Lewis Pairs

Elusive Silane–Alane Complex [Si–H…Al]: Isolation, Characterization, and Multifaceted Frustrated Lewis Pair Type Catalysis**

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Abstract: The super acidity of the unsolvated $Al(C_6F_5)_3$ enabled isolation of the elusive silane–alane complex [Si– H···Al], which was structurally characterized by spectroscopic and X-ray diffraction methods. The Janus-like nature of this adduct, coupled with strong silane activation, effects multifaceted frustrated-Lewis-pair-type catalysis. When compared with the silane–borane system, the silane–alane system offers unique features or clear advantages in the four types of catalytic transformations examined in this study, including: ligand redistribution of tertiary silanes into secondary and quaternary silanes, polymerization of conjugated polar alkenes, hydrosilylation of unactivated alkenes, and hydrodefluorination of fluoroalkanes.

ighly Lewis-acidic and chemically robust organoboranes, especially $B(C_6F_5)_3$, have proven their broad applications in catalysis for small-molecule transformation and macromolecular synthesis.^[1] Such boranes continue to receive much attention because of their recent success in frustrated Lewis pair (FLP) chemistry which was pioneered by Stephan and Erker.^[2] While earlier contributions emphasized the importance of orthogonal reactivity derived from sterically induced separation of the Lewis pairs, accumulated evidence suggests that electronically FLPs possessing a weak Lewis acid-Lewis base (LA-LB) bond can be effective as well.^[3] Indeed, a prototype can be traced back to 1996 when Parks and Piers^[4] reported the first example of the $B(C_6F_5)_3$ -catalyzed hydrosilvlation of C=O bonds with hydrosilanes by unusual Si-H bond activation rather than intuitive carbonyl activation.^[5] Such a reaction was proposed to proceed through the cleavage of the Si-H bond with a dissociating carbonylborane Lewis pair (i.e., FLP-type bond activation). Oestreich and co-workers further supported this hypothesis by proving the inversion of the chirality at Si of a chiral probe after the hydrosilylation step.^[6] Since then, much effort has been invested in the direct spectroscopic and structural characterizations of the proposed, yet elusive, silane-borane complex containing the crucial [Si-H...B] moiety, but the attempts with B(C₆F₅)₃ proved futile and only indirect spectroscopic clues pointing to this intermediate could be obtained. Almost 20 years after the original report, Piers and co-workers successfully isolated and structurally characterized the silane–borane adduct derived from Et₃SiH and 1,2,3-tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene, a perfluoroborole sophisticatedly tailored for higher Lewis acidity than B(C₆F₅)₃.^[7]

As compared with $B(C_6F_5)_3$, the congener alane $Al(C_6F_5)_3$ is a stronger LA^[8] as gauged, for example, by double activation of bridged metallocene dimethyls,^[9] fluoride ion affinity,^[10] stable adduct formation with weakly basic arenes,^[11] as well as by DFT calculations on the gas-phase Lewis acidity^[12] and the enthalpy of ion-pair formation in solution for the methide abstraction reaction.^[13] Despite its high Lewis acidity, the application of $Al(C_6F_5)_3$ in the area of FLP studies is much less explored.^[14] In 2002, we reported cleavage of a toluene C-H bond with the Al(C_6F_5)₃ and 2,6di-tert-butylpyridine pair.^[15] Subsequently, we and others have showed that the Lewis pair polymerization^[16] is typically much more effective with the alane than with the borane.^[17] Moreover, Krossing and co-workers noted that the analogous aluminum super LA [Al{OC(CF₃)₃]₃] forms stable adducts with PhF and Me₃SiF.^[10] Interestingly, the fluorosilane adduct [Me₃Si-F···Al{OC(CF₃)₃]₃] was viewed as a Janus-like bifunctional LA with a soft electrophilic Si site and a hard electrophilic Al site for different substrates.^[18]

We hypothesized that, as a result of the demonstrated superior Lewis acidity and activity in many catalytic reactions by the alane compared to the borane, $Al(C_6F_5)_3$ could lead to the isolable and characterizable simple silane–alane complex $[R_3Si-H\cdots Al(C_6F_5)_3]$, and thus uncover its potentially unique catalytic utilities. In this context, we communicate herein the isolation and structural characterization of silane–alane complexes with a hydride or fluoride bridge. Excitingly, the silane–alane complex effectively catalyzes (or is involved in) a variety of transformations, including four different types of catalytic reactions: ligand redistribution of silanes, polymerization of polar alkenes, hydrosilylation of unactivated alkenes, and hydrodefluorination of fluoroalkanes.

Mixing of Et₃SiH with $[Al(C_6F_5)_3(toluene)_{0.5}]^{[19]}$ failed to generate the silane–alane adduct because arenes such as toluene are stronger donors than Et₃SiH, as shown for the isoelectronic silylium ions.^[20] Hence, it is crucial to use the unsolvated $Al(C_6F_5)_3^{[19]}$ and avoid donor or even aromatic solvents for the generation of the desired silane–alane complex. Accordingly, addition of a slight excess of Et₃SiH to a suspension of the unsolvated $Al(C_6F_5)_3$ in hexanes led to immediate dissolution of $Al(C_6F_5)_3$ (the alane itself is

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Scheme 1. Synthesis of Janus-like silane–alane complexes and their multifaceted catalytic reactions with diverse substrates.

insoluble in hexanes). Colorless crystals of the corresponding hydrosilane–alane complex, [Et₃Si–H···Al(C₆F₅)₃], were developed at -30 °C overnight. In contrast, the analogous fluorosilane–alane adduct [Et₃Si–F···Al(C₆F₅)₃] was isolated directly using Et₃SiF and [Al(C₆F₅)₃(toluene)_{0.5}] (Scheme 1). These results indicate the donor strength of the four weak bases (reagents or solvents) involved here follows this trend: Et₃SiF > C₇H₈ > Et₃SiH > C₆H₁₄.

The formation of the desired adduct $[Et_3Si-H\cdots Al(C_6F_5)_3]$ was first revealed by a multinuclear NMR study. In aromatic solvents such as C_6D_6 and C_6D_5Br , this adduct exhibited ¹H and ¹⁹F NMR signals essentially identical to those of the free silane and arene-coordinated alane, and they result from the displacement of the complexed silane by the more coordinating arene. Nonetheless, the 1:1 composition of the complex was quantified using C_6F_5H as an internal reference to correlate the ¹H and ¹⁹F NMR integration values (see Figure S4 in the Supporting Information). More conclusive evidence for the [Si-H-A1] moiety in solution was derived



Figure 1. Comparison of ¹H NMR spectra of Et_3SiH (top), $Et_3SiH/AI(C_6F_5)_3$ (2:1, middle), and the $[Et_3SiH-AI(C_6F_5)_3]$ adduct (bottom).

from NMR spectra in C₆D₁₂ as a noncoordinating solvent (Figure 1). The ¹H resonance of Si*H* appears at $\delta = 3.38$ ppm with concomitant ¹*J*_{Si-H} = 104 Hz (c.f., free Et₃Si*H*: $\delta = 3.71$ ppm, ¹*J*_{Si-H} = 180 Hz), thus indicating that the Si–H bond is activated by coordination to the alane. The free and coordinated silanes established a rapid equilibrium in solution as addition of another equivalent of Et₃SiH shifted the one

and only Si*H* signal to $\delta = 3.51$ ppm (¹J_{Si-H} = 132 Hz). In contrast to [Si-H···Al], the [Si-F···Al] interaction is detectable even in C₆D₅Br by ¹⁹F NMR spectroscopy (see Figure S7 in the Supporting Information). In addition to the signals originating from aromatic fluorines, there is a broad signal at $\delta = -163.1$ ppm which is assigned to the bridging fluoride ($\delta = -175.0$ ppm for free Et₃SiF). The ²⁹Si resonance downfield shifted from $\delta = 31.6$ ppm for free Et₃SiF to $\delta = 77.4$ ppm for the adduct, and is consistent with the reduction of the electron density at the Si center.

Two pieces of solid-state structural information offer unambiguous insight into the σ -bonded [Si–H···Al] complex. FT-IR spectroscopy measurements performed on the crystals of the adduct revealed a characteristic, asymmetric stretching frequency at 1996 cm⁻¹ (see Figure S5 in the Supporting Information), and is consistent with previous studies for a typical v_{asym} (Si-H) activated by silylium and borole LAs.^[7,21]



Figure 2. X-ray structure (50% thermal displacement) of [Et₃Si-H…Al-(C₆F₅)₃], the highlighted geometry at Al, and intermolecular Al…F interactions in the crystal lattice. Hydrogen atoms except the bridging hydrogen omitted for clarity.

The structure of the adduct was also confirmed by X-ray diffraction analysis (Figure 2). The bridging H atom was clearly found on the difference density map and refined without any restraint or constraint, thus featuring a Si-H distance of 1.475(16) Å, an Al···H distance of 1.865(16) Å, and a Si-H. Al angle of 174.0(11)°. While the Si-H bond length is slightly shorter than that of the silane-borole adduct [1.51(2) Å],^[7] the Al···H distance is comparable to that of $\{(\mu-H)[Al(C_6F_5)_3]_2\}^-$ (1.818 Å).^[14e] Given the short Al···H distance, it was expected that this Si-H…Al interaction would be sufficient enough to render considerable pyramidalization of the Al center. However, the $\Sigma_{\text{C-Al-C}}$ of 356.5° is deviated from a perfect trigonal geometry by only 3.5°, which stands in contrast to the pseudo-tetrahedral geometry of the Al center observed in $\{(\mu-H)[Al(C_6F_5)_3]_2\}^{-.[14e]}$ A closer examination of the structure revealed the presence of a secondary interaction, trans to the coordinated Et₃SiH, between the Al center and a meta F atom of an adjacent molecule (Figure 2). This interaction is rather weak, given the long Al1...F2' distance of



2.6792(9) Å and the unaffected F2'-C3' bond length of 1.3489(15) Å. As a result, the geometry at Al is best described as a distorted trigonal bipyramid. This intermolecular Al-F interaction also leads to an extended structure featuring a herringbone pattern for the Si-H···Al···F motif (Figure 2). It is worth noting that such a secondary intermolecular interaction is also present in $PhF \cdot Al(OC(CF_3)_3)_3$ (Al. F: 2.770(8) Å),^[10] but it is absent in $\{(\mu-H)[Al(C_6F_5)_3]_2\}^{-[14e]}$ and $[Me_3SiF \cdot Al\{OC(CF_3)_3\}_3]$.^[18] In the present case, Et₃SiH, as a weak LB, is not electron-donating enough to effectively stabilize the unsolvated $Al(C_6F_5)_3$ so it seeks for additional stabilization by interacting with a fluorine atom from a second molecule. In comparison, the geometry at the Al center in the F-bridged complex, $[Et_3Si-F\cdotsAl(C_6F_5)_3]$, features more pronounced pyramidalization, with a Si-F distance of 1.725(2) Å, an Al…F contact of 1.841(2) Å, and a Σ_{C-Al-C} of 348.1°, all of which are averaged from three independent molecules (see Figure S22 in the Supporting Information).

The utility of the present silane–alane complex has been examined for applications in four types of catalytic reactions. First, strong activation of silanes by the super-Lewis-acidic alane promotes silane ligand redistribution,^[22] thus converting



Scheme 2. Silane ligand redistribution through silane-alane complexation.

tertiary silanes into secondary and quaternary silanes (Scheme 2; see Table S1 in the Supporting Information). Thus, heating a solution of Et₃SiH in ortho-dichlorobenzene at 80 °C for 4 hours with 5 mol% of $Al(C_6F_5)_3$ led to 96% conversion into Et₄Si and Et₂SiH₂. In the case of PhSiMe₂H, the reaction proceeded even at 25°C in C₆D₅Br to produce Ph₂SiMe₂ and Me₂SiH₂ (95% in 3 h). Noteworthy is that $B(C_6F_5)_3$ was essentially ineffective to promote this transformation under the same reaction conditions (3% in 12 h), although it can mediate other types of reactions.^[23] The mechanistic scenario is proposed to be in line with that reported for silvlium-mediated ligand exchange between the cationic and neutral Si centers.^[24] In the present case, silane activation through silane-alane complexation generates a cationic Si center, which interacts with an incoming silane molecule via intermediate A (Scheme 2), and subsequent hydride-aryl (or alkyl) ligand exchange at two Si centers (A to B) yields the quaternary silane and gaseous secondary silane.

Second, tandem catalysis in both FLP silane activation and non-FLP carbonyl activation by $Al(C_6F_5)_3$ enables effective polymerization of conjugated polar alkenes such as methyl methacrylate (MMA) by in situ hydrosilylation of monomer (Scheme 3). In this hypothesized tandem catalytic



Scheme 3. Tandem catalysis in polymerization of MMA by the silane/ alane system: FLP and non-FLP catalysis working in concert.

sequence, the alane plays a dual role in catalyzing hydrosilvlation of MMA to produce a silvl ketene acetal (SKA) initiator, Me₂C=C(OMe)OSiR₃, through FLP-type silane activation, and subsequent chain propagation involving nucleophilic attack of the SKA onto the activated monomer through monomer carbonyl activation.^[25] To test this hypothesis, we first examined the ability of $Al(C_6F_5)_3$ to catalyze hydrosilylation of C=O bonds. As anticipated, $Al(C_6F_5)_3$ exhibited much lower reactivity for hydrosilylation of ketones than $B(C_6F_5)_3$ (see Table S2 in the Supporting Information), which is attributed to the high oxophilicity and Lewis acidity of $Al(C_6F_5)_3$, both of which impair the dissociation of the ketone-alane adduct to form the silane-alane intermediate responsible for hydrosilylation. In fact, this finding provides further evidence, derived from the varied Lewis acidity and oxophilicity of the LA, to support the aforementioned FLPtype silane activation mechanism proposed by Piers and coworkers.^[4-7] Polymerization of the reactive *n*-butyl acrylate by in situ hydrosilylation of monomer catalyzed by $B(C_6F_5)_3$ was reported recently by Kakuchi and co-workers,^[26] but in our hands the borane/silane system exhibited no polymerization activity towards the less reactive and more sterically hindered MMA (in a MMA/Et₃SiH/B(C₆F₅)₃ ratio of 400/1/1 in C_6H_5F or 30/1/0.01 in CH_2Cl_2 at RT for 24 h). The reason is that, although $B(C_6F_5)_3$ can effectively catalyze 1,4-hydrosilvlation of the monomer, it provides insufficient activation of the monomer for the polymerization step. In contrast, the alane/silane system effectively polymerizes MMA (see Table S4 in the Supporting Information), thanks to its capacity to perform required tandem catalysis for this polymerization. Thus, with a loading of 2.0 or 1.0 mol% $Al(C_6F_5)_3$ (toluene)_{0.5}/PhSiMe₂H, MMA was quantitatively polymerized after 4 hours (or 16 h) into PMMA with $M_n =$ 1.14×10^4 g mol⁻¹ (or 1.45×10^4 g mol⁻¹). When the unsolvated $Al(C_6F_5)_3$ was employed, a 1.6-fold polymerization rate enhancement was observed.

Third, with the super Lewis acidity of $Al(C_6F_5)_3$, the silane/alane system exhibits a high activity towards hydrosilylation of weak basic substrates such as unactivated alkenes (Scheme 4 and see Table S3 in the Supporting Information). With the FLP-type silane activation in mind, we envisioned



Scheme 4. Highly effective hydrosilylation of the unactivated alkene by $[Et_3SiH\cdot Al(C_6F_5)_3].$

that switching the carbonyls to weaker basic or nucleophilic substrates such as alkenes would diminish the alane-substrate binding, thereby facilitating the silane activation. Hydrosilylation of unactivated alkenes by borane- or alane-based LA catalysts still remains rare,^[27] but the related organofluorophosphonium Lewis acid $[FP(C_6F_5)_3]^{+[28]}$ catalyzes efficient hydrosilylation of olefins and alkynes.^[29] Excitingly, the silane/alane complex $[Et_3SiH \cdot Al(C_6F_5)_3]$ (5.0 mol%) was shown to be very effective for hydrosilylation of 1-hexene, thus achieving 98% conversion into the corresponding alkyl silane in 0.5 hours and giving a turnover frequency (TOF) of 39 h⁻¹. In comparison, the activity of $[Al(C_6F_5)_3(toluene)_{0.5}]$ was considerably lower, with $TOF = 19 h^{-1}$. In particular, $B(C_6F_5)_3$, a far better catalyst for hydrosilylation of carbonyl substrates, is now a far inferior catalyst for alkene substrates such as 1-hexene with $TOF = 1.5 h^{-1}$, thus representing a 26fold rate enhancement when comparing $Al(C_6F_5)_3$ with $B(C_6F_5)_3$.

Fourth, $[Et_3SiH \cdot Al(C_6F_5)_3]$ mediates rapid hydrodefluorination^[30] of Ph₃CF, thus reaching a TOF of 600 h⁻¹ (see the



Scheme 5. Proposed mechanism for hydrodefluorination of Ph_3CF by [Et₃SiH·Al(C_6F_5)₃] with all the elemental steps being independently verified.

Supporting Information). A closer look at the possible mechanism (Scheme 5) revealed that the hydride-bridged complex serves as the precatalyst and the fluoride-bridged species as the true catalyst, based on the following observations: 1) reaction of $[Et_3SiH \cdot Al(C_6F_5)_3]$ with equimolar amounts of Ph₃CF readily yielded $[Et_3SiF \cdot Al(C_6F_5)_3]$ with concomitant formation of Ph₃CH (see Figure S17 in the Supporting Information); 2) Et₃SiF forms a more stable and readily detectable adduct with the alane in C₆D₅Br, while Et₃SiH is replaced by the arene for coordination to the alane and more importantly, there were no changes in NMR chemical shifts upon mixing a stoichiometric amount of $[Et_3SiF Al(C_6F_5)_3]$ with Et_3SiH (see Figure S18 in the Supporting Information); 3) $[Et_3SiF \cdot Al(C_6F_5)_3]$ reacts with Ph₃CF to produce free Et₃SiF and $[Ph_3C]^+[FAl(C_6F_5)_3]^-$ (see Figure S19 in the Supporting Information); and 4) the trityl salt further abstracts a hydride from Et₃SiH (see Figure S19), thereby closing the catalytic cycle by regenerating the catalyst $[Et_3SiF \cdot Al(C_6F_5)_3].$

In conclusion, the super acidity of the unsolvated Al-(C_6F_5)₃ enabled isolation and structural characterization of the elusive silane–alane complex [Et₃SiH·Al(C_6F_5)₃]. The Janus-like nature of this adduct, coupled with strong silane activation through such complexation, effects multifaceted FLP or non-FLP-type catalysis which, when compared with silane activation by the congener borane B(C_6F_5)₃, offers unique features or clear advantages in the four types of catalytic transformations examined in this study. First, strong activation of silanes by the alane promotes the ligand redistribution of tertiary silanes into secondary and quaternary silanes, while borane promotes no such transformation. Second, tandem catalysis in both FLP silane activation and non-FLP carbonyl activation by $Al(C_6F_5)_3$ enables effective polymerization of polar alkene MMA by in situ hydrosilylation of monomer, while the borane accomplishes only the first step of the process and thus yields no polymer products under low catalyst loading conditions. Third, in catalytic hydrosilvlation of the unactivated alkene 1-hexene, the silane/alane system shows a 26-fold rate enhancement over the silane/ borane system. Fourth, in hydrodefluorination of fluoroalkanes, the silane-alane complex $[Et_3SiH \cdot Al(C_6F_5)_3]$ is not only highly effective, it also offers mechanistic insight into each elemental step of the catalytic cycle where all the intermediates involved can be independently verified through stoichiometric control reactions. Efforts on elucidating detailed mechanisms for the aforementioned catalytic processes enabled by the silane-alane complex and extending substrate scope are currently underway.

Keywords: alanes \cdot Lewis acids \cdot silanes \cdot structure elucidation \cdot X-ray diffraction

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- Selected reviews: a) W. E. Piers, Adv. Organomet. Chem. 2005, 52, 1-76; b) E. Y.-X. Chen, T. J. Marks, Chem. Rev. 2000, 100, 1391-1434; c) Lewis acids in organic synthesis (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, 2000; d) W. E. Piers, T. Chivers, Chem. Soc. Rev. 1997, 26, 345-354.
- [2] Selected reviews: a) D. W. Stephan, Acc. Chem. Res. 2015, 48, 306-316; b) D. W. Stephan, G. Erker, Chem. Sci. 2014, 5, 2625-2641; c) "Frustrated Lewis Pairs I & II": Topics in Current Chemistry, Vols. 332 & 334 (Eds.: D. W. Stephan, G. Erker), Springer, New York, 2013; d) D. W. Stephan, G. Erker, Angew. Chem. Int. Ed. 2010, 49, 46-76; Angew. Chem. 2010, 122, 50-81.
- [3] S. J. Geier, D. W. Stephan, J. Am. Chem. Soc. 2009, 131, 3476– 3477.
- [4] D. J. Parks, W. E. Piers, J. Am. Chem. Soc. 1996, 118, 9440-9441.
- [5] a) W. E. Piers, A. J. V. Marwitz, L. G. Mercier, *Inorg. Chem.* 2011, 50, 12252–12262; b) D. J. Parks, J. M. Blackwell, W. E. Piers, *J. Org. Chem.* 2000, 65, 3090–3098.
- [6] a) M. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* 2015, 44, 2202–2220; b) S. Rendler, M. Oestreich, *Angew. Chem. Int. Ed.* 2008, 47, 5997–6000; *Angew. Chem.* 2008, 120, 6086–6089.
- [7] A. Y. Houghton, J. Hurmalainen, A. Mansikkamaki, W. E. Piers, H. M. Tuononen, *Nat. Chem.* 2014, 6, 983–988.
- [8] A review: E. Y.-X. Chen, e-Encycl. Reag. Org. Syn. 2012, DOI: 10.1002/047084289X.rn01382.
- [9] E. Y.-X. Chen, W. J. Kruper, G. Roof, D. R. Wilson, J. Am. Chem. Soc. 2001, 123, 745-746.
- [10] L. O. Müller, D. Himmel, J. Stauffer, G. Steinfeld, J. Slattery, G. Santiso-Quinones, V. Brecht, I. Krossing, *Angew. Chem. Int. Ed.* 2008, 47, 7659–7663; *Angew. Chem.* 2008, 120, 7772–7776.
- [11] G. S. Hair, A. H. Cowley, R. A. Jones, B. G. McBurnett, A. Voigt, J. Am. Chem. Soc. 1999, 121, 4922–4923.
- [12] A. Y. Timoshkin, G. Frenking, Organometallics 2008, 27, 371– 380.
- [13] K. Vanka, M. S. W. Chan, C. C. Pye, T. Ziegler, *Organometallics* 2000, 19, 1841–1849.

Angewandte Communications

- [14] a) G. Ménard, D. W. Stephan, Dalton Trans. 2013, 42, 5447–5453; b) G. Ménard, J. A. Hatnean, H. J. Cowley, A. J. Lough, J. M. Rawson, D. W. Stephan, J. Am. Chem. Soc. 2013, 135, 6446–6449; c) G. Ménard, T. M. Gilbert, J. A. Hatnean, A. Kraft, I. Krossing, D. W. Stephan, Organometallics 2013, 32, 4416–4422; d) G. Ménard, D. W. Stephan, Angew. Chem. Int. Ed. 2012, 51, 4409–4412; Angew. Chem. 2012, 124, 4485–4488; e) G. Ménard, D. W. Stephan, Angew. Chem. Int. Ed. 2012, 51, 8272–8275; Angew. Chem. 2012, 124, 8397–8400; f) M. A. Dureen, C. C. Brown, D. W. Stephan, Organometallics 2010, 29, 6594–6607; g) M. A. Dureen, D. W. Stephan, J. Am. Chem. Soc. 2009, 131, 8396–8397.
- [15] D. Chakraborty, E. Y.-X. Chen, *Macromolecules* 2002, 35, 13– 15.

[16] A review: E. Y.-X. Chen, Top. Curr. Chem. 2013, 334, 239-260.

- [17] a) J. Chen, E. Y.-X. Chen, Isr. J. Chem. 2015, 55, 216–225;
 b) T. Q. Xu, E. Y.-X. Chen, J. Am. Chem. Soc. 2014, 136, 1774–1777;
 c) Y. B. Jia, W. M. Ren, S. J. Liu, T. Q. Xu, Y. B. Wang, X. B. Lu, ACS Macro Lett. 2014, 3, 896–899;
 d) J. H. He, Y. T. Zhang, L. Falivene, L. Caporaso, L. Cavallo, E. Y.-X. Chen, Macromolecules 2014, 47, 7765–7774;
 e) J. H. He, Y. T. Zhang, G. M. Miyake, M. G. John, L. Falivene, L. Caporaso, L. Cavallo, E. Y.-X. Chen, Dalton Trans. 2012, 41, 9119–9134;
 g) Y. T. Zhang, G. M. Miyake, E. Y.-X. Chen, Angew. Chem. Int. Ed. 2010, 49, 10158–10162; Angew. Chem. 2010, 122, 10356–10360.
- [18] M. Rohde, L. O. Muller, D. Himmel, H. Scherer, I. Krossing, *Chem. Eur. J.* 2014, 20, 1218–1222.
- [19] a) S. Feng, G. R. Roof, E. Y.-X. Chen, *Organometallics* 2002, 21, 832–839; b) C. H. Lee, S. J. Lee, J. W. Park, K. H. Kim, B. Y. Lee, J. S. Oh, *J. Mol. Catal. A* 1998, *132*, 231–239; c) P. Biagini, G. Lugli, L. Abis, P. Andreussi, U. S. Pat. 5, 602269, 1997.
- [20] a) S. J. Connelly, W. Kaminsky, D. M. Heinekey, *Organometallics* 2013, *32*, 7478–7481; b) H. F. T. Klare, M. Oestreich, *Dalton Trans.* 2010, *39*, 9176–9184; c) J. B. Lambert, S. Zhang, C. L. Stern, J. C. Huffman, *Science* 1993, *260*, 1917–1918.
- [21] M. Nava, C. A. Reed, Organometallics 2011, 30, 4798-4800.

- [22] Ligand scrambling of Et₃SiH was also observed with a cationic aluminum species [AlEt₂]⁺: R. J. Wehmschulte, M. Saleh, D. R. Powell, *Organometallics* **2013**, *32*, 6812–6819.
- [23] a) Polymerization of the more reactive primary PhSiH₃ into branded polymers at elevated temperature: A. Feigl, I. Chiorescu, K. Deller, S. U. H. Heidsieck, M. R. Buchner, V. Karttunen, A. Bockholt, A. Genest, N. Rosch, B. Rieger, *Chem. Eur. J.* 2013, *19*, 12526–12536; b) Stoichiometric metathesis between Et₃SiH and B(C₆F₅)₃ to generate Et₃SiC₆F₅ and HB(C₆F₅)₂: D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* 1998, *17*, 5492–5503.
- [24] a) R. Labbow, F. Reiss, A. Schulz, A. Villinger, *Organometallics* 2014, *33*, 3223–3226; b) K. Müther, P. Hrobarik, V. Hrobarikova, M. Kaupp, M. Oestreich, *Chem. Eur. J.* 2013, *19*, 16579–16594; c) A. Schäfer, M. Reissmann, S. Jung, A. Schafer, W. Saak, E. Brendler, T. Müller, *Organometallics* 2013, *32*, 4713–4722; d) A. Schäfer, M. Reissmann, A. Schafer, W. Saak, D. Haase, T. Müller, *Angew. Chem. Int. Ed.* 2011, *50*, 12636–12638; *Angew. Chem.* 2011, *123*, 12845–12848.
- [25] E. Y.-X. Chen, Chem. Rev. 2009, 109, 5157-5214.
- [26] K. Fuchise, S. Tsuchida, K. Takada, Y. G. Chen, T. Satoh, T. Kakuchi, ACS Macro Lett. 2014, 3, 1015–1019.
- [27] a) M. Rubin, T. Schwier, V. Gevorgyan, J. Org. Chem. 2002, 67, 1936–1940; b) Y. S. Song, B. R. Yoo, G. H. Lee, I. N. Jung, Organometallics 1999, 18, 3109–3115.
- [28] M. Pérez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky, D. W. Stephan, *Science* **2013**, *341*, 1374–1377.
- [29] M. Pérez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky, D. W. Stephan, J. Am. Chem. Soc. 2013, 135, 18308–18310.
- [30] Selected reviews and examples: a) T. Stahl, H. F. T. Klare, M. Oestreich, ACS Catal. 2013, 3, 1578–1587; b) C. B. Caputo, D. W. Stephan, Organometallics 2012, 31, 27–30; c) C. Douvris, O. V. Ozerov, Science 2008, 321, 1188–1190; d) R. Panisch, M. Bolte, T. Müller, J. Am. Chem. Soc. 2006, 128, 9676–9682.

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