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Zinc Catalysts for On-Demand Hydrogen Generation and Carbon Dioxide Functionalization

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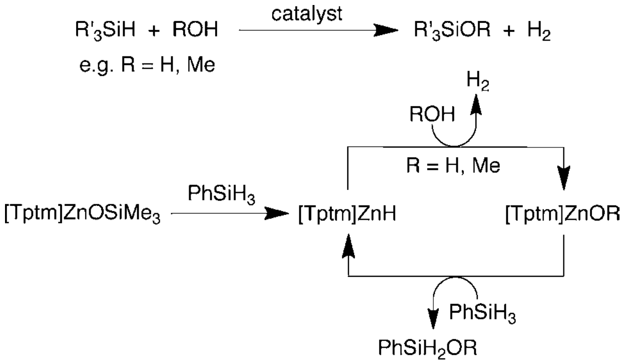
Supporting Information

ABSTRACT: [Tris(2-pyridylthio)methyl]zinc hydride, [κ^3-Tptm]ZnH, is a multifunctional catalyst that is capable of achieving (i) rapid release of hydrogen by protolytic cleavage of silanes with either water or methanol and (ii) hydrosilylation of aldehydes, ketones, and carbon dioxide. For example, [κ^3-Tptm]ZnH catalyzes the release of 3 equivalents of H_2 by methanolysis of phenylsilane, with a turnover number of 10^5 and a turnover frequency surpassing 10^6 h^{-1} for the first 2 equivalents. Furthermore, [κ^3-Tptm]ZnH also catalyzes the formation of triethoxysilyl formate by hydrosilylation of carbon dioxide with triethoxysilane. Triethoxysilyl formate may be converted into ethyl formate and *N*,*N*-dimethylformamide, thereby providing a means for utilizing carbon dioxide as a C_1 feedstock for the synthesis of useful chemicals.

Considerable effort is currently being directed towards (i) the implementation of a "hydrogen economy", in which hydrogen serves as a fuel,[1] and (ii) the use of ubiquitous carbon dioxide as a renewable C_1 source for the synthesis of useful chemicals.[2−5] However, the practical realization of both of these objectives presents daunting challenges. For example, a principal problem with respect to the utilization of carbon dioxide as a chemical feedstock is concerned with the fact that it is not only thermodynamically a very stable molecule ($\Delta G^0_f = -394$ kJ mol^{-1}), but is also kinetically resistant to many chemical transformations. Likewise, the energy-efficient storage of hydrogen with a high volumetric energy density is a critical prerequisite to the implementation of a hydrogen economy.[6] As such, attention is turning to the use of chemical methods to provide hydrogen on demand.[7] The discovery of new catalytic methods that rely on earth-abundant elements for (i) the rapid generation of hydrogen and (ii) the functionalization of CO_2 are crucial for advancing the use of hydrogen as a fuel and for utilizing CO_2 as an effective C_1 source for commodity chemicals. Therefore, it is significant that we describe herein a multifunctional zinc hydride catalyst that not only is capable of achieving the rapid generation of hydrogen on demand from liquid storage materials, but also achieves the hydrosilylation of aldehydes, ketones, and, most notably, CO_2. Of these, the last reaction provides a means to convert CO_2 into commodity chemicals such as ethyl formate and *N*,*N*-dimethylformamide.

Scheme 1. H_2 Production from Silanes via Hydrolysis and Alcoholysis



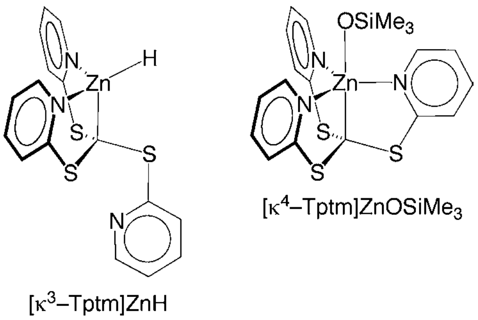


Figure 1. Zinc catalysts for hydrogen generation and for hydrosilylation.

Chemical methods for producing hydrogen on demand have focused on the use of ammonia-borane and related compounds,[8,9] organic heterocycles,[10,11] formic acid,[12] and organosilanes[13−16] as storage materials. Although there are drawbacks associated with each of these materials,[6,17] organosilanes are attractive from several perspectives: (i) many organosilanes are storable liquids that are thermodynamically capable of generating hydrogen by protolytic cleavage of the Si−H bonds with either water or alcohols (Scheme 1); (ii) organosilanes that are rich in Si−H groups, e.g., cyclo-$(CH_2SiH_2)_3$ and $C(SiH_3)_4$, have high hydrogen storage capabilities in the range 5.0−6.9 wt % for cleavage with water;[18] and (iii) the products of hydrolysis and alcoholysis have commercial value, with applications in materials chemistry and organic synthesis.

However, although the hydrolysis of Si−H bonds is thermodynamically favorable[19] and could provide a simple method of generating hydrogen on demand, the reaction is kinetically slow. Both homogeneous[13,14,20] and heterogeneous[21−23] catalysts have been reported for this reaction, but the majority feature precious metals such as rhenium, ruthenium,

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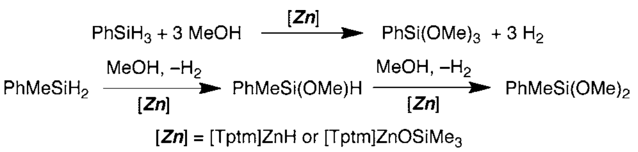
silver, and gold that are in short supply. For this reason, it is important to develop effective catalysts that are based on more abundant non-precious metals.[24] It is, therefore, significant that we have discovered that zinc, an abundant post-transition metal, can serve as a catalyst for the hydrolysis of Si−H bonds. Specifically, the [tris(2-pyridylthio)methyl]zinc hydride complex, [κ^3-Tptm]ZnH[25] (Figure 1), is an effective room-temperature catalyst for the release of 3 equivalents of H_2 from $PhSiH_3$, a commercially available trihydrosilane.[26] A proposed mechanism for the first cycle of H_2 elimination is illustrated in Scheme 1, in which the hydride complex [κ^3-Tptm]ZnH reacts with H_2O to release H_2 and form a hydroxide species that subsequently reacts with $PhSiH_3$ to regenerate [κ^3-Tptm]ZnH. In addition to [κ^3-Tptm]ZnH serving as a catalyst for the hydrolysis of Si−H bonds, the trimethylsiloxide complex [κ^4-Tptm]$ZnOSiMe_3$ (Figure 1) may be employed as an effective precatalyst because it reacts with $PhSiH_3$ to generate the hydride complex (Scheme 1).[25]

As an illustration of the effectiveness of [κ^4-Tptm]$ZnOSiMe_3$ as a precatalyst, 1 mol % (per Si−H bond) is capable of achieving quantitative liberation of 3 equivalents of H_2 from a mixture of $PhSiH_3$ and water, with a turnover frequency (TOF) of 1.0×10^4 h^{-1} for release of the first equivalent. These data are particularly noteworthy because the only other homogeneous catalyst for which quantitative data for hydrolysis of $PhSiH_3$ have been reported is a rhenium(V) compound, which releases only 2 equivalents of H_2 over a period of 2−4 h,[13,14] whereas [κ^4-Tptm]$ZnOSiMe_3$ liberates 2 equivalents in less than 2 min. It is, therefore, evident that the zinc hydride complex, [κ^3-Tptm]ZnH, is a more effective catalyst than is the rhenium compound. Furthermore, in contrast to the rhenium system, for which the silane cannot be used in excess because it reduces the oxorhenium compound to an inactive form,[13,14] the zinc catalyst operates effectively in the presence of excess silane (>30 equivalents).

Alcoholysis also provides a means to liberate H_2 from silanes,[14−16,27] and, in this regard, the zinc-catalyzed methanolysis of $PhSiH_3$[28,29] (Schemes 1 and 2) is even more efficient than is the hydrolysis reaction. For example, only 0.001 mol % (per Si−H bond) of [κ^4-Tptm]$ZnOSiMe_3$ can achieve quantitative liberation of 3 equivalents of H_2 from a mixture of $PhSiH_3$ and MeOH in toluene, corresponding to a turnover number (TON) of 10^5. The evolution of H_2 is also very rapid, with release of the first equivalent occurring in less than 2 min, corresponding to an impressive TOF of 1.6×10^6 h^{-1}. In the presence of 0.1 mol % [κ^4-Tptm]$ZnOSiMe_3$, the reaction is extremely fast, with 85% H_2 evolution being observed within 5 s. Not only is catalysis by this zinc system rapid, but the catalyst remains active for an extended period of time, as illustrated by monitoring the release of H_2 upon sequential injection of methanol at hourly intervals into a solution of $PhSiH_3$ containing [κ^4-Tptm]$ZnOSiMe_3$ (Figure 2).

The above results demonstrate that [κ^4-Tptm]$ZnOSiMe_3$ is highly effective for achieving the catalytic methanolysis of $PhSiH_3$, with catalyst loadings that are orders of magnitude lower than have previously been employed for this transformation.[15] Furthermore, the $PhSiH_3$/MeOH/[κ^3-Tptm]ZnH system is the most effective means to date for on-demand hydrogen generation by catalytic silane alcoholysis. For comparison, the most efficient system previously reported for silane alcoholysis employs a precious metal ruthenium catalyst, [$RuCl_2$(*p*-cymene)]$_2$, for which a TOF of 3.67×10^5 h^{-1} was observed with a catalyst loading of 0.1 mol %.[27d] However, a lower catalyst loading of 0.001 mol % resulted in only 78% completion, whereas H_2 release remains quantitative at a catalyst loading of 0.001 mol % for the $PhSiH_3$/MeOH/[κ^3-Tptm]ZnH system.

Scheme 2. Zinc-Catalyzed Methanolysis of Silanes



$$PhSiH_3 + 3\ MeOH \xrightarrow{[Zn]} PhSi(OMe)_3 + 3\ H_2$$

$$PhMeSiH_2 \xrightarrow[{[Zn]}]{MeOH,\ -H_2} PhMeSi(OMe)H \xrightarrow[{[Zn]}]{MeOH,\ -H_2} PhMeSi(OMe)_2$$

[*Zn*] = [Tptm]ZnH or [Tptm]$ZnOSiMe_3$

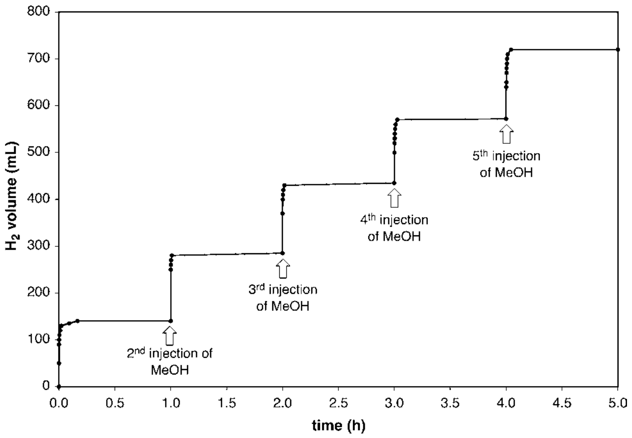
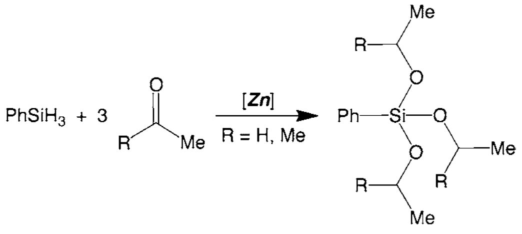


Figure 2. Generation of hydrogen on demand via sequential injection of methanol at hourly intervals into a toluene solution of $PhSiH_3$ containing 0.1 mol % [κ^4-Tptm]$ZnOSiMe_3$ at room temperature.

Although there are no other reports of zinc-catalyzed methanolysis of $PhSiH_3$, a comparison with related zinc-catalyzed alcoholysis reactions[27b,c] attests further to the efficacy of [κ^3-Tptm]ZnH and [κ^4-Tptm]$ZnOSiMe_3$. Thus, while 10 mol % of the [tris(4,4-dimethyl-2-oxazolinyl)phenylborate]zinc hydride complex converts a 1:1 mixture of $PhMeSiH_2$ and MeOH to an approximately 9:1 ratio of mono- and disubstituted products, PhMeSiH(OMe) and $PhMeSi(OMe)_2$, over 10 h at 45 °C (corresponding to a TOF of 1 h^{-1} based on $PhMeSiH_2$ consumed),[27b] the corresponding reaction employing only 0.3 mol % [κ^3-Tptm]ZnH (Scheme 2) occurs within 30 min at room temperature (corresponding to a TOF of 258 h^{-1}). Furthermore, in the presence of excess MeOH, the disubstituted product $PhMeSi(OMe)_2$ is obtained exclusively over a period of ca. 6 min at room temperature (corresponding to a TOF of 2.98×10^3 h^{-1}).

It is of note that the byproducts of hydrogen generation from silane alcoholysis reactions are siloxanes, a class of molecules that have varied applications. Siloxanes can also be synthesized by the hydrosilylation of aldehydes and ketones,[30] and, in this regard, [κ^3-Tptm]ZnH is also a hydrosilylation catalyst. For example, [κ^3-Tptm]ZnH catalyzes the insertion of acetaldehyde and acetone into all three Si−H bonds of $PhSiH_3$ to give $PhSi(OEt)_3$ and $PhSi(OPr^i)_3$, respectively (Scheme 3).[31] While the metal-catalyzed insertion of aldehydes and ketones into Si−H bonds is well established, the insertion into three Si−H bonds has not been reported as a general approach for synthesizing $PhSi(OR)_3$ derivatives; nevertheless, this transformation represents a useful method for the synthesis of such compounds. Aryltrialkoxysilanes are a class of molecules that are more commonly synthesized via the reaction of Grignard or lithium reagents with

Scheme 3. Zinc-Catalyzed Hydrosilylation of Aldehydes and Ketones



[*Zn*] = [Tptm]ZnH or [Tptm]ZnOSiMe$_3$

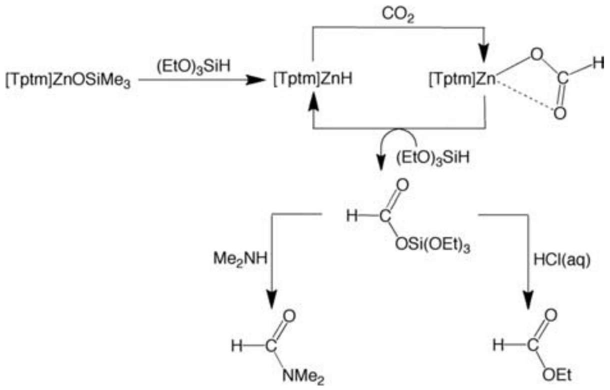
$Si(OR)_4$[32] and have found applications in cross-coupling reactions.[33]

In view of the ability of [κ^3-Tptm]ZnH to hydrosilylate carbonyl functionalities, we turned our attention to CO_2, a renewable C_1 resource that has been identified as a feedstock for a variety of chemicals,[2] as illustrated by the metal-catalyzed formation of polycarbonates by copolymerization with epoxides.[34−36] The use of CO_2 as a feedstock for formic acid and formates has also garnered much attention[37,38] because the principal industrial method for the synthesis of formic acid involves an intensive sequence comprising (i) hydrogenation of CO to methanol, (ii) carbonylation of methanol to methyl formate, and (iii) hydrolysis of methyl formate.[39]

Hydrosilylation of CO_2 is a more thermodynamically favorable process than is hydrogenation, with the first catalytic formation of silyl formates having been reported in 1981 for ruthenium compounds.[40] Despite subsequent interesting developments over the decades,[41] ruthenium remains the metal of focus for such transformations[42−45] and provides the only catalysts for which multigram quantities of silyl formates have been isolated. Therefore, in view of the impetus for developing catalysts that do not utilize precious metals,[24] we considered the possibility that zinc-catalyzed hydrosilylation of CO_2 could also be achieved in a similar manner to that observed above for hydrosilylation of aldehydes and ketones.

It is, therefore, noteworthy that the hydride complex [κ^3-Tptm]ZnH provides the first example of zinc-catalyzed hydrosilylation of CO_2. Specifically, [κ^3-Tptm]ZnH catalyzes the formation of triethoxysilyl formate, $HCO_2Si(OEt)_3$, by reaction of CO_2 with $(EtO)_3SiH$ at 100 °C (Scheme 4). As an illustration, [κ^3-Tptm]ZnH (0.1 mol %) catalyzes the hydrosilylation of CO_2 with $(EtO)_3SiH$ on a 20 g scale, with a TON of 10^3 and a TOF of 2.9 h^{-1}. Moreover, the trimethylsiloxide [κ^4-Tptm]ZnOSiMe$_3$ (0.25 mol %) is an effective precatalyst, achieving a TON of 400 and a TOF of 4.2 h^{-1}. Of note, these TOFs are within the range observed for ruthenium-catalyzed hydrosilylation of CO_2 (0.7−233 h^{-1}).[40,43]

Scheme 4. Zinc-Catalyzed Hydrosilylation of CO_2



A possible mechanism for the catalytic cycle is illustrated in Scheme 4. In support of this proposed mechanism, the hydride complex [κ^3-Tptm]ZnH is known to react with CO_2 to give the formate derivative, [κ^4-Tptm]ZnO$_2$CH,[25] which has been identified by ^1H NMR spectroscopy as the resting state and may also be employed as a catalyst.[46] The ability of zinc to effect the hydrosilylation of CO_2 provides an interesting complement to the prominent role that zinc plays in CO_2 chemistry in nature, namely the catalytic hydration of CO_2 by carbonic anhydrase to give protons and bicarbonate ions.

The formation of silyl formates by hydrosilylation of CO_2 provides a useful synthetic method for this class of molecules that are otherwise obtained via the reactions of silyl halides or triflates with formic acid in the presence of a base (e.g., pyridine or Et_3N).[47] Also of significance is the fact that the zinc-catalyzed hydrosilylation can be performed without the use of additional solvent, which is in contrast to a ruthenium-catalyzed reaction between Et_3SiH and CO_2 that preferentially gives the siloxane $Et_3SiOSiEt_3$ in the absence of a solvent, but HCO_2SiEt_3 in acetonitrile solution.[44]

Access to silyl formates from CO_2 is of interest because they have potential for serving as formylating agents, thereby providing a means to convert CO_2 into other useful compounds. In this regard, $HCO_2Si(OEt)_3$ reacts immediately with Me_2NH to give *N*,*N*-dimethylformamide (Scheme 4). By comparison, amines do not react with simple alkyl esters under these conditions in the absence of a catalyst. Furthermore, treatment of $HCO_2Si(OEt)_3$ with HCl(aq) immediately gives ethyl formate (Scheme 4).

In summary, the zinc hydride complex [κ^3-Tptm]ZnH is an effective catalyst for the rapid generation of hydrogen on demand and for the functionalization of CO_2, thereby producing a useful formylating agent. These results provide further evidence that, in suitable ligand environments, inexpensive and abundant non-transition metals can perform reactions that are typically catalyzed by compounds that contain precious metals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) For example, on the basis of the following bond energies [Me_3Si-H (90.3 kcal mol^{-1}),[a] Me_3Si-OH (128 kcal mol^{-1}),[a] H−H (104.2 kcal mol^{-1}),[b] H−OH (116.0 kcal mol^{-1}),[b] the hydrolysis of Me_3SiH to give H_2 and Me_3SiOH is exothermic by 26 kcal mol^{-1}: (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246−252. (b) Darwent, B. deB. *Nat. Stand. Ref. Data. Ser., Nat. Bur. Stand. (U.S.)*, 31 Jan 1970.

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