ChemPubSoc Europe

DOI: 10.1002/chem.201600971

CHEMISTRY
A European Journal
Communication

Homogeneous Catalysis

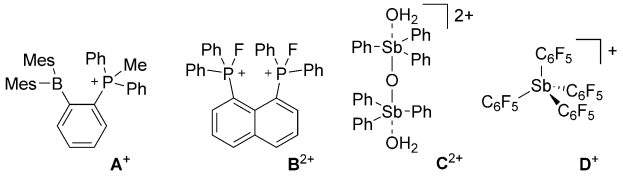
Promoting the Hydrosilylation of Benzaldehyde by Using a Dicationic Antimony-Based Lewis Acid: Evidence for the Double Electrophilic Activation of the Carbonyl Substrate

Masato Hirai, Junsang Cho, and François P. Gabbaï*[a]

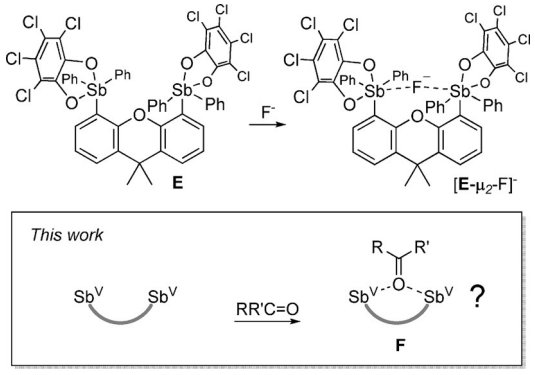
Abstract: The concomitant activation of carbonyl substrates by two Lewis acids has been investigated by using $[1,2\text{-}(Ph_2MeSb)_2C_6H_4]^{2+}$ ($[\mathbf{1}]^{2+}$), an antimony-based bidentate Lewis acid obtained by methylation of the corresponding distibine. Unlike the simple stibonium cation $[Ph_3MeSb]^+$, dication $[\mathbf{1}]^{2+}$ efficiently catalyzes the hydrosilylation of benzaldehyde under mild conditions. The catalytic activity of this dication is correlated to its ability to doubly activate the carbonyl functionality of the organic substrate. This view is supported by the isolation of $[\mathbf{1}\text{-}\mu_2\text{-}DMF][OTf]_2$, an adduct, in which the DMF oxygen atom bridges the two antimony centers.

Electrophilic phosphonium cations are attracting an increasing interest as Lewis acids for the complexation of small anions or for the activation of various organic reactions.[1] The unique Lewis acidic properties displayed by these saturated derivatives arise from the ability of phosphorus to form hypervalent compounds, a phenomenon facilitated by the introduction of electron-withdrawing ligands.[1a,b,2] Another methods that has been explored as a means to achieve greater Lewis acidity is based on the incorporation of two electrophilic moieties positioned to cooperatively interact with an incoming nucleophile. This is, for example, the case with the phosphonium borane derivative $\mathbf{A}^+$, which acts as a bidentate Lewis acid toward fluoride.[3] The Stephan group has recently investigated the Lewis acidic properties of the bis-fluorophosphonium species ($\mathbf{B}^{2+}$) and found that the proximity of the two Group 15 cations leads to enhanced catalytic activity in a range of reactions, including Friedel Crafts, hydrosilylation, and hydrodefluorination reactions.[2e,4]

Organoantimony(V) derivatives are another class of Lewis acidic derivatives drawing attention.[5] Such derivatives, including $\mathbf{C}^{2+}$[6] and $\mathbf{D}^+$,[7] are emerging as air-stable Lewis acids, which can be used to promote C–C bond-forming reactions or



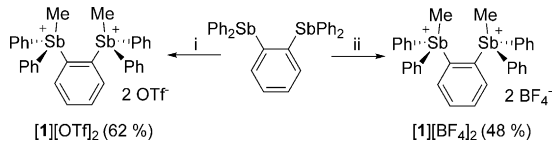
to activate strong element-fluorine bonds. As part of our contribution to the chemistry of these new Lewis acids, we have also synthesized bidentate distiboranes, such as **E**, and found evidence of strong cooperativity between the two Lewis acidic centers in the binding of fluoride anions.[8] Encouraged by these ongoing developments, we have now decided to test whether bidentate antimony derivatives could also be used as catalysts for the double electrophilic activation of organic carbonyls, as illustrated in **F**.[9] Herein, we present a series of results, which support this possibility.



To initiate our studies, we decided to target a bifunctional antimony Lewis acid with a binding pocket that is readily substrate accessible. This consideration led us to target the *ortho*-phenylene derivative $[\mathbf{1}]^{2+}$, which features two Lewis acidic antimony sites predisposed to interact with incoming nucleophiles. Distibonium salts $[\mathbf{1}][OTf]_2$ and $[\mathbf{1}][BF_4]_2$ could be conveniently generated by treatment of *o*-phenylene-bis(diphenylstibine)[10] with methyl trifluoromethylsulfonate (MeOTf) and trimethyloxonium tetrafluoroborate ($[Me_3O][BF_4]$), respectively (Scheme 1). Both $[\mathbf{1}][OTf]_2$ and $[\mathbf{1}][BF_4]_2$ have been fully characterized, and their compositions have been verified by elemental analyses. The ^1H NMR spectrum of $[\mathbf{1}][OTf]_2$ and $[\mathbf{1}][BF_4]_2$ in

[a] M. Hirai, J. Cho, Prof. Dr. F. P. Gabbaï
Department of Chemistry, Texas A&M University
College Station, Texas 77843 (USA)
Fax: (+1) 979-845-4719
E-mail: francois@tamu.edu
Homepage: http://www.chem.tamu.edu/rgroup/gabbai/

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201600971.



Scheme 1. Synthesis of [**1**][OTf]$_2$ and [**1**][BF$_4$]$_2$: i) 4 equiv MeOTf, toluene, 90 °C; ii) 2.05 equiv [Me$_3$O][BF$_4$], 1,2-C$_2$H$_4$Cl$_2$/toluene 1:2, 90 °C.

CD_2Cl_2 showed a diagnostic methyl resonance at $\delta = 2.18$ and 2.17 ppm, respectively, indicative of the formation of the methylstibonium moiety. Both [**1**][OTf]$_2$ and [**1**][BF$_4$]$_2$ are very soluble in CH_2Cl_2, THF, and CH_3CN and sparingly soluble in $CHCl_3$. Salt [**1**][BF$_4$]$_2$ is stable over prolonged periods of time and showed no tendency towards decomposition by fluoride transfer from the BF_4^- anion to the Lewis acidic antimony center. For comparison, we also prepared the monofunctional model compound [Ph$_3$MeSb][OTf][11] and [Ph$_3$MeSb][BF$_4$],[12] which have both been previously described.

With these compounds in hand, we first decided to quantitatively examine their Lewis acidity by applying the Gutmann–Beckett method, which relies on the ^{31}P NMR chemical-shift change observed upon coordination of Et_3PO to a Lewis acid.[13] In the case of the monofunctional Lewis acids [Ph$_3$MeSb][OTf] and [Ph$_3$MeSb][BF$_4$], CH_2Cl_2 solutions of Et_3PO (7.5×10^{-2} M) containing an eightfold excess of the stibonium salt feature a broad ^{31}P NMR signal at $\delta = 57.0$ ppm, downfield shifted from the free Et_3PO ($\delta = 51.0$ ppm) by 6.0 ppm. This suggests that these two salts display similar Lewis acidity despite the differing counteranions. When the same measurement was repeated with the distibonium salts [**1**][OTf]$_2$ and [**1**][BF$_4$]$_2$ by using CH_2Cl_2 solutions of Et_3PO (7.5×10^{-2} M) containing a fourfold excess of the distibonium, the ^{31}P NMR chemical shift of the phosphine oxide was observed at $\delta = 61.4$ and 62.2 ppm, respectively. These resonances are significantly more downfield than those observed with the simple stibonium salts [Ph$_3$MeSb][OTf] and [Ph$_3$MeSb][BF$_4$] indicating that the distibonium salts [**1**][OTf]$_2$ and [**1**][BF$_4$]$_2$ are more Lewis acidic and more effectively polarize the P=O bond of Et_3PO. This suggests that this greater Lewis acidity arises from the preorganization of the two stibonium moieties and their ability to simultaneously interact with the oxygen atom of the phosphine oxide. Last, we note a small influence of the counteranions for the bifunctional derivatives, with the BF_4^- salt displaying a slightly higher Lewis acidity than its triflate counterpart.

Although we failed to crystallize the above-mentioned Et_3PO adducts, single crystals of the distibonium salt [**1**][OTf]$_2$ were obtained as colorless blocks by diffusion of Et_2O into a CH_2Cl_2 (Figure 1).[14] In the crystal, one of the triflate anions is well separated from the distibonium complex. In contrast, the other triflate anion bridges the two antimony centers resulting in Sb1–O1 and Sb2–O2 separations of 2.8541(12) and 2.9838(13) Å, respectively. These Sb–O distances are shorter than the Sb–O separation of 3.1518(16) Å found in the monofunctional analog [Ph$_3$MeSb][OTf], the structure of which was also determined for the purpose of this study (see the Supporting Information).[14] In turn, coordination of the triflate anion in [**1**][OTf]$_2$

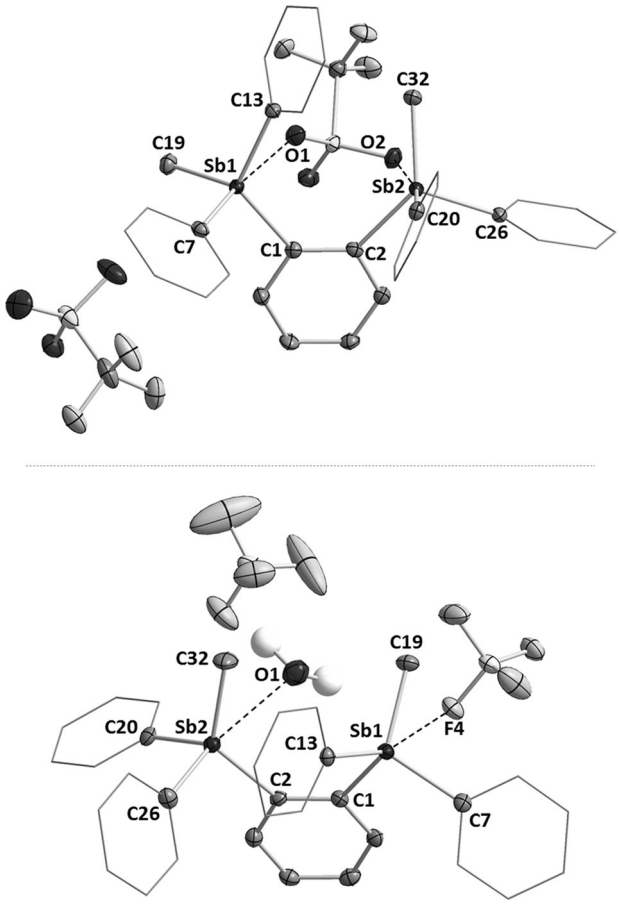


Figure 1. Solid-state structure of [**1**][OTf]$_2$ (top) and [**1**-OH$_2$][BF$_4$]$_2$ (bottom). Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity, except for the water molecule in [**1**-OH$_2$][BF$_4$]$_2$. Pertinent metric parameters can be found in the text.

cannot be overlooked and likely diminishes the Lewis acidity of the antimony centers. Next, we moved to the crystallization of [**1**][BF$_4$]$_2$.[14] In all attempts that involved a variety of solvents or solvent mixtures, this salt only precipitated in a powder form. In a few cases, we observed that precipitation of [**1**][BF$_4$]$_2$ was accompanied by formation of a small number of single crystals. Analysis of these crystals indicate that they correspond to the hydrate [**1**-OH$_2$][BF$_4$]$_2$, which probably results from the presence of adventitious water in the solvent (Figure 2). The water molecule interacts with one of the antimony centers (Sb2), as indicated by a Sb2–O1 distance of 2.938(3) Å. The other antimony atom interacts with a tetrafluoroborate anion, as indicated by the Sb1–F4 contact of 3.066(6) Å.

Encouraged by these results, we next investigated the catalytic properties of these stibonium compounds in the hydrosilylation of benzaldehyde by using triethylsilane in $CDCl_3$ (Scheme 2). Although [Ph$_3$MeSb][OTf] and [Ph$_3$MeSb][BF$_4$] (3 mol%) did not promote the reaction at room temperature, we observed some moderate catalytic activity in the case of [**1**][OTf]$_2$ (1.5 mol%), with 11% conversion after 8 h. A surprisingly contrasting behavior was observed in the case of [**1**][BF$_4$]$_2$ (1.5 mol%), which proves to be much more active leading to

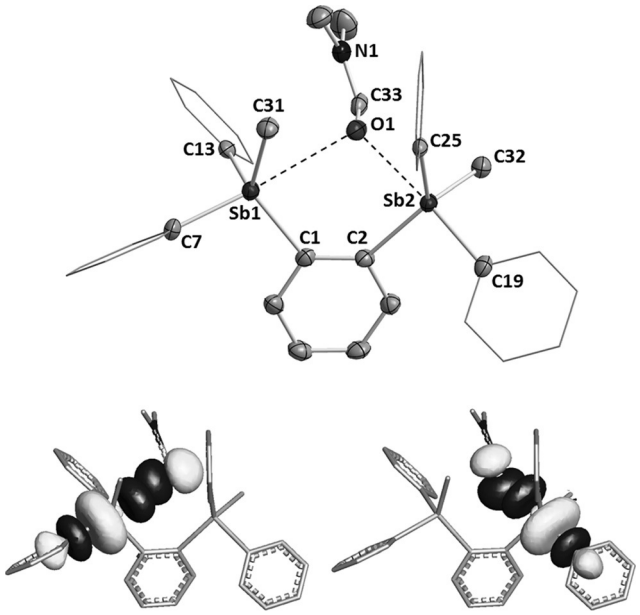
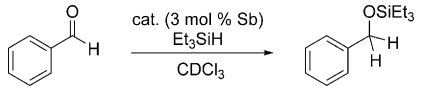


Figure 2. Top: Solid-state structure of [**1**-μ_2-DMF][OTf]$_2$. Thermal ellipsoids are drawn at the 50% probability level. The triflate anions and the hydrogen atoms are omitted for clarity. Pertinent metric parameters can be found in the text. Bottom: NBO plot (isovalue 0.05) showing two representative lp(O)→σ*(Sb–C_{Ph}) donor–acceptor interactions.



Scheme 2. Hydrosilylation of benzaldehyde.

complete conversion after 8 h. This reaction is unaffected by addition of 3 mol% of Mes_3P as a Brønsted acid scavenger indicating that protons are not responsible for the observed catalytic activity.[15] We also note that Et_3SiH reacts with acids making the involvement of protons an even more remote possibility. These results showed that: 1) the distibonium catalysts are more active that their monofunctional analogs; and 2) the tetrafluoroborate salt of the distibonium is significantly more active than the triflate salt. We propose that: 1) the higher activity of the distibonium catalysts arises from their ability to doubly activate the carbonyl functionality of the aldehyde; and 2) the higher activity of [**1**][OTf]$_2$ versus [**1**][BF_4]$_2$ results from the more weakly coordinating nature of the BF_4^- anion. To support the concept of double electrophilic activation of the carbonyl substrate by [**1**]$^{2+}$ in these reactions, we failed to isolate the benzaldehyde adduct. An adduct was obtained with the more basic carbonyl substrate DMF and [**1**][OTf]$_2$.[14] Elucidation of the structure of this adduct revealed a DMF molecule bridging the two antimony centers in an unsymmetrical fashion (Figure 2). The resulting Sb1–O1 (2.555(2) Å) and Sb2–O1 (2.992(2) Å) bonds are well within the sum of the van der Waals radii of the two elements (Sb–O 3.75 Å).[16] The DMF oxygen atom is positioned directly *trans* from a phenyl ligand (∡(O1-Sb1-C7) 175.44(10)°, ∡(O1-Sb2-C19) 175.49(11)°) leading to distorted trigonal bipyramidal geometries at each antimony center.[5a] The solid-state IR spectrum of single crystals of [**1**-μ_2-DMF][OTf]$_2$ displayed a weakening of the C–O bond, when the stretching frequency was lowered to 1634 cm^{-1} from 1675 cm^{-1} in neat DMF (see the Supporting Information). A natural bond orbital analysis carried out by using the crystal geometry of [**1**-μ_2-DMF]$^{2+}$ supported the concomitant interaction of the DMF oxygen atom with each antimony center, as illustrated by the presence of multiple O"Sb interactions involving filled oxygen p orbitals as donor orbitals and vacant Sb–C_{Ph} σ* orbitals as acceptor orbitals (Figure 2). The energy of these O"Sb interactions was estimated to be approximately 12 kcal mol^{-1} by using the NBO deletion protocol.[17]

The four stibonium salts investigated in this study have also been evaluated for the hydrosilylation of 4-nitro-, 4-trifluoromethyl-, 4-methoxy-, and 4-dimethylaminobenzaldehyde. Hydrosilylation reaction was not observed for these substrates. We propose that this lack of activation arises from the relatively weak Lewis acidity of the stibonium cations and their inability to activate weakly basic substrates, such as 4-nitro- and 4-trifluorobenzaldehyde or overcome the stability of electron-rich substrates, such as 4-methoxy- and 4-dimethylaminobenzaldehyde. To support this proposal, we have also tested the reactivity of 4-fluorobenzaldehyde and found that it undergoes clean hydrosilylation with [**1**][BF_4]$_2$ and Et_3SiH as silane. However, the fluorine atom appears to play a slight deactivating role with the reaction only proceeding when heated to 60 °C. We have also tested a few other tertiary silanes and found that *i*Pr_3SiH, Ph_2MeSiH, and Ph_3SiH are not reactive toward benzaldehyde in the presence of [**1**][BF_4]$_2$. We assign this lack of reactivity to the bulk of these silanes. Finally, the ^{1}H NMR spectrum of Et_3SiH remained unchanged upon mixing with [**1**][BF_4]$_2$. This observation suggests that a mechanism involving Si–H bond activation as with catalysts such $B(C_6F_5)_3$[18] or $[(C_6F_5)_3FP]^+$[4] is unlikely;[19] instead, it suggests that the catalyst may be directly activating the carbonyl substrate, as was observed for other main-group catalysts.[20] Collectively, these results can be reconciled by invoking the double electrophilic activation of benzaldehyde by [**1**]$^{2+}$ followed by silane reduction as depicted in Figure 3.

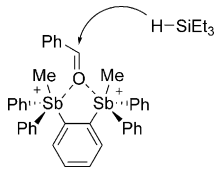


Figure 3. Double electrophilic activation of benzaldehyde by [**1**]$^{2+}$.

In summary, we described the synthesis and structure of a distibonium dication, which promotes the hydrosilylation of benzaldehyde under mild conditions. The unusual catalytic properties of this dication are proposed to result from its ability to doubly activate the carbonyl functionality of the substrate. This proposal is supported by the fact that simple stibonium monocations failed to promote this reaction, as well as by the isolation of the DMF adduct [**1**-μ_2-DMF][OTf]$_2$, in which the DMF oxygen atom is engaged with the two antimony centers.

Experimental Section

Synthesis of [1][OTf]$_2$: MeOTf (0.21 mL, 1.9×10^{-3} mol) was added to a solution of *o*-phenylene-bis(diphenylstibine) (302 mg, 4.8×10^{-4} mol) in toluene (3 mL). The mixture was sealed under N_2 atmosphere in a 25 mL Schlenk tube and heated for 90 °C for 12 h, after which a white precipitate was formed. The solid was filtered, washed with Et_2O (3×5 mL), and dried in vacuo to give [**1**][OTf]$_2$ in 62% yield (285 mg, 3.0×10^{-4} mol). Single crystals of [**1**][OTf]$_2$ were obtained as colorless blocks by diffusing Et_2O into a CH_2Cl_2 solution. ^{1}H NMR (399.508 MHz, CD_3CN, 25 °C, TMS): $\delta=7.88$–7.84 (m; 4H; C_6H_4), 7.71 (pseudo t; ^3J (H,H) = 6.0 Hz, 4H; *p-Ph*), 7.56 (pseudo t; ^3J (H,H) = 6.4 Hz, 8H; *o-Ph*), 7.49 (pseudo d; ^3J (H,H) = 6.4 Hz, 8H; *m-Ph*), 2.14 ppm (s; 6H; Sb-CH_3); ^{13}C{^{1}H NMR (125.60 MHz, CD_3CN, 25 °C, TMS): $\delta=141.38$ (*o*-phenylene), 136.61 (*o*-Ph), 134.91 (*p*-Ph), 134.91 (quat. Ph), 134.81 (*o*-phenylene), 134.05 (quat. *o*-phenylene), 131.93 (*o*-Ph), 124.46 (*o*-phenylene), 120.8 (q; $CF_3SO_3^-$), 6.43 ppm (Sb–CH_3); elemental analysis calcd (%) for $C_{34}H_{30}F_6O_6S_2Sb_2$: ($M_w$ 956.24): C 42.71, H 3.16; found: C 42.85, H 3.20.

Synthesis of [1][BF$_4$]$_2$: [Me_3O][BF_4] (49 mg, 3.3×10^{-4} mol) was added to a solution of **1** (101 mg, 1.6×10^{-4} mol) in a mixture of 1,2-dichloroethane (1 mL) and toluene (2 mL). The mixture was sealed in a 25 mL Schlenk tube under N_2 atmosphere and heated for 90 °C for 12 h, after which a white precipitate was formed. The solid was filtered, washed with Et_2O (3×5 mL), and dried in vacuo to give [**1**][BF_4]$_2$ in 48% yield (64 mg, 7.7×10^{-5} mol). Single crystals of [**1**-OH_2][BF_4]$_2$ were obtained in low yield as colorless blocks by layering pentane on a saturated CH_2Cl_2 solution of [**1**][BF_4]$_2$. ^{1}H NMR (399.508 MHz, CD_2Cl_2, 25 °C, TMS): $\delta=7.74$ (broad s; 4H), 7.66 (m; 4H), 7.55 (pseudo t; ^3J (H,H) = 6.0 Hz, 8H; *o-Ph*), 7.47 (pseudo d; ^3J (H,H) = 6.0 Hz, 8H; *m-Ph*), 2.16 ppm (s; 6H; Sb–CH_3); ^{13}C{^{1}H} NMR (125.60 MHz, CD_2Cl_2, 25 °C, TMS): δ 139.55 (*o*-phenylene), 134.89 (*o*-Ph), 133.21 (*o*-phenylene), 132.86 (*p*-Ph), 130.56 (*m*-Ph), 30.60 ppm (Sb–CH_3). The Sb-bound quaternary carbon could not be detected. Elemental analysis calcd (%) for $C_{32}H_{30}B_2F_8Sb_2$ (M_w 831.72): C 42.21, H 3.64; found: C 42.44, H 3.58. This elemental analysis was performed on the bulk product; it points to the absence of water in bulk [**1**][BF_4]$_2$.

Synthesis of [1-μ$_2$-DMF][OTf]$_2$: A sample of [**1**][OTf]$_2$ (32 mg; 3.3×10^{-5} mol) was placed in a vial and dissolved in 0.5 mL of DMF. Et_2O was slowly diffused into this mixture leading to the crystallization of [**1**-μ$_2$-DMF][OTf]$_2$ in 64% yield (22 mg, 2.1×10^{-5} mol). The ^{1}H NMR data showed that the adduct is fully dissociated in solution. ^{1}H NMR (399.508 MHz, CD_3CN, 25 °C, TMS): $\delta=7.89$ (broad; 1H; C(O)*H*), 7.88–7.84 (m; 4H; C_6H_4), 7.71 (pseudo t; ^3J (H,H) = 6.0 Hz, 4H; *p-Ph*), 7.56 (pseudo t; ^3J (H,H) = 6.4 Hz, 8H; *o-Ph*), 7.49 (pseudo d; ^3J (H,H) = 6.4 Hz, 8H; *m-Ph*), 2.88 (s; 3H; DMF-CH_3), 2.76 (s; 3H; DMF-CH_3), 2.14 ppm (s; 6H; Sb-CH_3); elemental analysis calcd (%) for $C_{35}H_{37}F_6NO_7S_2Sb_2$ (M_w 1029.33): C 43.17, H 3.62, N 1.36; found: C 43.22, H 3.55, N 1.38.

Hydrosilylation reactions: In a glovebox, an NMR tube was charged with benzaldehyde (0.023 mL, 2.0×10^{-4} mol), triethylsilane (0.064 mL, 4.0×10^{-4} mol), hexamethylbenzene (1.8 mg, 1.1×10^{-5} mol), and the corresponding stibonium salts (1.5 mol% [**1**][OTf]$_2$, 1.5 mol% [**1**][BF_4]$_2$, 3.0 mol% [Ph_3MeSb][OTf], 3.0 mol% [Ph_3MeSb][BF_4] with all concentrations based on benzaldehyde) in dry $CDCl_3$ (1 mL). After recording an initial ^{1}H NMR spectrum, the NMR samples were kept at room temperature and monitored periodically. For 4-fluorobenzaldehyde (21 μL, 0.2 mmol) with [**1**][BF_4]$_2$ (1.5 mol%) as a catalyst, no reaction was observed at room temperature. Placing the NMR tube in an oil bath heated to 60 °C gave a conversion of 33% after 8 h and >95% after 22 h.

Synthesis and isolation of (benzyloxy)triethylsilane: Triethylsilane (0.319 mL, 2.0×10^{-3} mol), hexamethylbenzene (9.0 mg, 5.6×10^{-5} mol), and [**1**][BF_4]$_2$ (12.5 mg, 1.5×10^{-5} mol; 1.5 mol%) were mixed in 4 mL of dry $CHCl_3$, and the reaction mixture was stirred at ambient temperature. After 12 h, the reaction mixture was directly transferred to a short silica plug and chromatographed by using hexanes/Et_3N (99:1) mixture as an eluent. The solvent was removed in vacuo to give the pure product as a colorless oil in 88% isolated yield (195.7 mg, 8.8×10^{-4} mol). The ^{1}H NMR spectrum of the product is in agreement with that previously reported.[19b] ^{1}H NMR (399.508 MHz, $CDCl_3$): $\delta=7.41$–7.32 (m; 4H; *o-* and *m-Ph*), 7.28–7.25 (m; 1H; *p-Ph*), 4.70 (s; 2H; CH_2), 0.97 (t; ^3J (H,H) = 8.0 Hz, 9H; CH_3CH_2Si,), 0.68 ppm (q; ^3J (H,H) = 8.0 Hz, 6H, CH_3CH_2Si).

Acknowledgements

Financial support from the Welch Foundation (A-1423), the National Science Foundation (CHE-1300371), Texas A&M University (A.E. Martell Chair), and the Laboratory for Molecular Simulation at Texas A&M University (software and computation resources) is gratefully acknowledged.

Keywords: antimony · homogeneous catalysis · cations · hydrosilylation · Lewis acids

[1] a) M. Perez, C. B. Caputo, R. Dobrovetsky, D. W. Stephan, *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 10917–10921; b) M. Pérez, Z.-W. Qu, C. B. Caputo, V. Podgorny, L. J. Hounjet, A. Hansen, R. Dobrovetsky, S. Grimme, D. W. Stephan, *Chem-Eur J* **2015**, *21*, 6491–6500; c) W. Zhao, P. K. Yan, A. T. Radosevich, *J. Am. Chem. Soc.* **2015**, *137*, 616–619; d) K. D. Reichl, A. T. Radosevich, *Chem. Commun.* **2014**, *50*, 9302–9305; e) T. Mukaiyama, S. Matsui, K. Kashiwagi, *Chem. Lett.* **1989**, *18*, 993–996; f) T. Mukaiyama, K. Kashiwagi, S. Matsui, *Chem. Lett.* **1989**, *18*, 1397–1400.

[2] a) C. B. Caputo, L. J. Hounjet, R. Dobrovetsky, D. W. Stephan, *Science* **2013**, *341*, 1374–1377; b) L. J. Hounjet, C. B. Caputo, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 2629–2635; c) M. Pérez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky, D. W. Stephan, *J. Am. Chem. Soc.* **2013**, *135*, 18308–18310; d) M. H. Holthausen, M. Mehta, D. W. Stephan, *Angew. Chem. Int. Ed.* **2014**, *53*, 6538–6541; *Angew. Chem.* **2014**, *126*, 6656–6659; e) M. H. Holthausen, R. R. Hiranandani, D. W. Stephan, *Chem. Sci.* **2015**, *6*, 2016–2021; f) M. Mehta, M. H. Holthausen, I. Mallov, M. Pérez, Z.-W. Qu, S. Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.* **2015**, *54*, 8250–8254; *Angew. Chem.* **2015**, *127*, 8368–8372.

[3] T. W. Hudnall, Y.-M. Kim, M. W. P. Bebbington, D. Bourissou, F. P. Gabbaï, *J. Am. Chem. Soc.* **2008**, *130*, 10890–10891.

[4] M. H. Holthausen, J. M. Bayne, I. Mallov, R. Dobrovetsky, D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 7298–7301.

[5] a) A. P. M. Robertson, S. S. Chitnis, H. A. Jenkins, R. McDonald, M. J. Ferguson, N. Burford, *Chem. Eur. J.* **2015**, *21*, 7902–7913; b) A. P. M. Robertson, N. Burford, R. McDonald, M. J. Ferguson, *Angew. Chem. Int. Ed.* **2014**, *53*, 3480–3483; *Angew. Chem.* **2014**, *126*, 3548–3551; c) I.-S. Ke, M. Myahkostupov, F. N. Castellano, F. P. Gabbaï, *J. Am. Chem. Soc.* **2012**, *134*, 15309–15311; d) C. R. Wade, F. P. Gabbaï, *Organometallics* **2011**, *30*, 4479–4481; e) M. Jean, *Anal. Chim. Acta* **1971**, *57*, 438–439; f) L. H. Bowen, R. T. Rood, *J. Inorg. Nucl. Chem.* **1966**, *28*, 1985–1990.

[6] N. Li, R. Qiu, X. Zhang, Y. Chen, S.-F. Yin, X. Xu, *Tetrahedron* **2015**, *71*, 4275–4281.

[7] B. Pan, F. P. Gabbaï, *J. Am. Chem. Soc.* **2014**, *136*, 9564–9567.

[8] M. Hirai, F. P. Gabbaï, *Angew. Chem. Int. Ed.* **2015**, *54*, 1205–1209; *Angew. Chem.* **2015**, *127*, 1221–1225.

[9] a) J. Vaugeois, J. D. Wuest, *J. Am. Chem. Soc.* **1998**, *120*, 13016–13022; b) M. Tschinkl, A. Schier, J. Riede, F. P. Gabbaï, *Organometallics* **1999**, *18*, 1747–1753; c) I. D. Kostas, G.-J. M. Gruter, O. S. Akkerman, F. Bickelhaupt, H. Kooijman, W. J. J. Smeets, A. L. Spek, *Organometallics* **1996**,

15, 4450 – 4458; d) J. D. Wuest, *Acc. Chem. Res.* **1999**, *32*, 81 – 89; e) J. B. King, F. P. Gabbaï, *Organometallics* **2003**, *22*, 1275 – 1280; f) T. Ooi, M. Takahashi, M. Yamada, E. Tayama, K. Omoto, K. Maruoka, *J. Am. Chem. Soc.* **2004**, *126*, 1150 – 1160.

[10] W. Levason, C. A. McAuliffe, S. G. Murray, *J. Organomet. Chem.* **1975**, *88*, 171 – 174.

[11] B. A. McCortney, B. M. Jacobson, M. Vreeke, E. S. Lewis, *J. Am. Chem. Soc.* **1990**, *112*, 3554 – 3559.

[12] M. C. Henry, G. Wittig, *J. Am. Chem. Soc.* **1960**, *82*, 563 – 564.

[13] M. A. Beckett, D. S. Brassington, S. J. Coles, M. B. Hursthouse, *Inorg. Chem. Commun.* **2000**, *3*, 530 – 533.

[14] CCDC 1448773 ([**1**][OTf]$_2$), 1448774 ([**1**][BF$_4$]$_2$), 1448775 ([**1**-μ_2-DMF][OTf]$_2$), 1448776 ([Ph$_3$MeSb][OTf]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

[15] R. K. Schmidt, K. Müther, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.* **2012**, *134*, 4421 – 4428.

[16] S. S. Batsanov, *Inorg. Mater.* **2001**, *37*, 871 – 885.

[17] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899 – 926.

[18] a) D. J. Parks, W. E. Piers, *J. Am. Chem. Soc.* **1996**, *118*, 9440 – 9441; b) D. J. Parks, J. M. Blackwell, W. E. Piers, *J. Org. Chem.* **2000**, *65*, 3090 – 3098.

[19] a) S. E. Denmark, Y. Ueki, *Organometallics* **2013**, *32*, 6631 – 6634; b) J. Koller, R. G. Bergman, *Organometallics* **2012**, *31*, 2530 – 2533.

[20] a) A. L. Liberman-Martin, R. G. Bergman, T. D. Tilley, *J. Am. Chem. Soc.* **2015**, *137*, 5328 – 5331; b) R. Calas, *J. Organomet. Chem.* **1980**, *200*, 11 – 36; c) J. L. Fry, M. Orfanopoulos, M. G. Adlington, W. P. Dittman, S. B. Silverman, *J. Org. Chem.* **1978**, *43*, 374 – 375; d) M. P. Doyle, C. T. West, S. J. Donnelly, C. C. McOsker, *J. Organomet. Chem.* **1976**, *117*, 129 – 140.

Received: March 1, 2016
Published online on March 16, 2016