Mild and Selective Carbon Dioxide Hydroboration to Methoxyboranes Catalyzed by Mn(I) PNP Pincer Complexes

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Well-defined Mn(I)-PNP pincer-type complexes were tested as non-precious transition metal catalysts for the selective reduction of CO_2 to boryl-protected MeOH in the presence of hydroboranes (HBpin, 9-BBN) and borates as Lewis acids (LA) additives. The best performance was obtained under mild reaction conditions (1 bar CO_2, 60 °C) in the presence of the hydridocarbonyl complex [MnH(PNP^{NH}–*i*Pr)$(CO)_2$] and $B(OPh)_3$ as co-catalyst. Preliminary mechanistic studies suggest that the initial activation step may occur by cationization of the metal center by the strong LA, and that both metal-catalyzed and metal-free steps are present in the overall catalytic system.

Introduction

In recent years, the increasing concentration of anthropogenic greenhouse gases in the atmosphere[1] and the need for more sustainable, fossil-free routes to chemicals and fuels, fostered a new momentum in the use CO_2 as C1 building block for chemical synthesis. Indeed, the transformation and utilization of CO_2 is now considered as a desirable alternative to its storage, at least for small scale, targeted applications.[2] Successful examples of CO_2 utilization include: a) transition metal, acid and/or base catalyzed *addition* of CO_2 to reactive substrates such as epoxides, alcohols, amines and alkynes to form new C–O, C–N, and C–C bonds,[3] and b) CO_2 chemical, electrochemical, or photochemical *reduction* to formic acid, formaldehyde, methanol, methane and CO.[4] Among the possible products that can be obtained from CO_2 reduction, methanol (MeOH), with more than 95 million metric tons annually produced worldwide,[5] is a highly desired target molecule. It can find use as fuel additive, bulk chemical, solvent and energy carrier, the latter by either reforming or catalytic dehydrogenation to produce hydrogen on demand. The principle advantages of MeOH as potential fuel for mobile engines are the compatibility with the existing distribution infrastructure and the high energy density of 22.7 MJ kg^{-1} at ambient conditions. In the last two decades various authors, and in particular Olah, Prakash and co-workers, put forward a strong case for the use of MeOH as an alternative for hydrogen as the new global fuel for a clean future.[6] This technology, based on CO_2 hydrogenation, found production scale application in the CRI plant in Grindavik (Iceland), producing MeOH from recycled CO_2 with an expected capacity of about 5 million litres per year.[7] The success is also linked to the low cost of electricity in Iceland, coming from geothermal sources, allowing for the cost-effective production of renewable hydrogen from water electrolysis.

The major hurdles for the efficient, widespread use of CO_2 as C1 synthon are the thermodynamic stability and kinetic inertness, in turn requiring forcing reaction conditions to obtain the desired 6-electron reduction to MeOH. The current technology requires high temperatures (190–270 °C) and pressures (> 90 bar) to synthesize MeOH from syngas (CO/H_2) in the presence of heterogeneous catalysts of type $Cu/ZnO/Al_2O_3$. As a general drawback, heterogeneous catalysts have often the tendency to decrease their selectivity and activity over time by metal leaching and/or surface passivation. The development of efficient, cost-effective, highly selective homogeneous catalysts for the synthesis of MeOH from CO_2 under mild conditions is therefore of high interest for the chemistry community worldwide, both at academic and industrial level.[2a]

Examples of organometallic catalysts able to bring about CO_2 hydrogenation to MeOH under homogeneous conditions have been described, involving the use of both noble (Ru, Ir) and earth-abundant (Co, Fe, Mn) transition metals.[8,9] The majority of the reported systems work under basic conditions, for example in the presence of amines, and involve a preliminary 2-electron reduction step of CO_2 to formic acid or formate, followed by hydrogenation of formamide intermediate to MeOH, as shown by Milstein,[10] Sanford,[11] Olah and Prakash,[12,13,14] Wass,[15] Martins and Pombeiro,[16] Hazari and Bernskoetter[17] and respective co-workers. CO_2 hydrogenation under acidic conditions was also demonstrated, for example by Huff and Sanford in a presence of a three-catalysts cascade system based on Ru and Sc,[18] by Himeda, Laurenczy and co-workers using an Ir(III) catalyst in H_2O/H_2SO_4,[19] and by Klankermayer, Leitner and co-workers using a Ru(triphos) complex (triphos = 1,1,1–tris (diphenylphosphinomethyl)ethane) in the presence of $HNTf_2$ ($HNTf_2$ = bis(trifluoromethane)sulfi-

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mide) at 140 °C, 20 bar CO_2 and 60 bar H_2, obtaining MeOH with high TONs and with the possibility to reuse the catalyst for consecutive repressurization cycles.[20,21] Among first-row transition metals, cobalt-catalyzed CO_2 hydrogenation to MeOH under acidic conditions was demonstrated by de Bruin and co-workers via intermediate ester hydrogenation,[22] and by Beller and co-workers in the presence of triphos and $Co(acac)_3$ with $HNTf_2$ in THF/ethanol, reaching a TON of 50.[23] Further optimization was then carried out, and in the presence of modified triphos ligands and $Co(NTf_2)_2$ as metal precursor, TON was increased up to 125.[24]

Although H_2 is the most atom-efficient, economical and sustainable reductant when produced from non-fossil, renewable feedstocks, some concerns are still present, due to safety risks connected with the use of flammable, pressurized gas. For this reason, chemists have looked for alternative reductants to bring about CO_2 reduction to MeOH. Hydrosilanes and hydroboranes have been successfully applied to replace H_2 under mild reaction conditions, due to the fact that E–H bonds (E = Si, B) are weaker than the H–H bond, and that the formation of stronger E–O bonds constitutes a driving force for the reaction. Although atom-efficiency is lower than using hydrogen, these reagents are in general liquid at room temperature, hence easier and safer to handle and store.[25,26,27]

Boron-based compounds are generally Lewis acidic and oxophilic enough to enable activation of the C=O bond of carbon dioxide.[28] Essentially, CO_2 can be reduced stepwise by a hydroborane (Scheme 1) to give formoxyborane (A), bis(boryl) acetal (B), methoxyborane (C) and bis(boryl)ether (D).

The first step in CO_2 hydroboration is generally a hydride transfer to the CO_2 carbon atom, and this may occur with a catalyst that can be either a metal hydride complex, an ambiphilic compound, a strong Lewis base or a hydroborate compound.[28,29] Examples of transition metal hydride catalysts for the selective CO_2 hydroboration to methoxyboranes have been previously described (Figure 1).[28,29,30] Guan and co-workers described in 2010 the first Ni hydrido complex supported by a POCOP pincer-type ligand [POCOP = 2,6-($tBu_2PO)_2C_6H_3$], that was able to catalyze CO_2 hydroboration with catecholborane (1,3,2-benzodioxaborole, HBcat), obtaining CH_3OBcat [CH_3OBcat = methoxycatecholborane)] with a TON of 495, carrying out the reaction in benzene at room temperature for 1 h, using 0.2 mol% of catalyst and 1 bar CO_2.[31] In 2012, Sgro and Stephan reported the use of a frustrated-Lewis pair (FLP) Ru hydrido complex of ligand $N[(CH_2)_2NHPiPr_2)(CH_2)_2NPiPr_2)(CHCH_2NHPiPr_2)]$ as catalyst for this reaction using pinacolborane (4,4,5,5-tetramethyl-1,3,2-dioxaborolane, HBpin), yielding CH_3OBpin [CH_3OBpin = methoxypinacolborane] and $O(Bpin)_2$. A moderate TON of 9 was obtained with 100 equiv. of HBpin, in CD_2Cl_2 at 50 °C after 96 h.[32] In the same year, Bontemps, Sabo-Etienne and co-workers disclosed the use of $[Ru(H)_2(H_2)_2(PCy_3)_2]$ as catalyst (10 mol%) using HBpin in C_6D_6, obtaining CH_3OBpin in 39% yield after either 22 days at room temperature or 5 h at 70 °C.[33] Another Ru-based system was reported in 2016 by Song and co-workers, namely complex $[Ru(CO)H(daf)(PPh_3)_2]$ (daf = 4,5-diazafluorenyl) as a catalyst for CO_2 hydroboration at 100 °C.[34] Rather unusually, the first step of the catalytic cycle was found to be the C–H borylation of the ligand, releasing hydrogen, followed by CO_2 insertion into the C–B bond rather than into the Ru–H bond. The resulting boryl derivative was then further reduced to different products including (OC(H)O)Bpin [(OC(H)O)Bpin = formoxypinacolborane] and CH_3OBpin (maximum yield = 54% after 45 h at 100 °C in C_6D_5Br). Alkali metal complexes were also described as active catalysts for CO_2 hydroboration to the methoxy level. Hill and co-workers showed that Mg and Ca hydride β-diketiminato compounds gave complete and selective conversion of HBpin to CH_3OBpin using 10 mol% of catalyst, 1 bar $^{13}CO_2$ at 60 °C in THF, after 6 or 4 days, respectively.[35] Among early transition metals, Trovitch and co-workers described the use of bis(imino)pyridine-type molybdenum catalyst [(κ^6–*P,N,N,N,C,P*-^{Ph2PPr}PDI)MoH] for CO_2 hydroboration with HBpin, with 97% borane utilization using 0.1 mol% of catalyst, after 8 h at 90 °C in C_6D_6, and CH_3OBpin formation with turnover frequency (TOF) of ca. 40 h^{-1}.[36]

More recently, the potential of Ir, Pd and Ni pincer complexes was examined in detail, focusing on the effects of type of ligands and hydroboranes in determining the selectivity of the reaction. In 2018, Rendón, Suarez and co-workers showed that Ir carbonyl pincer complexes stabilized by a deprotonated lutidine-derived CNP* ligand selectively catalyzed the hydroboration of CO_2 under 1–2 bar, 30 °C either to methoxyborane using HBcat (TOF = 56 h^{-1}, maximum yield = 28%, TON = 84) or to formoxyborane with the more sterically demanding HBpin (TOF = 1245 h^{-1}) in either THF/H_2O or THF, respectively.[37] One year later, Hazari and co-workers examined the correlations

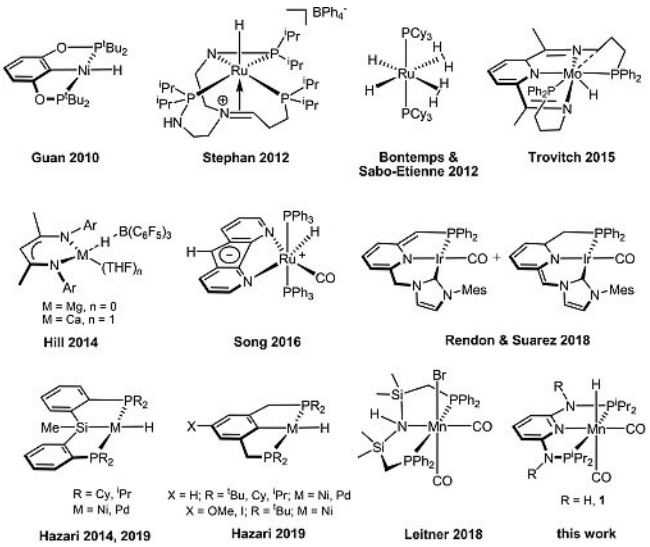
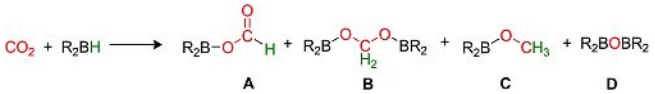


Figure 1. Examples of well-defined molecular catalysts for the selective CO_2 hydroboration to methoxyborane.



Scheme 1. Product distribution for CO_2 hydroboration.

between catalyst and borane structure and the level and rates of catalytic CO_2 reduction using Pd and Ni complexes, supported by PSiP and PCP pincer ligands, varying systematically their steric and electronic properties (Figure 1).[38] Results showed that a complex network of effects is active upon varying, together with the catalyst and the borane, the reaction conditions (CO_2 pressure, reaction time, catalyst concentration), ruling the activity and selectivity of the catalytic system. Remarkably, it was shown that, using HBpin, the product selectivity could be switched from formoxy- to methoxyborane by adding a Lewis acid (LA) such as $B(OPh)_3$. A maximum yield of 72% in CH_3OBpin was obtained with [(^{Cy}PSiP)PdH] in C_6D_6 at room temperature under the following conditions: [catalyst] = 0.0007 M, [HBpin] = 0.07 M, [$B(OPh)_3$] = 0.007 M, 1 atm of CO_2, 2 days. By using the less sterically demanding (but more expensive) HBcat, without any addition of borate, almost quantitative formation of CH_3OBcat was observed with [(^{tBu}PCP)PdH] under the conditions: [catalyst] = 0.0007 M, [HBcat] = 0.07 M, 1 atm of CO_2, room temperature, C_6D_6, 16 h.

In recent years, the cost effectiveness of chemical processes has become an important issue, thus the possibility to replace expensive platinum group metals with first-row, earth abundant counterparts in catalysis has grown in interest. Excellent results for CO_2 hydroboration catalysed by [Fe(H_2)(dmpe)] (dmpe = 1,2-bis(dimethylphosphino)ethane),[39a] and by iron and copper complexes[39b] of triphosphine and triphosphinite tripodal ligands PhSi{CH_2PPh_2}$_3$ and PhSi{$OPPh_2$}$_3$ were reported. Among first-row metals, manganese complexes have recently found new applications, paving the way for a more extensive use of such metal in catalytic reactions, including CO_2 reduction.[13,40] We recently disclosed the first examples of successful use of the Mn(I) hydridocarbonyl complexes [MnH(PNP^{NH}–*i*Pr)(CO)$_2$] (**1**) and [MnH(PNP^{NMe}–*i*Pr)(CO)$_2$] (**2**), supported by PNP pincer-type ligands based on a bis(aminophosphine)pyridyl scaffold (R = H, **1**; R = Me, **2**) for CO_2 hydrogenation to formate[41] and CO_2 hydrosilylation to methoxysilanes[42] under mild conditions, reaching high productivities and selectivities to the desired products. In 2018, Leitner and co-workers showed the first example of Mn(I)-catalyzed CO_2 hydroboration to methoxyborane. The Mn(I) complex [MnBr({$Ph_2PCH_2SiMe_2$}$_2$NH)(CO)$_2$] was able to bring about the selective CO_2 hydroboration to CH_3OBpin under solventless conditions, using HBpin (2.76 mmol), 0.036 mol% of catalyst, NaO*t*Bu (0.1 mol%) at 100 °C for 14 h, reaching a TON of 883.[43] Having the use of manganese in CO_2 hydroboration been established, we thought of interest to apply our Mn(I) complexes as catalysts for this reaction, varying systematically the main reaction parameters to study the effects on the reaction selectivity and activity, and the results are hereby reported.

Results and Discussion

The catalytic tests were carried out on NMR tube scale, using 1 bar of CO_2 and monitoring the increase of the yields of C1-products over time by ^{1}H NMR spectroscopy (see Experimental Section). Additional ^{11}B, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were collected to obtain more details. In particular, ^{11}B NMR gave qualitative information on the presence of other B-containing products such as bis(boryl)ethers and allowed the identification of unknown species formed by unproductive side reactions (*vide infra*). Initially, very mild conditions were applied (25 °C, 1 bar CO_2), in the presence of HBpin (0.224 mmol) and complex **1** (1.0 mol% with respect to HBpin), choosing [D_6]dmso as solvent. This solvent was chosen as it was previously demonstrated that it can assist CO_2 activation, for example in hydrosilylation reactions.[42,44] Under these conditions and using this solvent, the reaction gave (OC(H)O)Bpin, identified by the ^{1}H NMR signal at 8.18 ppm and the ^{11}B NMR broad signal at 21.21 ppm, as the only C1-product in ca. 56.5% maximum yield already after 5 h, without further increase at 24 h. Under the same reaction conditions, by changing solvent from [D_6]dmso to either [D_8]THF or C_6D_6, no C1-products were formed. The effect of temperature on the reaction was then investigated, repeating the previous tests at 60 °C, in the three different solvents mentioned above. The results obtained at 60 °C are summarized in Table 1.

It was observed that also at 60 °C, in both [D_6]dmso and C_6D_6, (OC(H)O)Bpin was formed as the only C1-product, albeit in moderate yields or with sluggish reactivity. Interestingly, in [D_8]THF a small amount of CH_3OBpin (5.0%) formed after ca. 5 h of reaction, reaching a maximum 5.5% yield after 24 h. In all cases, incomplete HBpin conversion, responsible for the low yields, was qualitatively assessed from the persistence of the characteristic signals at 27.3 ppm and 28.7 ppm in the corresponding final ^{11}B NMR spectra.

The use of Lewis acids (LA) as co-catalysts in CO_2 hydroboration was demonstrated by Hazari and co-workers as a powerful tool to drive the reaction selectivity to the desired methoxyborane species.[38] Accordingly, we repeated the tests adding $B(OPh)_3$ to the reaction mixture (10 mol% respect to HBpin). Whereas the addition of LA had the effect to increase the yield of (OC(H)O)Bpin in [D_6]dmso, that was confirmed as the only C1-product obtained in this solvent, the selective formation of the desired CH_3OBpin was detected in C_6D_6 and [D_8]THF. The formation of O(Bpin)$_2$ (product D in Scheme 1, R = Bpin) was observed in the corresponding ^{11}B NMR spectra. Product CH_3OBpin was characterized in [D_8]THF by ^{1}H NMR signals at 3.50 ppm and ^{11}B NMR signals at 20.93 ppm, whereas O(Bpin)$_2$ gave a broad signal at 21.90 ppm in the ^{11}B NMR spectra (Figures S11 and S12, Supporting Information). The

Table 1. Solvent effect for CO_2 hydroboration in the presence of **1**.[a]

t [h]	[D_6]dmso[b]	C_6D_6[b]	[D_8]THF
1	37.7	0.0	18.1[b]
3	37.7	7.6	26.9[b]
5	37.7	9.9	38.5[b], 5.0[c]
24	37.7	13.3	42.2[b], 5.5[c]

[a] Reaction conditions: **1** (2.24×10^{-3} mmol), HBpin (0.224 mmol), CO_2 (1 bar), 60 °C, solvent (0.4 mL). C1-product yields (%) obtained by ^{1}H NMR signals integration against a mesitylene internal standard (0.056 mmol). [b] Yield (%) of (OC(H)O)Bpin. [c] Yield (%) of CH_3OBpin.

yields (%) of C1-products, monitored during the course of the tests in the different solvents, are reported in Table 2. From the data summarized in Table 2, it can be observed that the best yields of CH_3OBpin were obtained in [D_8]THF, that was therefore chosen as preferred solvent for the rest of the study.

A closer inspection of the ^{11}B NMR spectrum showed, together with the signals due to CH_3OBpin and $O(Bpin)_2$, the presence of a signal at 21.80 ppm that, to the best of our knowledge, was not previously reported in other studies on CO_2 hydroboration. The corresponding $^{13}C\{^1H\}$ NMR spectrum showed the presence of three signals due to $O(Bpin)_2$ (83.06 ppm), CH_3OBpin (82.74 ppm) and a signal at 83.61 ppm. Based on literature data,[45] it was possible to assign the new signals to 4,4,5,5-tetramethyl-2-phenoxy-1,3,2-dioxaborolane (PhOBpin), formed in a side reaction between HBpin and $B(OPh)_3$ (Scheme 2).

An additional confirmation of the observed uncatalyzed side reactivity was obtained in a separate NMR test, monitoring the stoichiometric reaction (1:1) of HBpin and $B(OPh)_3$ in [D_8]THF at 60 °C, in the absence of CO_2 and catalyst. After 4 h, signals due to PhOBpin and BH_3 (q, −0.79 ppm) were observed in the corresponding ^{11}B NMR spectrum (Figure S37, Supporting Information), as expected according to the reaction shown in Scheme 2. Finally, in order to confirm that CO_2 was exclusively converted into methoxyborane, the catalytic test run in [D_8]THF was repeated using $^{13}CO_2$ under otherwise identical conditions. The reaction was monitored by ^1H and $^{13}C\{^1H\}$ NMR. The latter spectra initially showed as expected a signal at 124.2 ppm due to $^{13}CO_2$, that gradually decreased in intensity in favor of a growing signal at 52.5 ppm due to $^{13}CH_3OBpin$ (Figures S15 and S16, Supporting Information).

The main reaction parameters were then systematically varied to obtain process optimization and understand the effect of each component of the reaction. The effects of nature and acidity of LA additives were screened by repeating the catalytic tests with **1** in [D_8]THF at 60 °C, using an inorganic salt (LiOTf), a boron trihalide (BCl_3) and two other borates of different Lewis acidity,[46] such as $B(OCH_3)_3$ and $B(OCH_2CF_3)_3$ [$B(OCH_2CF_3)_3$ = tris(2,2,2-trifluoroethyl)borate], and comparing the results with those obtained with $B(OPh)_3$. The use of LiOTf did not favor the reaction, and only 3.41% of CH_3OBpin was observed after 24 h. Similarly, BCl_3 acted rather as an inhibitor than a promoter, as no C1-products were obtained after the same reaction time. On the other hand, a difference in reactivity was observed using the three selected borates (Table 3). Whereas the addition of $B(OCH_3)_3$ gave CH_3OBpin in ca. 48% yield after 24 h, tris(2,2,2-trifluoroethyl)borate gave the highest promoting effect after 5 h, giving CH_3OBpin in 53.6% against 44.3% yield, observed in the presence of $B(OPh)_3$. It was however observed that this effect levelled off on the 24 h reaction time, and a lower final yield in the desired product (68.5 vs. 78.3% with $B(OPh)_3$) was obtained. Thus, $B(OPh)_3$ was confirmed as the best choice as additive for CO_2 hydroboration under our reaction conditions.

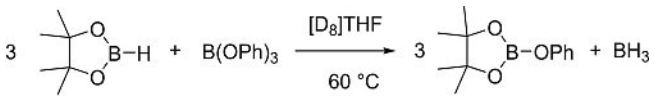
A control (blank) experiment showed that after 24 h in [D_8]THF at 60 °C, ca. 8% of CH_3OBpin was obtained even in the absence of catalyst (Figure S18, Supporting Information). Next, the effect of catalyst amount was examined, using HBpin, **1** (0.25, 0.5, 1.0, 2.0 mol% with respect to HBpin), $B(OPh)_3$ (10 mol%) in [D_8]THF at 60 °C for 24 h (Table 4). At all chosen catalyst to substrate ratios, CO_2 hydroboration proceeded selectively to the formation of CH_3OBpin as the only C1-product, with final yields varying in the range of *ca.* 61 to 78%, showing that the effect of catalyst concentration on the reaction is minor. Catalyst concentration of 1.0 mol% was confirmed as the most suitable to obtain the highest yield in CH_3OBpin.

The effect of $B(OPh)_3$ concentration was then studied, and the results are shown in Table 5. The use of 5 mol% of LA showed to be detrimental to the reaction, as only 55% yield of

Table 2. CO_2 hydroboration in the presence of **1** and $B(OPh)_3$ in different solvents.[a]

t [h]	[D_6]dmso[b]	C_6D_6[c]	[D_8]THF[c]
1	73.6[d]	0.0	18.8
3	73.6[d]	8.6	35.3
5	73.6[d]	9.4	44.3
24	73.6[d]	10.3	78.3[d]

[a] Reaction conditions: **1** (2.24×10^{-3} mmol), HBpin (0.224 mmol), $B(OPh)_3$ (2.24×10^{-2} mmol), CO_2 (1 bar), 60 °C, solvent (0.4 mL). C1-product yields (%) obtained by ^1H NMR signals integration against a mesitylene internal standard (0.056 mmol). [b] Yield (%) of (OC(H)O)Bpin. [c] Yield (%) of CH_3OBpin. [d] Full HBpin conversion observed from ^{11}B NMR spectra.



Scheme 2. Side reaction between HBpin and $B(OPh)_3$ giving PhOBpin.

Table 3. LA screening in CO_2 hydroboration in the presence of **1**.[a]

t [h]	$B(OCH_3)_3$[b]	$B(OPh)_3$[b]	$B(OCH_2CF_3)_3$[b]
1	4.2	18.8	30.0
3	17.0	35.3	45.4
5	24.2	44.3	53.6
24	48.1	78.3[c]	68.5[c]

[a] Reaction conditions: **1** (2.24×10^{-3} mmol), HBpin (0.224 mmol), LA (2.24×10^{-2} mmol), CO_2 (1 bar), 60 °C, [D_8]THF (0.4 mL). [b] Yields (%) of CH_3OBpin obtained by ^1H NMR signal integration against a mesitylene internal standard (0.056 mmol). [c] Full HBpin conversion observed from ^{11}B NMR spectra.

Table 4. Catalyst **1** amount screening in CO_2 hydroboration.[a]

t [h]	0.25 mol%[b]	0.5 mol%[b]	1.0 mol%[b]	2.0 mol%[b]
1	26.9	25.3	18.8	32.1
3	36.2	38.8	35.3	47.9
5	45.9	44.8	44.3	58.2
24	60.8	70.7[c]	78.3[c]	70.3[c]

[a] Reaction conditions: **1** ($0.56/1.12/2.24/4.48\times10^{-3}$ mmol), HBpin (0.224 mmol), $B(OPh)_3$ (2.24×10^{-2} mmol), CO_2 (1 bar), 60 °C, [D_8]THF (0.4 mL). [b] Catalyst amount (% mol respect to HBpin). In the columns, yields (%) of CH_3OBpin at different times, obtained by ^1H NMR signal integration against a mesitylene internal standard (0.056 mmol). [c] Full HBpin conversion observed from ^{11}B NMR spectra.

Table 5. $B(OPh)_3$ amount screening in CO_2 hydroboration with **1**.[a]

t [h]	5 mol %[b]	10 mol %[b]	20 mol %[b]
1	16.5	18.8	48.6
3	27.2	35.3	66.3
5	34.4	44.3	73.2
24	55.1	78.3	74.5

[a] Reaction conditions: **1** (2.24×10^{-3} mmol), HBpin (0.224 mmol), $B(OPh)_3$ ($1.12/2.24/4.48\times10^{-2}$ mmol), CO_2 (1 bar), 60 °C, [D_8]THF (0.4 mL). [b] LA amount (% mol respect to HBpin). In the columns, yields (%) of CH_3OBpin at different times, obtained by ^1H NMR signal integration against a mesitylene internal standard (0.056 mmol).

CH_3OBpin was obtained after 24 h. When 20 mol % of $B(OPh)_3$ were used, the major effect was mainly observed on the rate of the reaction, that was nearly completed already after 5 h, with a final yield in the desired product comparable to that obtained using 10 mol % of $B(OPh)_3$.

By replacement of $B(OPh)_3$ by NaO*t*Bu,[43] under otherwise identical conditions described above in the presence of **1**, after 24 h heating to 60 °C in [D_8]THF the reaction gave only traces of (OC(H)O)Bpin together with the formation of B_2Pin_3, identified by a ^{11}B NMR signal at 21.4 ppm and $^{13}C\{^1H\}$ NMR signals at 81.22 and 79.50 ppm.[47]

Additional screening included testing the activity and selectivity of our catalytic protocol with another hydroborane, such as 9-borabicyclo[3.3.1]nonane (9-BBN). Under standard reaction conditions, slightly adapted to account for the different solubility of 9-BBN in [D_8]THF (see Experimental Section), the reaction gave 9-methoxy-9-borabicyclo[3.3.1]nonane (CH_3O-9-BBN), 9,9′-oxybis(9-borabicyclo[3.3.1]nonane) [O(9-BBN)$_2$] and the side product 9-phenoxy-9-borabicyclo[3.3.1]nonane (PhO-9-BBN) shown in Scheme 3.

The products were identified by ^{11}B NMR signals at 61.3, 59.9 and 60.8 ppm, respectively, and by the ^1H NMR signal at 3.70 ppm for CH_3O-9-BBN. Full substrate conversion was observed in the ^{11}B NMR spectrum after 5 h at 60 °C in [D_8]THF, with a yield of 74.4 % of CH_3O-9-BBN. The effects of the type of

Scheme 3. CO_2 hydroboration in the presence of **1** and 9-BBN.

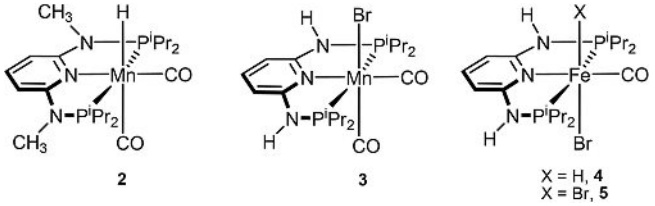


Figure 2. Other PNP pincer-type Mn and Fe complexes tested as catalysts for CO_2 hydroboration.

metal and ligands were then briefly investigated by testing other catalysts structurally related to **1** in CO_2 hydroboration with HBpin in the presence of $B(OPh)_3$ (Figure 2). It was previously reported that, in various catalytic reactions, slight changes in the PNP ligand backbone, *i.e.* replacing the N–H group with a N-CH_3 counterpart, may affect the substrate activation mechanisms, by either involving or suppressing metal-to-ligand cooperation (MLC), respectively.[41,48] Complex [MnH(PNP^{NMe}-*i*Pr)(CO)$_2$] (**2**) was thus tested under the optimized conditions described above. The need for a hydrido ligand was verified by testing the bromide analogue of **1**, namely [MnBr (PNP^{NH}—*i*Pr)(CO)$_2$] (**3**). Finally, two Fe(II) complexes isoelectronic to **1** and bearing the PNP^{NH}—*i*Pr ligand, *i.e. trans*-[FeBr(H) (PNP^{NH}—*i*Pr)(CO)] (**4**) and *trans*—[FeBr$_2$(PNP^{NH}—*i*Pr)(CO)] (**5**), were also tested to compare the activity of iron *vs.* manganese complexes. The results are summarized in Table 6.

In the case of the Mn complexes, a very modest yield (8 %) was obtained after 24 h with **2**, whereas a final yield of 31.3 % of CH_3OBpin was reached with **3**, confirming that pincer ligands with N–H moieties in the backbone must be preferred. Reaction monitoring by $^{31}P\{^1H\}$ NMR showed that **3** was slowly converted into **1** via bromide exchange with hydride during the reaction, as demonstrated by the decrease of the singlet at 135.86 ppm accompanied by the appearance of the singlet at 160.21 ppm due to **1**. In the case of the Fe complexes, the highest yield of CH_3OBpin was obtained with **4** (42.1 % *vs.* 22.6 % for **5**) after 24 h. Incomplete HBpin conversion was observed for these tests in the corresponding ^{11}B NMR spectra. Complex **3** was also tested in a Schlenk tube scale reaction under the conditions described by Leitner and co-workers for their manganese bromide catalyst,[42] and in this case a very small amount of CH_3OBpin (6.5 %) was obtained after 24 h (Supporting Information).

Finally, we decided to test ligand PNP^{NH}-*i*Pr as possible metal-free catalyst for CO_2 hydroboration. By replacing **1** with PNP^{NH}—*i*Pr (2.24×10^{-3} mmol), in the presence of HBpin (0.224 mmol), $B(OPh)_3$ (2.24×10^{-2} mmol), CO_2 (1 bar), 60 °C, [D_8] THF (0.4 mL), CH_3OBpin was obtained after 24 h in *ca.* 33 % yield. This unexpected result suggests that the catalytic mechanism may include both metal-mediated and metal-free activation steps.

$^{31}P\{^1H\}$ NMR monitoring of the catalytic run in the presence of **1**, HBpin and $B(OPh)_3$ under the conditions reported in Table 2 showed (Figure S14, Supporting Information) that the initial singlet at 160.3 ppm due to **1** gradually disappeared in

Table 6. Metal and ligand effects screening in CO_2 hydroboration.[a]

t [h]	**2**[b]	**3**[b]	**4**[b]	**5**[b]
1	–	7.3	19.0	4.2
3	–	13.0	24.7	6.7
5	5.1	16.7	29.6	8.5
24	8.0	31.3	42.1	22.6

[a] Reaction conditions: catalyst (2.24×10^{-3} mmol), HBpin (0.224 mmol), B(OPh)$_3$ (2.24×10^{-2} mmol), CO_2 (1 bar), 60 °C, [D_8]THF (0.4 mL). [b] Yields (%) of CH_3OBpin at different times, obtained by ^1H NMR signal integration against a mesitylene internal standard (0.056 mmol).

favor of a new singlet at 133.0 ppm (main species), already after 1 h at 60 °C. After 5 h, other signals were observed at 73.8 and 25.8 ppm, respectively, that were accompanied by another singlet at ca. 34.9 ppm after 24 h. The signal due to free ligand PNP^{NH}-*i*Pr, expected at 45.4 ppm in [D_8]THF, was not observed.

In a separate NMR experiment, **1** was mixed in 1:1 ratio with $B(OPh)_3$ in [D_8]THF and, after leaving the sample standing for several hours at room temperature, a singlet at 133.0 ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum, while the signal due to **1** disappeared. The corresponding ^{11}B NMR spectra showed the disappearance of the broad singlet at 16.10 ppm due to initial $B(OPh)_3$, replaced by a new signal at 2.28 ppm, a chemical shift value in the range compatible for $[HB(OPh)_3]^-$.[49] We assign these signals to the formation of the cationic complex [Mn(PNP^{NH}—*i*Pr)$(CO)_2$][$HB(OPh)_3$] (**1**$^+$) that is likely obtained by hydride abstraction from **1** by $B(OPh)_3$. As further confirmation, complex **3** was reacted in an NMR tube scale reaction with a small excess of Ag_2SO_4 as bromide scavenger, obtaining [Mn(PNP^{NH}—*i*Pr)$(CO)_2]_2(SO_4)$, characterized by a $^{31}P\{^1H\}$ NMR singlet at 133.0 ppm. Attempts to assign the other $^{31}P\{^1H\}$ NMR signals observed during the catalytic test were inconclusive. At the current stage, partial ligand release by de-coordination and following interaction with HBpin and/or $B(OPh)_3$ cannot be ruled out.

A tentative mechanistic proposal may involve the initial activation of CO_2 by the highly electrophilic species **1**$^+$, allowing for the first kinetically sluggish reaction with HBpin to give formoxyborane. This is then sequentially converted to the final methoxyborane product by metal-free steps in the presence of HBpin and a Lewis acid, that may in turn assist the activation of the B–H bond. A similar mechanism has been recently proposed for CO_2 hydrosilylation in the presence of $B(C_6F_5)_3$.[50] DFT calculations to describe the full catalytic cycle and pinpoint the role of the N–H moiety will be carried out and reported in due time.

Conclusions

In summary, the present study showed that Mn(I) complexes supported by PNP pincer-type ligands bearing N–H moieties in the backbone were able to bring about the efficient and selective hydroboration of CO_2 to methoxyboranes, as an example of CO_2 utilization as C1 building block for chemical synthesis catalyzed by earth-abundant transition metals. In particular, high yields of the desired product were obtained using as low as 0.5 mol% of catalyst under mild reaction conditions (1 bar CO_2, 60 °C) within 24 h. In addition, the role of Lewis acids in promoting the catalytic activity was described, together with the identification of previously unobserved side reactions and products.

Experimental Section

Typical procedure for CO_2 hydroboration tests. A stock solution containing the catalyst (0.56 to 4.48×10^{-3} mmol), HBPin (0.224 mmol) and mesitylene as internal standard (0.056 mmol) in the desired solvent (0.4 mL) was added in glove-box under nitrogen to a J-Young NMR tube, with or without a Lewis Acid (LA) additive (1.12 to 4.48×10^{-2} mmol). In the experiments with 9-BBN as borane, the tests were run using catalyst **1** (1.12×10^{-3} mmol), 9—BBN (0.112 mmol), $B(OPh)_3$ (1.12×10^{-2} mmol) and mesitylene as internal standard (0.028 mmol) in [D_8]THF (0.4 mL). Once prepared, the sample was degassed via three freeze-pump-thaw cycles and then CO_2 (1 bar) was added using a Schlenk line. The NMR tube was then placed in an oil bath kept at the desired temperature (25 or 60 °C) for the set reaction time. The formation of C1-products was monitored throughout the duration of the experiment using ^1H NMR spectroscopy and quantified by signals integration versus the mesitylene internal standard. Additional $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{11}B NMR spectra were also run to obtain further qualitative information. Each test was repeated at least twice to check for reproducibility. The yields of C1-products were obtained with an average error of ca. 6%.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: carbon dioxide hydroboration · manganese · pincer complexes · methanol · homogeneous catalysis

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