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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

Wesley Sattler and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027, United States

S Supporting Information

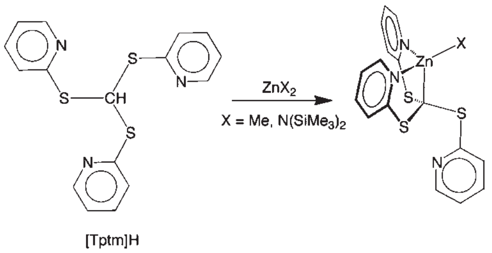
ABSTRACT: Tris(2-pyridylthio)methane, [Tptm]H, has been employed to synthesize the mononuclear alkyl zinc hydride complex, [κ^3-Tptm]ZnH, which has been structurally characterized by X-ray diffraction. [κ^3-Tptm]ZnH provides access to a variety of other [Tptm]ZnX derivatives. For example, [κ^3-Tptm]ZnH reacts with (i) R_3SiOH (R = Me, Ph) to give [κ^4-Tptm]$ZnOSiR_3$, (ii) Me_3SiX (X = Cl, Br, I) to give [κ^4-Tptm]ZnX, and (iii) CO_2 to give the formate complex, [κ^4-Tptm]ZnO_2CH. The bis(trimethylsilyl)-amide complex [κ^3-Tptm]$ZnN(SiMe_3)_2$ also reacts with CO_2, but the product obtained is the isocyanate complex, [κ^4-Tptm]ZnNCO. The formation of [κ^4-Tptm]ZnNCO is proposed to involve initial insertion of CO_2 into the Zn−$N(SiMe_3)_2$ bond, followed by migration of a trimethylsilyl group from nitrogen to oxygen to generate [κ^4-Tptm]$ZnOSiMe_3$ and Me_3SiNCO, which subsequently undergo CO_2-promoted metathesis to give [κ^4-Tptm]-ZnNCO and $(Me_3SiO)_2CO$.

Zinc hydride species are of considerable interest in view of their use in organic transformations[1] and their role in the Cu/ZnO-catalyzed synthesis of methanol from a mixture of CO, CO_2, and H_2.[2] Well-defined mononuclear zinc complexes that feature terminal hydride ligands are, however, rare,[3−5] due to the propensity of the hydride ligand to bridge two zinc centers.[6] Furthermore, structurally characterized mononuclear compounds that feature both alkyl and hydride ligands are unknown.[7−9] Here, we describe the synthesis, structural characterization, and reactivity of a mononuclear alkyl zinc hydride complex, including the facile insertion of CO_2 into the Zn−H bond. In addition, we also describe the ability of CO_2 to promote the displacement of siloxide ligands.

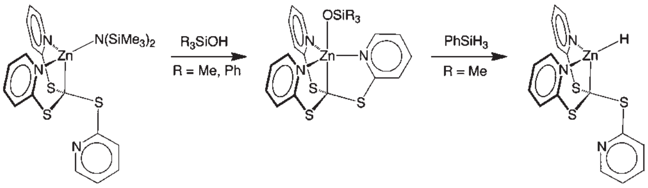
We previously utilized the tris(3-*tert*-butylpyrazolyl)hydroborato ligand to synthesize [Tp^{Bu^t}]ZnH, the first structurally authenticated monomeric zinc hydride complex,[3] in which the multidentate nature of the [Tp^{Bu^t}] ligand allows isolation of a compound that features a terminal hydride moiety.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

The key starting material for the synthesis of [κ^3-Tptm]ZnH is the bis(trimethylsilyl)amide derivative, [κ^3-Tptm]$ZnN(SiMe_3)_2$,[11] that is obtained via the reaction of [Tptm]H with $Zn[N(SiMe_3)_2]_2$, as illustrated in Scheme 1. Subsequent treatment of [κ^3-Tptm]$ZnN(SiMe_3)_2$ with Me_3SiOH yields the siloxide [κ^4-Tptm]$ZnOSiMe_3$[12,13] that reacts with $PhSiH_3$ to give the hydride complex, [κ^3-Tptm]ZnH (Scheme 2). The molecular structure of [κ^3-Tptm]ZnH has been determined by X-ray

Scheme 1



Scheme 2



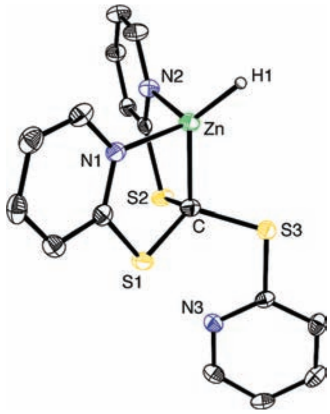


Figure 1. Molecular structure of [κ^3-Tptm]ZnH.

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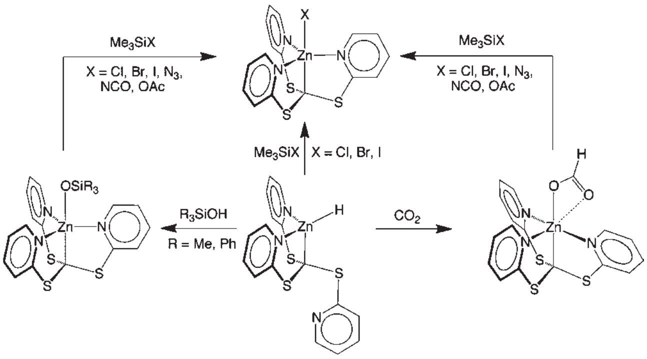
Scheme 3



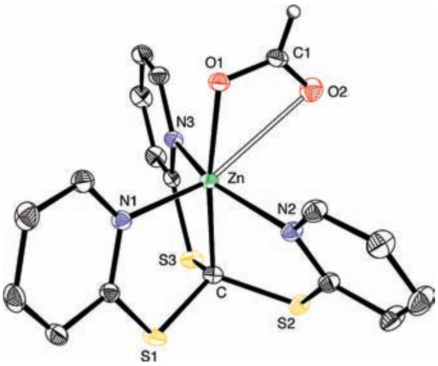


Figure 2. Molecular structure of [κ^4-Tptm]ZnO_2CH.

diffraction (Figure 1), which demonstrates that the compound exists as a discrete mononuclear complex in which the [Tptm] ligand coordinates in a κ^3-manner. The Zn−H moiety of [κ^3-Tptm]ZnH is characterized by a Zn−H bond length of 1.51(3) Å,[14] a singlet at δ 5.60 in the ^1H NMR spectrum, and an absorption at 1729 cm^{-1} in the IR spectrum, which shifts to 1242 cm^{-1} for the zinc deuteride isotopologue [κ^3-Tptm]ZnD [$\nu_H/\nu_D = 1.39$]. The zinc methyl counterpart, [κ^3-Tptm]ZnMe, has also been synthesized via the reaction of [Tptm]H with Me_2Zn (Scheme 1) and has a distorted tetrahedral geometry similar to that of [κ^3-Tptm]ZnH. For example, the C−Zn−H [132(1)°] and C−Zn−CH_3 [135.8(1)° and 134.1(1)° for two different crystalline forms] bond angles are distinctly greater than the tetrahedral value.

[κ^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 [κ^3-Tptm]ZnH is (i) protolytically cleaved by R_3SiOH (R = Me, Ph) to give [κ^4-Tptm]$ZnOSiR_3$ and (ii) undergoes metathesis with Me_3SiX (X = Cl, Br, I) to give [κ^4-Tptm]ZnX.[15,16] Of most note, however, is the fact that [κ^3-Tptm]ZnH reacts rapidly with CO_2 to give the formate complex, [κ^4-Tptm]ZnO_2CH (Scheme 3 and Figure 2), which may also be obtained from the reaction of [κ^3-Tptm]ZnH with HCO_2H.[17] 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.[2] The insertion of CO_2 into zinc hydride bonds is not, however, well precedented, and the only other examples involving monomeric zinc hydride complexes pertain to [Tp^R]ZnH derivatives.[3,4d,18] Both the formate and siloxide derivatives, [κ^4-Tptm]ZnO_2CH and [κ^4-Tptm]$ZnOSiR_3$, can be converted to a variety of other [κ^4-Tptm]ZnX derivatives upon treatment with Me_3SiX (X = Cl, Br, I, N_3, NCO, OAc), as illustrated in Scheme 3.

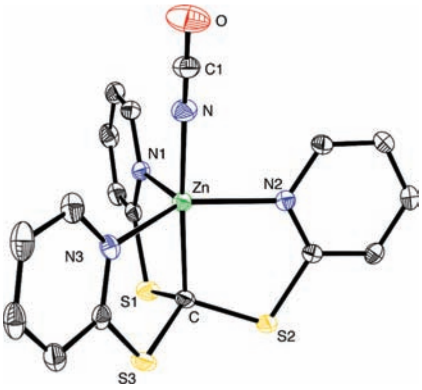
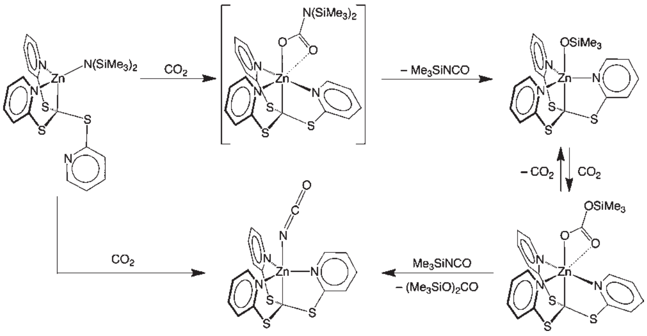


Figure 3. Molecular structure of [κ^4-Tptm]ZnNCO.

Scheme 4



In addition to its role in methanol synthesis,[2] the abundance of CO_2 has stimulated efforts to discover other synthetic methods that employ CO_2 as a C_1 building block,[19] as illustrated by the metal-catalyzed hydrogenation to formic acid and formates,[20] and the formation of polycarbonates by copolymerization with epoxides.[21] The reactivity of CO_2 towards metal compounds has, therefore, been the focus of much attention.[19,22] For example, the insertion of CO_2 into M−NR_2 bonds to give carbamato derivatives has been widely studied.[23] In contrast, however, there are few reports concerned with the reactivity of CO_2 towards bis(trimethylsilyl)amido complexes.[24] It is, therefore, notable that [κ^3-Tptm]$ZnN(SiMe_3)_2$ reacts with CO_2 to give the isocyanate complex, [κ^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_nMNR_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.[25,26] The formation of the isocyanate complex [κ^4-Tptm]ZnNCO also provides a contrast to the reaction of $Zn[N(SiMe_3)(Ad)]_2$ (Ad = adamantyl) with CO_2, which gives AdN=C=NAd and unidentified trimethylsiloxide species.[27]

The generation of [κ^4-Tptm]ZnNCO is necessarily a multistep process, of which the initial sequence is proposed to involve insertion of CO_2 into the Zn−$N(SiMe_3)_2$ bond to give [Tptm]$Zn[O_2CN(SiMe_3)_2]$, which subsequently converts to the trimethylsiloxide derivative [κ^4-Tptm]$ZnOSiMe_3$ and Me_3SiNCO (Scheme 4). In support of this proposal, both [κ^4-Tptm]$ZnOSiMe_3$ and Me_3SiNCO are observed by ^1H NMR spectroscopy during the course of the reaction. Interestingly, however, although the simplest rationalization for the formation of [κ^4-Tptm]ZnNCO from [κ^4-Tptm]ZnOSiMe$_3$ and Me$_3$SiNCO involves direct metathesis, additional experiments suggest that this is *not* the operative mechanism. Specifically, while an independent experiment indicates that [κ^4-Tptm]ZnNCO is formed upon treatment of [κ^4-Tptm]ZnOSiMe$_3$ with Me$_3$SiNCO, the reaction is extremely slow by comparison to the formation of [Tptm]ZnNCO upon treatment of [κ^3-Tptm]ZnN(SiMe$_3$)$_2$ with CO$_2$. The formation of the isocyanate complex [Tptm]ZnNCO is, however, accelerated if CO$_2$ is added to a mixture of [κ^4-Tptm]ZnOSiMe$_3$ and Me$_3$SiNCO. On this basis, it is proposed that the formation of [κ^4-Tptm]ZnNCO is promoted by insertion of CO$_2$ into the Zn−OSiMe$_3$ bond to give the carbonate derivative, [κ^4-Tptm]ZnO$_2$COSiMe$_3$, that is more susceptible towards metathesis with Me$_3$SiNCO than is [κ^4-Tptm]ZnOSiMe$_3$.

Evidence for facile reversible insertion of CO$_2$ into the Zn−OSiMe$_3$ bond is provided by variable-temperature ^{1}H and ^{13}C{^{1}H} NMR spectroscopic studies that allow for observation of [κ^4-Tptm]ZnO$_2$COSiMe$_3$ at temperatures ≤ 5 °C, as illustrated by a signal at 157.9 ppm in the ^{13}C{^{1}H} NMR spectrum attributable to the carbonate moiety. In addition, the reaction between [κ^3-Tptm]ZnN(SiMe$_3$)$_2$ and CO$_2$ is accompanied by formation of the carbonate (Me$_3$SiO)$_2$CO, an observation that is in accord with Me$_3$SiNCO undergoing metathesis with [κ^4-Tptm]ZnO$_2$COSiMe$_3$ rather than with [κ^4-Tptm]ZnOSiMe$_3$. Two factors that may contribute to the more facile cleavage of the Zn−OC(O)OSiMe$_3$ bond than the Zn−OSiMe$_3$ bond are (i) insertion of the CO$_2$ group displaces the OSiMe$_3$ 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.[28] Thus, while the insertion of CO$_2$ into M−OSiR$_3$ bonds has been little investigated,[29,30] 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;[31] 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 κ^4 or κ^3 manner. Specifically, κ^4-coordination is observed in the solid state for [κ^4-Tptm]ZnI, [κ^4-Tptm]ZnNCO, [κ^4-Tptm]ZnN$_3$, [κ^4-Tptm]ZnOSiR$_3$ (R = Me, Ph), [κ^4-Tptm]ZnO$_2$CH, and [κ^4-Tptm]ZnO$_2$CMe,[32] while κ^3-coordination is observed for [κ^3-Tptm]ZnH and [κ^3-Tptm]ZnMe. Low-temperature ^{1}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 [κ^3-Tptm]ZnH, [κ^3-Tptm]ZnMe, and [κ^3-Tptm]ZnN(SiMe$_3$)$_2$ at ca. −10 °C, consistent with κ^3-coordination. In contrast, the low-temperature ^{1}H NMR spectra of [κ^4-Tptm]ZnX [X = Cl, Br, I, NCO, N$_3$, OSiR$_3$ (R = Me, Ph), O$_2$CMe, O$_2$CH] exhibit chemically equivalent pyridyl groups indicative of κ^4-coordination.[33] This observation is in accord with density functional theory calculations which predict that the preference for κ^4- versus κ^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 κ^3-coordination while the bulky triphenylsiloxide derivative adopts κ^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 κ^4-coordination correlates well with the electronegativity of X, a trend which suggests that κ^4-coordination becomes more favored with increasing charge on the zinc center.[34]

In summary, the mononuclear alkyl zinc hydride complex, [κ^3-Tptm]ZnH, may be synthesized via treatment of [κ^4-Tptm]ZnOSiMe$_3$ with PhSiH$_3$. [κ^3-Tptm]ZnH exhibits a variety of different reaction pathways, including insertion of CO$_2$ to give the formate complex, [κ^4-Tptm]ZnO$_2$CH. The bis(trimethylsilyl)amide complex [κ^3-Tptm]ZnN(SiMe$_3$)$_2$ also reacts with CO$_2$, but the product obtained is the isocyanate complex, [κ^4-Tptm]ZnNCO, that results from a multistep sequence of which the initial steps are insertion of CO$_2$ into the Zn−N(SiMe$_3$)$_2$ bond followed by rearrangement to [κ^4-Tptm]ZnOSiMe$_3$ and Me$_3$SiNCO. An important discovery, however, is that the final metathesis step to give [κ^4-Tptm]ZnNCO is promoted by CO$_2$, an observation which indicates that the carbonate complex [κ^4-Tptm]ZnO$_2$COSiMe$_3$ is more susceptible towards metathesis than is the siloxide derivative, [κ^4-Tptm]ZnOSiMe$_3$. 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.

■ AUTHOR INFORMATION

Corresponding Author

parkin@columbia.edu

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

(33) The observation of equivalent pyridyl groups for [κ^4-Tptm]-ZnO_2CR (R = H, Me) implies that access to the freely rotating κ^1-O_2CR isomer is facile.

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