Reaction Mechanisms

Experimental and Computational Insights into Carbon Dioxide Fixation by RZnOH Species


Dedicated to Professor Herbert W. Roesky on the occasion of his 80th birthday

Abstract: Organozinc hydroxides, RZnOH, possessing the proton-reactive alkylzinc group and the CO₂-reactive Zn–OH group, represent an intriguing group of organometallic precursors for the synthesis of novel zinc carbonates. Comprehensive experimental and computational investigations on 1) solution and solid-state behavior of tBuZnOH (1) species in the presence of Lewis bases, namely, THF and 4-methylpyridine; 2) step-by-step sequence of the reaction between 1 and CO₂; and 3) the effect of a donor ligand and/or an excess of tBuZn as an external proton acceptor on the reaction course are reported. DFT calculations for the insertion of carbon dioxide into the dinuclear alkylzinc hydroxide 1 are fully consistent with ¹H NMR spectroscopy studies and indicate that this process is a multistep reaction, in which the insertion of CO₂ seems to be the rate-determining step. Moreover, DFT studies show that the mechanism of the rearrangement between key intermediates, that is, the primary alkylzinc bicarbonate with a proximal position of hydrogen and the secondary alkylzinc bicarbonate with a distal position of hydrogen, most likely proceeds through internal rotation of the dinuclear bicarbonate.

Introduction

Over the last decade, fixation approaches for CO₂ sequestration have received much attention because of their great environmental significance and very promising practical applications in materials chemistry.[1] Indeed, in Nature, CO₂ is the most abundant C-1 building block that is widely used to synthesize complex organic molecules in living organisms. In synthetic chemistry, CO₂ can be also utilized as a C-1 chemical feedstock for the preparation of useful carbon-containing organic compounds in metal-catalyzed systems.[1c–g] However, the construction of functional materials based on CO₂–metal carbonate conversion is much less explored and such materials are mostly isolated accidentally.[2] Particularly intriguing examples of CO₂ fixation concern reaction systems patterned on the active center of carbonic anhydrase (CA), which contains the Zn–OH group.[3]

Surprisingly, although a number of zinc complexes supported by multidentate ligands and terminal or bridging hydroxide ligation have been widely investigated experimentally as synthetic analogues of CA,[3,4] related organozinc hydroxide compounds have not been explored in this context.[5] Recently our group demonstrated that RZnOH-type moieties featuring a CO₂-reactive Zn–OH group and a proton-reactive Zn–C bond (Scheme 1a) possessed the unique ability to fix CO₂ and afford various zinc carbonate products (Scheme 1b). These preliminary investigations provided the first example of a structurally characterized alkylzinc hydroxide, tBuZnOH (1),[6] which, in the presence of CO₂, can form different nanomaterials based on CO₂ as a templating ion, for example, zinc carbonate nanoparticles (NPs) or discrete alkylzinc carbonate cluster 2 (Scheme 1b).[7] Moreover, the introduction of an auxiliary ligand, L, to the RZnOH system,[8] followed by the reaction with CO₂, led to the formation of the nanosized cluster ([L₂Zn]([ZnCO₃])₂ (L = deprotonated 8-hydroxyquinoline; Scheme 1b), which self-assembled into noncovalent porous material WUT-1.[9] Thus, aside from its fundamental novelty, organozinc hydroxides, in combination with CO₂, have appeared...
as very promising precursors of zinc carbonate based functional materials.

The unprecedented reactivity of the RZnOH/CO₂ system in different coordination environments prompted us to carry out the detailed experimental and computational mechanistic study reported herein. We selected 1 as a model system for CO₂ fixation. In particular, we were interested in 1) the solution and solid-state behavior of 1 in the presence of Lewis bases, namely, THF and 4-methylpyridine (py-Me); 2) the sequence of elementary steps of the reaction between 1 and CO₂; and 3) the effect of a Lewis base and an excess of RBuZn upon crystallization from a solution of RBuZn.

**Results and Discussion**

**Structure of adducts of 1 with Lewis bases**

We demonstrated previously that 1 exists in the solid state as a hexameric cluster [RBuZn(μ-OH)]₆ (1₆). To better understand the reaction between 1 and CO₂, first we investigated the character of aggregates that 1 forms in the presence of donor solvents, namely, THF and py-Me. Diffusion-ordered NMR spectroscopy (DOSY) revealed that 1 in [D₆]THF exists as a mixture of the hexameric cluster 1₆ (M_iso = 837 g mol⁻¹; M_exptl = (845 ± 70) g mol⁻¹) and a dimeric species solvated by THF, [RBuZn(μ-OH)(THF)]₂ (1₂ THF; M_iso = 423 g mol⁻¹, M_exptl = (436 ± 44) g mol⁻¹; Scheme 2a, see also Figure S2 and Table S2 in the Supporting Information). The DOSY NMR spectroscopy experiment for an equimolar mixture of 1 and py-Me in [D₆]THF revealed that, in this case, only the dimeric alkylzinc hydroxide adduct with py-Me [RBuZn(μ-OH)(py-Me)]₂ (1₂ py-Me; M_iso = 465 g mol⁻¹, M_exptl = (539 ± 54) g mol⁻¹) was spectroscopically detectable (Scheme 2a and Figure S4 and Table S3 in the Supporting Information). Recrystallization of an equimolar mixture of 1 and py-Me from a solution in THF at 273 K afforded colorless crystals of a new hexanuclear aggregate stabilized by two py-Me molecules, [RBuZn₆(μ₂-OH)₂(μ-OH)₂(py-Me)₂] (3), as the least soluble product (Scheme 2b). We note that 3 was also isolated in high yield from a mixture of 1₂ with 0.33 equivalents of py-Me (for details, see the Supporting Information). In THF, compound 3 dissociates to form solvated dimeric aggregates of 1₂(py-Me)(THF)ₓ, (in which x = 0, 1, or 2), as indicated by DOSY NMR spectroscopy experiments (Figure S3 and Table S3 in the Supporting Information). Single-crystal XRD analysis revealed that, in the solid state, compound 3 occurs as a Zn₆O₄ cage-like structure composed of two ZnO₄ rings in the fused boat conformation (Figure 1). Its molecular structure can be described as being derived from the opening of two opposite edges of the hexagonal prism of 1₆. In the Zn₆O₄ core, two types of hydroxide groups can be distinguished: four of them adopt μ₁-OH and two of them μ-OH coordination modes. The Zn—O bond lengths in Zn—μ₁-O fall within the range of 2.03–2.13 Å and the mean distance of Zn—μ-O is equal to 1.95 Å. In the case of the hexanuclear aggregate 3 stabilized by two py-Me molecules, the described structural features may be attributed to the latent Lewis acidity of the alkylzinc hydroxide cluster, and this behavior resembles the reactions of hexanuclear tert-butylalumoxane with amines.
Reactivity of 1 towards CO₂ in the presence of Lewis bases

To investigate the sequence of elementary steps of the reaction between 1 and CO₂ in the presence of Lewis bases, we monitored this reaction by using ¹H NMR spectroscopy (Figure 2). Upon exposure of a solution of 1 in [D₈]THF to CO₂ at 298 K, we initially observed broadening of the parent Zn–OH signal, which suggested that the zinc-bound hydroxide groups interacted with CO₂ to form incipient complexes (Figure 2a and Figure S5 in the Supporting Information). After 10 min, new signals at δ = 1.16 and 9.86 ppm emerged; these could be attributed to the bicarbonate species [²BuZn(HCO₂)]⁻.[13] The resulting highly acidic bicarbonates undergo further transformations by promoting protonolysis of the alkylzinc moieties; this is accompanied by the evolution of isobutane (the corresponding signal appears in the spectrum after ca. 40 min) and the formation of a [ZnCO₃]⁻ species (Scheme 3).

Scheme 3. Proposed sequence of elementary steps in the reaction of 1₂–L₂ (L = THF or py-Me) with CO₂.

After 5 h, the only signal that remained in the spectrum was that of isobutane, which indicated that all Zn–OH groups were involved in a stepwise CO₂ fixation process. A gel-like, insoluble substance containing ZnCO₃ NPs was recovered from the NMR tube after the reaction ended.[21]

To test the effect of py-Me as a strong Lewis base on the reactivity between RZnOH species and CO₂, we examined the reactivity of the py-Me adduct 3 towards CO₂ in [D₈]THF at 298 K. Again, significant broadening of ZnOH signals was observed (Figure 2b and Figure S6 in the Supporting Information); however, resonances attributed to [²BuZn(HCO₂)]⁻ emerged shortly (after around 10 min) and simultaneously signals belonging to 1 (δ = 1.05 and 4.49 ppm) decreased.[14] Strikingly, for the 3/CO₂ system, we essentially did not observe any signals of isobutane during the first 90 min of the reaction. It is reasonable to assume that at this stage of the process it is the formation of putative dinuclear aggregates (1a) and (1b) that occurs predominantly (Scheme 3). We noted that in the meantime partial protonolysis of the ²Bu–Zn group occurred, leading to a complex aggregate that probably contained [²BuZn(HCO₂)]⁻ and [ZnCO₃]⁻ moieties, and supported by py-Me molecules. After 24 h, the reaction mixture became cloudy and an insoluble solid formed. Many attempts to obtain single crystals suitable for single-crystal XRD analysis failed and the composition of the resulting product was only qualitatively elucidated as [²BuZn(HCO₂)]⁻[ZnCO₃]⁻[py-Me]⁺ by elemental analysis (see the Experimental Section).[13] CPMAS NMR spectroscopy [resonances characteristic for carbon atoms from carbonates (δ = 168.0 ppm, broad signal), ²Bu–Zn group (δ = 34.3 ppm), and py-Me (δ = 20.6, 125.27, 149.81 ppm); see Figure S9 in the Supporting Information] and FTIR spectroscopy. IR bands assignable to the carbonate and bicarbonate species were observed at 9 = 3420 (v(OH)), 1684 (v₂(CO)), 1508 (v₁(CO)) 1463 (v₁(CO) (the most intense band), 1380 (v₂(CO)), and 1236 cm⁻¹ (v₁(OCO)) (see Figure S10 in the Supporting Information).[15]

Based on the above investigations, it is reasonable to conclude that the consumption of ZnOH moieties takes place faster in the 1/CO₂/py-Me system compared with that in the 1/CO₂/THF system, with the concomitant formation of relatively stable alkylzinc bicarbonate [²BuZn(HCO₂)]⁻, species (Scheme 3).

Figure 2. a) ¹H NMR spectra for CO₂ fixation by 1 in [D₈]THF; a) inset showing an enlarged spectrum range. b) ¹H NMR spectra for CO₂ fixation by 3 in [D₈]THF. c) ¹H NMR spectra for CO₂ fixation by the 1/tBuZn reaction system in [D₈]THF. Characteristic signals are marked as follows: ·: tBuZn, Zn(OH) groups from 1 or 3; ·: tBuZn groups from tBuZn; ¤, □, ▽: tBuZn groups of the putative bicarbonate 1a and 1b (L = THF or py-Me); ·: acidic proton from bicarbonate species.
In this case, the protonolysis of the tBu–Zn group affording zinc carbonates and isobutane is much less pronounced than that in the 1/CO₂/THF system; this can be attributed to more efficient stabilization of the putative bicarbonate intermediate 1b₁ by py-Me. Strong donor ligands are liable to significantly modulate the internal rearrangement of the resulting bicarbonate ion and its reactivity; this hypothesis is in agreement with prior theoretical studies of biomimetic systems in which the presence of indirect (external) supporting residues facilitate the proton relay of zinc-bound bicarbonate.[16]

Reactivity of 1 towards CO₂ in the presence of tBu₂Zn

In our previous studies, we demonstrated that the presence of tBu₂Zn had a strong influence on the reaction between 1 and CO₂, yielding the alkylzinc carbonate complex 2.[7] We hypothesized that in this system excess tBu₂Zn acted as an external proton acceptor and quenched acidic protons in the bicarbonate intermediates 1a₁ or 1b₁ (Scheme 3). To investigate the 1/CO₂/tBu₂Zn system, first we ensured that 1 itself was not reactive towards tBu₂Zn. A control ¹H NMR spectroscopy experiment carried out under ambient conditions for an equimolar mixture of 1 and tBu₂Zn in THF and toluene showed that the characteristic signals of both compounds were present and their intensities were unaltered (see the Supporting Information for details). In the next step, we monitored the reaction of 1 with CO₂ in the presence of tBu₂Zn in [D₈]THF by using ¹H NMR spectroscopy. Figure 2c reveals that signals attributed to 1 (δ = 1.05 and 4.44 ppm) and tBu₂Zn (δ = 0.98 ppm) disappeared quickly (see also Figure S6 in the Supporting Information), and isobutane was formed during the first 10 min of the reaction. The signals of tBuZn gradually disappeared within a few hours, and during the reaction course we did not observe signals characteristic for bicarbonate species (see above). This indicates that the fast transformation of the bicarbonate species into alkylzinc carbonate 2 is triggered by protonolysis of tBu₂Zn molecules. Similar results were obtained in the case of 3/6/tBu₂Zn in [D₈]THF exposed to CO₂. As for the 1/CO₂/tBu₂Zn system, we did not observe any presence of bicarbonate species (Figure S8 in the Supporting Information). Notably, the reaction of 3/6/tBu₂Zn with CO₂ yielded alkylzinc carbonate 2 in high yield (75%).[17]

DFT calculations

DFT calculations were performed at the PBE0/6-31G + + (2d,2p) level[21] to determine the pathway of CO₂ insertion into the dimeric unit [tBuZn(µ-OH)]₂ (1₂). We focused on the energy profiles of various elementary steps of the reaction between 1₂ and CO₂, as well as on the mechanism associated with intramolecular rearrangements of the dinuclear [tBuZn(µ-OH)][tBuZn(HCO₃)] bicarbonate intermediate (Figure 3). We note that theoretical studies considering the mechanism of CO₂ fixation mediated by dinuclear systems are relatively scarce,[19] in contrast to many computational studies on mononuclear CA model systems over the last three decades.[16,20]

The reaction path for the fixation of one molecule of CO₂ into the dimeric 1₂ unit is presented in Figure 3. In the first stage of the reaction, the separated reactants form an encounter complex (a local minimum on the energy pathway) 1₂CO₂ (a₁), although the binding energy of −4.9 kJ mol⁻¹ does not indicate a strong interaction between the subunits. The closest contact between the hydroxyl oxygen and the CO₂ carbon atom (2.93 Å) for a₁ is shorter than the van der Waals separation estimated from the van der Waals radii (3.22 Å).[21] The next step, in which the bicarbonate TS a₂ is formed, seems to be the most limiting due to the relatively high energetic barrier of +52.5 kJ mol⁻¹. At this point, the deviation from linearity of the CO₂ molecule is 32.1°. This barrier exceeds approximately twice that calculated for mononuclear CA model systems.[16]

The reaction is then expected to proceed to the primary bicarbonate [tBuZn(µ-OH)][tBuZn(HCO₃)] (a₃) as a local minimum (corresponding to the primary bicarbonate 1a₁ in Scheme 2)[22] with a six-membered heterocyclic ring and a bicarbonate proton in the proximal position.

In the case of the CA model systems, at the stage of CO₂ fixation, an intramolecular proton transfer (Lipscomb mechanism) or an internal rotation (Lindskog mechanism) of the bicarbonate species are usually considered.[3c,16,20] In the present case, the activation energy corresponding to direct proton transfer between primary bicarbonate a₃ and secondary bicarbonate a₇ has a value of +82.7 kJ mol⁻¹ (see Figure S11 in the Supporting Information). The appearance of such a big energy gap in the absence of proton acceptors[23] strongly suggests that the rotation-type mechanism should be expected. During the formation of the bicarbonate group, internal proton transfer to the ternary carbon atom in the tBu group may also occur. This
competitive process, however, was found to be endothermic (see Figure S12 in the Supporting Information) and had an extremely high activation barrier of $+167.4 \text{ kJ mol}^{-1}$. Indeed, the energy profile presented in Figure 3 clearly indicates that for the dinuclear $\text{[}t\text{BuZn(µ-OH)}][t\text{BuZn(HCO}_2})\text{]}$ intermediate the rotation-type pathway is favored for the transformation from primary bicarbonate a3 to secondary bicarbonate a7 and proceeds via local minimum a5 and two TSs, a4 and a6. The Zn1–O2 bond in structure a3 first undergoes a transformation to the a5 local minimum with a four-membered Zn$_2$O$_2$ ring. This transformation proceeds via TS a4, and represents an almost negligible energy barrier of 3.4 kJ mol$^{-1}$. After rotation around the carbon–oxygen bond, separated by TS a6, the final product a7 is obtained (denoted as 1a$_{eq}$ in Scheme 4). The rotation-type pathway of the dinuclear $\text{[}t\text{BuZn(µ-OH)}][t\text{BuZn(HCO}_2})\text{]}$ intermediate rearrangement shows considerable similarity to that commonly encountered in bicarbonate intermediates of mononuclear CA model systems. Notably, the CO$_2$ fixation process can occur on two sides of 1$_1$ (both Zn–OH groups can be involved in the CO$_2$ fixation), leading to the formation of dinuclear $\text{[}t\text{BuZn(µ-OH)}][t\text{BuZn(HCO}_2})\text{]}$ and $\text{[}t\text{BuZn(HCO}_2})\text{]}$ bicarbonates. DFT calculations indicate that for both insertion steps the activation energies have comparable values (see Figure S13 in the Supporting Information), which is consistent with our experimental observations (see above).

Moreover, the DFT data indicate that, in the 1/CO$_2$, systems, bicarbonate intermediates 1a$_1$ and 1b$_1$ are likely to exist as an equilibrated mixture of the primary bicarbonate 1a$_1$ (or 1b$_1$; with proximal position of hydrogen) and the secondary bicarbonate 1a$_2$ (or 1b$_2$; with distal position of hydrogen). It is reasonable to propose that 1a$_2$ and 1b$_2$ are energetically favored, as represented in Scheme 4. In the next step, we considered the proton-transfer process in a reaction between the dimeric bicarbonate $\text{[}t\text{BuZn(HCO}_2})\text{]}$ and tBu$_2$Zn. The corresponding path is presented in Figure 4, and the diagram shows that the reaction starts with the formation of $\text{[}t\text{BuZn(HCO}_2})\text{]}$, tBu$_2$Zn (b1), which involves the secondary bicarbonate conformer with the distal position of hydrogen.[24]

As expected, the corresponding binding energy is negative, −8.8 kJ mol$^{-1}$, mainly due to electrostatic interactions between the oxygen atom on the bicarbonate subunits and the zinc atom from the acceptor molecule. The crucial step of the presented path is then the formation of TS b2, which corresponds to the reaction barrier of $+14.7 \text{ kJ mol}^{-1}$. The formation of TS b2 enables protonolysis of the Zn–C bond in the external molecule with the formation of a mixed carbonate product $\text{[}t\text{BuZn(HCO}_2})\text{]}$ (b3) and isobutane. Finally, the overall energy gain of the reaction yields a total value of $-153.8 \text{ kJ mol}^{-1}$, which is likely to render it essentially irreversible. In conclusion, the DFT calculations, in conjunction with spectroscopic studies, clearly indicate that the presence of tBu$_2$Zn in the 1/CO$_2$ system greatly accelerates proton transfer from the intermediate bicarbonate species 1b$_{neq}$ and supports the formation of the alkylzinc carbonate $\text{[}t\text{BuZn(CO}_2})\text{]}$, as shown in Scheme 5.[22]

**Figure 4.** Reaction profile with energetic minima and TSs for the $\text{[}t\text{BuZn(HCO}_2})\text{]}$/tBu$_2$Zn reaction system. Energy values [kJ mol$^{-1}$] were obtained at the PBE0/6-31G $+$ (+2d,2p) level of theory.

**Scheme 5.** Proposed transformation of the intermediate bicarbonate 1b$_{neq}$ in the presence of tBu$_2$Zn.

**Conclusion**

We provided a comprehensive experimental and theoretical study that afforded a detailed mechanistic picture of the reaction between RZnOH species and CO$_2$. We demonstrated that species of 1 in the presence of donor ligand L readily formed dimeric species $\text{[}t\text{BuZn(µ-OH)(L)}\text{]}$ (L = THF, py-Me) in solution. The $^1$H NMR spectroscopy studies supported by DFT calculations indicated that in the reaction of 1$_1$ with CO$_2$, both Zn–OH groups were involved in the fixation of CO$_2$ to form putative primary and secondary dinuclear bicarbonate intermediates. The resulting acidic bicarbonates underwent further transformations by promoting protonolysis of the alkylzinc moieties, which was accompanied by the evolution of isobutane and the formation of Zn(CO$_2$)$_2$ species. In the case of the 1/CO$_2$/py-Me system, protonolysis of tBu–Zn group was much less pronounced than that in the 1/CO$_2$/THF system. Further-
more, our studies indicated that the presence of tBu$_2$Zn in the 1/CO$_2$ system greatly accelerated proton transfer from the inter- mediate bicarbonate species and supported the formation of alkylzinc carbonate cluster 2. In both systems, 1/CO$_2$ and 1/ tBu$_2$Zn, proton transfer from the bicarbonate to the alkyl- zinc species or external tBu$_2$Zn molecule, respectively, was irre- versible and became the driving force for the formation of the final carbonate products. Finally, our studies underlined the in- creasing potential of simple organozinc precursors that fea- tured CO$_2$-reactive Zn–OH groups and proton-reactive Zn–C bonds for the design of new functional materials based on zinc carbonate components.

**Experimental Section**

**Methods and materials**

All manipulations were conducted under a nitrogen atmosphere by using standard Schlenk techniques. Di-tert-butylzinc[25] and 1[7] were prepared as described previously. All other reagents were purchased from commercial vendors (py-Me (Aldrich), CO$_2$ 99.999% (Multai), and solvents were dried and distilled from Na/K alloy prior to use. Solution NMR spectra were acquired on Varian Mercury 400 MHz and Varian Inova 500 MHz spectrometers. Solid-state NMR spectra were acquired on a Bruker Avance I 500 MHz spectrometer. IR spectra were recorded on an FTIR PerkinElmer System 2000 spectrometer.

**Synthesis of 3**

Lewis base py-Me (16 μL, 0.16 mmol, 0.33 equiv) was added to a freshly prepared solution (12.0 mL) of 1$_1$ (0.420 g, 0.50 mmol) in THF. The prepared solution was stirred at room temperature for 1 h. Compound 3 was obtained as colorless plate-like crystals after recrystallization from THF at $-20^\circ$C (0.312 g, 81%); $^1$H NMR (CD$_2$$_2$THF, 400.10 MHz, 298 K): $\delta=7.11$ (d, 2H; CH$_3$); 8.38 (d, 2H; CH$_{py}$); 4.49 (s, 1H; Zn=NH); 2.32 (s, 3H; CH$_3$); 1.05 ppm (s, 9H; Zn(C(CH$_3$)$_2$)$_2$); IR (Nujol): $\tilde{\nu}=3648$ (s), 3607 (s), 2954 (s), 2924 (s), 2854 (s), 2805 (s), 2746 (w), 2688 (w), 1622 (s), 1461 (s), 1377 (s), 1070 (w), 1023 (m), 914 (s), 803 (s), 722 (m), 656 cm$^{-1}$ (s); elemental analysis calcd (%) for C$_{24}$H$_{36}$O$_4$Zn: (1023.31 gmol$^{-1}$): C 42.23, H 7.23, N 2.74; found: C 42.32, H 7.29, N 2.70;

**Reaction of the 3/6 tBu$_2$Zn system with CO$_2$**

A solution of tBu$_2$Zn (0.270 g, 1.50 mmol) in THF (3.0 mL) was added to a freshly prepared solution of 3 (0.256 g, 0.25 mmol) in THF (4.0 mL). The resultant solution was allowed to warm to room temperature and exposed to a CO$_2$ atmosphere in a Schlenk flask without stirring. Colorless rhomboid crystals of 2 were obtained after recrystallization from the parent mixture at room temperature after 24 h (0.392 g, 88%).

**Reaction of 3 with CO$_2$**

Freshly dissolved 3 (0.268 g, 0.25 mmol) in toluene (4.0 mL) was exposed to a CO$_2$ atmosphere in a Schlenk flask without stirring. A white, insoluble in organic solvent precipitate was obtained after 24 h. $^1$H NMR (CD$_2$$_2$THF, 400.10 MHz, 298 K): $\delta=7.18$ (d, 2H; CH$_3$); 7.12 (d, 2H; CH$_3$); 7.12 (d, 2H; CH$_3$); 2.30 (s, 3H; CH$_3$); 1.05 ppm (s, 9H; Zn(C(CH$_3$)$_2$)$_2$); CP-MAS $^1$C NMR: $\delta=20.6$ (4-py-CH$_3$)$_2$, 34.3 (C(CH$_3$)$_2$), 125.3, 149.8 (4-py-Me), 168.0 (CO$_2$)$_2$ ppm; IR (Nujol): $\tilde{\nu}=3383$ (w), 2954 (s), 2923 (s), 2853 (s), 1623 (s), 1506 (w), 1463 (s), 1456 (s), 1377 (s), 1232 (s), 1212 (m), 1069 (m), 1033 (s), 842 (s), 814 (s), 722 cm$^{-1}$ (m); elemental analysis calcd (%) for [tBu$_2$Zn(CO$_2$)$_3$(Me-Py)$_3$]$_3$: C$_{36}$H$_{36}$N$_4$O$_{12}$Zn$_3$ (1285.31 gmol$^{-1}$): C 39.22, H 5.76, N 2.17; Zn 30.58; found: C 35.58, H 2.61, N 2.71, Zn 45.48.

Elemental analysis indicated 1) that the molar ratio of py-Me/Zn was 1.5 in the precipitate, which corresponded to the composi- tion of starting compound 3 (py-Me/Zn molar ratio 1.3); and 2) the lower content of carbon (in comparison with [tBu$_2$Zn(CO$_2$)$_3$(Me-Py)$_3$]) suggested partial hydrolysis of tBu$_2$Zn and the formation of carbonate species.

**Crystallographic data**

Data were collected by using the oil drop technique to mount crystals on a Nionus Kappa-CCCD equipped with an Oxford Cryos- stream low-temperature device.

**Crystal data for 3: C$_{24}$H$_{36}$O$_4$Zn; M = 1023.31; crystal dimensions 0.34 x 0.28 x 0.24 mm$^3$; triclinic; space group P1 (no. 2); a = 10.5370(4), b = 14.4060(6), c = 15.7430(5) Å; $\alpha = 90.830(2)$, $\beta = 99.4812(3)$, $\gamma = 96.747(2)$; $\mu = 2.339.36(15)$ Å$^2$; $\tau = 2$; $F(000) = 1064$; $\rho_{calc} = 1.453$ gcm$^{-3}$; $\tau = 100(2)$ K; $\mu(\text{MoK\textalpha}) = 3.065$ mm$^{-1}$; $\theta_{max} = 24.71$°; 7957 unique reflections. The structure was solved by direct methods by using the SHELXS97[25] program and was refined by full-matrix least squares on $F^2$ by using the program SHELXL97.[27]

All non-hydrogen atoms were refined with anisotropic displace- ment parameters. The hydrogen atoms were introduced at geo- metrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.2. Refinement converged at $R = 0.0751$, $wR2 = 0.1595$ for all data and 471 parameters ($R1 = 0.0576$, $wR2 = 0.1371$ for 6155 reflections with $I_{obs} > 2\sigma(I_{obs})$). The Goof on $F^2$ was 1.023. A weighting scheme $w = (\sigma(F_n^2) + 0.0418P^2 + 3.1964P)^{-1}$, in which $P = (F^2 + 2F_e^2)/3$ was used in the final stage of the refinement. The residual electron density is $+0.85/-0.75$ eÅ$^{-3}$.

CCDC-866666 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Computational details**

The geometries of the compounds studied herein were optimized with the PBE0[28] functional in the 6-31G + + (2p,2d) basis set (double zeta with the addition of polarized and diffuse functions). The selection of the functional was based on its reliable per- formance in related calculations when considering mostly higher- row transition-metal complexes,[29,30] and the results were usually comparable or better to those obtained with the popular B3LYP functional for minima and TSs.[31,32] However, contrary to B3LYP, PBE0 represents a parameter-free DFT model.[28]

The nature of the minima and maxima obtained after the optimiza- tion process was confirmed by frequency analysis, and zero-point energy corrections were added to the corresponding electronic en- ergies for the basis set superposition error. Additionally, the intrinsic reaction coordinate calculations and the analysis of frequen- cies were performed for the TSs to check whether the corre- sponding minima had been correctly located. All calculations were performed with the Gaussian suite of codes.[36] Figures were prepared with the CYLview visualization software.[34]
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Keywords: carbon dioxide fixation · computational chemistry · density functional calculations · reaction mechanisms · zinc · zinc hydroxide


[2] The room-temperature $^1$H NMR spectrum of a freshly prepared solution of 1 in [D$_2$]THF features partly overlapping resonances that correspond to different Ru analogs. To obtain interpretable data that were well re- solved in the diffusion domain, multivariable analysis was used (see the Supporting Information).


[5] Zinc bicarbonate has been an elusive species for spectroscopic characterization for decades, and the bicarbonate ion was only very recently identified with a tris(3-tert-butyl-5-methylphenyl)azo)hydroborato zinc complex by low-temperature $^1$H NMR spectroscopy studies (δ = 13.2 ppm, C$_2$D$_2$, C$_3$H$_8$, 19 K), see: W. Sattler, G. Parkin, Polyhedron 2012, 31, 41–48; more recently these authors reported the first terminal zinc bicarbonate complexes to be structurally characterized by using XRD; for details, see [4a].

[6] For comparison, in the 1/COSY system, we observed a relatively weak intensity of the signal attributed to the acidic proton of the bicarbonate species at δ = 9.86 ppm, which suggested rapid proton migration from Zbi(THC) to a species with a thermodynamically favorable energetic minimal Zn(CO$_3$).


[9] This observation is in agreement with another control experiment in which BuZn is added only 5 h after 3 and CO$_2$ are mixed (when 1b·Me is observed; according to $^1$H NMR spectroscopy studies). This gave 2 in almost quantitative yield.

[10] The selection of the function with respect to other functionals tested, and its reliability was confirmed within the transition-metal study.


To simplify DFT calculations, we did not include donor solvent molecules in the initial structures.


Herein, we only consider the interaction between tBu2Zn and the secondary bicarbonate with the distal position of hydrogen. The interaction involving the primary bicarbonate intermediate with the proximal position of hydrogen exhibits significant steric hindrance that does not allow for the stabilization of any TSs.


