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Four-electron reduction of CO₂: from formaldehyde and acetal synthesis to complex transformations

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The expansive and dynamic field of the CO₂ Reduction Reaction (CO₂RR) seeks to harness CO₂ as a sustainable carbon source or energy carrier. While significant progress has been made in two, six, and eight-electron reductions of CO₂, the four-electron reduction remains understudied. This review fills this gap, comprehensively exploring CO₂ reduction into formaldehyde (HCHO) or acetal-type compounds (EOCH₂OE, with E = [Si], [B], [Zr], [U], [Y], [Nb], [Ta] or -R) using various CO₂RR systems. These encompass (photo)electro-, bio-, and thermal reduction processes with diverse reductants. Formaldehyde, a versatile C₁ product, is challenging to synthesize and isolate from the CO₂RR. The review also discusses acetal compounds, emphasizing their significance as pathways to formaldehyde with distinct reactivity. Providing an overview of the state of four-electron CO₂ reduction, this review highlights achievements, challenges, and the potential of the produced compounds – formaldehyde and acetals – as sustainable sources for valuable product synthesis, including chiral compounds.

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1. Introduction

Research in CO₂ transformations conducted by the Carbon Capture and Utilization (CCU) community is driven by both fundamental and applicative motivations. On the fundamental side, the goal is to find the keys to transform this thermodynamically and kinetically stable molecule. On the practical side, there is a desire to emulate nature by using CO₂ either as a synthetic building block or as an energy carrier. These objectives gain urgency due to the increasing concentration of atmospheric CO₂ and the inevitable depletion of fossil



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resources. Given its significance and broad scope, the field of CO₂ transformation has been extensively covered in numerous reviews and books. Early reviews¹ and comprehensive perspectives² provide authoritative insights. Other reviews focus specifically on the use of CO₂ as an energy carrier³ or as a synthetic reagent.⁴ From an applied perspective, the importance of Life Cycle Assessment (LCA)⁵ has been considered to evaluate the industrial potential of various processes.⁶ From a thermodynamic standpoint, this expansive field can be categorized into reactions involving a redox event at the carbon atom of CO₂ (CO₂ Reduction Reaction: CO₂RR) or those that do not.^{4a} Motivations for the CO₂RR include using CO₂ as an energy carrier, as energy is formally stored during CO₂ reduction, and as a sustainable source of carbon. In the CO₂RR, comprehensive reviews have focused on the type of reduction used, whether it involves thermal reduction with dihydrogen,⁷ hydroboranes,⁸ or hydrosilanes,⁹ (photo)electro reduction¹⁰ or bio-catalysed reduction.¹¹ Other reviews explore the homogeneous¹² or heterogeneous¹³ nature of the catalytic system.

Within the CO₂RR, the level of reduction of CO₂ is arguably the most important parameter to consider. Since the carbon atom of CO₂ is fully oxidized (+IV), it can be reduced by as much as 8e⁻ giving rise to four possible even reduction states shown (Scheme 1). The +II, 0, -II and -IV carbon atom oxidation states can be reached by electroreduction or hydrogenation of CO₂. The corresponding C₁ reduction products are represented in Scheme 1(a): CO₂¹⁴ and HCOOH¹⁵ (2e⁻), HCHO and ROCH₂OR (4e⁻), CH₃OH^{15a,16} (6e⁻) and CH₄ (ref. 17) (8e⁻). As shown in Scheme 1(b), the same oxidation states are reached with hydroelementation (E-H) reactions. Using mostly hydroborane (E = BR₂) and hydrosilane (E = SiR₃), HCOOE (2e⁻), EOCH₂OE and HCHO (4e⁻), CH₃OE (6e⁻) and CH₄ (8e⁻) have indeed been reported. Although it does not correspond to a formal hydroelementation, the catalytic formation of CO (2e⁻) was reported with hydroborane¹⁸ and with diborane.¹⁹ The 4e⁻ reduction products of CO₂ – namely formaldehyde and acetal compounds

– occupy a distinct position compared to other C₁ reduction products (Scheme 1c). The reasons for this are explained below.

1.1. Why reducing CO₂ by 4e⁻ to formaldehyde?

In the context of an increasing demand for complex transformations of CO₂ beyond the simple C₁ building blocks mentioned earlier^{20,21} and the desire for long-term CO₂ storage, formaldehyde offers unparalleled potential in terms of reactivity and versatility.²² More than 30 million tons of formaldehyde are produced and used annually by the chemical industry. This commodity compound is typically synthesized from the partial oxidation of methanol under energy-demanding conditions, representing over 35% of the total methanol transformation.^{22a,23} A mild and sustainable synthesis of formaldehyde from CO₂ would thus represent a significant advancement for the chemical industry. Most industrial applications use formaldehyde as a reticulating agent in condensation reactions leading to various C-N, C-O, C-S, and C-C bonds.

Furthermore, formaldehyde serves as a precursor to more complex molecules, including chiral ones,²⁴ being a C₁ and a C_n source in aldol²⁵ and formose reactions,²⁶ notably. These transformations are beyond the reach of other CO₂ reduction products.

However, there is still no selective and sustainable synthesis of formaldehyde from CO₂. This can be attributed to two major issues: (i) the 4e⁻ reduction stage requires any catalytic system to overcome the energy barriers for both the 2 and 4e⁻ reduction steps while preventing the 6e⁻ reduction, and (ii) the detection of formaldehyde (HCHO) is challenging due to its intrinsic instability, limiting further development and optimization. Depending on the reaction media (pH, solvent, co-substrates), formaldehyde can polymerize, precipitate, or react with other chemicals present in the mixture, making its characterization difficult. Several detection methods have been used, such as optical methods, chemical derivatization for HPLC and GC analysis, or chemical conversion for colorimetric method analysis (established by Nash in the 1950s).²⁷ Recently,



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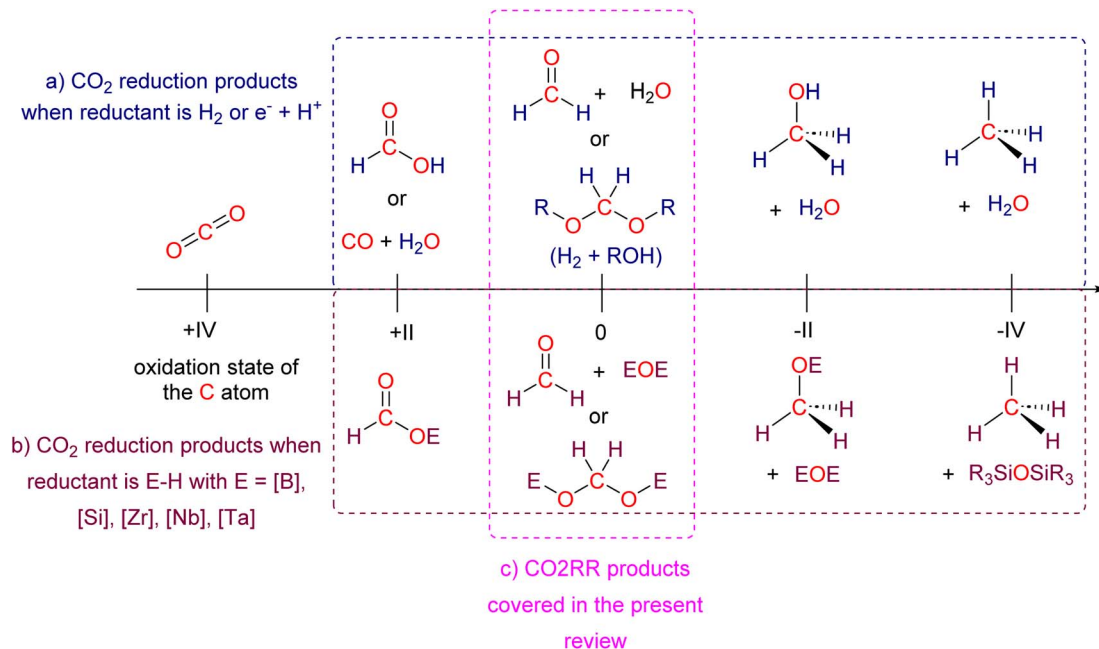
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Scheme 1 C₁ products generated from CO₂ reduction by (a) hydrogenation or electroreduction or (b) hydroelementation reactions. (c) Formaldehyde and acetal compounds as the products of four-electron reduction of CO₂ covered in the present review.

a new and simple method for trapping and quantifying formaldehyde in aqueous solutions by ¹H NMR was designed, otherwise allowing for isotope labelling experiments and thus unambiguous demonstration that the HCHO production arises from CO₂ reduction.²⁸

1.2. Why reducing CO₂ by 4e⁻ to acetal compounds?

The formation of acetal (EOCH₂OE) from hydroelementation of CO₂ is an important process linked to formaldehyde, because

(i) Some of these acetal compounds were shown to quantitatively release formaldehyde, offering an efficient and selective access to it under particularly mild conditions and with isotope labelling proving the origin of formaldehyde. The generated formaldehyde was subsequently used as C₁ and also C_n sources,²⁹ and notably in the first enantioselective transformation of CO₂ into a C₄ carbohydrate,³⁰ representing the highest level of complexity obtained from CO₂ at that time.³¹

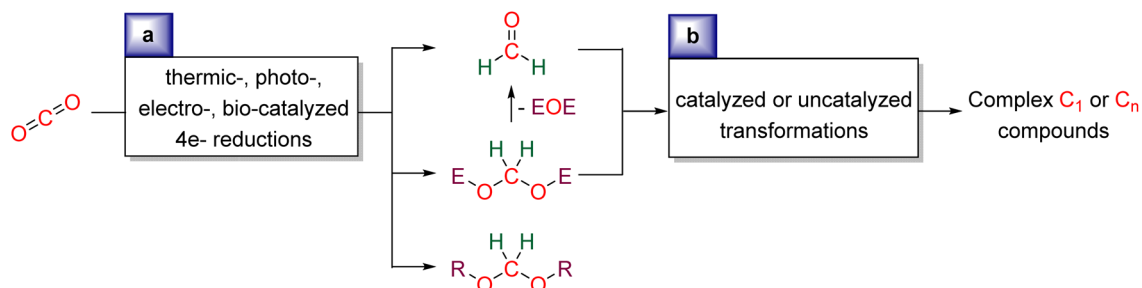
(ii) Beyond the release of formaldehyde, acetal compounds were also involved in transformations related to but distinct

from formaldehyde, notably when used as a C_n source. Interestingly, in one case, boryl moieties remained on the product, demonstrating a difference in reactivity compared to formaldehyde.³² This finding should open opportunities to use the boryl or silyl functional groups as an integral part of new compounds as opposed to a waste moiety.

(iii) Finally, mild conditions and organic solvents used in hydroelementation enable *in situ* NMR monitoring leading to easier proofs of the origin of the acetal or formaldehyde by isotopic labelling experiments.

1.3. Objective and organization of the review

We aim at presenting the challenges and mechanistic considerations associated with formaldehyde³³ and acetal synthesis from CO₂ (Scheme 2a), as well as highlighting the reactions in which these reduction products have been involved (Scheme 2b). This review is organized by the type of reduction system: Hydrosilylation (Section 2), Hydroboration (Section 3), Other hydroelementation reactions (Section 4), Hydrogenation



Scheme 2 General scheme presenting the current review: (a) synthesis of formaldehyde or acetal compounds from CO₂RR and (b) utilisation of formaldehyde and acetal as C₁ and C_n sources.



(Section 5), Electroreduction (Section 6), Photo(electro)reduction (Section 7), and Bio-catalysed reduction (Section 8). In each section, the reduction and subsequent transformations of the $4e^-$ reduction products are presented, with special attention drawn to the mechanisms involved.

2. Hydrosilylation

Hydrosilylation of multiple C=C, C=O and C=N bonds has been intensely investigated, fuelling applications in the silicon industry as well as in synthetic chemistry, in asymmetric reductions in particular.³⁴ Hydrosilylation of CO₂ involves the addition of a Si-H bond to the C=O bond, transferring the hydride to the carbon atom and forming a Si-O bond. This reaction is favoured kinetically and thermodynamically by the polarity of the Si-H bond (electronegativity (E. N.) of H = 2.2, Si = 1.9) and the formation of a strong Si-O bond (>500 kJ mol⁻¹),³⁵ respectively. As a consequence, CO₂ hydrosilylation usually operates under mild conditions of temperature and pressure.

CO₂ hydrosilylation was first reported in 1981 with Ru- and Pd-based catalysts, independently.³⁶ In both cases, the reduction process led to formoxysilane ($2e^-$ reduction product). Hydrosilylation beyond the $2e^-$ reduction stage was hypothesized in these two initial reports based on the observation of bis(silyl) ether (R₃SiOSiR₃) and of a small amount of formaldehyde (<4% yield) with the Ru-based catalyst.^{36b} In 1989, an Ir-based catalyst enabled unambiguous observation of the hydrosilylation of CO₂ beyond the $2e^-$ reduction stage. In this pioneering study, it was remarkable that the 2, 4 and $6e^-$ reduction products – formoxysilane, bis(silyl)acetal (BSA) and methoxysilane, respectively – were subsequently observed.³⁷ Finally, the first report of CO₂ hydrosilylation into methane was published in 2006 by Matsuo and Kawaguchi with a [Zr]/B(C₆F₅)₃ catalytic system.³⁸

Since these initial reports, the reduction of CO₂ by $4e^-$ with hydrosilane witnessed a growing attention. The present section aims to cover in detail (i) the formation of BSA and formaldehyde in part 2.1, (ii) the mechanisms accounting for their generation in part 2.2, (iii) the proposed origin of the selectivity toward BSA in part 2.3, and (iv) their use as reactive intermediates in reductive functionalization reactions leading to more complex products in part 2.4 (Scheme 3).

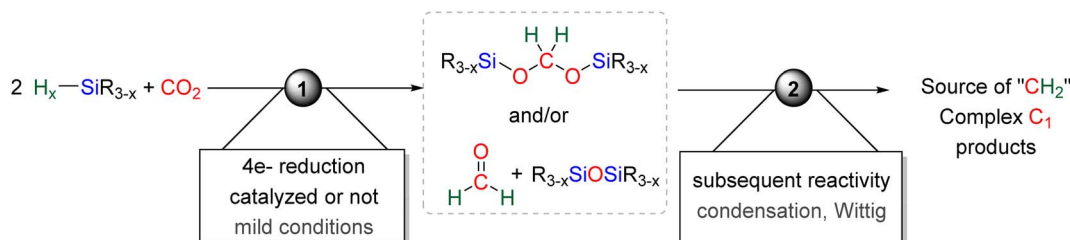
2.1. Hydrosilylation of CO₂ into bis(silyl)acetals (BSAs) and formaldehyde

2.1.1. Description of BSA 1 to BSA 11. Bis(silyl)acetals (BSAs) are obtained from the double hydrosilylation of one

molecule of CO₂. They feature an acetal core with two stabilizing silyl moieties attached to both oxygen atoms. Reported BSAs are depicted in Scheme 4 and their NMR characterizations are given in Table 1. Currently, eleven BSAs (**BSA 1–11**) have been reported in the literature. **BSA 1–6** have been generated from tertiary silanes HSiMe₃, HSiEt₃, HSiPh₃, HSiMe₂Et, HSiPh₂Me and HSiPhMe₂, respectively, in excellent NMR yields (79 to 99%) regardless of the nature of silane substituents (trialkyl, triaryl or mixed silanes). Among them, only **BSA 2** and **3** were isolated with best yields of 94 and 95% with **C4** and **C17**, respectively. The utilization of secondary and primary silanes led to the formation of **BSA 7–10**. None of them was isolated. **BSA 10a** was characterized from a quasi-stoichiometric control experiment between a Co-formate complex and phenylsilane.⁴² The use of only three equivalents of silane enabled the characterization of **BSA 10a** as the sole (silyl)acetal, in contrast to the observation of several BSA signals under the catalytic conditions. The presence of more than one hydride as reductive entities on the silicon atom with primary or secondary silanes indeed leads to the observation of multiple (silyl)acetal signals. This was clearly exemplified by Eisenberg *et al.* when using the dialkylsilanes, Me₂SiH₂ and Et₂SiH₂ (**BSA 7–8**, respectively).³⁷ In both cases, three ¹³C and ¹H NMR signals characteristic of BSA were observed. Despite the ill-defined nature of the acetal mixture, the characteristic NMR chemical shifts and the absence of other signals in this area enable not only the detection but also the quantification of the (silyl)acetal entities. As shown in Table 1, a narrow range of methylene chemical shifts was observed in ¹H NMR (4.96 to 5.80 ppm) and in ¹³C NMR (83 to 85.7 ppm) with ¹J_{CH} coupling constants between 161.5 and 164.4 Hz. In addition, conclusive labelling studies were reported with ¹³CO₂. ²⁹Si NMR data are restricted to **BSA 2**, **4–6**, and **11** with chemical shifts of 18.3, 17.7, –2.74, 6.99 and 24.0 ppm, respectively.

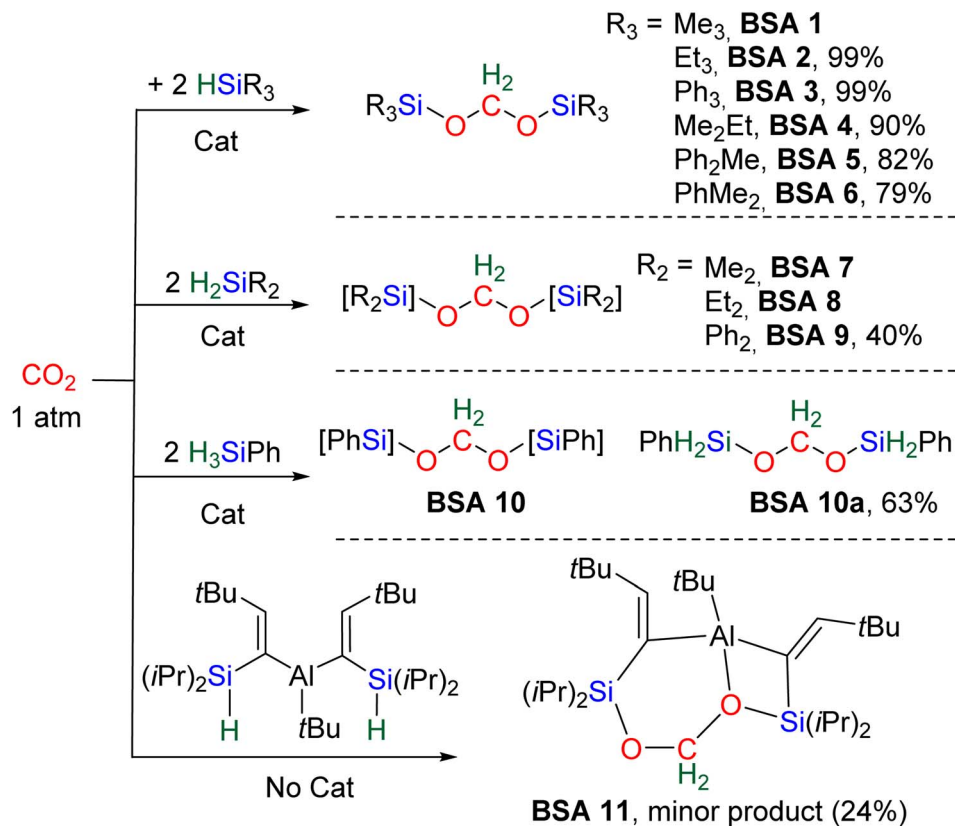
Most of the characterized BSA features tertiary silane moieties (**BSA 1–6** and **BSA 11**). Three of them were isolated (**BSA 2**, **3** and **11**) and the latter two were characterized by XRD. The higher stability of (silyl)acetals featuring tertiary silyl moieties is discussed in the mechanism section, Section 2.2. Catalysts were necessary to generate BSA but for **BSA 11**, which was derived from the hydrosilylation of CO₂ by an aluminum complex featuring two hydrosilane pendent moieties. **BSA 11** was generated as a minor product in 24% yield and features an acetal fragment stabilized by the Lewis acidic alane moiety.⁴³

2.1.2. Catalytic systems. Selective (**C1–C25**) and non-selective (**C26–C36**) catalytic systems leading to the formation of **BSA 1–10** are described separately below. We consider



Scheme 3 General scheme of Section 2: CO₂ hydrosilylation.





Scheme 4 Synthesis of BSA 1–11. The yields indicated are the best reported yields.

Table 1 NMR characterization of BSA 1–11

| BSA | Solvent | $^{13}\text{C}(\text{CH}_2)$ | | | | Ref. |
|------------------------|---------------------------------|------------------------------|------------------------|--|----------------------------|------|
| | | δ (ppm) | $^1J_{\text{CH}}$ (Hz) | $\delta_{\text{H}}(\text{CH}_2)$ (ppm) | δ_{Si} (ppm) | |
| 1 | C_6D_6 | — | 164 | 5.03 | — | 37 |
| 2 ^a | C_6D_6 | 84.6 | — | 5.03 | 18.3 | 39 |
| 3 ^a | $\text{C}_4\text{D}_3\text{Br}$ | 85.5 | — | 5.55 | — | 38 |
| | C_6D_6 | 85.7 | 164.4 | 5.45 | — | 38 |
| 4 | C_6D_6 | 84.0 | — | 5.02 | 17.72 | 40 |
| 5 | C_6D_6 | 84.9 | — | 5.21 | −2.74 | 40 |
| 6 | C_6D_6 | 84.5 | — | 5.06 | 6.99 | 40 |
| 7 | C_6D_6 | 85.4 | 164 | 5.02 | — | 37 |
| | | 84.5 | — | 5.08 | — | |
| | | 83.8 | — | 5.12 | — | |
| 8 | — | — | — | — | — | 37 |
| 9 | CD_3CN | 83 | — | 5.8 | — | 41 |
| 10 | C_6D_6 | 85.6 | — | — | — | 42 |
| 11 ^a | C_6D_6 | 87.6 | — | 5.04 | 24.0 | 43 |
| | | | | 5.18 | | |

^a Isolated.

a system selective when it affords BSA as the major product even if at a low conversion rate of silane. Catalysts **C1–C25** are depicted in Fig. 1. The specific mode of action of these catalysts indicated with a colour code in Fig. 1 (bottom right) are discussed in detail in the mechanism section, Section 2.2.

Table 2 gathers the catalytic performances (turnover number – TON, turnover frequency – TOF, yield) of catalysts **C1–25**. Key features are the mild conditions in terms of temperature (ranging from 25 to 80 °C) and CO_2 pressure (from stoichiometric quantities to 6 atm). We have selected the conditions affording the best performances in terms of TON, TOF and/or yield for each catalytic system. TOFs are not given at the initial rate because such data were available only for **C5** (Table 2). All BSA derivatives were obtained selectively with the exception of **BSA 1**, **7** and **8**. Most of the TON values are in between 10 and 89. The catalysts **C1**, **C8**, **C11**, **C12**, **C17** and **C25** afford high TONs of 203, 395, 285, 620, 178 and 670, respectively. Only catalysts **C4** and **C8** led to exceptionally high TON values of 3400 and 1200, respectively. Moreover, **C8** and **C25** led to maximum TOFs of 55.8 and 52 h^{-1} , respectively, while all the other catalysts led to TOFs between 0.1 and 10.4 h^{-1} .

In addition to TON and TOF, yields are important to assess the selectivity of a given system. This is particularly important when the synthesized BSA is intended to be used as an intermediate in one-pot transformation (see reductive functionalization, Section 2.4). Most of the catalysts afforded BSA in yields higher than 73%. **BSA 2** was notably isolated from **C8**-catalyzed CO_2 hydroxylation on the NMR scale, while larger scales of **BSA 2** (570 mg, 2.1 mmol) and **BSA 3** (2.67 g, 4.7 mmol) were isolated with **C4**- and **C17**-catalyzed reactions, in 94 and 95% yield respectively. This preparative scale notably facilitated the utilization of **BSA 3** in subsequent transformations (see reductive



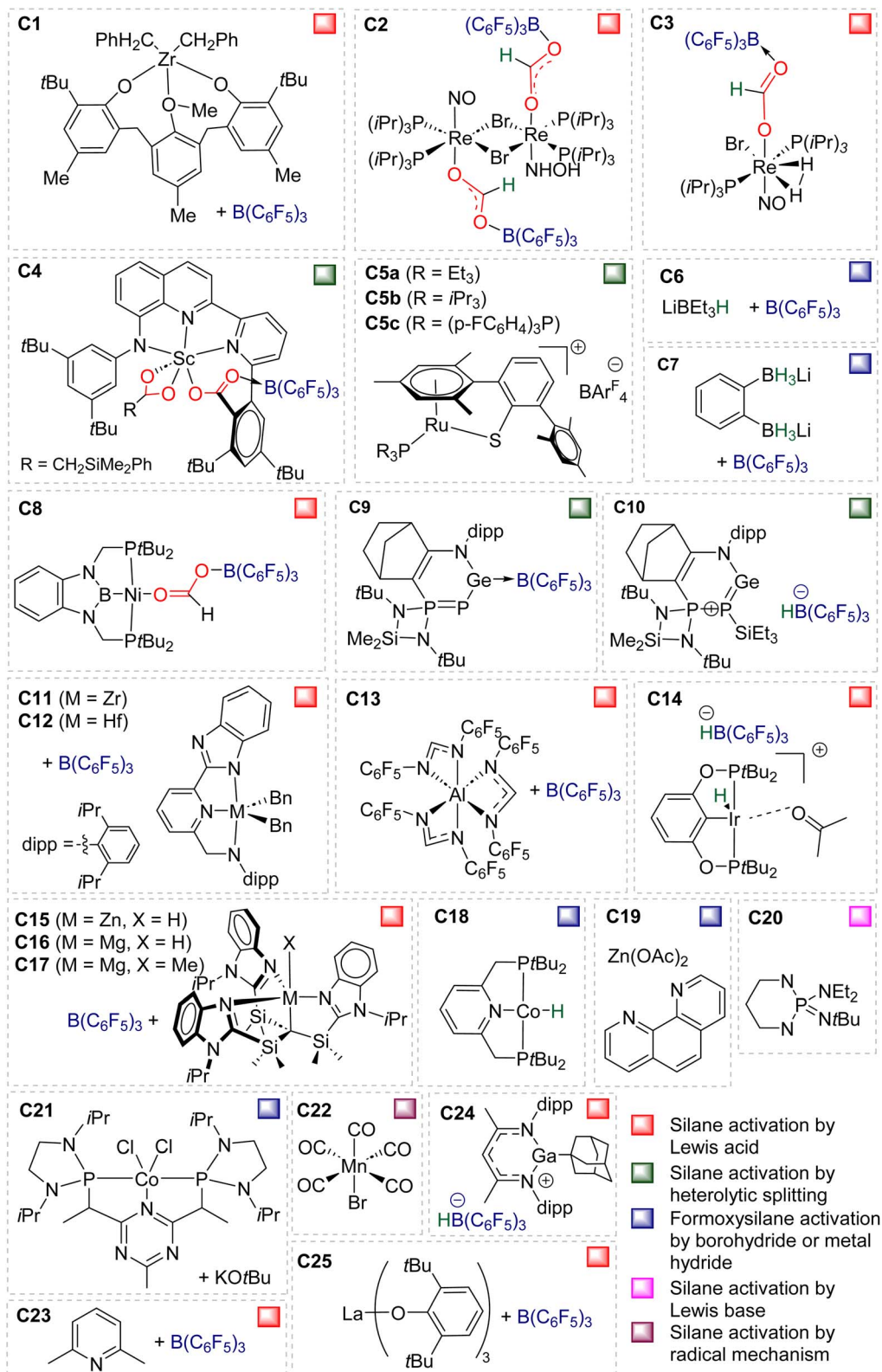


Fig. 1 Catalysts C1–C25 leading to the selective formation of BSA.

functionalization, Section 2.4). The yields for hydrosilylation of CO_2 are given based on the hydrosilane and not on the CO_2 conversion in the vast majority of the cases. This is due to the

difficulty in controlling the amount and conversion of CO_2 as a gas with ^{13}C NMR titration and to the fact that silane is considered to be the most expensive reactant. Yields based on



Table 2 Catalytic performances of the selective catalysts C1–C25 for the synthesis of BSA 2–6, 9 and 10

| BSA | Catalyst | TON ^a | TOF (h ⁻¹) | Yield ^b (%) | P _{CO₂} ^f | T (°C) | Time (h) | [Cat] (%) | Ref. |
|-----------------|----------|---------------------|-------------------------|------------------------|--|--------|----------|-----------|------|
| 2 | C1 | 203 | 1.2 | 82 | 1 | 25 | 165 | 0.9 | 38 |
| | C2 | 89 | 5.9 | 87 | 5 | 80 | 15 | 1 | 44 |
| | C3 | 95 | 7.3 | 89 | 5 | 80 | 13 | 1 | |
| | C4 | 1000 | 10.4 | 94 ^e | 4 | 65 | 96 | 0.1 | 45 |
| | C5a | 3400 | n.d | 94 ^e | 4 | 65 | n.d | 0.02 | |
| | | 25 | 6.2/11 ^c | 99 | 5 | 80 | 4 | 4 | 40 |
| | C5b | 49 | 1.5/8.6 ^c | 80 | 5 | 80 | 32 | 2 | |
| | | 25 | 0.51/<0.01 ^c | 89 | 5 | 80 | 48 | 4 | |
| | C5c | 25 | 0.34/0.00 ^c | >99 | 5 | 80 | 72 | 4 | |
| | C6 | n.d | n.d | 91 | 1 | 50 | 24 | 10 | 46 |
| | C7 | n.d | n.d | 54 | 1 | 50 | 41 | 10 | |
| | C8 | 1200 | 55.8 | 60 ^d | 4 | 70 | 21.5 | 0.05 | 39 |
| | | 910 | 26.8 | 91 ^d | 4 | 70 | 34 | 0.1 | |
| | C9 | 20 | 0.8 | 82 | 3 | 60 | 24 | 5 | 47 |
| | C10 | | | | | | | | |
| | C11 | 395 | 6.6 | 76 | 1 | 22 | 60 | 0.24 | 48 |
| | C12 | 285 | 5.9 | 55 | 1 | 22 | 48 | 0.24 | |
| | C13 | 9 | 0.69 | 60 | 6 | 80 | 13 | 1.5 | 49 |
| | C22 | 57 | 57.3 | 86 | 4 | 50 | 1 | 1.5 | 50 |
| | C24 | 17 | 0.3 | 85 | 2 | 60 | 58 | 10 | 51 |
| C25 | 99 | 99 | 99 | 5 | 25 | 1 | 1 | 52 | |
| 3 | C1 | 50 | 0.13 | 64 | 1 | 25 | 384 | 2 | 38 |
| | C14 | 36 | 2 | 100 | 1 | 23 | 22.7 | 2.5 | 53 |
| | C15 | 12 | 0.1 | n.d | 1 | 25 | 120 | 2 : 10 | 54 |
| | C16 | 83 | 1.2 | n.d | 1 | 25 | 69 | 0.5 : 2.5 | |
| | C17 | 178 | 2.5 | n.d | 1 | 25 | 72 | 0.5 : 2.5 | 29a |
| | | n.d | n.d | 95 ^e | 1 | 25 | 672 | 1 | |
| | C25 | 670 | 52 | 67 | 5 | 80 | 13 | 1 | 52 |
| 4 | C5a | 31 | 0.57/7.8 ^c | 64 | 5 | 80 | 55 | 2 | 40 |
| | | 25 | 2.3/12 ^c | 90 | 5 | 80 | 11 | 4 | |
| 5 | C5a | 17 | 0.23/3.9 ^c | 24 | 5 | 80 | 73 | 2 | 40 |
| | | 25 | 0.69/12 ^c | 79 | 5 | 80 | 36 | 4 | |
| | C8 | 620 | 16.5 | 62 ^d | 4 | 70 | 37.5 | 0.1 | 40 |
| 6 | | 137 | 18.3 | 82 ^d | 4 | 70 | 7.5 | 0.6 | |
| | C5a | 32 | 0.44/6.2 ^c | 55 | 5 | 80 | 73 | 2 | 40 |
| | | 24 | 0.32/9.5 ^c | 79 | 5 | 80 | 75 | 4 | |
| | C8 | 121 | 40 | 78 | 4 | 70 | 3 | 0.6 | 39 |
| 9 ^g | C13 | 3.5 | 0.07 | 31 | 6 | 80 | 48 | 1 | 49 |
| | C19 | 40 ⁱ | 1.7 ⁱ | 40 ⁱ | 1 mmol | 25 | 24 | 1 | 55 |
| | C20 | 5.6 | 1.4 | 7 | 5 | 25 | 4 | 1.25 | 56 |
| 10 ^h | C18 | 32/126 ^j | 1.2/4.8 ^j | 63 | 0.4 mmol | 25 | 26 | 2 | 42 |

^a TON = silane converted/catalyst loading unless otherwise stated. ^b *In situ* yield unless otherwise stated. ^c Initial rate measured after 1 hour. ^d No other product detected. ^e Isolated yield. ^f atm unless otherwise stated. ^g 2 eq. vs. CO₂. ^h 4 eq. vs. CO₂. ⁱ Based on hydrosilane and on CO₂ conversion. ^j Based on CO₂ conversion.

CO₂ conversion are nonetheless significant because (i) it allows for more complete description of a given catalytic system by reporting its performances based on both reactants and (ii) silane is not necessarily the most expensive substrate, notably when isotopically labelled CO₂ is used. Performance data based on CO₂ conversion are particularly important when ¹¹CO₂ and ¹⁴CO₂ are used for radiochemistry.⁵⁷

Compounds C26,⁵⁸ C27,³⁷ C28,⁵⁹ C29,⁶⁰ C30,⁶¹ C31,⁴¹ C32,⁶² C33,⁴⁹ C34,⁴⁹ C35⁶³ and C36⁶⁴ were shown to catalyse the hydrosilylation of CO₂ affording BSA as a minor product (Fig. 2). Most of these systems were optimized for the generation of methoxysilane and/or methane and not for BSA. The observation of BSA as intermediates in many cases confirms that (silyl)

acetals are very often on the reaction pathway to the 6 and 8e⁻ reduction products in hydrosilylation processes.

2.1.3. Formaldehyde. The observation of formaldehyde from CO₂ hydrosilylation was only reported at 100 °C with Ru(Cl)₂(PPh₃)₃ as the catalyst in 1981 (Scheme 5).^{36b} It was however observed in less than 4% yield and detailed experimental data are lacking to know if free formaldehyde was observed by a direct or indirect method after derivatization. Based on current knowledge, one can wonder if the detected formaldehyde may result from BSA evolution, although the authors explicitly indicated that no experimental proofs were found for BSA generation.

More recently, BSA was utilized as an intermediate to selectively access formaldehyde (Scheme 6). The air stable **BSA 3**



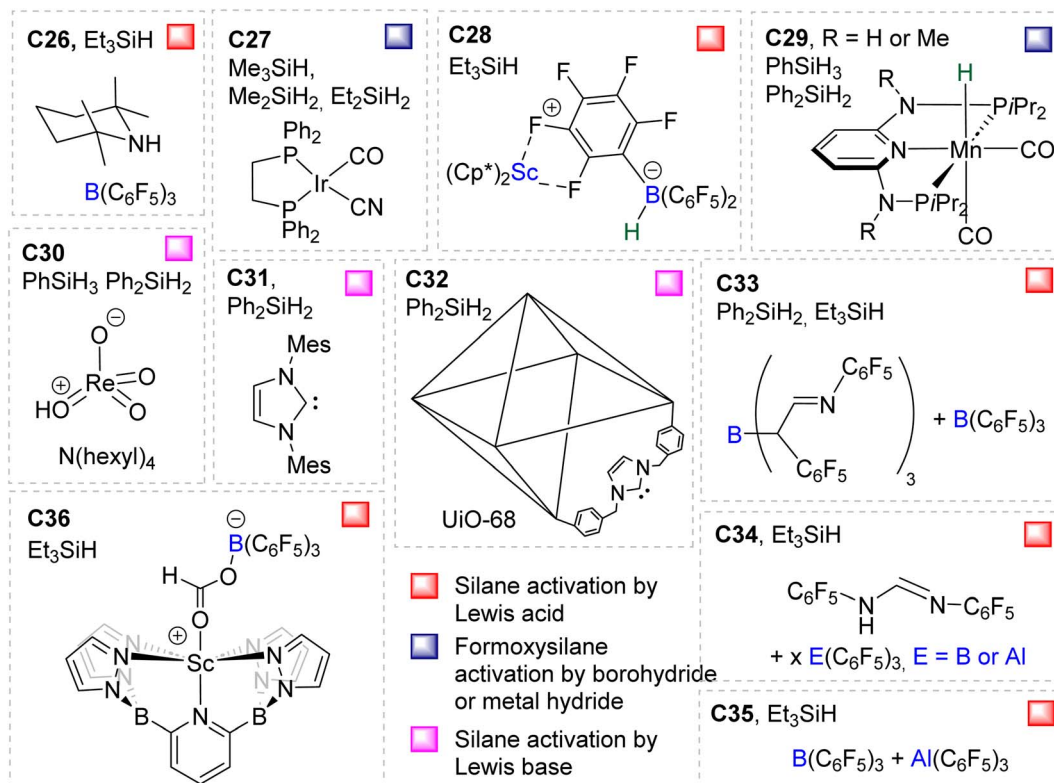
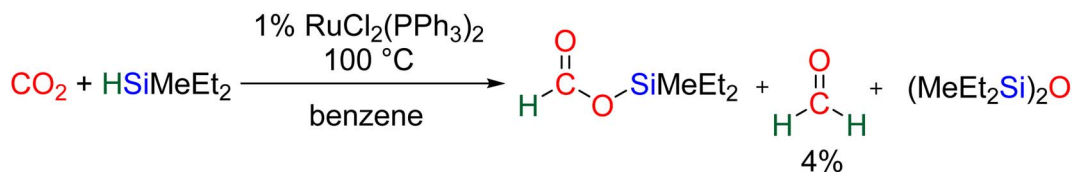
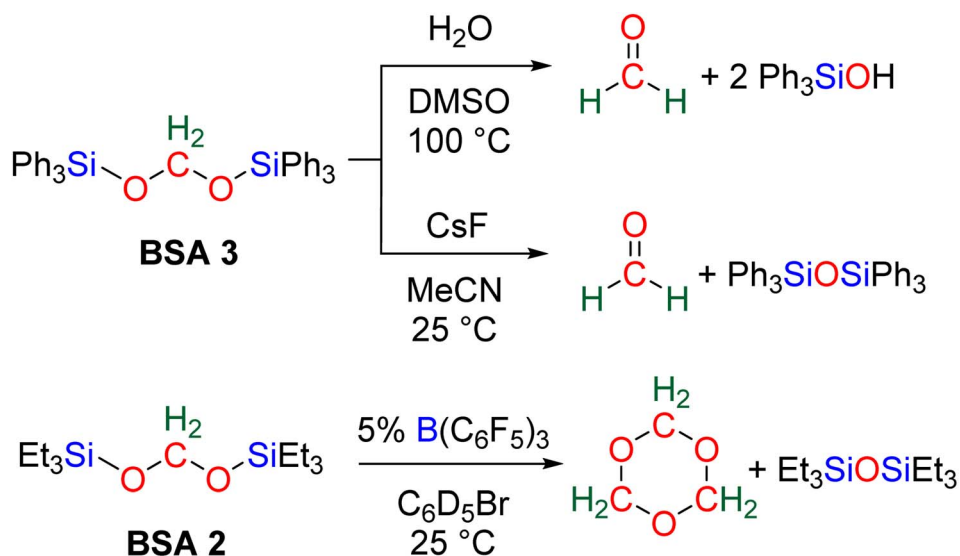


Fig. 2 Unselective catalytic systems C26–C36 and hydrosilane employed.



Scheme 5 Early observation of formaldehyde from CO₂ hydrosilylation.



Scheme 6 Quantitative generation of formaldehyde from BSA 2 and 3.



featuring triphenylsilyl groups was shown to quantitatively deliver formaldehyde in DMSO/H₂O at 100 °C or in the presence of H₂SO₄ at room temperature.^{29a} Alternatively, CsF promoted the generation of formaldehyde at room temperature, presumably *via* the breaking of the Si–O bond after fluoride attack on the silicon centre.

In another study, **BSA 2** featuring triethylsilyl moieties was shown to quantitatively release formaldehyde in the form of trioxane within 1 h in the presence of 5 mol% of B(C₆F₅)₃ as the catalyst at room temperature.⁶³ Conversely, **BSA 3** did not release formaldehyde in the presence of 22 mol% of B(C₆F₅)₃ in 10 days at room temperature.^{29a} These contrasting reactivities between **BSA 2** and **BSA 3** highlight the influence of the silyl fragment on the reactivity of the BSA.

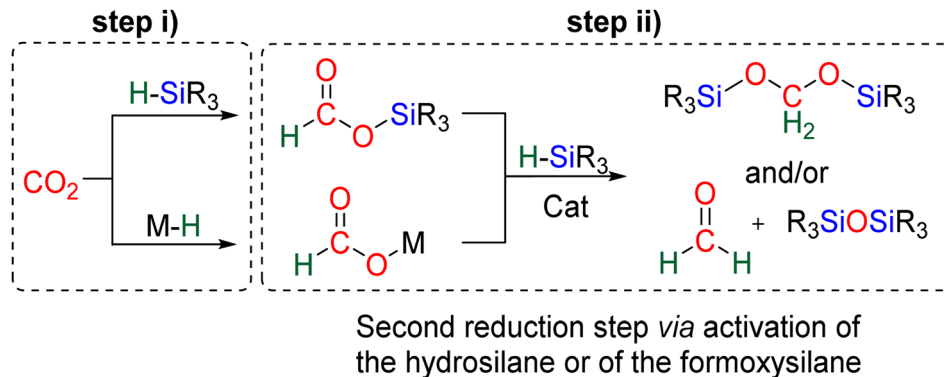
2.2. Mechanistic considerations

The 4e[−] reduction of CO₂ into bis(silyl)acetal (BSA) or formaldehyde by hydrosilane takes place along two steps: (i) the 2e[−] reduction of CO₂ into either formoxysilane or metal formate (Scheme 7, step (i)), followed by (ii) the hydrosilylation of the intermediate into the corresponding 4e[−] reduction products (Scheme 7, step (ii)). The elementary reactions accounting for step (i) have been already investigated both experimentally and theoretically in reviews focusing on CO₂ hydrosilylation.⁹ We will focus here on the less investigated second reduction step leading to the 4e[−] reduction products. A thorough evaluation of

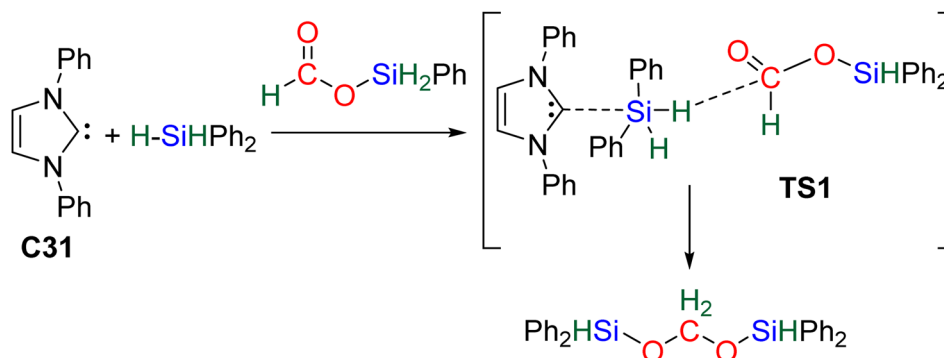
the different mechanisms showed that the role of the catalyst is to activate either the hydrosilane or the formoxysilane, along different activation modes depending on the nature of the catalyst which are described hereafter for the catalysts **C1–36**. A summary of the different activation modes is given in Section 2.2.7 with a general scheme, Scheme 13.

2.2.1. Activation of the hydrosilane by a Lewis base. The N-Heterocyclic Carbene (NHC) **C31** has been shown to catalyse the hydrosilylation of CO₂ into methoxysilane with the observation of BSA as an intermediate.⁴¹ DFT investigations have suggested that the NHC activates the hydrosilane to trigger a hydride transfer to the formoxysilane and the generation of the BSA (Scheme 8).⁶⁵ The calculated transition state (**TS1**) of the rate determining step involves three key components: **C31** acting as the LB activator, Ph₂SiH₂ as the reductant and finally the formoxysilane intermediate. A subsequent – almost barrier less – step regenerates the catalyst **C31** along with the BSA release. Although not yet proven, the action mode of **C20**,⁵⁶ **C30**⁶¹ and **C32**⁶² may be similar to that of **C31** because of their high Lewis basicity. Theoretical investigations on the hydrosilylation of CO₂ catalysed by the perrhenate anion **C30** also support such views with a similar activation pathway of the hydrosilane for the first reduction step to formoxysilane.

2.2.2. Activation of the hydrosilane by a Lewis acid. Hydrosilanes are typically activated by strong Lewis acids promoting the transfer of a silylium “Si⁺” moiety. The cationic



Scheme 7 Two mechanistic pathways for the 4e[−] reduction of CO₂ by hydrosilanes.



Scheme 8 Schematic view of the computed transition state (**TS1**) of the Lewis basic activation of hydrosilane by catalyst **C31**.

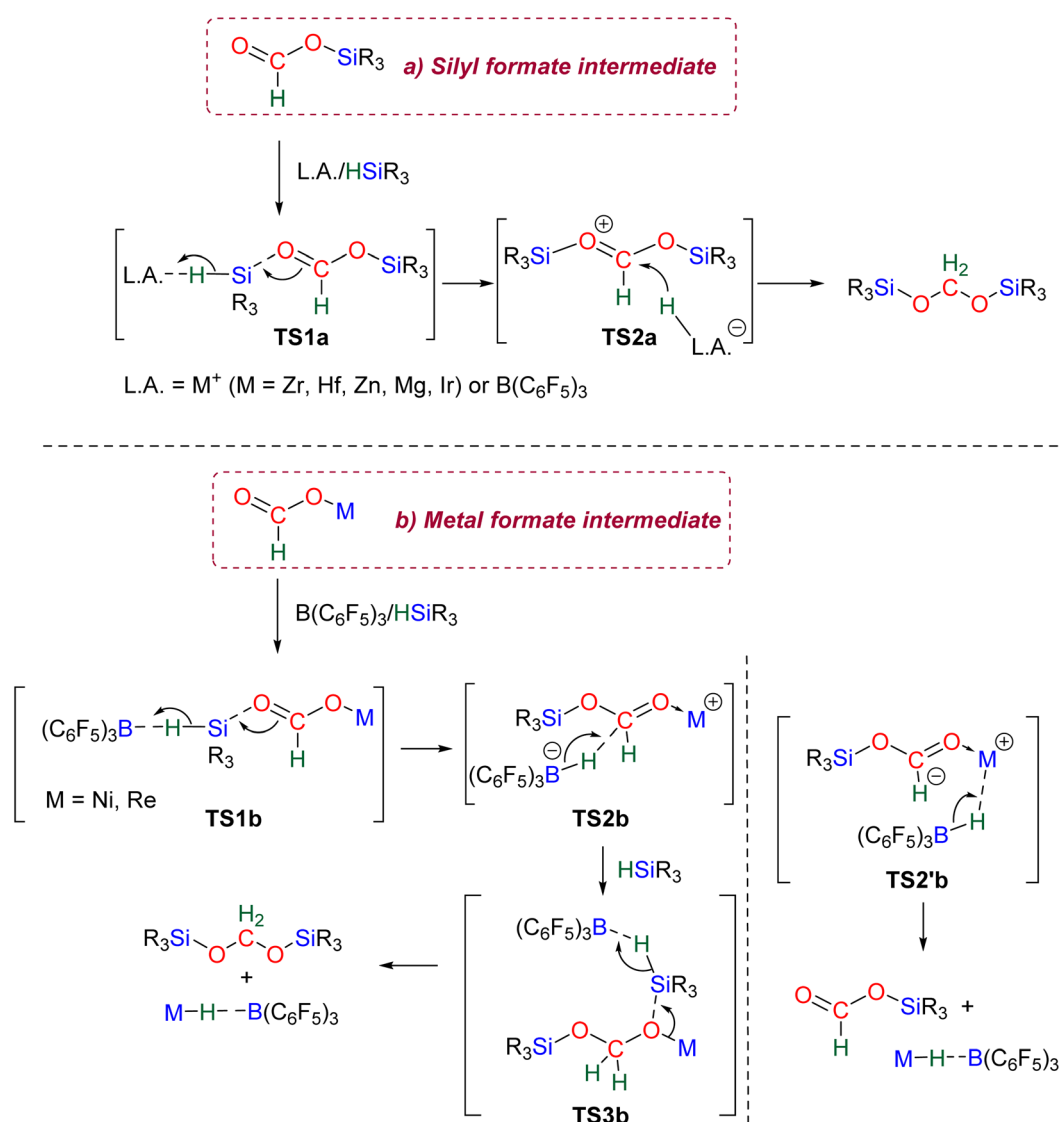


Ir-based complex **C14** and $B(C_6F_5)_3$ are two prototypical compounds known to catalyse the activation of hydrosilanes in various transformations.⁶⁶ In such Lewis acid-catalysed generation of BSA, combined cationic TM-based complexes and $B(C_6F_5)_3$ were proposed to catalyse hydrosilylation either of a silylformate or of a metal formate as illustrated in Scheme 9a and b, respectively.

2.2.2.1. Silyl formate intermediate. Scheme 9a describes the mechanism associated with a Lewis acidic system promoting the silylium “Si⁺” transfer to *silyl formate* species. Such a reaction occurred in an SN₂-type activation going through the transition state **TS1a**. The resulting intermediate is then involved in a second elementary step through the transition state in which the hydride abstracted by the Lewis acid (H-LA) is transferred to the carbon atom of the carbonyl function to form the corresponding BSA derivative while regenerating the Lewis acid. Such a mechanism was computed for **C14**,^{53,67} **C26**,^{58,68} and **C35**.⁶³

In the cases of **C14** and **C26**, **TS1a** was found to be higher in energy than **TS2a**, while the reverse was found with **C35**. The catalysts **C1**, **C11–13**, **C15–17**, **C24–25**, **C28** and **C36** are proposed to follow a similar pathway. The catalysts **C18**, **C33** and **C34** could also follow a similar pathway but the observed induction period points toward a more complex process.

2.2.2.2. Metal formate intermediate. Scheme 9b describes the mechanism associated with the Lewis acidic system promoting the silylium “Si⁺” transfer to metal formate species. In the cases of **C2**, **C3** and **C8**, the second reduction step indeed occurred at a metal formate intermediate. The mechanism involving **C8** has been investigated by DFT (Scheme 9b).⁶⁹ Both **TS1b** and **TS2b** are similar to **TS1a** and **TS2a** respectively (Scheme 9a). The acetal obtained after these two first steps is a metal silyl acetal. After a second activation of the hydrosilane by $B(C_6F_5)_3$, this metal silyl acetal intermediate is converted into the corresponding BSA derivative along with the regeneration of the



Scheme 9 Calculated Lewis acid activation of (a) silylformate or (b) metal formate intermediates. Only TS are shown for the sake of simplicity, and the movement of the electrons is schematically shown with arrows.



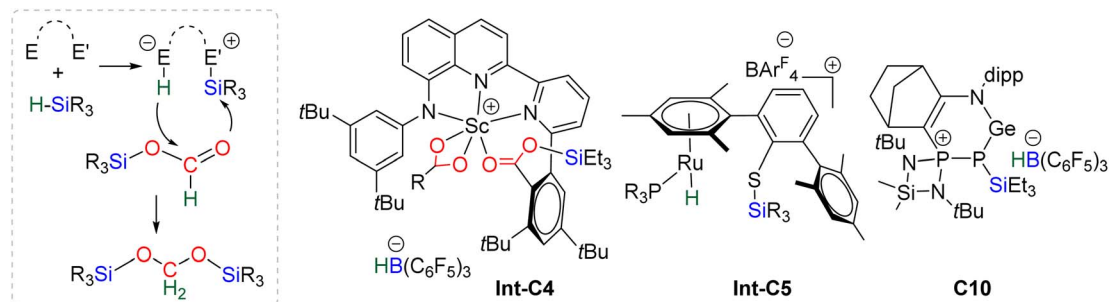


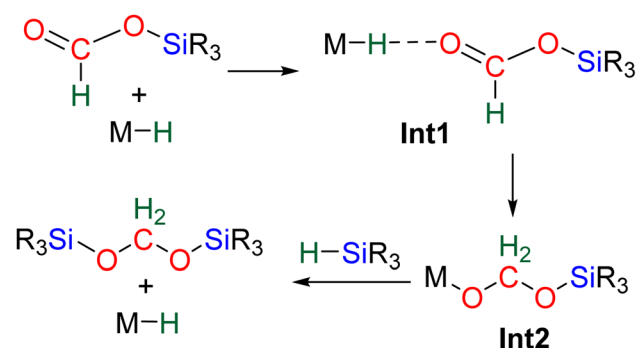
Fig. 3 Complexes resulting from the heterolytic splitting of hydrosilane prior to CO₂ hydrosilylation.

active catalyst. An alternative pathway involving **TS2'** was also calculated to be iso-energetic.⁶⁹

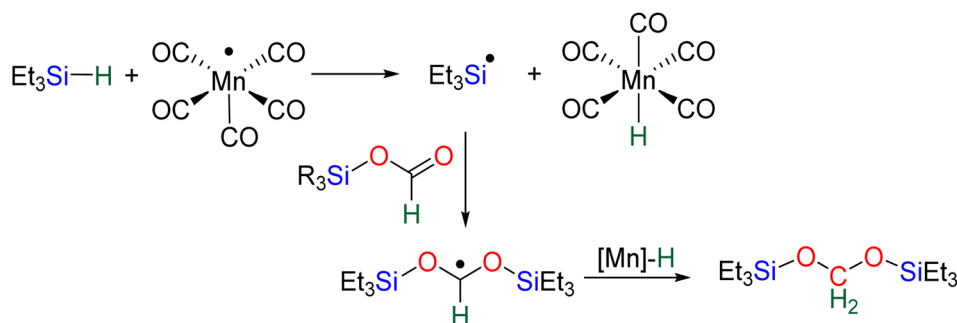
2.2.3. Heterolytic cleavage of the hydrosilane by bifunctional activation. While the catalytic systems **C4–5**^{40,45} and **C9**⁴⁷ are structurally different systems, the proposed mechanism of activation is similar: heterolytic cleavage of the hydrosilane prior to the reduction of the formoxysilane (Fig. 3, left). To support this assumption, catalysts **C4–5** and **C9** were shown to heterolytically cleave hydrosilanes to afford the three species **Int-C4**,⁴⁵ **Int-C5**⁷⁰) and **C10** (Fig. 3).⁴⁷ In addition, **C10** was isolated and used as a catalyst in place of **C9**, showing similar catalytic activity toward CO₂ hydrosilylation to that of **C9**. These compounds are proposed to transfer both silylium and hydride moieties to the formoxysilane intermediate to form the corresponding BSA derivative. Based on previous results concerning the hydrosilylation of other substrates, Oestreich *et al.* proposed the initial transfer of the silylium moiety followed by hydride transfer in a two elementary step mechanism with **Int-C5**.⁴⁰ Such a two-step pathway would be very similar to the calculated pathway for the Lewis acid activation of hydrosilane described above.

2.2.4. Homolytic cleavage of the hydrosilane by a radical initiator. Mn(CO)₅Br complex **C22** was shown to catalyse the hydrosilylation of CO₂ into **BSA 2** with triethylsilane.⁵⁰ **C22** was proposed to generate a radical complex upon loss of a bromine atom which would then activate triethylsilane in a homolytic manner (Scheme 10). Although no mechanism for the second step was proposed, following the logic of the first reduction step suggests that addition of the silyl radical to the silylformate could take place, followed by hydrogen transfer from a Mn hydride species.

2.2.5. Activation of the formoxysilane by a metal-hydride moiety. As shown in Scheme 11, formoxysilane may be activated by metal hydride species by its formal addition into the M–H bond, leading to a metal(silyl)acetal which will then release the corresponding BSA. Catalytic systems **C18**, **C21**, **C27** and **C29** are proposed to follow this pathway. Detailed pathways were calculated with **C29**⁶⁰ and **C21**.⁷¹ The in-depth theoretical investigation on catalyst **C21** points toward the insertion of the formoxysilane into the Co–H bond leading to the formation of a metal silyl acetal intermediate.⁷¹ Following this addition, the metal centre is able to activate the hydrosilane *via* an oxidative addition leading to the transfer of the silyl ligand to produce BSA. Moreover, calculations enabled comparison of the three distinct catalytic cycles leading to the formoxysilane, the BSA and the methoxysilane products. The authors compared the



Scheme 11 Computed pathway for the hydrosilylation of formoxysilane to BSA with M–H catalyst **C29** and **C21**.



Scheme 10 Proposed mechanism for the radical activation of Et₃SiH by **C22** based on experimental results.



energy gap values δE between the most stable intermediate and the highest transition state for each cycle. The smaller value (24.2 kcal mol⁻¹) found for the formation of the formoxysilane compared to the values for the BSA (28.9 kcal mol⁻¹) and the methoxysilane (29.9 kcal mol⁻¹) explain why formoxysilane could be obtained selectively. The small difference between the δE of BSA vs. δE of methoxysilane explains the difficulty in selectively generating BSA in these systems. These calculations reproduced the experimental selectivity obtained under different reaction conditions of temperature and pressure. We hypothesize that the catalytic system **C19** followed this pathway as well, based on the assumption that the combination of the bidentate ligand (*i.e.*, 1,10-phenanthroline) and Zn(OAc)₂ would generate a Zn-H moiety in the presence of a hydrosilane under catalytic conditions.

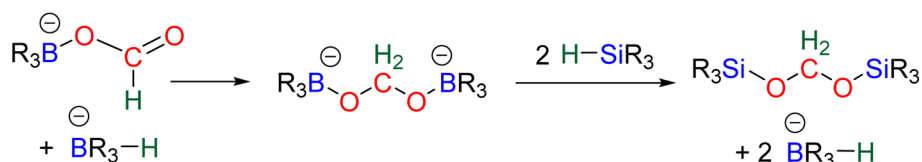
2.2.6. Activation of the formate by a borohydride. Catalyst systems **C6** and **C7** are the only borohydride compounds reported so far to catalyse the hydrosilylation of CO₂ into BSA.⁴⁶ No theoretical investigations were conducted. Based on experimental findings, the proposed mechanism involves the insertion of CO₂ into two B-H bonds of borohydride catalyst leading to a dianionic acetal intermediate (Scheme 12). This assumption is based on the observed reactivity of **C7** with CO₂ and bromobenzoic acid as the CO₂ surrogate. The reactivity of **C7**

toward CO₂ was indeed immediate but led to an insoluble material difficult to analyse. However, the reactivity toward bromobenzoic acid led to the reaction of the two borohydride fragments with two equivalents of the carbonyl part. While no further insights were gathered with theoretical investigations for these specific systems, the ability of borohydride to insert CO₂ was observed previously in various studies.⁷² An alternative BR₃/SiR₃ exchange after each borohydride addition may also be at play and would avoid any charge build-up.

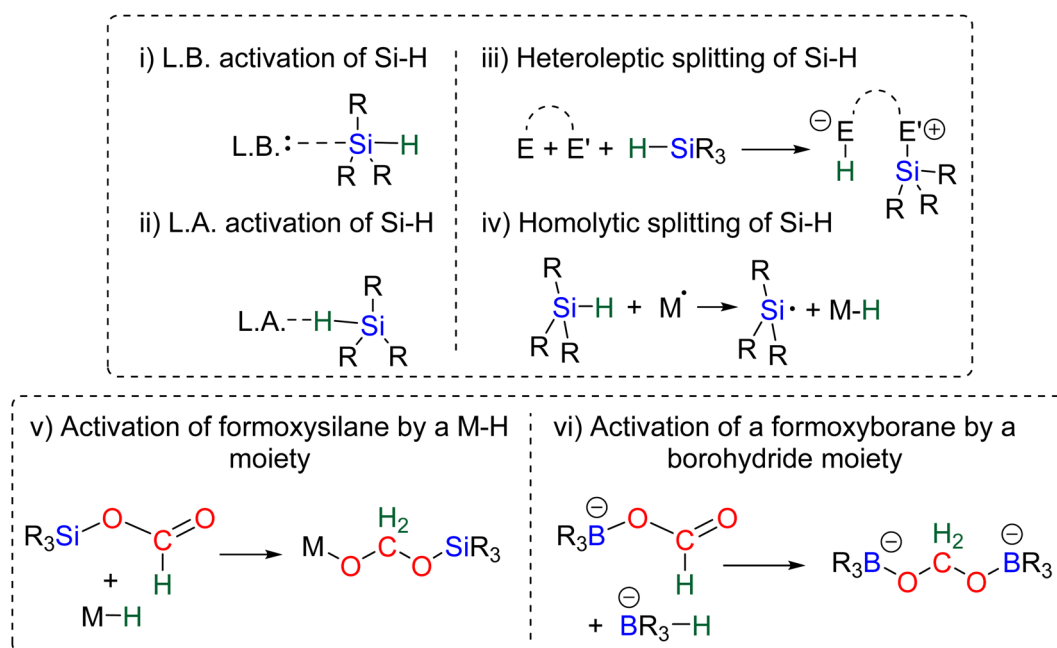
2.2.7. Summary of the activation modes of hydrosilane or formoxysilane. Most of the catalytic systems activate the hydrosilane reductant either *via* (i) Lewis base (LB), (ii) Lewis acid (LA), (iii) heterolytic splitting of the Si-H bond in a bifunctional manner or (iv) homolytic cleavage by a radical initiator. The Lewis acid activation is at play in the majority of the examples. In fewer cases, the silyl- or boryl-formate intermediates are activated by (v) a metal or (vi) a borohydride species. The different activation modes are summarized in Scheme 13.

2.3. Origin of the selectivity for BSA

The control or simply the understanding of the selectivity for bis(silyl)acetal (BSA) is a challenge. In this section we describe some of the main parameters which have been shown to favour



Scheme 12 Proposed mechanism for **C6** and **C7** catalytic systems based on experimental results.



Scheme 13 Activation modes of hydrosilane or formoxysilane leading to (silyl) acetals BSA (LB = Lewis base, LA = Lewis acid).

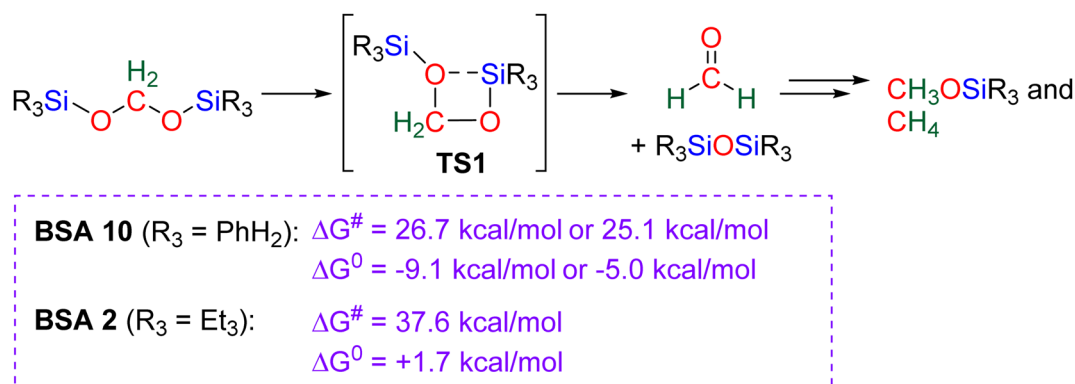


BSA accumulation either upon thermodynamic stabilization or by disfavoring further reduction to methoxysilane or methane.

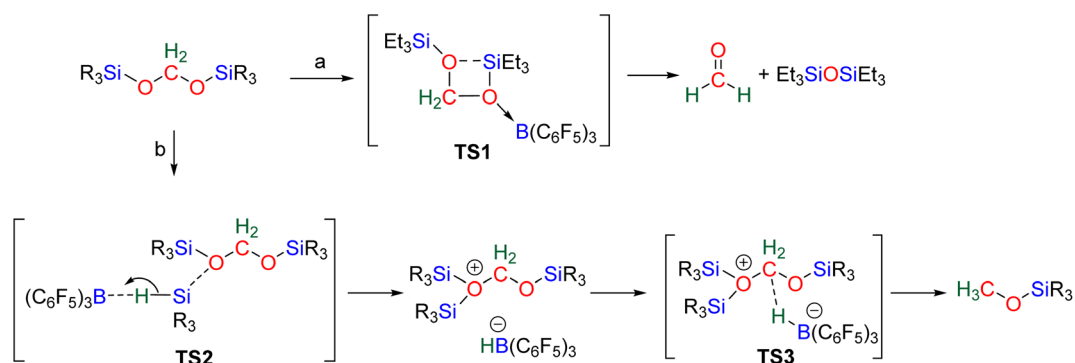
2.3.1. Thermodynamic and kinetic stabilization of BSA by the nature of the silyl groups. Although no specific study was conducted on the role of the silyl group in the stabilization of BSA, two theoretical investigations provided some reactivity trends. These calculations suggested that BSA evolves to formaldehyde *via* **TS1**, and the formaldehyde is then further reduced to methoxysilane and/or methane (Scheme 14). This process was calculated in two independent studies with phenylsilyl groups (SiH_2Ph) to be thermodynamically favoured by -9.1 and -5.0 kcal mol^{-1} , with an activation barrier of 25.1 and 26.7 kcal mol^{-1} .^{65,73} When the same transformation was calculated with triethylsilyl (SiEt_3) groups, the reaction was then thermodynamically disfavoured by $+1.7$ kcal mol^{-1} with a barrier of 37.6 kcal mol^{-1} .⁶³ It thus appears that SiEt_3 groups bring both kinetic (>10 kcal mol^{-1}) and thermodynamic (about 8 kcal mol^{-1}) stability compared to phenylsilyl moieties. Although care must be taken while comparing different theoretical studies, these investigations point toward a higher stability of a BSA featuring tertiary silyl moieties as compared to BSA featuring primary silyl moieties. This corroborates the predominance of tertiary silanes for the selective generation of **BSA 1–6**, and **11**. Moreover, some catalysts were shown to favour BSA when tertiary silanes were employed, but methoxysilane and methane when secondary and primary silanes were

employed. This is the case for example with **C1** and **C15–17**, while most of the other selective catalysts have not been tested with primary or secondary silanes. Finally, every isolated BSA featured trisubstituted silyl groups (**BSA 2, 3** and **11**).

2.3.2. Sequestration of $\text{B}(\text{C}_6\text{F}_5)_3$. The origin of selectivity for BSA of the catalytic systems **C4** and **C8** employing $\text{B}(\text{C}_6\text{F}_5)_3$ is proposed to be the result of the formation of a Lewis pair between $\text{B}(\text{C}_6\text{F}_5)_3$ and an oxygen atom present on the complex. This so-called sequestration of $\text{B}(\text{C}_6\text{F}_5)_3$ during the process is proposed to prevent further reduction. ^{39,45,69} $\text{B}(\text{C}_6\text{F}_5)_3$ has indeed been shown to favour further reduction to methoxysilane or methane. Two modes of action were calculated (Scheme 15, paths a and b). In path a, $\text{B}(\text{C}_6\text{F}_5)_3$ catalyses the transformation of BSA into formaldehyde *via* **TS1**. This result was obtained within the same study presented just above with **BSA 2** featuring triethylsilyl moieties.⁶³ The $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reaction was calculated to be 10 kcal mol^{-1} lower in energy compared to the uncatalyzed transformation. Moreover, the reaction was probed experimentally: while **BSA 2** was stable for a day in solution, it was transformed into formaldehyde within 1 h in the presence of 5% of $\text{B}(\text{C}_6\text{F}_5)_3$. The second mode of activation b occurs *via* an SN_2 -type activation of the hydrosilane by the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ leading to silylium transfer (**TS2**) and finally hydride (**TS3**) transfer to form methoxysilane (Scheme 15, path b). These transformations were calculated in the cases of **C14** (ref. 67) and **C26**.⁶⁸ In accordance with this mechanism proposal, various

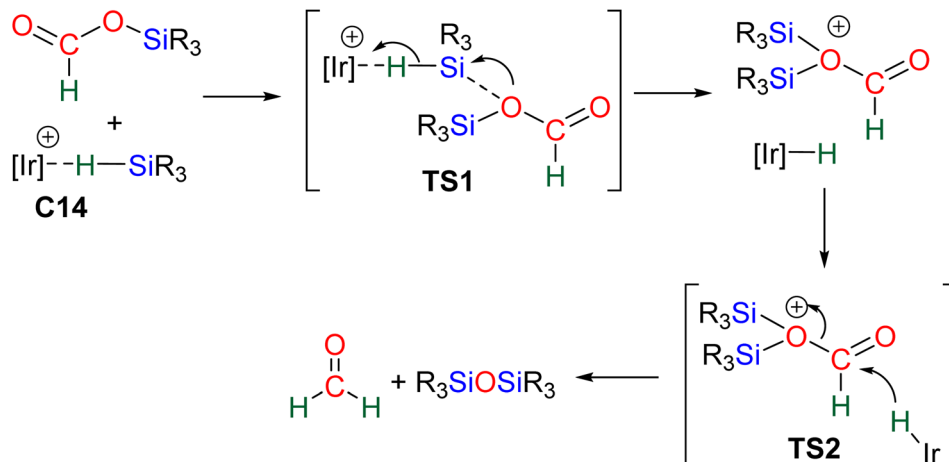


Scheme 14 Computational findings regarding the capability of BSA to liberate HCHO based on the type of silyl moiety.



Scheme 15 Computed $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed conversion of BSA into formaldehyde or methoxysilane.





Scheme 16 Calculated pathway for the generation of formaldehyde from formoxysilane with the Ir-based catalytic system C14.

selective systems reported further reduction when an additional catalytic amount of $B(C_6F_5)_3$ was added to the system. This was notably the case for C4, C8 and C15–17.

2.3.3. Stoichiometry. In most of the CO_2 hydrosilylation reactions reported, an excess of CO_2 gas was employed. In order to influence the level of reduction of the hydrosilylation reaction, 2 and 4 equivalents of CO_2 vs. silane were used with catalytic systems C18 and C19, respectively. Under such stoichiometric or quasi-stoichiometric conditions, it was possible to observe the formation of BSA in 40 and 63% yields for C18 and C19, respectively. The importance of the stoichiometry conditions was proven for C18 since a larger ratio of CO_2 gave rise to formoxysilane whereas a larger amount of silane led to methoxysilane.

2.3.4. Hydrosilylation of CO_2 to formaldehyde without the intermediary of BSA. While formaldehyde was experimentally shown to be obtained from BSA with further insights from calculations, its generation without the intermediary of BSA remains an open question. Besides its experimental observation early on in less than 4%, there is only one theoretical investigation reporting such generation with the Ir-based catalytic system C14.⁶⁷ As depicted in Scheme 16, the cationic [Ir]-hydride complex was calculated to promote silylium transfer to the OSiR₃ moiety of the formoxysilane intermediate in TS1, ultimately leading to formaldehyde via TS2. However, the same calculation showed that the silylium transfer to the oxygen atom of the carbonyl leading to BSA was favoured explaining why formaldehyde was not observed experimentally during the reaction.

2.4. Bis(silyl)acetal as an intermediate in reductive functionalization of CO_2

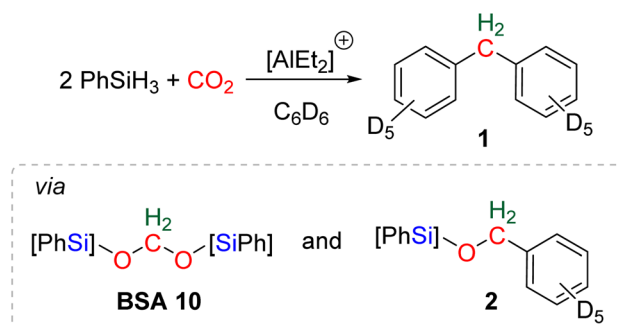
The reductive functionalization of CO_2 refers to the reduction of CO_2 combined with the functionalization of the reduced product with a co-reactant. The term was first employed in the case of the hydrosilylation of CO_2 into formoxysilane, intercepted with amines to afford formamide, formamidine or methylamine derivatives.^{20c,74} An early reaction of this type can

be traced back to a report on the preparation of formamide from CO_2 reduction in the presence of amine in 1988.⁷⁵ In this case, the reductant was not hydrosilane but dihydrogen. Although unexpected, the first reductive functionalization of CO_2 via the generation of a bis(silyl)acetal (BSA) intermediate was reported in a study devoted to the use of cationic Al-based species for catalysing the hydrosilylation of CO_2 to methane.⁷⁶ In the course of the reaction, the formation of deuterated diphenylmethane **1** featuring a bridged-methylene moiety was observed (Scheme 17). Experimental proofs showed that transiently generated BSA reacted with the deuterated solvent via electrophilic catalysis by the cationic Al-based compound to afford compound **1** via compound **2**.

Following this preliminary report, subsequent studies reported the use of BSA as a key intermediate for the generation of more complex products in the presence of various co-reactants. Such strategies considerably enlarged the scope of compounds obtained from CO_2 in using BSA as a source of methylene for the formation of C–N, C–C, C–S and C–O bonds.

2.4.1. Reductive functionalization of CO_2 via a transient BSA intermediate

2.4.1.1. TBD/PhSiH₃: a pioneering reduction system in reductive functionalization. Formation of C–N and C–C bonds. The first system describing a reductive functionalization of CO_2 with



Scheme 17 First example of reductive functionalization of CO_2 into product **1**, involving a BSA intermediate and compound **2**.

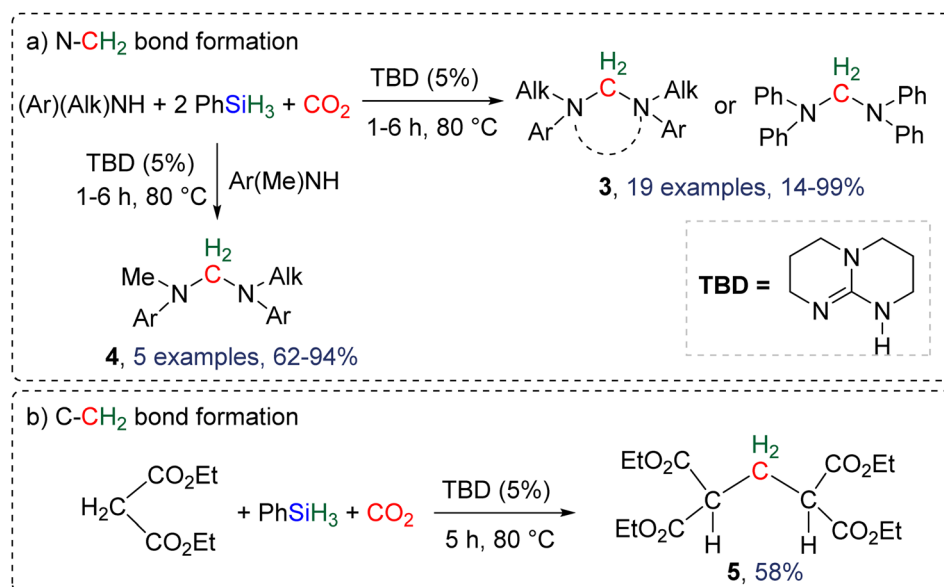


hydrosilane with the intermediary of BSA was reported in 2015 (Scheme 18).⁷⁷ It included the use of TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) which catalysed the hydrosilylation of CO₂ with phenylsilane into the corresponding BSA, although it was never directly observed or characterized. Besides TBD, other Lewis basic catalysts including 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), Verkade's base and NHC (IPr and ItBu) were tested to catalyse the reduction step. Slightly lower yields of the final products were obtained. Various co-substrates featuring N-H (Scheme 18a) or C-H functionalities (Scheme 18b) acted as functionalizing agents in intercepting the transiently formed BSA leading to the formation of methylene-bridged "N-CH₂-N" and "C-CH₂-C" moieties. In total, 19 cyclic or acyclic symmetrical aminal products **3** were generated selectively with yields ranging from 14 to 99% (larger than 70% in most cases, Scheme 18a). In addition, 5 dissymmetric aminal products **4** were also generated using two different amines with yields ranging from 62 to 94% (Scheme 18a). For the synthesis of these dissymmetric aminal compounds, a key factor was to employ two amines featuring different nucleophilicities, enabling the most nucleophilic amine to first react with BSA, which affords an intermediate aminosilylacetal. Subsequently, the second (less nucleophilic) amine reacts with the aminosilylacetal intermediate yielding the corresponding aminal compound. Replacing the amine co-reactant with 2 equivalents of the nucleophilic malonate compound led to the unique formation of two C-C bonds in 58% yield (compound **5**, Scheme 18b).

2.4.1.2. Extension of the scope with the TBD/PhSiH₃ reduction system. The TBD/PhSiH₃ system was proven to be reliable and versatile to insert one or two methylene units in complex structures. To do so, 10–20 mol% of TBD was used at temperatures ranging from 100 to 120 °C and reaction times from 6 to 30 h (Scheme 19). Indolepyrrolidine derivatives were engaged as co-reactants leading to cyclisation reactions with the formation

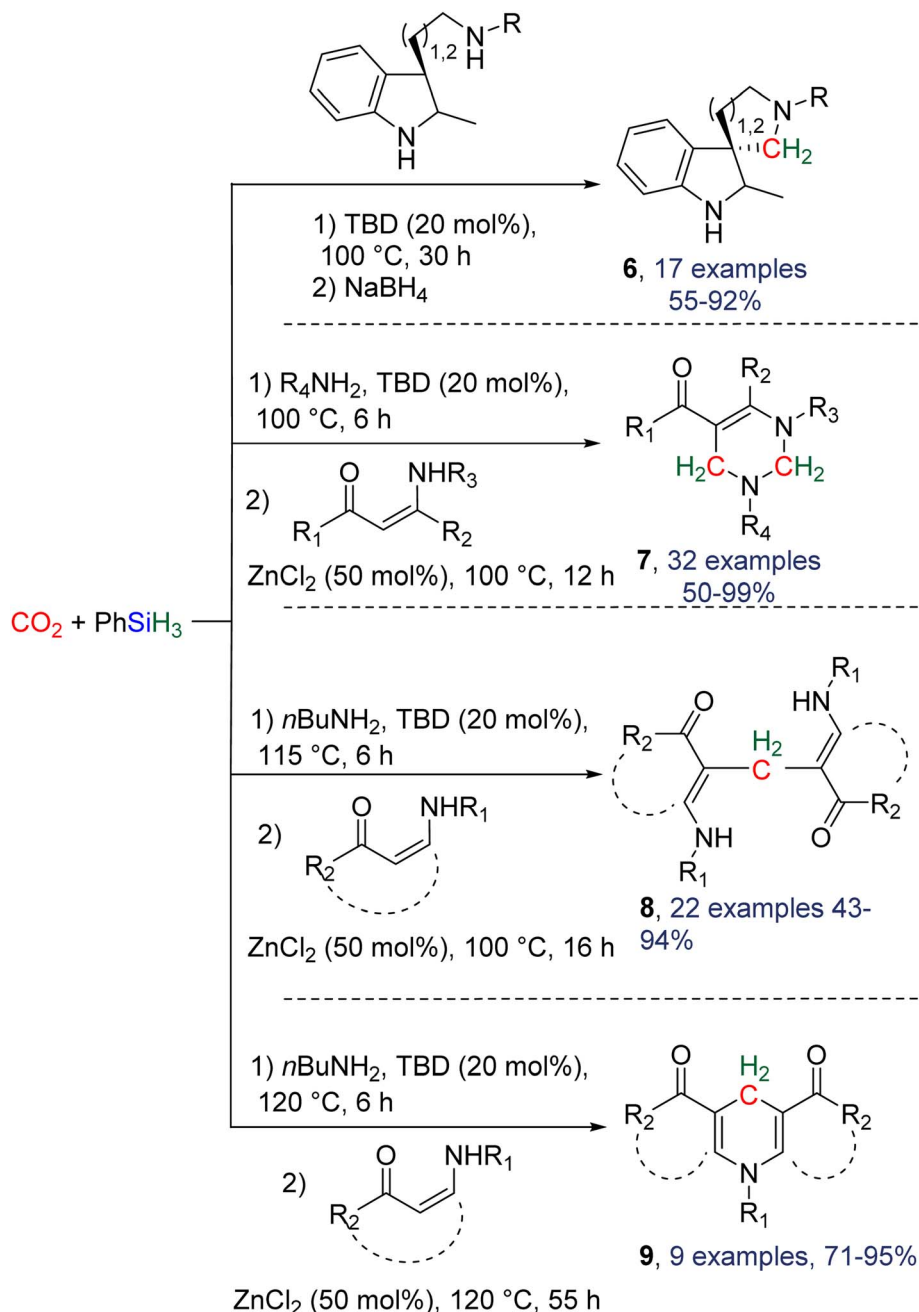
of C-CH₂ and N-CH₂ bonds. A second enantioselective reduction step of the pyrrolidine ring afforded spiro-indolepyrrolidine products **6** (Scheme 19), and 17 different compounds have been obtained in good to very good yields (55–92%).⁷⁸ Reductive functionalization with amine was then used to incorporate two methylene units from the hydrosilylation of CO₂ (Scheme 19, compounds **7**).⁷³ Key features of these transformations include the use of (i) a primary amine leading to the generation of an imine intermediate and (ii) a Lewis acid-catalysed cyclization reaction with various enaminones. The scope of the reaction was evaluated with 32 identified examples of tetrahydropyrimidine compounds with isolated yields (based on the enaminone) ranging from 50 to 99% (in most cases larger than 80%). The mechanism for the formation of compounds **7** was also investigated by DFT (Scheme 20). TBD was calculated to catalyse the hydrosilylation of CO₂ into **BSA 10** followed by the liberation of formaldehyde. The imine is then generated from the condensation of the primary amine with formaldehyde (step i). Controlled experiment proved that a stable imine can be formed when a bulky bis(diisopropyl)aniline is used. The enaminone nucleophilically adds to the intermediate imine *via* a Lewis acid/TBD-catalysed reaction (step ii) leading to an aza-diene compound after phenylamine elimination (step iii). The Diels–Alder reaction between the aza-diene intermediate and a second equivalent of *in situ* generated imine finally furnishes the tetrahydropyrimidine **7** (step iv). This elegant strategy employing a primary amine as a first functionalization step transformation was further used to generate enaminones (Scheme 19, compounds **8**, 22 examples, 43–94%) and 1,4-dihydropyridines (Scheme 19, compounds **9**, 9 examples, 71–95%).⁷⁹

2.4.1.3. Development of new catalysts. Besides the utilization of TBD as a catalyst, two other catalytic systems were employed for reductive functionalization with hydrosilanes. The



Scheme 18 First selective reductive functionalization of CO₂ *via* the generation of a BSA intermediate leading to the formation of (a) C–N and (b) C–C bonds.





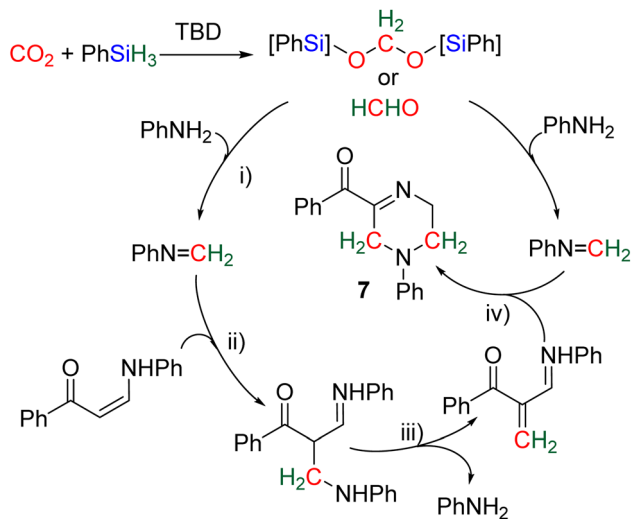
Scheme 19 Extension of the product scope upon reductive functionalization of CO₂ with hydrosilanes.

combination of [CpFe(CO)₂]₂ and P(*n*Bu)₃ was shown to catalyse the hydrosilylation of CO₂ with phenylsilane in the presence of tryptamine derivatives to afford a variety of tetrahydro-β-carbolines and other nitrogen-containing heterocycles **10** after 36 h at 60 °C (Scheme 21).⁸⁰ In total, 19 heterocycles were obtained in yields ranging from 50 to 94%. The [CpFe(CO)₂]₂/P(*n*Bu)₃ system is proposed to catalyse the hydrosilylation of CO₂ into BSA which is then involved in a Pictet–Spengler-type cyclization. Other Fe-based precursors did not afford any conversion, while diphenylsilane or other tertiary phosphine afforded the expected compounds although in lower yields. Another report described the use of a phosphorus ylide to intercept the

reduction intermediate *via* a Wittig reaction (Scheme 21, compounds **11**).⁸¹

If the first tests were conducted with the TBD/PhSiH₃ system in acetonitrile, optimization conditions revealed the beneficial role of an inorganic base and notably of sodium *tert*-butoxide (NaOtBu) in DMF in catalysing the hydrosilylation of CO₂ with PMHS (polymethylhydrosiloxane) – a waste of the silicone industry. This process led to the synthesis of 20 olefins in yields ranging from 30 to 85%. Ionic liquids²²⁴ and covalent organic frameworks⁸³ were also employed as catalysts in a similar synthesis of amina by CO₂ reductive functionalization.





Scheme 20 Proposed mechanism for the synthesis of tetrahydropyrimidine 7.

2.4.2. Reductive functionalization of CO₂ via an isolated BSA intermediate (BSA 3). In contrast to the previous examples in which BSA was not isolated or observed, BSA 3 could be isolated before being involved in subsequent transformations.^{29a} Such a process avoids compatibility issues between the reduction and the functionalization steps since they are performed independently. Using the Mg-based catalytic system C17, BSA 3, featuring triphenylsilyl groups, was isolated in high yield on a 3 g scale (95% yield, Table 2). As presented in Section 2.1.3, BSA 3 was found to quantitatively release formaldehyde either in DMSO at 100 °C, in the presence of CsF at room temperature or under acidic conditions (H₂SO₄) at room

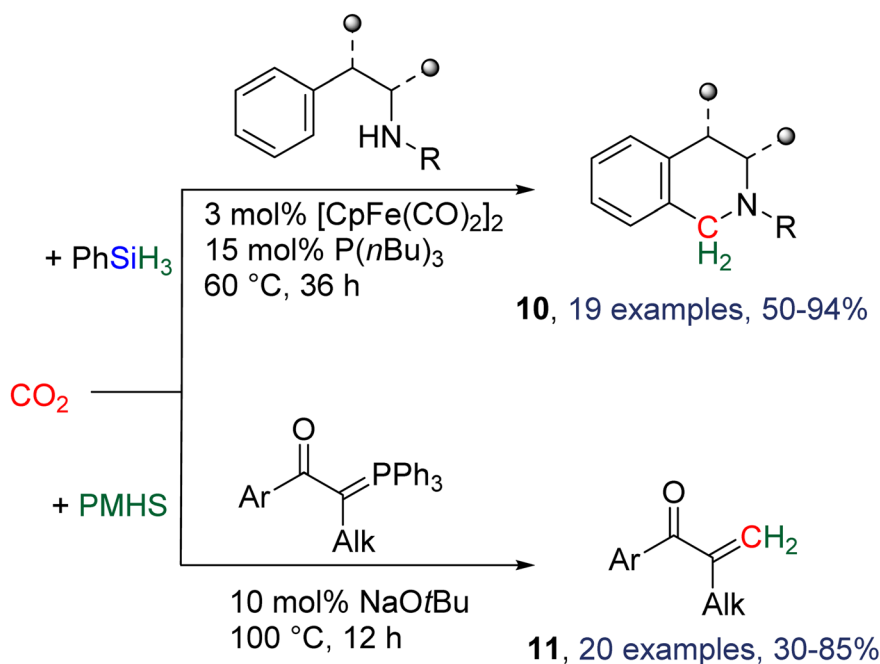
temperature (Scheme 6). Under these conditions, BSA 3 was then engaged in further transformations (Scheme 22).

In the presence of diol or di-thiol substrates under acidic conditions, the cyclic compounds 12 were generated in good yields forming CH₂-O (69% yield) and CH₂-S bonds (51% yield), respectively. The reaction with hydrazine proved to be efficient to generate a CH₂=N bond (compound 13, 62% yield), while reactions with molecules comprising primary amine and thiol or secondary amine function led to benzimidazole and benzothiazole compounds 14 (95 and 57% yields), respectively. Finally, the reaction with ammonia afforded hexamethylene tetra-amine 15 in 77% yield. In addition, C-C bonds were also generated (i) with malonate leading to 5,5-dimethylcyclohexane-1,3-dione compound 16 (89% yield), (ii) through a Wittig reaction leading to the acrylate compounds 17 (80 and 87% yields) and finally (iii) through a Pictet-Spengler-type cyclization reaction leading to compound 18 (82% yield). It must be noted that ¹³C-labelled BSA 3 could also be efficiently generated and isolated from the catalytic hydrosilylation of ¹³CO₂ and was used as a dry source of ¹³C-labelled HCHO.

2.4.3. Conclusion on the reductive functionalization of CO₂. Reductive functionalization of CO₂ with hydrosilanes led to the synthesis of a very broad range of various products in which the intermediate BSA was used as a methylene source to form C-N, C-O, C-S and even C-C bonds. In these reactions, BSA is generated either transiently when PhSiH₃ is the reductant – although not observed – or isolated when Ph₃SiH is the reductant.

2.5. Conclusion and perspectives

In conclusion, the four-electron reduction of CO₂ with hydrosilane is noteworthy for several reasons. Firstly, it distinguishes itself with a considerable number and variety of selective



Scheme 21 New catalysts for reductive functionalization with hydrosilanes.



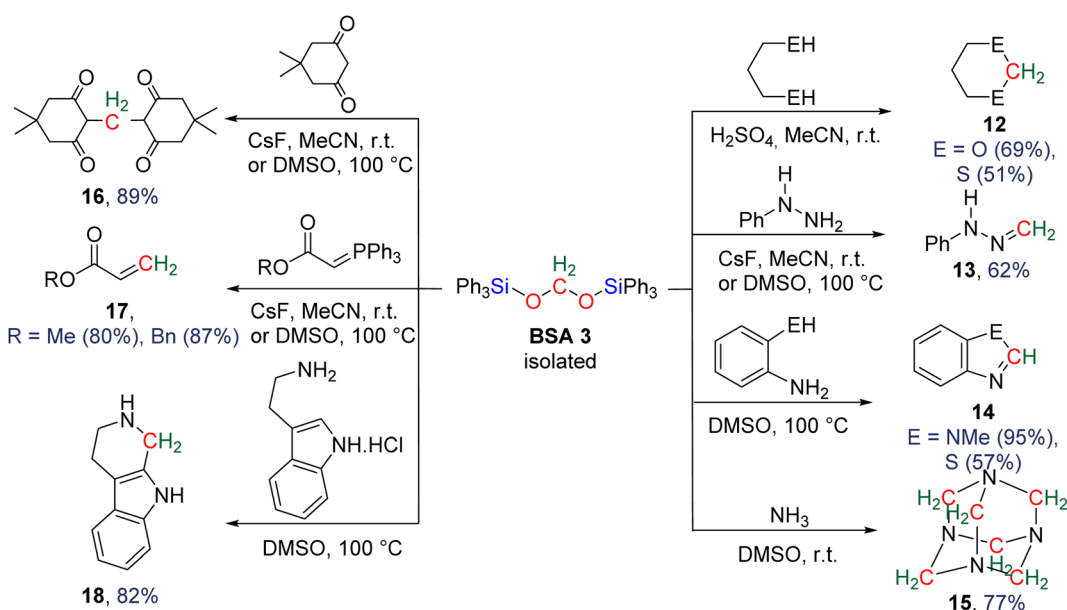
catalytic systems (C1–24), primarily based on the combination of transition metal-based complexes and $B(C_6F_5)_3$. Comprehensive experimental and theoretical studies have revealed five distinct activation modes, elucidating the 2 to 4 electron reduction stage. Despite the highest reported TON of 3400 and TOF of 10.4 h^{-1} , there is room for further enhancements. Secondly, it stands out due to the diverse array of characterized and isolated bis(silyl)acetal (BSA) compounds, with a current total of 11 reported. These isolated BSAs were predominantly obtained from tertiary silanes, demonstrating high selectivity (79 to 99% yields) under mild conditions. Finally, the process is notable for numerous transformations involving BSA in reductive functionalization, ranging from simple condensation to multi-step reactions with co-reactants. Interestingly, when primary silanes were employed, BSA formation was never observed, likely due to its high reactivity. In contrast, tertiary silanes led to the isolation of BSA before engaging in subsequent functionalization through formaldehyde release.

Perspectives in the field of $4e^-$ CO_2 hydrosilylation could involve rationalizing the stability of the generated bis(silyl) acetal (BSA) based on the choice of hydrosilane. Generating BSAs with intermediate stability holds particular interest, offering potential for expanding the reactivity scope of BSA compounds. A significant breakthrough would be utilizing BSAs as a C_n source for producing high-value added products, an area yet to be explored compared to their borylated counterparts discussed in the next section. However, the primary challenge remains the treatment of the siloxane by-product produced during CO_2 hydrosilylation, currently considered as waste. Exploring potential uses for these siloxane moieties or designing a regeneration system for the sustainable recycling of hydrosilane presents a promising avenue for further research.

3. Hydroboration

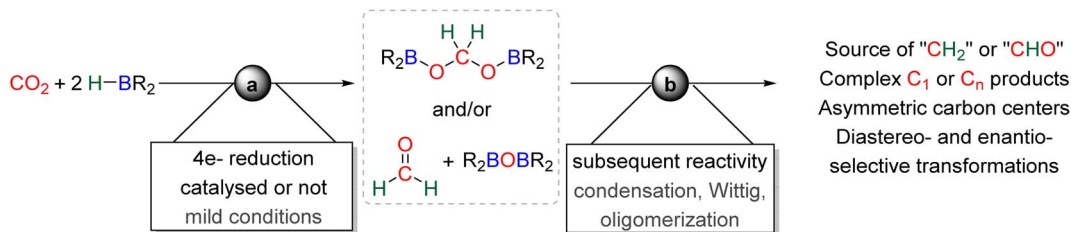
In the realm of hydroelementation reactions, hydroboration holds an important and specific place. Since the discovery of hydroboration of olefins,⁸⁴ this reaction has been largely developed for the reduction of unsaturated bonds.^{8b,85} Beyond reduction, the formal addition of B–H bonds is used as a privileged access to organoboron compounds which are then used as reagents in coupling reactions.⁸⁶ Hydroboration of CO_2 involves the addition of a B–H bond to the C=O bond, transferring the hydride to the carbon atom and forming a B–O bond. It is favoured both kinetically and thermodynamically by the polarity of the B–H bond (E. N. of H = 2.2, B = 2.0) and the strength of the formed B–O bond (BDE(B–O) >500 kJ mol^{-1}),⁸⁷ respectively. As a consequence, CO_2 hydroboration reactions, like CO_2 hydrosilylation ones, operate under much milder conditions – usually room temperature and 1 atm of CO_2 – than CO_2 hydrogenation.^{8a} However, it is noticeable that the catalytic systems used for the hydroboration or the hydrosilylation of CO_2 are different in most cases.

The first catalytic hydroboration of CO_2 was reported in 2010 with a Ni-based catalytic system and was shown to afford the $6e^-$ reduction product, methoxyborane, readily hydrolysed to methanol.⁸⁸ While the $2e^-$ reduction product – formoxyborane – was observed, no $4e^-$ reduction product was detected, although formaldehyde was proposed as an elusive intermediate.^{88,89} The Ni-based pincer system used as the catalyst remains one of the most efficient catalyst of CO_2 hydroboration into methoxyborane with TOF and TON of 495 and 495 h^{-1} , respectively. It is worth noticing that an earlier report described the use of borane in the reduction of CO_2 . However, it was not a hydroboration reaction, but the reduction of CO_2 into CO by B_2pin_2 and a (NHC)Cu-based catalyst.^{19b} It was only in 2012 and 2014 that



Scheme 22 Products obtained from the functionalization of HCHO released from BSA 3.



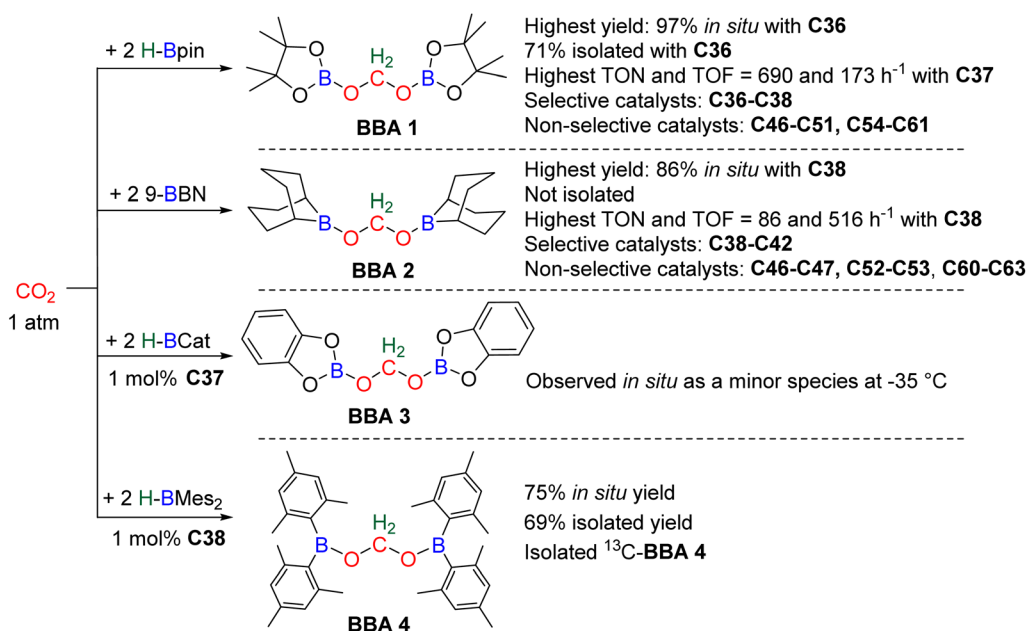
Scheme 23 General scheme for Section 3: CO₂ hydroboration.

bis(boryl)acetal (BBA)⁹⁰ and formaldehyde⁹¹ were respectively characterized from the hydroboration of CO₂, although not in a selective manner. Later on, the efficient and selective generation of BBA derivatives was reported using different hydroboranes as reductants. These transformations (Scheme 23, step a) will be presented in the first part 3.1 and the mechanism will be discussed in part 3.2. Finally, the use of these 4e⁻ reduced products as reactants in further transformations (Scheme 23, step b) will be described in part 3.3 and a general conclusion will be drawn in part 3.4.

3.1. Hydroboration of CO₂ into bis(boryl)acetals (BBAs) and formaldehyde

In total, 7 BBA derivatives have been synthesized by the hydroboration of CO₂.⁹² **BBA 1–4** were obtained from the hydroboration of CO₂ (Scheme 24) catalysed by compounds **C36–C45** (selective catalysts, Fig. 4) and **C46–C63** (unselective catalysts, Fig. 4). **BBA 5–7** were obtained in the absence of a catalytic system (Scheme 25). **BBA 2** and **4** were shown to be key intermediates leading to formaldehyde in high yields. These transformations are described hereafter.

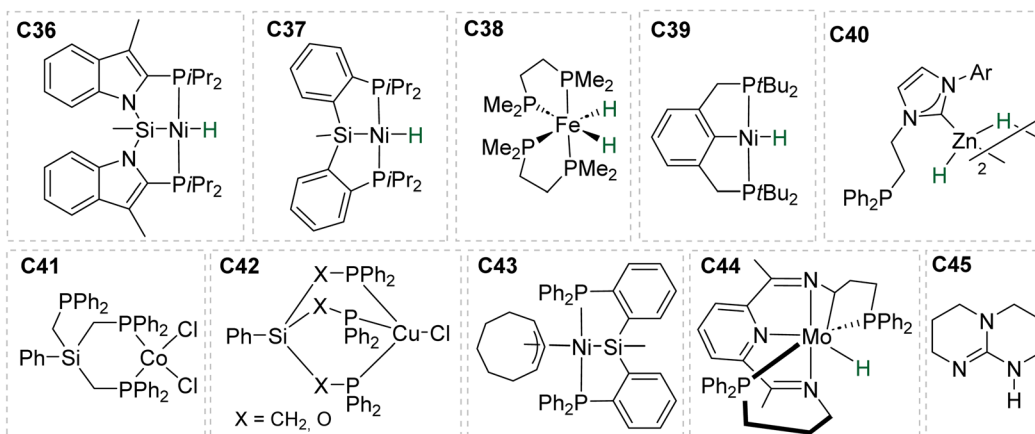
3.1.1. Catalytic hydroboration of CO₂ into BBA 1–4 catalysed by C36–C63. **BBA 1**, featuring pinacolboryl moieties (Scheme 24), was the first BBA reported in the literature in 2012. It was characterized *in situ* as a minor product with Ru-based catalysts **C46–C47** bearing a tricyclohexylphosphine (PCy₃) ligand.⁹⁰ Its selective generation was reported with **C38** albeit with a low yield of 30%.⁹³ It was only in 2017 that the use of 0.2% of the Ni hydride catalyst **C36** led to its selective generation at room temperature, with high *in situ* yields of 84% and 97% after reaction times of 1 h and 4 h, respectively.⁹⁴ Such high selectivity enabled the isolation of **BBA 1** by precipitation in 71% yield. This currently remains the only example in which **BBA 1** was isolated. Under optimized reaction conditions, benzene was the solvent of choice. While cyclohexane gave a similar result, the use of THF induced a net decrease (30% yield). **C43**⁹⁵ (15 min at room temperature with 2% of the Ni-based precatalyst) and **C44**⁹⁶ (2 h at 90 °C with 1% of the Mo-based catalyst) were shown to afford **BBA 1** as the major product. It must be noted that **BBA 1** was observed as a minor product in hydroboration reactions catalysed by compounds **C46–C47**,⁹⁰ **C48–C50**,^{94,97} **C51**,⁹⁸ and **C54–C61**.^{99,100}



Scheme 24 Catalytic generation of BBA 1–4 with C36–C63 catalysts.



a) Selective catalysts (BBA as major product)



b) Other catalysts (BBA as minor product)

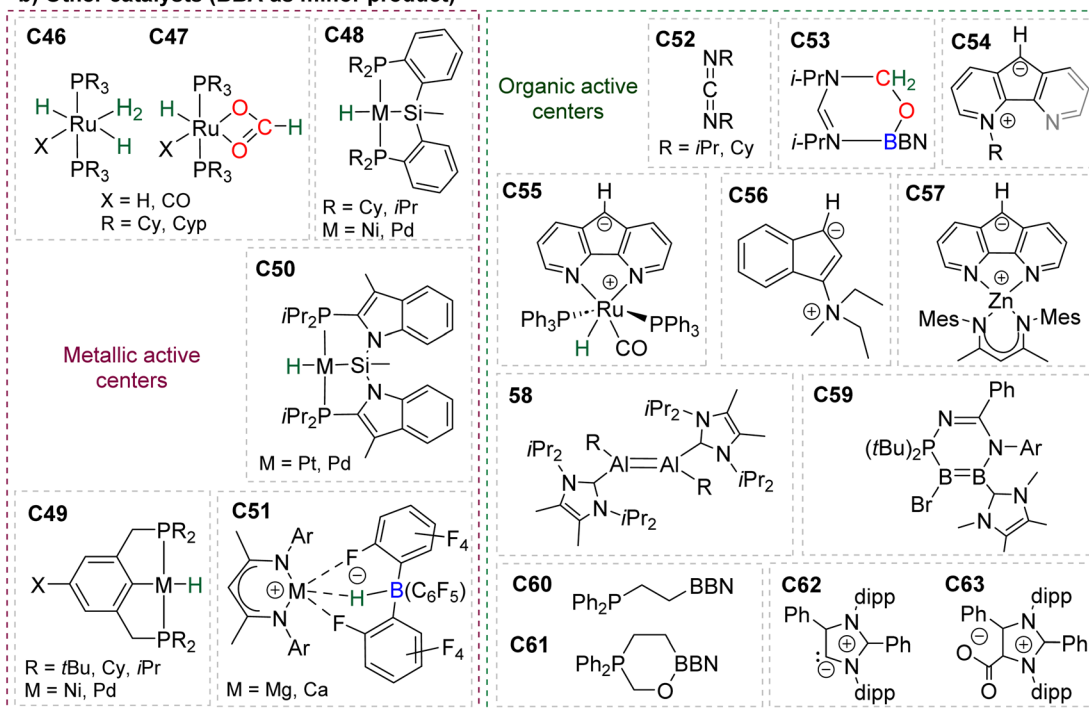
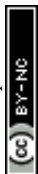


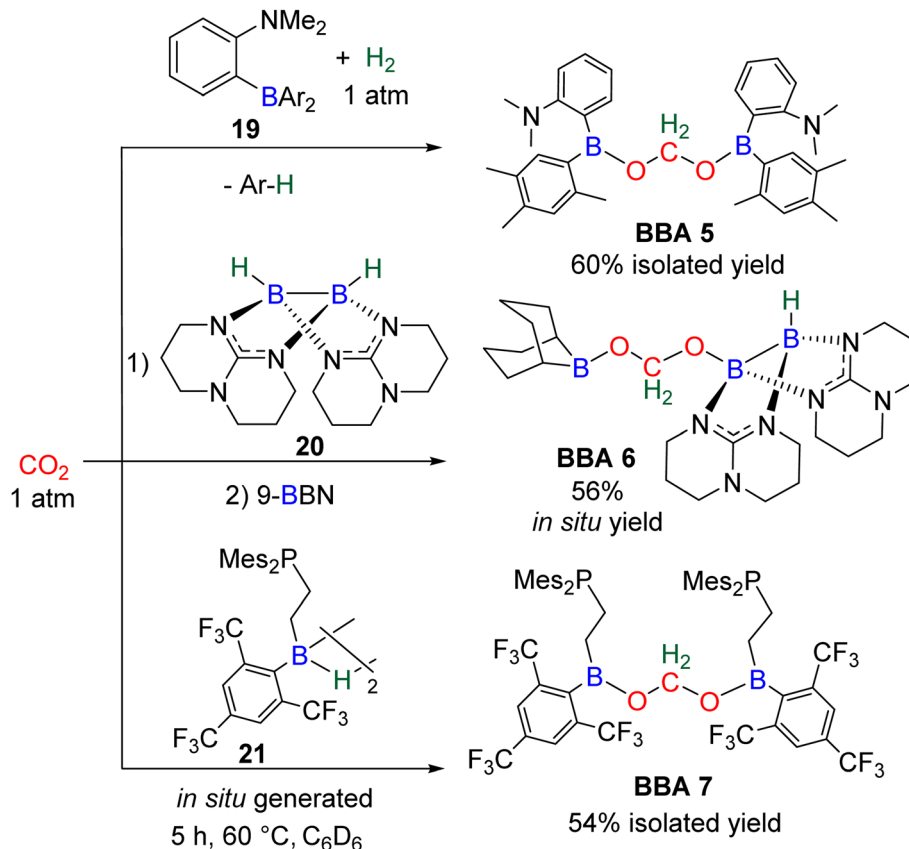
Fig. 4 Catalysts C36–C63 for the generation of BBA 1–7 and formaldehyde: (a) selective catalysts C36–C45 and (b) unselective catalysts C46–C63.

BBA 2 was reported for the first time in 2014 in CO₂ hydroboration catalysed by the nitrogen-based Lewis base TBD (C45).¹⁰¹ This study focused on the reduction of CO₂ to the methoxyborane compound with various metal-free catalysts and hydroboranes. Using 9-BBN and 2.5 mol% of catalyst C45, **BBA 2** was detected as the major intermediate after 1 h (85% ratio) before decaying, leading to the final methoxyborane compound. The selective generation of **BBA 2** and yield quantification (instead of ratio) were then described with C37–C39.

In 2015, the well-defined iron dihydride bis-diphosphine catalyst C38 was used at room temperature and under 1 atm of CO₂ to afford **BBA 2** in 85% yield (TOF = 109 h⁻¹) with a catalyst loading of 1 mol%.⁹³ The importance of the THF

solvent was identified since such selectivity was not observed with benzene or toluene. Moreover, a high TOF of 516 h⁻¹ was measured upon increasing the temperature to 60 °C with the generation of **BBA 2** in 86% yield in only 10 min. In 2016, the well-defined [Co]- and [Cu]-precatalysts C41 and C42 were shown to generate **BBA 2** as the major product after 24 h at room temperature and 60 °C, respectively.¹⁰² Beyond these selective systems, catalysts C46–C47,⁹⁰ C52–C53,¹⁰³ C60–C61¹⁰⁴ and C62–C63¹⁰⁵ were also reported to catalyze the generation of **BBA 2** as a minor product under mild conditions. **BBA 3** has only been partially characterized once as a minor compound, despite numerous studies using HBCat for CO₂ hydroboration. This is in marked contrast with the selective generation of **BBA 1** and





Scheme 25 Catalyst free generation of BBA 5–7.

BBA 2, and might be explained by the ability of HBCat to readily reduce CO₂ to the methoxyborane stage (*vide infra* in mechanistic consideration).

In this context, **BBA 3** was characterized *in situ* as a minor intermediate, during methoxyborane preparation with catalyst C37.⁹⁷ Following the reaction, a minor signal was observed by ¹H NMR in the characteristic area of acetals. Its broadness suggested the reversible formation of **BBA 3**. This assumption was confirmed by its sharpening at –35 °C leading to the first characterization of the acetal moiety of **BBA 3**. When ¹³CO₂ was used, this acetal signal appeared as a doublet, which finally disappeared upon further reduction to the methoxyborane product. **BBA 4** was obtained from the CO₂ hydroboration with HBMe₂ catalysed by the iron hydride catalyst C38 with an *in situ* yield of 75%.³⁰ This BBA exhibits higher stability as compared to **BBA 1–3**, as shown by an isolated yield of 69% and its characterization by X-ray diffraction analysis.³⁰ Moreover, **BBA 4** featuring a ¹³C-labelled methylene fragment was also isolated in similar yield from ¹³CO₂ hydroboration. The stability of **BBA 4** was used to perform enzymatic transformations (*vide infra*). It is noteworthy that catalyst C38 is able to catalyse the selective generation of three BBA derivatives, namely, **BBA 1, 2** and **4**.

The performances of catalysts C36–C42 for the selective generation of **BBA 1–2** and **BBA 4** are reported in Table 3. The performances of catalysts C43–C45 are not indicated because

only the ratio between the detected products were measured and not the quantitative yields. The performances of catalysts C46–C63 are not given since **BBA 1–3** were only observed as minor compounds. Among the seven selective catalytic systems (C36–C42), one can notice that all of them are transition metal (TM)-based catalysts and five based on 3d-TM (C36–C39, C41). The active centre is a metal hydride fragment either present in the initial catalyst or presumably generated *in situ* during the reaction with the hydroborane. The best performances in terms of TON and TOF were obtained with C37 (487 and 122 h^{–1}) and C38 (85, 109 h^{–1} at room temperature and 86, 516 h^{–1} at 60 °C) for the generation of **BBA 1** and **BBA 2**, respectively. The best yields were obtained with catalysts C36 (97% yield) and C38 (86% yield) for the generation of **BBA 1** and **2**, respectively. The selectivity is an important factor to be considered when the generated BBA is further engaged in additional reactions (see Section 3.3). If a catalytic system exhibits high TON and TOF but poor selectivity, the presence of other products or of the remaining hydroborane may be detrimental for the subsequent reactions.

3.1.2. Catalyst-free generation of BBA 5–8. Currently, three BBA derivatives, **BBA 5–7**, have been obtained without any catalyst (Scheme 25). **BBA 5** features two different aryl substituents on each boryl moiety, 2,4,5-Me₃C₆H₂ and *o*-NMe₂-C₆H₄ groups (Scheme 25). It resulted from the reaction of the ambiphilic ortho amino-borane compound **19** with H₂ and CO₂ (72 h,



Table 3 Catalytic performances of the selective formation of BBA 1, 2 and 4 with catalysts C36–C42

| BBA | Catalyst | TON | TOF (h ⁻¹) | Yield ^a (%) | P _{CO₂} (atm) | T (°C) | Time ^b | Cat loading (%) | Ref. |
|-----|----------|-----|------------------------|------------------------|-----------------------------------|--------|-------------------|-----------------|------|
| 1 | C36 | 487 | 122 | 97 71 ^c | 1 | rt | 4 | 0.2 | 94 |
| | C37 | 690 | 173 | 69 | 1 | rt | 4 | 0.1 | 97 |
| | C38 | 6 | 1.2 | 30 | 1 | 25 | 5 | 5 | 93 |
| 2 | C38 | 85 | 109 | 85 | 1 | rt | 47 min | 1 | 93 |
| | | 86 | 516 | 86 | 1 | 60 | 10 min | 1 | |
| | C39 | 32 | 2 | 64 | 1 | rt | 16 | 1 | 97 |
| | C40 | 15 | 3.8 | 75 | 1 | rt | 4 | 5 | 106 |
| | C41 | 25 | 1 | 38 | 1 | 60 | 24 | 1.5 | 102 |
| | C42 | 53 | 2 | 79 | 1 | rt | 24 | 1.5 | |
| 4 | C38 | 75 | 75 | 75 69 ^c | 1 | 25 | 1 | 1 | 30 |

^a *In situ* yield unless otherwise stated. ^b Hour unless otherwise stated. ^c Isolated yield.

room temperature). **BBA 5** was isolated in 60% yield as a monocrystal suitable for the first X-ray diffraction analysis of a BBA. DFT investigations suggested that H₂ led to the protoborylation of compound **19** giving rise to a monohydroborane compound (not observed) which would formally doubly add to CO₂ and generate **BBA 5**. **BBA 6** is a dissymmetric BBA featuring one diboryl and one BBN moieties (Scheme 25).¹⁰⁷ It is the only dissymmetric BBA reported to date and was obtained in two consecutive steps. Compound **20**, so-called diborane (**4**), was proposed to be nucleophilic enough to readily transfer a hydride to CO₂ affording a formoxyborane intermediate, which was characterized *in situ* in a mixture of compounds in 70% yield. In a second step, 9-BBN reduced the formoxy fragment to afford **BBA 6** within 5 h with an *in situ* NMR yield of 80% (56% overall yield). **BBA 7** features boryl units bearing two different substituents at the boron atom, a perfluoroaryl group (1,3,5-tris(trifluoromethyl)phenyl) and an alkyl phosphine group (2-dimesitylphosphino-ethyl, Scheme 25).¹⁰⁸ It was readily synthesized in 5 h at 60 °C and isolated in 54% yield from the *in situ* generated phosphino-hydroborane dimer **21**. **BBA 7** was characterized by XRD analysis.

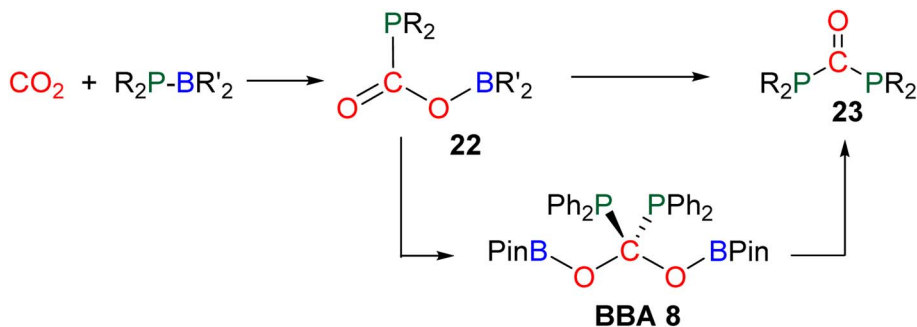
3.1.3. Summary of the generation of BBA 1–7. In total, seven BBA derivatives resulting from CO₂ hydroboration have

been characterized so far in the literature since the first report in 2012. **BBA 1–4** were obtained using commercially available pinacolborane (HBPin), 9-borabicyclo[3.3.1]nonane (9-BBN) and catecholborane (HBCat) and the non-commercially available dimesitylborane (HBMe₂), respectively (Scheme 24). It is worth mentioning that the commercially available hydroborane BH₃ led to the reduction of CO₂ to the methoxyborane stage.^{104,109} To our knowledge, detection of a corresponding BBA was never reported. NMR analysis was used as a key tool to characterize these species that are often difficult to isolate. The methylene moiety was indeed easily characterized by ¹H and ¹³C NMR in a narrow range of chemical shifts: 4.90 < δ¹H < 5.72 and 81.9 < δ¹³C < 91.3 (Table 4). Moreover, ¹³C-labelled control experiments with ¹³CO₂ allowed confirmation of the origin of the carbon atom in the product. Boron chemical shift is not characteristic of BBA since the boron atom substituents have a strong impact. They also influence the stability of BBA as observed in the case of BSA derivatives. This general feature is illustrated in BBA compounds by (i) the rather ease of generating **BBA 1** and **2** as opposed to **BBA 3**, (ii) the stability of **BBA 4**, **5** and **7** which could be isolated and crystallized while **BBA 2** was never isolated and (iii) the possibility to generate BBA in the absence of a catalyst in the cases of **BBA 5–7**.

Table 4 Selected NMR chemical shifts for BBA 1–7

| BBA | Isolated | XRD | Solvent | δ ¹³ C(CH ₂) | δ ¹ H(CH ₂) | δ ¹¹ B | Ref. |
|-----|----------|-----|---------------------------------|-------------------------------------|---|-------------------|------|
| 1 | Yes | No | C ₆ D ₆ | 85.7 | 5.51 | 22.8 | 94 |
| | | | | 85.4 | 5.49 | — | 90 |
| 2 | No | No | THF- <i>d</i> ₈ | 87.0 | ¹ J _{HC} = 167.2 Hz | 58.6 (ref. 100c) | 93 |
| | | | | | 5.54 | | |
| 3 | No | No | C ₆ D ₆ | 81.9 | 5.27 | n.d | 97 |
| 4 | Yes | Yes | THF- <i>d</i> ₈ | 89.6 | 5.49 | 48.5 | 30 |
| 5 | Yes | Yes | C ₆ D ₆ | 90.9 | 5.72 | 46.1 | 110 |
| 6 | No | No | CD ₂ Cl ₂ | 91.3 | 5.20 | −5.4 | 107 |
| | | | | | | 6.8 | |
| 7 | Yes | Yes | C ₆ D ₆ | 88.5 | 4.90 | 55.5 | 32 |
| | | | | | | 51.0 | |



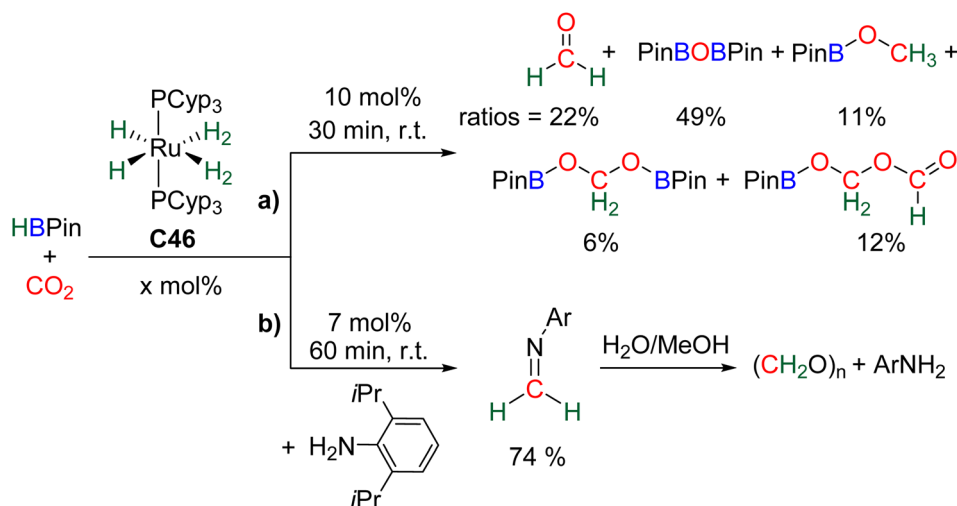
Scheme 26 Synthesis of **BBA 8** by the phosphoborylation of CO_2 .

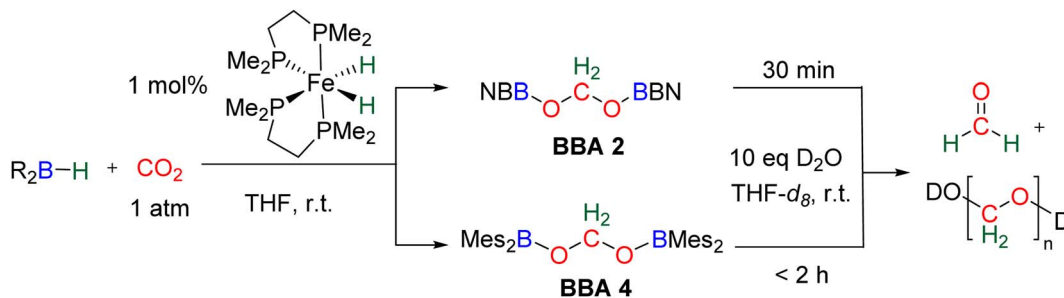
3.1.4. Miscellaneous BBA 8. **BBA 8** is an additional bis(boryl)acetal that is not presented with the other BBAs because it does not result from a double hydroboration of CO_2 but rather from formal double phosphoborylation (Scheme 26).¹¹¹ This compound features a central acetal core that is substituted by two diphenylphosphino substituents. The reactivity of a series of phosphinoborane compounds (R_2PBR_2) toward CO_2 led to a single insertion (compound **22**) and then ultimately to the formation of diphosphoacetal compound **23**. **BBA 8** was shown experimentally, with support from theoretical calculation, to be an intermediate and was synthesized and crystallized enabling its XRD analysis at low temperature. However, its instability precluded any further characterization in solution.

3.1.5. Hydroboration of CO_2 into formaldehyde. The direct observation of free formaldehyde from the hydroboration reaction has been described only once, in 2014, with the ruthenium catalyst **C46** featuring two tricyclopentylphosphine (PCyp_3) ligands and HBpin as the reductant (Scheme 27a).⁹¹ Under optimized conditions, HBpin was consumed in 30 min at room temperature with 10 mol% catalyst loading. Formaldehyde was observed as the major reduction product (ratio of 22%) along with other borylated products including **BBA 1** and

methoxyborane (CH_3OBPin). Labelling experiments using ^{13}C confirmed the generation of free formaldehyde with its characteristic resonances in ^1H and ^{13}C NMR spectra (8.74 and 193.0 ppm, respectively in C_6D_6). In order to drive the selectivity toward formaldehyde, 2,6-bis(diisopropyl)aniline was added in the reaction mixture before CO_2 pressurization. The related imine resulting from the condensation reaction between formaldehyde and the aniline was generated after 1 h at room temperature in 74% and 85% yields based on CO_2 and aniline, respectively (Scheme 27b). Upon hydrolysis of the generated imine, a formalin solution was obtained.

Observation of formaldehyde from CO_2 hydroboration was also mentioned in two other studies.^{95,112} In both cases, it appears to result from the evolution of **BBA 1**. Using the selective formation of BBA as a tool to access formaldehyde was further developed recently. **BBA 2** and **BBA 4** were selectively generated with catalyst **C38**, and subsequently hydrolysed with 10 equivalents of D_2O . This led to their complete hydrolysis into formaldehyde at room temperature within 30 min and less than 2 h for **BBA 2** and **BBA 4**, respectively (Scheme 28). The generated formaldehyde was then further transformed in organo-^{29b} or enzymatic³⁰-catalyzed reactions (see Section 3.3). It is remarkable that **BBA 2** and **BBA 4** were stable enough to be

Scheme 27 Hydroboration of CO_2 into formaldehyde: (a) generation and (b) selective trapping of HCHO .



Scheme 28 Generation of formaldehyde from BBA 2 and BBA 4 hydrolysis.

generated selectively – and even isolated in the case of **BBA 4** – and yet efficiently released formaldehyde under mild hydrolytic conditions.

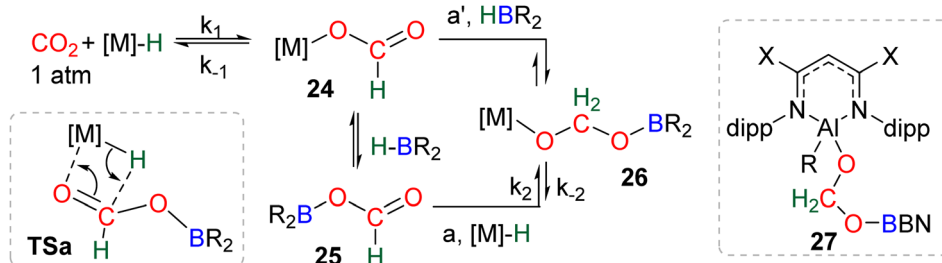
3.2. Mechanistic considerations

This section is dedicated to mechanistic considerations for the formation of bis(boryl)acetal (BBA) or formaldehyde. It is divided into three parts: (i) metal-hydride catalysis (**C36–C44**, **C46–C51**), (ii) organic catalysis (**C45**, **C52–C63**) and (iii) uncatalyzed generation of **BBA 5–7**.

3.2.1. Metal hydride catalysis. The catalysts **C36–C44** and **C46–C51** feature a metal hydride moiety or are believed to generate such a function upon reaction with the hydroborane (**C41–C43**). This hydride is proposed to be the key species of the catalytic process leading to BBA. As shown in Scheme 29, the elementary steps accounting for the $2e^-$ reduction of CO_2 are the insertion of CO_2 into the M–H bond leading to the formate complex **24**, followed by a σ -bond metathesis with the hydroborane leading to formoxyborane **25**. We will not describe further this $2e^-$ reduction of CO_2 since it was reviewed elsewhere.⁸ Our discussion will rather concentrate on the ensuing reduction step leading to BBA and formaldehyde. At present, theoretical^{89,113} and experimental^{90,91,97,112,114} studies are converging on the central role of metal boryl acetal compound **26**, which is proposed to result from the reaction of **25** with M–H (step a, Scheme 29). The corresponding transition state (**TSa**, Scheme 29) is characterized by a hydride attack on the electrophilic carbon atom of **25**, as proposed by several DFT calculations on Ni,^{89,115} Ru,¹¹³ Fe,^{113a} Os^{113a} and Mn¹¹⁶ systems. The concomitant M–O interaction is often calculated to occur but does not seem mandatory. The likely involvement of

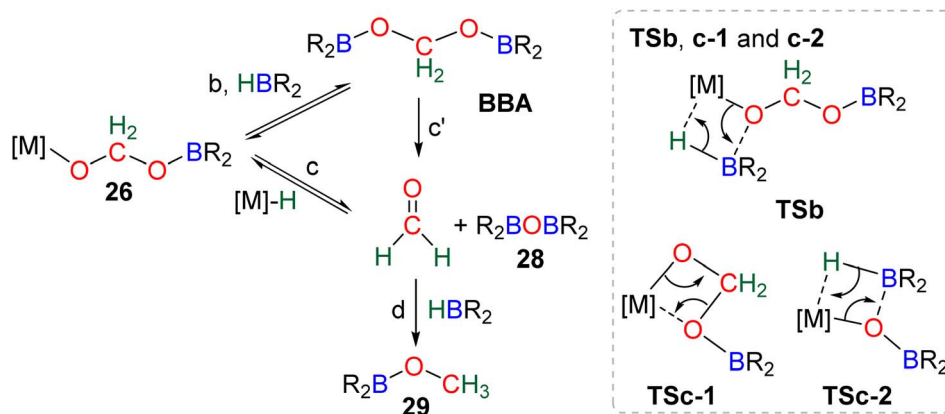
a formoxyborane species **25** as an intermediate to the $4e^-$ and $6e^-$ stages was experimentally asserted when a formoxyborane featuring a pinacolboranyl moiety was shown to give similar rate and product distribution to that in CO_2 hydroboration with catalyst **C46**.¹¹²

Numerous experimental proofs demonstrated that formate complex **24** obtained from CO_2 insertion into M–H bond could be used in hydroboration reactions.^{8a,90,91} However, although the metal boryl acetal species **26** has been calculated to be central for the $4e^-$ reduction of CO_2 , identification and/or isolation of these species are still lacking. The aluminum compound **27** is the only metal boryl acetal compound characterized without ambiguity (Scheme 29).¹¹⁴ It was obtained from the subsequent reaction of the corresponding [Al]–H with CO_2 and then with 9-BBN and **27** was fully analysed by NMR and X-ray diffraction (XRD) studies. It is noticeable that only 9-BBN gave access to this metal boryl acetal structure. Analogous structures could indeed neither be observed with HBpin because of the lack of reactivity nor with HBCat or BH_3 because of subsequent reduction processes. It is also important to notice that like boron, aluminium is a group 13 element and that despite mimicking important steps of CO_2 hydroboration, neither the starting Al hydride complex nor complex **27** catalyses the CO_2 hydroboration reaction because the initial Al–H species is not regenerated under the reaction conditions. Step a' (Scheme 29) is an alternative step to generate **26** from the direct hydroboration of the formate complex **24**. To the best of our knowledge, it has not been reported in DFT investigations but we believe that it should not be discarded *ipso facto*. Compound **26** is a key intermediate because it serves as a bifurcation point either toward BBA (Scheme 30, step b) or



Scheme 29 Calculated elementary steps (a and a') leading to the generation of the elusive intermediate **26** and structure of the only metal boryl acetal (**27**) so far characterized.





Scheme 30 Calculated elementary steps (b, c, c', d) and transition states (TSb, TSc-1 and TSc-2) from metallic boryl acetal.

formaldehyde (Scheme 30, step c). BBA is formed from the hydroboration of the metallic acetal intermediate **26**. **TSb** represents the type of transition state calculated to account for this step. It formally corresponds to an M–O metathesis. Step c illustrates the route leading to formaldehyde and the boryl ether **28** which eventually leads to the $6e^-$ reduction hydroboration product **29** through step d. This last step was experimentally identified with the Ru–H complex **C46** that was shown to catalyse the hydroboration of formaldehyde into methoxyborane with HBpin. The first transition state **TSc-1** does not involve HBR_2 and is simply a rearrangement of the metal boryl acetal **26**. The aliphatic chain rearranges to enable the interaction of the second oxygen atom with the metal centre. This reorganization weakens the M–O bond of the first oxygen atom and the O–CH₂ bond of the second oxygen atom. This leads to the release of formaldehyde and the formation of an M–OBR₂ intermediate which is subsequently hydroborated to regenerate the metal hydride and affords the ether compound **28** via **TSc-2**.

The factors influencing the selectivity have been explored in a thorough study involving the use of various hydride pinners of Ni- and Pd-based catalysts and three different hydroboranes, namely, HBpin, HBCat and 9-BBN.⁹⁷ The origin of the selectivity between the $2e^-$ and $4e^-$ reduction products was proposed to be dependent on the relative rate of reaction between the metal hydride fragment (M–H) and either (i) CO₂ to afford the formoxyborane **25** (k_1) or (ii) the formoxyborane intermediate **25** to afford the metal boryl acetal **26** (k_2) (Scheme 29). It was indeed shown that a lower pressure of CO₂ led to a higher selectivity toward the $4e^-$ reduction product presumably by disfavouring k_1 . It was also proposed that k_2 could be favoured by (i) increasing the concentration of the hydroborane, (ii) decreasing the steric hindrance of the boryl unit, (iii) increasing its electrophilicity and (iv) using a Lewis acid to co-activate the formoxyborane.

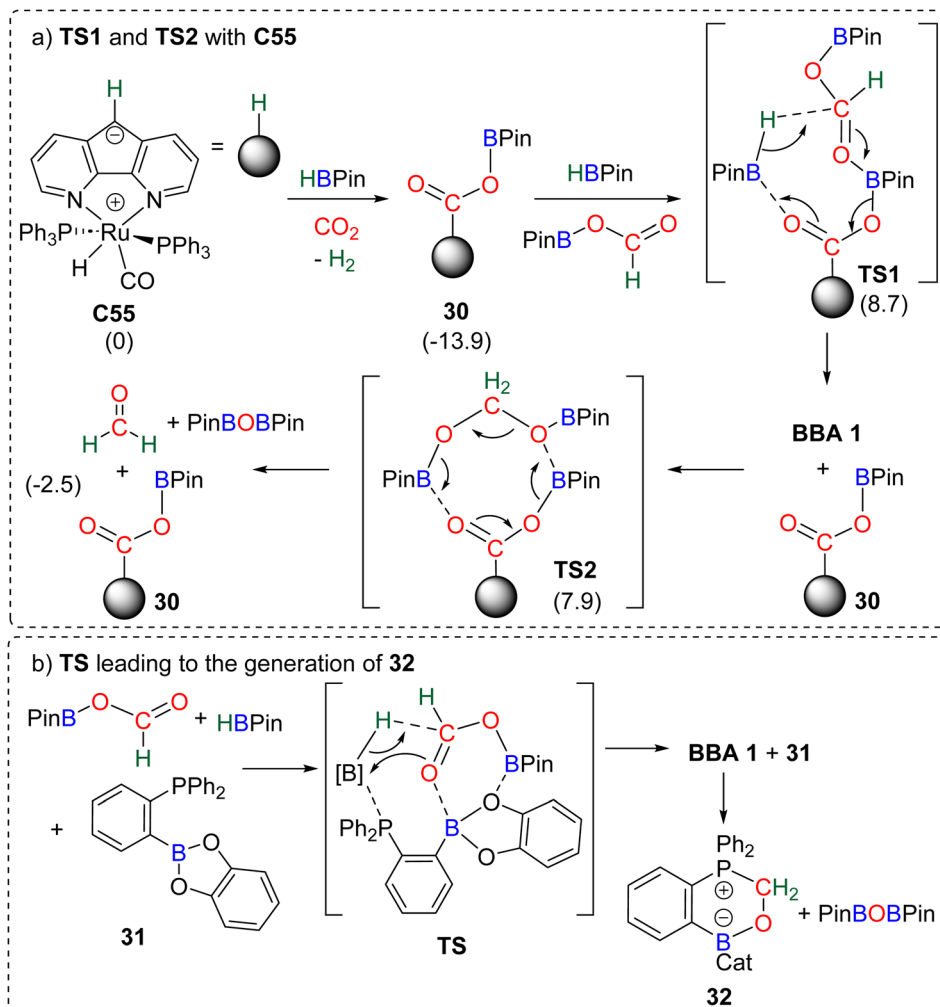
The origin of the selectivity between the $4e^-$ and the $6e^-$ reduction products appears to be the preference between the formation of BBA and the formation of formaldehyde, since the latter readily leads to further reduction. However, the factors influencing the preference toward BBA or formaldehyde remain to be disclosed. In addition, the formation of BBA was shown to

be reversible which eventually led to the final generation of the more stable methoxyborane in various systems.^{90,97} This feature explains the key role that the boryl moieties may play in the kinetic and/or thermodynamic stabilization of the corresponding BBA. Step c' is an alternative path generating formaldehyde directly from BBA (Scheme 30). Such evolution has not been proposed as a plausible path for M–H catalysis but for organic catalysis (*vide infra*).^{96,98} The direct generation of a methoxyborane compound **29** from the metal boryl acetal **26** has not been identified so far.

3.2.2. Organic catalysis. As shown in the first section, compounds **C45** (TBD) and **C52–63** are able to catalyse the hydroboration of CO₂ without any metal centre. The metal ions in compounds **C55** and **C57** are not believed to be the active catalytic centres. The suggested mechanism with **C55** and **C57** indeed follows a similar pathway to that with **C54** and **C56**, as it involves the anionic carbon moiety as the active catalytic centre. This was based on the theoretical investigations conducted on the Ru-based system **C55** and is depicted in Scheme 31(a).^{82,117}

The carbanion located on the backbone of the ligand of the complex was found to react both with HBPin and CO₂ to produce the catalytic species **30**. Compound **30** was proposed to activate the formoxyborane intermediate **25** and HBPin concomitantly through **TS1** to afford **BBA 1**. The regenerated catalyst **30** could then be involved in the transformation of **BBA 1** into formaldehyde via an 8-membered-ring (**TS2**). In this reaction, formaldehyde was not experimentally observed but was proposed to be a transient intermediate *en route* to the observed methoxyborane structure. The ambiphilic phosphine borane **31** was shown to catalyse CO₂ hydroboration into methoxyborane with different hydroboranes (HBCat, HBPin, 9-BBN and BH₃) (Scheme 31b).¹¹⁸ Although no free formaldehyde nor BBA was observed, a pathway, similar on various aspects to the previous one (Scheme 31a), was proposed. Theoretical investigations notably concluded on the co-activation of HBPin and formoxyborane (**TS**, Scheme 31b) to afford **BBA 1**. **BBA 1** then evolves to formaldehyde which ultimately reacts with compound **31** to form the formaldehyde adduct **32**. Interestingly, labelling experiments proved that the formaldehyde moiety of compound **32** was not reduced further to afford the

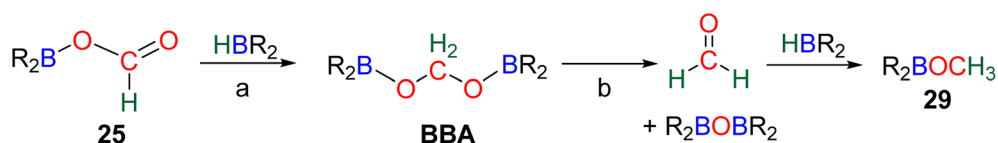




Scheme 31 Calculated elementary steps for the 4e⁻ reduction mechanism of CO₂ with (a) C55 (energies indicated in parenthesis are ΔG values in kcal mol⁻¹) and (b) compound 31.

methoxyborane.^{109a} Instead, the adduct 32 acts as a more effective catalyst in the hydroboration of CO₂ into methoxyborane with the various boranes tested. This feature is responsible for an observed induction period, which was also noticed (i) in the CO₂ hydroboration reactions with catalyst C52 leading to the generation of C53,^{103,119} (ii) in the hydroboration of CO₂ with PtBu₃ in which a formaldehyde derived intermediate (compound 36, Scheme 33) was also observed,¹²⁰ and (iii) when using catalyst C60 leading to C61 which was proven to be a more active catalyst.¹⁰⁴ The similar pathway identified in these two studies implies (i) the reduction of CO₂ into formoxyborane as the 2e⁻ reduction intermediates are observed with metal

hydride catalysts and (ii) the subsequent generation of BBA (Scheme 32, step a) and then formaldehyde (Scheme 32, step b) before further reduction to the 6e⁻ reduction product.¹²¹ This latter feature stands in contrast with the metal hydride systems in which BBA and formaldehyde are not generated along the same pathway (Scheme 30). This common pathway remains to be confirmed by further studies on additional organo-catalysed systems. Generalizing such a mechanism remains highly hypothetical because of (i) the very small number of reported theoretical investigations, (ii) the large variety of organic catalysts C45 and C52–C63 and (iii) the difficulty to study very reactive intermediates experimentally. A general trend is the



Scheme 32 Elementary steps a and b for the reduction of formoxyborane 25 to methoxyborane 29 calculated with compound 32.



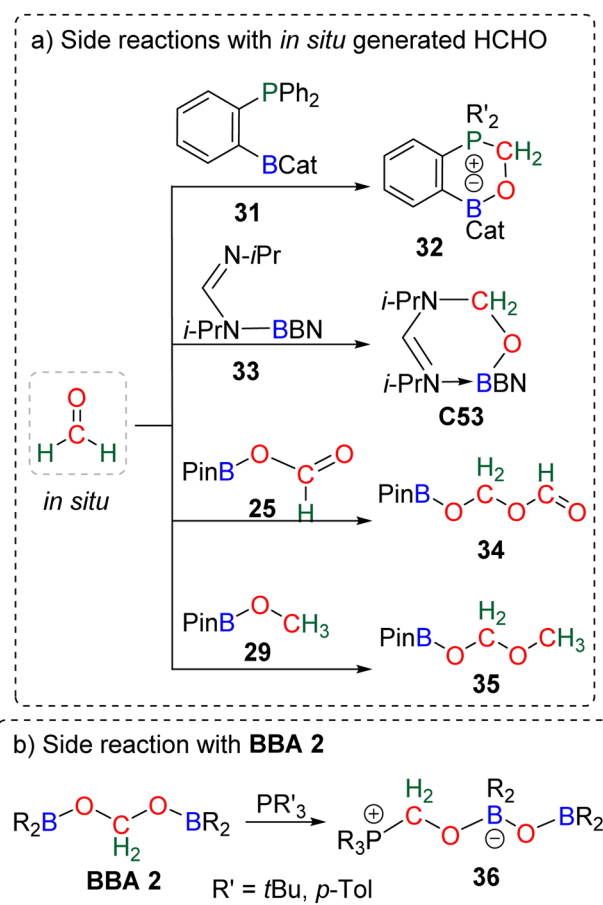
ability of these main group organic catalysts to co-activate several substrates and/or intermediates (CO₂, hydroborane, formoxyborane). This feature highlights the powerful synergy observed between moderately reactive centres (moderate Lewis acid and Lewis base fragments) for the transformation of very stable molecules such as carbon dioxide.

3.2.3. Uncatalyzed hydroboration for the generation of BBA 5–7. No DFT investigations have been performed to rationalize the catalyst-free generation of **BBA** 5–7. At first glance, the presence of a pendent N- or P-based Lewis base on the boryl unit in all three cases is a striking feature. Based on the ability of main group organic compounds to catalyse CO₂ hydroboration, one could assume that the pendent Lewis base plays a role either in the intramolecular B–H activation or in an intermolecular CO₂ anchoring/activation.⁴³ Another role could lie in the stabilization of the formed BBA, even though no interaction of the pendant Lewis base was detected in the XRD analyses of **BBA** 4, 5 and 7. Finally, the uncatalyzed addition of the hydroborane **21** to CO₂ affording **BBA** 7 is surprising if one considers the hydride transfer as being the first elementary step for such transformation. Indeed, the presence of a perfluoroaryl substituent on the boron atom certainly decreases the hydricity of the B–H bond.¹²² With this reactive trend in mind, one would assume that the B–H bond hydricity in compound **21** is lower than the one in HBPIn, HBCat and 9-BBN which were proved unreactive toward CO₂ in the absence of a catalyst. That the empty p orbital at the boron atom might be at play in the first elementary step is worth considering at least in the latter case.

3.3. Use of formaldehyde and bis(boryl)acetal as C₁ and C_n sources

The known high reactivity of formaldehyde was first evidenced in four side reactions involving CO₂ reduction. In these reactions, *in situ* generated formaldehyde reacted with other products or catalysts present in solution (Scheme 33a).

The formation of compounds **32**^{109a,118} and **C53**¹⁰³ was postulated from calculation to arise from the reaction between transiently generated formaldehyde and the ambiphilic compounds **31** and **33**, respectively. Compounds **34**^{90,112,123} and **35**⁹¹ were shown experimentally to arise from the reaction of formaldehyde with **25** and **29**, respectively, which was confirmed by labelling experiments. BBA compounds were also shown to readily react under mild conditions. We believe that the characterization of compound **36** was the first observation of such BBA reactivity (Scheme 33b).¹²⁰ Although the authors did not elaborate on the mechanism of its formation, we propose that **36** could be formed from the reaction of **BBA 2** with the phosphine used as the catalyst, on the basis of a similar reaction later observed between **BBA 2** and an NHC leading to compound **48** (Scheme 37) analogous to compound **36**. These examples showed that BBA intermediates or formaldehyde is prone to react. Such “undesired” yet attractive reactivities may pave the way to more controlled transformations. Along this idea, we present hereafter different examples using BBA or formaldehyde in subsequent reactions either (i) as a C₁ source for the formation of C–O, C–N, C–P and C–C bonds, or (ii) as a C_n

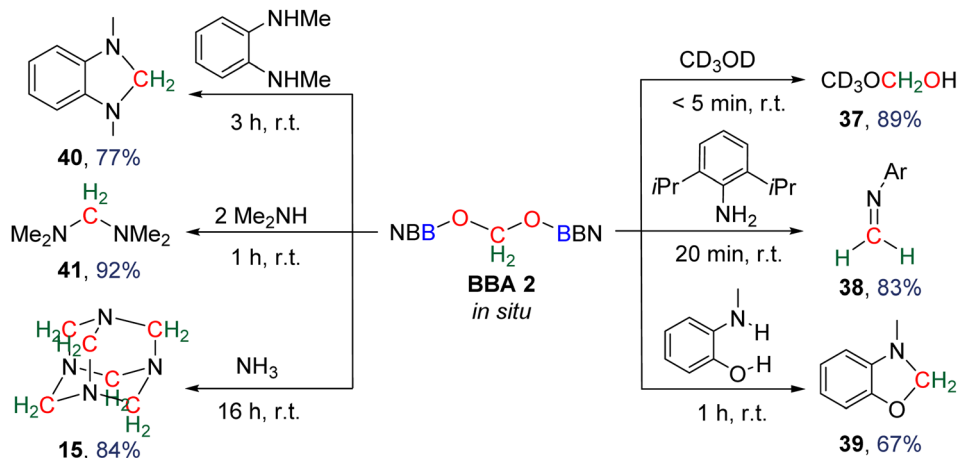


Scheme 33 Side reactions obtained with *in situ* generated HCHO (a) and BBA 2 (b).

source in oligomerization reactions leading to the formation of carbon chains and the synthesis of chiral carbon centres.

3.3.1. BBA as a C₁ source in the formation of H₂C–O, H₂C–N and H₂C–P bonds. **BBA 2** was the first BBA involved in reductive functionalization.^{93,124} Although **BBA 2** has never been isolated so far, its selective and efficient generation in 85% yield after 47 min at room temperature from ¹²CO₂ and ¹³CO₂ hydroboration enabled probing of its reactivity toward various E–H substrates (E = RO or R₂N, Scheme 34).⁹³ Its reaction with methanol and (diisopropyl)aniline led to the characterization of the hemiacetal compound **37** (89% yield, <5 min) and imine **38** (83% yield, 20 min), respectively. These short reaction times and high yields were the first evidence that **BBA 2** could indeed be used as a formaldehyde surrogate leading to the transfer of a methylene fragment for the formation of H₂C–O and H₂C=N bonds. The reactivity was further extended to the generation of the hemiaminal **39** (67% yield, 1 h) and both cyclic and acyclic aminal compounds **40** (77% yield, 3 h) and **41** (84% yield, 1 h), respectively. Finally, the reaction with ammonia afforded the cage compound hexamethylenetetramine **15** in 84% yield after 16 h. In the latter example, it is remarkable that the six fully deoxygenated carbon atoms are issued from **BBA 2** and thus from CO₂. **BBA 1** was also used as a source of methylene in



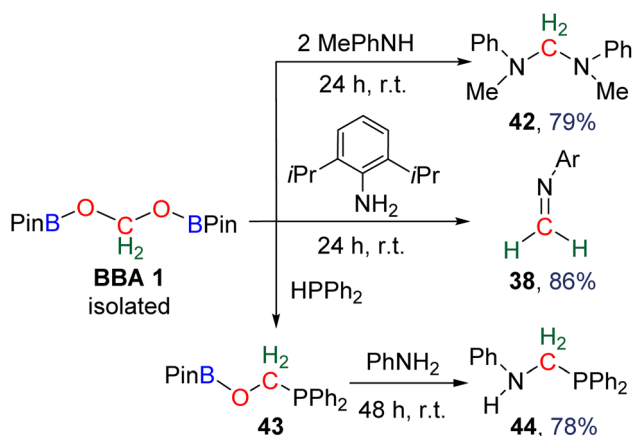


Scheme 34 Formation of $\text{CH}_2\text{-N}$, $\text{CH}_2=\text{N}$ and $\text{CH}_2\text{-O}$ bonds from **BBA 2**: generation of compounds **15**, **37–41**.

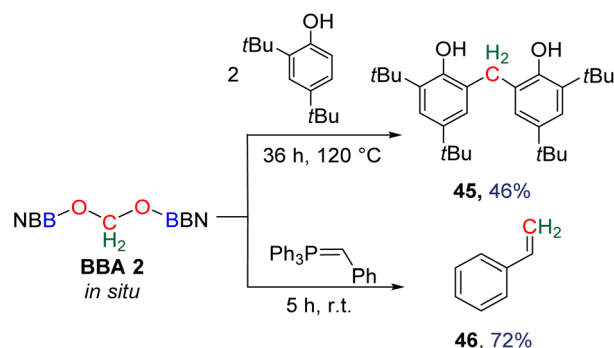
reductive functionalization reactions (Scheme 35).⁹⁴ Being selectively generated (71% isolated yield), its reactivity was explored first with (diisopropyl)aniline giving rise to the corresponding imine **38** (86% yield, 24 h). It is interesting to note that similar yields were obtained starting from both **BBA 1** and **BBA 2** (*i.e.*, 83% and 86% yields, respectively) but with longer reaction time with **BBA 1** (24 h) than with **BBA 2** (20 min). The reaction with phenylmethylamine afforded the aminor **42** (79% yield, 24 h). Finally, the reaction with diphenylphosphine gave rise to a single product assigned to compound **43**. Subsequent reaction with phenylamine led to the isolation of compound **44** (78% yield, 48 h) featuring for the first time a C–P bond.

3.3.2. CO_2 as a C_1 source in the formation of C–C bonds. The formation of C–C bonds from CO_2 reduction is of high interest, yet challenging. Such a process was first described with the condensation reaction between **BBA 2** and 2 equivalents of a substituted phenol derivative, leading to the generation of the methylene-bridged compound **45** (46% yield, 36 h, 120 °C, Scheme 36). **BBA 2** was also used in a Wittig reaction, producing styrene **46** (72% yield, 5 h, room temperature). These two examples showed that the formation of C–C and C=C bonds could be successfully achieved from CO_2 .⁹³

3.3.3. BBA as a C_n source: oligomerization of BBA and formaldehyde. The conversion of CO_2 into C_n compounds by the construction of a carbon chain is an appealing process because of the higher complexity and diversity of the C_n products as compared to the C_1 products. However, this reaction is highly challenging in terms of conditions, selectivity and scope of products.^{3b,21a-c} In particular, no asymmetric carbon atom was generated from CO_2 . So far, the $4e^-$ reduction of CO_2 by hydrogenation, hydrosilylation and hydroboration aimed at employing CO_2 exclusively as a C_1 source. While the difficulties encountered in controlling the $4e^-$ reduction processes may have been the main reason for this, the long-known possibilities of oligomerizing formaldehyde – the so-called formose reaction – were strongly calling for using CO_2 $4e^-$ reduction products as a C_n source.¹²⁵ This was first accomplished upon reacting **BBA 2**, generated *in situ* from CO_2 hydroboration, with N-heterocyclic carbene (NHC, Scheme 37).³² Ender's NHC carbene **47** is a classical organo-catalyst able to catalyse the formation of C–C bonds of carbonyl compounds and notably the oligomerization of formaldehyde.¹²⁶ Its stoichiometric reactivity with **BBA 2** was first probed, leading to the formation and isolation of compound **48** (40% yield, 3 h, 10 °C) (Scheme 37). This reaction resulted from the formal isomerization of **BBA 2** triggered by the addition of the NHC on the electrophilic methylene moiety of

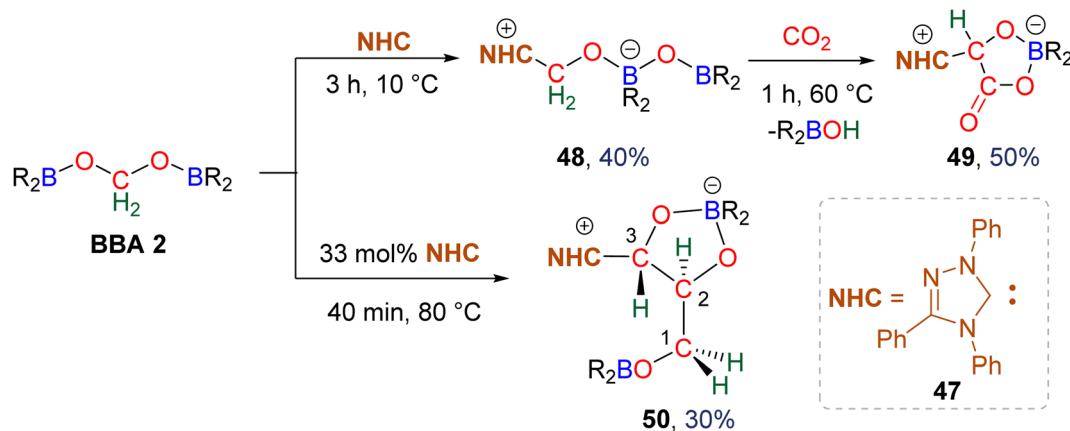


Scheme 35 Generation of $\text{CH}_2\text{-N}$ and $\text{CH}_2\text{-P}$ bonds from **BBA 1**.



Scheme 36 Generation of C–C and C=C bonds from **BBA 2**.



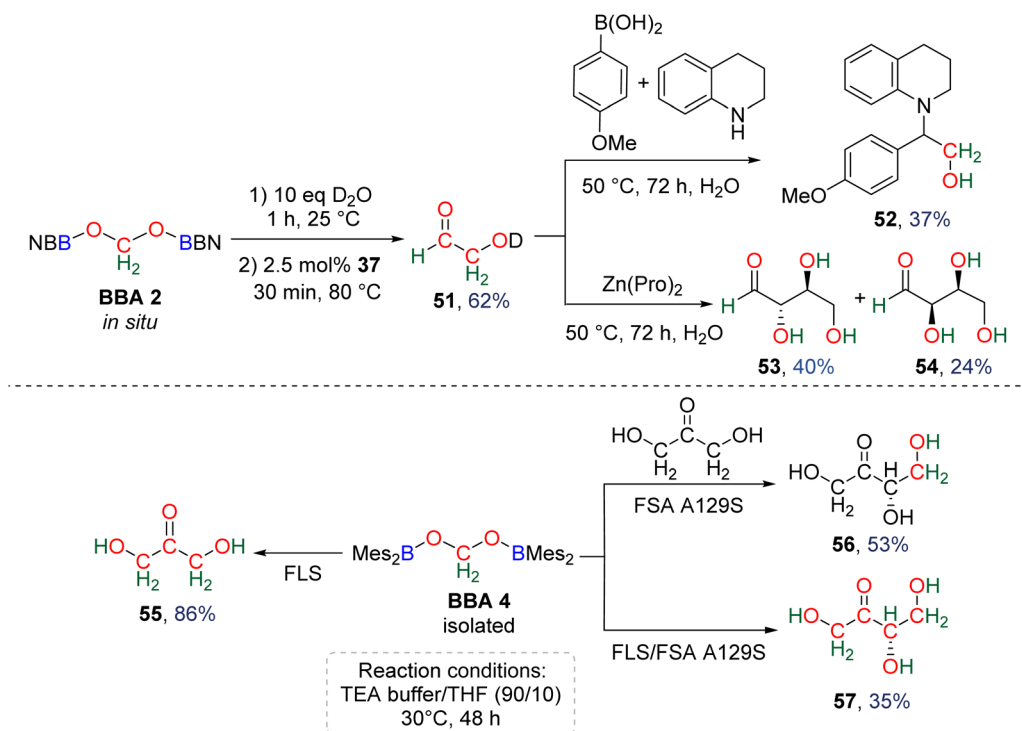


Scheme 37 Homocoupling of BBA 2 resulting in the formation of compounds 49 and 50.

BBA 2 via an S_N2 type mechanism, as proposed by DFT investigations.³² This reaction illustrated that a Lewis base can promote the migration of an O- BR_2 fragment onto the other Lewis acid moiety of a BBA molecule, which is reminiscent of the generation of compound **36** from the reaction of **BBA 2** with tertiary phosphines (Scheme 33b). The intermediate **48** was shown to further react with CO_2 to form compound **49** (50% yield, 1 h, 60 °C), which was notably characterized by X-ray diffraction analysis. This compound was obtained from the loss of a borinic acid moiety (R_2BOH), possibly generating a transient original O-borylated Breslow intermediate which was then able to trap a CO_2 molecule in a bifunctional manner.¹²⁷

Compound **49** features a new C-C bond between two carbon atoms arising from two CO_2 molecules. In this reaction, the new

C-C bond was formed thanks to the nucleophilic character of the carbon atom linked to the NHC. This Umpolung process – classical of organocatalyzed C-C bond formation with such a carbene – was further used to generate compound **50** from the homocoupling of three **BBA 2** molecules in the presence of 33 mol% of NHC, generating a chain of three carbon atoms (C^1 , C^2 , C^3) arising from three CO_2 molecules. It must be pointed out that two of the three carbon atoms (C^2 , C^3) of the chain are asymmetric carbons and were generated with a high diastereocontrol, thanks to the presence of the boryl moiety. DFT investigations were conducted to get insights on the elementary steps accounting for these transformations,³² which stand as the first reported example of the generation of asymmetric carbon centres from CO_2 . In the process leading to **50**, it should



Scheme 38 Chemo- and enzyme-catalysed oligomerization of BBA 2 and 4.



be noticed that formaldehyde is never released from **BBA 2**. The oligomerization reaction involves BBA without the intermediary of formaldehyde, as shown from the presence of boryl moieties in the final product **50**. The possibility that formaldehyde could be released from BBA – in the same vein as what was explored with **BSA 3** – before its engagement in the oligomerization process, was recently explored with **BBA 2** and **BBA 4** (Scheme 38). Despite its powerful nature, the formose reaction remains a challenging reaction due to the difficulty in controlling both the length of the carbon chain and the chirality of the generated carbohydrates.^{26,126,128}

As presented earlier, **BBA 2** was shown to quantitatively release formaldehyde after 1 h at room temperature in the presence of 10 equivalents of D₂O. Optimization of both the hydrolysis and the formose steps led to the synthesis of the C₂ carbohydrate glycolaldehyde **51** in 62% yield after 30 min at 80 °C using 2.5 mol% of NHC **47** as the catalyst (Scheme 37).^{29b} Glycolaldehyde was further engaged in one-pot reactions leading to the formation of compound **52** (37% isolated yield) *via* a Petasis–Borono–Mannich reaction or to the formation of the C₄ carbohydrates erythrose (**53**, 40% yield) and threose (**54**, 24% yield) generated from Zn(pro)-catalysed dimerization reactions (pro = proline).

In a parallel study, **BBA 4** was identified as a promising candidate to conduct enzymatic transformations.³⁰ Its isolation, in contrast to **BBA 2**, was seen as an important feature toward this aim. If it was stable enough for isolation, **BBA 4** was nonetheless shown to readily release formaldehyde upon hydrolysis under relatively similar conditions to those with **BBA 2**. Enzymatic transformations were then thought about in order to control the length of the generated carbon chain and the chirality of the product. While formaldehyde is usually responsible for enzyme inhibition and even denaturation,¹²⁹ D-fructose-6-phosphate aldolase (FSA) and formolase (FLS) were shown to catalyse aldolization and formose transformations of formaldehyde, respectively.^{24,130} These enzymes were thus selected to perform the transformation of formaldehyde released from **BBA 4**. The enzymatic transformations were conducted at 30 °C for 48 h in a triethanolamine (TEA) buffered solution (25 mM, pH 7.0 with 1 mM MgSO₄ and 0.1 mM thiamine pyrophosphate (TPP)) with THF. The presence of 10% THF was found optimal to ensure the solubility of **BBA 4**, while limiting the detrimental effect of this organic solvent on FLS and FSA activities (Scheme 38).³⁰ Under these conditions, **BBA 4** was oligomerized by FLS into dihydroxyacetone (**55**) in 86% yield. **BBA 4** was then reacted with commercial dihydroxyacetone in the presence of the mono-mutant FSA A129S¹³¹ to afford the corresponding C₄ carbohydrate, L-erythrulose (**56**) in 53% yield with a perfect enantiocontrolled aldol reaction. In this case, one carbon atom of the carbon chain arose from **BBA 4**. Following recently reported cascade reactions with formaldehyde,¹³² these two enzymes were then combined in a one-pot cascade reaction to achieve the transformation of **BBA 4** into L-erythrulose **57** in 35% yield. All four carbon atoms of the carbohydrate arose from CO₂, including the chiral one. This reaction corresponds to the first cell-free enantioselective transformation of CO₂.

3.4. Conclusion and perspectives

In conclusion, the 4e⁻ hydroboration of CO₂ stands out for several reasons: (i) the uncatalyzed formation of three bis(boryl) acetal (BBA) compounds derived from specific hydroboranes; (ii) the highest reported turnover frequency (TOF) at 516 h⁻¹ among hydroelementation reactions; (iii) the reactive nature of BBA at room temperature, facilitating condensation reactions or formaldehyde release; (iv) the utilization of BBA as a C_n source with or without formaldehyde release, wherein the reaction without formaldehyde release results in the formation of an O-borylated C₃ compound; (v) the use of BBA in the pioneering enantioselective generation of a carbon centre from CO₂.^{30–32} This significant breakthrough was achieved through formaldehyde release and subsequent enzymatic cascade reactions.

As perspectives in CO₂ hydroboration, the primary challenge lies in the stoichiometric utilization of hydroborane and thus the stoichiometric amount of borinic acid (R₂BOH) generated as a co-product following the hydrolysis of BBA compounds. Since there is currently no sustainable process for regenerating hydroborane from this co-product, CO₂ hydroboration is scarcely applicable unless the product synthesized from BBA holds a very high value. For example, carbohydrates, particularly rare and non-natural ones, are of significant interest to the pharmaceutical industry. Their synthesis from CO₂, especially with isotope labelling, could be an avenue worth exploring for generating chiral complex C_n products from CO₂. On the other hand, the prospect of generating O-borylated C_n products could open new avenues to retain boryl moieties in CO₂ transformation products, instead of treating them as waste after B–O bond hydrolysis. This would allow for further functionalization of the generated compounds. To achieve these objectives, future efforts could focus on exploring a broader variety of hydroboranes with diverse properties. Such a range of hydroboranes could lead to the formation of a diverse array of BBA compounds with varying stability and reactivity, suitable for various applications. Additionally, other CO₂ hydroelementation reactions, beyond hydrosilylation and hydroboration, may provide an even greater variety of acetal compounds with unique properties. Specific CO₂ hydroelementation reactions involving early transition-metal hydride species are discussed in the subsequent section of this review.

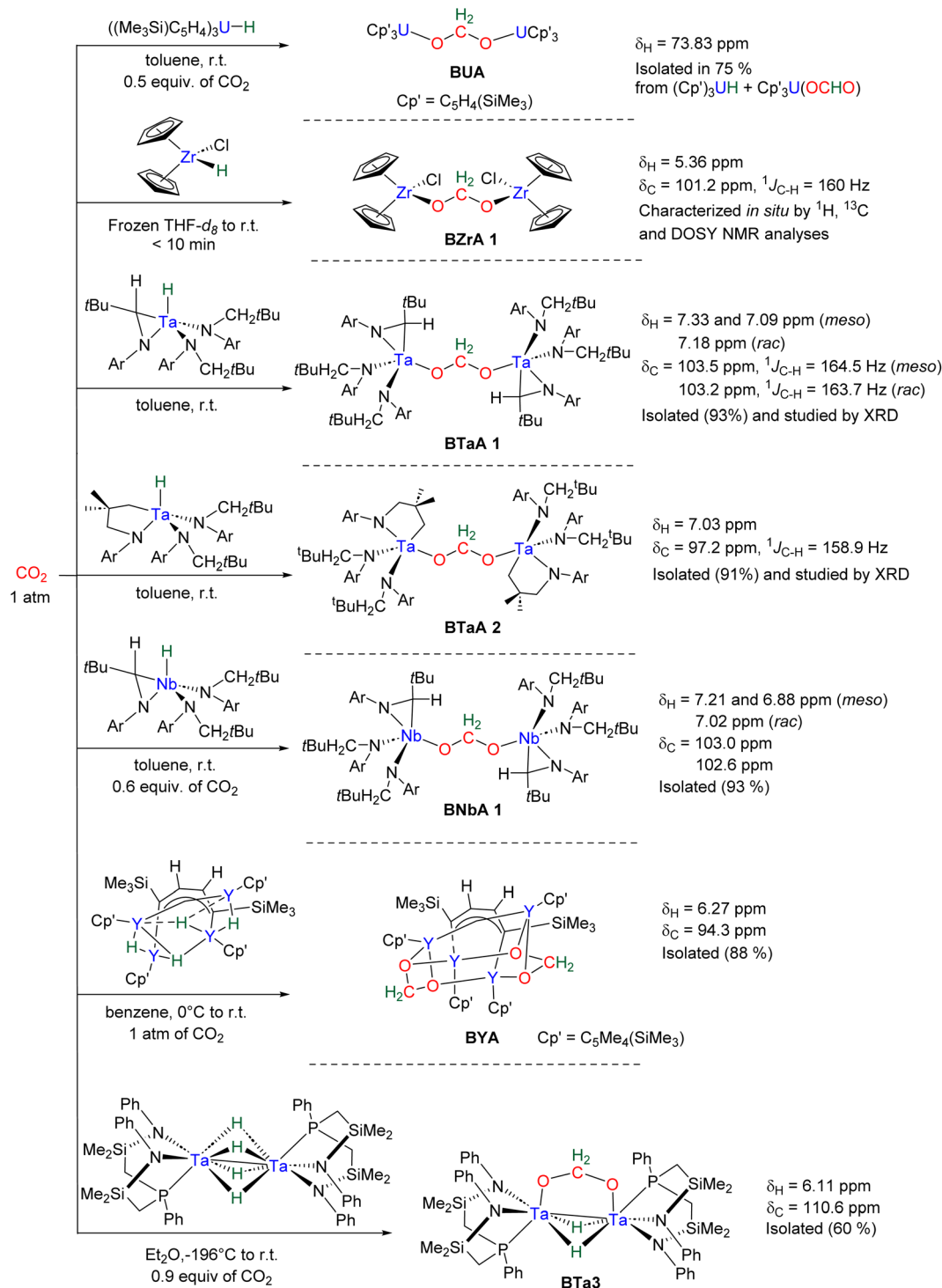
4. Other hydroelementation reactions

The CO₂ hydroelementation involving metal hydrides and phosphines has seen limited development. We have compiled these results in this concise standalone section, separated from the broader and more extensive sections.

4.1. Hydroelementation with actinide, early TM and rare earth metal hydride species to acetal complexes

Hydride complexes of U, Zr, Ta, Nb and Y were shown to react with CO₂ under mild conditions to afford the bi-metallic acetal or methylene diolate complexes shown in Scheme 39. The reaction of the U(IV) hydride complex (Cp')₃U(H) (Cp' =



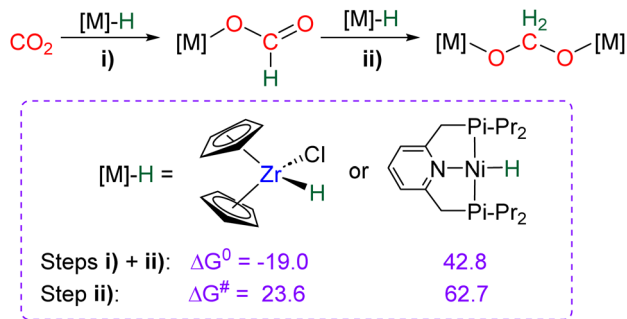


Scheme 39 Generation of BZrA 1, BTaA 1, BTaA 2 and BNbA 1.

$\text{C}_5\text{H}_4(\text{SiMe}_3)$) with 1 atm CO_2 led to the expected formoxy uranium $(\text{Cp}'_3)\text{U}(\text{OCHO})$. However, when only 0.5 equiv. of CO_2 was introduced in an NMR tube, the bis(uranyl)acetal complex (**BUA**) was generated.¹³¹ This complex was also isolated by crystallization from the stoichiometric reaction of $(\text{Cp}'_3)_3\text{U}(\text{OCHO})$ with $(\text{Cp}'_3)_3\text{U}(\text{H})$ in 75% yield after 4 h at 70°C . The methylene fragment was characterized at 73.83 ppm in ^1H NMR

due to the proximity with the paramagnetic uranium centre. The reaction of the Schwartz's reagent, $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$, was investigated with $^{13}\text{CO}_2$.¹³⁴ A frozen $\text{THF}-d_8$ solution of the Zr complex was prepared and reaction with $^{13}\text{CO}_2$ was investigated at an early stage. After initiating the reaction by a gentle shaking of the frozen solution, the acetal **BZrA 1** could be observed by ^1H NMR analysis for only 10 min. To further characterize the acetal





Scheme 40 DFT investigations for the formation of metallic acetal upon reaction of [Ni]-H and [Zr]-H hydrides with CO₂ (free enthalpies in kcal mol⁻¹).

species, ¹H and ¹³C{¹H} NMR analyses were conducted at 235 K.^{134b} The methylene signal appeared at $\delta^1\text{H} = 5.36$ ppm and $\delta^{13}\text{C} = 101.2$ ppm. Low temperature diffusion ordered NMR spectroscopy (DOSY) confirmed the dimeric nature of **BZrA 1** in solution.^{134a} The reduction of CO₂ was also investigated with Ta-H and Nb-H complexes. The acetal complexes **BTaA 1**, **BTaA 2** and **BNbA 1** were isolated and characterized, notably by XRD in the case of the two former ones (Scheme 39).¹³⁵ Two diastereoisomers with diastereotopic methylene protons, the *rac* and *meso* forms, were observed for **BTaA 1** and **BNbA 1**, being the result of a C₂ and C_s symmetry, respectively. The [Ta]- and [Nb]-based hydride complexes featured a peculiar aziridine-metallacycle which was shown to generate a 5-membered cycle leading to **BTaA 2**. Another Ta acetal complex **BTaA 3** was later reported from the reaction of a dinuclear Ta tetrahydride complex with 0.9 equivalent of CO₂ at low temperature.¹³⁴ The methylene signal was characterized in solution at $\delta^1\text{H} = 6.11$ ppm and $\delta^{13}\text{C} = 110.6$ ppm and the complex was structurally characterized by X-ray diffraction analysis. Finally, a tetranuclear yttrium tetrahydride complex was also shown to readily react with 1 atm of CO₂ to afford **BYA** featuring two methenediolate bridge fragments maintaining the tetranuclear

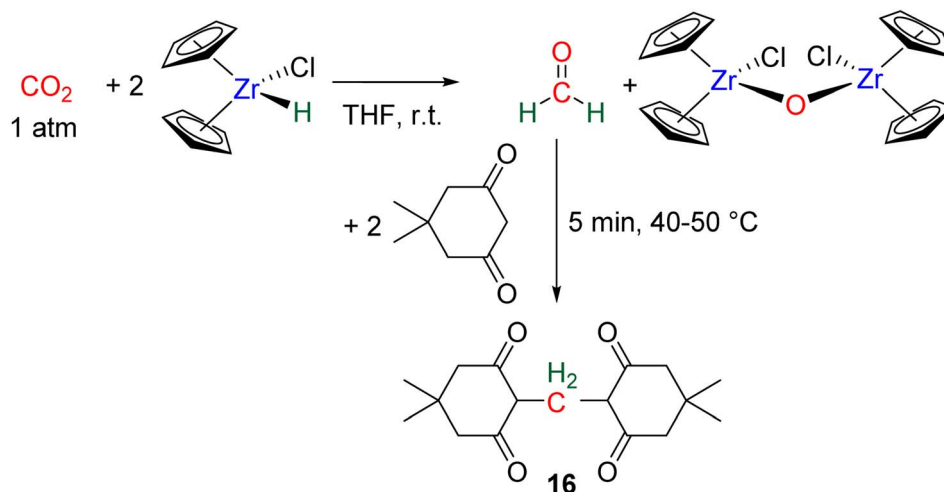
structure. The complex was analysed in the solid state by X-ray diffraction and in solution by NMR (CH₂ fragment: $\delta^1\text{H} = 6.27$ ppm and $\delta^{13}\text{C} = 94.3$ ppm).¹³⁷

The methylene signal of these acetal products appeared at a lower field in ¹H NMR (6.11 ppm < $\delta^1\text{H}$ < 7.33 ppm) as compared to BBA, BSA and **BZrA 1** structures while the ¹³C{¹H} NMR chemical shifts of the early-TM acetals are in a slightly lower field area as compared to the ones obtained from BBA and BSA derivatives (101.2 ppm < $\delta^{13}\text{C}$ < 103.5 ppm).

DFT investigations⁸⁹ were conducted to compare the reactivity of CO₂ toward the Schwartz's reagent [Zr]-H complexes¹³⁴ vs. [Ni]-H complexes used as catalysts in CO₂ hydroboration,⁸⁸ regarding the formation of the corresponding metallic acetal species (Scheme 40). This study disclosed a rare comparison between the reactivities of early and late TM complexes toward CO₂.¹³⁸ The formation of the acetal from two equivalents of [M]-H and CO₂ (steps (i) + (ii), Scheme 36) is exergonic with $\Delta G^0 = -19.0$ kcal mol⁻¹ for the Zr complex, while it is endergonic for the Ni analogue by +42.8 kcal mol⁻¹. Replacing the bulky ^tBu group of the pincer system on Ni led to a more accessible, yet still endergonic reaction by +26.9 kcal mol⁻¹. The thermodynamic barriers (ΔG^\ddagger) for step (ii) were calculated to equal 23.6 and 62.7 kcal mol⁻¹ for the Zr-H and Ni-H, respectively. These calculations explained why the bis-nickel acetal was never observed in contrast to the Zr analogue.⁸⁹

4.2. Hydroelementation to formaldehyde and reductive functionalization

While the formation of **BZrA 1** is favourable as shown in experiments and upon DFT calculations, it is not stable at room temperature, in contrast to **BTaA 1**, **BTaA 2** and **BNbA 1**. The reaction of group IV elements toward CO₂ has been studied for a long time, with an early report in the 1970s.¹³⁹ Using Schwartz's reagent as the reductant, CO₂ was readily reduced to formaldehyde at room temperature (Scheme 41).^{139a,b} Besides the formation of a [ZrOZr] complex, the proof for the formation of formaldehyde was obtained by *in situ* condensation with 5,5-



Scheme 41 Condensation of a cyclohexanedione with formaldehyde generated from CO₂ hydrozirconation.



dimethylcyclohexane-1,3-dione to afford the corresponding maledone compound **16** which displays a methylene-bridged structure. This study reported the actual first example of reductive CO₂ functionalization.^{139a,140}

4.3. Hydrophosphination

CO₂ hydrophosphination was reported to afford the corresponding formate compound.¹⁴¹ Despite similar electronegativity values for P and H atoms, 1,3,2-diazaphospholene (NHP-H) exhibits zwitterionic properties¹⁴² leading to the 2e⁻ reduction of CO₂ into a phosphorus formate moiety in high yield (93% isolated yield). However, no further reduction to the 4, 6 or 8e⁻ reduction levels was evidenced. One can imagine that further structural modification would be necessary to achieve further reduction.

4.4. Conclusion

In conclusion, the 4e⁻ hydroelementation with early TM presented in this section stands out by the fact that (i) only four examples were reported so far; (ii) formaldehyde is spontaneously released at low temperature from **BZrA 1**; and (iii) the insertion of CO₂ into the early TM hydride bond is uncatalyzed.

As perspectives, hydroelementation of CO₂ to the 4e⁻ reduction level might offer a wide range of reactivity *via* the modification of the coordination sphere of the metal fragment.

5. Hydrogenation

The hydrogenation of CO₂ into HCOOH, HCHO, CH₃OH and CH₄ are reactions of utmost importance in the actual momentum of producing green H₂ from water electrolysis.^{13f,15a,16a,143} As opposed to hydroelementation, hydrogenation of CO₂ is a 100% atom economical reaction making CO₂ perfectly fitted to store energy and/or to afford key C₁ building blocks for the chemical industry. As a consequence, these transformations have been intensively investigated but for

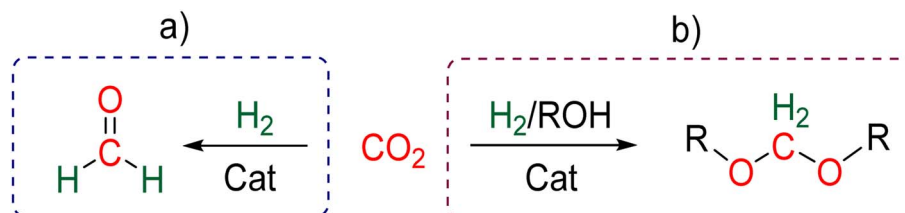
formaldehyde synthesis. There are indeed currently only five catalytic systems, including heterogeneous and homogeneous processes, which have reported the generation and detection of formaldehyde in CO₂ hydrogenation (Scheme 42a). These systems are presented in Section 5.1. Three of these examples generated formaldehyde as the major product and none disclosed its isolation. Reasons are because of (i) the disfavoured thermodynamic parameters in gas and in liquid phases, (ii) the highly reactive nature of formaldehyde and (iii) its volatility as a gas under atmospheric conditions.

To circumvent such hurdles, the hydrogenation reaction conducted in the presence of alcohol as the solvent and co-reactant led to the stabilization of the 4e⁻ reduction stage in the form of acetals (Scheme 42b) as described in Section 5.2, which is in line with the formation of BSA and BBA presented in the previous sections. The specific roles of H₂ and alcohol are thoroughly explained in the mechanism described in Section 5.2.3.

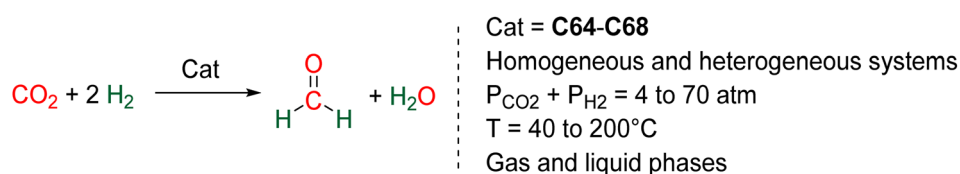
5.1. Hydrogenation of CO₂ into formaldehyde

Catalysts **C64–C68** were reported to generate formaldehyde from CO₂ hydrogenation (Scheme 43). The catalytic conditions and performances are presented in Table 5. It is worth mentioning that the origin of the detected HCHO was not confirmed with ¹³CO₂ labelling experiments in any of these cases.

C65,¹⁴⁵ **C67**¹⁴⁷ and **C68**¹⁴⁸ gave rise to the generation of formaldehyde as the major product. **C64**¹⁴⁴ is the only reported molecular homogeneous system and operates in liquid media similarly to **C67** and **C68**, while **C65** and **C66**¹⁴⁶ operate in the gas phase. Reaction temperatures range between 40 and 200 °C, while the total gas pressure ($P_{\text{CO}_2} + P_{\text{H}_2}$) ranges between 4 and 70 atm. The positive impact of a high $P_{\text{H}_2}/P_{\text{CO}_2}$ ratio on the selectivity toward HCHO formation is a common feature observed for **C64**, **C65** and **C67**. It can also be noticed that both selective systems, **C65** and **C67**, relied on a Pt-based catalyst system. The small number of catalytic systems and their disparities preclude



Scheme 42 CO₂ hydrogenation into 4e⁻ reduction products: (a) formaldehyde (Section 5.1) and (b) acetals (Section 5.2).



Scheme 43 CO₂ hydrogenation into formaldehyde catalysed by **C64–C68**.

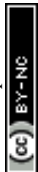


Table 5 Properties of reported systems for CO₂ hydrogenation into formaldehyde catalysed by C64–C68

| | K[Ru(EDTA-H)Cl]·H ₂ O | Pt–Cu/SiO ₃ | Ni–Co NPs | Pt–Ni and Pt–Cu/Al ₂ O ₃ | Ru/LDH |
|-----------------------------------|--|--|---|--|--|
| Catalytic systems | C64 ¹⁴⁴ | C65 ¹⁴⁵ | C66 ¹⁴⁶ | C67 ¹⁴⁷ | C68 ¹⁴⁸ |
| Performances | Rate = 2.79×10^{-2} M h ⁻¹ | 5.22×10^{-3} M g _{cat} ⁻¹ h ⁻¹ | CO ₂ conv. = 0.24% HCHO ratio = 30% | 0.41×10^{-5} M g _{cat} ⁻¹ h ⁻¹ | 0.037 M g _{cat} ⁻¹ h ⁻¹ |
| T (°C) | 40 | 150 | 200 | 25 | 50 |
| P _{CO₂} (atm) | 17 | 0.3 | 1 | 4 | 10 |
| P _{H₂} (atm) | 17 | 5.7 | 3 | 66 | 10 |
| Medium | H ₂ O | CO ₂ gas | CO ₂ gas | CH ₃ OH | H ₂ O |
| HCHO as the major product? | No | Yes | No | Yes | Yes |

further general considerations. C64–C68 systems are described separately hereafter in a chronological order.

The first report of formaldehyde generation dates back to 1989 with the use of the homogeneous Ru-based catalyst C64.¹⁴⁴ The reaction was performed in water at 40 °C with a total gas pressure ($P_{\text{CO}_2} + P_{\text{H}_2}$) of 34 atm. Under these catalytic conditions, CO₂ hydrogenation led to the generation of HCOOH and HCHO which then decomposed into CO and H₂O. The generation of CO was monitored by GC analysis while formation of HCOOH and HCHO was followed spectrophotometrically upon reaction with Nash's reagent.¹⁴⁹ Kinetic investigation showed that the decrease of P_{CO_2} while keeping P_{H_2} constant led to a rate increase in HCHO formation. The initial rate of formation of formaldehyde was measured at 2.79×10^{-2} M h⁻¹ using 1 mmol of catalyst loading with an estimated activation energy of 8.3 kcal mol⁻¹. The rate of formation of formaldehyde was found to be lower than its rate of decomposition, explaining the lack of formaldehyde build-up within the system. In addition, the rate of formation of formic acid was always higher than that of formaldehyde explaining the favoured selectivity towards formic acid. In 2001, an impregnated Pt/Cu (ratio = 0.03) on SiO₂ surface (C65) was shown to afford formaldehyde and methanol with a total gas pressure ($P_{\text{CO}_2} + P_{\text{H}_2}$) of 6 atm in the gas phase.¹⁴⁵ The reaction was monitored by temperature programmed surface reaction spectroscopy indicating an optimum temperature of 150 °C for the formation of formaldehyde. While methanol was favoured at a $P_{\text{H}_2}/P_{\text{CO}_2}$ ratio of 3, the selectivity was reversed when this ratio was increased to 20. At this ratio, the rate of formation reached 0.12 g_{cat}⁻¹ h⁻¹ for methanol and 5.22×10^{-3} g_{cat}⁻¹ h⁻¹ for formaldehyde, respectively. In the absence of Pt, the analogous Cu-based catalyst afforded only methanol. The importance of Pt in the formation of formaldehyde was attributed to the known ability of Pt to adsorb H₂. Indeed, the Pt activation of H₂ along with a higher pressure of H₂ was proposed to favour a higher concentration of H₂ in the proximity of the Cu centres, responsible for shifting the product formation from methanol to formaldehyde. These observations suggest that the formation of formaldehyde and methanol follows two distinct competitive pathways and that the accessibility of activated H₂ is part of the rate determining step for formaldehyde but not for methanol. In 2015, bimetallic Ni–Co nanoparticles (NPs) (C66) were produced in a bottom-up approach and their ability to catalyse CO₂ hydrogenation was studied.¹⁴⁴ Their catalytic activity was evaluated after deposition of the Ni–Co NPs on a mesoporous silica support and exposition to a CO₂:H₂:He (6.6:20.7:14.7) gas mixture at a total pressure of 6 atm. At 200 °C, a low conversion of CO₂ (0.24%) was observed by GC analysis with 30% selectivity for formaldehyde and 70% selectivity for CO generated as the major product. Only a trace amount of formaldehyde was detected upon increasing the temperature to 350 °C. Pt–Ni and Pt–Cu (C67) catalysts selectively afforded formaldehyde in methanol medium at 25 °C and a total gas pressure ($P_{\text{CO}_2} + P_{\text{H}_2}$) of 70 atm.¹⁴⁷ The catalysts were prepared by a wet impregnation method using γ -alumina as the support. The final Pt–Ni and Pt–Cu supported catalysts contained 10 wt% Ni or Cu content and 1 wt% Pt content. Once again, a high $P_{\text{H}_2}/P_{\text{CO}_2}$ ratio (16) led to the generation of formaldehyde with a molar yield of



$0.9 \times 10^{-4} \text{ M g}_{\text{cat}}^{-1}$ in 22 h corresponding to $0.41 \times 10^{-5} \text{ M g}_{\text{cat}}^{-1} \text{ h}^{-1}$. This activity is still lower than the one reported with the C65 catalyst ($5.22 \times 10^{-3} \text{ M g}_{\text{cat}}^{-1} \text{ h}^{-1}$).

Compound C68 is a heterogeneous catalyst consisting of highly dispersed Ru on layered double hydroxide (LDH). The use of 0.5 wt% Ru was recently shown to catalyse the hydrogenation of CO_2 ($P_{\text{CO}_2} = 10 \text{ atm}$, $P_{\text{H}_2} = 10 \text{ atm}$) into $0.446 \text{ M g}_{\text{cat}}^{-1}$ of formaldehyde in water as the solvent in 12 h, corresponding to $0.037 \text{ M g}_{\text{cat}}^{-1} \text{ h}^{-1}$.¹⁴⁸ The detection and quantification of formaldehyde was performed using the colorimetric method with 3-methyl-2-benzothiazolinone hydrazone (MBTH) and high-performance liquid chromatography (HPLC), respectively. In the same study, dihydrogen was replaced by glycerol as a transfer hydrogenation reagent. In a 0.2 M aqueous glycerol solution, catalytic transfer hydrogenation (CTH) of CO_2 afforded formaldehyde in a slightly better yield at 0.1 and 3 wt% Ru under otherwise the same conditions. It is worth mentioning that in the proposed mechanism, initiation of the reaction *via* the dehydrogenation of glycerol into the C_3 carbohydrate dihydroxyacetone (DHA) or glyceraldehyde is proposed. However, the possibility that glycerol – notably *via* the generation of these carbohydrates – could be a source of formaldehyde prior to the CTH of CO_2 was not investigated.¹⁵⁰

5.2. Hydrogenation of CO_2 into acetals

As presented above, the selective $4e^-$ hydrogenation of CO_2 into HCHO is still a widely open challenge. In contrast, the selective $4e^-$ hydrogenation of CO_2 into acetal was pioneered rather recently in 2016 and 2017 with homogeneous Ru- and Co-based catalytic systems.¹⁵¹ The formation of an acetal from CO_2 hydrogenation consists in the addition of alcohol to stop at the $4e^-$ reduction stage with the formation of acetal species (Scheme 42b). Mechanistic investigations have shown that formaldehyde is never formed during the process which alternates between reduction (hydrogenation) and functionalization (with the alcohol) steps giving rise to the acetal. The interest in the formation of dialkoxymethane derivatives is dual. First, it provides a selective access to formaldehyde since some of them were found to release HCHO in strong acidic media,¹⁵³ although to our knowledge, the proof of concept from CO_2 has never been reported. Second, dialkoxymethane derivatives are compounds of interest as fuel additives to lower the formation of soot because of their high oxygen content and the absence of C–C bonds.^{151,153} The catalytic performances of the reported systems, the in-depth optimization of the catalytic conditions, the proposed mechanism and the extent of the scope of alcohols employed are presented hereafter.

5.2.1. Catalytic systems for CO_2 hydrogenation into dimethoxymethane (DMM). Currently, 10 catalytic systems (C69–C78) have been reported for the hydrogenation of CO_2 in the presence of methanol as the solvent and co-substrate affording dimethoxymethane (DMM). Their structures are depicted in Fig. 5 and the catalytic conditions and performances are reported in Table 6. It must be noted that in all reported studies, the reactions were monitored by ^1H and ^{13}C NMR spectroscopy and the products characterized and quantified *in situ*.

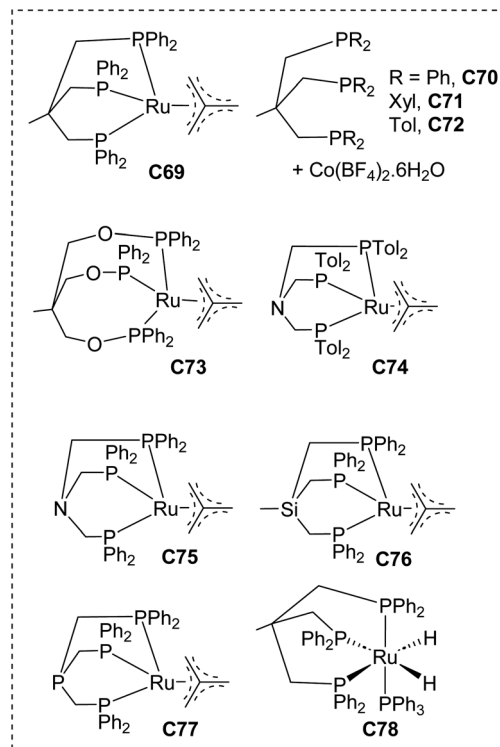


Fig. 5 Catalytic systems C69–C78 leading to the hydrogenation of CO_2 into DMM.

The characteristic methylene signal of DMM was observed at 4.39 ppm in the ^1H NMR analysis in CD_3OD . With the Ru-based precatalyst C69 featuring a triphosphine ligand (Scheme 44) and a Lewis acid co-catalyst ($\text{Al}(\text{OTf})_3$), the hydrogenation of CO_2 in methanol was shown to afford the $2e^-$ reduction product methoxyformate (MF) and the $4e^-$ reduction product dimethoxymethane (DMM) (Scheme 5).^{151a} Among the different conditions tested (variation of the Ru-based precatalyst, temperature, pressure, nature of the acid and time), the best TON of 214 was found with C69 under the following conditions: $P_{\text{CO}_2} = 20 \text{ atm}$, $P_{\text{H}_2} = 60 \text{ atm}$, 18 h, $80 \text{ }^\circ\text{C}$, 2 mL of CH_3OH , 12.5 μmol of Ru-based precatalyst and 25 μmol of $\text{Al}(\text{OTf})_3$ (Table 6, entry 1). The selectivity toward DMM *vs.* MF was 67%. Following this initial report, catalytic systems C70–C78 were investigated in the same reaction (Fig. 5).

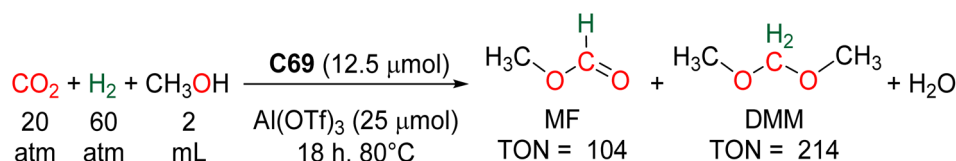
Pre-catalysts C70–C72 are Co-based in contrast to all the other catalysts which are Ru-based.^{151b} C70–C72 were found to generate DMM with slightly lower TON of 92 to 157 than C69 (Table 6, entries 2–4 *vs.* entry 1, resp.), with an interesting maximal selectivity of 81% for DMM. Better TONs were observed by replacing $\text{Al}(\text{OTf})_3$ with $\text{HN}(\text{Tf})_2$ as the acid, longer reaction time (22 h) and a higher temperature ($100 \text{ }^\circ\text{C}$). The impact of the triphosphine ligand was also probed. The use of triphosphine ligands featuring $\text{P}(\text{Xyl})_2$ and $\text{P}(\text{Tol})_2$ moieties increased the TON to 120 and 157 for C71 and C72, respectively. Optimization of the Ru-based system was further explored in detail by another group.^{154–156} C73–C75 were tested in a first study.¹⁵⁴ While the phosphinite moieties in C73 gave lower TONs than the other reported catalytic systems (Table 6, entry 5), replacement of the



Table 6 Catalytic conditions and performances of C69–78

| Entry | Cat, <i>n</i> (μmol) | Acid, <i>n</i> (μmol) | <i>P</i> _{H₂} (atm) | <i>P</i> _{CO₂} (atm) | <i>V</i> _{CH₃OH} (mL) | Time (h) | <i>T</i> (°C) | TON | TOF (h ⁻¹) | Sel ^a (%) | Ref. |
|-------|----------------------|------------------------------|---|--|---|----------|---------------|------|------------------------|----------------------|------|
| 1 | C69, 12.5 | Al(OTf) ₃ , 25 | 60 | 20 | 2 | 18 | 80 | 214 | 12 | 67 | 151 |
| 2 | C70, 15 | HN(Tf) ₂ , 45 | 60 | 20 | 2 | 22 | 100 | 92 | 4 | 74 | 151b |
| 3 | C71, 15 | HN(Tf) ₂ , 45 | 60 | 20 | 2 | 22 | 100 | 120 | 5 | 79 | 151b |
| 4 | C72, 15 | HN(Tf) ₂ , 45 | 60 | 20 | 2 | 22 | 100 | 157 | 7 | 81 | 151b |
| 5 | C73, 1.5 | Al(OTf) ₃ , 6.25 | 60 | 20 | 0.5 | 18 | 80 | 32 | 2 | 28 | 154 |
| 6 | C74, 1.5 | Al(OTf) ₃ , 6.25 | 60 | 20 | 0.5 | 18 | 80 | 221 | 12 | 71 | 154 |
| 7 | C75, 1.5 | Al(OTf) ₃ , 6.25 | 60 | 20 | 0.5 | 18 | 80 | 292 | 16 | 72 | 154 |
| 8 | C75, 1.5 | Al(OTf) ₃ , 6.25 | 90 | 5 | 0.5 | 18 | 90 | 97 | 5 | 92 | 154 |
| 9 | C75, 0.38 | Al(OTf) ₃ , 1.56 | 90 | 20 | 0.5 | 18 | 90 | 786 | 44 | 60 | 154 |
| 10 | C75, 0.075 | Al(OTf) ₃ , 3.576 | 105 | 12.5 | 0.55 | 21 | 105 | 2761 | 131 | 61 | 155 |
| 11 | C75, 0.75 | Al(OTf) ₃ , 35.76 | 100 | 15 | 0.5 | 20 | 100 | 3874 | 194 | 73 | 155 |
| 12 | C76, 0.38 | Al(OTf) ₃ , 3.13 | 90 | 20 | 0.5 | 18 | 90 | 685 | 38 | 60 | 156 |
| 13 | C77, 0.38 | Al(OTf) ₃ , 3.13 | 90 | 20 | 0.5 | 18 | 90 | 439 | 24 | 46 | 156 |
| 14 | C78, 3.1 | Al(OTf) ₃ , 25 | 20 | 100 | 5 | 20 | 100 | 1176 | 59 | 70 | 157 |

^a Selectivity = TON(DMM)/[TON(MF) + TON(DMM)].



Scheme 44 DMM synthesis with C69.

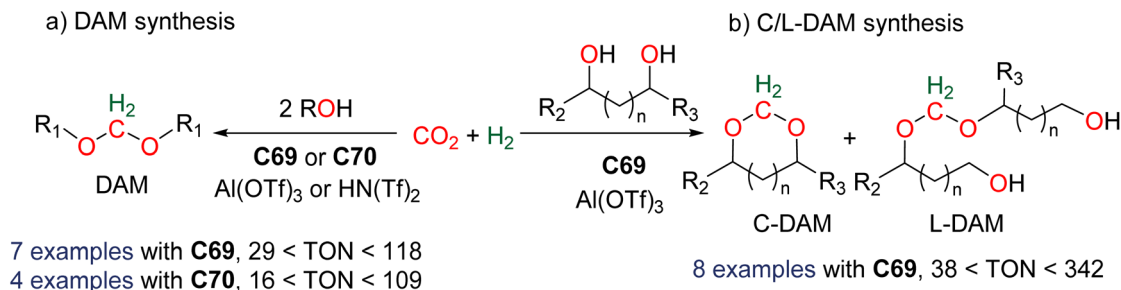
central C atom of the backbone of the ligand by a N atom in C74 and C75 enabled slight increase of the TON to 221 and 292, respectively (Table 6, entries 6 and 7). With C75, the optimization conditions led to a net increase of either the selectivity for DMM to 92% but with a TON of 97 (Table 6, entry 8) or of the TON to 786 but with a selectivity for DMM reduced to 60% (Table 6, entry 9). The quantities of the catalyst and co-catalyst were shown to be the main factor enabling this TON increase. In this optimization study for C75, all possible parameters were carefully optimized individually (univariate optimization) to improve the TON from 214 to 786 (Table 6, entries 1 and 9, resp.) which represents a 367% increase in TON. A subsequent study using a multivariate optimization led to a larger improvement of TON. The pre-catalyst C75 indeed provided TONs of 2761 and 3874 with a 10 fold increase of the scale of the reaction leading to the formation of 2.88 mmol of DMM (Table 6, entries 10 and 11, resp.).¹⁵⁵ This corresponds to a significant improvement of further 493% from the univariate optimization (Table 6, entry 9). These impressive results were made possible mainly by acting on the quantities of the catalyst and co-catalyst. In another report, the replacement of the heteroelement of the backbone by Si or P atoms (C76 and C77, respectively) did not enable any further increase of the catalytic performances or selectivity (Table 6, entries 12 and 13).¹⁵⁶ In order to have a closer look at the active catalyst, dihydride compound C78 was synthesized and tested (Table 6, entry 14).¹⁵⁷ Pre-catalysts C69–77 are indeed sought to generate M–H species which act as the active catalyst in the reaction. This study showed the beneficial aspect of adding tertiary phosphine or phosphite in order to prevent catalyst deactivation by the

formation of a carbonyl ligand from the CO₂ decarbonylation. Overall, optimization strategies presented with catalysts C69–C78 were dedicated to the improvement of TON as the most important parameter. Although interesting selectivities of DMM vs. MF were obtained, the lesser attention to this parameter can be explained by the possibility of hydrogenating MF into DMM in a second step.^{154,156} However, the TOF parameter was not optimized. As indicated in Table 6, it ranges between 2 and 194 h⁻¹, leaving room for improvement in these systems.

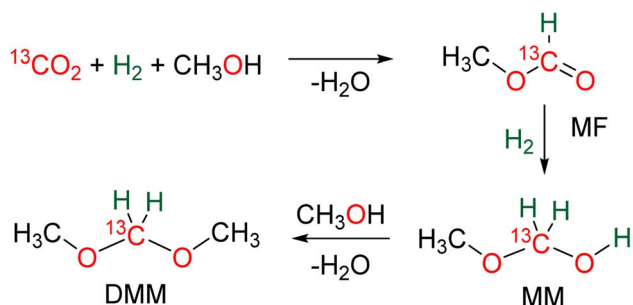
5.2.2. Extension to other dialkoxyethanes (DAMs). Other alcohols beside methanol were tested to generate dialkoxyethane (DAM) compounds. Using C69^{151a} and C70 (Fig. 5),^{151b} 11 examples were obtained and characterized with TON ranging from 16 to 118 (Scheme 45a). Aliphatic alcohols used included linear chain (containing 2 to 10 carbon atoms), branched (^tBuOH and ⁱPrOH) and benzyl alcohol. In a subsequent study, the authors used bio-sourced diols to increase the sustainability of the process and the product scope.¹⁵⁸ These diols were shown to afford either a cyclic acetal (C-DAM) or a linear acetal (L-DAM) (Scheme 45b). In total, eight products were characterized and selectivity toward either C-DAM or L-DAM was reached depending on the nature of the diol substrate (*n* = 1–6). A selectivity of 92% was notably observed toward the formation of the C-DAM, 4-methyl-1,3-dioxane, while reversed selectivity of 99% to L-DAM was obtained with the diol featuring a 5-carbon linker.

5.2.3. Mechanism. In the initial description of the formation of DMM from CO₂, the intermediary of methoxyformate (MF) and methoxymethanol (MM) was demonstrated





Scheme 45 Synthesis of (a) linear DAM with C69 or C70 and (b) cyclic or linear C-DAM or L-DAM, respectively, with C69.



Scheme 46 Proposed mechanism for the formation of DMM.

(Scheme 46).^{151a} MF and MM were indeed observed during the reaction and the expected ¹³C-labelled products and intermediates were characterized when starting from ¹³CO₂ and ¹²CH₃OH reactants. In this reaction mechanism, formaldehyde was not an intermediate. One methanol molecule was indeed involved in the first reduction step leading to MF. Compared to formic acid, the methylated analogue MF was hypothesized to “activate” this reduction stage enabling further hydrogenation into MM under rather mild conditions compared to the CO₂ hydrogenation reaction to methanol in the absence of alcohol. It is reminiscent of pioneering strategies using alcohol¹⁵⁹ or amine^{20b,160} to promote the hydrogenation of CO₂ into methanol under mild conditions in cascade reactions. One additional molecule of methanol is finally reacted with the MM intermediate affording DMM.

Two recent in-depth studies published concomitantly in 2021 proved to be particularly complementary since one is an experimental investigation of the most used C75/Al(OTf)₃ catalytic system,¹⁶¹ while the other is a DFT investigation on the Co-based C70/HN(Tf)₂ system.^{153b} It is noteworthy that these studies confirmed the elementary steps proposed initially in 2016. The C75/Al(OTf)₃ catalytic system was investigated by *in situ* infrared (IR) spectroscopy at three relevant temperatures: 333 K, 353 K and 373 K enabling the determination of rate constants and activation parameters for the three steps: CO₂ to MF, MF to MM and MM to DMM.¹⁶¹ These key steps were included in a reaction network analysis. The rate determining step (rds) was shown to be the first CO₂ to MF step with an activation parameters Δ*G*[#] (333 K) of 119.0 kJ mol⁻¹ and the lowest rate constant of 1.41 × 10⁻⁶ s⁻¹ M⁻² at the same temperature. In accord with the experiment, the competitive

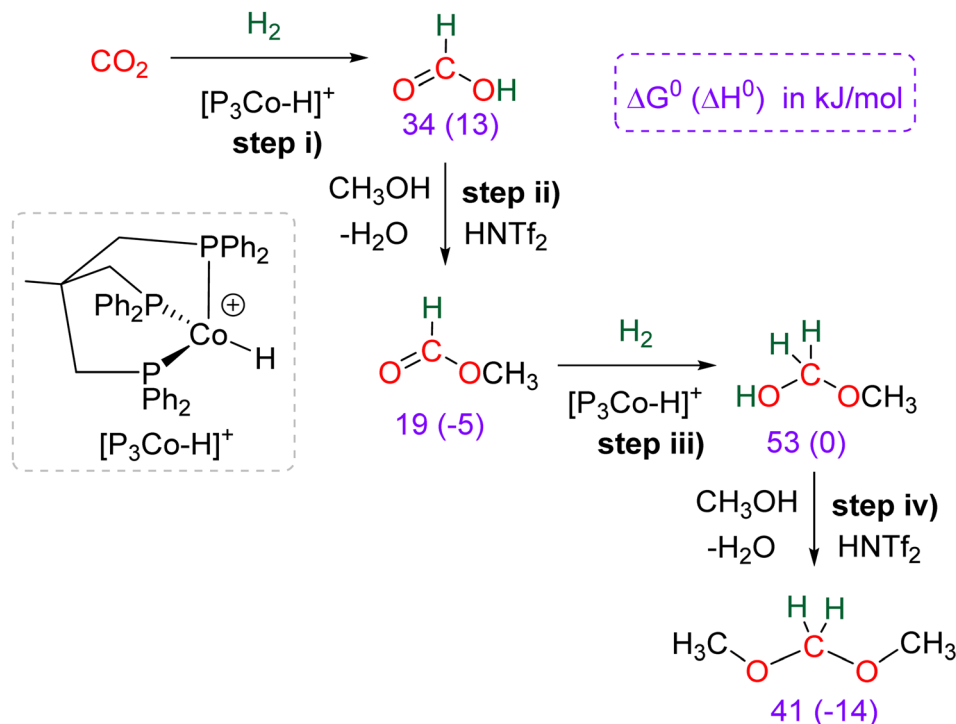
formation of CH₃OH from the hydrogenation of MM was shown to be accessible at higher temperature and the formation of DMM was favoured by the large excess of CH₃OH used as the solvent. Furthermore, this reaction network analysis was also used as a predictive tool to propose new experimental conditions that would favour one product over the other. The positive effect of H₂O removal on the formation of DMM was notably proposed.

The DFT study of the C70/HN(Tf)₂ system proposed a detailed kinetic and thermodynamic analysis of each elementary step accounting for the formation of DMM but also for the over-reduction to CH₃OH.^{153b} The thermodynamic values Δ*G*⁰ for the subsequent formation of formic acid, MF, MM and DMM, indicated in Scheme 47, have been calculated to be 34, 19, 53 and 41 kJ mol⁻¹, respectively. A major input of this study was to define the exact role of the TM-based catalyst and the acid co-catalyst. The active Co-based species were calculated to be the monohydride cationic Co complex ([P₃Co-H]⁺) depicted in Scheme 47 (purple box) and was calculated to be the catalyst responsible for the hydrogenation of CO₂ into formic acid and of MF into MM. The two steps (i) and (iii) have been calculated with Δ*G*[#] of 79 and 98 kJ mol⁻¹, respectively. On the other hand, the esterification of formic acid into MM (step ii) and the etherification of MM into DMM (step iv) are catalysed by the acid catalyst HN(Tf)₂. It was found that the methylating agent responsible for the etherification of MM to DMM was not directly methanol, but CH₃O-NTf₂ *in situ* generated from the reaction of CH₃OH with HN(Tf)₂. Nonetheless, the calculated Gibbs free energy barrier from the most stable Co-formate species is 179 kJ mol⁻¹ for the last step (iv), making it the rate determining step (rds) of the whole process. As in the previous study, the access to DMM *via* formaldehyde was calculated to be higher in energy and thus discarded. The formation of formaldehyde as an intermediate to DMM was proposed in a related Ru-based system using ethanol instead of methanol, but not with the same level of kinetic or thermodynamic investigations.¹⁶²

5.3. Conclusion

In conclusion, the selective 4e⁻ reduction of CO₂ by hydrogenation stands out for several reasons: (i) the development of highly active catalytic systems resulting in the reduction of CO₂ into acetals, achieving the highest reported turnover number (TON) of 3874 for this reduction stage, following extensive





Scheme 47 Mechanism of formation of DMM based on calculations.

optimization studies; (ii) the synthesis of acetals, which are of interest as fuel additives, in contrast to bis(silyl)acetal (BSA) and bis(boryl)acetal (BBA) compounds that lack known applications. Consequently, a variety of DAM derivatives have been synthesized, utilizing various alcohols, particularly those derived from biomass.

As perspectives, future endeavours could focus on broadening the applicability of DAM, encouraging additional investigations into acetal syntheses *via* CO₂ hydrogenation, and exploring diverse catalytic processes beyond [P₃Ru] and [P₃Co] systems.¹⁶³ It would be intriguing to explore the potential use of the generated acetal as both C₁ and C_n sources, similar to what has been described with BSA and BBA. However, the hydrogenation of CO₂ into formaldehyde is still in its early stages, with only three selective systems described so far, operating in gas or liquid phases, involving catalysts C65, C67, and C68. Moreover, no isolation or utilization of the generated formaldehyde has been reported to date. Given its perfect atom efficiency and the reactive nature of formaldehyde, the primary challenge lies in developing an efficient system for hydrogenating CO₂ into formaldehyde, enabling its isolation and/or utilization.

Finally, although the processes of 4e⁻ reduction of CO₂ into formaldehyde and into acetal are at very different stages of maturity, it is noteworthy that the stabilization of the 4e⁻ reduction stage in the form of acetal parallels the stabilization of monomeric formaldehyde (HCHO) in the form of acetals of various lengths in formalin solution – the common commercial source of formaldehyde for chemical or biochemical transformations.^{24–26,128a–130,132,164} It is indeed noticeable that the two examples described in liquid medium for the

hydrogenation of CO₂ with C64 and C67 were conducted in H₂O, CH₃OH or glycerol. Presumably, these solvents stabilize the reactive *in situ* generated monomeric formaldehyde in the form of methanediol or acetal derivatives while avoiding its polymerization as paraformaldehyde.

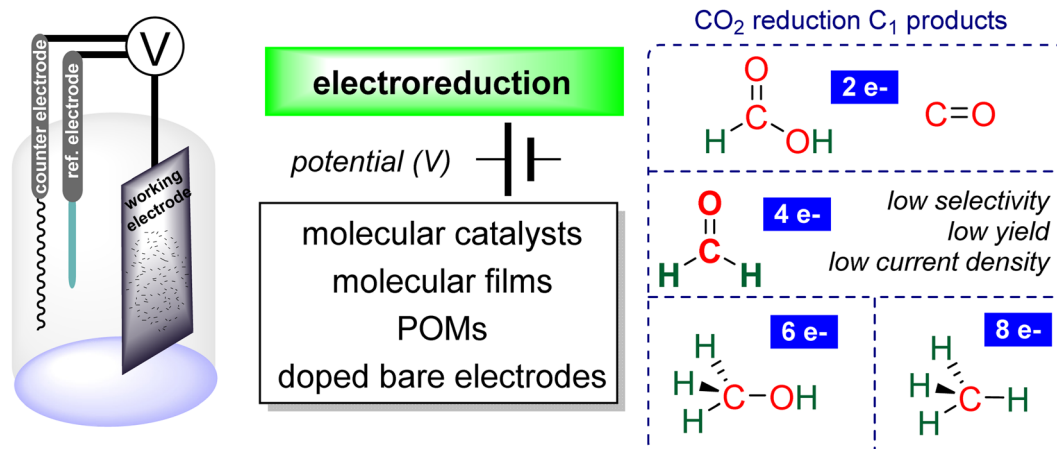
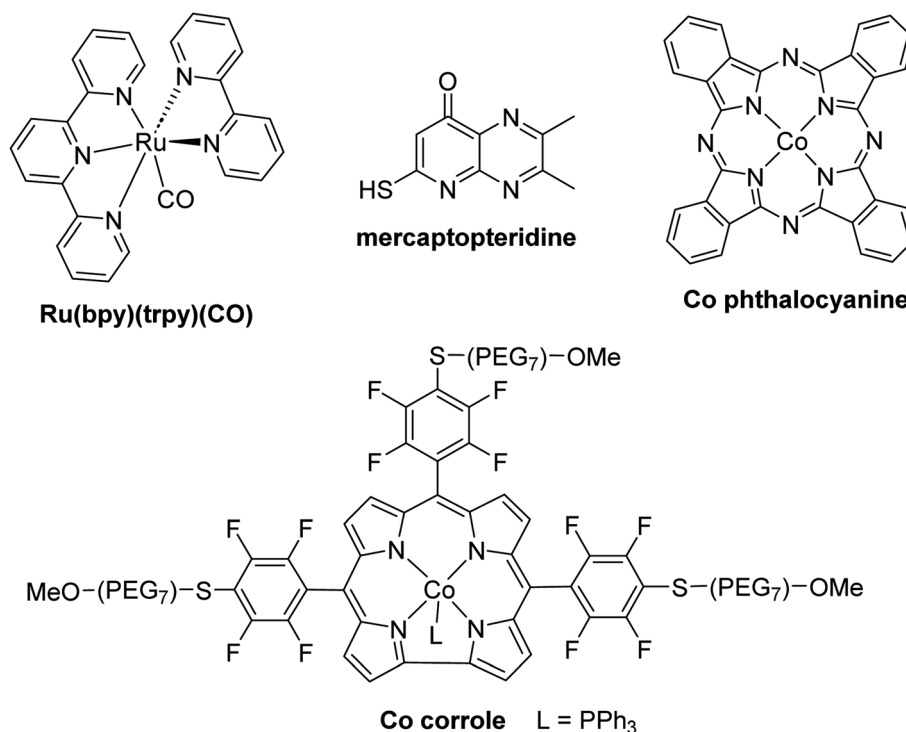
6. Electroreduction

Electrochemical CO₂ reduction reaction (eCO₂RR) offers a green and sustainable approach for converting this gas into various products, under mild conditions (room temperature and pressure) and both in organic or aqueous media. Regarding C₁ products, while the formation of 2e⁻ reduction products has been performed with several catalysts with high selectivity and rate,^{10a} the formation of 4, 6 and 8e⁻ reduction products has been much more rarely observed (Scheme 48).¹⁶⁵ If methanol and methane have been produced in a few cases, formaldehyde remains an elusive product to date.

6.1. Electrocatalytic systems

One of the early examples of CO₂ electrochemical reduction to formaldehyde concerned the use of a Ru based complex with a terpyridine–bipyridine ligand (Fig. 6) which was shown to produce a small amount of HCHO, through the formation of a formyl complex, in a mixture of water and ethanol, at low temperature (–20 °C) upon electrolysis at an Hg pool working electrode ($E = -1.70 \text{ V vs. Ag/AgCl}$).¹⁶⁶ A faradaic efficiency (FE) of *ca.* 5% was obtained for HCHO, while methanol and remarkably C–C coupling products were also identified (H(O)CCOOH, HOCH₂COOH). Unexpectedly, a metal-free organic



Scheme 48 Electrochemical reduction of CO₂ into C₁ products.Fig. 6 Examples of molecular catalysts capable of generating formaldehyde from CO₂ electroreduction.

catalyst, 6,7-dimethyl-4-hydroxy-2-mercaptopteridine (a natural cofactor, Fig. 6) was reported to electrocatalyze CO₂ reduction to various products, including not only formate, but also methanol and formaldehyde (not quantified).¹⁶⁷ The reaction was conducted in a phosphate buffered solution at a reticulated vitreous carbon electrode ($E = -0.65$ V vs. Ag/AgCl), and it was suggested that CO₂ was first reduced to formate, which was subsequently reduced to formaldehyde and methanol (the latter product was obtained with FE 10–23%) *via* a carbamate compound. Recently, a transition metal based polyoxometalate (TOA)₆[a-SiW₁₁O₃₉-Co(_)] (TOA: tetraoctyl ammonium, _ = vacant position at the Co atom) was shown to electroreduce CO₂ under homogeneous

conditions in dichloromethane as the solvent, and a potential of -1.5 V vs. Hg₂Cl₂/Hg at a Hg electrode.¹⁶⁸ In the presence of an acid as a co-reactant (water and H₂SO₄), the products were identified as CO, with about 13% FE, and formaldehyde with a maximum efficiency (FE) of *ca.* 25%. The use of an organic and reducible solvent (which is shown to generate HCHO under an Ar atmosphere), limits the development of the process but this example is an interesting case of molecular electrochemical approach for CO₂-to-HCHO conversion. Another molecular cobalt complex, a Co corrole (triphenylphosphine 5,10,15-tris(2,3,5,6-tetrafluoro-4-(MeO-PEG(7)thiophenyl)), Fig. 6) modified at the para positions with thiol bound poly(ethylene



glycol) chains terminated by methoxy groups was adsorbed at the carbon paper electrode and then investigated for the eCO₂RR into methanol and ethanol.¹⁶⁹ In 0.1 M phosphate buffer solutions with 0.1 M NaClO₄ at potentials ranging from -0.51 V to -0.8 V vs. NHE, low formaldehyde efficiencies from 10 to 1%, respectively, were obtained among other liquid phase products (formate, acetate, glyoxal), corresponding to low current densities (from 0.2 to 0.02 mA cm⁻² respectively).

Another strategy was developed upon polymerizing electrode films of metal complexes at the surface of conductive carbon. Cr, Co and Fe bis-terpyridine complexes bearing the vinyl group were used to grow electroactive films upon oxidation, which were further employed as catalysts in aqueous solutions with 0.1 M NaClO₄.¹⁷⁰ At potentials close to -1.1 V vs. Ag/AgCl, faradaic yields of 28% (Fe), 39% (Co) and 87% (Cr) were reported for formaldehyde, thus showing very high activity for first row transition metals while second and third row transition metals (Ru and Os respectively) gave barely any reactivity, which was assigned to the presence of metal-based redox processes in the former cases compared to ligand-based redox processes in the latter. The CO₂ to CO conversion being now a well-controlled reaction, and CO being a possible intermediate towards formaldehyde production, a parallel approach was developed using CO directly as the reactant and supramolecular catalysts: thin films of Co phthalocyanine and 4,4',4'',4'''-tetracarboxyphthalocyanine made at the carbon fibre were investigated and shown to produce mainly formaldehyde as the CO reduction product with very little methanol, at a potential of -0.7 V vs. SCE (Saturated Calomel Electrode) in sulfuric acid solutions.¹⁷¹ Recently, it was further shown that CO reduction with a phthalocyanine monomer complex also led to formaldehyde with unambiguous confirmation from labelled studies.¹⁷² These results opened the door to understanding the mechanism of formaldehyde pathway from both CO₂ and CO as reactants, with possibilities of tuning the quantity of formaldehyde being produced and the ratio between HCHO and methanol. It also opens the possibility of setting a cascade approach in which the CO produced from CO₂ reduction could further be used to generate HCHO. A very recent study explored such electroreduction of CO to HCHO with Co phthalocyanine deposited at a carbon paper electrode. Upon optimization of the pH (12) and of the electrode potential, a partial current density of 0.64 mA cm⁻² (17.5% faradaic efficiency) was achieved for HCHO, with a maximum ratio between HCHO and CH₃OH of ca. 7.5. Mechanistic insights illustrate that the binding of CO to the metal cobalt site is strong enough for further reducing it, while controlling the amount of protons and the electrode potential is key to favouring formaldehyde formation and release at the expense of methanol production.¹⁷³ A puzzling discovery was made upon direct electroreduction of CO₂ in various solutions (methanol, water and even sea water) at boron doped diamond (BDD) electrodes without any additional catalyst.¹⁷⁴ These materials have several advantages, including a large potential window, high stability and furthermore the presence of sp³-bonded carbon atoms on BDD which are believed to be active sites for triggering chemical transformations. Upon 1 h electrolysis at $E = -1.7$ V vs. Ag/AgCl, a maximum yield (FE) of 74%

was obtained for formaldehyde, along with formic acid and a very small amount of dihydrogen as a by-product. The formaldehyde was deemed to be formed from the 2e⁻ reduction of formic acid initially obtained from CO₂ conversion, while current densities were low, typically in the range of 0.1 to 0.2 mA cm⁻². Finally, an elegant indirect approach has been proposed with methanol as the solvent. While methanol itself was oxidized to formaldehyde in the anodic compartment, electroreduction of CO₂ at the Sn electrode led to formic acid, which reacted with the solvent to give methyl formate. Finally, the latter was reduced to formaldehyde, with faradaic efficiencies for HCHO from 10 to 50% depending on the electrolyte conditions.¹⁷⁵

6.2. Conclusion and perspectives

In conclusion, the electrochemical reduction of CO₂ to formaldehyde poses a formidable challenge, with only a limited number of examples identified thus far. These cases exhibit low yields, low current density, and, in many instances, uncertainties regarding the origin of the produced formaldehyde. The challenge of obtaining formaldehyde also arises from its susceptibility to further transformation at the electrode into more reduced products, such as methanol. Additionally, the precise catalytic mechanisms involved in these processes remain elusive with only very few mechanistic studies.¹⁷³

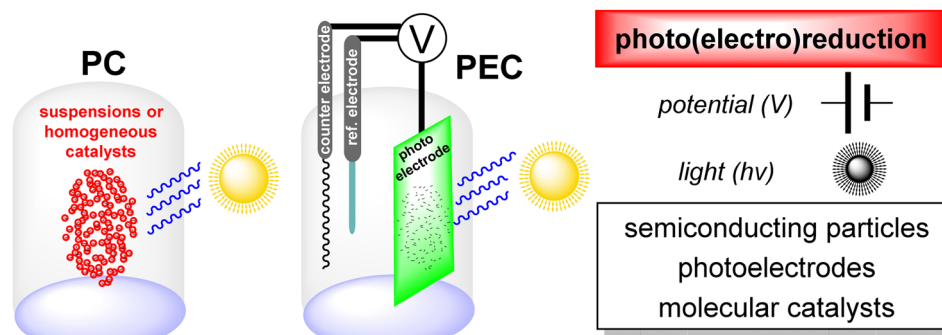
As perspectives, the prospect of *in situ* generating a substantial quantity of formaldehyde under mild conditions across a range of precisely controlled potentials is enticing. This potential development could pave the way for utilizing formaldehyde in subsequent chemical reactions, particularly in coupling reactions. As an early illustrative example, co-reduction scenarios involving CO₂ (or CO) with nitrogen-containing species like nitrite (NO₂⁻)¹⁷⁶ or nitrate (NO₃⁻)^{176b,177} could facilitate C-N bond formation, yielding a diverse array of products, including amines and urea. The exploration of these processes, along with related ones, under the controlled conditions afforded by electrochemistry is poised to yield new and stimulating results.

7. Photo(electro)reduction

The photochemical (PC) and photoelectrochemical (PEC) reduction of CO₂ (Scheme 49), mostly using semiconducting materials, have been extensively studied in the last four decades.¹⁷⁸ However, if compared to other reduction products such as CO or formate, only a limited number of studies so far reported the formation of formaldehyde as a major product and even less studies report a selective HCHO production, mainly because of its high reactivity.¹⁷⁹ Moreover, very few of these studies conducted proper isotope labelled measurements to confirm the origin of the carbon atom, which constitutes a severe drawback.¹⁸⁰

A very early report questioned the possible formation of formaldehyde from water and CO₂ as the first stage of the photosynthetic process forming carbohydrates.¹⁸¹ This study showed that an aqueous solution, free of catalyst, containing carbon dioxide gives formaldehyde when irradiated with





Scheme 49 Photochemical and photoelectrochemical reduction of CO₂.

UV-light ($\lambda = 200$ nm) in a first stage, and that subsequent irradiation with lower energy light ($\lambda = 290$ nm) induced the polymerization of HCHO to sugars. It also showed that the formation of HCHO can be photocatalyzed under visible light through the use of “coloured basic substances” such as malachite-green or methyl-orange. Remarkably, the role of HCHO in the course of the photochemically induced formation of highly reduced compounds from CO₂ was thus already questioned a century ago. Later, a pioneer work reported that using suspensions of various semiconductors (TiO₂, ZnO, CdS, GaP and SiC, Table 7, entries 1–5) in CO₂-saturated purified water, the generation of formic acid, formaldehyde and methanol was observed up to the millimolar concentration range after 7 h of visible light illumination (500 W Xe or Hg lamp).¹⁸² Trace of methane was also detected. The reduction products were quantified by gas chromatography although no labelled experiment was conducted to assert the origin of the products. The yield in methanol was observed to increase as the conduction band (CB) of the material was more negative compared to the reduction potential of the CO₂-to-CH₃OH reaction. A quantum yield of *ca.* 5×10^{-4} was reported for the formaldehyde production with both TiO₂ and SiC photocatalysts. Using semiconductor electrodes polarized at -1.5 V vs. SCE, CO₂ reduction to formic acid, formaldehyde and methanol was also observed with non-illuminated TiO₂ and illuminated GaP. Since this seminal paper, the majority of studies published so far have explored various semiconductors,¹⁹⁸ based on metal and metal oxides, doped or not, eventually in combination with co-catalysts,^{3c,199} in the form of suspensions, bulk materials or thin films. Some other examples, albeit quite rare, employed either a fully molecular, a heterogeneous material or even a photo-enzymatic approach.

7.1. Suspension of a semiconductor

Aqueous suspensions of semiconducting SiTiO₃, WO₃ and TiO₂ under both Hg lamp or natural sunlight were reported to generate a mixture of methanol (a few μmol per hour) and formaldehyde (a few tens of μmol per hour) from dissolved carbon dioxide, as quantified by gas chromatography (CH₃OH) and colorimetric (HCHO) measurements (Table 7, entries 6–8).¹⁸³ Traces of methane were also detected. In a follow-up study,¹⁸⁴ aqueous suspensions of strontium titanate (SrTiO₃)

treated with various transition metal–TiO₂ deposits, namely Rh, Pt, In and Au, and saturated with CO₂ were irradiated with a 75 W Hg-lamp or a solar concentrator. When using Ir oxide as an additive (4.55 mol%), formic acid was the main product with a rate of *ca.* $1 \mu\text{mol h}^{-1}$. With Ru oxide (4.55 mol%) as the additive, methanol was the main product. The highest rate for formaldehyde formation was obtained with SrTiO₃ with 0.5 mole % of lanthanum chromite (LaCrO₃) as an additive (Table 7, entry 9). However, the change in selectivity with the nature of the additive was not discussed. Aqueous suspensions of n-type semiconductors such as bismuth (Bi₂S₃) and cadmium (CdS) sulphides were reported to generate formic acid and formaldehyde at *ca.* 10^{-5} M concentration after 1 h under wide spectrum irradiation (55 mW cm^{-2}) when H₂S was present in the system (Table 7, entries 10 and 11).¹⁸⁵ This was explained by a sequential process producing first formic acid by $2e^-/2\text{H}^+$ transfers then formaldehyde by additional electron transfers. The catalysis, which was shown to be proportional to the light intensity, stopped due to the poisoning deposition of elemental sulphur at the surface of the particles. The formation of HCHO as the only CO₂ reduction product was also observed at a rate up to $0.25 \mu\text{mol h}^{-1}$ with a CO₂ saturated aqueous suspension of TiO₂ at 333 K under 500 W high pressure Xe lamp irradiation (Table 7, entry 12), but the origin of such selectivity is unknown.¹⁸⁶ TiO₂ doping with 0.1 mol% WO₃ further increased this rate up to $0.42 \mu\text{mol h}^{-1}$ (Table 7, entries 13 and 14). The deposition of Rh on TiO₂ led to the formation of HCOOH (major), CH₃OH (secondary) and HCHO (minor) up to a total rate of $0.67 \mu\text{mol h}^{-1}$ (Table 7, entry 15). The doping of TiO₂ with Au was more thoroughly studied. At 7 bars and 80 °C, a reactor containing 0.6 g of 0.1–0.5 wt% loading of Au/TiO₂ composites led to the highest yield of formaldehyde ($270 \text{ mmol kg}_{\text{cat}}^{-1} \text{ h}^{-1}$, Table 7, entry 16).¹⁸⁷ Another study reported the use of a gold nanoparticle decorated TiO₂ photonic crystal as the photocatalyst (Au-PMTiNTs).¹⁸⁸ When irradiated with an AM1.5 G source, methane was the main reduction product ($302 \mu\text{mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$, 89.3% selectivity), whereas, under the irradiation of a UV-poor white lamp, formaldehyde ($420 \mu\text{mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$) and CO ($323 \mu\text{mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$) were the major products (Table 7, entry 17). This so-called optical control of selectivity was explained by the plasmonic effects of the gold surface involving hot electrons but no discussion was made on the hydrogen atom source.



Table 7 Catalytic performance of photochemical and photoelectrochemical systems for CO₂ reduction to formaldehyde^a

| Entry | Catalyst | Loading | Conditions | Light source | Products | Yield ($\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$) | Ref. |
|-------|--|------------------------|---|------------------------------------|-------------------------------------|--|------|
| 1 | TiO ₂ | 1 g/100 mL | Water | 500 W Xe or h.-p. Hg arc lamp | HCOOH CH ₃ OH | n.d 3.3 | 182 |
| 2 | ZnO | 1 g/100 mL | Water | 500 W Xe or h.-p. Hg arc lamp | HCOOH CH ₃ OH | 15.7 5 | 182 |
| 3 | CdS | 1 g/100 mL | Water | 500 W Xe or h.-p. Hg arc lamp | HCHO HCOOH CH ₃ OH | 17.1 n.d 16.7 | 182 |
| 4 | GaP | 1 g/100 mL | Water | 500 W Xe or h.-p. Hg arc lamp | HCHO HCOOH CH ₃ OH | 28.6 n.d 15.7 | 182 |
| 5 | SiC | 1 g/100 mL | Water | 500 W Xe or h.-p. Hg arc lamp | HCHO HCOOH CH ₃ OH | 13.3 n.d 15.7 | 182 |
| 6 | SrTiO ₃ | 4–10 g L ⁻¹ | Water | 70 W h.-p. Hg lamp (>300 nm) | CH ₃ OH HCHO | 1.79 0.01 | 183 |
| 7 | WO ₃ | 4–10 g L ⁻¹ | Water | 70 W h.-p. Hg lamp (>300 nm) | CH ₃ OH HCHO | 1.26 0.05 | 183 |
| 8 | TiO ₂ | 4–10 g L ⁻¹ | Water | 70 W h.-p. Hg lamp (>300 nm) | CH ₃ OH HCHO | 0.51 0.08 | 183 |
| 9 | SrTiO ₃ + 0.5 mole % LaCrO ₃ | 1 g/160 mL | Water | 70 W h.-p. Hg lamp (>300 nm) | HCOOH CH ₃ OH | 0.98 0.065 | 184 |
| 10 | CdS | 0.33 g L ⁻¹ | Water | 100 W quartz-iodine lamp (>350 nm) | HCOOH HCHO | 0.042 1.22 | 185 |
| 11 | Bi ₂ S ₃ | 0.5 g L ⁻¹ | H ₂ S 0.097 M Water | 100 W quartz-iodine lamp (>350 nm) | HCOOH HCHO | 1.95 1.0 | 185 |
| 12 | TiO ₂ (MGB) | 0.3 g | H ₂ S 0.097 M Water | 500 W h.-p. Xe lamp | HCOOH HCHO | 1.58 0.94 | 186 |
| 13 | TiO ₂ + 0.1 mole % WO ₃ | 0.3 g | Water | 500 W h.-p. Xe lamp | HCHO | 1.98 | 186 |
| 14 | TiO ₂ + 2 mole % WO ₃ | 0.3 g | Water | 500 W h.-p. Xe lamp | HCHO | 1.18 | 186 |
| 15 | 1 mole % Rh/TiO ₂ | 0.3 g | Water | 500 W h.-p. Xe lamp | HCOOH CH ₃ OH | 0.69 0.53 | 186 |
| 16 | 0.1 wt% Au/TiO ₂ | 0.6 g/1.2 L | Water, Na ₂ SO ₃ 0.85 g L ⁻¹ 80 °C 7 bar CO ₂ | med.-p. Hg lamp (254–364 nm) | HCHO HCOOH CH ₃ OH | 0.37 148 721 | 187 |



Table 7 (Contd.)

| Entry | Catalyst | Loading | Conditions | Light source | Products | Yield ($\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$) | Ref. |
|-----------------|---|--|---|------------------------------------|--|--|------|
| 17 | Au/TiO ₂ NT photonic crystals | 85 $\mu\text{g Au}$ per TiO ₂ wafer | Water vapor | 50 W white-cold LED (>400 nm) | CO | 323 | 188 |
| 18 | TiO ₂ | 0.5 g L ⁻¹ | Water 80 °C 7 bar CO ₂ | 125 W med.-p. Hg lamp (254–364 nm) | HCHO HCOOH HCHO | 420 102 2954 | 189 |
| 19 | TiO ₂ /ZrO ₂ (ZrO ₂ 40 weight%) | 0.2 g spread on a Cu plate | “Wet” (70% humidity) | Real sunlight | CH ₃ OH HCHO | 16 537 732 | 190 |
| 20 | NaTaO ₃ -C (annealed at 650 °C) | 100 mg/200 mL | Water | Pen ray lamp (254 nm) | HCHO | 1392 | 191 |
| 21 | Pd/TiO ₂ -Fe ₂ O ₃ | 0.05 g/50 mL | Water pH 8.5 Na ₂ CO ₃ | 500 W Xe lamp | HCHO | 33.5 | 192 |
| 22 | CoPe/TiO ₂ (1% mass ratio, calcined at 400 °C) | 10 g/100 mL | 0.1 N NaOH aq. sln | 500 W tungsten-halogen lamp | C ₂ H ₅ OH CH ₃ CO ₂ H HCOOH | 101.7 51 15.7 | 193 |
| 23 | RuL10H/TiO ₂ (0.125 μM Ru complex per g_{cat}) | 10 mg/10 mL | 0.8 mM TEOA aq. sln | 250 W lamp (>420 nm) | CO CH ₃ OH CH ₄ | 1 0.5 0.8 | 194 |
| 24 | Sn ₇₅ -Cu ₂₅ /C ₃ N ₄ | 1.5 mg/3.5 mL | 0.1 M KHCO ₃ | 300 W Xe lamp (>420 nm) | HCHO | 2.5 | 195 |
| 25 ^b | K ₂ Ti ₆ O ₁₃ + 0.3 wt% Pt | 0.3 g/4 mL | Water r.t. | 150 W Hg-lamp | H ₂ | 68 | 196 |
| 26 ^b | Cu/ZnO/K ₂ Ti ₆ O ₁₃ + 0.3 wt% Pt | 0.3 g/4 mL | Water r.t. | 150 W Hg-lamp | HCOOH CH ₄ HCHO | 0.23 0.2 0.476 | 196 |
| 27 ^b | K ₂ Ti ₆ O ₁₃ + 0.3 wt% Pt | 0.3 g/4 mL | Water 274 °C | Concentrated sunlight | H ₂ HCOOH CH ₄ HCHO | 17 3.04 0.27 0.57 | 196 |
| 28 | TiO ₂ | 30 mg/20 mL | Aq. sln pH 6.5, NADH 5 mM, [Cp*Rh(bpy)(H ₂ O)] ²⁺ , 0.25 mM | 23 W UV lamps (max 365 nm) | HCHO (PB buff.) HCHO (NaOH-EDTA buff.) | 27.6 5.59 548 | 197 |



Table 7 (Contd.)

| Suspensions | | | | | | | |
|-----------------|---|-----------------|---|--------------------------------------|--|---|------|
| Entry | Catalyst | Loading | Conditions | Light source | Products | Yield ($\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$) | Ref. |
| 29 | TiO ₂ coupled to FDH : FADH (ratio 1 : 03) loaded membrane | 30 mg/20 mL | Aq. sln pH 5.5, NADH 5 mM, [Cp*Rh(bpy)(H ₂ O)] ²⁺ 0.25 mM | 23 W UV lamps (max 365 nm) | HCHO (PB buff.) HCHO (NaOH-EDTA buff.) | 13.5 345 | 197 |
| Photoelectrodes | | | | | | | |
| Entry | Catalyst | Bias (V) | Conditions | Light source | Products | Yield ($\mu\text{mol h}^{-1} \text{cm}^{-2}$) | Ref. |
| 30 | Polyaniline coated p-Si | -1.9 V vs. SCE | 0.1 M LiClO ₄ aq. sln | Xe lamp (150 mW cm ⁻²) | HCOOH HCHO | 60.5 15 | 200 |
| 31 | p-GaAs | -0.5 V vs. SCE | 4 M HCl aq. sln with 0.32 M V(III)/V(III) couple, 50 °C | 150 W tungsten or Xe lamp | HCOOH CH ₃ OH HCHO | n.d. | 201 |
| 32 | Bifunctional TiO ₂ with Ru N719 dye | No bias | 2 M NaOH aq. sln pH 10 | 300 W Xe lamp (cutoff > 420 nm) | HCOOH CH ₃ OH HCHO | 16.7 35.6 25.8 | 202 |
| 33 ^b | Cu ₂ O film on Cu | No bias | 0.1 M Na ₂ CO ₃ /NaHCO ₃ aq. sln pH 9.0 | 125 W h.-p. Hg lamp | CH ₃ OH HCHO | 9.5 125 | 203 |
| 34 | 040-BiVO ₄ /Cu | +0.9 V vs. RHE | 0.5 M NaCl aq. sln | 300 W Xe lamp with an AM 1.5G filter | HCHO CH ₃ OH C ₂ H ₅ OH | 108 ^c n.d. n.d. | 204 |
| 35 | Cu/rGO/PVP/Nafion | +0.68 V vs. RHE | 0.1 M NaOH aq. sln | 300 W Xe lamp with a KG3 filter | HCHO | 1.18 | 205 |

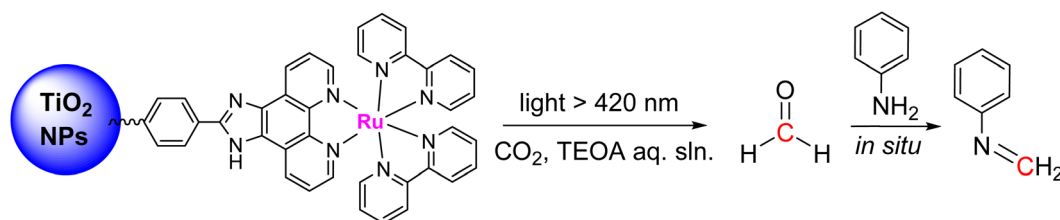
^a n.d: not determined. ^b Catalyst deposited on a wet paper filter at the bottom of the reaction vessel. ^c In $\mu\text{mol L}^{-1} \text{h}^{-1} \text{cm}^{-2}$ (reactor volume not specified).

Another example of TiO₂ based photocatalysis was reported in which sodium sulfite was used as the reducing agent in order to fill in photogenerated holes. Under 7 bars of CO₂, at 80 °C and at a TiO₂ loading of 0.5 g⁻¹ in basic (pH 14) aqueous solutions, the formation of H₂ (102 μmol h⁻¹ g_{cat}⁻¹), formaldehyde (16 537 μmol h⁻¹ g_{cat}⁻¹) and formic acid (2954 μmol h⁻¹ g_{cat}⁻¹) were measured depending on experimental conditions (time and pH) under UV irradiation from a medium pressure Hg vapor 125 W lamp introduced into the photoreactor (Table 7, entry 18).¹⁸⁹ The higher formation rate for formaldehyde was observed at the beginning of the reaction (few hours), which was explained by a branched mechanism, with on one hand a CO₂-to-formic acid reduction later generating gaseous products (only detected after several hours of irradiation once the hole scavenger is consumed), and on the other hand the direct reduction of carbonates into HCHO. Composites made of nanometre-sized TiO₂ particles and micrometre-sized zirconium oxide (ZrO₂) particles have been reported to generate high yields of formaldehyde and methanol (maximum 300 μmol g_{cat}⁻¹ total after only 300 s) under real solar light illumination (Table 7, entry 19).¹⁹⁰ For that, the composite was scattered on a copper plate and allowed to humidify in a fridge to form a thin layer of water on the composite surface. The assembly was then placed in a gas-barrier plastic bag (allowing CO₂ diffusion only) containing ambient air and then was illuminated with solar light. It was proposed that reduction products originated from the reduction of bicarbonate ions resulting from the dissolution of CO₂ contained (from ambient air) in the thin layer of water. A highly crystalline carbon-doped NaTaO₃ perovskite was also reported to reduce CO₂ to formaldehyde in neutral aqueous solutions at room temperature and under 254 nm irradiation (4.4 mW cm⁻²), at the optimal rate of 39 μmol g_{cat}⁻¹ after 2 h (Table 7, entry 20).¹⁹¹ This rate, determined through complexometric measurements, was shown to be dependent on the annealing temperature used to prepare the material as well as the carbon content since the undoped material showed very low formaldehyde yield. Three hematite-based materials, namely Fe₂O₃, TiO₂-Fe₂O₃ and Pd/TiO₂-Fe₂O₃ were suspended as nanoparticles in an aqueous sodium carbonate solution (pH 8.5) and illuminated with a 500 W xenon lamp. After 2 hours, the highest rate for formaldehyde was obtained with Pd/TiO₂-Fe₂O₃ (1338 μmol L⁻¹ g_{cat}⁻¹, Table 7, entry 21), when compared with the simple Fe₂O₃ (878 μmol L⁻¹ g_{cat}⁻¹) and TiO₂-Fe₂O₃ (399 μmol L⁻¹ g_{cat}⁻¹) and was explained by the hydrogenation of formic acid with hydrogen atoms on the photocatalyst surface.¹⁹² An example of a system combining a semiconducting material and

a molecule consisted of cobalt phthalocyanine loaded TiO₂ nanoparticles (CoPc/TiO₂) of ca. 11 nm diameter prepared by a sol-gel method and dispersed in alkaline (NaOH) aqueous solutions under a CO₂ atmosphere.¹⁹³ When irradiated with a tungsten-halogen 500 W lamp, a mixture of products containing CO, HCOOH, CH₃OH, CH₄ and HCHO was produced at a maximum yield of 407 μmol g_{cat}⁻¹ after 20 h under optimized conditions (CoPc/TiO₂ mass ratio, calcination temperature), the latter accounting for ca. 50 μmol g_{cat}⁻¹ (Table 7, entry 22). The CO₂ reduction to formaldehyde utilizing a heteroleptic ruthenium metal complex covalently linked to TiO₂ nanoparticles was also reported to occur in aqueous medium at pH 7 under visible light (λ > 420 nm) illumination.¹⁹⁴ When the hybrid catalyst was dispersed in neutral water, in the presence of TEOA (triethanolamine) as a sacrificial donor agent, the formation of formaldehyde as the major product (maximum TON of 720 after 5 h, corresponding to a formation rate of 18 μmol h⁻¹ g_{cat}⁻¹, Table 7, entry 23) was observed in the liquid phase as determined by HPLC, with CO and CH₄ as minor (TON 136 and 64, respectively), gaseous, products. Moreover, recyclability tests showed that the loss of activity was limited to 10–15% after the sixth cycle, due to some material loss during washing steps. In addition, this system used the *in situ* generated formaldehyde in a condensation reaction with amine, generating new H₂C–N bonds (Scheme 50). To the best of our knowledge, this represents the only example of reductive functionalization of CO₂ *via* formaldehyde in (photo)electroreduction systems.

Very recently,¹⁹⁵ a single-atom catalyst with dual-atom sites (DAS) composed of neighbouring Sn(II) and Cu(I) centres embedded in a C₃N₄ framework was reported to generate HCHO from CO₂ with a selectivity of 61% and a productivity of 259.1 μmol g⁻¹ (Table 7, entry 24) after 24 h irradiation. The catalyst was dispersed in a CO₂-saturated 0.1 M aqueous KHCO₃ containing 10 vol% triethylamine (TEA) as the sacrificial electron donor and was irradiated using a 300 W Xe lamp equipped with a 420 nm cut-off filter. The best productivity was obtained with the Sn₇₅-Cu₂₅/C₃N₄ composition, and the production of HCHO from CO₂, asserted by ¹³C labelled experiments and FTIR and NMR characterization, was attributed to the 2e⁻ reduction of HCHO through the synergetic action of the two metals.

An original strategy was also tested with a Pt-loaded potassium hexatitanate (Pt-K₂Ti₆O₁₃) photocatalyst (0.3 mg) deposited on a filter at the bottom of a flask containing 4 mL of water under a CO₂ atmosphere.¹⁹⁶ Upon illumination with a 150 W Hg-lamp, formaldehyde was detected as a secondary reduction product (H₂ as the main one) by GC at a rate of 0.48 μmol h⁻¹



Scheme 50 Visible light reduction of CO₂ into formaldehyde followed by *in situ* condensation with an amine.¹⁹⁴



g_{cat}^{-1} , together with CH_4 and HCOOH (Table 7, entry 25). When combined with a Cu/ZnO catalyst, the resulting composite produced HCHO as the secondary product (H_2 – major) at a rate of $0.57 \mu\text{mol h}^{-1} g_{\text{cat}}^{-1}$ along with CH_4 and HCOOH (Table 7, entries 26 and 27).

Finally, semiconductors can also be associated with an enzymatic process. For example, a very recent study reported the immobilization of two kinds of dehydrogenases, namely formate dehydrogenase (FDH) and formaldehyde dehydrogenase (FADH) (see Section 8 for more details on these enzymes), on the surface of polyethylene hollow fibre membranes, coupled with UV induced, TiO_2 -based photocatalytic coenzyme regeneration.¹⁹⁷ In this system, the excitation of TiO_2 causes charge separation and electrons are transferred to the NAD^+ formed during the enzymatic cascade CO_2 reduction, for coenzyme NADH regeneration, using EDTA as the electron donor and pentamethylcyclopentadienyl rhodium bipyridine ($[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$) as the redox mediator. In the absence of an enzyme, HCHO was formed at a maximum rate of 0.207 mM (with H_2O as the electron donor) and 4.11 mM (with EDTA as the electron donor), at pH 6.5 and after 5 h UV irradiation (365 nm max). With the photo-enzyme assembly, the best results were obtained at pH 5.5 with EDTA as the electron donor, reaching 2.59 mM of formaldehyde after 5 h of reaction (Table 7, entries 28 and 29). The production of HCHO proceeded for 48 h with limited loss of activity.

7.2. Photoelectrodes

A p-type Si photoelectrode was coated with a polyaniline film of ca. 50 nm thickness upon electro polymerization. Under illumination with a Xe lamp (150 mW cm^{-2}) at a bias potential of -1.9 V vs. SCE , the photocathode immersed in a CO_2 -saturated 0.1 M LiClO_4 aqueous solution generated several micromoles of formic acid and formaldehyde as determined by a colorimetric method (Table 7, entry 30).²⁰⁰ The bare photoelectrode did not show any activity towards CO_2 reduction. The total faradaic yield reached 20 to 28% even though no methane or methanol could be detected by gas chromatography. In the presence of the $\text{V(II)}-\text{V(III)}$ chloride redox couple presumably acting as an electron relay, a p-type GaAs photoelectrode was reported to generate formic acid, formaldehyde and methanol in low yields (from 1 to 3% faradaic yields) in an acidic (4 M HCl) aqueous solution under visible light illumination (tungsten-halogen lamp, 980 mW cm^{-2}) at a bias potential of -0.5 V vs. SCE and at $50 \text{ }^\circ\text{C}$ (Table 7, entry 31).²⁰¹

The sequential formation of formic acid (detected by HPLC), formaldehyde (UV-Vis) and methanol (GC) was reported with a bifunctionalized TiO_2 film under visible-light irradiation (300 W Xe lamp with a cut-off filter) in acetonitrile solution containing DMPIImI electrolyte and the iodide/triiodide couple as a redox mediator.²⁰² The film was separated into two zones, a sensitized area containing a ruthenium complex (N719) as the dye and a catalytic area composed of a pure TiO_2 zone. Under illumination, electrons generated in the sensitized zone migrate to the catalytic one through TiO_2 particles. This film was used as the reduction half-cell in a H-type reactor with Pt as the anode

material, in order to prevent re-oxidation of CO_2 reduction products. Formic acid was generated first, then formaldehyde and methanol, with a respective yield of ca. $0.05 \text{ mmol cm}^{-2}$ after 5 h (Table 7, entry 32). This yield was enhanced when an external voltage was applied between the reference electrode and the anode thus enabling the regeneration of the redox mediator and consequently of the dye. The effect of the bias potential and the pH on the product distribution was studied with a PEC assembly composed of the $\text{Cu}/\text{Cu}_2\text{O}$ electrode irradiated with a 125 W high pressure mercury lamp.²⁰³ In $0.1 \text{ M Na}_2\text{CO}_3/\text{NaHCO}_3$ electrolyte (pH 9.0) saturated with CO_2 , a high rate for HCHO was observed at 0 V bias (Table 7, entry 33), whereas methanol was the main product at $+0.2 \text{ V}$ bias. At the positive potential bias, some HCHO was also observed at pH 8 to 11 as a minor product.

A PEC assembly consisting of a (040)-facet engineered BiVO_4 plate as the photoanode (040-BVO) and a Cu plate immersed in NaCl electrolyte as the cathode has been reported to generate various C_1 products from CO_2 when illuminated with solar light under an external bias potential.²⁰⁴ Depending on the applied potential, the selectivity could be tuned towards a specific product, with a general trend showing that at low potentials, kinetically favourable products are dominant, whereas at high potentials, thermodynamically stable products are dominant. Formaldehyde is produced with 85% faradaic efficiency at an applied potential of 0.90 V vs. RHE , corresponding to a yield of $143 \mu\text{M h}^{-1}$ (Table 7, entry 34). Very recently, it has been shown that a system combining calcium and iron co-doped TiO_2 films as the photoanode and multilayered Cu based dark electrode as the cathode was able to selectively generate formaldehyde and/or acetaldehyde at the cathode surface by tuning the anode bias potential.²⁰⁵ Both electrodes were immersed in a 0.1 NaOH aqueous electrolyte saturated with CO_2 , and formaldehyde was detected as the only product with a reduced graphene oxide (rGO) coated copper electrode (Table 7, entry 35). The highest yield was $470 \mu\text{M cm}^{-2}$ after 8 h (25% faradaic efficiency) under solar simulated irradiation with an applied bias of 0.68 V vs. RHE . It is important to note that in the last example ^{13}C labelled experiments were conducted to confirm the origin of the products.

7.3. Solid material approaches

Some studies were also conducted with catalytic solid materials. Two Mo-based heterogeneous catalysts, namely a mixed-valence polyoxomolybdate cluster and composite consisting of a molybdenum keplerate cluster embedded in reduced graphene oxide (RGO), were shown to reduce CO_2 and oxidize water at the same time, generating sub-mmol amounts of formic acid as the main product and formaldehyde as the secondary product, as quantified by HPLC.²⁰⁶ Experiments were conducted in pure water with no sensitizer and light irradiation was set at 373 nm (19 mW cm^{-2}). The turnover number and frequency for formic acid (not calculated for formaldehyde) were claimed to reach ca. 10^6 and ca. $6 \times 10^2 \text{ s}^{-1}$, respectively. This study shows the possibility of using cheap metal oxides such as oxometallates as catalytic materials for both CO_2 reduction and water oxidation.



7.4. Molecular approaches

To the best of our knowledge, only two studies employing a fully molecular approach have been reported. A homogeneous system employing pyridine as a catalyst in aqueous solution in the presence of Ru(phen)₃ photosensitizer, ascorbic acid as an electron donor and KCl as an electrostatic stabilizing agent reported the formation, under 470 nm monochromatic illumination, of formate (NMR quantified) as the main product with methanol (GC-MS) as the minor product and traces of formaldehyde detected by NMR.²⁰⁷ Two ruthenium(II) polypyridyl complexes covalently modified with a pendant pyridyl function have also been shown to be active towards CO₂ reduction under both electrochemical and photochemical conditions in a DMF : water mixture. In the presence of TEA (triethylamine) as a sacrificial donor agent and under 470 nm irradiation, the formation of formate (main product), formaldehyde and methanol (minor) was observed after 1 h irradiation albeit with a very low TON of 16, 7 and 1, respectively.²⁰⁸ The rapid loss of activity was attributed to ligand photolabilization leading to complex degradation. In neither of these examples has the mechanism been elucidated.

7.5. Conclusion and perspectives

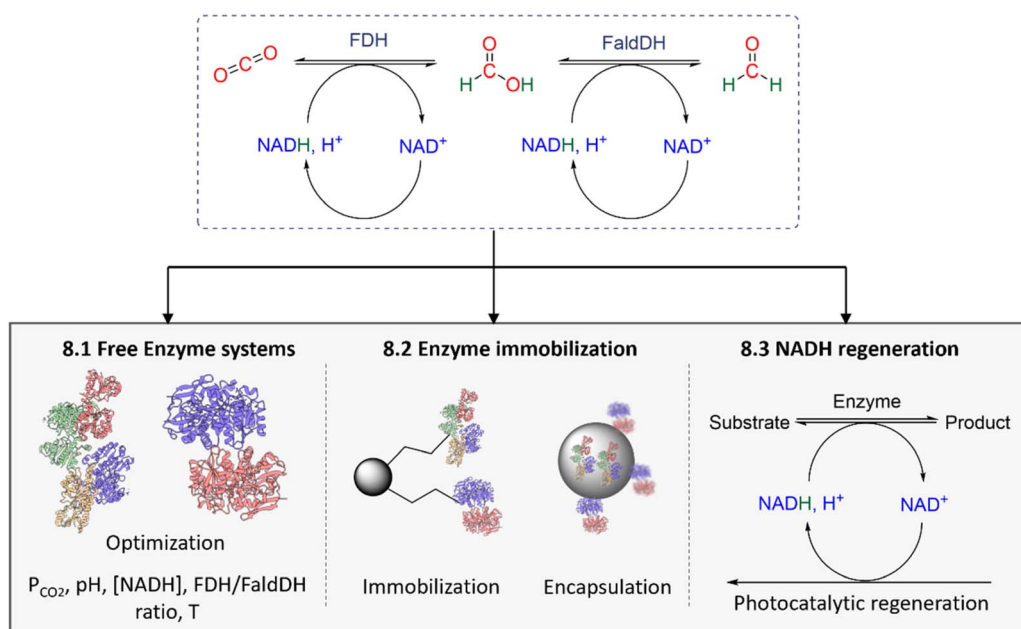
In conclusion, achieving the selective conversion of CO₂ into formaldehyde (HCHO) using light as the primary, if not the sole, energy source is far from realized, as outlined in Table 7 with key examples. The predominant outcome in the majority of studies involves a product mixture, lacking control over selectivity, with low yields and demonstrating limited mechanistic understanding. The inherent high reactivity of HCHO poses a clear challenge to its detection. Therefore, improvements in analytical detection methodologies are imperative. The use of

visible (solar) light still remains scarce, with most systems requiring UV light.

As perspectives, functionalized materials, in particular associating a photoactive material and molecular tuneable unit, open new possibilities to finely control the local environment of the catalytic site and thus to favour the formaldehyde pathway.

8. Enzyme-catalysed CO₂ reduction into formaldehyde

Biological fixation of CO₂ occurs through six major pathways including the Calvin–Benson–Bassham (CBB) cycle which represents the most common pathway.²⁰⁹ Interestingly, the transformation of CO₂ into carbohydrates in the CBB cycle was initially hypothesized to occur *via* a formaldehyde pathway.^{181,210} However, it was later demonstrated that the CBB cycle does not involve the intermediate formation of formaldehyde, but the CO₂ fixation to form a carboxylate which is then further reduced in subsequent steps.²¹¹ It is only with isolated enzymes that HCHO and CH₃OH were obtained from CO₂. The dehydrogenases, formate dehydrogenases (FDHs, EC 1.2.1.2),²¹² formaldehyde dehydrogenase (FaldDH, EC 1.2.1.46)²¹¹ and alcohol dehydrogenase (ADH, EC 1.1.1.1)²¹³ are able to catalyse the reduction of CO₂, HCOOH and HCHO into HCOOH, HCHO and CH₃OH, respectively.^{11b,214} Although most of the reports focused on the selective generation of formate, notably because of its implication as an intermediate in the Wood–Ljungdah pathway in acetogens²¹⁵ or methanol,²¹⁶ only a handful of studies focused on the selective generation of formaldehyde. The two-step enzyme cascade combining formate dehydrogenase (FDH) and formaldehyde dehydrogenase (FaldDH) is currently the only reported process (Scheme 51) for the enzymatic conversion of CO₂ into HCHO. Both enzymes are commercially available and



Scheme 51 Enzymatic sequential generation of formate and formaldehyde with FDH (formate dehydrogenase) and FaldDH (formaldehyde dehydrogenase).



Table 8 Conditions and performances of bio-cascade systems for CO₂ reduction into formaldehyde^a

| Entry | Immobilization | Substrate | P or [C] | NADH regeneration | Time (h) | HCHO generation (mmol L ⁻¹) | Ref. |
|-------|-----------------------|--------------------|------------------------|-------------------|----------|---|------|
| 1 | Free enzymes | KHCO ₃ | 100 mM | No | 72 | 0.060 | 217 |
| 2 | Free enzymes | CO _{2(g)} | 0.5 MPa | No | 12 | 0.901 | 218 |
| 3 | HDMMC-based system | CO _{2(g)} | 0.3 MPa | No | 8 | 0.022 | 219 |
| 4 | TiO ₂ -NPs | CO _{2(g)} | 0.3 MPa | No | 4 | — | 220 |
| 5 | NPSCs | CO _{2(g)} | 0.3 MPa | No | 4 | 0.125 | 221 |
| 6 | MCF-MP | KHCO ₃ | 200 mM | No | — | 0.037 | 222 |
| 7 | 3% TCPP@ZIF-8 | NaHCO ₃ | 10 μM | Yes | 8 | 0.008 | 223 |
| 8 | PE-HFMs | CO _{2(g)} | 3 mL min ⁻¹ | Yes | 4 | 0.034 | 197 |

^a HDMMCs = hybrid double membrane microcapsules, NPs = nanoparticles, NPSCs = nanoparticle-stabilized capsules, MCF-MP = siliceous mesostructured cellular foams functionalized with mercaptopropyl groups, TCPP = 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin, ZIF = zeolite-like imidazole framework material, PE-HFMs = polyethylene hollow fibre membranes.

have similar pH and temperature optima. Each step of the cascade is endowed with a 2e⁻ reduction of CO₂ and requires one equivalent of NADH (nicotinamide adenine dinucleotide hydride) as a co-factor, serving as the reductant. Two molecules of NADH are thus oxidized into the corresponding NAD⁺ during the biocatalyzed reduction of CO₂ to formaldehyde.

The main parameters and performances of these selective catalytic systems are summarized in Table 8. The results are described in three sections: (i) optimized reaction conditions with free enzyme systems, (ii) immobilized and compartmentalized enzymes and, finally, (iii) systems coupled to the NADH regeneration process.

8.1. Optimization of the reaction conditions with free enzyme systems

Studies have shown that FDH/FalDDH ratio lower than 1 is beneficial for the production of formaldehyde over formate since the formate is a good substrate for the FDH (Table 8, entry 1).²¹⁷ In the same vein, an excess of NADH (NADH/NAD⁺ molar ratio > 2000) was also found necessary to drive the reaction. Under optimized conditions, 60 μM of formaldehyde was produced from KHCO₃ instead of CO₂ in 72 h with 15 g L⁻¹ of FalDDH and 1 g L⁻¹ of FDH. The formaldehyde concentration was quantified using a colorimetric test (Nash reagent)¹⁴⁹ as it was found that indirect detection through UV quantification of NADH disappearance could be erroneous due to interaction with CO₂. Following this study, the same cascade was explored with gaseous CO₂ (Table 8, entry 2).²¹⁸ Higher amount of FalDDH as compared to FDH was again necessary and the study disclosed the positive impact of a high CO₂ pressure (from 0.2 to 0.5 MPa) to generate a high amount of formaldehyde. Under optimized conditions, 901 μM of formaldehyde was produced (0.5 MPa of CO₂) after 12 h. A plateau was found at 10–12 h before a net decrease of formaldehyde, tentatively explained by the consumption of formaldehyde *via* the reverse reaction (*i.e.*, oxidation of HCHO into CO₂) and/or the instability of formaldehyde in the reaction medium.

8.2. Enzyme immobilization and compartmentalization

Immobilized systems were explored to improve the performances of the FDH/FalDDH cascade with the aim to increase

enzyme stability, activity²²⁴ and reusability compared to the enzymes freely diffusing systems. FDH and FalDDH were immobilized and spatially separated at organic–inorganic hybrid double membrane microcapsules (HDMMCs) (Table 8, entry 3).²¹⁹ FDH was encapsulated in the lumen of the HDMMCs while FalDDH was encapsulated in the intermembrane space. The study showed an improved activity with formaldehyde production of 22 μmol compared to the control experiment with free enzymes (9 μmol). The same group encapsulated FDH in Ti nanoparticles (NPs) while FalDDH was immobilized at the surface of the particles (Table 8, entry 4).²²⁰ The size of the NPs (from 75 to 375 nm) was shown to have a significant impact on the reaction. The best performances were obtained with NP size of 75 nm. The recycling stability of the enzyme-containing NPs was evaluated and displayed a loss of half of the initial performance after 10 cycles. It was improved in a following report describing the preparation of nanoparticle-stabilized capsules (NPSCs) containing FDH entrapped in the capsule and FalDDH conjugated on the capsule surface (Table 8, entry 5).²²¹ Furthermore, the distance between both enzymes was evaluated using Förster resonance energy transfer (FRET) analysis on the enzyme labelled with carbocyanine dyes (Table 8, entry 6).²²² While no detectable FRET was observed free in the enzyme system with an estimated distance of 40 nm between the two enzymes, co-immobilization of the enzymes in the silica materials displayed an increased transfer efficiency >50% with an estimated distance of less than 10 nm. This feature was proposed to be responsible for the enhanced activity in the particles compared to the enzyme free system, due to probability increase of direct substrate transfer between the two enzymes.

8.3. NADH regeneration

NADH is a co-factor that is regenerated in biological systems. When implemented *in vitro*, its stoichiometric use negatively impacts the atom-efficiency of any given transformation. The regeneration of NADH from NAD⁺ has thus been the subject of intense investigation with the development of bio-, electro- and photo-regeneration systems.²²⁵ In the case of the FDH/FalDDH cascade reaction transforming CO₂ into formaldehyde, only two reports described the combination of the cascade with a regeneration process. FDH and FalDDH were co-immobilized in the cavities of the zeolitic imidazolate framework-8 (ZIF-8)



combined with 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (TCPP) as a photosensitizer fixed to the surface of the zeolite (Table 8, entry 7).²²³ Triethanolamine (TEOA) was used as an electron donor, Cp*Rh(bpy)Cl (M, Cp* = pentamethylcyclopentadienyl, bpy = bipyridine) as an electron mediator and water as a proton donor. Under optimum conditions (1 mg mL⁻¹ 3% TCPP@ZIF-8, pH = 8.0) the NADH regeneration reached 75% yield after 3 h under visible-light exposure. Combining this regeneration system with FDH/FalDDH (2 : 1 ratio) afforded the conversion of 10 μM of NaHCO₃ into 7.74 μM of formaldehyde (conversion rate 77%) after 8 h under visible-light exposure. The use of titanium dioxide (TiO₂) in a photocatalytic system¹⁸² was also probed with immobilized FDH/FalDDH on the surface of polyethylene (PE) hollow fibre membranes (HFMs) (Table 8, entry 8).¹⁹⁷ Despite side reactions due to the known ability of the UV/TiO₂ system to photoreduce CO₂ into various products (*e.g.*, CO, HCOOH, HCHO, CH₃OH, CH₄),¹⁸² NADH regeneration was observed and 34 μM of formaldehyde was generated under the best conditions (ratio FDH : FalDDH = 1 : 0.3, CO₂ 3 mL min⁻¹, H₂O as the electron donor, PB buffer, pH 7.0, [NADH] = 1 mmol L⁻¹, exposure to two 23 W UV lamps at λ = 365 nm).

8.4. Conclusion and perspectives

In conclusion, the enzymatic conversion of CO₂ into formaldehyde is still at an early stage of development. Only a few reports have highlighted the selective formation of formaldehyde in cascade reactions involving FDH and FalDDH. Strategies for enzyme immobilization were identified to enhance both the reusability and activities of FDH and FalDDH when compared to free enzyme systems.

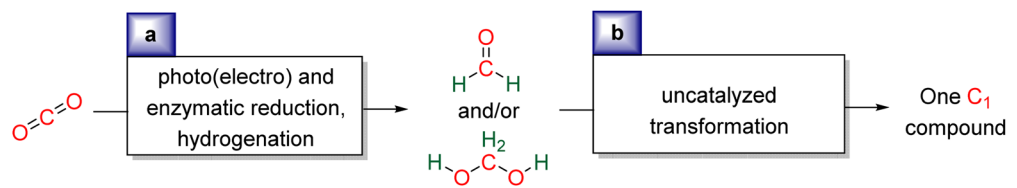
As perspectives, discovering more active and/or robust enzymes from diverse organisms or engineering existing enzymes for improved stability and activity is crucial for advancing current strategies. Additionally, the development of

efficient co-factor regeneration systems is essential to establish an energetically sustainable and cost-effective process. The design of an effective co-immobilized system for enzymes coupled with a co-factor regeneration process remains undisclosed. An attractive approach involves substituting the natural co-factor NADH with a more sustainable electron and proton supplier system, as previously demonstrated in the biocatalyzed generation of formate or methanol from CO₂.^{11b,213} Similarly, electrochemically driven enzymatic systems represent a promising avenue. Finally, the biocatalyzed four-electron reduction of CO₂ to formaldehyde has yet to be explored in subsequent transformations. While such processes are enticing, the undefined form taken by the generated formaldehyde and its instability in the enzymatic reaction medium have so far hindered its isolation or utilization in subsequent transformations for the synthesis of more complex products.

9. General conclusions

In this comprehensive review, we have examined the reduction of CO₂ with four electrons, leading to the production of formaldehyde and acetal derivatives through thermal (hydrogenation or hydroelementation reactions), electrochemical, photoelectrochemical, and bio-driven processes. Formaldehyde holds considerable appeal for both energy carrier applications and use as a chemical feedstock. Particularly noteworthy is its versatility for the latter application compared to formic acid, methanol, or methane obtained from the CO₂ reduction reaction (CO₂RR). Despite its promising attributes, synthesizing and isolating formaldehyde from the CO₂RR remains significantly more challenging than the aforementioned C₁ compounds. To date, only a limited number of systems have been reported to generate formaldehyde from CO₂ as the major product, and in many cases, conclusive evidence regarding the origin of formaldehyde is lacking. The most notable performances of these systems are summarized in Table 9.

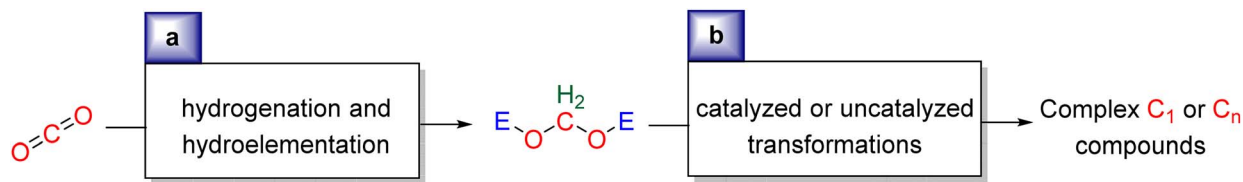
Table 9 Best catalytic performances of the different reduction systems reported for the generation of formaldehyde from electro-, photoelectrochemical, enzymatic and hydrogenation processes and further use as a C₁ source in subsequent transformations



| Reduction system | Hydrogenation | Electroreduction | Photoelectroreduction |
|--|--|------------------|--|
| Yield | 0.037 M g _{cat} ⁻¹ h ⁻¹ | | 400–500 μmol h ⁻¹ g _{cat} ⁻¹ (1 bar CO ₂) 16 500 μmol h ⁻¹ g _{cat} ⁻¹ (7 bars CO ₂) |
| TON | — | 10 ⁴ | |
| Selectivity (%) | — | 90 | 60–70 |
| Faradaic efficiency (%) | n.a | 85–90 | NA |
| Current density (mA cm ⁻²) | n.a | 0.1–0.2 | NA |
| C ₁ source | ✗ | ✗ | CH ₂ -N |
| C _n source | ✗ | ✗ | ✗ |
| Asymmetric C center | ✗ | ✗ | ✗ |



Table 10 Best catalytic performances of the different reduction systems reported for the generation of acetal compounds and further use of the acetals as C_1 and/or C_n sources in subsequent transformations



| Reduction system | Hydrogenation | Hydrosilylation | Hydroboration | Hydrozirconation |
|---------------------|---------------|----------------------|--|------------------|
| TON | 3874 | 3400 | 690 | — |
| TOF (h^{-1}) | 194 | 10.4 | 516 | — |
| Yield (%) | — | 99 | 97 | — |
| Scale | 2.88 mmol | 4.70 mmol | 0.55 mmol | — |
| C_1 source | ✗ | $CH_2-N, -O, -S, -C$ | $CH_2-N, -O, -P, -C$ | CH_2-C |
| C_n source | ✗ | ✗ | C_2, C_3, C_4 | ✗ |
| Asymmetric C center | ✗ | ✗ | Diastereo- and enantio-selective transformations | ✗ |

In hydrogenation reactions, the highest reported yield of formaldehyde (HCHO) was $0.037 M g_{cat}^{-1} h^{-1}$ achieved with a Ru-based heterogeneous catalyst in an aqueous medium.¹⁴⁸ Another notable instance involved electroreduction, where a film of electropolymerized chromium vinylterpyridine complex exhibited 90% faradaic efficiency (FE) and a turnover number (TON) of 10^4 .¹⁷⁰ In photoelectroreduction, optimal performances were observed at $16\ 500 \mu mol h^{-1} g_{cat}^{-1}$ under 7 bars of CO_2 and $80^\circ C$ with a TiO_2 catalyst, achieving 70% selectivity.¹⁸⁹ Remarkably, in all these systems, the generated formaldehyde was utilized only once as a substrate in a cascade reaction to form a C–N bond, leaving significant untapped potential in this area for future exploration.¹⁹⁴ Further investigations are thus imperative, both for fundamental understanding and catalyst development, and it is crucial to gather solid evidence regarding the origin of the generated formaldehyde in each case. In addition to the challenge of generating formaldehyde, detecting and isolating it proves to be a formidable task due to its reactive nature.

On the other hand, the reduction of CO_2 into acetal products has seen successful developments in thermic processes, specifically in (i) the hydrogenation of CO_2 in the presence of alcohol and (ii) hydroelementation reactions involving hydrosilanes, hydroboranes, and early transition metal hydride species. In contrast to the synthesis of formaldehyde, numerous acetal compounds were selectively and efficiently generated, and eventually isolated. Notably, the formation of acetals from the CO_2RR currently stands as the sole pathway to formaldehyde, enabling its consistent use not only as a C_1 source but also as a C_n source. Bis(silyl)acetal (BSA) and bis(boryl)acetal (BBA) were indeed shown to release formaldehyde, which was then employed in subsequent C_1 and C_n transformations. It was also demonstrated that these acetals could serve as a formaldehyde surrogate without releasing formaldehyde. The primary drawback of the acetal approach is its lack of atom efficiency. While the regeneration of hydroborane or hydrosilane in a sustainable reduction process would be an ideal solution, the formation of high value-added compounds *via*

complex transformations may compensate for this issue to some extent. Table 10 compiles the highest reported performances (TON, TOF, yield, selectivity) in each of the reductive processes leading to acetal compounds. While the chemistry of formaldehyde is well-established and developed, the acetal compounds obtained from the four-electron reduction of CO_2 are, for the most part, novel molecules, and their reactivities are still under investigation. Pioneering studies on their reactivity have led to the utilization of several BSA, BBA, and **BZrA 1** as a C_1 source in multicomponent reactions. This facilitated the incorporation of one carbon atom from CO_2 into very diverse molecules in the form of methylene. Table 10 also summarizes the types of C–E bonds ($E = N, O, S, P$) formed from BSA, BBA, and **BZrA 1**. Moreover, two BBA compounds (**BBA 2** and **4**) were employed as a C_n source, generating $C_2, C_3,$ and C_4 carbohydrates. In the case of the latter two, asymmetric carbon centres were even generated in a diastereo- and enantioselective manner, respectively. Formaldehyde was directly observed only once in 4% yield with hydrosilanes and only once among a mixture of other products with hydroboranes. The intermediary of acetals (**BSA 3**, **BBA 2** and **4**, **BZrA 1**) was essential for the selective generation of formaldehyde, as it was quantitatively released either spontaneously, from hydrolysis, or from CsF activation depending on the acetal properties.

To conclude, the $4e^-$ reduction of CO_2 is a two-face journey. On one hand, the generation of acetal compounds witnessed important advances both to control this challenging reduction stage and to use it in subsequent complex transformations but at the expense of low atom-efficiency. On the other hand, the generation of formaldehyde from hydro(electro)reduction is more sustainable, but still in its infancy compared to other C_1 reduction compounds such as CO or methanol.

We believe that intertwined processes from the different fields involved in the CO_2RR (single *vs.* cascade processes, coupling between electro- and organo-catalysis) may be instrumental in addressing the challenging and sustainability issues associated with the $4e^-$ reduction of CO_2 .



Data availability

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Author contributions

S. B. conceptualized the review. S. B, S. D., J. B. and M. R. wrote and edited the review.

Conflicts of interest

The authors declare no competing financial interest.

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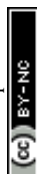
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