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Reaction Mechanisms

Catalytic Reduction of CO_2 to CO by Using Zinc(II) and In Situ Generated Carbodiphosphoranes**

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Much of the anthropomorphic contributions to atmospheric CO_2 has arisen from the consumption of fossil fuels over the last 200 years.[1] The deleterious impact of this greenhouse gas has prompted worldwide efforts to reduce CO_2 emissions. While methods for the capture and sequestering of CO_2 have garnered much attention, strategies targeting CO_2 reduction are also being investigated. Olah and co-workers are advocates for methanol economy.[2] The direct reduction of CO_2 to methanol would provide a liquid fuel that would fit into the existing distribution infrastructure and thus be a carbon-neutral and green replacement for fossil fuels.

The development of catalysts capable of effecting CO_2 reduction has evolved in two major directions. Direct hydrogenation of CO_2 to formic acid or methanol has drawn considerable attention. An alternative strategy is focused on the conversion of CO_2 into CO.[3] This latter transformation was achieved in 2005 when Sadighi et al. developed an N-heterocyclic carbene (NHC) supported organocopper(I) catalyst for the reduction of CO_2 in the presence of a diboron reagent. This reaction yielded CO and a stable B–O–B by-product.[3g] Electrocatalytic methods for CO_2 reduction have also been shown to give CO and CO_3.[4] In a related fashion, disproportionation of CO_2 to CO and CO_3^{2-} is metal mediated in the reaction of $Li_2[W(CO)_5]$ with CO_2.[5]

Nonmetal systems for CO_2 reduction to CO have also garnered some attention. For example, Ying et al.[3j] have shown that an NHC catalyst can convert CO_2 into CO with an aldehyde serving as the oxygen acceptor, thus forming a carboxylic acid as the oxidation product.[6] In a creative and interesting application of a frustrated Lewis pair (FLP), Ashley et al. demonstrated the reduction of CO_2 to methanol in the presence of a sterically encumbered phosphine and boranes at 140 °C for nine days.[7] Subsequently we showed that a RP/AlX_3 FLP system could be used to effect the reduction of CO_2 to either methanol or CO under ambient conditions.[8] However, these transformations are limited to stoichiometric reductions because of the oxophilicity of the Lewis acids employed. Most recently, Cantat et al. have used amidines or carbenes with silanes to promote efficient formylation of amines with CO_2.[9] Herein, we have targeted related systems which display analogous cooperative action of Lewis acids and bases to effect catalytic CO_2 reduction, however we reasoned that to effect catalytic reductions, a weakly oxophilic Lewis acid was necessary. We sought to both activate CO_2 and also ensure release of the reduction products. Herein we report the discovery of the catalytic reduction of CO_2 to CO with the concurrent oxidation of phosphine. The mechanism of this facile CO_2 reduction is shown to proceed by the activation of CO_2 using an in situ generated carbodiphosphorane and zinc(II).

In an initial experiment, a solution of Et_3P, a readily oxidizable phosphine, in CH_2Cl_2 was placed under an atmosphere of CO_2. Monitoring this solution showed very slow conversion into CO and Et_3PO over a period of weeks. Repetition in bromobenzene showed neither evidence of reduction of CO_2 to CO nor oxidation of the phosphine to Et_3PO. Addition of CH_2I_2 to the bromobenzene solution prompted the reduction to occur. In this case, CH_2I_2 (4 mol %) and an excess of Et_3P (1:25) in C_6H_5Br were exposed to an atmosphere of $^{13}CO_2$ (2 atm) at 25 °C. Over a period of several weeks, slow conversion of CO_2 into CO and the generation of Et_3PO was observed (Table 1, entry 1). Raising the temperature to 100 °C accelerated the reaction, thus yielding a 56 % conversion of the excess phosphine into phosphine oxide after 56 hours (Table 1, entry 2). To facilitate the reduction of CO_2 in this fashion, a catalytic amount of the Lewis acid, $ZnBr_2$, was added to the reaction mixture. Under reaction conditions similar to those described above, 33 % of the phosphine was oxidized at 25 °C within 175 hours (Table 1, entry 3), while at 100 °C, virtually all of the phosphine was oxidized with the corresponding release of CO within 5 hours (Table 1, entry 4). The corresponding reduction of CO_2 and formation of the phosphineoxide were

Table 1: Catalytic conversion of CO_2 and Et_3P into CO and Et_3PO, respectively.

$$Et_3P + CO_2 \xrightarrow[C_6H_5Br]{\text{catalyst}\; CH_2I_2/(ZnBr_2)} Et_3P{=}O + CO$$

Entry	$Et_3P/CH_2I_2/ZnBr_2$[a]	T [°C]	t [h]	Conv. [%]	TON[b]	TOF
1	25:1:–	25	600	21	5.3	–
2	25:1:–	100	56	56	14	0.25
3	25:1:1	25	175	33	8.3	0.05
4	25:1:1	100	5	99	24.8	4.95

[a] Molar ratio. [b] Turnover number (TON) and turnover frequency (TOF) calculated on the basis of the integration of the peaks in the ^{31}P NMR spectra.

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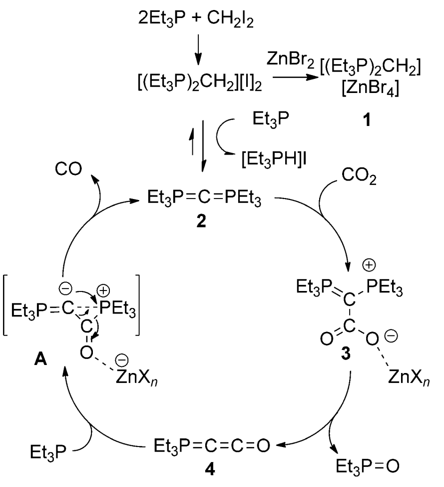
also observed using either Cy_3P or tBu_3P with $CH_2Cl_2/ZnBr_2$, although these reactions proceeded much more slowly. Similarly the poor solubility of $ZnCl_2$ appeared to inhibit the reaction when it was used in place of $ZnBr_2$. In addition, control experiments confirmed that phosphine and $ZnBr_2$ in the absence of CH_2Cl_2 resulted in neither reduction of CO_2 nor oxidation of phosphine.

The reaction of phosphine and CH_2I_2 results in equilibria among several species. Attempts to isolate the initial species in stoichiometric reactions of phosphine and CH_2I_2 led to the generation of phosphonium salts. In the presence of $ZnBr_2$ the species $[(Et_3P)_2CH_2][ZnBr_4]$ (**1**) could be isolated. This species exhibited a ^{31}P NMR signal at $\delta = 37.6$ ppm. This species is analogous to the $[(Ph_3P)_2CH_2]^{2+}$ salt isolated by Alcarazo and co-workers.[10] The anion of this species clearly results from halide redistribution and may reflect solubility properties.

In the presence of excess phosphine, equilibria are established in which **1** is deprotonated to generate the carbodiphosphorane $[(Et_3P)_2C]$ (**2**) and the phosphonium by-product $[Et_3PH][X]$. This was confirmed by variable-temperature $^{31}P\{^1H\}$ NMR studies of the reaction of excess PEt_3 with CH_2I_2. At 100 °C, the resonance attributable to $[(Et_3P)_2C]$ was observed at $\delta = 28.0$ ppm. Similar observations were made for the analogous reaction of nBu_3P with CH_2I_2.[11] Efforts to independently synthesize **2** were plagued with purification issues. Similar to the Me_3P analogue described by Gasser and Schmidbaur,[12] this species was extremely reactive, presumably because of both the basicity and diminished steric demands in comparison to the isolated carbodiphosphorane $(Ph_3P)_2C$.[13]

Subsequent reaction of **2** with CO_2 is proposed to generate $[(Et_3P)_2CCO_2]$ (**3**) which reacts by a Wittig-type reaction, thus eliminating Et_3PO and generating the phosphoranylideneketene $Et_3P{=}C{=}C{=}O$ (**4**; Scheme 1). This reaction sequence is supported by the established chemistry of PPh_3, where the bis(ylide) $Ph_3P{=}C{=}PPh_3$ has been shown to react with CO_2 to yield the carbodiphosphorane CO_2 adduct $[(Ph_3P)_2CCO_2]$.[13] Thermolysis of this latter product has also been shown to result in the release of phosphine oxide and formation of the phosphoranylideneketene $(Ph_3P{=}C{=}C{=}O)$.[13] In contrast to this PPh_3 ketene species, which proved to be remarkably stable, **4** is attacked by an additional Et_3P and leads to subsequent loss of CO and the regeneration of the bis(ylide) **2** . The zinc Lewis acid is thought to participate in this reaction as the rate of CO evolution is accelerated in its presence. Thus, the greater basicity and lesser steric demands of Et_3P compared to that of PPh_3, together with the assistance of the Lewis acidity of the zinc ion, facilitate the attack of the phosphaketene. This addition of Lewis acid and base to the ketene amounts to an FLP addition to the ketene, not unlike other FLP additions to CO_2,[14] olefins,[15] or alkynes.[16] It is the last step of CO liberation and reformation of **2** that completes the catalytic cycle and allows the oxidation of the phosphine with concurrent liberation of CO.

To garner further insight, the reaction was performed under the latter reaction conditions and monitored periodically by ^{31}P NMR spectroscopy. The resonance attributable to the substrate Et_3P ($\delta = -19.7$ ppm) disappears over the course of the reaction. At the same time the corresponding resonance from Et_3PO ($\delta = 51.2$ ppm) grows in. After five hours of reaction time at 100 °C the phosphine is consumed and the phosphineoxide is the major phosphorus-containing species. In addition to these signals, the formation of the minor side product **5** is indicated by the appearance of the doublets at $\delta = 23.0$ and $\delta = 26.2$ ppm with a P–P coupling of $J = 63$ Hz. Integration of the peak is consistent with the formation of this species from about 80 % of the 4 mol % CH_2I_2 precatalyst added. Interestingly addition of $LiNiPr_2$ to the reaction mixture resulted in the elimination of **5** and $^{13}C\{H\}$ NMR data revealed additional formation of ^{13}CO.[11] For the reaction employing $^{13}CO_2$, the ^{31}P resonances from **5** exhibited coupling to ^{13}C of $J = 47$ and 2 Hz. Furthermore, characterization of **5** was achieved by the fortuitous isolation of crystals of **5** from the reaction mixture. X-ray crystallography confirmed the formulation of **5** as $[Et_3P{=}CH(PEt_3)(COZnBr_3)]$ (Figure 1).[11] This species is best described as an ylide derivative in which the substituents on the ylide carbon



Scheme 1. Proposed catalytic cycle of CO_2 reduction and phosphine oxidation (X = I, Br; n = 2, 3).

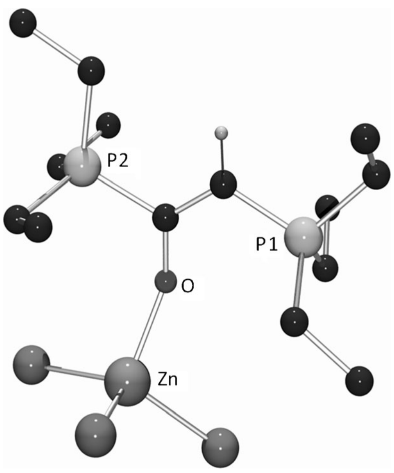


Figure 1. POV-ray depiction of **5**. Hydrogen atoms were omitted for clarity.

atom are a hydrogen and a carbonyl fragment in which a second phosphine is bound to C and the oxygen atom is coordinated to a $ZnBr_3$ unit. The P−C bond of the ylide portion is 1.760(2) Å, while the phosphonium-CO bond is 1.831(2) Å. The C−O bond is 1.287(3) Å and the Zn−O bond distance was found to be 1.987(2) Å. The central C−C bond linking the ylide to the carbonyl fragment was determined to 1.366(3) Å, which is consistent with conjugation across the P-C-C-O fragment.

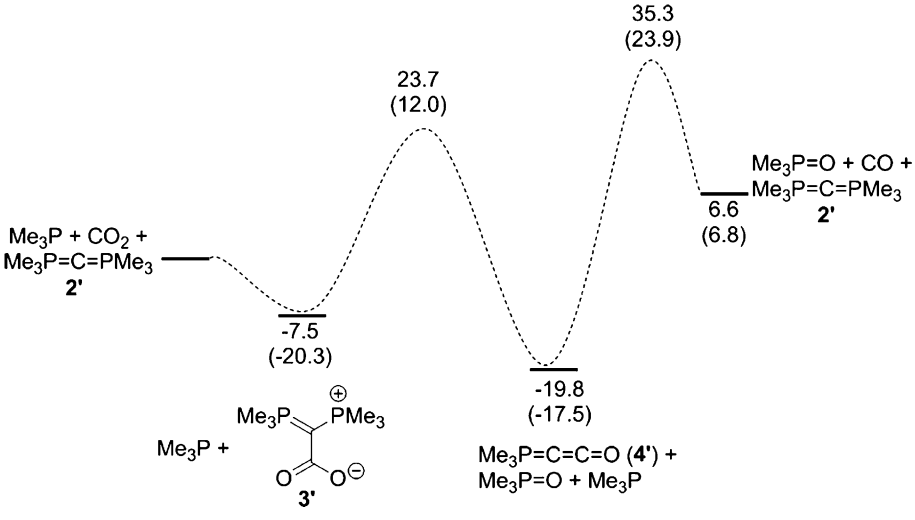
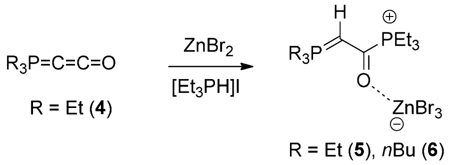


Figure 2. Gibbs energy diagram showing enthalpy values (kcal mol^{-1}) for the reaction of CO_2 with Me_3P and CH_2I_2.

The formation of the minor product **5** arises from the interception of the ketene **4** by $[Et_3PH][ZnBr_3]$, which protonates **A** to give **5** [Eq. (1)]. Fortunately the poor solubility of the $[Et_3PH]^+$ in bromobenzene limits the formation of **5**, thus allowing the reduction of CO_2 to proceed with the precipitation of salts of $[Et_3PH]^+$ from the reaction mixture. In contrast, when using nBu_3P as the substrate, the solution remains homogeneous and thus $[nBu_3PH][ZnX_3]$ (X = Br or I) is available in solution and thus results in the formation of $[nBu_3P{=}CH(PBu_3)(COZnBr_3)]$ (**6**) [Eq. (1)]. NMR data show this species is formed in 91 % yield based on CH_2I_2 in a C_6H_6Br solution and indeed no catalytic liberation of CO is observed. Interestingly, when performing the reaction in toluene, where the phosphonium salt $[nBu_3PH][ZnX_3]$ (X = Br or I) is less soluble, catalysis with a TON of 4 is observed to generate nBu_3PO and CO. The corresponding reactions of Cy_3P or tBu_3P in CH_2Cl_2 proceed catalytically but rather slowly, even at elevated temperatures.



(1)

To further support this mechanism we performed preliminary DFT calculations at the B2PLYP-D/6-311 + G(d,p) level of theory[17] for the model reactions of Me_3P, CO_2, and the corresponding carbodiphosphorane (Figure 2).[11] Interestingly, the overall process is calculated to be endothermic by 6.6 kcal mol^{-1}. However, the intermediates **3′** and **4′** were calculated to form in exothermic reactions of −20.3 and −17.5 kcal mol^{-1}, with net negative Gibbs energies for the successive steps of −7.5 kcal mol^{-1} and −19.8 kcal mol^{-1}, respectively. This is consistent with formation of the previously reported synthesis of $(Ph_3P{=}C{=}C{=}O)$.[13] The liberation of CO from phosphaketene with concurrent reformation of the (bis)ylide was computed to be endothermic by 24.3 kcal mol^{-1} with an activation energy from **4′** of 55.1 kcal mol^{-1}. The computed barrier is consistent with the slow CO release at room temperature in the absence of Lewis acid. While the overall driving force for this step is thought to be the irreversible liberation of CO, the barrier is lowered by 8 kcal mol^{-1} in the presence of zinc(II) (**4′**−ZnF_3).[11] These data are consistent with the slow CO release and the requirement for elevated temperatures.

In conclusion, we have described the reduction of CO_2 to CO using CH_2I_2 to generate the catalytically active species, $Et_3P{=}C{=}PEt_3$ in situ. This (bis)ylide reacts with CO_2, subsequently eliminating phosphine oxide and generating the transient phosphaketene. While this reaction is accelerated by the presence of catalytic $ZnBr_2$, the zinc ion and phosphine also act on the phosphaketene to regenerate the (bis)ylide, with concurrent CO elimination. While the present results demonstrate the catalytic reduction of CO_2 to CO, we are continuing to examine related systems for CO_2 reduction catalysis targeting oxygen-atom delivery to other substrates.

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[11] See the Supporting Information. CCDC 909071 and 909072 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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