



Review

Boron-mediated activation of carbon dioxide

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ABSTRACT

Carbon dioxide is a very abundant molecule that is used as building block by nature. It would be a sustainable resource for our carbon-based societies if we could emulate nature in transforming CO₂ under mild conditions. Despite the high thermodynamic stability of CO₂, the last decade witnessed increasing interests in the homogeneous reduction of CO₂ with dihydrogen, hydroborane or hydrosilane as reducing agents. With the last two reductants very mild conditions could be used ($T < 100$ °C, $P_{\text{CO}_2} < 5$ atm), mechanistic insights were gained and a variety of compounds were described including more complex molecules resulting from the reductive functionalization of CO₂ with amines. The versatile properties of boron-containing molecules are key to activate CO₂ in various ways, and not only via hydroboration of CO₂. At the stoichiometric level, Lewis pairs featuring a strong Lewis acidic borane moiety are shown to form CO₂ adducts, whereas formatoborate compounds can be obtained by the reaction of CO₂ with hydroborates or with metal hydride complex mediated by boranes. Catalytic reductions of CO₂ can be achieved (i) with hydroboranes when the hydride transfer is catalyzed by a metal hydride complex, an amphiphilic compound, a strong Lewis base or a hydroborate, (ii) with diborane or silylborane to promote the abstraction of one oxygen atom to afford CO and (iii) with hydrosilane activated by strong Lewis acidic perfluorinated borane compound.

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1. Introduction

Carbon dioxide is a very attractive source of carbon because it is very abundant and rather non-toxic when compared to the other C1 sources employed by the chemical industry. Its use has thus attracted a lot of interest in many fields of chemistry from the most fundamental researches to the most applied one [1–16]. However it is also a very thermodynamically stable molecule and only in few cases the balance between the cost of the required energy input (physical or chemical energy) and the created value of the product is economically favorable [17–19]. Many interconnected factors – going beyond chemistry – have an impact on this balance. At the fundamental level, a more efficient and controlled activation of CO₂ would allow one to (i) decrease the level of energy input and/or (ii) increase the molecular complexity of the product and as a consequence the added-value of the compounds synthesized from CO₂. The last decade witnessed intense interests in the homogeneous reduction of CO₂ with dihydrogen [20–23], hydrosilane [24] and hydroborane as reducing agents. While CO₂ hydrogenation appears as the ideal reaction in term of atom economy, a sustainable source of “carbon free” dihydrogen and milder reaction conditions remain to be described. The use of hydrosilanes and hydroboranes to reduce CO₂ is not economically interesting when simple molecules are synthesized. However, very mild conditions were used ($T < 100\text{ }^{\circ}\text{C}$, $P_{\text{CO}_2} < 3\text{ atm}$) that allowed one to gain mechanistic insights and to synthesize a variety of compounds including more complex molecules resulting from the reductive functionalization of CO₂ with amines. In addition, the versatile properties of boron-containing molecules allow one to activate CO₂ in various ways, and not only via hydroboration of CO₂. The present review focuses on these different modes of activation (Scheme 1). At the stoichiometric level, (a) Lewis pairs containing a strong Lewis acidic borane moiety form CO₂ adducts, whereas (b) formatoborate compounds can be obtained from the reaction of CO₂ with hydroborates or with metal hydride complexes mediated by boranes. Catalytic reductions of CO₂ are achieved (c) with hydroboranes when the hydride transfer is catalyzed by a metal hydride bond, an amphiphilic compound, a strong Lewis base (L.B.) or a hydroborate, (d) with diborane or silylborane to promote the abstraction of one oxygen atom to afford CO and (e) with hydrosilane activated by strong Lewis acidic perfluorinated borane.

2. Activation of CO₂ by a Lewis pair

No CO₂-borane adduct has been reported so far while only strong Lewis bases form stable adduct with CO₂. However, when combining borane with a Lewis base – even L.B. that does not activate CO₂ by itself – CO₂ adducts **1–14**, **16–21**, were characterized. The Lewis base – a phosphine or an amine – coordinates to the electrophilic central carbon, while the borane coordinates to the nucleophilic oxygen atom of CO₂, formally generating a zwitterionic molecule featuring phosphonium or ammonium and borate moieties (Scheme 2). If an amphiphilic compound is used – the Lewis base and the borane are connected – a cyclic zwitterion is obtained.

2.1. Phosphine/borane activation

In 2009, Grimme, Stephan, Erker et al. first reported the activation of CO₂ by a Frustrated Lewis Pair (FLP). The Lewis pair PtBu₃/B(C₆F₅)₃ gives rise to the adduct **1** (Scheme 3) [25], and a recent theoretical analysis studied the motion involved in the formation of this compound, showing an influence of the relative volume of the Lewis acid and Lewis base [26]. An intramolecular

FLP containing dimesitylphosphine (–PMes₂) as the L.B. and a perfluorinated borane as the L.A. connected by an ethylene linker activates CO₂ to afford compound **2**. Following similar strategies, the CO₂ adducts **3–14** were characterized (Scheme 3). The same authors have explored other FLP systems and isolated compounds **3–9** [27]. The combination of triisopropylphosphine (PiPr₃) with B(C₆F₅)₃ does not afford the expected CO₂ adduct. The fluoride in *para*-position of the C₆F₅ group was indeed substituted by the phosphine [28]. However, when using unsubstituted B(C₆F₄H)₃ at the *para* position, the reaction with PiPr₃ and PtBu₃ in the presence of CO₂ affords adducts **3** and **4**, respectively. In compounds **5–9**, PtBu₃ was used as the Lewis base whereas B(C₆F₄H)₂R with different R groups (**5**: hexyl, **6**: Cy, **7**: norbornyl, **8**: Cl and **9**: Ph) was used as the Lewis acid counterpart. The experimental data and theoretical calculations show that the different properties of the R groups have little impact on the CO₂ activation energy profile by the Lewis pair, or on the stability of the resulting compounds. Equilibrium constants for the formation of **6** were determined by a microfluidic approach in order to circumvent the time scales and diffusion issues encountered when measuring gas–liquid interaction parameters [29]. In addition, abstraction of the chloride in compound **6** gave rise to a more robust structure due to the increased Lewis acidity of the borane moiety [30]. Stephan et al. have subsequently used diborane compounds as Lewis acid to afford compounds **10–13**. With a diborane featuring an O-bridge or an *ortho*-phenylene linker, the isolated CO₂ adducts **10** [31] and **11** [32] exhibit a single B–O coordination. However, with a sp² C-bridge linker, the CO₂ adducts **12** and **13** were isolated in which each oxygen atom of the CO₂ molecule interacts with a borane moiety. The same year, Slootweg, Lammertsma et al. used an intramolecular FLP system with a methylene linker between a phosphine and a non-fluorinated borane moieties. Interestingly, despite a less Lewis acidic borane, CO₂ is activated and compound **14** isolated [33]. A similar structure was also found with an alane moiety in place of the borane [34]. In 2012, Maerten, Baceiredo et al. subjected a boryl(phosphine)carbene [35] to 1 atm of CO₂ [36]. The outcome is completely different from the previous examples since the carbene is driving the reaction with its insertion into the C=O bond of CO₂. The resulting compound **15** features a phosphacumulenylium with the oxygen atom from CO₂ trapped between the phosphorus and the boron atoms (Scheme 3).

Experimental and theoretical data for **1–14** are reported in Table 1. Compounds **1–9** and **11–13** form reversibly. Compound **1** loses CO₂ at 80 °C under vacuum and the other compounds are isolated at low temperature since the release of CO₂ is observed upon warming. The less stable adducts (**2**, **5–9**) release CO₂ between –20 or –14 °C. The energy of formation of adducts **2**, **5**, **6** and **8** have indeed been calculated between –2.9 and –4.7 kcal mol^{–1}. In contrast, compound **13** and **14** are stable under vacuum at 100 and 80 °C, respectively. The computed formation energy of 20.3 kcal mol^{–1} for compound **13** is thus in good agreement with the experience. The solution and solid state characterizations are also reported but no clear general trend emerges from it. In the case of δ¹³C, the data are comprised between 160.5 and 161.3 ppm, but for **12**, **13** and **14** which exhibit comparatively deshielded signals at 170.9, 169.7 and 167.8 ppm, respectively, and for **10** which exhibit shielded signal at 156.3 ppm. The νCO stretching frequencies are much weaker in the case of **12** and **13** (1617 and 1608 cm^{–1}) than in the other compounds (1686 to 1719 cm^{–1}). The expected change of geometry from linear to bent for the activated-CO₂ is observed, but since the variations are minimal between the different compounds (between 123.9(3)° and 129.5(4)°), this measure is hardly an indicator of the degree of activation. While the two C–O bond distances are identical in each diborane compounds **12** and **13**, the other compounds exhibit markedly shorter C=O distances for the oxygen not involved in the coordination with the borane moiety.

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