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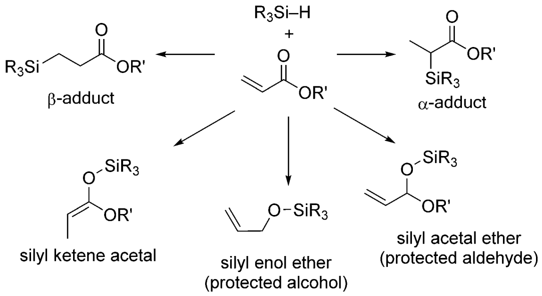
Cerium-Catalyzed Hydrosilylation of Acrylates to Give α-Silyl Esters

*Aradhana Pindwal, Smita Patnaik, William C. Everett, Arkady Ellern, Theresa L. Windus, and Aaron D. Sadow**

Abstract: *The homoleptic organocerium complex Ce{C(SiHMe$_2$)$_3$}$_3$ (**1**) reacts with B(C$_6$F$_5$)$_3$ to produce the zwitterionic bis(alkyl) hydridoborato Ce{C(SiHMe$_2$)$_3$}$_2$HB(C$_6$F$_5$)$_3$ (**2**). NMR and IR spectroscopy and X-ray crystallography indicate that each alkyl ligand contains two bridging Ce←H-Si interactions in both **1** and **2**. Compound **2** serves as a precatalyst for the hydrosilylation of acrylates to give α-silyl esters at room temperature with a turnover number of 2200.*

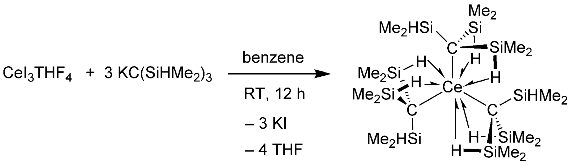
Catalytic hydrosilylation enables synthesis to impact wide ranging technological applications such as adhesives, electronics, and medical devices.[1] Conversions that give SiH-containing products are particularly valuable in many applications that employ, for example, oxidation or cross-coupling.[2] Late-transition-metal catalysts have been extensively studied in hydrosilylations,[3] and first row metal-based catalysts have recently attracted attention.[4] While early-metal complexes are active for SiH additions to olefins, these oxophilic systems typically have limited functional-group tolerance.[5] Carbonyl hydrosilylations catalyzed by reducible titanocene-based complexes notably overcome this limitation.[6] Alternatively, hypervalent silane intermediates are proposed in a calcium-catalyzed ketone hydrosilylation,[7] and a scandium hydridoborate catalyzes CO$_2$ reductive hydrosilylation.[8]

Hydrosilylation of acrylates may generate mixtures of silyl ketene acetals, silyl ethers, α- and β-adducts, and polyacrylates depending on the catalyst system (Scheme 1).[9] This selectivity challenge may be addressed by new reaction pathways and new catalysts. Recently, B(C$_6$F$_5$)$_3$ was discovered to catalyze the addition of tertiary silanes to α,β-unsaturated esters giving silyl ketene acetals which isomerize to α-silyl esters through a B(C$_6$F$_5$)$_3$-catalyzed rearrangement.[10] This system is best with substituted esters such as cinnamates, while acrylate and methacrylate conversions are not reported. In contrast, we observed that a zwitterionic magnesium hydridoborate complex produces silyl ketene acetals in hydrosilylations of methacrylates without subsequent rearrangement.[11] The hydridoborate functionality of this catalyst appeared to be important, and this idea motivated consideration of other [M]HB(C$_6$F$_5$)$_3$ complexes in catalytic hydrosilylations. Larger rare-earth centers might influence the selectivity in these hydrosilylations, and thus compounds of the type [Ln]HB(C$_6$F$_5$)$_3$ were targeted.



Scheme 1. Possible products from acrylate hydrosilylations. Polymerization (not shown) is also a common pathway with oxophilic early metal centers.

Hydride abstraction, by reaction of β-SiH main-group or rare-earth alkyl compounds and B(C$_6$F$_5$)$_3$, provides a straightforward route to [M]HB(C$_6$F$_5$)$_3$.[12] We therefore employed a suitable precursor, Ce{C(SiHMe$_2$)$_3$}$_3$ (**1**), synthesized by reaction of CeI$_3$THF$_4$ and 3 equivalents of KC(SiHMe$_2$)$_3$ [Eq. (1)].



1, 79%

(1)

The ^{1}H NMR spectrum of **1** (298 K) contained broad signals at $\delta = 5.0$ (9H, SiH) and 1.1 ppm (54H, SiMe) in the diamagnetic region, whereas a spectrum acquired at 206 K showed three sharp methyl resonances at $\delta = -11.6$, 9.3 and 10.6 ppm (18H each). In addition, peaks at $\delta = -19.7$ (6H) and 24.5 (3H) ppm were assigned to Ce←H-Si and terminal SiH groups, respectively. The IR spectrum of **1** contained bands at 2107 and 1829 cm^{-1}, assigned to ν_{SiH} of terminal and bridging groups. Crystallography revealed a trigonal-planar geometry for the CeC$_3$ core (Figure 1), long Ce–C distances [2.651(2), 2.659(2), and 2.672(2) Å], and short Ce–H and Ce–Si distances.[13] Trigonal coordination by the carbon centers contrasts the pyramidal structures and the much shorter Ce–C distances of Ce{CH(SiMe$_3$)$_2$}$_3$ [2.475(7) Å]. The latter tris(alkyl)cerium compound and Ce{N(SiMe$_3$)$_2$}$_3$ are notable for their pyramidal (non-VSEPR) geometries.[14]

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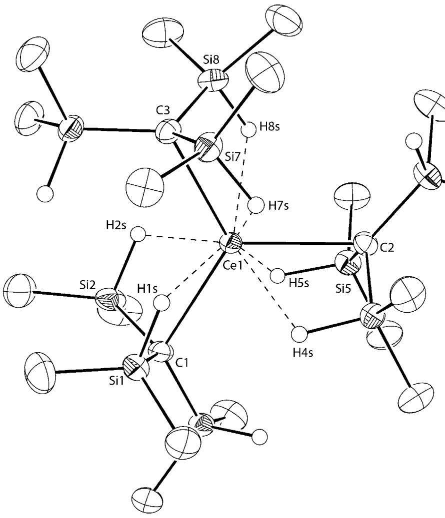


Figure 1. ORTEP diagram of Ce{C(SiHMe$_2$)$_3$}$_3$ (**1**) plotted at 50% probability. The H atoms included in the image are bonded to Si and were objectively located.

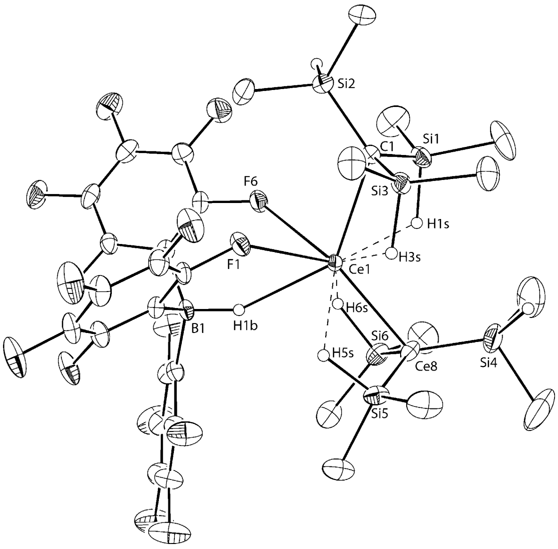
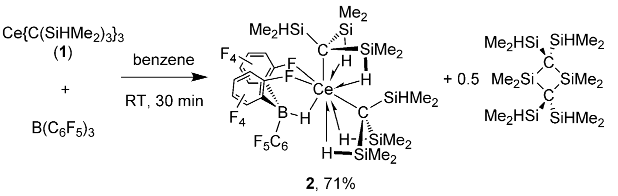


Figure 2. ORTEP diagram of Ce{C(SiHMe$_2$)$_3$}$_2$HB(C$_6$F$_5$)$_3$ (**2**) plotted at 35% probability. The H atoms included in the image are bonded to either Si or B and were objectively located.

Compound **1** and B(C$_6$F$_5$)$_3$ yield the desired zwitterionic Ce{C(SiHMe$_2$)$_3$}$_2$HB(C$_6$F$_5$)$_3$ (**2**) and 0.5 equivalents of the disilacyclobutane [(Me$_2$HSi)$_2$C-SiMe$_2$]$_2$ [Eq. (2)]. Formation of HB(C$_6$F$_5$)$_3$$^-$ rather than (Me$_2$HSi)$_3$C-B(C$_6$F$_5$)$_3$$^-$ suggests that the reaction proceeds by an intermolecular β-hydrogen abstraction.[12]



2, 71%

(2)

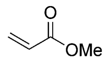
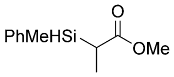
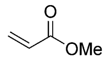
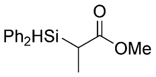
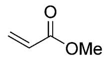
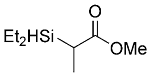
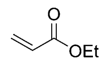
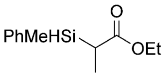
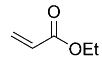
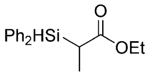
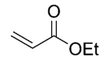
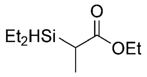
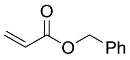
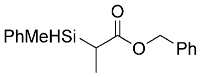
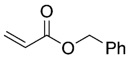
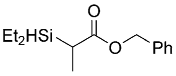
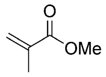
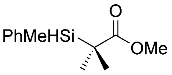
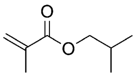
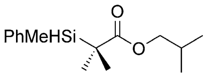
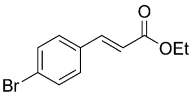
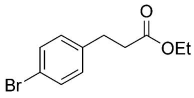
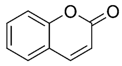
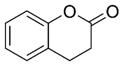
The ^{1}H NMR spectrum of **2** contained one signal at $\delta = 3.99$ ppm, and unlike **1**, this peak could not be resolved at low temperature. A broad signal at $\delta = -45$ ppm in the ^{11}B NMR spectrum indicated that the hydridoborate anion coordinated to the Ce center. Peaks at 2117 and 1795 cm^{-1} in the IR spectrum of **2** were assigned to the two Si-H groups in classical and bridging groups, respectively.

A single-crystal X-ray diffraction study of **2** reveals that two C(SiHMe$_2$)$_3$ groups coordinate to the Ce center in a fashion similar to that in **1** (Figure 2).[15] The third ligand is the tridentate HB(C$_6$F$_5$)$_3$. The sum of C-Ce-C and C-Ce-centroid angles is 360° (with the centroid defined as the average position of the H1b, F1, and F6 atoms), thus suggesting that the three ligands are arranged in a planar geometry as in **1**. The only other structurally characterized cerium hydridoborate compound reported in the Cambridge Crystallographic Data Centre is [{1,2,4-*t*Bu$_3$C$_5$H$_2$}$_2$Ce(H)BPh$_3$].[16] The Ce–C, Ce–Si, and Ce–H distances in **2** are shorter than in **1**. For example, the Ce1–C1 and Ce1–C2 distances are 2.582(3) and 2.615(2) Å, respectively. The Ce–Si distances (in the Ce↼H-Si structures) in **2** are (3.15 ± 0.01) Å, which is 0.05 Å shorter than the average Ce–Si distance in **1** [(3.20 ± 0.01) Å]. Interestingly, the average C$_{\text{central}}$–Si distance [(1.835 ± 0.003) Å] associated with the bridging Ce↼H-Si interactions is shorter than those associated with non-bridging SiHMe$_2$ groups [(1.855 ± 0.001) Å] for both **1** and **2**. Although the β-SiH-containing alkyls in both compounds do not react to spontaneously eliminate silene, the perturbation of distances over the whole ligand suggests there are whole-ligand consequences resulting from the agostic-like structures.

Compound **2** catalyzes the hydrosilylation of acrylates and methacrylates with secondary silanes to give α-silyl esters (Table 1). These results contrast the catalytic action of To$^{\text{M}}$MgHB(C$_6$F$_5$)$_3$ noted above, as this magnesium hydridoborate catalyst provides silyl ketene acetals in additions of both secondary and tertiary silanes to methacrylates, but not acrylates.[11] Neither divalent zwitterionic YbC(SiHMe$_2$)$_3$HB(C$_6$F$_5$)$_3$[12a] nor the trivalent neutral **1** provide either hydrosilylation product under related reaction conditions. To identify the thermodynamically favored silane product, the relative energies (ΔG) of six rotational isomers of the silyl ketene acetal Me(H)C=C(OSiHPh$_2$)OMe and twelve rotational isomers of the α-silyl ester Me(Ph$_2$HSi)HCCO$_2$Me were compared by computation, and the latter was found to be more stable by 9.5 to 12.2 kcal mol^{-1}.

The α-silyl ester products were unambiguously characterized by NMR and infrared spectroscopy. For example, the ^{1}H NMR spectrum of methyl α-diphenylsilylpropionate contained a doublet at $\delta = 4.94$ ppm, which was assigned to an SiH ($^3J_{\text{HH}} = 3.0$ Hz, $^1J_{\text{SiH}} = 205$ Hz). This SiH signal coupled to a quartet of doublets at $\delta = 2.73$ ppm ($^3J_{\text{HH}} = 7.2$ Hz), assigned to an α-methine, which coupled to the doublet at $\delta = 1.35$ ppm representing a methyl group. These signals correlated with the ^{29}Si NMR signal at $\delta = -9.33$ ppm in a ^{1}H-^{29}Si HMBC experiment. The ^{1}H NMR spin system and two-dimensional Hetcor experiment establish the presence of a Si–C bond. Moreover, correlation in a ^{1}H-^{13}C HMBC experiment was

Table 1: **2**-catalyzed hydrosilylation of acrylates and methacrylates.

Silane	Acrylate	Product[a]	Yield [%] (isolated)
$PhMeSiH_2$			84 (82)
Ph_2SiH_2			81 (80); 72[b] (72)[c]
Et_2SiH_2			82 (81)
$PhMeSiH_2$			88 (85)
Ph_2SiH_2			77 (74)
Et_2SiH_2			82 (79)
$PhMeSiH_2$			83 (81)
Et_2SiH_2			78 (77)
$PhMeSiH_2$			89 (88)[d]
$PhMeSiH_2$			82 (81)
Ph_2SiH_2			85 (82)
Et_2SiH_2			84 (81)

[a] Reaction conditions: 1 mol% **2**, $CHCl_3$, RT, 10 min. [b] [D$_6$]benzene. [c] Toluene. [d] 0 °C, 1 h.

observed between the carbonyl resonance at $\delta = 175.93$ ppm and the ^1H NMR signal of the α-methyl. Finally, a band in the infrared spectrum at 1725 cm^{-1} was consistent with the ν_{CO} of an ester.

Although the transformation occurs efficiently in chloroform, reactions performed in other solvents including benzene, toluene, and methylene chloride also afford α-silyl esters. In addition, the catalyst is extremely active, thus giving full conversion of methyl acrylate and $PhMeSiH_2$ with 0.05 mol% **2** within 5 minutes. During these reactions, the pale yellow reaction mixture turns colorless upon catalyst deactivation. The timing of this color change, the yield determined by NMR spectroscopy (from reactions that deactivate before complete conversion), and the catalyst/substrate ratio provides turnover number of 2200 and an estimate of the turnover frequency of 37 s^{-1} (133 200 h^{-1}).

Because $B(C_6F_5)_3$ catalyzes the addition of tertiary silanes to esters[17] and α,β-unsaturated esters to give 1,2-addition and α-silyl esters, respectively,[10] and small amounts of $B(C_6F_5)_3$ could be present in the reaction from dissociation of **2**, differentiation of **2** from $B(C_6F_5)_3$ required study of the latter's catalytic chemistry with secondary silanes. In contrast to the reactions of tertiary silanes, $PhMeSiH_2$ and methyl acrylate react in the presence of 1 mol% $B(C_6F_5)_3$ to give a complex mixture of unidentified species. Additional evidence distinguishing the chemistry of **2** versus $B(C_6F_5)_3$ involves the latter's proposed two-step pathway for formation of α-silyl esters by 1,4-addition to give silyl ketene acetals and subsequent retro-Brook rearrangement. This pathway was tested for **2**-catalyzed hydrosilylation by treatment of the proposed silyl ketene acetal intermediate $Me_2C{=}C(OSiPhMeH)OCH_2Ph$, synthesized by $To^MMgHB(C_6F_5)_3$-catalyzed hydrosilylation of benzyl methacrylate with phenylmethylsilane,[11] with either **2** or $B(C_6F_5)_3$. However, the α-silyl ester product $Me_2(PhMeHSi)CCO_2CH_2Ph$ was not detected in either reaction mixture after even 1 day.

Moreover, Ph_2SiH_2 and either methyl methacrylate or *trans*-4-ethyl bromocinnamate react in the presence of $B(C_6F_3)_3$ to give mixtures involving C−O cleavage. In contrast, the apparent hydrogenation products 3,4-dihydro-*trans*-4-ethyl bromocinnamate and dihydrocoumarin are obtained upon addition of either Ph_2SiH_2 or Et_2SiH_2 with the corresponding cinnamate ester or lactone in the presence of a catalytic amount of **2** (after chromatographic workup of the silyl ketene acetal). These results indicate that the catalytic hydrosilylation chemistry of **2** with secondary silanes is distinct from that of $B(C_6F_5)_3$ in terms of the identity of the active species and its mode of action, as well as the nature of accessible silane and α,β-unsaturated esters reaction partners.

Although the active catalytic species is not observed under the reaction conditions, alkane byproducts such as $HC(SiHMe_2)_3$ are not detected during the rapid conversions. From this outcome, we infer that tris(dimethylsilyl) groups remain bonded to the Ce center during and after catalysis. The relatively inert nature of the Ce-$C(SiHMe_2)_3$ coordination may be related to the two Ce↼H-Si interactions per ligand found in the precatalyst and its new homoleptic tris(alkyl) cerium precursor. As noted above, these interactions are characterized by low-energy SiH in IR spectra, fluxional processes frozen at low temperature in NMR studies, and distorted structures revealed by X-ray crystallography. Remarkably, the observed Si−C bond formation is not impeded by the oxophilic Ce and Si centers in the catalyst and reductant. Furthermore, the apparent ancillary nature of the alkyl groups suggest that other ancillary ligands may be accessible for controlling enantioselectivity in these addition reactions.

Acknowledgments

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cerium · homogeneous catalysis · hydrosilylation · structure elucidation · X-ray diffraction

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[1] a) B. Marciniec, *Comprehensive handbook on hydrosilylation*, Pergamon Press, Oxford, **1992**; b) B. Marciniec, *Hydrosilylation: a comprehensive review on recent advances*, Springer, Berlin, **2009**.

[2] a) G. R. Jones, Y. Landais, *Tetrahedron* **1996**, *52*, 7599 – 7662; b) S. E. Denmark, R. F. Sweis, *Acc. Chem. Res.* **2002**, *35*, 835 – 846; c) S. E. Denmark, C. S. Regens, *Acc. Chem. Res.* **2008**, *41*, 1486 – 1499.

[3] a) B. Marciniec, *Coord. Chem. Rev.* **2005**, *249*, 2374 – 2390; b) S. Park, M. Brookhart, *Organometallics* **2010**, *29*, 6057 – 6064; c) I. E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J.-P. Declercq, *Science* **2002**, *298*, 204 – 206; d) S. B. Duckett, R. N. Perutz, *Organometallics* **1992**, *11*, 90 – 98; e) A. J. Chalk, J. F. Harrod, *J. Am. Chem. Soc.* **1965**, *87*, 16 – 21.

[4] a) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, *Science* **2012**, *335*, 567 – 570; b) A. J. Ruddy, C. M. Kelly, S. M. Crawford, C. A. Wheaton, O. L. Sydora, B. L. Small, M. Stradiotto, L. Turculet, *Organometallics* **2013**, *32*, 5581 – 5588; c) R. J. Trovitch, *Synlett* **2014**, 1638 – 1642; d) A. Rit, A. Zanardi, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2014**, *53*, 13273 – 13277; *Angew. Chem.* **2014**, *126*, 13489 – 13493.

[5] a) T. I. Gountchev, T. D. Tilley, *Organometallics* **1999**, *18*, 5661 – 5667; b) F. Buch, J. Brettar, S. Harder, *Angew. Chem. Int. Ed.* **2006**, *45*, 2741 – 2745; *Angew. Chem.* **2006**, *118*, 2807 – 2811; c) V. Leich, T. P. Spaniol, L. Maron, J. Okuda, *Chem. Commun.* **2014**, *50*, 2311 – 2314; d) P.-F. Fu, L. Brard, Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1995**, *117*, 7157 – 7168.

[6] M. B. Carter, B. Schiott, A. Gutierrez, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 11667 – 11670.

[7] J. Spielmann, S. Harder, *Eur. J. Inorg. Chem.* **2008**, 1480 – 1486.

[8] F. A. LeBlanc, W. E. Piers, M. Parvez, *Angew. Chem. Int. Ed.* **2014**, *53*, 789 – 792; *Angew. Chem.* **2014**, *126*, 808 – 811.

[9] a) K. Takeshita, Y. Seki, K. Kawamoto, S. Murai, N. Sonoda, *J. Org. Chem.* **1987**, *52*, 4864 – 4868; b) E. Yoshii, Y. Kobayashi, T. Koizumi, T. Oribe, *Chem. Pharm. Bull.* **1974**, *22*, 2767 – 2769; c) S. A. Bruno (duPont), US 4785126A, **1988**; d) S. A. Bruno (duPont), US5332852A, **1994**.

[10] Y. Kim, S. Chang, *Angew. Chem. Int. Ed.* **2016**, *55*, 218 – 222; *Angew. Chem.* **2016**, *128*, 226 – 230.

[11] N. L. Lampland, A. Pindwal, S. R. Neal, S. Schlauderaff, A. Ellern, A. D. Sadow, *Chem. Sci.* **2015**, *6*, 6901 – 6907.

[12] a) K. Yan, G. Schoendorff, B. M. Upton, A. Ellern, T. L. Windus, A. D. Sadow, *Organometallics* **2013**, *32*, 1300 – 1316; b) K. Yan, B. M. Upton, A. Ellern, A. D. Sadow, *J. Am. Chem. Soc.* **2009**, *131*, 15110 – 15111.

[13] $C_{21}H_{63}CeSi_9$: M_r 708.64; $P\bar{1}$; $a = 11.504(1)$, $b = 11.542(1)$, $c = 16.704(2)$, $\alpha = 100.352(2)$, $\beta = 98.519(2)$, $\gamma = 114.706(2)$, $V = 1919.3(3)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.226$, $\mu = 1.477$, $\lambda = 0.7173$ Å; 173 K; reflect. measured: 30348, independent: 9901; R_{int} 0.0365, R 0.0303, wR 0.0661. CCDC 1507399 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[14] a) A. G. Avent, C. F. Caro, P. B. Hitchcock, M. F. Lappert, Z. N. Li, X. H. Wei, *J. Chem. Soc. Dalton Trans.* **2004**, 1567 – 1577; b) T. Fjeldberg, R. A. Andersen, *J. Mol. Struct.* **1985**, *129*, 93 – 105.

[15] $C_{32}H_{43}BCeF_{15}Si_6$, M_r 1032.13; $P\bar{1}$; $a = 11.477(2)$, $b = 13.408(2)$, $c = 15.194(2)$, $\alpha = 82.826(2)$, $\beta = 76.552(2)$, $\gamma = 75.376(2)$, $V = 2194.9(6)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.563$, $\mu = 1.288$, $\lambda = 0.7173$ Å; 173 K; reflect. measured: 29404, independent: 8949; R_{int} 0.0322, R 0.0286, wR 0.0661. CCDC 1507398 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[16] E. L. Werkema, R. A. Andersen, A. Yahia, L. Maron, O. Eisenstein, *Organometallics* **2009**, *28*, 3173 – 3185.

[17] D. J. Parks, W. E. Piers, *J. Am. Chem. Soc.* **1996**, *118*, 9440 – 9441.

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Communications

Hydrosilylation

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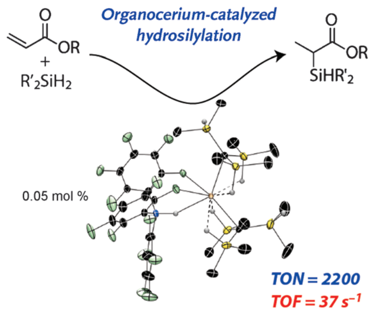
Cerium-Catalyzed Hydrosilylation of Acrylates to Give α-Silyl Esters



Zwitter: A zwitterionic organocerium hydridoborato complex is highly active for the catalytic addition of acrylates and secondary silanes to give α-silyl esters. The ester functionality is not reduced under these reaction conditions despite the oxophilicity of the cerium catalyst. NMR and IR spectroscopy and X-ray crystallography indicate that each alkyl ligand forms two bridging Ce←H-Si interactions. TOF = turnover frequency, and TON = turnover number.