–Pl 1.747(6), Cl–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).

comparable with the one supported by β -diketiminate ligand [RAI(OCH₂O)₂AIR] (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

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



Scheme 4. DFT Studies of Catalytic CO_2 Hydroboration with BH_3 ·SMe₂ from Complexes A to H, Showing the Three C-H Bond Formations from CO_2^{a}

 $^{a}\Delta G$ in kcal/mol, calculated at 298 K.

methoxyborane **3a** (yield: 78%) and bis(boryl)oxide **3b**. Similarly, **4**-catalyzed hydroboration of CO_2 with $BH_3 \cdot SMe_2$ in C_6D_6 at 110 °C formed $[B(OMe)_3]$ (**3e**, yield: 98%) in 60 min. 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 $BH_3 \cdot SMe_2$ 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 equiv of BH₃·SMe₂ in C_6D_6 to form a mixture of bis(iminophosphoranyl)methanido compounds, confirmed by ³¹P NMR spectroscopy (seven 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 BH_3 ·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, high-resolution mass spectrometry (HRMS) was performed, and we were able to detect the presence of such intermediates (Schemes 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/zcalcd 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 CO₂ with BH₃·SMe₂ is proposed (Schemes 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 ($\Delta G = -24.8 \text{ kcal}/$ 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} ($\Delta G = -1.8$ kcal/mol) to form compound C ($\Delta G = -20.5$ 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} ($\Delta G = -3.5$ kcal/mol) to form complex D ($\Delta G = -27.8$ 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 BH₃·SMe₂ 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 isoenergetic ($\Delta G = -30.0$ kcal/ mol) via TS_{E-F} ($\Delta G = -12.1$ 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 ($\Delta G = -34.3$ kcal/mol), in a facile



Scheme 5. DFT Studies of Catalytic CO₂ Hydroboration with BH·SMe₂ from H to the Formation of 3e and Regeneration of B^a

 $^{a}\Delta G$ in kcal/mol, calculated at 298 K.

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} ($\Delta G = -5.3$ kcal/mol) resulting in the cleavage of the O-C bond and the formation of MeOBH₂ coordinated to the Al center in complex H ($\Delta G = -41.0 \text{ kcal/mol}$). 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, $\Delta G = -70.9$ kcal/mol). The associated TS_{H-I} is found at $\Delta G = -33.5$ 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-I} ($\Delta G = -41.6$ kcal/mol), requiring ~29 kcal/mol, due to increased steric crowding. Upon coordination, a B-H bond interacts with the Al center in complex J ($\Delta G = -61.1$ 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 ($\Delta G = -61.1 \text{ kcal/mol}$). In this complex, a formate OC(O)H, a methoxyborane MeOBH₂, and BH₃-coordinated OBH₂ moieties are bound to Al, which is

thus pentacoordinated. Decoordination 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 $O(BH_2)_2$ 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 $O(BH_2)_2$ 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 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 CO_2 with HBpin is proposed (Scheme 6). First, 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.

Following the hydroboration of CO_2 , the catalytic ability of complex **2** toward the hydroboration of carbonyl, alkyne, and

Scheme 6. Catalytic Cycle for the Hydroboration of CO_2 with HBpin



nitrile derivatives was further examined. First, we verified that there were no reactions between substrates with HBpin in $C_{4}D_{4}$ at room temperature or at 110 °C without a 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 and 5c, MeOC₆H₄ 5f) and -withdrawing substituents (MeCO₂C₆H₄ 5d, F₃CC₆H₄ 5e) was completed in 1 h using 5 mol % of 2 at 60 °C. The corresponding borate esters were obtained in high yield. Second, moderate yield was achieved for the hydroboration of nonaromatic aldehydes 5g-5k. Third, 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. Fourth, 10 mol % of **2** catalyzed the hydroboration of aromatic nitriles $ArC \equiv N$ (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 [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.

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





"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 the consumed carbonyl compound and R(R')C(H)OBpin resonances. Isolated yields are reported in parentheses. ^bReaction temperature: 110 °C ^cCatalytic loading of **2**: 10 mol %. All the catalytic trials were repeated in triplicate.

particular, complex 2 efficiently reduces CO_2 with $BH_3 \cdot SMe_2$ to form $B(OMe)_3$. Its activity is higher than that of known base-metal catalysts used for such a reaction. We have observed that the additions to form the formate AlOCHO and the acetal AlOCH₂OAl 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 a Na/K alloy and distilled prior to use. C_6D_6 was dried over K metal and distilled prior to use. CDCl₃ was dried over CaH₂ and distilled prior to use. Chemicals were purchased from

Table 2. Catalytic Hydroboration of Nitriles



^{*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 ¹H NMR spectroscopy on the basis of the integration of the consumed nitrile compound and $RCH_2N(Bpin)_2$ resonances. Isolated yields are reported in parentheses. All the catalytic trials were repeated in triplicate.

Sigma-Aldrich. They were degassed when received and then stored in a glovebox. They were used directly without further purification. When chemicals were stored under air, they were dried, distilled, and degassed by standard Schlenk techniques before use. The ¹H, ¹¹B{¹H}, ¹³C{¹H}, and ³¹P{¹H} 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 SiMe₄ for ¹H, ¹³C, and ²⁹Si; BF₃:Et₂O for ¹¹B; and 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. Control experiments are written in the Supporting Information.

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 h 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 (92%, 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, P_2C), 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, C_6D_6) δ 38.98 (s). HRMS (ESI): m/zcalcd for $C_{43}H_{45}N_2AIP_2CI$: 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 min, the reaction mixture was dried under vacuum to yield a white precipitate. Yield: 1.51 g (100%). ¹H 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) 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 freezepump-thaw degassed thrice. CO2 gas (1 bar) was streamed into the flask using a Schlenk line along with vigorous stirring. Upon stirring for 16 h, white precipitates were observed in the flask. The reaction mixture was dried under vacuum and extracted with a DCM (10 mL) and hexane (1 mL) mixture. The resulting filtrate was left to stand at 0 °C to yield colorless crystals of 4-D. Yield: 0.08 g (5.3%). ¹H NMR $(395.9 \text{ MHz}, C_6 D_{67} \text{ ppm}): \delta 8.24 (s, 4H, OCH_2 O), 8.02 (m, 16H, m-$ 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, C_6D_{62} ppm): δ 161.3 (s, O- CH_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-CH₃), 20.3 (s, Mes o-CH₃), not observable (PCP). ${}^{31}P{}^{1}H{}$ NMR (121.5 MHz, C₆D₆, 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 CO₂ 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 (0.064 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 48 h. The yield was calculated based on the total number of protons converted into the methoxy product with reference to the integral of internal standard. Yield = 78.4%.

Complex 2 Catalyzed Hydroboration of CO₂ with BH₃·SMe₂. In a J. Young NMR tube, complex 2 (0.0035 g, 0.005 mmol) was 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 h. CH₃ protons of SMe₂ were used as the internal standard for calculating yield. Yield was calculated based on the total number of protons converted into a methoxy product. Yield = 97.6%.

Complex 2 Catalyzed Hydroboration of CO₂ 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 h. Yield was calculated based on total number of protons converted into the 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 a 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 the 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 the 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 was dried under vacuum and characterized by NMR spectroscopy. Isolated yields of selected products were subsequently obtained by weight.

Table 3. Catalytic Hydroboration of Alkynes



^{*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 ¹H 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.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03507.

Experimental procedures; X-ray data collection and structural refinement; DFT calculations; and selected spectra (PDF)

Theoretical studies (XYZ)

Accession Codes

CCDC 2042750–2042751 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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