

Lewis Acidity of Bis(perfluorocatecholato)silane: Aldehyde Hydrosilylation Catalyzed by a Neutral Silicon Compound

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S Supporting Information

ABSTRACT: Bis(perfluorocatecholato)silane $\text{Si}(\text{cat}^{\text{F}})_2$ was prepared, and stoichiometric binding to Lewis bases was demonstrated with fluoride, triethylphosphine oxide, and N,N' -diisopropylbenzamide. The potent Lewis acidity of $\text{Si}(\text{cat}^{\text{F}})_2$ was suggested from catalytic hydrosilylation and silylcyanation reactions with aldehydes. Mechanistic studies of hydrosilylation using an optically active silane substrate, R -(+)-methyl-(1-naphthyl)phenylsilane, proceeded with predominant stereochemical retention at silicon, consistent with a carbonyl activation pathway. The enantiospecificity was dependent on solvent and salt effects, with increasing solvent polarity or addition of $\text{NBu}_4\text{BAR}^{\text{F}}_4$ leading to a diminished enantiomeric ratio. The medium effects are consistent with an ionic mechanism, wherein hydride transfer occurs prior to silicon–oxygen bond formation.

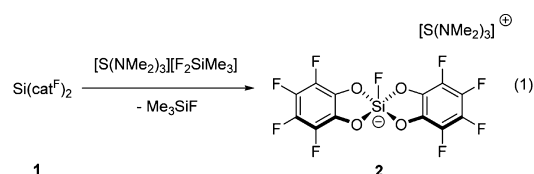
Lewis acidic main group compounds have emerged as broadly applicable reagents. In particular, $\text{B}(\text{C}_6\text{F}_5)_3$ and other electron-deficient boranes can serve as activators for transition metal compounds,¹ and as alternatives to metal-based catalysts.²

In contrast to group 13 species, silicon Lewis acids remain relatively rare.³ Silicon tetrachloride is the common silicon-based Lewis acid of choice in catalytic applications;⁴ however, the reactive Si–Cl bonds are readily cleaved by nucleophilic reagents, limiting its utility. Several recent reports have shown that cationic silylium ions promote catalytic imine reduction and Diels–Alder reactions.⁵ Silylium compounds, in combination with phosphines, engage in frustrated Lewis pair reactions that activate carbon dioxide and dihydrogen.⁶ Additionally, Leighton and co-workers have demonstrated that chiral silicon complexes can serve as reagents for asymmetric crotylation reactions and as catalysts for Diels–Alder additions.⁷ Based on these promising results, we were interested in exploring the behavior of neutral silicon compounds as potent Lewis acids. Herein, we report the synthesis and reactivity of a neutral bis(perfluorocatecholato)silane Lewis acid, which represents the first example of a neutral silicon species that catalyzes aldehyde hydrosilylation.

The bis(catecholato)silane motif was selected due to its ease of preparation and stability, and fluorinated catechol ligands were employed to enhance the Lewis acidic properties. The novel complex bis(perfluorocatecholato)silane, $\text{Si}(\text{cat}^{\text{F}})_2$ (**1**), was easily prepared by treatment of silicon tetrachloride with 2 equiv of tetrafluorocatechol in acetonitrile. In the absence of

Lewis bases, **1** has very limited solubility in standard organic solvents including benzene, dichloromethane, and acetonitrile.

Reactions with simple anionic and neutral Lewis bases were investigated to probe the binding properties of $\text{Si}(\text{cat}^{\text{F}})_2$. First, addition of tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) to $\text{Si}(\text{cat}^{\text{F}})_2$ in tetrahydrofuran led to the immediate formation of a bis(perfluorocatecholato)fluorosilicate complex (**2**, eq 1). Single crystal X-ray diffraction confirmed the



structure of **2**, which exhibits an approximate square pyramidal geometry at silicon (Figure 1). There is π -stacking between the

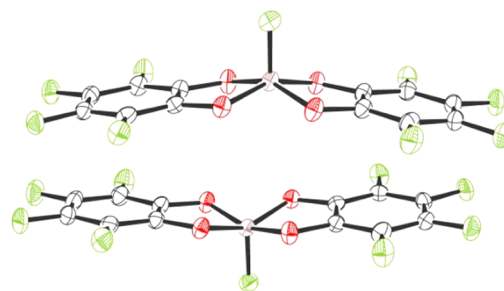


Figure 1. ORTEP diagram of **2**, with thermal ellipsoids at 50% probability. Tris(dimethylamino)sulfonium cations are omitted for clarity.

perfluorocatechol rings of two silicate units in the solid state ($d = 3.08$ – 3.61 Å).⁸ The Si–F bond distance in **2** (1.602(2) Å) is nearly identical to that reported previously for $[\text{Si}(\text{cat})_2\text{F}][\text{NEt}_4]$.⁹ This fluoride binding demonstrates that $\text{Si}(\text{cat}^{\text{F}})_2$ can readily accommodate an added Lewis base to form a pentacoordinate species, a general step that is necessary for catalytic applications.

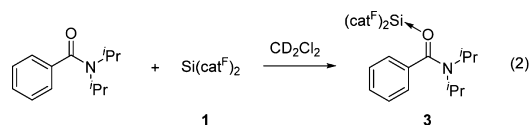
To apply the Gutmann–Beckett method as a gauge of Lewis acidity, the binding of triethylphosphine oxide to $\text{Si}(\text{cat}^{\text{F}})_2$ was evaluated on the basis of the change in the ³¹P NMR chemical

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shift of OPEt_3 upon complexation.¹⁰ A change of +35.9 ppm in the ^{31}P NMR chemical shift of OPEt_3 was observed upon treatment with 1 equiv of $\text{Si}(\text{cat}^{\text{F}})_2$ in dichloromethane- d_2 . Only a slightly smaller change in chemical shift was observed using $\text{Si}(\text{cat})_2$ ($\Delta\delta = +32.5$ ppm). These differences are substantially larger than the change observed upon binding to $\text{B}(\text{C}_6\text{F}_5)_3$ ($\Delta\delta = +26.6$ ppm) and suggest that $\text{Si}(\text{cat}^{\text{F}})_2$ is a stronger Lewis acid toward OPEt_3 than $\text{Si}(\text{cat})_2$ or $\text{B}(\text{C}_6\text{F}_5)_3$, although both silicon complexes induce large changes in ^{31}P NMR chemical shifts upon complexation.

In contrast to the strong Lewis acidity implied by the Guttmann–Beckett analysis with OPEt_3 , $\text{Si}(\text{cat}^{\text{F}})_2$ does not readily bind aldehydes or ketones. The combination of 1 equiv of *trans*-crotonaldehyde and $\text{Si}(\text{cat}^{\text{F}})_2$ resulted in negligible (<2%) conversion to a $\text{Si}(\text{cat}^{\text{F}})_2$ -crotonaldehyde adduct (assessed by ^1H NMR spectroscopy in dichloromethane- d_2). This suggests that $\text{Si}(\text{cat}^{\text{F}})_2$ displays a substantially diminished affinity for “soft” Lewis bases relative to typical boron Lewis acids, which readily coordinate to carbonyl groups.^{2a,11}

Replacing aldehyde moieties with the strongly coordinating amide functional group promoted coordination, and quantitative adduct formation was observed between *N,N'*-diisopropylbenzamide and $\text{Si}(\text{cat}^{\text{F}})_2$ (3, eq 2). Upon binding to either



$\text{Si}(\text{cat}^{\text{F}})_2$ or $\text{B}(\text{C}_6\text{F}_5)_3$, the two N-bound isopropyl groups of the benzamide appear as separate, sharp signals, whereas there is coalescence of these signals in the room temperature ^1H NMR spectrum of the free benzamide.¹² This behavior can be rationalized by invoking strong nitrogen π -donation upon formation of the Lewis acid–base adduct, which slows the exchange of the *E* and *Z* isopropyl groups via rotation about the C(amide)–N bond. In contrast to 1, the parent bis(catecholato)silane complex $\text{Si}(\text{cat})_2$ does not react with *N,N'*-bisdiisopropylbenzamide (by NMR spectroscopy in dichloromethane- d_2 solvent), indicating that the perfluoro derivative displays an enhanced binding affinity for this substrate.

Single crystals of 3 were grown from a mixture of *o*-difluorobenzene and toluene at -30 °C (Figure 2). In comparison to the analogous $\text{B}(\text{C}_6\text{F}_5)_3$ adduct, the C(amide)–O bond of 3 is shorter (1.32(1) vs 1.304(3) Å) and the C(amide)–N bond is longer (1.28(1) vs 1.297(3) Å).¹² The C=O stretching frequency of 3 ($\nu_{\text{CO}} = 1606$ cm^{-1}) is

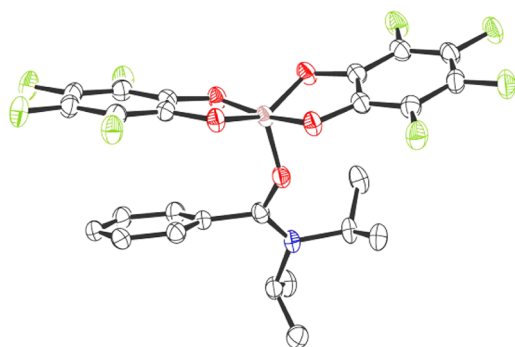


Figure 2. ORTEP diagram of compound 3 with all thermal ellipsoids shown at 50% probability.

intermediate between values for free benzamide and the $\text{B}(\text{C}_6\text{F}_5)_3$ adduct (1625 and 1570 cm^{-1} , respectively). Thus, both bond length and IR spectroscopic comparisons suggest that $\text{B}(\text{C}_6\text{F}_5)_3$ is more activating than 1 toward benzamides.

Hydrosilylation of aldehydes was used to assess the catalytic properties of $\text{Si}(\text{cat}^{\text{F}})_2$. Main-group-catalyzed hydrosilylation is well-known for both neutral and cationic boron Lewis acids.^{2a,13} In contrast, only cationic silylium ions have previously been reported as hydrosilylation catalysts.^{2b,14} These silylium-ion catalyzed carbonyl reductions often result in over-reduction to the deoxygenated hydrocarbon products, rather than the presumed initial silyl ether complex.

Initial studies showed that $\text{Si}(\text{cat}^{\text{F}})_2$ is an efficient catalyst for the hydrosilylation of 4-nitrobenzaldehyde with triethylsilane at room temperature, to exclusively form the corresponding silyl ether product (Table 1, entry 1). In contrast, we found the

Table 1. Hydrosilylation Trials with Neutral Silicon Catalysts^a

entry	catalyst	time (h)	temp (°C)	yield (%)
1	$\text{Si}(\text{cat}^{\text{F}})_2$	0.5	25	>95
2	$\text{Si}(\text{cat})_2$	48	25	2
3	$\text{Si}(\text{C}_6\text{F}_5)_4$	48	45	0

^aReaction conditions: 4-nitrobenzaldehyde (0.30 M), triethylsilane (0.30 M), and catalyst (0.015 M) in dichloromethane- d_2 (0.5 mL).

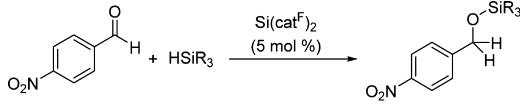
previously reported $\text{Si}(\text{cat})_2$ and $\text{Si}(\text{C}_6\text{F}_5)_4$ complexes to be essentially inactive as catalysts (Table 1, entries 2, 3). To our knowledge, $\text{Si}(\text{cat}^{\text{F}})_2$ represents the first neutral silicon Lewis acid to serve as a catalyst for aldehyde hydrosilylation.

Catalytic amounts of $\text{Si}(\text{cat}^{\text{F}})_2$ also promoted the silylcyanation of 4-nitrobenzaldehyde with trimethylsilylcyanide at 45 °C (eq 3). Previous studies of main group silylcyanation catalysis



typically involve (i) combinations of Lewis acid and Lewis base catalysts, such as the Shibasaki bifunctional aluminum and phosphine oxide system,¹⁵ or (ii) simple Lewis base activators, including fluoride, phosphines, and amines.¹⁶ In the current study, $\text{Si}(\text{cat}^{\text{F}})_2$ behaves as a single component Lewis acid silylcyanation catalyst.

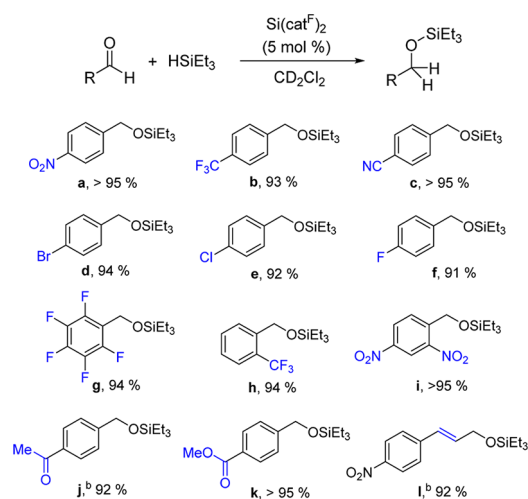
Hydrosilylation catalysis was further evaluated through study of the silane substrate scope (Table 2). Tertiary alkyl and aryl silanes exhibited high activity in hydrosilylations of 4-nitrobenzaldehyde (entries 1–4). Bulky silanes such as triisopropylsilane and bis(trimethylsilyl)phenylsilane were also tolerated (entries 5, 6). In contrast, $\text{B}(\text{C}_6\text{F}_5)_3$ does not react with these sterically demanding substrates, which has been attributed to front strain that prevents silane coordination.^{2b} Silanes incorporating trimethylsiloxy- and dimethylamido- groups were also efficiently transformed (entries 7, 8). Secondary silanes underwent hydrosilylation in low conversion (entry 9), and the primary silanes surveyed (H_3SiPh and $\text{H}_3\text{Si}^t\text{Bu}$) were completely inactive.

Table 2. Silane Scope for Hydrosilylation Catalysis^a


entry	silane	time (h)	yield (%)
1	HSiPh ₃	1	94
2	HSiPh ₂ Me	0.5	>95
3	HSiPhMe ₂	0.5	>95
4	HSi ^t BuMe ₂	0.5	91
5	HSi ⁱ Pr ₃	0.5	>95
6	HSi(SiMe ₃) ₂ Ph ^b	1	93
7	HSi(OSiMe ₃) ₂ Me	0.5	>95
8	HSi(NMe ₂) ₂ Me	0.5	92
9	H ₂ SiPhMe	2	42

^aReaction conditions: 4-nitrobenzaldehyde (0.30 M), silane (0.30 M), and **1** (0.015 M) in CD₂Cl₂ at 25 °C. Yields were determined by ¹H NMR integration relative to an internal standard. ^b45 °C.

A variety of benzaldehydes were investigated for conversion to the corresponding silyl ethers (Scheme 1). Electron-deficient

Scheme 1. Hydrosilylation Aldehyde Scope^a

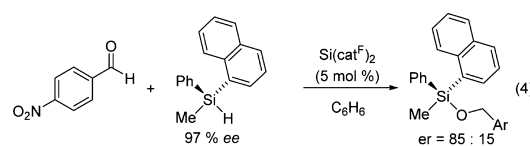
^aReaction conditions: aldehyde (0.30 M), triethylsilane (0.30 M), and **1** (0.015 M) in CD₂Cl₂ at 25 °C. Yields were determined by ¹H NMR integration relative to an internal standard. ^b0.45 M HSiEt₃.

aldehydes were required for productive catalysis. The nitrile functional group was tolerated (entry c), whereas many Lewis acid catalysts, notably B(C₆F₅)₃, are inactive in the presence of these strongly coordinating groups.^{2b} No inhibitory effect was observed for *ortho* substituents (entries h, i). Aldehydes were selectively and exclusively hydrosilylated in the presence of ketones and esters (entries j, k). Lastly, an electron-deficient cinnamaldehyde derivative underwent exclusive 1,2-addition (entry l).

In order to distinguish between possible mechanistic pathways, experiments were performed to determine whether Si(cat^F)₂ binds to and activates the aldehyde or silane substrate during hydrosilylation catalysis.¹⁷ No changes were observed in the ¹H NMR spectrum of HSiEt₃ upon addition of Si(cat^F)₂ (in dichloromethane-*d*₂). Previous work by the Piers and Bergman groups has cited loss of *J*_{HH} coupling between the Si–H and CH₂ protons of silicon-bound alkyl groups as evidence for the intervention of a transient Lewis acid adduct.^{2b,18} Additionally,

no scrambling occurred between a 1:1 mixture of HSiPhMe₂ and DSiPh₂Me upon treatment with 10 mol % Si(cat^F)₂ in dichloromethane-*d*₂. Attempts to observe hydrosilylation of alkenes or silylation of phenols with catalytic Si(cat^F)₂ were unsuccessful. In contrast, B(C₆F₅)₃, which is known to operate via a silane activation mechanism, is efficient for these catalytic transformations.^{2d,19} Taken together, these observations suggest that Si(cat^F)₂, unlike B(C₆F₅)₃, does not bind to the silane substrate during catalysis.

An optically active silane substrate was employed to provide further mechanistic insight. Analogous enantiospecificity studies have been reported as evidence for the silane coordination mechanism operative for B(C₆F₅)₃ and transition metal catalysts.²⁰ Reactions were performed with 5 mol % Si(cat^F)₂ for the hydrosilylation of 4-nitro-benzaldehyde with enantiopure *R*-(+)-methyl-(1-naphthyl)phenylsilane²¹ to furnish the silyl ether product in 95% yield (eq 4). The reaction proceeded with

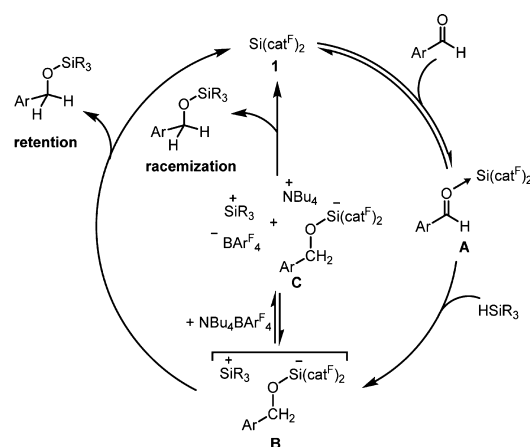


predominant stereochemical retention; however, the enantiomeric excess was highly dependent on solvent polarity, with increased racemization in more polar media (70% ee in benzene, 40% ee in *o*-dichlorobenzene, and 12% ee in dichloromethane).

To investigate the decrease in enantiospecificity, studies were performed in the presence of tetrabutylammonium tetrakis-(pentafluorophenyl)borate, NBu₄BAR^F₄. Salt effects on organic S_N1 reactions have provided insight into ionic dissociation steps, typically in polar solvents;²² however, there are fewer examples of salt effects in nonpolar solvents.²³ For the hydrosilylation shown in eq 4, the addition of NBu₄BAR^F₄ had a deleterious effect on the enantiospecificity (26% ee in the presence of 150.0 mM NBu₄BAR^F₄, compared to 70% ee in the absence of salt).

A proposed mechanism that accounts for the predominant stereochemical retention, as well as the observed solvent and salt effects, is shown in Scheme 2. The aldehyde first coordinates to Si(cat^F)₂ (**A**), which is followed by hydride transfer from the silane substrate to the activated aldehyde. We suggest that this leads to a silylium alkoxy silicate intimate ion pair intermediate (**B**) that can undergo rapid silicon–oxygen bond formation, with

Scheme 2. Proposed Hydrosilylation Mechanism



displacement of the catalyst, within the ion pair prior to silylium rotation, resulting in stereochemical retention. Loss of stereospecificity is caused by the formation of a solvent separated ion pair or ion aggregate (C), which is favored in more polar solvents or upon increasing salt concentration. An alternative mechanism featuring a four-membered cyclic transition state has been proposed for related silane additions to activated carbonyls.²⁴ This concerted, asynchronous addition should afford complete stereochemical retention and is inconsistent with the observed racemization under more polar conditions. For comparison, a catalytically competent silane–Si(cat^F)₂ adduct should lead to inversion in the major product,^{20a} allowing us to exclude this possible mechanism.

In conclusion, bis(perfluorocatecholato)silane (1) was prepared, and reactions to assess its Lewis acidity were investigated. Coordination of fluoride, triethylphosphine oxide, and *N,N'*-diisopropylbenzamide demonstrate the ability of Si(cat^F)₂ to bind several common classes of Lewis bases. Additionally, hydrosilylation and silylcyanation of electron-deficient aldehydes were catalyzed by Si(cat^F)₂ under mild conditions. A stereogenic silicon substrate was employed in combination with solvent and salt effect studies to provide evidence for a carbonyl activation mechanism involving an ionic intermediate. We hope that future work will expand upon the use of neutral, yet potent, silicon Lewis acids in catalytic transformations.

■ ASSOCIATED CONTENT

Supporting Information

Additional experimental information, characterization, X-ray crystallographic details, and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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