

# Synthesis, Structure, and Reactivity of a Mononuclear Organozinc Hydride Complex: Facile Insertion of $CO_2$ into a Zn-H Bond and $CO_2$ -Promoted Displacement of Siloxide Ligands

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# Supporting Information

ABSTRACT: Tris(2-pyridylthio)methane, [Tptm]H, has been employed to synthesize the mononuclear alkyl zinc hydride complex,  $[\kappa^3$ -Tptm]ZnH, which has been structurally characterized by X-ray diffraction.  $[\kappa^3$ -Tptm]ZnH provides access to a variety of other [Tptm]ZnX derivatives. For example,  $[\kappa^3$ -Tptm]ZnH reacts with (i) R<sub>3</sub>SiOH (R = Me, Ph) to give  $[\kappa^4$ -Tptm]ZnOSiR<sub>3</sub>, (ii) Me<sub>3</sub>SiX (X = Cl, Br, I) to give  $\lceil \kappa^4$ -Tptm $\rceil$ ZnX, and (iii) CO<sub>2</sub> to give the formate complex,  $[\kappa^4$ -Tptm]ZnO<sub>2</sub>CH. The bis(trimethylsilyl)amide complex  $[\kappa^3$ -Tptm]ZnN(SiMe<sub>3</sub>)<sub>2</sub> also reacts with CO<sub>2</sub>, but the product obtained is the isocyanate complex,  $[\kappa^4$ -Tptm]ZnNCO. The formation of  $[\kappa^4$ -Tptm]ZnNCO is proposed to involve initial insertion of CO2 into the  $Zn-N(SiMe_3)_2$  bond, followed by migration of a trimethylsilyl group from nitrogen to oxygen to generate  $[\kappa^4$ -Tptm]ZnOSiMe<sub>3</sub> and Me<sub>3</sub>SiNCO, which subsequently undergo CO<sub>2</sub>-promoted metathesis to give  $[\kappa^4$ -Tptm]-ZnNCO and  $(Me_3SiO)_2CO$ .

Zinc hydride species are of considerable interest in view of their Zuse in organic transformations<sup>1</sup> and their role in the Cu/ZnOcatalyzed synthesis of methanol from a mixture of CO, CO<sub>2</sub>, and H<sub>2</sub>.<sup>2</sup> Well-defined mononuclear zinc complexes that feature terminal hydride ligands are, however, rare,<sup>3-5</sup> due to the propensity of the hydride ligand to bridge two zinc centers.<sup>6</sup> Furthermore, structurally characterized mononuclear compounds that feature both alkyl and hydride ligands are unknown.<sup>7-9</sup> Here, we describe the synthesis, structural characterization, and reactivity of a mononuclear alkyl zinc hydride complex, including the facile insertion of CO<sub>2</sub> into the Zn–H bond. In addition, we also describe the ability of CO<sub>2</sub> to promote the displacement of siloxide ligands.

We previously utilized the tris(3-*tert*-butylpyrazolyl)hydroborato ligand to synthesize  $[Tp^{Bu^{t}}]ZnH$ , the first structurally authenticated monomeric zinc hydride complex,<sup>3</sup> in which the multidentate nature of the  $[Tp^{Bu^{t}}]$  ligand allows isolation of a compound that features a terminal hydride moiety. Using a similar approach, we have now employed a multidentate alkyl ligand derived from tris(2-pyridylthio)methane, [Tptm]H,<sup>10</sup> to permit isolation of a monomeric alkyl hydride complex, namely  $[\kappa^{3}-Tptm]ZnH$ .

The key starting material for the synthesis of  $[\kappa^3$ -Tptm]ZnH is the bis(trimethylsilyl)amide derivative,  $[\kappa^3$ -Tptm]ZnN(SiMe\_3)<sub>2</sub>,<sup>11</sup> that is obtained via the reaction of [Tptm]H with Zn[N-(SiMe\_3)<sub>2</sub>]<sub>2</sub>, as illustrated in Scheme 1. Subsequent treatment of  $[\kappa^3$ -Tptm]ZnN(SiMe\_3)<sub>2</sub> with Me\_3SiOH yields the siloxide Scheme 1



Scheme 2





Figure 1. Molecular structure of  $[\kappa^3$ -Tptm]ZnH.

 $[\kappa^4$ -Tptm]ZnOSiMe<sub>3</sub><sup>12,13</sup> that reacts with PhSiH<sub>3</sub> to give the hydride complex,  $[\kappa^3$ -Tptm]ZnH (Scheme 2). The molecular structure of  $[\kappa^3$ -Tptm]ZnH has been determined by X-ray

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#### Scheme 3





**Figure 2.** Molecular structure of  $[\kappa^4$ -Tptm]ZnO<sub>2</sub>CH.

diffraction (Figure 1), which demonstrates that the compound exists as a discrete mononuclear complex in which the [Tptm] ligand coordinates in a  $\kappa^3$ -manner. The Zn–H moiety of [ $\kappa^3$ -Tptm]ZnH is characterized by a Zn–H bond length of 1.51(3) Å,<sup>14</sup> a singlet at  $\delta$  5.60 in the <sup>1</sup>H NMR spectrum, and an absorption at 1729 cm<sup>-1</sup> in the IR spectrum, which shifts to 1242 cm<sup>-1</sup> for the zinc deuteride isotopologue [ $\kappa^3$ -Tptm]ZnD [ $\nu_{\rm H}/\nu_{\rm D}$  = 1.39]. The zinc methyl counterpart, [ $\kappa^3$ -Tptm]ZnMe, has also been synthesized via the reaction of [Tptm]H with Me<sub>2</sub>Zn (Scheme 1) and has a distorted tetrahedral geometry similar to that of [ $\kappa^3$ -Tptm]ZnH. For example, the C–Zn–H [132(1)°] and C–Zn–CH<sub>3</sub> [135.8(1)° and 134.1(1)° for two different crystalline forms] bond angles are distinctly greater than the tetrahedral value.

 $[\kappa^3$ -Tptm]ZnH serves as a precursor to a variety of other [Tptm]ZnX derivatives, as illustrated in Scheme 3. For example, the zinc hydride bond of  $[\kappa^3$ -Tptm]ZnH is (i) protolytically cleaved by  $R_3$ SiOH (R = Me, Ph) to give  $[\kappa^4$ -Tptm]ZnOSiR<sub>3</sub> and (ii) undergoes metathesis with Me<sub>3</sub>SiX (X = Cl, Br, I) to give  $[\kappa^4$ -Tptm]ZnX.<sup>15,16</sup> Of most note, however, is the fact that  $[\kappa^3$ -Tptm]ZnH reacts rapidly with CO<sub>2</sub> to give the formate complex,  $[\kappa^4$ -Tptm]ZnO<sub>2</sub>CH (Scheme 3 and Figure 2), which may also be obtained from the reaction of  $[\kappa^3$ -Tptm]ZnH with HCO<sub>2</sub>H.<sup>17</sup> Such reactivity is of particular interest in view of the fact that formate species are proposed intermediates in the ZnO- and Cu/ZnO-catalyzed synthesis of methanol.<sup>2</sup> The insertion of CO<sub>2</sub> into zinc hydride bonds is not, however, well precedented, and the only other examples involving monomeric zinc hydride complexes pertain to [TpR]ZnH derivatives.<sup>3,4d,18</sup> Both the formate and siloxide derivatives,  $[\kappa^4$ -Tptm]ZnO<sub>2</sub>CH and  $[\kappa^4$ -Tptm]ZnOSiR<sub>3</sub>, can be converted to a variety of other



**Figure 3.** Molecular structure of  $[\kappa^4$ -Tptm]ZnNCO.

Scheme 4



 $[\kappa^4$ -Tptm]ZnX derivatives upon treatment with Me<sub>3</sub>SiX (X = Cl, Br, I, N<sub>3</sub>, NCO, OAc), as illustrated in Scheme 3.

In addition to its role in methanol synthesis,<sup>2</sup> the abundance of CO<sub>2</sub> has stimulated efforts to discover other synthetic methods that employ  $CO_2$  as a  $C_1$  building block,<sup>19</sup> as illustrated by the metal-catalyzed hydrogenation to formic acid and formates,<sup>20</sup> and the formation of polycarbonates by copolymerization with epoxides.<sup>21</sup> The reactivity of  $CO_2$  towards metal compounds has, therefore, been the focus of much attention.<sup>19,22</sup> For example, the insertion of CO2 into M-NR2 bonds to give carbamato derivatives has been widely studied.<sup>23</sup> In contrast, however, there are few reports concerned with the reactivity of CO2 towards bis(trimethylsilyl)amido complexes.<sup>24</sup> It is, therefore, notable that  $[\kappa^3$ -Tptm]ZnN(SiMe<sub>3</sub>)<sub>2</sub> reacts with CO<sub>2</sub> to give the isocyanate complex,  $[\kappa^4$ -Tptm]ZnNCO, which has been structurally characterized by X-ray diffraction (Figure 3). Thus, rather than undergoing only a simple insertion reaction of the type that is observed for  $L_n MNR_{2}^{23}$  the reaction is accompanied by deoxygenation of  $CO_2$ , a transformation that is made possible by the formation of strong Si–O bonds.<sup>25,26</sup> The formation of the isocyanate complex  $[\kappa^4$ -Tptm]ZnNCO also provides a contrast to the reaction of Zn[N(SiMe<sub>3</sub>)(Ad)]<sub>2</sub> (Ad = adamantyl) with CO<sub>2</sub>, which gives AdN=C=NAd and unidentified trimethylsiloxide species.<sup>2</sup>

The generation of  $[\kappa^4$ -Tptm]ZnNCO is necessarily a multistep process, of which the initial sequence is proposed to involve insertion of CO<sub>2</sub> into the Zn-N(SiMe<sub>3</sub>)<sub>2</sub> bond to give [Tptm]-Zn[O<sub>2</sub>CN(SiMe<sub>3</sub>)<sub>2</sub>], which subsequently converts to the trimethylsiloxide derivative  $[\kappa^4$ -Tptm]ZnOSiMe<sub>3</sub> and Me<sub>3</sub>SiNCO (Scheme 4). In support of this proposal, both  $[\kappa^4$ -Tptm]ZnO-SiMe<sub>3</sub> and Me<sub>3</sub>SiNCO are observed by <sup>1</sup>H NMR spectroscopy during the course of the reaction. Interestingly, however, although the simplest rationalization for the formation of  $[\kappa^4$ -Tptm]ZnNCO from  $[\kappa^4$ -Tptm]ZnOSiMe<sub>3</sub> and Me<sub>3</sub>SiNCO involves direct metathesis, additional experiments suggest that this is not the operative mechanism. Specifically, while an independent experiment indicates that  $[\kappa^4-Tptm]ZnNCO$  is formed upon treatment of  $[\kappa^4$ -Tptm]ZnOSiMe<sub>3</sub> with Me<sub>3</sub>SiNCO, the reaction is extremely slow by comparison to the formation of [Tptm]ZnNCO upon treatment of  $[\kappa^3$ -Tptm]ZnN(SiMe\_3)<sub>2</sub> with CO<sub>2</sub>. The formation of the isocyanate complex [Tptm]ZnNCO is, however, accelerated if  $CO_2$  is added to a mixture of  $[\kappa^4$ -Tptm]ZnOSiMe<sub>3</sub> and Me<sub>3</sub>SiNCO. On this basis, it is proposed that the formation of  $[\kappa^4$ -Tptm]ZnNCO is promoted by insertion of CO2 into the Zn-OSiMe3 bond to give the carbonate derivative,  $[\kappa^4$ -Tptm]ZnO<sub>2</sub>COSiMe<sub>3</sub>, that is more susceptible towards metathesis with Me<sub>3</sub>SiNCO than is  $[\kappa^4$ -Tptm]ZnOSiMe<sub>3</sub>.

Evidence for facile reversible insertion of CO<sub>2</sub> into the Zn– OSiMe<sub>3</sub> bond is provided by variable-temperature <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopic studies that allow for observation of  $[\kappa^4\text{-}Tptm]ZnO_2COSiMe_3$  at temperatures  $\leq 5 \,^{\circ}$ C, as illustrated by a signal at 157.9 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum attributable to the carbonate moiety. In addition, the reaction between  $[\kappa^3\text{-}Tptm]$ -ZnN(SiMe<sub>3</sub>)<sub>2</sub> and CO<sub>2</sub> is accompanied by formation of the carbonate (Me<sub>3</sub>SiO)<sub>2</sub>CO, an observation that is in accord with Me<sub>3</sub>SiNCO undergoing metathesis with  $[\kappa^4\text{-}Tptm]ZnO_2CO$ -SiMe<sub>3</sub> rather than with  $[\kappa^4\text{-}Tptm]ZnOSiMe_3$ . Two factors that may contribute to the more facile cleavage of the Zn–OC-(O)OSiMe<sub>3</sub> bond than the Zn–OSiMe<sub>3</sub> bond are (i) insertion of the CO<sub>2</sub> group displaces the OSiMe<sub>3</sub> group from the metal center, thereby reducing steric interactions, and (ii) the presence of the C(O) group allows for a six-membered transition state.

The ability of  $CO_2$  to promote the overall displacement of a siloxide ligand has implications with respect to the fact that siloxides find frequent use as ancillary ligands.<sup>28</sup> Thus, while the insertion of  $CO_2$  into  $M-OSiR_3$  bonds has been little investigated,<sup>29,30</sup> it is evident from the above studies that the presence of  $CO_2$  could provide a general means to enhance reactivity of compounds with  $M-OSiR_3$  bonds;<sup>31</sup> correspondingly, it suggests that the presence of  $CO_2$  could be detrimental for situations in which the siloxide ligand is intended to play the role of a spectator.

Finally, it is pertinent to comment on the fact that the [Tptm]ZnX complexes described herein belong to two structural classes that differ according to whether the [Tptm] ligand binds in a  $\kappa^4$  or  $\kappa^3$ manner. Specifically,  $\kappa^4$ -coordination is observed in the solid state for  $[\kappa^4$ -Tptm]ZnI,  $[\kappa^4$ -Tptm]ZnNCO,  $[\kappa^4$ -Tptm]ZnN<sub>3</sub>,  $[\kappa^4$ -Tptm]-ZnOSiR<sub>3</sub> (R = Me, Ph),  $[\kappa^4$ -Tptm]ZnO<sub>2</sub>CH, and  $[\kappa^4$ -Tptm]-ZnO<sub>2</sub>CMe,<sup>32</sup> while  $\kappa^3$ -coordination is observed for  $[\kappa^3$ -Tptm]-ZnH and  $[\kappa^3$ -Tptm]ZnMe. Low-temperature <sup>1</sup>H NMR spectroscopic studies suggest that these coordination modes are also preserved in solution. Specifically, although all [Tptm]ZnX complexes exhibit three chemically equivalent pyridyl groups at room temperature, a 2:1 pattern emerges for  $[\kappa^3$ -Tptm]ZnH,  $[\kappa^3$ -Tptm]ZnMe, and  $[\kappa^3$ -Tptm]ZnN(SiMe<sub>3</sub>)<sub>2</sub> at ca. -10 °C, consistent with  $\kappa^3$ -coordination. In contrast, the low-temperature <sup>1</sup>H NMR spectra of  $[\kappa^4$  -Tptm]ZnX [X = Cl, Br, I, NCO, N<sub>3</sub>, OSiR<sub>3</sub>  $(R = Me, Ph), O_2CMe, O_2CH]$  exhibit chemically equivalent pyridyl groups indicative of  $\kappa^4$ -coordination.<sup>33</sup> This observation is in accord with density functional theory calculations which predict that the preference for  $\kappa^4$ - versus  $\kappa^3$ -coordination in [Tptm]ZnX for monodentate X ligands increases in the sequence Me < N- $(SiMe_3)_2 < H < I < OSiMe_3 < Br < Cl < N_3 < NCO < F.$  In view of the fact that the hydride derivative adopts  $\kappa^3$ -coordination while the bulky triphenylsiloxide derivative adopts  $\kappa^4$ -coordination, it is evident that steric factors do not dictate the differences in coordination mode. A consideration of [Tptm]ZnX derivatives in which X is monoatomic (X = F, Cl, Br, I, and H), however, indicates that the preference for  $\kappa^4$ -coordination correlates well with the electronegativity of X, a trend which suggests that  $\kappa^4$ -coordination becomes more favored with increasing charge on the zinc center.<sup>34</sup>

In summary, the mononuclear alkyl zinc hydride complex,  $[\kappa^3$ -Tptm]ZnH, may be synthesized via treatment of  $[\kappa^4$ -Tptm]-ZnOSiMe<sub>3</sub> with PhSiH<sub>3</sub>. [ $\kappa^3$ -Tptm]ZnH exhibits a variety of different reaction pathways, including insertion of CO2 to give the formate complex,  $[\kappa^4$ -Tptm]ZnO<sub>2</sub>CH. The bis(trimethylsilyl)amide complex  $[\kappa^3$ -Tptm]ZnN(SiMe<sub>3</sub>)<sub>2</sub> also reacts with CO<sub>2</sub>, but the product obtained is the isocyanate complex,  $[\kappa^4$ -Tptm]ZnNCO, that results from a multistep sequence of which the initial steps are insertion of CO<sub>2</sub> into the Zn-N- $(SiMe_3)_2$  bond followed by rearrangement to  $[\kappa^4$ -Tptm]ZnO-SiMe<sub>3</sub> and Me<sub>3</sub>SiNCO. An important discovery, however, is that the final metathesis step to give  $[\kappa^4$ -Tptm]ZnNCO is promoted by CO2, an observation which indicates that the carbonate complex  $[\kappa^4$ -Tptm]ZnO<sub>2</sub>COSiMe<sub>3</sub> is more susceptible towards metathesis than is the siloxide derivative,  $[\kappa^4$ -Tptm]ZnOSiMe<sub>3</sub>. As such, this finding has ramifications with respect to inducing reactivity of other siloxide compounds.

# ASSOCIATED CONTENT

**Supporting Information.** Experimental details, computational data, crystallographic data (CIF), and complete ref 19c. This material is available free of charge via the Internet at http:// pubs.acs.org.

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(31) In this regard, we have also observed that  $CO_2$  promotes formation of [ $\kappa^4$ -Tptm]ZnX (X = Cl, Br) upon treatment of [ $\kappa^4$ -Tptm]-ZnOSiR<sub>3</sub> (R = Me, Ph) with Me<sub>3</sub>SiX.

(32)  $[\kappa^4$ -Tptm]ZnCl also exhibits  $\kappa^4$ -coordination; see ref 15.

(33) The observation of equivalent pyridyl groups for  $[\kappa^4$ -Tptm]-ZnO<sub>2</sub>CR (R = H, Me) implies that access to the freely rotating  $\kappa^1$ -O<sub>2</sub>CR isomer is facile.

(34) Accordingly, DFT studies indicate that the difference in energies between  $[\kappa^3$ -Tptm]ZnX and  $[\kappa^4$ -Tptm]ZnX (X = F, Cl, Br, I, H) correlates well with the NBO charges on zinc (Supporting Information).