Frustrated Lewis Pair Catalyzed Reduction of Carbon Dioxide Using Hydroboranes: New DFT Mechanistic Insights

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Catalytic CO₂ reduction is attractive for the sustainable production of value-added fuels and chemicals. Prevented by an unclear mechanistic picture, only a few frustrated Lewis pair (FLP) catalysts are known for the efficient CO₂ reduction under mild conditions using hydroboranes as reductant. For the first time, based on extensive DFT calculations, very efficient mechanisms for all steps of the FLP-catalyzed reduction of CO₂ to various products of boryl formate, H₂CO, bis(boryl) acetal and methoxyborane are revealed. Zwitterionic B/P FLP-H₂CO adducts are confirmed as active catalyst via the Lewis-basic CH₃O “oxide” center. Strong O and N Lewis-bases are very active in promoting hydride transfer from hydroboranes to CO₂ and strongly bound to the boryl group of reduced species. This can be modulated by Lewis acids in FLP catalysts for well-balanced catalytic activity, which is crucial for further design of novel catalytic process.

The worldwide dependence on non-renewable energy sources and chemical feedstock is detrimental to the environment. There is enormous interest in the development of alternative sustainable resources in order to meet our global energy and commodity chemical demands. Carbon dioxide (CO₂) is an appealing renewable carbon source for the production of value-added fuels and commodity chemicals due to its low cost, high abundance and relative lack of toxicity.[1] However, since CO₂ is the most oxidized form of carbon that is thermodynamically and kinetically quite stable, catalysis is crucial to the efficient reduction of CO₂ to value-added products using reducing reagents such as dihydrogen (H₂), hydroborane and hydrosilane.[2] The direct hydrogenation of CO₂ to methanol is the most atom-efficient route, but currently requires transition-metal-based catalysts (such as pincer iron) under relatively harsh conditions.[3] Alternatively, both metal[4] and non-metal[5] catalysts have been developed for the efficient hydroboration or hydroisylation of CO₂ under mild conditions. In particular, metal-free frustrated Lewis pair (FLP) systems[5c-e,i,l-o,6] are usually more environment-friendly thus quite attractive for sustainable synthesis of high-value fine chemicals. Despite of stoichiometric bis(boryl) oxide byproduct, the products of CO₂ hydroboration can be useful for the transfer of formyl, methylene and methyl groups into organic compounds.[7] Mechanistic insights into such catalytic CO₂ hydroboration reactions is of great importance for the further design of novel catalytic process.

Catalytic CO₂ reduction is generally thought to be initialized by hydride transfer from the metal or boron center to the CO₂ molecule activated by the catalyst[4a,k,l-m,n,r,b]. However, only a few FLP catalysts are known to be active for CO₂ reduction under mild conditions; three typical examples of known hydroboration are shown in Scheme 1. In 2013, Fontaine et al. demonstrated the first intramolecular B/P FLP 1a for CO₂ reduction using catecholborane (HBcat),[5j] and subsequently suggested the FLP-H₂CO adduct as the actual catalyst. In 2014, using Lewis-basic phosphine tBu₃P and reactive 9-...
As seen in Figure 1, HBcat may bind to the CH₂O “oxide” site of 1af, leading to transient 2a that is 2.8 kcal/mol higher in free energy with an evidently elongated (by 0.16 Å) CH₂O–Bcat bond and a highly reductive hydroborate center. Facile hydride transfer from 2a to CO₂ and its reduced intermediates (boryl formate 4a and H₂CO) may occur via similar transition structures T51a, T52ac and T53ac, respectively, leading via intermediate H₂CO to the methoxyl borane 6a as the final product. The initial catalytic reduction of CO₂ into 1af-bound boryl formate HCOOBcat (4a) is −7.6 kcal/mol exergonic over a moderate barrier of 24.1 kcal/mol (T51a); the complex 3α needs only 1.4 kcal/mol to release the boryl formate 4a and regenerated 1af with a recovered CH₂O–Bcat bond. As suggested previously[5f] the Bcat oxygen atoms of 1af may also promote hydride transfer from HBcat to CO₂ (via T51o), which is however kinetically 2.1 kcal/mol less favorable. Similar CH₂O oxided promoted hydride transfer from HBcat to 4a is −19.3 kcal/mol exergonic over a barrier of 26.7 kcal/mol (T52ac), forming free H₂CO (along with OBcat), and regenerated 1af via ionic O−B recombination) that can be more readily reduced by 1af-promoted hydride transfer (T53ac) into the methoxyl borane H₂COBcat (6a). Alternatively, direct C=O hydroboration of 3a with HBcat is −20.4 kcal/mol exergonic over a barrier of 25.4 kcal/mol (T52a) to form the bis(boryl) acetali H₂(BOBcat)₂ (5a) (along with regenerated 1af) that can be more readily reduced by another HBcat via 1af-aided OBcat− abstraction from and hydride transfer to 5a (T53a), leading again to 6a as the final product, which is kinetically 1.3 kcal/mol more favorable. In contrast, C=O hydroboration reactions of CO₂, 4a and H₂CO using HBcat without catalyst are prevented by high barriers of 43.1, 35.9 and 32.1 kcal/mol (see ESI Table S1), respectively. The Lewis-basic CH₂O “oxide” center is thus proven very active in promoting hydride transfer, even partially quenched by the Lewis-acidic Bcat group as base shuttle within the FLP catalyst 1af to realize well-balanced catalytic steps.

In contrast, a similar CH₂O “oxide” site is also found in the tBu₅P–CH₂O–BbnOCHO complex but without additional acidic stabilization, which is also active for catalytic CO₂ reduction using reactive diborane (HBBn), but with a relatively low product selectivity (methoxyl borane H₂COBbn together with significant amount of HCOOBbn and H₂(BOBbn)₂ as products).[5] Our DFT calculations (see ESI Figure S3 and Table S2) show that the hydride transfer from the tBu₅P–CH₂O–BbnH complex to CO₂ is −16.1 kcal/mol exergonic over a rather low barrier of 7.2 kcal/mol, indicating a very active oxide center in promoting hydride transfer. The tBu₅PCH₂O center is strongly bound to the boryl group of HCOOBbn, H₂COBbn, H₂COBbn and HBBn species by −21.1, −7.1, −3.8 and −9.6 kcal/mol, respectively, making possible the release of H₂COBbn, and H₂COBbn (via transient H₂CO over low barriers within 15 kcal/mol) but not HCOOBbn as product by HBBn up-taking. The C=O hydroboration of the tBu₅PCH₂O-bound HCOOBbn is −4.0 kcal/mol exergonic over a moderate barrier of 17.9 kcal/mol to form the tBu₅PCH₂O-bound H₂COBbn₂. After fast HBBn up-taking, the further reduction of H₂COBbn₂ into H₂COBbn is prevented by a sizeable barrier of 23.2 kcal/mol (see below) thus is the slowest reduction step.

Figure 1. DFT computed free energy paths (in kcal/mol, at 298 K and 1 M concentration) for the FLP-H₂CO adduct 1af-catalyzed CO₂ reduction using HBcat. Less competing paths are shown in red lines. Crucial H, B, C, N, O and P atoms are high-lighted as white, pink, grey, blue, red and orange balls, with partially breaking bonds indicated by dashed lines and selected bond lengths shown in Å. See also ESI Figure S1 for a complete catalytic cycle.
More recently, the novel Si/N FLP catalyst 1b was proven active for the CO$_2$ reduction using reactive (HBbn)$_2$ in THF solution. The proposed mechanism via H/Cl exchange between HBbn and 1b$^{[5e]}$ is examined at first.

As shown in Figure 2, the diborane (HBbn), may dissociate with the help of a coordinating THF molecule over a moderate barrier of 23.1 kcal/mol (TS1) into monomeric HBbn species. The CO$_2$ hydroboration via HBbn is $-4.4$ kcal/mol exergonic over a sizable barrier of 30.3 kcal/mol (TS2) to form the boryl formate 3b (a higher barrier of 36.5 kcal/mol via dimeric (HBbn)$_2$, see ESI Table S3) and should be slow at room temperature. On the other hand, the H/Cl exchange between HBbn and 1b is shown to be 15.4 kcal/mol exergonic to form the Si–H bond containing complex 1bH. Further hydride transfer from 1bH to CO$_2$ is $-14.8$ kcal/mol exergonic over a low barrier of only 15.7 kcal/mol (TS3) and thus should be efficient even at room temperature. However, this effectively leads to a high barrier of 31.1 kcal/mol for the 1b-catalyzed CO$_2$ hydroboration that is kinetically even worse than the case without any catalyst.

Experimentally, 1b reacts reversibly (in 30% conversion) with CO$_2$ to form the neutral adduct 2b in THF solution.$^{[5e]}$ As shown in Figure 3, according to our DFT calculations, this reaction is indeed only 0.4 kcal/mol exergonic over a low barrier of 15.5 kcal/mol (TS1b), excluding 2b as stable off-cycle resting state as suggested previously.$^{[5e]}$ Moreover, the proposed$^{[5e]}$ C=$\equiv$O hydroboration of 2b via monomeric HBbn is $-4.4$ kcal/mol exergonic but prevented by a sizable barrier of 27.1 kcal/mol (TS2b) to form the boryl formate 4b and regenerated catalyst 1b. Since the B=O binding of 4b to 1b is actually $-3.7$ kcal/mol exergonic to form the adduct 4b.1b, the effective barrier for such catalytic CO$_2$ hydroboration would be 30.8 kcal/mol thus again kinetically not favorable.

Again, facile hydride transfer from HBbn to CO$_2$ promoted by the N-base center of 1b is found in our DFT calculations. The cooperative binding of HBbn to 1b is $-0.6$ kcal/mol exergonic over a barrier of 20.2 kcal/mol (TS3b), leading to the complex 3b with the B–H bond partially activated by the Si/N centers. Further hydride transfer to CO$_2$ is $-7.5$ kcal/mol exergonic over a low barrier of 18.0 kcal/mol (TS4b) to form the complex 4b.1b. When the Lewis-acidic SiMe$_3$Cl is replaced by the neutral methyl group, such barrier can be further reduced to only 11.0 kcal/mol, indicating again a highly active N-base site in promoting hydride transfer. Direct C=$\equiv$O hydroboration of 4b.1b by HBbn is $-14.0$ kcal/mol exergonic over a low barrier of 18.3 kcal/mol (TS5b) to form the bis(boryl) acetal H$_2$C(OBbn)$_2$ 5b and released 1b, which is kinetically 7.5 kcal/mol more favorable than the alternative pathway via the hydroboration of free 4b that may lead to H$_2$CO instead of 5b. If present, the addition of H$_2$CO to the FLP 1b is $-14.2$ kcal/mol exergonic over a rather low barrier of 11.8 kcal/mol, leading to the separated ions of 1bf$^+$ and Cl$^-$ in THF solution. The bis(boryl) acetal 5b can be directly reduced by HBbn, which is $-26.2$ kcal/mol exergonic over a sizable barrier of 23.2 kcal/mol (via novel cyclic TS6b) to reach the methoxyl borane 6b. Very similar mechanism is also found when less reactive HBCat is used as reductant, despite that 1b-bound H$_2$C(OBcat)$_2$ (5c) is involved in the final (also slowest) reduction using HBcat over a sizable barrier of 28.3 kcal/mol (see ESI Figure S2 and Table S4), suggesting lower catalytic reactivity than 1af. Our new mechanism of FLP-catalyzed CO$_2$ reduction is thus kinetically
very efficient, limited by the reduction of the bis(boryl) acetal intermediates.

In summary, for the first time, very efficient new mechanisms are revealed by extensive DFT calculations for the complete steps of FLP-catalyzed CO reduction using hydroboranes. Zwitterionic B/P FLP...ächtet, J. Chem. Soc., Perkin Trans. 1986, 14, 1885–1890.

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Conflict of Interest

The authors declare no conflict of interest.

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