

Synthesis, Structure, and Reactivity of a Terminal Magnesium Hydride Compound with a Carbatrane Motif, [Tism^{Pr^{'Benz}}]MgH: A Multifunctional Catalyst for Hydrosilylation and Hydroboration

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Supporting Information

ABSTRACT: The *tris*[(1-isopropylbenzimidazol-2-yl)dimethylsilyl)]methyl ligand, [Tism^{Pr'Benz}], has been employed to form the magnesium carbatrane compound, [Tism^{Pr'Benz}]MgH, which possesses a terminal hydride ligand. Specifically, [Tism^{Pr'Benz}]MgH is obtained via the reaction of [Tism^{Pr'Benz}]MgMe with PhSiH₃. The reactivity of [Tism^{Pr'Benz}]MgMe and [Tism^{Pr'Benz}]MgH allows access to a variety of other structurally characterized carbatrane derivatives, including [Tism^{Pr'Benz}]MgX [X = F, Cl, Br, I, SH, N(H)Ph, CH(Me)Ph, O₂CMe, S₂CMe]. In addition, [Tism^{Pr'Benz}]MgH is a catalyst for (i) hydrosilylation and hydroboration of styrene to afford the Markovnikov products, Ph(Me)C(H)SiH₂Ph and Ph(Me)C(H)Bpin, and (ii) hydroboration of carbodiimides and pyridine to form *N*-boryl formamidines and *N*-boryl 1,4- and 1,2dihydropyridines, respectively.

B y comparison to other main group elements, terminal hydride compounds of the alkaline earth Group 2 metals are rare.¹ For example, although we reported the first monomeric terminal beryllium hydride, [Tp^{Bu'}]BeH, in 1992,^{2,3} structurally authenticated monomeric terminal magnesium hydride compounds remained unknown until 2010, when Jones and Stasch reported [Nacnac^{But}]Mg(DMAP)H.⁴⁻⁶ Moreover, structurally characterized terminal calcium hydride compounds are currently unknown.⁷ Despite their paucity, however, terminal hydride compounds of these elements offer much potential, and are often invoked as intermediates in a variety of catalytic cycles, including hydrosilvlation, hydroboration, hydroamination, and hydrogenation.^{1,8,9} Such transformations involving Mg and Ca are of particular interest because these are two of the most abundant elements in the Earth's crust. As such, efficient catalysis using Mg and Ca offers potential societal benefits, especially considering that, for example, industrial hydrosilylation reactions typically employ precious metal catalysts.¹⁰ Therefore, we describe here the synthesis, structure, reactivity, and catalytic applications of the terminal magnesium hydride compound, [Tism^{Pr'Benz}]MgH, which features a carbatrane motif provided by the tris-[(1-isopropylbenzimidazol-2-yl)dimethylsilyl]methyl ligand.

We recently described the use of the [Tism^{Pr'Benz}] ligand to afford the methyl magnesium carbatrane compound, [Tism^{Pr'Benz}]MgMe (1).^{11,12} Here, we report that the reactivity associated with the Mg-Me bond provides access to a variety of other [Tism^{Pr'Benz}]MgX derivatives (Schemes 1 and 2),^{13,14} each of which has been structurally characterized by X-ray diffraction. For example, protolytic cleavage of the Mg-Me bond by H₂S and PhNH₂ affords uncommon terminal hydrosulfido^{15,16} and anilido¹⁷ magnesium compounds, namely [Tism^{PriBenz}]MgSH (2) and [Tism^{PriBenz}]MgN(H)Ph (3). Metathesis of [Tism^{PriBenz}]MgMe with Me₃SnX [X = F (4), Cl (5), Br (6), I (7)] provides the series of halide derivatives [Tism^{PriBenz}]MgX, with [Tism^{PriBenz}]MgF being most noteworthy because terminal magnesium fluoride compounds are rare.^{14a}





While each of the $[Tism^{Pr^{i}Benz}]MgX$ compounds adopts an idealized trigonal bipyramidal geometry, a noteworthy difference pertains to the location of the X substituent. Specifically, the X substituents of $[Tism^{Pr^{i}Benz}]MgX$ [X = Me, F, Cl, Br, N(H)Ph] adopt an axial position that is *trans* to the atrane C-atom, whereas the X substituents of $[Tism^{Pr^{i}Benz}]MgX$ [X = I, SH] adopt an equatorial position. These two geometries are associated with different coordination modes for the $[Tism^{Pr^{i}Benz}]$ ligand. Thus, an axial X substituent is associated with a local C_3 coordination mode of the $[Tism^{Pr^{i}Benz}]$ ligand (with a trigonal arrangement of

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Scheme 2. Synthesis and Reactivity of [Tism^{PrⁱBenz}]MgH



N-atoms), whereas an equatorial X substituent is associated with an idealized seesaw coordination mode (with a T-shaped arrangement of N-atoms).

In addition to metathesis reactions, the Mg-Me bond is also subject to insertion reactions. Thus, CO₂ and CS₂ insert into the Mg-Me bond to afford the acetate and dithioacetate derivatives, [Tism^{Pr'Benz}]Mg(κ^2 -O₂CMe) (8) and [Tism^{Pr'Benz}]Mg(κ^2 -S₂CMe) (9), as illustrated in Scheme 1. The molecular structures of [Tism^{Pr'Benz}]Mg(κ^2 -O₂CMe) and [Tism^{Pr'Benz}]Mg(κ^2 -S₂CMe) were determined by X-ray diffraction, thereby revealing that the acetate and dithioacetate ligands coordinate to the Mg center in a κ^2 -manner, with the [Tism^{Pr'Benz}] ligand adopting a seesaw coordination mode (Scheme 1). While magnesium acetate compounds are well known,^{18,19} there are no structurally characterized magnesium dithioacetate compounds listed in the CSD.

The formation of $[Tism^{Pr^{i}Benz}]Mg(\kappa^{2}-O_{2}CMe)$ is of some relevance to the mechanism of action of Rubisco, the most abundant protein on Earth.²⁰ Specifically, Rubisco is involved in carbon fixation and employs Mg to mediate the formation of a C-C bond between CO₂ and the C2 position of D-ribulose 1,5-bisphosphate to form a carboxylate derivative.²⁰ The 2-carboxy-D-arabinitol 1,5-bisphosphate transition state analogue has been shown to possesses a magnesium–carboxylate interaction,²¹ and so the formation of $[Tism^{Pr^{i}Benz}]Mg(\kappa^{2}-O_{2}CMe)$ from CO₂ resembles an aspect of the mechanism of action of Rubsico, which has otherwise received little attention from a synthetic analogue perspective.^{22,23}

The most significant transformation of $[Tism^{Pr'Benz}]MgMe$ involves the metathesis reaction with PhSiH₃, which provides access to the terminal magnesium hydride compound, $[Tism^{Pr'Benz}]MgH$ (**10**, Scheme 2).²⁴ The molecular structure of $[Tism^{Pr'Benz}]MgH$ was determined by X-ray diffraction (Figure 1), thereby demonstrating that the compound exists as a welldefined monomeric species with a terminal hydride ligand in the axial site of a trigonal bipyramidal coordination environment. The Mg-H bond length is 1.85(3) Å, which is comparable to the sum of the covalent radii (1.72 Å).^{13,25} Spectroscopically, the Mg-H moiety of $[Tism^{Pr'Benz}]MgH$ is characterized by a singlet at δ 6.78 in the ¹H NMR spectrum.²⁶

Parallel to the reactivity observed for $[Tism^{Pr^{i}Benz}]MgMe$, the hydride complex may likewise be employed to form $[Tism^{Pr^{i}Benz}]MgSH$, $[Tism^{Pr^{i}Benz}]MgN(H)Ph$, and $[Tism^{Pr^{i}Benz}]MgX (X = F, Cl, Br, I)$ via the respective metathesis reactions with H₂S, PhNH₂, and Me₃SnX (cf. Scheme 1). In addition, a particularly noteworthy example of metathesis is



Figure 1. Molecular structures of $[Tism^{Pr^{i}Benz}]MgH$ and $[Tism^{Pr^{i}Benz}]MgCH(Me)Ph$.

provided by the observation that an EXSY experiment demonstrates that the Mg-H and Si-H groups of $[Tism^{Pr'Benz}]MgH$ and PhSiH₃ undergo degenerate exchange on the NMR time scale.²⁷

The reactivity of $[Tism^{Pr'Benz}]MgH$ is not restricted to metathesis reactions. In particular, the Mg-H bond of $[Tism^{Pr'Benz}]MgH$ undergoes insertion of styrene to afford the 1-phenylethyl derivative $[Tism^{Pr'Benz}]MgCH(Me)Ph$ (11, Scheme 2), which provides the first structurally authenticated (Figure 1) example of the insertion of an olefin into a terminal magnesium hydride bond.^{28,29} Of note, the alkyl ligand of $[Tism^{Pr'Benz}]MgCH(Me)Ph$ occupies an equatorial site of a trigonal bipyramid, whereas that of $[Tism^{Pr'Benz}]MgMe$ is located in an axial site.

Another interesting feature of the insertion of styrene is that it affords selectively the branched 1-phenylethyl derivative, $[Tism^{Pr'Benz}]MgCH(Me)Ph$, rather than the less sterically demanding linear 2-phenylethyl derivative, $[Tism^{Pr'Benz}]MgCH_2CH_2Ph$. Although the 2-phenylethyl derivative is less sterically demanding, density functional theory calculations demonstrate that the branched isomer, $[Tism^{Pr'Benz}]MgCH(Me)Ph$, is 5.0 kcal mol⁻¹ more stable than the corresponding linear isomer, $[Tism^{Pr'Benz}]MgCH_2CH_2Ph$.

With respect to the observed selectivity, it is pertinent to note that the insertion of an olefin into a M-H bond to afford a linear isomer is often associated with the primary alkyl derivative being generally more stable than secondary and tertiary derivatives.^{30,31} Electron-withdrawing substituents on the olefin, however, favor formation of the branched isomer,^{32–34} which Jones attributed to the insertion reaction being driven by the formation of the isomer with the stronger C-H bond.³⁴ On this basis, [Tism^{PrBenz}]MgCH(Me)Ph would be more thermodynamically stable than [Tism^{PrBenz}]MgCH₂CH₂Ph because the former possesses a strong methyl C-H bond whereas the latter possesses a weaker benzylic C-H bond.³⁴

Analogous to [Tism^{PrⁱBenz}]MgMe, the Mg-C bond of [Tism^{PrⁱBenz}]MgCH(Me)Ph also undergoes metathesis with PhSiH₃ to form the magnesium hydride complex, [Tism^{PrⁱBenz}]MgH, releasing Ph(Me)C(H)SiH₂Ph and providing a means by which [Tism^{Pr Benz}]MgH may serve as a catalyst for hydrosilylation of styrene (Scheme 3).³⁵ The proposed mechanism for the catalytic cycle is illustrated in Scheme 2, and analysis of the reaction via ¹H NMR spectroscopy indicates that the resting state of the system is the alkyl form, [Tism^{PrⁱBenz}]MgCH(Me)Ph.

Furthermore, since $[Tism^{Pr^{i}Benz}]MgH$ is obtained upon treatment of $[Tism^{Pr^{i}Benz}]MgMe$ with $PhSiH_{3}$, $[Tism^{Pr^{i}Benz}]MgMe$ may also serve as a precatalyst. Although the activity is not high,³⁶ the observation represents the first example of hydrosilylation of an olefin catalyzed by a magnesium hydride compound.³⁷ In addition, since styrene inserts into the Mg-H bond to afford selectively the 1-phenylethyl isomer, [Tism^{Pr'Benz}]MgCH(Me)Ph, the hydrosilylation proceeds in a Markovnikov manner, in contrast to the anti-Markovnikov selectivity that is commonly observed for transition metal catalysts.^{38–40}

Scheme 3. Catalytic Activity of [Tism^{PrⁱBenz}]MgH



 $[Tism^{Pr'Benz}]MgH$ and $[Tism^{Pr'Benz}]MgMe$ likewise effect catalytic hydroboration of styrene to form the Markovnikov product, Ph(Me)C(H)Bpin. Although the activity is low,³⁶ the observation is noteworthy because alkylboronic esters are of much utility in organic synthesis,⁴¹ and there are no other reports of Mg-catalyzed hydroboration of olefins.⁴²

In addition to hydroboration of styrene, [Tism^{PriBenz}]MgH is also a catalyst for hydroboration of carbodiimides and pyridine (Scheme 3). Hydroboration of carbodiimides has received relatively little attention,⁴³ and so it is of note that [Tism^{PrⁱBenz}]MgH catalyzes the formation of N-boryl formamidines, RN = C(H)N(R)Bpin, by addition of HBpin to RN=C=NR (R = Cy, Prⁱ). Significantly, [Tism^{Pr'Benz}]MgH is an effective catalyst³⁶ at room temperature, more active than the only other reported catalyst for this transformation.^{43a} Finally, [Tism^{PrⁱBenz}]MgH and [Tism^{PrⁱBenz}]MgMe also effect catalytic addition of HBpin to pyridine to afford N-boryldihydropyridine, pinBNC₅H₆, as a mixture of 1,4- and 1,2-isomers, of which the former is obtained preferentially.^{44,45} The latter transformation is of relevance because dearomatization is a useful strategy in organic synthesis,⁴⁶ and the dearomatization of pyridine is of particular note because dihydropyridines (i) are a component of pharmaceuticals and natural products and (ii) serve as hydride sources in reductions.⁴⁷

In summary, the terminal hydride compound, [Tism^{Pr'Benz}]MgH, has been synthesized via the reaction of [Tism^{Pr'Benz}]MgMe with PhSiH₃. [Tism^{Pr'Benz}]MgH exhibits diverse reactivity with a variety of substrates to afford [Tism^{Pr'Benz}]MgX [X = F, Cl, Br, I, SH, N(H)Ph, CH(Me)Ph]. Of particular interest, [Tism^{Pr'Benz}]MgH undergoes insertion of styrene into the Mg-H bond to afford the branched 1phenylethyl derivative, [Tism^{Pr'Benz}]MgCH(Me)Ph. The latter compound reacts with PhSiH₃ to afford [Tism^{Pr'Benz}]MgH and Ph(Me)C(H)SiH₂Ph, thereby providing a means by which [Tism^{Pr'Benz}]MgH can serve as a catalyst for Markovnikov hydrosilylation. In addition to hydrosilylation, [Tism^{Pr'Benz}]MgH is also a catalyst for hydroboration of styrene, carbodiimides, and pyridine.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b06719.

Experimental details and computational data (PDF) Crystallographic data (ZIP)

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The authors declare no competing financial interest.

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