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Magnesium-catalyzed hydrosilylation of α,β -unsaturated esters[†]

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To^MMgHB(C₆F₅)₃ (**1**, To^M = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) catalyzes the 1,4-hydrosilylation of α,β -unsaturated esters. This magnesium hydridoborate compound is synthesized by the reaction of To^MMgMe, PhSiH₃, and B(C₆F₅)₃. Unlike the transient To^MMgH formed from the reaction of To^MMgMe and PhSiH₃, the borate adduct **1** persists in solution and in the solid state. Crystallographic characterization reveals tripodal coordination of the HB(C₆F₅)₃ moiety to the six-coordinate magnesium center with a \angle Mg–H–B of 141(3)°. The pathway for formation of **1** is proposed to involve the reaction of To^MMgMe and a PhSiH₃/B(C₆F₅)₃ adduct because the other possible intermediates, To^MMgH and To^MMgMeB(C₆F₅)₃, react to give an intractable black solid and To^MMgC₆F₅, respectively. Under catalytic conditions, silyl ketene acetals are isolated in high yield from the addition of hydrosilanes to α,β -unsaturated esters with **1** as the catalyst.

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Introduction

Catalytic addition reactions, such as hydrosilylation¹ and hydroboration² 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-coupling3 or oxidation.4 Transition-metal, main-group metal, and rare earth metal complexes catalyze hydrosilvlation through a range of pathways including 2-electron metal-centered redox chemistry, single-electron processes, σ -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(C₆F₅)₃ catalyzes hydrosilylation of alkenes and carbonyls by action upon silanes,5 through frustrated Lewis Pairs in the presence of a bulky base,6 or through its combination with a metal center.7

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. α , β -Unsaturated carbonyls can be particularly difficult because they may be susceptible to 1,2-addition to the carbonyl, 1,4-additions, α - or β -additions to the olefin, or polymerizations. The 1,4-addition products, silyl enol ethers or silyl ketene acetals, are valuable versatile nucleophiles in Mukaiyama aldol, Michael reactions,8 arylations,9 and haloketone or ketol formations. Since Wilkinson's and Karstedt's catalysts were shown to give selective 1,4-addition of R₃SiH to α,β-unsaturated ketones,¹⁰ mainly platinum-group metals have been studied as catalysts for 1,4-hydrosilylation of α,β-unsaturated esters.¹¹ Examples using more earth-abundant metals, such as main group or first row transition-metals, are less common and largely limited to Cu systems.12

There are only a few examples of alkene hydrosilylation catalyzed by heavy group 2 metal complexes (Ca, Sr, Ba),¹³ and carbonyl hydrosilylation is even less common. This is likely a result of the oxophilicity of magnesium and its heavier congeners. In fact, [{Me-Nacnac^{Dipp}}CaH·THF]₂ (Me-Nacnac^{Dipp} = ((2,6-iPr₂C₆H₃)NCMe)₂CH) provides a rare example of a group 2 catalyzed 1,2-hydrosilylation of ketones.¹⁴ In the stoichiometric dearomatization of pyridine and quinoline derivatives utilizing [{Me-Nacnac^{Dipp}}MgⁿBu] and PhSiH₃, it was found that PhSiH₃ is insufficiently reactive to provide catalytic turnover.¹⁵ 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,¹⁶ or with main group catalysts in hydroborations.¹⁷ In a magnesium catalyzed

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hydroboration of esters, the α,β -unsaturated ester reacts through C-O bond cleavage while the C=C bond is unaffected.17b In that system, an important postulated intermediate, $To^{M}Mg{H(RO)Bpin}$ ($To^{M} = tris(4,4-dimethyl-2-oxazolinyl)phe$ nylborate; Bpin = boron pinacol ester), contains a boronhydrogen bond. The [M]{H(RO)Bpin} motif contains features also associated with $[M]{HB(C_6F_5)_3}$ complexes,¹⁸ including oxygen or fluorine coordination to the metal center and a B-H \rightarrow M interaction featuring a long M-H distance and nonlinear B-H-M angle. Recently, a {Me-Nacnac^{Dipp}}MHB(C_6F_5)₃ complex (M = Mg, Ca) was reported to catalyze the hydroboration of carbon dioxide,19 and this may suggest that hydroborates derived from $B(C_6F_5)_3$ or HBpin may lead to new chemistry. Alternatively, a terminal magnesium hydride supported by a tetradentate monoanionic trimethylated tetraazacyclododecane ligand is stabilized by AliBu₃, which coordinates to the amide moiety in the ancillary ligand rather than the nucleophilic hydride.20 The tris(oxazolinyl)borato magnesium catalyst precursors studied for hydroboration, namely To^MMgMe or To^MMgOR, do not mediate hydrosilvlation of esters under the conditions tested, further suggesting that the boron center in To^MMg{H(RO)Bpin} provides a key feature for magnesiumcatalyzed conversions of oxygenates.

The present study follows this idea to develop magnesiumcatalyzed reductions of oxygenates employing organosilanes, rather than pinacolborane, as stoichiometric reductants. Here, we have incorporated the [M]HB(C₆F₅)₃ motif into the complex To^MMgHB(C₆F₅)₃ (1) and report its reactivity as the first magnesium-catalyzed hydrosilylation. This transformation provides silyl ketene acetals through 1,4-hydrosilylation of α , β unsaturated esters.

Results and discussion

The monomeric magnesium methyl To^MMgMe reacts slowly with organosilanes to provide Me–Si bond-containing compounds. For example, To^MMgMe and PhSiH₃ react in toluene- d_8 to form PhMeSiH₂ over 3 h at 100 °C (eqn (1)).



The presumed magnesium-containing product, $To^M MgH$, 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 $To^M MgNHR$ and hydrosilanes that provide Si–N bond-containing products²¹ and in 1 : 1 reactions of $To^M MgMe$ and HBpin that afford Me-Bpin.^{17b} As a result, the identity of $To^M MgH$ is assumed based on reaction stoichiometry and its apparent reactivity as a catalytic intermediate.²¹ In order to obtain more evidence for $To^M MgH$, we attempted to trap it as a Lewis acid adduct with $B(C_6F_5)_3$. A mixture of $To^M MgMe$, $PhSiH_3$, and $B(C_6F_5)_3$ gives $PhMeSiH_2$ and 1 (eqn (2)). Notably, this reaction occurs at room temperature over 10 min, whereas the direct interaction of $To^M MgMe$ and $PhSiH_3$ requires the forcing conditions noted above. The optimized preparation of 1 involves dropwise addition of $To^M MgMe$ to a mixture of $PhSiH_3$ and $B(C_6F_5)_3$ dissolved in benzene.



The ¹H NMR spectrum of **1** (benzene- d_6 , r.t.) contained one set of oxazoline resonances, which is consistent with a pseudo- C_{3v} -symmetric structure and tridentate coordination of To^M to the magnesium center. In addition, the hydrogen bonded to boron was observed at 2.7 ppm as a 1 : 1 : 1 : 1 quartet ${}^{1}J_{BH} =$ 69 Hz). In the ¹¹B NMR spectrum, a singlet at -18.2 ppm was assigned to the tris(oxazolinyl)borate ligand, and a doublet at $-21.1 \text{ ppm} (^{1}J_{\text{HB}} = 69 \text{ Hz})$ characterized the HB(C₆F₅)₃ group. The C₆F₅ are equivalent and freely rotating on the NMR timescale at room temperature, as indicated by the three resonances observed in the ¹⁹F NMR spectrum at -134.2, -156.5 and -161.4 ppm. The chemical shift of the *ortho*-F are similar to $Cp_{2}^{*}ZrH{HB(C_{6}F_{5})_{3}}$ ($Cp^{*} = C_{5}Me_{5}$), while the *meta*-F and *para*-F signals of 1 are downfield with respect to the zirconium hydride complex.²² The $\delta_{para} - \delta_{meta}$ of 5 ppm²³ suggests coordination of $HB(C_6F_5)_3$ to the Mg center. On the basis of these data and the single-crystal X-ray diffraction study (see below), ¹⁹F NMR spectra were acquired from 298 to 180 K; however, these signals did not vary over that temperature range. A single infrared band at 1579 cm⁻¹ assigned to the oxazoline $\nu_{\rm CN}$ also supported the assignment of tridentate To^M-coordination. In addition, B-H bond formation was evidenced by an IR band at 2372 cm^{-1} .

A single crystal X-ray diffraction study confirms the identity of compound **1** as $To^{M}MgHB(C_{6}F_{5})_{3}$, the tridentate coordination mode of the To^M ligand, and the tripodal Mg-HB(C₆F₅)₃ interaction (Fig. 1). The six coordinating groups (three N from To^{M} , two F and one H from $HB(C_{6}F_{5})_{3}$) form a distorted octahedral coordination geometry. Thus, the pseudo-trans disposed N1-Mg1-H1 angle is 162.3(7) and the N2-Mg1-F10 and N3-Mg1-F11 angles are 169.28(9) and 173.33(9)°. The Mg1-H1 and B1-H1 interatomic distances are 2.06(3) Å and 1.24(3) Å, respectively. The Mg1-H1 distance is longer than in the bridging Mg–H–Mg of [{Me-Nacnac^{Dipp}}Mg(μ -H)]₂ (1.95(3) Å)²⁴ and [{tBu-Nacnac^{Dipp}}Mg(µ-H)]₂ (1.80(5) and 1.91(5) Å; tBu-Nacnac^{Dipp} = $((2,6-iPr_2C_6H_3)NCtBu)_2CH)$. It is also longer than in the terminal magnesium hydride $\{tBu-Nacnac^{Dipp}\}$ MgH(DMAP) (1.75(7) Å).²⁵ The Mg1-H1 distance, however, is shorter than the related Mg-H distance of 2.19(3) Å in ${\rm To}^M Mg H_2 Bpin.^{17b}$ In $[\{Me\text{-Nacnac}^{\rm Dipp}\} Mg B H_4]_2,$ there are two types of Mg-H-B interactions, a Mg-H-B bridge (1.95(2) and 1.96(2) Å) containing shorter distances than in 1, and Mg, Mg, B-

 μ^3 -H 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*₂ZrH{HB(C₆F₅)₃}.²² Additionally, the B–H distance in 1 is similar to that of Cp*₂SmHB(C₆F₅)₃ (1.18(5) A),^{18b} Cp*₂ScHB(C₆F₅)₃ (1.14(3) Å),^{18a} and {Me-Nacnac^{Dipp}} CaHB(C₆F₅)₃ (1.16(2) Å).¹⁹

The nonlinear \angle Mg1–H1–B1 (141(3)°) angle is likely strongly influenced by the magnesium–fluorine interactions rather than from a Mg-(η²-H–B) interaction because the Mg1–B1 distance is long (3.149(4) Å). However, the Mg–H–B angle in To^MMgH₂Bpin 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 tridentate coordination mode of HB(C₆F₅)₃ is similar in 1, MC(SiHMe₂)₃{HB(C₆F₅)₃}THF₂ (M = Ca, Yb),^{18d} and {Me-Nacnac^{Dipp}}CaHB(C₆F₅)₃.¹⁹ Cp*₂SmHB(C₆F₅)₃ contains two Sm–F interactions from the aryl rings and a possible interaction between Sm and the hydride.^{18b} 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*₂ZrH{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 $To^M MgMe$ and $B(C_6F_5)_3$ to give $To^M MgMeB(C_6F_5)_3$ (2), followed by reaction of this species with PhSiH₃ to give PhMeSiH₂ and **1** (Path **A**). In Path **B**, the reaction of $To^M MgMe$ and PhSiH₃ forms $To^M MgH$, which is trapped by $B(C_6F_5)_3$ to give **1**. Alternatively, PhSiH₃ and $B(C_6F_5)_3$ could interact to give a transient adduct [PhH₂-SiHB(C₆F₅)₃], and this intermediate reacts with $To^M MgMe$ to give the products (Path C). Methide abstraction by $B(C_6F_5)_3$ in Path **A** is well established,²⁸ supporting the possible intermediate $To^M MgMeB(C_6F_5)_3$. Furthermore, $Cp^*_2 ZrMe\{(\mu-Me) B(C_6F_5)_3\}$ is reported to undergo hydrogenation with H₂ to give



Fig. 1 Rendered thermal ellipsoid diagram of $To^M MgHB(C_6F_5)_3$ (1) plotted at 50% probability. The H1, bridging between Mg1 and B1, was located objectively in the difference Fourier map and was refined isotropically. Two molecules of toluene and the H atoms on To^M are not included in the depiction for clarity.

$$\begin{split} Cp*_2ZrH\{HB(C_6F_5)_3\},^{22,28} \text{ and } (C_5R_5)_2MMe\{(\mu\text{-}Me)B(C_6F_5)_3\} \ (M=Zr, Hf; C_5R_5=C_5H_5, C_5H_4Me, C_5Me_5) \ \text{and silanes react to give} \\ (C_5R_5)_2MH\{HB(C_6F_5)_3\}.^{29} \ \text{These reactions, however, may involve} \\ methyl-hydride exchange through the conversion of [M]H\{(\mu\text{-}Me)B(C_6F_5)_3\} \ \text{to } [M]Me\{(\mu\text{-}H)B(C_6F_5)_3\} \ \text{rather than direct} \\ hydrogenolysis of a M-Me-B bridge required for Path A. Path C \\ is supported by proposed silane-borane adducts in B(C_6F_5)_3- \\ catalyzed hydrosilylations with tertiary silanes, ^{5b} \ \text{and recently a} \\ tris(pentafluorophenyl)-boraindene \ \text{and triethylsilane adduct} \\ was isolated \ \text{and fully characterized.}^{30} \end{split}$$

Path **B** is immediately ruled out by the apparent reaction kinetics, which require forcing conditions to slowly generate $To^{M}MgH$ from PhSiH₃ and $To^{M}MgMe$. This reaction time and temperature contrasts the rapid formation of **1** from $To^{M}MgMe$ and PhSiH₃ in the presence of B(C₆F₅)₃. To test the feasibility of Path **A**, the proposed intermediate, $To^{M}MgMeB(C_6F_5)_3$ (2), was independently synthesized by addition of B(C₆F₅)₃ dissolved in pentane to a benzene solution containing $To^{M}MgMe$ (eqn (3)).



The product immediately precipitates giving analytically pure 2. Reactions in benzene- d_6 or methylene chloride- d_2 provide To^MMgMeB(C₆F₅)₃ as a partially soluble species that may be quickly characterized by solution-phase spectroscopy. However, once solvent is removed and To^MMgMeB(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 an ¹H-¹¹B HMBC experiment, the resonance assigned to the MeB(C₆F₅)₃ at 1.27 ppm correlated with a singlet ¹¹B NMR signal at -15.5 ppm. However as 2 stands in benzene d_6 , the signals for To^MMgMeB(C₆F₅)₃ decrease as the new species To^MMgC₆F₅ (3) and BMe₃ form. After 7 h,



Scheme 1 Possible pathways to $To^{M}MgHB(C_{6}F_{5})_{3}$ (1).

 $To^MMgMeB(C_6F_5)_3$ is still the major component, but it is completely consumed over 20 h. This transformation occurs more rapidly in methylene chloride- d_2 ($t_{1/2} = 1$ h).

Compound 3 is most conveniently prepared and isolated by the reaction of 1 equiv. of TO^MMgMe and 1 equiv. of $B(C_6F_5)_3$ in benzene- d_6 over 24 h, but also forms from the reaction of 0.3 equiv. of $B(C_6F_5)_3$ with TO^MMgMe (eqn (4)). Solid $TO^MMgC_6F_5$ 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 To^M ancillary ligand. Two peaks were observed in the ¹¹B NMR spectrum at 86.5 and -18.3 ppm assigned to BMe₃ and To^M, 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 ν_{CN} band in the infrared spectrum at 1594 cm⁻¹. These values are similar to those of crystallographically characterized To^MMgMe (¹⁵N NMR: -157 ppm; ν_{CN} : 1592 cm⁻¹).³² 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.³³

The reaction of *in situ* generated 2 and PhSiH₃ at room temperature in benzene- d_6 gives only starting materials after 30 min. Over *ca.* 24 h, To^MMgMeB(C₆F₅)₃ undergoes C₆F₅ transfer to the magnesium center, and PhSiH₃ remains unconsumed. Micromolar-scale reactions in methylene chloride- d_2 yield a mixture of To^MMgC₆F₅, 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 To^MMgHB(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- d_6 , 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-2*H*-pyran-2-one react with PhMeSiH₂ or BnMe₂SiH in the presence of **1**.

Table 1 1-catalyzed hydrosilylation of α,β -unsaturated esters^{*a*}

Reaction	mol% catalyst ^b	Time (h)	Isolated% yield
BnMe ₂ SiH OSiBnMe ₂ + CO ₂ Me OMe	1	0.5	99
$(H_2C=CH)Me_2SiH /= OSiMe_2 + OSiMe_2 + OMe + OMe$	1	0.5	92
$\begin{array}{c} Ph_2SiH_2 \\ + \\ CO_2Me \end{array} \xrightarrow{OSiHPh_2} \\ OMe \end{array}$	1	0.5	96
PhMeSiH ₂ OSiHMePh + CO ₂ Me OMe	1	7 ^c	97
$\begin{array}{c} \text{MePhSiH}_2 \\ + \\ + \\ CO_2C_4H_9 \end{array} \xrightarrow{OSiHMePh}_0 \\ \end{array}$	2.5	8	41
MePhSiH ₂ OSiHMePh + CO ₂ CH ₂ Ph OCH ₂ Ph	2.5	4	99
$ \overset{\text{PhMeSiH}_2}{+} \overset{\text{O}}{\longrightarrow} \overset{\text{OiHMePh}}{\overset{\text{O}}{\longrightarrow}} $	10	5	80
$ \overset{BnMe_2SiH}{\overset{+}{\longrightarrow}} \overset{O}{\overset{O}{\longrightarrow}} \overset{SiMe_2Bn}{\overset{O}{\longrightarrow}} $	1	0.5^d	83
$\begin{array}{c} \text{MePhSiH}_2 \\ + \\ 2 \\ \text{CO}_2 \text{Me} \end{array} \xrightarrow{\text{OMe}} 0^{\text{OMe}} 0^{\text{OMe}} \end{array}$	5	12 ^e	32

^{*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 To^MMgX compounds (X = Me, C_6F_5 , MeB(C_6F_5)₃, B(C_6F_5)₄) were investigated as catalysts for hydrosilylation of methyl methacrylate. A catalytic amount of To^MMgMe reacts instantaneously with methyl methacrylate and PhMeSiH₂ in benzene- d_6 to give insoluble materials likely resulting from polymerization. Even though some of the silane is consumed in this reaction, neutral To^MMgMe is not a viable hydrosilylation catalyst. Moreover, this further demonstrates that the silicon–oxygen bond formation is unlikely to involve σ -bond metathesis of silanes and a magnesium alkoxide.

In addition, ¹H NMR spectra of catalytic mixtures of methyl methacrylate, PhMeSiH₂ and 10 mol% To^MMgMeB(C₆F₅)₃ show only resonances assigned to methyl methacrylate and PhMeSiH₂, and signals associated with the hydrosilylation product were not detected. To^MMgMeB(C₆F₅)₃ is converted to To^MMgC₆F₅ under these conditions, and independent experiments show that To^MMgC₆F₅ is also not catalytically active. Hydridoborate-free magnesium compounds were tested next. The reaction of To^MMgMe and [Ph₃C][B(C₆F₅)₄] in benzene-*d*₆ at room temperature gives [To^MMg][B(C₆F₅)₄] as a precipitate after 15 min. However, this complex is not an ester hydrosilylation catalyst, and PhMeSiH₂ and methyl methacrylate are unchanged after 2 d at 80 °C in the presence of 10 mol% [To^MMg][B(C₆F₅)₄].

Alternatively, $B(C_6F_5)_3$ is known as a hydrosilylation catalyst that mediates 1,2-addition of tertiary silanes to esters.5b Free $B(C_6F_5)_3$ 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 α,β -unsaturated esters was probed. However upon treatment with 10 mol% B(C₆F₅)₃, BnMe₂SiH or (H₂C=CH)Me₂SiH and methacrylates provide mixtures containing the 1,4-addition product contaminated with at least 2 other species (see ESI[†] for spectra). The reactions of PhMeSiH₂ and methyl methacylate, as catalyzed by 1 or 1 mol% $B(C_6F_5)_3$, 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 formed as part of a mixture. The $B(C_6F_5)_3$ catalyzed reaction of PhMeSiH₂ and benzyl methacylate gives a complicated mixture. Interestingly, lower $B(C_6F_5)_3$ 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 $B(C_6F_5)_3$ when 1 is used as the catalyst. The $B(C_6F_5)_3$ -catalyzed reaction of Et_3SiH and methyl methacrylate, however, gives the silyl ketene acetal quantitatively, as does the same conversion catalyzed by 1. Thus, B(C₆F₅)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 ¹H and ¹¹B NMR spectroscopy. In the ¹H 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 BnMe₂SiH, and new, albeit small, oxazoline methyl and methylene signals were observed. The new oxazoline

signals are not sufficiently abundant to account for all of the previous To^M signals. Moreover, the quartet at 2.7 ppm for $HB(C_6F_5)_3$ was not visible after addition of excess organosilane, although a number of broad signals appeared in that region. The SiH of BnMe₂SiH appeared as a sharp multiplet and was apparently unchanged in the presence of 1. The broad doublet at -21 ppm in the ¹¹B NMR spectrum of 1 decreased in intensity, and a new signal at -24 ppm appeared. The new upfield ¹¹B NMR signal appeared in the region typical of $HB(C_6F_5)_3$, but H-B coupling was not resolved in the broad signal. At low temperature (190 K), the ¹¹B NMR signal at -24 was not detected, and the doublet at -21 is the major HB(C₆F₅)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 ¹¹B NMR signal at -18 ppm for To^M was sharp at 190 K, broad at 260 K, and again sharpened at 280 K. These data suggest that BnMe₂SiH and To^MMgHB(C₆F₅)₃ interact to disrupt the hydridoborate coordination to magnesium resulting in a dynamic system, but the $HB(C_6F_5)_3$ moiety remains intact. Moreover, ¹¹B NMR spectra acquired during catalytic conversions reveal signals at -18 and -24 ppm assigned to the boron centers in To^{M} and $HB(C_{6}F_{5})_{3}$. These two ¹¹B NMR signals were also observed after complete conversion of methyl methacrylate via hydrosilylation. ¹H 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_2SiH_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 Ph₂SiH₂ 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 PhMeSiH₂ 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 To^M-containing ¹H NMR resonances observed in the catalytic reaction mixture (in methylene chloride- d_2) were those assigned to To^MMgC₆F₅. On the basis of faster conversion of $To^{M}MgMeB(C_{6}F_{5})_{3}$ to $To^{M}MgC_{6}F_{5}$ in methylene chloride than in benzene, the lack of activity of To^MMgC₆F₅ as a hydrosilylation catalyst, and the lower catalytic activity in methylene chloride than in benzene, we suggest that catalyst deactivation occurs through C₆F₅ 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 note-worthy 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 $To^{M}MgMe$, $To^{M}MgHB(C_{6}F_{5})_{3}$ (1), $To^{M}MgMeB(C_{6}F_{5})_{3}$ (2), and $To^{M}MgC_{6}F_{5}$ (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, To^MMgMe, and B(C₆F₅)₃. The catalysis requires [HB(C₆F₅)₃]⁻, and no catalysis is observed with $[B(C_6F_5)_4]^-$ or with neutral magnesium alkyls To^MMgMe or To^MMgC₆F₅, providing additional support for the bifunctional role of **1** in this hydrosilvlation, as proposed in frustrated Lewis pair chemistry.³⁴ Moreover, $To^{M}MgMeB(C_{6}F_{5})_{3}$ is not a viable hydrosilylation precatalyst, in contrast to $To^{M}MgHB(C_{6}F_{5})_{3}$. 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 To^MMgC₆F₅. To^MMgC₆F₅ 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 $To^{M}MgC_{6}F_{5}$ 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-innocent counterion.

Experimental

$To^{M}MgHB(C_{6}F_{5})_{3}(1)$

A solution of To^{M} MgMe (0.134 g, 0.32 mmol) dissolved in benzene was added in a dropwise 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 To^MMgHB(C₆F₅)₃ (0.286 g, 0.31 mmol, 97.6%). Once isolated, To^MMgHB(C₆F₅)₃ is soluble in benzene or toluene, and X-ray quality single crystals were grown from a concentrated toluene solution at $-30 \,^{\circ}\text{C}$. ¹H NMR (600 MHz, benzene- d_6): δ 0.82 (s, 18H, CNC Me_2 CH₂O), 2.72 (br q, ¹ J_{BH} = 69 Hz, 1H,

MgHB(C₆F₅)₃), 3.30 (s, 6H, CNCMe₂CH₂O), 7.38 (m, ${}^{3}J_{HH} = 7.2$ Hz, 1H, para-C₆H₅), 7.56 (m, ${}^{3}J_{HH} = 7.6$ Hz, 2H, meta-C₆H₅), 8.25 (d, $^{3}J_{\rm HH} = 7.2$ Hz, 2H, ortho-C₆H₅). $^{13}C{^{1}H}$ NMR (150 MHz, THF- d_{8}): δ 27.35 (CNCMe2CH2O), 66.13 (CNCMe2CH2O), 79.28 (CNCMe2- CH_2O , 130.24 (para-C₆H₅), 133.26 (meta-C₆H₅), 134.79 (C₆F₅), 135.74 (C₆F₅), 136.81 (C₆F₅), 137.49 (ortho-C₆H₅), 138.41 (C₆F₅), 142 (br, ipso-C₆H₅), 147.78 (C₆F₅), 149.35 (C₆F₅), 191 (CNCMe₂-CH₂O). ¹¹B NMR (192 MHz, benzene- d_6): δ –18.2 (To^M), –21.1 (d, ${}^{1}J_{\text{HB}} = 69 \text{ Hz}, \text{ MgHB}(\text{C}_{6}\text{F}_{5})_{3}$). ${}^{19}\text{F} \text{ NMR} (544 \text{ MHz}, \text{ benzene-}d_{6}): \delta$ -134.2 (ortho-C₆F₅), -156.5 (para-C₆F₅), -161.4 (meta-C₆F₅). ¹⁵N NMR (60 MHz, benzene- d_6): δ –162. IR (KBr, cm⁻¹): ν 2976 (s), 2937 (s), 2372 (w br, BH), 1642 (m), 1579 (s), 1511 (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 C₃₉H₃₀B₂-F₁₅MgN₃O₃: 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. $C_{39}H_{30}B_2$ - $F_{15}MgN_3O_3(C_7H_8)_{2.5}, M = 1149.94$, triclinic, $a = 11.7916(18), b = 13.460(2), c = 18.239(3), \alpha = 86.434(3), \beta = 88.133(3), \gamma = 69.802(3), V = 2711.3(7) Å^3, T = 173 K, space group <math>\overline{P1}$, Z = 2, 15 346 reflections measured, 9197 unique ($R_{int} = 0.0303$). The final $R_1(F^2)$ and $wR_2(F^2)$ for $I > 2\sigma(I)$ were 0.0492 and 0.161.

Representative catalytic hydrosilylation

Reaction of Ph₂SiH₂ and methyl methacrylate. To^MMgHB(C₆- F_{5}_{3} (0.011 g, 0.012 mmol), methyl methacrylate (0.117 g, 1.17 mmol), and Ph₂SiH₂ (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- d_6): δ 1.64 (s, 3H, C=CM e_2), 1.69 (s, 3H, C=CMe₂), 3.29 (s, 3H, OMe), 5.84 (s, 1H, SiH), 7.17 (m, 6H, C₆H₅), 7.74 (m, 4H, C₆H₅). ${}^{13}C{}^{1}H$ NMR (150 MHz, benzene d_6 : δ 16.79 (C=CMe₂), 17.42 (C=CMe₂), 57.92 (OMe), 91.74 $(C=CMe_2)$, 130.47 (C_6H_5) , 131.12 (C_6H_5) , 134.16 $(ipso-C_6H_5)$, 135.49 (C₆H₅), 136.39 (C₆H₅), 150.93 (C=CMe₂). ²⁹Si (119 MHz, benzene- d_6) δ –14.5 (d, ${}^{1}J_{SiH}$ = 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 C₁₇H₂₀O₂Si: C, 71.79; H, 7.09. Found C, 71.61; H, 7.32.

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