

An Air- and Water-Tolerant Zinc Hydride Cluster That Reacts Selectively With CO₂**

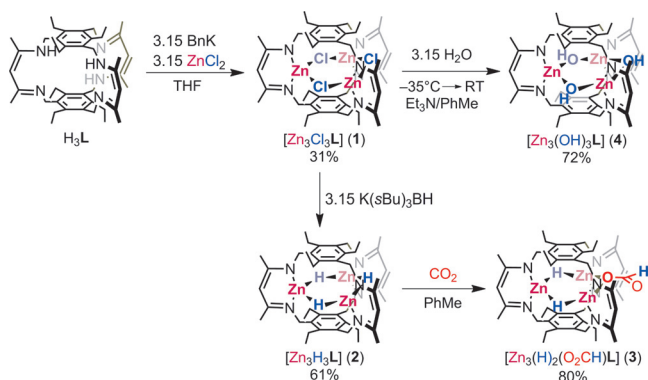
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Abstract: The reaction of [Zn₃Cl₃L], in which L^{3−} is a tris(β-diketiminato) cyclophane, with K(sBu)₃BH afforded [Zn₃(μ-H)₃L] (**2**), as confirmed by NMR spectroscopy, NOESY, and X-ray crystallography. The complex **2** was air-stable and unreactive towards water, methanol, and other substrates (e.g., nitriles) at room temperature over 24 h but reacted with CO₂ (ca. 1 atm) to generate [Zn₃(μ-H)₂(μ-1,1-O₂CH)] (**3**). In contrast, [Zn₃(OH)₃L] (**4**) was found to be unreactive toward CO₂ over the course of several days at 90 °C.

Amid concerns over global warming resulting from the atmospheric level of carbon dioxide, there is interest in developing chemical strategies to utilize carbon dioxide as a C₁ source. This however requires either the electrochemical or chemical reduction of CO₂ to more reactive molecules (e.g., acids, alcohols).^[1,2] High selectivity by the reactive species for carbon dioxide over other substrates (e.g., H⁺) reduces the need for purification of the CO₂ stream.^[1g,3] Two approaches for CO₂ reduction are the use of either low-valent metal centers or metal hydrides.^[2b,4] The latter typically show poor selectivity for CO₂ and are susceptible to protonation,^[5] thus leading to competitive H⁺ reduction.^[1h,i,6] In particular, Zn hydrides are attractive, as zinc is earth-abundant, and reductive elimination or metal oxidation are disfavored. Zinc hydrides are typically highly nucleophilic; for example, (β-diketiminato)zinc hydrides react with CO₂ and many unsaturated organic substrates (e.g., alkynes, nitriles, and ketones).^[7] Parkin and Sattler demonstrated the reduction of carbon dioxide and carbonates by [(tptm)ZnH] (tptm = tris(2-pyridylthio)methane) complexes in tandem with silanes.^[8] However, there are no reports of the selective reaction of ZnH species with CO₂ over carbonyl- or nitrile-containing compounds, other heteroallenes, or protons. Herein, we report a trizinc tri(hydride) complex which is an air-tolerant solid

and reacts with carbon dioxide exclusively, with no observed reaction with the other substrates tested (e.g., MeCN).

The treatment of H₃L with benzyl potassium (BnK), followed by the addition of ZnCl₂, afforded Zn₃Cl₃L (**1**; 31 %, Scheme 1).^[9] We propose that **1** adopts a structure in which a hexagonal [Zn₃(μ₂-Cl)₃]³⁺ cluster is supported by the ligand.



Scheme 1. Synthesis and reactivity of **1–4**.

This structure is consistent with the *D*_{3h} symmetry observed for **1** in solution NMR spectra, and is analogous to that of [Fe₃(μ₂-NH₂)L].^[10] Complex **1** reacted readily with K(sBu)₃BH to yield [Zn₃H₃L] (**2**; 61 %), which also appeared to have *D*_{3h} symmetry in solution according to NMR spectroscopy. The assigned hydride resonance at 2.64 ppm was not coupled to any C atoms in **2** in gHSQC spectra and exhibited a strong NOE correlation with the -CH₂CH₃ hydrogen atoms of the ethyl groups on the benzene caps (δ = 2.54 ppm). These data suggest a [Zn₃(μ₂-H)₃]³⁺ core in **2**. The solid-state structure of **2**, in which each metal cation is in a distorted tetrahedral environment (τ₄ = 0.89–0.92) defined by the N,N chelate of a given β-diketiminato (nacnac) arm and two μ₂-H[−] donors, supports this assignment (Figure 1).^[11] Bond metrics observed in **2** are comparable to those in dimeric and monomeric nacnac and NHC zinc hydride complexes.^[12] The hydride resonance in **2** is shifted downfield by about 2 ppm relative to those reported for mono- and dinuclear zinc hydride complexes,^[12c,d,13] probably as a result of the ring currents of the cyclophane aromatic rings.^[14]

To our surprise, we observed no changes in either IR or NMR spectra of reaction mixtures of **2** with a large excess (> 150 equiv) of either RC≡N (R = Me, Ph), PhCHO, acetone, Me₃SiC≡CH, or CS₂ even after several days at room temperature (see Figures S12–S17 in the Supporting Information). All reactions remained homogeneous solutions, and only unreacted **2** and the substrate were observed. The

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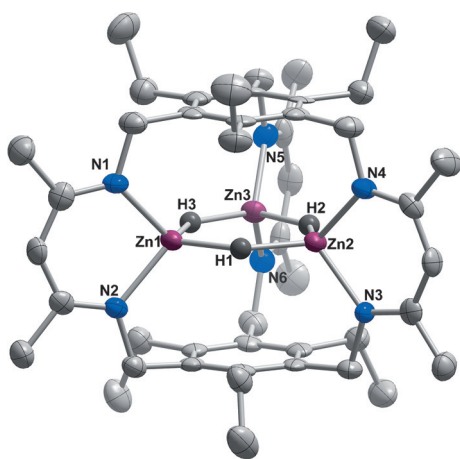


Figure 1. Solid-state structure of **2**. C, N, and Zn atoms are represented as light-gray, blue, and purple ellipsoids (90% probability), respectively. Hydride H atoms are depicted as dark-gray spheres. All other H atoms and solvent molecules of crystallization have been removed for clarity.

broad functional-group tolerance of **2** contrasts sharply with the reactivity profiles of mononuclear zinc hydride complexes. We then probed the reaction of **2** with water and methanol; however, we similarly observed no changes in the ^1H NMR spectrum (see Figures S18 and S19). On the basis of this result, we tested the air stability of **2**. As expected, spectra of both solid and solution samples of **2** stored on the bench top and exposed to air over the course of several days were unchanged and consistent with the starting complex (see Figures S20 and S21). To our knowledge, this complex is a unique example of an air- and water-stable zinc hydride.

In contrast to the substrates above, the addition of CO_2 to **2** resulted in the growth of a new singlet at 8.32 ppm and multiplets at 2.66 and 2.55 ppm with a concomitant decrease in the hydride resonance at 2.64 ppm in ^1H NMR spectra of the reaction mixture (Figure 2). The resonances at 8.32 ppm in the ^1H NMR spectrum and 164.7 ppm in the ^{13}C NMR spectrum of the reaction product are at comparable chemical shifts to those of other reported zinc-bound formates.^[7c,12b,15] Intense and sharp absorptions were present in the IR spectrum of the CO_2 reaction product at 1670 and 1228 cm^{-1} —comparable to values for C=O stretching modes of metal formates^[7c,d,12b]—and shifted to 1630 and 1207 cm^{-1} when $^{13}\text{CO}_2$ was used as the substrate (see Figure S30). A doublet at 8.32 ppm ($J_{\text{CH}} = 202\text{ Hz}$) in the ^1H NMR spectrum and a strong signal enhancement of the formate carbon-atom resonance in the ^{13}C NMR spectrum were also observed for the $^{13}\text{CO}_2$ reaction product (see Figure S22). Taken together, these spectral changes support the formation of a formate ligand derived from CO_2 . Notably, not all hydride ligands in the reaction mixture were consumed, which was surprising, as analogous mononuclear zinc hydrides react quantitatively with CO_2 . In multinuclear NMR and NOE spectroscopic experiments, we determined the molecular structure of the major product as $[\text{Zn}_3(\text{H})_2(\text{O}_2\text{CH})\text{L}]$ (**3**). The reaction was monitored by ^1H NMR spectroscopy to probe whether intermediates were formed during the reaction. No spectral

changes were observed at temperatures below 20°C . We subsequently collected spectra over 14 h at 20°C , by which time 82 % of **2** had been consumed to afford **3**, as based on the integral of the $-\text{OCHO}$ resonance (Figure 2, inset). The absence of additional downfield resonances—typical of metal formates—is in agreement with the NMR spectroscopic structural solution of **3** and supports differential reactivity of the three hydride ligands.

Although the solid-state structure is not of sufficient quality, we nonetheless observed electron density and partial occupancies for the formate ligands, consistent with our solution structure determination (see Figure S31). The formate is coordinated in a μ -1,1 bridging mode, which is not consistent with the apparent C_{2v} symmetry in room-temperature NMR spectra. In the spectrum of **3** at -85°C , we observed three resonances (4.80, 4.77, and 4.62 ppm) with approximately equivalent integrals for the three central $-\text{CH}$ hydrogen atoms in the nacnac arms. The resonances at 4.77 and 4.62 ppm broadened and coalesced upon warming to afford a single resonance at 25°C (see Figure S23). Similarly, the multiplet assigned to the ligand $-\text{CH}_2\text{CH}_3$ hydrogen atoms appeared as two distinct multiplets at -85°C ; these signals also coalesced upon warming to afford a quartet at 2.66 ppm (see Figure S23). These variable-temperature data agree with the crystallographic result, but point to fluxional coordination of the formate ligand at room temperature, probably as a result of a carboxylate shift through a μ -1,3 bridging mode (see Scheme S4 in the Supporting Information). The calcu-

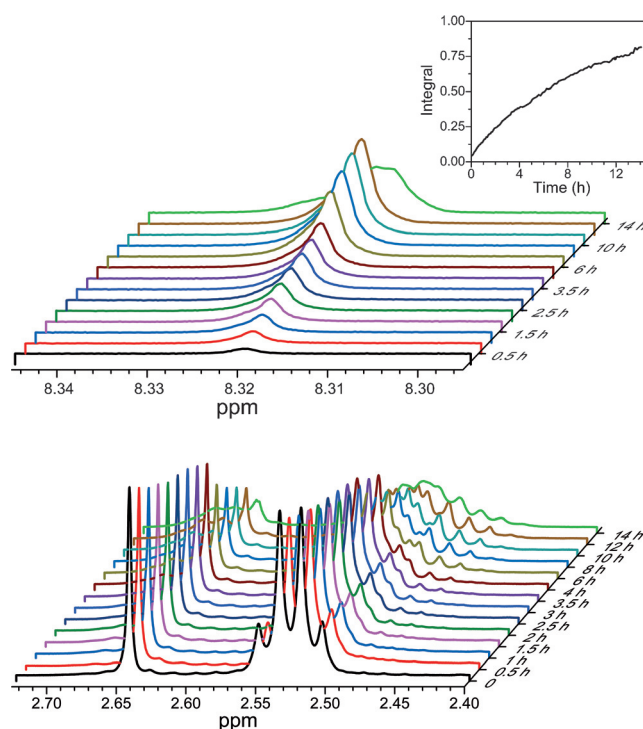


Figure 2. ^1H NMR spectra collected over 14 h after the addition of CO_2 to **2**. A new resonance observed at 8.32 ppm is consistent with the formation of a formate ligand (top) and the concomitant loss in intensity of the resonance for the hydride at 2.64 ppm (bottom). The inset is a plot of the integral of the peak at 8.32 ppm referenced to the 18 ligand $-\text{CH}_2\text{CH}_3$ protons versus time.

lated activation energy for this process is 10.0(8) kcal mol⁻¹ for a coalescence temperature of 238 K and is similar to $\Delta G^\ddagger$ values for carboxylate shifts in Zn^{II} acetates.^[16]

Given that zinc hydroxides typically react readily with CO₂ to afford bicarbonate complexes, we examined the reactivity of the hydroxide analogue of **2**. The addition of water to a suspension of **1** and excess NEt₃ in toluene afforded [Zn₃(OH)₃L] (**4**) in reasonable yield (72%). Like **2**, this complex had *D*_{3h} symmetry in solution, with $\delta(\text{Zn-OH}) = -1.12$ ppm.^[17] NOE and gHMBC experiments confirmed the close position of the -OH hydrogen atoms to the -CH₂CH₃ hydrogen atoms on the aromatic rings, as expected for μ_2 hydroxide ligands, and an absorption observed at 3684 cm⁻¹ in the IR spectrum of **4** is comparable to that of other metal hydroxides (see Figures S24, S25, and S28).^[17b,c] We observed no change in the NMR or IR spectrum during reactions of **4** with CO₂ in toluene even at temperatures up to 90 °C for 48 h. The lack of reactivity of **4** with CO₂ differs from prior synthetic and biological examples, in which terminal hydroxides coordinated to zinc capture atmospheric CO₂.^[18] Possible reasons for the difference observed in this case are an inability to access mononuclear or terminal ZnOH species, the unfavorable steric conditions for interaction with substrates, as dictated by the ligand, or improper orientation of the reactive electron pair on the bridging hydroxides as compared to the hydrides. Nonetheless, the reduced reactivity of the hydroxide congener correlates with the observed muted reactivity of [Zn₃H₃L] as compared to that of monometallic complexes.

To our knowledge, the selectivity for CO₂ and the differential reactivity of the three hydrides are unique to **2**. The ethyl substituents above and below the hydride ligands, as well as dynamic effects (e.g., rotation of the Et groups), may enforce steric constraints on the size and shape of potential substrates. However, lack of reactivity with H₂O or MeOH suggests that other effects also operate. From the electrostatic map calculated from an optimized structure of **2** in which the Et substituents are replaced with Me groups (see Figure S32), we observed that each hydride lies within a hydrophobic pocket, which may disfavor the approach of more polar substrates towards the reactive hydride. A higher bond distortion for the reaction of CS₂ versus CO₂ with frustrated Lewis pairs was recently proposed, and may also occur in the present case.^[19] For mononuclear zinc hydrides, substrate coordination to the metal center precedes hydride transfer.^[8c,20] Each Zn center in **2** is held within a pseudotetrahedral coordination environment with no obviously accessible site for substrate binding. Thus, hydride transfer could occur by direct nucleophilic attack by a μ_2 hydride. A similar mechanism was proposed for CO₂ reduction by iridium hydride complexes; these complexes are tolerant of water and have limited reactivity with substrates other than CO₂.^[2,21] Our results and these prior reports suggest that CO₂ selectivity can be controlled by limiting access to the metal coordination sphere prior to hydride transfer. However for (nacnac)metal hydrides, the mononuclear species are speculated to be reactive, whereas the hydride-bridged dimers are not.^[12d,22] Alternatively then, the Zn₃H₃ cluster could undergo a structural distortion to generate either an asymmetric bridging

hydride or a terminal hydride that reacts readily with CO₂. Once the first formate is installed, subsequent opening of the remaining M-H-M bonds may require significantly more energy or be retarded because of the fluxional coordination of the formate ligand, thereby reducing reactivity. Access to and the reactivity of isostructural clusters in which the metal-hydride bond strengths vary will provide valuable insight into the reaction mechanism.

In conclusion, [Zn₃H₃L] is a unique metal hydride complex, as it is air- and water-tolerant yet demonstrates exceptional selectivity for CO₂ over a variety of other substrates. ¹H NMR spectroscopic data support the formation of a [Zn₃(H)₂(O₂CH)L] complex, and ¹³CO₂ experiments confirmed the reduction of carbon dioxide to formate. Additional mechanistic studies, including the reactivity of the zinc hydride complex with other substrates, such as CO, are ongoing.

Keywords: carbon dioxide · cyclophanes · diketiminates · reduction · zinc hydrides

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