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Phosphine Catalyzed Reduction of CO$_2$ with Boranes†

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Phosphine is shown to catalyse the reaction of CO$_2$ with 9-BBN to give mixtures of HCO$_2$(B(C$_8$H$_{14}$)) 3, H$_2$C(OB(C$_8$H$_{14}$))$_2$ 4 and MeOB(C$_8$H$_{14}$) 5; at 0.02 mol% of tBu$_3$P 5 is obtained in 98% yield at 60 °C with TON of almost 5500 and a TOF of 170. Under stoichiometric conditions the species (R$_3$PCH$_2$O)(HC(O)O)B(C$_8$H$_{14}$) (R = tBu 1, 4-MeC$_6$H$_4$ 2) were isolated and characterized.

Prompted by concerns over global warming, climate changes and the need for renewable fuels, numerous research groups have undertaken efforts seeking to develop highly efficient methodologies to utilize CO$_2$ as a C1 source for organic synthesis.[1] To this end, a number of transition metal catalysts have been developed which effect the hydrogenation of CO$_2$ to formic acid[2] and methanol[3], the hydrosilylation of CO$_2$ to formic acid,[4] methanol[1k, 5] and methane[6], and the reduction of CO$_2$ with borane reagents into CO[7] and methoxide.[8] Sabo-Etienne and co-workers[9] provided an interesting example of the reduction of CO$_2$ by [RuH$_2$(H$_2$)$_2$(PCy$_3$)$_2$] and pinacolborane (HBpin) generating the formic acid ester, CH$_2$(OBpin$_2$)$_2$ and the methoxide MeOBpin. More recently, our group demonstrated a related CO$_2$ reduction with HBpin, catecholborane (HBcat) or 9-borabicyclo[3.3.1]nonane (9-BBN) to generate methoxyboranes using a Ru-$tris$(aminophosphine) catalyst.[10] Shintani and Nazaki have reported the copper-catalyzed hydroboration of CO$_2$ with HBpin yielding formic acid ester.[11]

While these strategies for CO$_2$ reduction exploit transition metal based catalysts, non-metal catalysts have also been developed. For example, N-Heterocyclic carbenes[1k, 5] have also been exploited for reduction of CO$_2$. In addition, frustrated Lewis pairs (FLPs) have been utilized to activate and reduce CO$_2$.[12] Piers and co-workers used B(C$_6$F$_5$)$_3$ and amines to transform CO$_2$ to methane with silanes.[13] We have reported use of Zn(II) and in $situ$ generated carbodiphosphines to reduce CO$_2$ to CO.[14] The Berke group used Re-H and B(C$_6$F$_5$)$_3$ as FLPs in the hydrogenation of CO$_2$ into

formate.[15] In recent efforts, Fontaine and coworkers[16] have demonstrated the catalytic activity of R$_2$PC$_6$H$_4$B(O$_2$C$_6$H$_4$) in the hydroboration of CO$_2$ to methoxyborane, utilimately generating methanol on hydrolysis. Recently, we reported the N,N'-diphosphanyl-imidazol-2-ylidene (NHC-P) ring expansion with 9-BBN to intramolecular FLPs which catalyze the hydroboration of CO$_2$ to methoxyborane.[17] In the present report, we demonstrate that an intermolecular FLP approach is also effective as catalytic amounts of phosphines in the presence of 9-BBN effect the reduction of CO$_2$, in one case achieving TON of over 5500.

The combination of tBu$_3$P and 9-BBN in bromobenzene-d_5 under ^{13}CO$_2$ (5 atm) at 25°C for 6 hours, resulted in the formation of new products as evidenced by ^{1}H NMR spectroscopy. Two doublets appeared at 8.74 ppm ($^1J_{C-H}$ = 208 Hz), 5.46 ppm ($^1J_{C-H}$ = 165 Hz) and one doublet of doublets appeared at 4.32 ppm ($^1J_{C-H}$ = 145 Hz, $^2J_{H-P}$ = 1 Hz). The first two signals were attributed to H^{13}COOB and CH$_2$(OB)$_2$ fragments, respectively by analogy to the known species HCOOBpin and CH$_2$(OBpin)$_2$.[9] These assignments were further confirmed by the corresponding ^{13}C NMR signals at 169.1 ppm (d, $^1J_{C-H}$ = 208 Hz) and 85.44 ppm (t, $^1J_{C-H}$ = 165 Hz). A peak at 52.45 ppm (dt, $^1J_{C-P}$ = 56 Hz, $^1J_{C-H}$ = 145 Hz) in the ^{13}C NMR spectrum also gave rise to the corresponding doublet at 43.3 ppm on ^{31}P{^{1}H} NMR spectrum were assigned to an [tBu$_3$P^{13}CH$_2$OBR$_2$] fragment.

The analogous stoichiometric reactions of other phosphines with CO$_2$ and 9-BBN afforded similar products (see supplementary data) as evidenced by ^{1}H, ^{31}P and ^{11}B and ^{13}C NMR spectra. In the case of Ph$_3$P, the product proved difficult to isolate. In the case of the corresponding mixture of Cy$_3$P, 9-BBN and ^{13}CO$_2$, the phosphine-borane adduct (Cy$_3$P)9-BBN was observed as the predominant species in solution as evidenced by the ^{31}P and ^{11}B NMR spectra, although trace amount of [Cy$_3$P^{13}CH$_2$OBR$_2$] species and HCOOBR$_2$ were observed (see supplementary data). This is consistent with the lesser steric demands and stronger basicity. The corresponding reaction of (4-MeC$_6$H$_4$)$_3$P with 9-BBN and ^{13}CO$_2$ afforded isolation

of ((4-MeC$_6$H$_4$)$_3$PCH$_2$O)(HC(O)O)B(C$_8$H$_{14}$) **2** (Scheme 1, Figure 1 (b)), which was spectroscopically similar to **1**.

Crystals of a product **1** and **2** were obtained from stoichiometric reaction of phosphine and 9-BBN (HBC$_8$H$_{14}$) under ^{13}CO$_2$ in bromobenzene-d_5 layered with hexanes. X-ray study of these crystals confirmed the formulations as (R$_3$PCH$_2$O)(HC(O)O)B(C$_8$H$_{14}$) (R = tBu **1**, 4-MeC$_6$H$_4$ **2**) (Figure 1), in which CO$_2$ is incorporated both as a formate and in the phosphonium methoxy-fragment. These zwitterions incorporate phosphonium fragments linked via a CH$_2$O linker to the borate center. The four coordinate B atoms in each case are also coordinated to a formate anion. The B-O bond distances ranging from 1.499 (2) to 1.568 (3) Å. The remaining metric parameters are unexceptional.
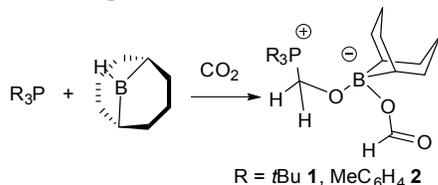
Scheme 1. Isolation of **1** and **2**.
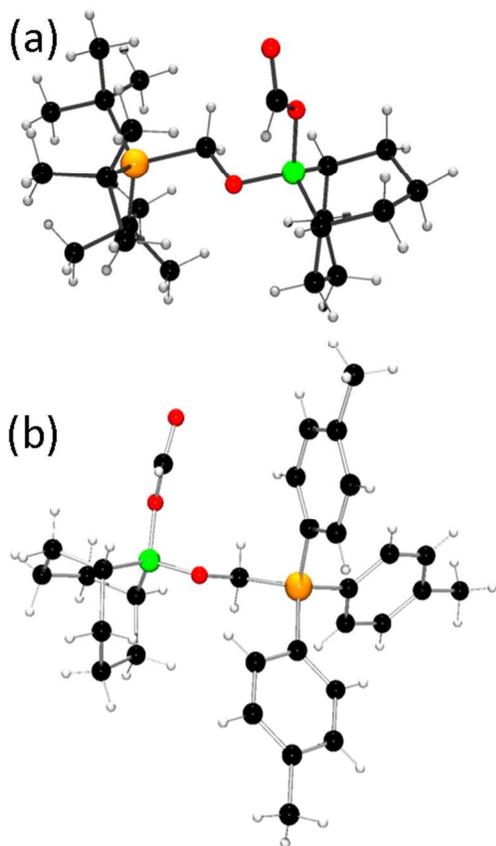
Figure 1. POV-ray depiction of (a) **1**, (b) **2**; C, black; O, red; B, green; P, orange; H, grey.

As the formation of these products illustrates the stoichiometric reduction of CO$_2$, we probed the reactions under catalytic conditions. Thus, 4 mol% of tBu$_3$P and 9-BBN (0.094 mmol) were combined with excess ^{13}CO$_2$ at room temperature (Table 1, entry 2). After 16 h,

the CO$_2$-reduction products include boron-bound formate species, HCO$_2$(B(C$_8$H$_{14}$)) **3**, the diolate-linked compound H$_2$C(OB(C$_8$H$_{14}$))$_2$ **4** and methoxide product MeOB(C$_8$H$_{14}$) **5** fragments in the ratio of **3: 4: 5** of 36: 15: 49 (Table 1, entry 2). The formate product **3** was evident from the ^{1}H NMR doublet at 8.91 ppm ($^1J_{C-H}$ = 199.7 Hz) and the ^{13}C NMR doublet at 166.9 ppm ($^1J_{C-H}$ = 200 Hz). The diolate derivative spectrum and a triplet at 85.44 ppm ($^1J_{C-H}$ = 165 Hz) in ^{13}C NMR spectrum. The boron-methoxide exhibited a doublet at 3.57 ppm ($^1J_{C-H}$ = 143 Hz) in ^{1}H NMR spectrum and a quartet at 52.69 ppm ($^1J_{C-H}$ = 143 Hz) in ^{13}C NMR spectrum consistent with the formulation as **5**. The electron deficient or sterically encumbered phosphines (C$_6$F$_5$)$_3$P, (2,4,6-Me$_3$C$_6$H$_2$)$_3$P and (2-MeC$_6$H$_4$)$_3$P showed no reactivity even at 60 °C. Employing 4 mol% Ph$_3$P, (4-MeC$_6$H$_4$)$_3$P and (3,5-Me$_2$C$_6$H$_3$)$_3$P were also effective in reduction of CO$_2$ producing mixtures of **3-5** (Table 1, Entry 3-5). Lowering the concentration of catalysts to 1-2 mol% increases the proportion of **5** in the products (Table 1, entry 6-8). In the case of tBu$_3$P lowering the concentration of tBu$_3$P to 0.2 and 0.02 mol% results in even higher production of 5 (Table 1, entry 9, 10); in the latter case 98% of the borane was converted to **5** with a minor amount of **4** (2%) after 31.5 h at 60 °C. This corresponds to a TON of 5556 and a TOF of 176.

Table 1 Product Ratios for Reduction of CO$_2$ with 9-BBN catalyzed by Phosphines[a]

Entry	Phosphines	Conc mol%	t/T h/°C	3	4	5
1	No catalyst	-	19/25	0	0	0
2	tBu$_3$P	4	16/25	36	15	49
3	Ph$_3$P	4	19/25	60	36	4
4	(4-MeC$_6$H$_4$)$_3$P	4	19/25	28	34	38
5	(3,5-Me$_2$C$_6$H$_3$)$_3$P	4	15/25	28	39	33
6	(4-MeC$_6$H$_4$)$_3$P[b]	1	30/25	7	30	63
7	Ph$_3$P[b]	1	20/25	8	41	51
8	tBu$_3$P[b]	2	13/25	19	24	57
9	tBu$_3$P[b]	0.2	16/25	3	29	68
10	tBu$_3$P[b]	0.02	32/60	0	2	98

[a] bromobenzene; ^{13}CO$_2$: 5 atm; all 9-BBN dimer (0.094 mmol) was consumed; ratios based on integration of resonances in ^{1}H NMR spectra using the protonated solvent as the internal standard. [b] 9-BBN dimer (0.410 mmol) was consumed.

The consumption of borane in these reactions was monitored in the reactions using 1.0 mol% tBu$_3$P, 1.0 mol% Ph$_3$P and 1.0 mol% (p-MeC$_6$H$_4$)$_3$P as the catalyst. These reactions were complete in 13, 20 and 30 h, respectively (Figure 2).

In the latter two cases, an induction period was observed. In these cases, doubling the phosphine concentration halved the observed induction period. This is consistent with the slow formation of a phosphine derivative which is subsequently and sequentially reduced to give **3**, **4** and **5**. In addition it suggests that as the concentration of the reduction product increase the reaction accelerates. This view is consistent with the observation of only traces of **3** during these induction periods. These data support a mechanism in which initial FLP-like binding of CO$_2$ takes place and is subsequently reduced (Scheme 2). The slow binding of CO$_2$ by the arylphosphines is consistent with the reduced steric demands

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prompting an equilibrium involving the classical Lewis P/B adduct. In the case of tBu$_3$P, steric demands preclude such adduct formation. In addition, the weaker basicity of the aryl-phosphines presumable slows nucleophilic attack of CO_2. The species **1** or **2** are generated in the reaction under stoichiometric conditions inferring that further reaction with borane effects the conversion to **4** and **5**. Indeed reaction of isolated **1** with 9-BBN at room temperature gave **4** and **5** in 10 min.

Figure 2. Consumption of borane in by phosphine catalysed CO_2 reduction using tBu$_3$P (1.0 mol%), Ph$_3$P (1.0 mol%) and (4-MeC$_6$H$_4$)$_3$P (1.0 mol% catalyst in C$_6$D$_5$Br); P($^{13}CO_2$): 5 atm; 25 °C).

Further monitoring of these reductions revealed the presence of two transient species with phosphine adjacent a methylene fragment. In the case of the tBu$_3$P reaction, this was evidenced by signals at 42.4 ppm (d, $^1J_{C-P}$ = 54 Hz) and 41.6 ppm (d, $^1J_{C-P}$ = 51 Hz) in ^{31}P NMR spectrum and 54.9 ppm (d, $^1J_{C-P}$ = 54 Hz) and 55.0 ppm (d, $^1J_{C-P}$ = 51 Hz) in ^{13}C{^{1}H} NMR spectrum. These species are attributed to the intermediate reductions species (Scheme 2).

Scheme 2. Proposed mechanism for phosphine catalysed CO_2 reduction with 9-BBN.

Conclusions

In conclusion, herein we have described a facile approach to the metal-free catalytic reductions of CO_2 in the presence of 9-BBN. These reactions proceed via an FLP-type CO_2 activation intermediate. Subsequent reaction with borane effects sequential reduction ultimately yielding the boron-methoxide. In the best case described herein, the catalyst tBu$_3$P gives rise to 5500 turnovers of hydride transfers to CO_2. Further studies of FLP systems for CO_2 reductions are the subject of continuing study in our laboratories.

Notes and references

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