ACS Catalysis
Research Article
pubs.acs.org/acscatalysis

Hydroboration of Carbon Dioxide Using Ambiphilic Phosphine–Borane Catalysts: On the Role of the Formaldehyde Adduct

Richard Declercq,[†,⊥,∥] Ghenwa Bouhadir,*[,†,⊥] Didier Bourissou,*[,†,⊥] Marc-André Légaré,[‡,∥] Marc-André Courtemanche,[‡] Karine Syrine Nahi,[‡] Nicolas Bouchard,[‡] Frédéric-Georges Fontaine,*[,‡] and Laurent Maron[§]

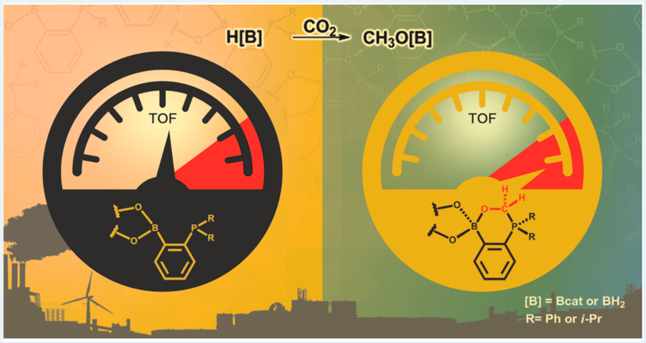
[†]Université de Toulouse, UPS, Laboratoire Hétérochimie Fondamentale et Appliqué (LHFA), 118 route de Narbonne, 31062 Toulouse, France

[⊥]CNRS, LHFA, UMR 5069, 31062 Toulouse, France

[‡]Département de Chimie, Université Laval, 1045 Avenue de la Médecine, Québec (Québec), Canada, G1V 0A6

[§]Université de Toulouse, INSA, UPS, LCPNO, CNRS, UMR 5215 CNRS-UPS-INSA, 135 avenue de Rangueil, 31400 Toulouse, France

Supporting Information



ABSTRACT: Ambiphilic phosphine–borane derivatives 1-$B(OR)_2$-2-PR'_2–C_6H_4 (R′ = Ph (**1**), *i*Pr (**2**); $(OR)_2$ = $(OMe)_2$ (**1a**, **2a**); catechol (**1b**, **2b**) pinacol (**1c**, **2c**), –$OCH_2C(CH_3)_2CH_2O$– (**1d**)) were tested as catalysts for the hydroboration of CO_2 using HBcat or $BH_3{\cdot}SMe_2$ to generate methoxyboranes. It was shown that the most active species were the catechol derivatives **1b** and **2b**. In the presence of HBcat, without CO_2, ambiphilic species **1a**, **1c**, and **1d** were shown to transform to **1b**, whereas **2a** and **2c** were shown to transform to **2b**. The formaldehyde adducts **1b·CH$_2$O** and **2b·CH$_2$O** are postulated to be the active catalysts in the reduction of CO_2 rather than being simple resting states. Isotope labeling experiments and density functional theory (DFT) studies show that once the formaldehyde adduct is generated, the CH_2O moiety remains on the ambiphilic system through catalysis. Species **2b·CH$_2$O** was shown to exhibit turnover frequencies for the CO_2 reduction using $BH_3{\cdot}SMe_2$ up to 228 h^{-1} at ambient temperature and up to 873 h^{-1} at 70 °C, mirroring the catalytic activity of **1b**.

KEYWORDS: *organocatalysis, carbon dioxide reduction, methanol, frustrated Lewis pairs, hydroboranes, ambiphilic systems*

INTRODUCTION

The general consensus of the scientific community on the role of greenhouse gases on global climate changes has led to several initiatives to limit their emissions. As a consequence, a large number of contributions on the search for economical and efficient ways to sequester and valorize carbon dioxide, the principal gas which causes climate change, have appeared. Nowadays, several technologies are used in order to capture carbon dioxide from flue exhausts of major producers but sequestration remains a costly solution.[1] One way to make the capture of CO_2 more economically viable is in its valorization by using this molecule as a C-1 building block for the synthesis of valuable chemicals.[2] One transformation that has attracted much attention is the reduction of carbon dioxide to methanol, which is at the core of the methanol economy, as promoted by Nobel laureate George A. Olah.[3] Several heterogeneous systems are known to catalytically reduce carbon dioxide to methanol, and some of these technologies are now commercialized.[3] Nevertheless, the search for novel catalysts is still ongoing, notably using homogeneous systems which give the promise for more active and selective processes. In that regard, some transition metal-based systems have been used for the reduction of carbon dioxide to formic acid,[4] formate,[5] formaldehyde,[6] methanol,[6d,7] methane,[8] acetals,[9] and carbon monoxide.[10]

In the past few years, there have been many important developments in the design of metal-free catalytic systems for the reduction of carbon dioxide. Indeed, some highly reactive species such as aluminum[11] and silylium cations[12] have been shown to reduce carbon dioxide with low selectivity to methane, methanol, and other alkylation side-products. FLP (frustrated Lewis pair) systems, even if they are known to bind carbon dioxide,[13] have demonstrated very limited efficiency in its reduction.[14,15] Since the seminal report by Ying and co-workers that *N*-heterocyclic carbenes can reduce carbon dioxide in the presence of hydrosilanes to methoxysilanes, which upon

Received: January 29, 2015
Revised: March 11, 2015

DOI: 10.1021/acscatal.5b00189
ACS Catal. 2015, 5, 2513–2520

hydrolysis yield methanol,[16] there have been few other organocatalytic systems reported for carbon dioxide reduction. Among these figures the report by Stephan that some phosphine−borane systems derived from 9-BBN catalyze the hydroboration of CO_2.[17] For their part, Cantat and co-workers demonstrated that strong nitrogen bases, such as guanidines and amidines can be used as organocatalysts for the reduction of CO_2 to formamides using hydrosilanes[18a] or to methoxyboranes using 9-borabicyclo[3.3.1]nonane (9-BBN) and, although with very low turnover frequency, HBcat (cat = catechol).[18b] It was recently reported that bidentate Lewis bases, such as proton sponge, can also act as a catalyst for the reduction of carbon dioxide using $BH_3{\cdot}SMe_2$ as a reductant[18c,d] and that even $NaBH_4$ can catalyze the reduction of carbon dioxide using BH_3 adducts.[18e] Moreover, Cantat and co-workers reported the methylation of amines with carbon dioxide and 9-BBN mediated by proazaphosphatrane superbases.[18f] However, these last systems, although active, exhibit either low turnover numbers or low turnover frequencies.

One of the most active metal-free systems for the reduction of carbon dioxide to date is 1-Bcat-2-PPh_2−C_6H_4 (**1b**), which can be generated in situ from the addition of HBcat to precatalyst Al(2-PPh_2−C_6H_4)$_3$.[19] **1b** can generate methoxyboranes of general formula CH_3OBR_2 from several hydroboranes (HBR_2), such as catecholborane, pinacolborane, and $BH_3{\cdot}SMe_2$, which in turn can be hydrolyzed to methanol.[20] Although such a process has limited commercial potential because of the cost of boranes, it serves as an excellent model to understand the mechanism of FLP-derivatives in the catalytic functionalization of unsaturated substrates such as carbon dioxide. Indeed, the very high turnover frequency (TOF), which can reach 973 h^{-1}, and the turnover numbers (TONs) obtained, which exceed 2950 at 70 °C, surpass that of the most active transition metal catalysts. An in-depth density functional theory (DFT) study of this system using HBcat as reductant allowed postulating that the activation of both the catecholborane and CO_2 in a concerted fashion led to much lower transition state energies than classical reduction pathways, a process that does not occur without catalyst.[21] In order to optimize this class of catalyst, we were interested in looking at the influence of the substituents on the phosphine and borane parts. Herein, we report that the influence of the phosphine and the borane moieties on the catalyst is of limited importance because of substitutions that occur prior to the beginning of the catalytic activity. Notably, the formaldehyde generated forms an adduct with the phosphine−borane that turns out to be an active catalyst for the reduction of carbon dioxide rather than only a resting state as previously postulated. DFT calculations suggest that the dual activation of the borane and carbon dioxide plays a key role in the reduction process.

■ RESULTS AND DISCUSSION

Efficiency of 1-B(OR)$_2$-2-PR′$_2$−C_6H_4 Derivatives As Catalysts for the HBcat Hydroboration of CO_2.

Phosphine−boranes of the general structure 1-BR_2-2-PR′$_2$−C_6H_4 have been reported before and used extensively as ligands for transition metals.[22] Some of these metal-free species have shown a large range of activities, notably in the fixation, splitting, and transfer of singlet dioxygen,[23a] in the bifunctional organo-catalyzed Michael addition[23b] and in the trapping of reactive intermediates of organic transformations.[23c,d] In order to better understand the importance of structural parameters of these phosphine−boranes derivatives on the catalytic activity, the synthesis of 1-B(OR)$_2$-2-PR′$_2$−C_6H_4 derivatives with diphenyl- and di-*iso*-propyl-phosphine moieties (R′ = Ph and *i*Pr) was envisioned (Figure 1).

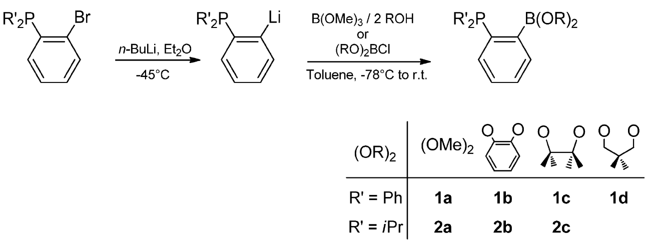


Figure 1. Synthesis of the various derivatives of general formula 1-B(OR)$_2$-2-R′$_2$P−C_6H_4 tested in the course of this study.

The 1-B(OR)$_2$-2-PPh_2−C_6H_4 derivatives (R_2 = catechol (**1b**), pinacol (**1c**), and −$OCH_2C(CH_3)_2CH_2O$− (**1d**)) were easily synthesized from the addition of the corresponding diols to in situ generated 1-B(OMe)$_2$-2-PPh_2−C_6H_4 (**1a**).[23b] The isolation of the latter compound was also possible on the gram scale but proved to be quite sensitive to hydrolysis. On the other hand, the reaction of catechol with 1-B(OMe)$_2$-2-P(*i*Pr)$_2$−C_6H_4 (**2a**) surprisingly did not yield the expected 1-Bcat-2-P(*i*Pr)$_2$−C_6H_4 (**2b**), although the generation of the pinacol derivative 1-Bpin-2-P(*i*Pr)$_2$−C_6H_4 (**2c**) was successful using a similar reaction pathway. It was however possible to synthesize the desired analogue **2b** by the electrophilic trapping of 1-Li-2-P(*i*Pr)$_2$−C_6H_4 with ClBcat. Unfortunately, species **2b** proved to be particularly unstable in solution (Figure S18 in the Supporting Information (SI)), which might be caused by redistribution of the catechol moiety promoted by the nucleophilic phosphine,[24] and had to be protected by coordination to borane, generating species 1-Bcat-2-[P(*i*Pr)$_2{\cdot}$$BH_3$]−$C_6H_4$ (**2b·BH$_3$**).

The catalytic activity of catalysts **1a−d**, **2a**, **2b·BH$_3$**, and **2c** toward the hydroboration of CO_2 was evaluated first using HBcat as a reducing agent under approximately 2 atm of CO_2 in C_6D_6.[25] As can be seen in Table 1 (entries 1−3, 6, and 9), species **1a−c**, **2a**, and **2c** exhibit similar catalytic activity for the formation of methoxyboranes, sustaining turnover frequencies between 46 to 56 h^{-1} range in the first 105 min of reaction. A stoichiometric amount of catBOBcat was also formed during the process, as previously characterized for this system.[20a] The exception is **2b·BH$_3$**, presumably because of the BH_3 protection of the phosphine moiety (entry 7). However, this problem is circumvented after some time since a TON of 74 was observed after 12 h of reaction (entry 8). Species **1d** is very slow to start (entry 4), showing insignificant production of methoxyboranes after 105 min of reaction, but with increasing activity as time goes, reaching TON of 48 after 4 h (entry 9).

Spectroscopic Monitoring of the Reduction Process. In order to rationalize the similarities in catalytic activity of the different phosphine−boranes species and explain the difference of reactivity for the neopentyl glycol derivative **1d**, the CO_2 reduction using HBcat was monitored using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. As previously reported, one species at −1.0 ppm was observed by $^{31}P\{^1H\}$ NMR spectroscopy when **1b** was used as catalyst, which was attributed to the formaldehyde adduct 1-Bcat-2-PPh_2−$C_6H_4{\cdot}CH_2O$ (**1b·CH$_2$O**). Interestingly, it was observed that **1b·CH$_2$O** was also present at the end of the CO_2 reduction catalytic experiments when using any of the **1a−d** derivatives as catalyst. In order to account for possible

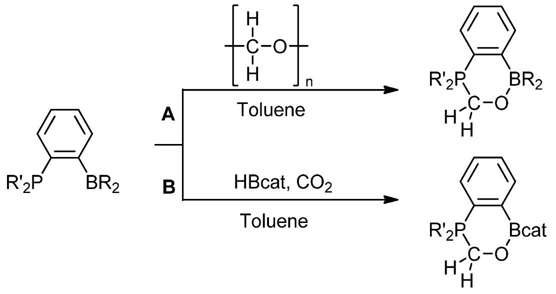
Table 1. Catalytic Hydroboration of 2 atm of CO_2 Using HBcat[a]

$$CO_2 + 3\ HBCat \xrightarrow[70°C,\ C_6D_6]{\text{PB catalyst}} H_3C{-}OBCat + CatBOBCat$$

entry	catalyst	borane	time (min)	TON[b]	TOF[b] (h^{-1})
1	**1a**	HBcat	105	92	53
2	**1b**	HBcat	98	98	56
3	**1c**	HBcat	105	81	46
4	**1d**	HBcat	105	1	<1
5	**1d**	HBcat	240	48	12
6	**2a**	HBcat	105	84	48
7	**2b·BH_3**	HBcat	105	0	0
8	**2b·BH_3**	HBcat	720	74	6
9	**2c**	HBcat	105	75	43

[a] Reaction conditions: In a J-Young NMR tube, 530 μmol of catecholborane (56.4 μL) was added to a mixture of 5.3 μmol of catalyst (~0.6 mL of stock solution at ~8.8 mmol/L) and an internal standard of hexamethylbenzene (2 mg, 3.3 g/L) in C_6D_6. The final concentration of catalyst is 8.1 mM. The J-young NMR tube was placed under ~2 atm of CO_2 and was heated at 70 °C. The catalysis was followed by ^1H NMR spectroscopy. [b] Turnover numbers (TONs) and turnover frequencies for the formation of CH_3OBcat according to the number of hydrogen atoms transferred to CO_2 based on NMR integration of the corresponding resonance with internal standard.

Scheme 1. Synthesis of Formaldehyde Adducts of Phosphine Boranes[a]



[a] **1b·CH_2O**: path A using **1b**, 80 °C, 16 h. **1b·$^{13}CH_2O$**: path B using **1b**, $^{13}CO_2$, 5 HBcat, 80 °C, 16 h. **1c·CH_2O**: path A, using **1c**, 70 °C, 15 min. **2b·CH_2O**: path B using **2c**, 3 HBcat, 80 °C, 12 h. **2c·CH_2O**: path A, using **2c**, 70 °C, 15 min.

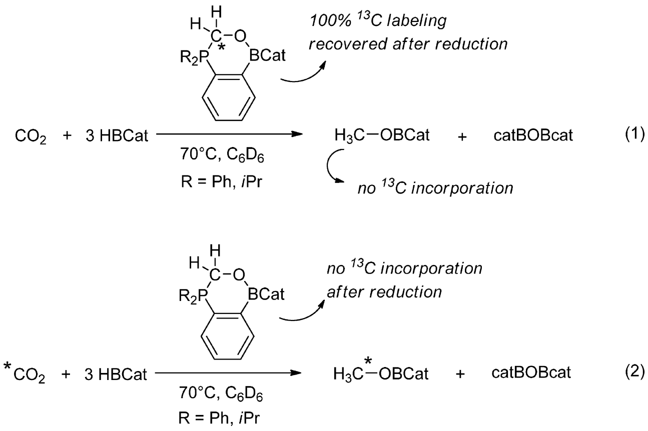
transformations of the catalyst during the reduction process, the reactions of species **1a−d** with HBcat were carried out. It was found that **1a**, **c**, and **d** readily convert to species **1b** when 5 equiv of catecholborane was added to these species in the absence of CO_2. However, species **1d** was shown to undergo such replacement more slowly than the other ambiphilic species. Monitoring the catalytic reduction of CO_2 with **1d** as a catalyst showed that catalysis did not begin until it transforms to **1b**. Similarly, the CO_2 reduction reactions using **2a**, **2b·BH_3**, or **2c** as catalysts allowed the observation of a single phosphorus containing species by $^{31}P\{^1H\}$ NMR at δ = 14.8 as the resting state of the reaction. The addition of HBcat to **2b·CH_2O** (vide infra) in solution without the presence of CO_2 gave the same resonance observed under catalytic conditions at ≈14 ppm, suggesting that the latter species consist in a Lewis adduct between **2b·CH_2O** and HBcat, presumably by an interaction between the HBcat and one O adjacent to B, although the exact mode of interaction could not be determined experimentally. This transformation implies the reduction of CO_2 to formaldehyde, as previously reported for the PPh_2 derivatives, but also the substitution of the pinacol moiety on boron by a catechol moiety. Similarly to the case of the $-PPh_2$ catalysts, the formaldehyde adduct **2b·CH_2O** is the resting state of the CO_2 reduction reaction.

Synthesis of the Formaldehyde Adducts and Labeling Experiments. As observed in Scheme 1, the formaldehyde adduct of **1b** can be prepared and isolated by heating the phosphine−boranes **1b** in the presence of excess paraformaldehyde. Unfortunately, other phosphine−boranes formaldehyde adducts based on the PPh_3 framework could not be isolated. In fact, **1a** decomposed when heated with paraformaldehyde. While **1c** is stable in the presence of paraformaldehyde, its binding of formaldehyde was found to be reversible and the adduct **1c·CH_2O** could not be isolated in the solid form. Consequently, **1c·CH_2O** could be prepared in situ and characterized by NMR spectroscopy, but its catalytic activity could not be quantified. In $CDCl_3$, the methylene resonances were observed by ^1H NMR spectroscopy at 5.37 ppm for both **1b·CH_2O** and **1c·CH_2O**, which is consistent with the change in hybridization of the carbon atom and with the loss of planarity of the aldehyde. In the $^{31}P\{^1H\}$ NMR spectra, **1c·CH_2O** was characterized by a singlet at −5.5 ppm, while **1b·CH_2O** resonates at δ = −3.5. The ^{11}B NMR spectra show signals consistent with tetravalent boron atoms at 5.7 and 8.8 ppm for **1c·CH_2O** and **1b·CH_2O**, respectively. The formaldehyde adducts of the P*i*Pr_2 derivatives appeared to be more stable than their PPh_2 counterparts. Species **2b·CH_2O** was isolated in quantitative yield by the addition of 3 equiv of HBcat to **2c** under 1 atm of CO_2 in C_6D_6 or by the addition of 30 equiv of HBcat to species **2c·CH_2O** (Scheme 1). This species has a ^{31}P NMR chemical shift of δ = 12.2 and the CH_2 resonance was observed at δ = 4.96 in the ^1H NMR spectrum. **2c·CH_2O** was isolated by the addition of paraformaldehyde to species **2c** in toluene at 70 °C and was characterized by ^{31}P NMR (δ = 7.7).

In order to verify if the aldehyde adduct is only a resting state or a significant part of the active catalyst, labeled **1b·$^{13}CH_2O$** and **2b·$^{13}CH_2O$** were prepared directly from $^{13}CO_2$. **1b·$^{13}CH_2O$** was synthesized by exposing **1b** to ca. 2 atm of $^{13}CO_2$ in a closed Schlenk vessel in the presence of 5 equiv of catecholborane. The resulting white precipitate was isolated and washed several times with toluene to yield pure **1b·$^{13}CH_2O$**. The $^{31}P\{^1H\}$ NMR spectrum for **1b·$^{13}CH_2O$** shows a characteristic doublet at −3.5 ppm with a $^1J_{C-P}$ of 57 Hz. In the ^1H NMR spectrum, the CH_2O resonance was found as a doublet at 5.37 ppm with a $^1J_{C-H}$ of 151 Hz. Interestingly, when this species was used as catalyst for the hydroboration of CO_2 using HBcat (Scheme 2, eq 1), no ^{13}C incorporation was observed in the methoxyborane formed and the $^{13}C-^{31}P$ coupling within the formaldehyde adduct could be observed by NMR spectroscopy throughout the catalytic process. Consistently, when **1b·CH_2O** and **2b·CH_2O** were used to reduce $^{13}CO_2$, no ^{13}C incorporation was observed in the formaldehyde adducts. These experiments demonstrate that the CH_2O fragment bridging P and B is not reduced but stays coordinated on the ambiphilic molecule. Thus, the formaldehyde adduct is more than a resting state and is in fact the active species responsible for the fast reduction of CO_2 in the presence of ambiphilic phosphine−boraness **1** and **2**.

DFT Studies of CO_2 Reduction Using Formaldehyde Adducts. In order to determine whether formaldehyde adduct **1b·CH_2O** and **2b·CH_2O** in the catalytic transformation, the possible interactions between HBcat and these species were

Scheme 2. Labeling Experiments Carried out with the Phosphine−Boranes Formaldehyde Adducts 1b·CH_2O and 2b·CH_2O



studied using computational chemistry. In order to compare the energies with our previous computational studies, calculations were performed at the same level of theory (B97D/6-31G**) with the solvation effects (benzene) accounted for by the SMD model. As shown in Figure 2, several possible adducts could be optimized where the borane interacts with one of the oxygen on the phosphine−boranes species, notably from the catechol and the aldehyde moieties. Although the previously reported formaldehyde adduct remains the most thermodynamically stable adduct, many other minima could be located on the energy surface. Unsurprisingly, all the isomers have very similar energy values, making difficult the identification of one ground-state structure, especially when keeping in account the uncertainty of the method (±5 kcal·mol^{-1}), and the possible involvement of fluxional processes and conformational changes.

Intrigued by the important number of isomers identified and by the possibility for the aldehyde adduct to be an active catalyst rather than a resting state, pathways for CO_2 reduction were investigated with **1b·CH_2O** acting as a catalyst. In the study of the reduction of CO_2 by **1b**, the lowest energy barriers were found upon simultaneous activation of the catecholborane by the Lewis base and of carbon dioxide by the Lewis acid. Direct reduction of carbon dioxide, once bound in a classical fashion by the phosphine and the borane of the catalyst, was found to require a much higher barrier (Scheme 3).[21]

After a thorough investigation of the possibilities for **1b·CH_2O** to act as a catalyst for CO_2 reduction, it was possible to find three new transition states which all involve simultaneous activation of HBcat and CO_2. In the first transition state, **TS1a** (−1.1 (28.6)), the H(2)−O(1) distance of 2.15 Å suggests that the Lewis acidic activation is achieved through hydrogen bonding with one of the hydrogen atoms of the bound-formaldehyde (Figure 3). Although unusual, the activation of CO_2 by hydrogen bonding was suggested before in the Ni(II)(cyclam) electrochemical reduction of CO_2 to CO by Sauvage and co-workers[26] and in the reduction of CO_2 to sodium formate by an Ir(III) pincer complex by Hazari and co-workers.[27] Another interesting aspect of this transition state is the difference in B−O bond lengths. While the B(1)−O(4) bond of 1.38 Å is in the expected range, the B(1)−O(3) bond of 2.27 Å is significantly elongated, showing that the catechol group is disconnected and that the B-catechol ring is opened. The second transition state also involved the formation of an oxygenate species with HBcat, but this time from the opening of the formaldehyde adduct (IM3) (**TS1b**; 1.9 (29.6) kcal·mol^{-1}). The oxygen atom of CO_2 is perfectly aligned with the Lewis acidic boron center. The B−O bond distance of 2.44 Å and the planar geometry around the boron center (sum of angles = 358.7°) suggest weak interaction with the carbon dioxide molecule. The third transition state with similar energy values than the two other transition states was also located starting from intermediate **IM5**, (**TS1c** −1.8 (26.3) kcal·mol^{-1}). It was found to occur by a simultaneous delivery of a boronium/hydridoborate ion pair which would be formed from the transfer of the hydride from one B-catechol moiety to the other. In all these intermediates, the formaldehyde adduct plays an important role, either by activating the borane or the carbon dioxide. Once the hydride and the Bcat moieties are transferred to generate the catBOC(O)H species, the B−O bond that was broken in the transition state (from the Bcat in pathway A and from B−OCH_2 in pathways B and C) is regenerated to reform species **1b·CH_2O**.

Comparing these transition states with the direct reduction of formaldehyde (**TS 1d**, 22.3 (38.8 kcal·mol^{-1})) supports the experimental observation that formaldehyde remains bound to the ambiphilic framework during catalysis. The transition states **TS1a−TS1c** were found to have free energies that are respectively 9.7, 8.7, and 12.0 kcal·mol^{-1} lower than the activation by the phosphine that was originally reported. Although it is likely that the initial formation of the aldehyde occurs through the phosphine−borane mechanism, the results reported herein show that the oxygen atoms are more potent than phosphorus in the activation of hydroboranes.

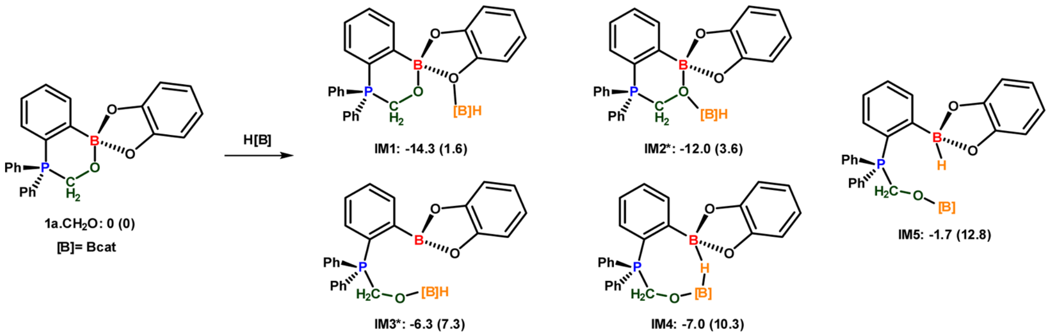
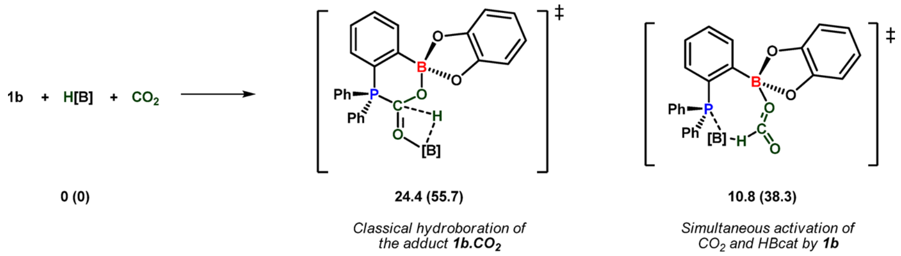


Figure 2. Some of the calculated adducts between the boranes ([B]H = HBcat) and species **1b·CH_2O** with calculated free enthalpy and free energy (kcal·mol^{-1}) computed at B97D/6-31G** with the experimental solvent (benzene) accounted for the SMD model. The * indicates that two minima were observed for two rotamers (see the SI).

Scheme 3. Previously reported transition states (and Energies in Kilocalories Per Mole) for the Hydroboration of CO_2 by 1b[a]



[a]H[B] = catecholborane.[21]

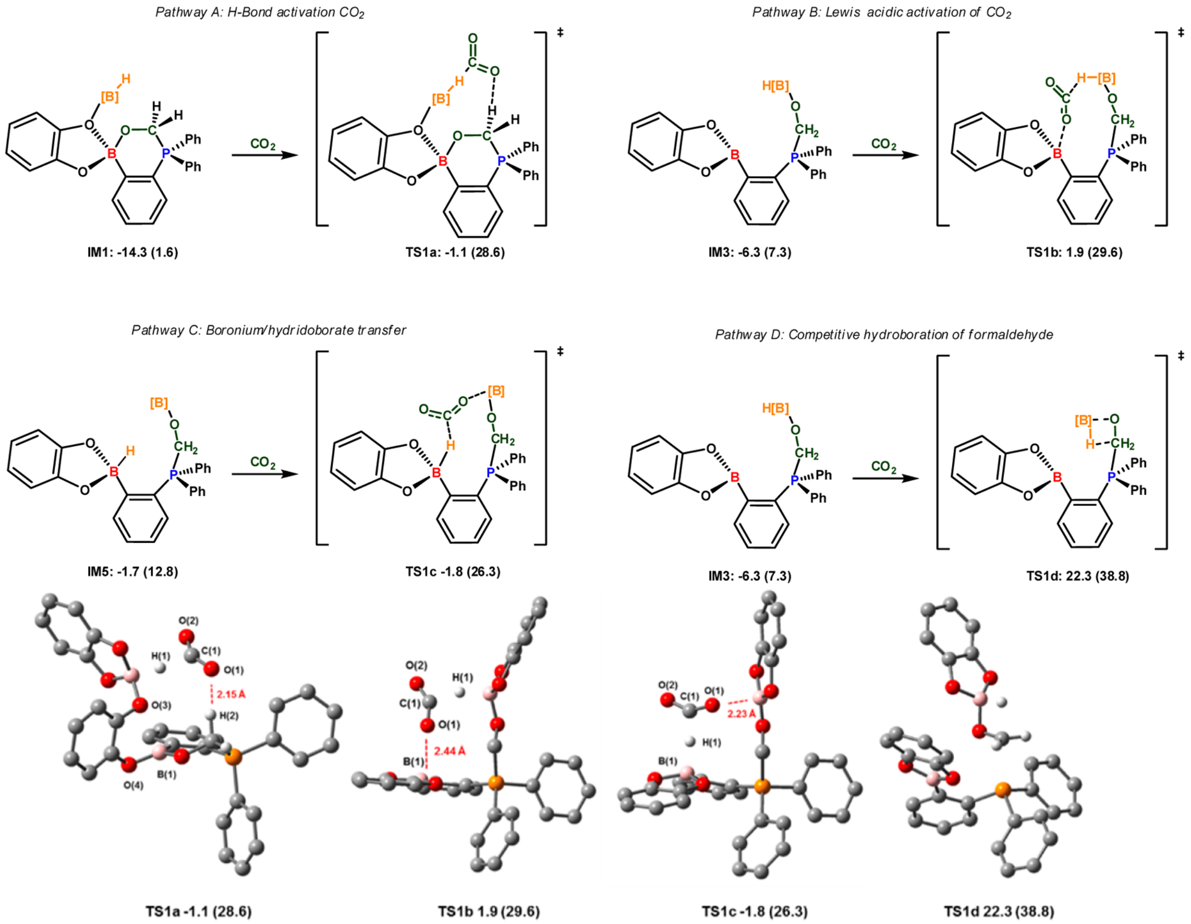


Figure 3. Transition state structures for the hydroboration of CO_2 by **1b·CH_2O** and HBcat. Calculated free enthalpy and free energy (kcal·mol^{-1}) computed at B97D/6-31G** with the experimental solvent (benzene) accounted for the SMD model.

Catalytic Efficiency of Aldehyde Adducts in the Reduction of CO_2 using BH_3·SMe_2. The efficiency of the aldehyde adducts was then evaluated in the reduction of CO_2 using the dimethylsulfide–borane adduct as a reducing agent. BH_3·SMe_2 is a reagent of choice for the hydroboration of CO_2 since it is less reactive and dangerous than the diborane reagent B_2H_6 while possessing high hydrogen content by having three transferable hydrides per boron atom. Interestingly, no transition metal system has been reported to use BH_3 adducts for the reduction of carbon dioxide and only a limited number of organocatalysts can do such reaction, including **1b** that proved the most active to date, with TOF of 973 h^{-1} at 70 °C.[20] To follow up on known literature, the values of TON and TOF were calculated according to the number of hydrogen atoms transferred on CO_2.

The catalytic reduction of CO_2 was carried out using **1a–1d** as catalysts (Table 2, entries 1–4). In these experiments, about 2 atm of CO_2 was added to a 8 mM solution of the catalyst in C_6D_6 containing 100 equiv of BH_3·SMe_2 in a J-Young NMR tube. As can be observed, both species **1a** and **1b** showed good activities, reaching TOF of 257 and 242 h^{-1} in the first hour of reaction (Table 2, entries 1 and 2, respectively). There is a significant decrease in activity when the pinacol derivative was used, since only a TOF of 43 h^{-1} was observed (Table 2, entry 3), whereas catalyst **1d** did not show significant activity (Table 2, entry 4). While the reduction of CO_2 using BH_3·SMe_2 and **1b** as catalyst proceeds rapidly at 70 °C, it was shown to be much slower at room temperature. As it was reported, the spectroscopic monitoring of the latter reaction reveals that it suffers from a long induction period before reaching its peak

Table 2. Catalytic Hydroboration of 2 atm of CO_2 Using $BH_3{\cdot}SMe_2$[a]

$$CO_2 + BH_3.SMe_2 \xrightarrow[C_6D_6]{\text{PB catalyst}} [B(OMe)O]_n + SMe_2$$

entry	catalyst	time (min)	T (°C)	TON[b]	TOF[b] (h^{-1})
1	**1a**	60	70	257	257
2[20a]	**1b**	67	70	271	242
3	**1c**	60	70	43	43
4	**1d**	60	70	<1	<1
5	**1b·CH_2O**	35	25	84	144
6	**2b·CH_2O**	30	20	114	228
7	**2b·CH_2O**	90	20	204	136
8	**2b·CH_2O**	30	70	297	594
9[c]	**2b·CH_2O**	30	70	435	873
10[c]	**2b·CH_2O**	90	70	1005	670

[a] Reaction conditions: In a J-Young NMR tube, 530 μmol of $BH_3{\cdot}SMe_2$ (56.4 μL) was added to a mixture of 5.3 μmol of catalyst (~0.6 mL of stock solution at ~8.8 mmol/L) and an internal standard of hexamethylbenzene (2 mg, 3.3 g/L) in C_6D_6 for entries 1−5, but in $CDCl_3$ for entries 6−10. The final concentration of catalyst is ~8.1 mM. The J-young NMR tube was placed under 2 atm of CO_2 and was heated at 70 °C. The catalysis was followed by ^1H NMR spectroscopy. [b] Turnover numbers (TONs) and turnover frequencies for the formation of $[B(OMe)O]_n$ according to the number of hydrogen atoms transferred to CO_2 based on NMR integration of the corresponding resonance with internal standard. [c] The reaction was performed under the same conditions but with a catalyst concentration of ~1.8 mM.

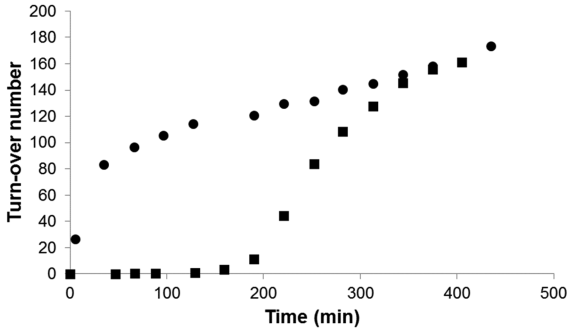


Figure 4. Number of turnovers for the reduction of CO_2 in $[B(OMe)O]_n$ in the presence of 100 equiv of $BH_3{\cdot}SMe_2$ as a reductant using 9 mM solution of (●) **1b·CH_2O** and (■) **1b** in C_6D_6. The reaction was carried out at room temperature using about 1−2 atm of CO_2 in a J-Young NMR tube. The exact pressure could not be measured, but under the loading present it is expected that CO_2 will be the limiting reagent since 1.5 atm is needed to obtain 100% yield (300 TON), explaining the lower rate at high conversion.

turnover frequency. The intermediates of the reaction were monitored using ^1H and ^{31}P NMR spectroscopy. As long as species **1b·BH_3** is the only one in solution, no significant reduction process is taking place. However, as soon as the presence of the formaldehyde adduct was observed, the catalytic reduction rate was shown to increase significantly, confirming that **1b·CH_2O** is playing a significant role on the catalytic reduction.

When carrying out the reduction of CO_2 in benzene at *room temperature* with **1b·CH_2O** as the catalyst, the rapid reduction of CO_2 was observed in the first minutes of reaction. In fact, within the 5 min needed for the acquisition of the first NMR spectrum, it was possible to ascertain a nominal TON value of 26 for the conversion of CO_2 to $[MeOBO]_n$, which can be associated with an initial TOF of >520 h^{-1} (Figure 4). This reaction rate is significantly superior to previously observed catalytic activities at ambient temperature when using **1b** as the starting catalyst, especially when considering that a significant amount of the catalyst was not dissolved at this time. After 35 min, a TON of 84 was observed, corresponding to a TOF of 144 h^{-1} (Table 2, entry 5).

The formaldehyde adduct **2b·CH_2O** was also evaluated with $BH_3{\cdot}SMe_2$ as a reductant. The catalytic tests were performed in $CDCl_3$ to ensure good solubility. Accordingly, it was found that a 1 mol % of species **2b·CH_2O** could give over 99% of the conversion expected within 30 min, giving TON of 114 and TOF over 228 h^{-1} at ambient temperature, which is slightly higher that the activity of **1b·CH_2O** (Table 2, entry 6). Letting the reaction run for 90 min increased the TON value to 204, while reducing the TOF to 136 h^{-1} (Table 2, entry 7). Looking at the reactivity at 70 °C it was possible to observe that catalyst **2b·CH_2O** converted almost quantitatively $BH_3{\cdot}SMe_2$ to methoxyboranes in 30 min, giving TON and TOF of 297 and 594 h^{-1} (Table 2, entry 8), respectively, which under NMR tube conditions surpass the catalytic activity of catalyst **1b**. Decreasing catalyst loading to 1.8 mM but keeping all the other parameters identical, it was possible to observe that catalyst **2b·CH_2O** could give a TON of 435 in the first 30 min (TOF of 873 h^{-1}), while running the reaction for 150 min increased the TON to 1005 (Table 2, entries 9 and 10). These results are of significant interest since some of the formaldehyde adducts exhibit higher stability than their phosphine−borane precursors, notably in the case of **2b**. Also, the high activity at ambient temperature and the absence of induction period contrasts drastically with all systems reported to date to reduce CO_2 using BH_3 derivatives which usually need induction periods and higher temperatures to proceed efficiently.

It should be noted that the increase in activity of the formaldehyde adducts compared to the ambiphilic phosphine−boranes is really counterintuitive, especially when comparing with the usual chemistry of Frustrated Lewis Pairs. Indeed, in latter systems, the activation of substrates such as molecular hydrogen and carbon dioxide is possible by preventing the formation of Lewis adducts between the two components of the FLP. Although such process is particularly important in hydrogen activation, it does not seem to play a similar role in the catalytic reduction of carbon dioxide. Indeed, the most important factor seems to be the activation of the reducing agent, which is done in the current system by interaction of the hydroborane with O atoms of the formaldehyde adduct; something that can be related to the activity of several borates in the reduction of carbon dioxide, including notably the BH_4^- salts that are well-known to reduce CO_2 in a stoichiometric fashion. It seems however that the simultaneous activation of the carbon dioxide by either hydrogen bonding or by a weak Lewis acid such as the boroncatecholate moiety is helping to lower significantly the transition state energy. As it was stated before, such weak Lewis acid can also prevent the formation of very stable formate adducts which might make difficult the release of the reduced species and high catalytic turnovers. The formaldehyde adducts **1b·CH_2O** and **2b·CH_2O** presented in this system have also the advantage to be quite stable to both air and water, which are significant advantages compared to some ambiphilic species, notably **2b**.

■ CONCLUSION

Ambiphilic species reported in this study all show the ability to hydroborate catalytically CO_2 to CH_3OBR_2 derivatives using catecholborane and $BH_3{\cdot}SMe_2$. However, in the presence of catecholborane, all species undergo transformations to generate respectively **1b·CH_2O** or **2b·CH_2O**, which are believed to be the active catalysts in the latter reaction. Although the exact mechanism for such transformation is unknown, derivatives of **1b** and **2b** seem to be the favored species in such system. The latter reaction also puts in evidence the importance of possible redistribution occurring in such systems with the B−O bonds being quite kinetically labile. As it was demonstrated by using **1b·$^{13}CH_2O$** and **2b·$^{13}CH_2O$** as catalysts, the interaction between the formaldehyde and the phosphine−borane moiety seems to remain intact throughout catalysis. DFT modeling of possible transition states show that the ambiphilic activation remains possible, as it was proposed for species **1b**, but this time one oxygen atom, either from the formaldehyde or the catechol moieties, acts as Lewis base to activate the reducing agent, whereas the CO_2 is activated either by one borane or by hydrogen bonding with one hydrogen of the formaldehyde adduct. Species **2b·CH_2O** was shown to be the best catalyst at room temperature reported for this system, obtaining TOF of 228 h^{-1}. Although it represents a much harder challenge, we are currently interested in using such concept for the hydrogenation of carbon dioxide.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00189.

> Detailed experimental procedures and additional DFT information (other calculated reaction pathways, Cartesian coordinates, free enthalpies, and energies) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: frederic.fontaine@chm.ulaval.ca (F.-G.F.).
*E-mail: bouhadir@chimie.ups-tlse.fr. Fax: 33 (0)5 61 55 82 04. Tel.: 33 (0)5 61 55 68 03 (G.B.).
*E-mail: dbouriss@chimie.ups-tlse.fr (D.B.).

Author Contributions

‖R.D. and M.-A.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Sciences and Engineering Research Council of Canada (NSERC, Canada) and the Centre de Catalyse et Chimie Verte (Quebec). M.-A. C., M.-A. L, and N.B. would like to thank NSERC and FQRNT for scholarships. The Centre National de la Recherche Scientifique (CNRS), the Université Paul Sabatier (UPS), and French MESR (Ph.D. grant to R.D.) are acknowledged for financial support of this work. We would like to thank R. Nadeau for the design of the TOC graphic.

■ REFERENCES

(1) *Carbon Dioxide Capture and Storage*; Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L., Eds.; Intergovernmental Panel on Climate Change (IPCC), Cambridge University Press: New York, 2005.

(2) Olah, G. A.; Goeppert, A.; Surya Prakash, G. K. *J. Org. Chem.* **2009**, *74*, 487−498.

(3) *Beyond Oil and Gas: The Methanol Economy*; Olah, G. A., Alain Goeppert, G. K.; Prakash, S., Eds.; Wiley-VCH: Weinheim, 2006.

(4) (a) Tanaka, R.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14168−14169. (b) Federsel, C.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 6254−6257. (c) Schaub, T.; Paciello, R. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 7278−7282.

(5) (a) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, *128*, 12362−12363. (b) Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P. J.; Scopelliti, R.; Laurenczy, G.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 9777−9780. (c) Langer, R.; Diskin-Posner, Y.; Leitus, G. W.; Shimon, L. J.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 9948−9952. (d) Schmeier, T. J.; Dobereiner, G. E.; Crabtree, R. H.; Hazari, N. *J. Am. Chem. Soc.* **2011**, *133*, 9274−9277. (e) Park, S.; Bézier, D.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134*, 11404−11407. (f) Huff, C. A.; Sanford, M. S. *ACS Catal.* **2013**, *3*, 2412−2416. (g) Jeletic, M. S.; Mock, M. T.; Appel, A. M.; Linehan, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 11533−11536. (h) Zhang, L.; Cheng, J.; Hou, Z. *Chem. Commun.* **2013**, *49*, 4782−4784.

(6) (a) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 1671−1674. (b) Bontemps, S.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 10253−10255. (c) Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **2014**, *136*, 4419−4425. (d) Metsänen, T. T.; Oestreich, M. *Organometallics* **2015**, *34*, 543−546.

(7) (a) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. *J. Am. Chem. Soc.* **2010**, *132*, 8872−8873. (b) Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. *Nature Chem* **2011**, *3*, 609 − 614. (c) Huff, C. A.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 18122−18125. (d) Wesselbaum, S.; von Stein, T.; Klankermayer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 7499−7502.

(8) (a) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, *128*, 12362−12363. (b) Park, S.; Bézier, D.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134*, 11404−11407. (c) Mitton, S. J.; Turculet, L. *Chem. - Eur. J.* **2012**, *48*, 15258−15262. (d) Berkefeld, A.; Piers, W. E.; Parvez, M.; Castro, L.; Maron, L.; Eisenstein, O. *Chem. Sci.* **2013**, *4*, 2152−2162.

(9) LeBlanc, F. A.; Piers, W. E.; Parvez, M. *Angew. Chem.* **2014**, *126*, 808−811.

(10) (a) Laitar, D. S.; Müller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 17196−17197. (b) Kleeberg, C.; Cheung, M. S.; Lin, Z.; Marder, T. B. *J. Am. Chem. Soc.* **2011**, *133*, 19060−19063. (c) Zhao, H.; Lin, Z.; Marder, T. B. *J. Am. Chem. Soc.* **2006**, *126*, 15637−15643.

(11) (a) Khandelwal, M.; Wehmschulte, R. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 7323−7326. (b) Wehmschulte, R. J.; Saleh, M.; Powell, D. R. *Organometallics* **2013**, *32*, 6812−6819.

(12) Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 2981−2984.

(13) (a) Mömming, C.; Otten, M.; Kehr, E. G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 6643−6646. (b) Appelt, C.; Westenberg, H.; Bertini, F.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K.; Uhl, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 3925−3928. (c) Boudreau, J.; Courtemanche, M.-A.; Fontaine, F.-G. *Chem. Commun.* **2011**, *47*, 11131−11133. (d) Peuser, I.; Neu, R. C.; Zhao, X.; Ulrich, M.; Schirmer, B.; Tannert, J. A.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G.; Stephan, D. W. *Chem. - Eur. J.* **2011**, *17*, 9640−9650. (e) Hounjet, L. J.; Caputo, C. B.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2012**, *51*, 4714 −4717. (f) Takeuchi, K.; Stephan, D. W. *Chem. Commun.* **2012**, *48*, 11304−11306. (g) Theuergarten, E.; Schlösser, J.; Schlüns, D.; Freytag, M.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. *Dalton Trans.* **2012**, *41*, 9101−9110. (h) Lu, Z.; Liu, Y. J.; Wang, Y.; Lin, J.; Li, Z. H.; Wang, H. *Organometallics* **2013**, *32*, 6753−6758. (i) Barry, B. M.; Dickie, D. A.; Murphy, L. J.; Clyburne, J. A. C.; Kemp, R. A. *Inorg. Chem.* **2013**, *52*, 8312−8314.

(14) (a) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 9839−9843. (b) Ménard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796−1797. (c) Ménard, G.; Stephan, D. W. *J.*

Am. Chem. Soc. **2010**, *132*, 1796−1797. (d) Roy, L.; Zimmerman, P. M.; Paul, A. *Chem. - Eur. J.* **2011**, *17*, 435−439. (e) Ménard, G.; Stephan, D. W. *Dalton Trans.* **2013**, *42*, 5447−5453. (f) Ménard, G.; Gilbert, T. M.; Hatnean, J. A.; Kraft, A.; Krossing, I.; Stephan, D. W. *Organometallics* **2013**, *32*, 4416−4422.

(15) (a) Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132*, 10660−10661. (b) Wen, M.; Huang, F.; Lu, G.; Wang, Z.-X. *Inorg. Chem.* **2013**, *52*, 12098 −12107.

(16) Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 3322−3325.

(17) Wang, T.; Stephan, D. W. *Chem. - Eur. J.* **2014**, *20*, 3036−3039.

(18) (a) Das Neves Gomes, C.; Jacquet, O.; Villiers, C.; Thuéry, P.; Ephritikhine, M.; Cantat, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 187−190. (b) Das Neves Gomes, C.; Blondiaux, E.; Thuéry, P.; Cantat, T. *Chem. - Eur. J.* **2014**, *20*, 7098−7106. (c) Légaré, M.-A.; Courtemanche, M.-A.; Fontaine, F.-G. *Chem. Commun.* **2014**, *50*, 11362−11365. (d) For a related system deriving from the [ClC(PPh$_2$NMes)Li] carbenoid, see: Ho, S. Y.-F.; So, C.-W.; Saffon-Merceron, N.; Mézailles. *Chem. Commun.* **2015**, *51*, 2107−2110. (e) Fujiwara, K.; Yasuda, S.; Mizuta, T. *Organometallics* **2014**, *33*, 6692−6695. (f) Blondiaux, E.; Pouessel, J.; Cantat, T. *Angew. Chem., Int. Ed.* **2014**, *53*, 12186−12190.

(19) Courtemanche, M.-A.; Larouche, J.; Légaré, M.-A.; Wenhua, B.; Maron, L.; Fontaine, F.-G. *Organometallics* **2013**, *32*, 6804−6811.

(20) (a) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2013**, *135*, 9326−9329. (b) Fontaine, F.-G.; Courtemanche, M.-A.; Légaré, M.-A. *Chem. - Eur. J.* **2014**, *20*, 2990−2996.

(21) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2014**, *136*, 10708−10717.

(22) (a) Bontemps, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *J. Am. Chem. Soc.* **2006**, *128*, 12056−12057. (b) Bontemps, S.; Bouhadir, G. D.; Apperley, C.; Dyer, P. W.; Miqueu, K.; Bourissou, D. *Chem. - Asian J.* **2009**, 428−435. (c) Bouhadir, G.; Amgoune, A.; Bourissou, D. Phosphine-Boranes and Related Ambiphilic Compounds: Synthesis, Structure, and Coordination to Transition Metals. *Advances in Organometalic Chemistry*; Elsevier, 2010; Vol. *58*, pp 1−107.

(23) (a) Porcel, S.; Bouhadir, G.; Saffon, N.; Maron, L.; Bourissou, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 6186−6189. (b) Baslé, O.; Porcel, S.; Ladeira, S.; Bouhadir, G.; Bourissou, D. *Chem. Commun.* **2012**, *48*, 4495−4497. (c) Moebs-Sanchez, S.; Bouhadir, G.; Saffon, N.; Maron, L.; Bourissou, D. *Chem. Commun.* **2008**, 3435−3437. (d) Bebbington, M. W. P.; Bontemps, S.; Bouhadir, G.; Bourissou, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 3333−3336.

(24) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorg. Chem.* **1993**, *32*, 2175−2182.

(25) The exact protocol described in the experimental section was carried out for all catalytic reactions. However, since the volume of the NMR tubes differ slightly and some small difference in temperature or pressure can occur when the CO_2 is transferred in the J-Young tube, the exact pressure cannot be known. In a typical experiment with HBcat the CO_2 will be in significant excess, but in the case of the reactions with $BH_3 \cdot SMe_2$, about 1.5 atm is needed for full conversion, which might alter the activity after more than 200 TON.

(26) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7461−7467.

(27) Schmeier, T. J.; Dobereiner, G. E.; Crabtree, R. H.; Hazari, N. *J. Am. Chem. Soc.* **2011**, *133*, 9274−9277.