Magnesium-catalyzed hydrosilylation of a,b-unsaturated esters

Nicole L. Lampland
_Iowa State University_

Aradhana Pindwal
_Iowa State University_

Steven R. Neal
_University of Tennessee - Knoxville_

Shealyn Schlauderaff
_Iowa State University_

Arkady Ellern
_Iowa State University, ellern@iastate.edu_

See next page for additional authors

Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs

Part of the Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/223. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Magnesium-catalyzed hydrosilylation of α,β-unsaturated esters

Abstract

$\text{To}^{\text{M}}\text{MgHB(C}_6\text{F}_5)_3$ (1, $\text{To}^{\text{M}} = \text{tris}(4,4\text{-dimethyl-2-oxazolinyl})\text{phenylborate}$) catalyzes the 1,4-hydrosilylation of α,β-unsaturated esters. This magnesium hydridoborate compound is synthesized by the reaction of $\text{To}^{\text{M}}\text{MgMe}$, PhSiH$_3$, and B(C$_6$F$_5$)$_3$. Unlike the transient $\text{To}^{\text{M}}\text{MgH}$ formed from the reaction of $\text{To}^{\text{M}}\text{MgMe}$ and PhSiH$_3$, the borate adduct 1 persists in solution and in the solid state. Crystallographic characterization reveals tripodal coordination of the HB(C$_6$F$_5$)$_3$ moiety to the six-coordinate magnesium center with a $\angle\text{Mg–H–B}$ of 141(3)$^\circ$. The pathway for formation of 1 is proposed to involve the reaction of $\text{To}^{\text{M}}\text{MgMe}$ and a PhSiH$_3$/B(C$_6$F$_5$)$_3$ adduct because the other possible intermediates, $\text{To}^{\text{M}}\text{MgH}$ and $\text{To}^{\text{M}}\text{MgMeB(C}_6\text{F}_5)_3$, react to give an intractable black solid and $\text{To}^{\text{M}}\text{MgC}_6\text{F}_5$, respectively. Under catalytic conditions, silyl ketene acetal s are isolated in high yield from the addition of hydrosilanes to α,β-unsaturated esters with 1 as the catalyst.

Keywords
catalysis, esters, Hydrosilylation, Crystallographic characterization, Hydrosilanes, Silyl ketene acetal

Disciplines
Chemistry

Comments
This article is from Chemical Science 6 (2015): 6901, doi: 10.1039/c5sc02435h. Posted with permission.

Rights
This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Authors
Nicole L. Lampland, Aradhana Pindwal, Steven R. Neal, Shealyn Schlauderaff, Arkady Ellern, and Aaron D. Sadow

This article is available at Iowa State University Digital Repository: http://lib.dr.iastate.edu/chem_pubs/223
Magnesium-catalyzed hydrosilylation of \(\alpha,\beta\)-unsaturated esters†

Nicole L. Lampland,a Aradhana Pindwal,a Steven R. Neal,‡b Shealyn Schlauderaff,a Arkady Ellerna and Aaron D. Sadow*a

To\(^{\text{M}}\)MgHB(C\(_6\)F\(_5\))\(_3\) (1, To\(^{\text{M}}\) = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) catalyzes the 1,4-hydrosilylation of \(\alpha,\beta\)-unsaturated esters. This magnesium hydridoborate compound is synthesized by the reaction of To\(^{\text{M}}\)MgMe, PhSiH\(_3\), and B(C\(_6\)F\(_5\))\(_3\). Unlike the transient To\(^{\text{M}}\)MgH formed from the reaction of To\(^{\text{M}}\)MgMe and PhSiH\(_3\), the borate adduct 1 persists in solution and in the solid state. Crystallographic characterization reveals tripodal coordination of the HB(C\(_6\)F\(_5\))\(_3\) moiety to the six-coordinate magnesium center with a \(\angle\text{Mg–H–B}\) of 141(3)°. The pathway for formation of 1 is proposed to involve the reaction of To\(^{\text{M}}\)MgMe and a PhSiH\(_3\)/B(C\(_6\)F\(_5\))\(_3\) adduct because the other possible intermediates, To\(^{\text{M}}\)MgH and To\(^{\text{M}}\)MgMeB(C\(_6\)F\(_5\))\(_3\), react to give an intractable black solid and To\(^{\text{M}}\)MgC\(_6\)F\(_5\), respectively. Under catalytic conditions, silyl ketene acylals are isolated in high yield from the addition of hydrosilanes to \(\alpha,\beta\)-unsaturated esters with 1 as the catalyst.

The availability of many reaction pathways creates a challenge to control the selective conversion of carbonyl or olefin functional groups in substrates that contain both moieties. \(\alpha,\beta\)-Unsaturated carbonyls can be particularly difficult because they may be susceptible to 1,2-addition to the carbonyl, 1,4-additions, \(\alpha\)- or \(\beta\)-additions to the olefin, or polymerizations. The 1,4-addition products, silyl enol ethers or silyl ketene acylals, are valuable versatile nucleophiles in Mukaiyama aldol, Michael reactions, arylations, and haloketone or ketol formations. Since Wilkinson’s and Karstedt’s catalysts were shown to give selective 1,4-addition of R3SiH to \(\alpha,\beta\)-unsaturated ketones, mainly platinum-group metals have been studied as catalysts for 1,4-hydrosilylation of \(\alpha,\beta\)-unsaturated esters. Examples using more earth-abundant metals, such as main group or first row transition-metals, are less common and largely limited to Cu systems.

There are only a few examples of alkene hydrosilylation catalyzed by heavy group 2 metal complexes (Ca, Sr, Ba), and carbonyl hydrosilylation is even less common. This is likely a result of the oxophilicity of magnesium and its heavier congeners. In fact, [(Me-Nacna\(_{\text{Dipp}}\))\(_2\)]CaH·THF, (Me-Nacna\(_{\text{Dipp}}\) = [(2,6-iPr\(_2\)C\(_6\)H\(_5\))NCMe]CH) provides a rare example of a group 2 catalyzed 1,2-hydrosilylation of ketones. In the stoichiometric deaeromatization of pyridine and quinoline derivatives utilizing [(Me-Nacna\(_{\text{Dipp}}\)]MgBu] and PhSiH\(_3\), it was found that PhSiH\(_3\) is insufficiently reactive to provide catalytic turnover. To the best of our knowledge, there are no previous reports of hydrosilylation catalyzed by homogeneous magnesium complexes.

More often, esters are cleaved under hydrosilylation conditions with first-row transition-metal catalysts, or with main group catalysts in hydroborations. In a magnesium catalyzed

---

**Introduction**

Catalytic addition reactions, such as hydrosilylation and hydroboration are important synthetic tools for the reduction of unsaturated moieties. These reactions also provide carbon-element, oxygen-element, and nitrogen-element bonds (element = silicon, boron, hydrogen) that allow further elaboration of organic and inorganic substances through cross-coupling or oxidation. Transition-metal, main-group metal, and rare earth metal complexes catalyze hydrosilylation through a range of pathways including 2-electron metal-centered redox chemistry, single-electron processes, \(\sigma\)-bond metathesis, or hydride abstraction reactions involving Lewis acid sites. Even a single compound can be involved in catalytic additions through a number of pathways that vary depending on the substrates, reductants, conditions and/or co-catalysts. For example, B(C\(_6\)F\(_5\))\(_3\) catalyzes hydrosilylation of alkenes and carboxyls by action upon silanes, through frustrated Lewis Pairs in the presence of a bulky base, or through its combination with a metal center.

---

*dDepartment of Chemistry, Iowa State University, 1605 Gilman Hall, Ames, IA 50011, USA. E-mail: sadow@iastate.edu

†Electronic supplementary information (ESI) available: General experimental, synthesis and characterization of magnesium compounds and catalysis products. CCDC 1411027. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc02435h

‡Current address: Department of Chemistry, University of Tennessee, 515 Dabney-Buehler Hall, 1420 Circle Dr., Knoxville, TN 37996, USA.

The article is licensed under a Creative Commons Attribution 3.0 Unported Licence.
hydroboration of esters, the \( \alpha,\beta \)-unsaturated ester reacts through C–O bond cleavage while the C=–C bond is unaffected.\(^{17}\) In that system, an important postulated intermediate, \( \text{ToM}^\text{H}(\text{R} | \text{O})\text{Bpin} \) \( (\text{ToM} = \text{tris}(4,4\text{-dimethyl-2-oxazolyl})\text{phenylborate}; \text{Bpin} = \text{boron pinacol ester}) \), contains a boron–hydrogen bond. The \([\text{M}](\text{H}(\text{R} | \text{O})\text{Bpin})\) motif contains features also associated with \([\text{M}](\text{H}(\text{C}_6\text{F}_5)\text{B})\) complexes,\(^{18}\) including oxygen or fluorine coordination to the metal center and a B–H \( \to M \) interaction featuring a long M–H distance and nonlinear B–H–M angle. Recently, a \([\text{Me-Nacnac}^{\text{Dipp}}] \text{MHB}(\text{C}_6\text{F}_5)\) complex \( (\text{M} = \text{Mg, Ca}) \) was reported to catalyze the hydroboration of carbon dioxide,\(^{19}\) and this may suggest that hydroborates derived from \( \text{B}(\text{C}_6\text{F}_5) \) or \( \text{HBpin} \) may lead to new chemistry.

Alternatively, a terminal magnesium hydride supported by a tetradeutate monoanionic trimethylated tetraazazacyclooctetacene ligand is stabilized by \( \text{AlBu}_3 \), which coordinates to the amide moiety in the ancillary ligand rather than the nucleophilic hydride.\(^{20}\) The tris(oxazolyl)borato magnesium catalyst precursors studied for hydroboration, namely \( \text{ToM}^\text{H}\text{Me} \) or \( \text{ToM}^\text{H}\text{OR} \), do not mediate hydrosilylation of esters under the conditions tested, further suggesting that the boron center in \( \text{ToM}^\text{H}(\text{H}(\text{R} | \text{O})\text{Bpin}) \) provides a key feature for magnesium-catalyzed conversions of oxygenates.

The present study follows this idea to develop magnesium-catalyzed reductions of oxygenates employing organosilanes, rather than pinacolborane, as stoichiometric reductants. Here, we have incorporated the \([\text{M}](\text{HB}(\text{C}_6\text{F}_5)\text{B})\) motif into the complex \( \text{ToM}^\text{H}\text{Me} \) and \( \text{ToM}^\text{H}\text{Me} \) rather than pinacolborane, as stoichiometric reductants. Here, \( \text{ToM}^\text{H}\text{Me} \) provides a key feature for magnesium-catalyzed hydrosilylation. This transformation provides silyl ketene acetals through 1,4-hydrosilylation of \( \alpha,\beta \)-unsaturated esters.

### Results and discussion

The monomeric magnesium methyl \( \text{ToM}^\text{H}\text{Me} \) reacts slowly with organosilanes to provide Me–Si bond-containing compounds. For example, \( \text{ToM}^\text{H}\text{Me} \) and \( \text{PhSiH}_3 \) react in toluene-\( \text{d}_6 \) to form \( \text{PhMeSiH}_2 \) over 3 h at 100 °C (eqn (1)).

\[
\begin{align*}
\text{PhB} & \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{PhSiH}_3 \\
\text{ToM}^\text{H}\text{Me} & \quad \text{PhMeSiH}_2
\end{align*}
\]

The presumed magnesium-containing product, \( \text{ToM}^\text{H}\text{H} \), is rapidly converted into an intractable black solid under these conditions. This black material is also formed as a byproduct in room temperature reactions of \( \text{ToM}^\text{H}\text{NHR} \) and hydrosilanes that provide Si–N bond-containing products\(^{21}\) and in \( 1:1 \) reactions of \( \text{ToM}^\text{H}\text{Me} \) and \( \text{HBpin} \) that afford Me–Bpin.\(^{17b}\) As a result, the identity of \( \text{ToM}^\text{H}\text{H} \) is assumed based on reaction stoichiometry and its apparent reactivity as a catalytic intermediate.\(^{21}\) In order to obtain more evidence for \( \text{ToM}^\text{H}\text{H} \), we attempted to trap it as a Lewis acid adduct with \( \text{B}(\text{C}_6\text{F}_5) \).

A mixture of \( \text{ToM}^\text{H}\text{Me} \), \( \text{PhSiH}_3 \), and \( \text{B}(\text{C}_6\text{F}_5) \) gives \( \text{PhMeSiH}_2 \) and 1 (eqn (2)). Notably, this reaction occurs at room temperature over 10 min, whereas the direct interaction of \( \text{ToM}^\text{H}\text{Me} \) and \( \text{PhSiH}_3 \) requires the forcing conditions noted above. The optimized preparation of 1 involves dropwise addition of \( \text{ToM}^\text{H}\text{Me} \) to a mixture of \( \text{PhSiH}_3 \) and \( \text{B}(\text{C}_6\text{F}_5) \) dissolved in benzene.

\[
\begin{align*}
\text{ToM}^\text{H}\text{Me} & \quad \text{PhSiH}_3 \\
+ & \quad \text{B}(\text{C}_6\text{F}_5) \\
r., 10 \text{~min} & \quad 1
\end{align*}
\]

The \( ^1\text{H} \) NMR spectrum of 1 (benzene-\( \text{d}_6 \), r.t.) contained one set of oxazoline resonances, which is consistent with a pseudo-

\[
\begin{align*}
\text{ToM} & \quad \text{Mg} \quad \text{H} \quad \text{Me} \quad \text{H} \quad \text{Me} \quad \text{Me} \quad \text{PhSiH}_2 \\
\text{ToM} & \quad \text{Mg} \quad \text{H} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{PhSiH}_2
\end{align*}
\]

\[
\begin{align*}
\text{ToM}^\text{H}\text{Me} \quad \text{PhSiH}_3 \\
+ \quad \text{B}(\text{C}_6\text{F}_5) & \quad 1
\end{align*}
\]

The \( ^1\text{H} \) NMR spectrum of 1 (benzene-\( \text{d}_6 \), r.t.) contained one set of oxazoline resonances, which is consistent with a pseudo-

\[
\begin{align*}
\text{ToM} & \quad \text{Mg} \quad \text{H} \quad \text{Me} \quad \text{H} \quad \text{Me} \quad \text{Me} \quad \text{PhSiH}_2 \\
\text{ToM} & \quad \text{Mg} \quad \text{H} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{PhSiH}_2
\end{align*}
\]

\[
\begin{align*}
\text{ToM}^\text{H}\text{Me} \quad \text{PhSiH}_3 \\
+ \quad \text{B}(\text{C}_6\text{F}_5) & \quad 1
\end{align*}
\]

The \( ^1\text{H} \) NMR spectrum of 1 (benzene-\( \text{d}_6 \), r.t.) contained one set of oxazoline resonances, which is consistent with a pseudo-

\[
\begin{align*}
\text{ToM} & \quad \text{Mg} \quad \text{H} \quad \text{Me} \quad \text{H} \quad \text{Me} \quad \text{Me} \quad \text{PhSiH}_2 \\
\text{ToM} & \quad \text{Mg} \quad \text{H} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{PhSiH}_2
\end{align*}
\]

\[
\begin{align*}
\text{ToM}^\text{H}\text{Me} \quad \text{PhSiH}_3 \\
+ \quad \text{B}(\text{C}_6\text{F}_5) & \quad 1
\end{align*}
\]

The \( ^1\text{H} \) NMR spectrum of 1 (benzene-\( \text{d}_6 \), r.t.) contained one set of oxazoline resonances, which is consistent with a pseudo-

\[
\begin{align*}
\text{ToM} & \quad \text{Mg} \quad \text{H} \quad \text{Me} \quad \text{H} \quad \text{Me} \quad \text{Me} \quad \text{PhSiH}_2 \\
\text{ToM} & \quad \text{Mg} \quad \text{H} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{PhSiH}_2
\end{align*}
\]

\[
\begin{align*}
\text{ToM}^\text{H}\text{Me} \quad \text{PhSiH}_3 \\
+ \quad \text{B}(\text{C}_6\text{F}_5) & \quad 1
\end{align*}
\]
µ"H1 with magnesium–hydrogen distances of 2.20(2) and 2.34(2) Å that are longer than 1.26. The B1–H1 distance of 1 is between the bridging (1.33(2) Å) and terminal (1.19(3) Å) B–H distances in diborane27 and much longer than in the terminal B–H (1.06(6) Å) of Cp*₂ZrH₂[HB(C₆F₅)₃].22 Additionally, the B–H distance in 1 is similar to that of Cp*₂SmHB(C₆F₅)₃ (1.18(5) Å).²⁶ Cp*₂ScHB(C₆F₅)₃ (1.14(3) Å),²⁸ and {MeNacnac⁡\text{dipp}}CaHB(C₆F₅)₃ (1.16(2) Å).²⁹

The nonlinear &lt; Mg1–H1–B1 (141(3)°) angle is likely strongly influenced by the magnesium–fluorine interactions rather than from a Mg–(π²–H–B) interaction because the Mg1–B1 distance is longer (3.149(4) Å). However, the Mg–H–B angle in To⁴MgH₂Bpin of 93(2)° is much smaller, and as a result the Mg–B distance of 2.520(8) Å in the pinacol borane compound is shorter than in 1. The trigonal coordination mode of HB(C₆F₅)₃ is similar in 1, MC(SiHMe₂)₃[HB(C₆F₅)₃]THF₂ (M = Ca, Yb),²⁹ and {MeNacnac⁡\text{dipp}}CaHB(C₆F₅)₃.²⁹ Cp*₂SmHB(C₆F₅)₃ contains two Sm–F interactions from the aryl rings and a possible interaction between Sm and the hydride.²⁹ Despite the size difference and the bulky tridentate oxazolinylborate ligand, Mg₂⁺ still forms an analogous structure to these larger divalent metal cations. In contrast, Cp*₂ScHB(C₆F₅)₃ (ref. 18a) and Cp*₂ZrH₂[HB(C₆F₅)₃] (ref. 22) are bidentate through two M–F interactions.

Three pathways were considered for the formation of 1 (Scheme 1). The first one involves the reaction of To⁴MgMe and B(C₆F₅)₃ to give To⁴MgMeB(C₆F₅)₃ (2), followed by reaction of this species with PhSiH₃ to give PhMeSiH₂ and 1 (Path A). In Path B, the reaction of To⁴MgMe and PhSiH₃ forms To⁴MgH₂, which is trapped by B(C₆F₅)₃ to give 1. Alternatively, PhSiH₃ and B(C₆F₅)₃ could interact to give a transient adduct [PhH₂–SiHB(C₆F₅)₃], and this intermediate reacts with To⁴MgMe to give the products (Path C). Methide abstraction by B(C₆F₅)₃ in Path A is well established,²⁸ supporting the possible intermediate To⁴MgMeB(C₆F₅)₃. Furthermore, Cp*₂ZrMe₂(μ-Me)B(C₆F₅)₃ is reported to undergo hydrogenation with H₂ to give Cp*₂ZrH₂[HB(C₆F₅)₃]₂,²²–²⁸ and (C₅R₅)₂MMe(μ-Me)B(C₆F₅)₃ (M = Zr, Hf; C₅R₅ = C₅H₅, C₅H₄Me, C₅Me₅) and silanes react to give (C₅R₅)₂MH[HB(C₆F₅)₃]₂.²⁹ These reactions, however, may involve methyl-hydride exchange through the conversion of [M][H][μ-Me]B(C₆F₅)₃ to [M][Me]([μ-H]B(C₆F₅)₃) rather than direct hydrogenolysis of M–Me–B bridge required for Path A. Path C is supported by proposed silane-borane adducts in B(C₆F₅)₃-catalyzed hydrosilylations with tertiary silanes,²⁶ and recently a tri(pentfluorophenyl)-boraindene and triethylsilane adduct was isolated and fully characterized.³⁰

Path B is immediately ruled out by the apparent reaction kinetics, which require forcing conditions to slowly generate To⁴MgH₂ from PhSiH₃ and To⁴MgMe. This reaction time and temperature contrasts the rapid formation of 1 from To⁴MgMe and PhSiH₃ in the presence of B(C₆F₅)₃. To test the feasibility of Path A, the proposed intermediate, To⁴MgMeB(C₆F₅)₃ (2), was independently synthesized by addition of B(C₆F₅)₃ dissolved in pentane to a benzene solution containing To⁴MgMe (eqn (3)).

The product immediately precipitates giving analytically pure 2. Reactions in benzene-δ₆ or methylene chloride-δ₂ provide To⁴MgMeB(C₆F₅)₃ as a partially soluble species that may be quickly characterized by solution-phase spectroscopy. However, once solvent is removed and To⁴MgMeB(C₆F₅)₃ is isolated, it becomes insoluble in benzene and methylene chloride and only partially redissolves in THF. As in 1, ¹H NMR spectra of in situ generated 2 revealed equivalent oxazoline groups. In a ¹H–¹B HMBC experiment, the resonance assigned to the MeB(C₆F₅)₃ at 1.27 ppm correlated with a singlet ¹B NMR signal at −15.5 ppm. However as 2 stands in benzene-δ₆, the signals for To⁴MgMeB(C₆F₅)₃ decrease as the new species To⁴MgC₆F₅ (3) and BMe₃ form. After 7 h,

![Fig. 1](image)

**Scheme 1** Possible pathways to To⁴MgH₂B(C₆F₅)₃ (1).
ToMgMgMeB(C₆F₅)₃ is still the major component, but it is completely consumed over 20 h. This transformation occurs more rapidly in methylene chloride-d₆ (t₁/₂ = 1 h).

Compound 3 is most conveniently prepared and isolated by the reaction of 1 equiv. of ToMgMe and 1 equiv. of B(C₆F₅)₃ in benzene-d₆ over 24 h, but also forms from the reaction of 0.3 equiv. of B(C₆F₅)₃ with ToMgMgMe (eqn (4)). Solid ToMgMgC₆F₅ was purified from the BMe₃ side product by washing with pentane.

The ¹H NMR spectrum of the crude reaction mixture contained a broad signal at 0.74 ppm assigned to BMe₃ (ref. 31) and singlet resonances at 0.98 and 3.38 ppm assigned to the ToM ancillary ligand. Two peaks were observed in the ¹³B NMR spectrum at 86.5 and −18.3 ppm assigned to BMe₃ and ToM, respectively. In addition, the tridentate coordination of the tris(oxazolinyl)borate ligand is supported by the ¹⁵N NMR chemical shift of −158 ppm and the F₂ bands in the infrared spectrum at 1594 cm⁻¹. These values are similar to those of crystallographically characterized ToMgMeB(C₆F₅)₃ (¹⁵N NMR: −157 ppm; F₂: 1592 cm⁻¹). Three signals in the ¹⁹F NMR spectrum included a downfield signal at −110 ppm assigned to the ortho-fluorine. For comparison, C₆F₅MgBr provides three sets of ¹⁹F NMR signals, with ortho-F resonance appearing 45 ppm upfield of the para-F peak.

The reaction of in situ generated 2 and PhSiH₃ at room temperature in benzene-d₆ gives only starting materials after 30 min. Over ca. 24 h, ToMgMgMeB(C₆F₅)₃ undergoes C₆F₅ transfer to the magnesium center, and PhSiH₃ remains un consumed. Micromolar-scale reactions in methylene chloride-d₆ yield a mixture of ToMgMeB(C₆F₅)₃, BMe₃, B(C₆F₅)₃, and PhSiH₃ after 2 h. On the basis of these observations, 2 is not an intermediate in the formation of the magnesium hydridoborate 1, and Path A is ruled out. Therefore, the currently preferred pathway for the formation of 1 involves methide abstraction by a transient borane-silane adduct (Scheme 1, Path C). In fact, the aryl group transfer from boron to magnesium may be a decomposition pathway for 1 in catalytic reactions (see below).

α,β-Unsaturated esters and silanes react through selective 1,4-hydrosilylation in the presence of catalytic amounts of ToMgH[B(C₆F₅)₃] (1). For instance, the reaction of methyl methacrylate, Ph₂SiH₂, and 1 mol% 1 gives complete conversion of methyl methacrylate after 30 min in benzene-d₆, as determined by ¹H NMR spectroscopy (eqn (5)).

A ¹H NMR spectrum of the isolated silyl ketene acetal product contained inequivalent methyl signals at 1.64 and 1.69 ppm, and singlets at 3.29 (3H) and 5.84 ppm (1H) assigned to the OMe and SiH groups. Olefinic signals, however, are not present in the product’s ¹H NMR spectrum. The ¹³C{¹H} NMR spectrum contained a resonance at 150.93 ppm assigned to the acetal carbon. In an ¹H–²⁹Si HMBC experiment, a ²⁹Si NMR signal at −14.5 ppm correlated to the SiH, inequivalent methyl signals, and phenyl resonances.

A range of silyl ketene acetals are prepared using 1 as the hydrosilylation catalyst (Table 1). Although transformations proceed with the low catalyst loadings of Table 1, scaled up reactions were performed with 20 mol% 1 to increase the rate of conversion. Secondary and tertiary silanes effectively hydrosilylate methyl methacrylate, and the products are isolated in good yield. In addition, the cyclic α,β-unsaturated ester 5,6-dihydro-2H-pyran-2-one react with PhMeSiH₂ or BnMe₂SiH in the presence of 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>mol% catalyst</th>
<th>Time (h)</th>
<th>Isolated% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrMe₂SiH + CO₂Me</td>
<td>1</td>
<td>0.5</td>
<td>99</td>
</tr>
<tr>
<td>Ph₂SiH₂ + CO₂Me</td>
<td>1</td>
<td>0.5</td>
<td>96</td>
</tr>
<tr>
<td>Me₂PhSiH₂ + CO₂Ph</td>
<td>1</td>
<td>7</td>
<td>97</td>
</tr>
<tr>
<td>PhMe₂SiH₂ + CO₂CH₂Ph</td>
<td>2.5</td>
<td>8</td>
<td>41</td>
</tr>
<tr>
<td>Me₂PhSH₂ + CO₂CH₂Ph</td>
<td>2.5</td>
<td>4</td>
<td>99</td>
</tr>
<tr>
<td>PhMe₂SiH₂ + CO₂CH₂Ph</td>
<td>10</td>
<td>5</td>
<td>80</td>
</tr>
</tbody>
</table>

a Reaction conditions: silane : acrylate = 1 : 1, benzene, r.t. b Catalyst loading given for NMR scale reactions. c 60 °C. d 35 °C. e 80 °C.
A number of experiments further test the key features of the catalyst structure and the reaction pathway. First, a series of ToMMgX compounds \([X = \text{Me}, \text{C}_6\text{F}_5\text{Me}, \text{MeB}(\text{C}_6\text{F}_5)_2, \text{B}(\text{C}_6\text{F}_5)_3]\) were investigated as catalysts for hydrosilylation of methyl methacrylate. A catalytic amount of ToMMgMe reacts instantaneously with methyl methacrylate and PhMeSiH\(_2\) in benzene-\(d_6\) to give insoluble materials likely resulting from polymerization. Even though some of the silane is consumed in this reaction, neutral ToMMgMe is not a viable hydrosilylation catalyst. Moreover, this further demonstrates that the silicon–oxygen bond formation is unlikely to involve \(\sigma\)-bond metathesis of silanes and a magnesium alkoxide.

In addition, \(^1\)H NMR spectra of catalytic mixtures of methyl methacrylate, PhMeSiH\(_2\), and 10 mol\% ToMMgMeB(\text{C}_6\text{F}_5)_3 show only resonances assigned to methyl methacrylate and PhMeSiH\(_2\), and signals associated with the hydrosilylation product were not detected. ToMMgMeB(\text{C}_6\text{F}_5)_3 is converted to ToMMgC\(_6\text{F}_5\) under these conditions, and independent experiments show that ToMMgC\(_6\text{F}_5\) is also not catalytically active. Hydridoborate-free magnesium compounds were tested next. The reaction of ToMMgMe and [\(\text{Ph}_3\text{C}\)][\text{B}(\text{C}_6\text{F}_5)_4] in benzene-\(d_6\) at room temperature gives [ToMMg][\text{B}(\text{C}_6\text{F}_5)_3] as a precipitate after 15 min. However, this complex is not an ester hydrosilylation catalyst, and PhMeSiH\(_2\) and methyl methacrylate are unchanged after 2 d at 80 °C in the presence of 10 mol\% [ToMMg][\text{B}(\text{C}_6\text{F}_5)_3].

Alternatively, B(\text{C}_6\text{F}_5)_3 is known as a hydrosilylation catalyst that mediates 1,2-addition of tertiary silanes to esters.\(^b\) Free B(\text{C}_6\text{F}_5)_3 might be present in the reaction mixture as a result of its dissociation from 1, so its catalytic mode of action in mixtures of silanes and \(\alpha,\beta\)-unsaturated esters was probed. However upon treatment with 10 mol\% B(\text{C}_6\text{F}_5)_3, BnMe\(_2\)SiH or \((\text{H}_2\text{C}==\text{CH})\text{Me}_2\)SiH and methacrylates provide mixtures containing the 1,4-addition product contaminated with at least 2 other species (see ESI† for spectra). The reactions of PhMeSiH\(_2\) and methyl methacrylate, as catalyzed by 1 or 1 mol% B(\text{C}_6\text{F}_5)_3, give inequivalent products. The product from the strong Lewis acid catalyst, in this case, does not contain an SiH, but is instead the double addition product PhMeSi[OC(OME)]=CMe\(_2\)\(_2\) formed as part of a mixture. The B(\text{C}_6\text{F}_5)_3-catalyzed reaction of PhMeSiH\(_2\) and benzyl methacrylate gives a complicated mixture. Interestingly, lower B(\text{C}_6\text{F}_5)_3 loadings generally result in increased amounts of the side products with respect to silyl ketene acetal. These data indicate that the hydrosilylation of the methacrylates is not catalyzed by B(\text{C}_6\text{F}_5)_3 when 1 is used as the catalyst. The B(\text{C}_6\text{F}_5)_3-catalyzed reaction of Et\(_2\)SiH and methyl methacrylate, however, gives the silyl ketene acetal quantitatively, as does the same conversion catalyzed by 1. Thus, B(\text{C}_6\text{F}_5)_3-catalyzed hydrosilylations are more sensitive to the substitution of the organosilane than conversions catalyzed by 1.

Next, the interaction of 1 and organosilane was probed by \(^1\)H and \(^{11}\)B NMR spectroscopy. In the \(^1\)H NMR spectrum, the intensity of methyl and methylene signals associated with the oxazoline ligand in 1 diminish by ca. 70% upon addition of 10 equiv. of BnMe\(_2\)SiH, and new, albeit small, oxazoline methyl and methylene signals were observed. The new oxazolines signals are not sufficiently abundant to account for all of the previous ToMMg signals. Moreover, the quartet at 2.7 ppm for HB(\text{C}_6\text{F}_5)_3 was not visible after addition of excess organosilane, although a number of broad signals appeared in that region. The SiH of BnMeSiH\(_2\) appeared as a sharp multiplet and was apparently unchanged in the presence of 1. The broad doublet at −21 ppm in the \(^{11}\)B NMR spectrum of 1 decreased in intensity, and a new signal at −24 ppm appeared. The new upfield \(^{11}\)B NMR signal appeared in the region typical of HB(\text{C}_6\text{F}_5)_3, but H–B coupling was not resolved in the broad signal. At low temperature (190 K), the \(^{11}\)B NMR signal at −24 was not detected, and the doublet at −21 is the major HB(\text{C}_6\text{F}_5)_3 resonance. As the temperature increased to 260 K, the broad signal at −24 ppm appeared while the doublet at −21 diminished.

At the same time, the \(^{11}\)B NMR signal at −18 ppm for ToMMg was sharp at 190 K, broad at 260 K, and again sharpened at 280 K. These data suggest that BnMeSiH\(_2\) and ToMMgHB(\text{C}_6\text{F}_5)_3 interact to disrupt the hydridoborate coordination to magnesium resulting in a dynamic system, but the HB(\text{C}_6\text{F}_5)_3 moiety remains intact. Moreover, \(^{11}\)B NMR spectra acquired during catalytic conversions reveal signals at −18 and −24 ppm assigned to the boron centers in ToMMg and HB(\text{C}_6\text{F}_5)_3. These two \(^{11}\)B NMR signals were also observed after complete conversion of methyl methacrylate via hydrosilylation. \(^1\)H NMR spectra of the catalytic reaction mixture, however, do not contain signals associated with 1. These data suggest that a fluxional derivative of 1 is involved in the catalytic conversion.

Under pseudo-first order conditions (using toluene-\(d_8\) as solvent) with excess methyl methacrylate, the half-life for the disappearance of Ph\(_2\)SiH\(_2\) is \(~3\) min at 64 °C, and over several minutes the silane is completely consumed. However, a methacrylate polymerization side-reaction interferes with kinetic measurements under these conditions. In the presence of excess Ph\(_2\)SiH\(_2\) with respect to the methacrylate, zero-order, first-order, and second-order kinetic plots of methyl methacrylate concentration vs. time are non-linear, and complete conversion of the methacrylate is not obtained. The decrease in catalytic rate is even more prominent in methylene-chloride-\(d_2\) than in benzene-\(d_6\). In benzene-\(d_6\), the addition of methyl methacrylate and PhMeSiH\(_2\) is catalyzed by 10 mol\% 1 in fewer than 10 min, while equivalent reaction conditions in methylene chloride-\(d_2\) give only 50% conversion after 24 h. Furthermore, the only ToMMg-containing \(^1\)H NMR resonances observed in the catalytic reaction mixture (in methylene chloride-\(d_2\)) were those assigned to ToMMgC\(_6\text{F}_5\). On the basis of faster conversion of ToMMgMeB(\text{C}_6\text{F}_5)_3 to ToMMgC\(_6\text{F}_5\) in methylene chloride than in benzene, the lack of activity of ToMMgC\(_6\text{F}_5\) as a hydrosilylation catalyst, and the lower catalytic activity in methylene chloride than in benzene, we suggest that catalyst deactivation occurs through C\(_6\text{F}_5\) migration from boron to magnesium.

**Conclusions**

The catalytic results above represent an unusual example of a magnesium-catalyzed hydrosilylation of C–O containing compounds. This catalytic transformation is particularly noteworthy in the context of the oxophilic magnesium center, and
the general challenge of catalytic turnover under such reducing conditions. While a kinetically-characterized catalytic mechanism is not accessible in the current system, plausible intermediates can be considered, and some may be ruled out, on the basis of the observed reactivity of ToMgMe, ToMgHB(C6F5)3 (1), ToMgMeB(C6F5)3 (2), and ToMgC6F5 (3). The catalytic intermediates might involve the coordination of the ester oxygen to the magnesium center, a boron–carbon bond-containing species, a silane adduct of a cationic magnesium center, and/or an enolate of magnesium or boron. As one possibility, a magnesium enolate and a borane–silane adduct might interact to give Si–O bond formation and regenerate 1, following the proposed pathway for the formation of 1 from PhSiH3, ToMgMe, and B(C6F5)3. The catalysis requires [HB(C6F5)3]− and no catalysis is observed with [B(C6F5)3]− or with neutral magnesium alkyls ToMgMe or ToMgC6F5, providing additional support for the bifunctional role of 1 in this hydrosilylation, as proposed in frustrated Lewis pair chemistry.8 Moreover, ToMgMeB(C6F5)3 is not a viable hydrosilylation precursor, in contrast to ToMgHB(C6F5)3. This result further supports the postulate that the hydridoborate is key to accessing the active magnesium species.

A catalyst deactivation pathway is suggested to involve the transfer of C6F5 from boron to magnesium to give ToMgC6F5. ToMgC6F5 is shown to be catalytically inert and to form more rapidly in methylene chloride than in benzene; the trend of faster catalyst deactivation in methylene chloride than in benzene parallels the faster formation of ToMgC6F5 in the former solvent. These observations are taken as evidence in support of C6F5 transfer as a pathway to catalyst deactivation. This catalyst deactivation pathway is somewhat unexpected, given that magnesium alkyls are much more potent nucleophiles and bases than magnesium alkoxides. That is, in the presence of oxygen-containing substrates, a magnesium catalyst is deactivated by magnesium–carbon bond formation rather than magnesium–oxygen bond formation. This, and the catalytic hydrosilylation of oxygenates employing a highly oxophilic metal center, further indicates that the combination of a strong Lewis acid with early metal centers can access new reaction pathways through cooperation between the metal center and non-ionic counterion.

**Experimental**

ToMgHB(C6F5)3 (1)

A solution of ToMgMe (0.134 g, 0.32 mmol) dissolved in benzene was added in a droppewise fashion into a benzene solution containing PhSiH3 (0.069 g, 0.64 mmol) and B(C6F5)3 (0.162 g, 0.32 mmol). A white precipitate formed as the reaction mixture stirred for 30 min. The precipitate settled after centrifugation, and the supernatant was decanted. The white solid was washed with pentane (3 × 5 mL) and dried under vacuum, providing analytically pure ToMgHB(C6F5)3 (0.286 g, 0.31 mmol, 97.6%). Once isolated, ToMgHB(C6F5)3 is soluble in benzene or toluene, and X-ray quality single crystals were grown from a concentrated toluene solution at ~30 °C. 1H NMR (600 MHz, benzene-d6): δ 0.82 (s, 18H, CNCMe2CH2O), 2.72 (br q, JHH = 69 Hz, 1H, MgHB(C6F5)3), 3.30 (s, 6H, CNCMe2CH2O), 7.38 (m, JHH = 7.2 Hz, 1H, para-C6H5), 7.56 (m, JHH = 7.6 Hz, 2H, meta-C6H5), 8.25 (d, JHH = 7.2 Hz, 2H, ortho-C6H5). 13C{1H} NMR (150 MHz, THF-d8): δ 27.35 (CNCMe2CH2O), 66.13 (CNCMe2CH2O), 79.28 (CNCMe2CH2O), 130.24 (para-C6H5), 133.26 (meta-C6H5), 134.79 (C6F5), 135.74 (C6F5), 136.81 (C6F5), 137.49 (ortho-C6F5), 138.41 (C6F5), 142 (br, ipso-C6F5), 147.78 (C6F5), 149.35 (C6F5), 191 (CNCMe2CH2O). 11B NMR (192 MHz, benzene-d6): δ −18.2 (ToMg), −21.1 (d, JHH = 69 Hz, MgHB(C6F5)3). 19F NMR (544 MHz, benzene-d6): δ −134.2 (ortho-C6F5), −156.5 (para-C6F5), −161.4 (meta-C6F5). 31N NMR (60 MHz, benzene-d6): δ −162. IR (KBr, cm−1): ν 2976 (s), 2937 (s), 2372 (w br, BH), 1642 (m), 1579 (s), 1459 (s br), 1373 (m), 1271 (m), 1199 (m), 1180 (m), 1161 (m), 1087 (s), 965 (s br), 843 (w), 804 (w), 735 (w), 705 (w). Anal. calcd for C39H30B2F15MgN3O3: C, 50.94; H, 3.29; N, 4.57. Found C, 51.38; H, 3.41; N, 4.31. Mp: 166–167 °C.

**Crystallography**

Crystal structure determination for compound 1. C39H30B2F15MgN3O3 (C>H3), M = 1149.94, triclinic, a = 11.7916(18), b = 13.4602(2), c = 18.2393(3), α = 86.434(3), β = 88.133(3), γ = 69.802(3), V = 2711.3(7) Å3, T = 173 K, space group P1, Z = 2, 15 346 reflections measured, 9197 unique (Rint = 0.0303). The final R1(F2) and wR2(F2) for I > 2σ(I) were 0.0492 and 0.161.

**Representative catalytic hydrosilylation**

Reaction of PhSiH3 and methyl methacrylate. ToMgHB(C6F5)3 (0.011 g, 0.021 mmol), methyl methacrylate (0.117 g, 1.17 mmol) and PhSiH2 (0.216 g, 1.17 mmol) were stirred in C6H6 for 30 min at room temperature. Benzene was removed under reduced pressure, leaving behind a colorless gel. The product was extracted with pentane, and the extracts were evaporated under reduced pressure to afford a colorless liquid (0.331 g, 1.13 mmol, 96.3%). 1H NMR (400 MHz, benzene-d6): δ 1.64 (s, 3H, C3H8), 1.69 (s, 3H, C3H8), 3.29 (s, 3H, OMe), 5.84 (s, 1H, SiH), 7.17 (m, 6H, C6H6), 7.74 (m, 4H, C6H4), 1.01 (d, 3JHH = 69 Hz, 1H, MgHB(C6F5)3). 13C{1H} NMR (150 MHz, benzene-d6): δ 16.79 (C–CMe2), 17.42 (C–CMe2), 57.92 (OMe), 91.74 (C–CMe2), 130.47 (C6H5), 131.12 (C6H5), 134.16 (ipso-C6H5), 135.49 (C6H5), 136.39 (C6H5), 150.93 (C–CMe2). 29Si (119 MHz, benzene-d6) δ −14.5 (d, JHH = 201 Hz). IR (KBr, cm−1): ν 3094 (m), 2931 (s), 2158 (s), 1716 (s), 1661 (w), 1598 (m), 1566 (w), 1548 (w), 1528 (w), 1437 (s), 1263 (m), 1169 (br s), 1029 (m), 949 (m), 858 (s), 738 (s), 701 (s), 671 (w). Anal. calcd for C39H30B2O2Si: C, 71.79; H, 7.09. Found C, 71.61; H, 7.32.

**Acknowledgements**

The authors gratefully thank the National Science Foundation (CHE-0955635) for financial support. Dr Sarah Cady and Dr Shu Xu are thanked for valuable NMR assistance.

**References**

