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Communication

Metal free mild and selective aldehyde cyanosilylation by a neutral penta-coordinate silicon compound⁺

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This study demonstrates the preparation and structural characterization of a Si(IV) hydride (PhC(NtBu)₂SiH(CH₃)Cl) (1) and its use as a catalyst for cyanosilylation of a variety of aldehydes. Compound 1 represents the first neutral penta-coordinate silicon(IV) species that catalyzes cyanosilylation of aldehydes under mild condition.

The use of neutral compounds with heavier *p*-block elements as single site catalysts is rapidly expanding for metal free hydroboration reactions.¹⁻¹² Cyanosilylation of aldehydes is amongst the most important strategies for the C-C bond formation and protection of alcohol functionality. There has been also an increased interest in nonmetallic catalytic systems for cyanosilylation of aldehydes.¹³ However, only a handful of well-defined neutral heavier main group compounds has been utilized as single site cyanosilylation catalyst (Scheme 1). Nagendran et al. reported a Ge(II) cyanide (A) for silvlcvanation of three aldehydes (R= iPr, Et, and CH(Ph)CH₃).¹⁴ Bergman and Tilley have demonstrated bis(perfluorocatecholato)silane $[Si(cat^{F})_{2}]$ (B) can promote the cyanosilylation of 4-nitro-benzaldehyde.¹⁵ Recently, the groups of Zhi, Parameswaran, and Roesky introduced a well-defined Al(III) hydride catalyst [(LAIH(OSO₂CF₃)) (L=HC(CMeNAr)₂, Ar=2,6- $iPr_2C_6H_3$), (**C**) and its derivatives for cyanosilylation of a range aldehydes and ketones.^{1,16} Among heavier *p*-block elements, catalysis with silicon compounds seems to provide many opportunities because silicon is the (a) isostere of carbon, (b) non-metal, (c) silicon precursors are inexpensive, and (d) the second most earth abundant element. Despite these priori favorable attributes as well as impetus from the theoretical studies,¹⁷ neutral well-defined silicon Lewis acids are relatively rare^{5,18,19} and largely confined to silylium ions²⁰ and metallosiloxanes.²¹ Here, we report the synthesis of a

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Si(IV) hydride (PhC(NtBu)₂SiH(CH₃)Cl) (1) using amidinato ligand and explored its potential as a catalyst for cyanosilylation of a variety of aldehydes at room temperature. To the best of knowledge, this is the first example of a neutral penta-coordinate Si(IV) compound that catalyzes aldehyde cyanosilylation.

Germanium(II) cyanide catalyzed: Nagendran, 2014¹⁴



Neutral Silicon(IV) compound catalyzed: Bergman and Tilley, 2015¹⁵



Aluminum hydride catalyzed: Zhi, Parameswaran, and Roesky, 2015



Scheme 1. Previous approaches towards cyanosilylation of aldehydes and ketones by single component neutral heavier main group catalysts.

Following the synthetic protocol that has been used for the preparation of $(PhC(NtBu)_2SiCl_3)^{22a}$ or $(PhC(NtBu)_2SiHCl_2)^{,22b}$ we reacted MeSiHCl₂ with *tert*-butyl carbodiimide and phenyl lithium to obtain $(PhC(NtBu)_2SiH(CH_3)Cl)$ (1) (Scheme 2). Compound 1 was crystallized in orthorhombic space group $P2_1$ and the selected bond lengths and angles are given in the legend of the Figure 1.²³ 1 exhibits an approximate trigonal bipyramidal geometry at the silicon atom. The Si–C bond is 1.852(8) Å in length, which is in good agreement with the previously reported Si–C single bonds.²⁴ The Si–H bond length

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[†]Dedicated to Professor K. C. Kumara Swamy on the occasion of his 60th birthday Experimental Details, single crystal X-ray data, and representative NMR spectra are given in the supporting information. CCDC Nos. are 1543755 (1) and 1543756 (Int-1). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.co.uk/data_request/cif.

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is of 1.350(7) Å, which is same to that in the previously reported LSiCl(H)N(H)-N=CPh₂ [L=PhC(NtBu)₂] [1.350 Å].²⁵ A resonance at δ 6.33 ppm at the ¹H NMR spectrum of **1** corresponds to Si–H protons. The five coordination of the Si atom is mirrored at the ²⁹Si NMR spectrum, which shows a resonance at δ –80.66 ppm. The IR spectrum of **1** shows an absorption band at 2160.70 cm⁻¹ corresponding to the Si–H bond. The molecular ion peak was observed at *m/z* 310 with the highest relative intensity.

also selectively cyanated under the regular conditions. These indicate that the catalytic system selectively activates the carbonyl function and keeps the heterocycles intact. Aldehydes were selectively and exclusively cyanosilylated in the presence of acid (2q), amide (2o) and ester (2p). Similar to A and B, the cyanosilylation of the ketones using 1 was not successful, which can be attributed to the higher coordination and sterics around the silicon atom.



Scheme 2. Preparation of Catalyst 1.

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Figure 1. Molecular structure of 1. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except H1 bonded to Si1) are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Si1–H1 1.35(7), Si1–Cl1 2.365(2), Si1–C16 1.852(8); N1–Si1–C16 118.0(3), N2–Si1–N1 69.7(3), C16–Si1–N2 97.7(3), N1–Si1–Cl1 100.9(2), C16–Si1–Cl1 94.5(3), N2–Si1–Cl1 167.1(2).

Next, we attempted the reaction of benzaldehyde with Me₃SiCN in a catalytic process using 1 (Scheme 3). Initial studies showed that 1 is an efficient catalyst for the cyanosilylation of benzaldehyde with Me₃SiCN at room temperature, to give the corresponding cyanosilylated product in 83% yield (Scheme 4, entry 2a) in 6 hrs using 3 mol% of the catalyst. This reaction does not proceed without the catalyst. We have also examined the reaction using $MeSiHCl_2$ (10 mol%) as a catalyst instead of 1 but no reaction took place even after prolonged heating. Scheme 4 shows the results of cyanosilylation experiments with a variety of aldehydes under optimal conditions of 3 mol% catalyst at room temperature with a 6 h reaction time. Aldehydes with electron-donating substituents were required for productive catalysis. Halogenated benzaldehydes can be converted to the cyanosilylated products and no σ -bond metathesis between the halogen moiety and Me₃SiCN was observed (entry 2c-2f). It should be noted that α, β -unsaturated carbonyl such as cinnamaldehyde was predominantly converted to the 1,2adducts, leaving the olefinic functionality intact (entry 2i). No conjugated addition product was observed. 1-Naphthaldehyde (entry 2I) and heteroaromatic aldehydes such as pyridyl 4carbaldehyde (entry 2j) and 2-fulfuraldehyde (entry 2k) were



Scheme 3. Silicon(IV) hydride mediated cyanosilylation of aldehydes

Scheme 4. Cyanosilylation aldehyde scope^{a,b}



^aReaction conditions: 3 mol% catalyst, 6h reaction at room temperature in benzene.
^bYields were determined by NMR spectroscopy on the basis of the consumption of the aldehyde. ^cheating at 55 °C.

Next, we sought to investigate the mechanism of the reaction. Previously, the groups of Yang, Parameswaran, and Roesky theoretically calculated the catalytic cycle for cyanosilylation of aldehydes and ketones by **C**, however, no intermediate was isolated.¹ Zhi et al. reported that the initial step is the donation of electron density from the N atom of the CN group, followed by the insertion of the C=O functionality into the Si–C bond of Me₃SiCN. However, the activation barrier was reported to be 32 kcal/mol. Moreover, we reasoned that as the Si atom in **1** is penta-coordinate, it would be difficult to accommodate an added Lewis base on silicon.

Penta-coordinate silicon compound as a catalyst is of interest in connection with mechanistic studies. Corriu, Tacke, and others suggested that nucleophilic substitution at the silicon atom in R_3SiX compounds can be driven by nucleophiles.^{13e,26}

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Monitoring a 1:1 mixture of Me₃SiCN and 1 in CDCl₃ at room temperature by ¹H NMR spectroscopy, there is a development of a new SiMe $_3$ peak at δ 0.05 with concomitant disappearance of the Me₃SiCN protons (δ 0.36 ppm). Similarly, the Si–*H* proton shifted upfield (δ 5.29 ppm) than that of **1**. The ²⁹Si NMR spectrum (in CDCl₃) exhibits new signals at δ 32 ppm reflecting the formation of Me₃SiCl during the reaction. The five coordination number of silicon is indicated by another $^{29}\text{Si-NMR}$ signal at δ –113.18 ppm, which is significantly highfield shifted with respect to that of 1 and thereby rules out the possibility of formation of any silylium ion, which usually appears in the downfield region.²⁷ Further, the IR spectrum of the mixture showed a new CN stretching band at 2189 cm⁻¹, different from 1. Taken together, these data reveal that a metathesis reaction between 1 and TMSCN took place and suggest the possible formation [LSi(H)(CH₃)CN] (Int-1) with the simultaneous liberation of Me₃SiCl.



Scheme 5. Conceivable mechanisms for amidinato silane catalyzed cyanosilylation.

The formation of **Int-1** was further confirmed by single crystal X-ray diffraction studies (Figure 2).²³ The structural features of **Int-1** are similar to those in **1**. The Si atom adopts distorted trigonal bipyramidal geometry. C17, N2, and H1 reside at the equatorial position whereas N1 and C16 occupy the axial position with an N1-Si1-C16 bond angle of 166.6(3)°. The Si–Me bond length is similar [1.845(7) Å] to that in **1**, however, the Si–H bond length [1.50(4) Å] has been increased while compared to that of **1** indicating a more electropositive Si(IV) center. The Si–CN bond length is of 1.960(8) Å, which is longer than the usual Si–C single bond presumably due to the sp-hybridization of the C atom. The C=N bond length 1.15(1) Å, which is about the same as in most free isocyanides (1.14 to 1.16 Å).^{28,29}

Based on our observations, a plausible mechanism for this cyanosilylation of aldehydes with **1** is shown in Scheme 5. Initially, **1** was transformed to **Int-1** by σ -bond metathesis reaction between **1** and Me₃SiCN along with the formation of Me₃SiCl. The **Int-1** contains a long Si–CN bond and the N_(amidinate) \rightarrow Si bond reduces the electrophilicity of the Si atom and enhances the cleavage tendency of the Si–CN bond. Consequently, **Int-1** reacts with aldehydes to result in the

alkoxy derivative (Int-2) with the simultaneous migration of the CN substituent from the Si atom to the C atom. The formation of Si-O bond in Int-2 may be attributed to driving this step. Finally, the alkoxides undergo σ -bond metathesis reaction with Me_3SiCl to result in cyanosilylated products and regenerate the catalyst. The conversion of Int-2 to the final cyanosilylated product was found to be favourable by 1.9 kcal/mol (ΔG value) [for further details, please see the Supporting Information (SI) file]. In order to check the formation of Int-2, we have performed the NMR tube reaction of Int-1 with benzaldehyde. The ¹H NMR spectrum indicates the formation of **Int-2** as a new resonance appeared at δ 5.11 ppm, while the Si–H proton exhibits a resonance at δ 6.24 ppm. However, the reaction mixture was accompanied by the formation of few undesired products that could not be characterized. In fact, the reaction product of Int-1 with benzaldehyde was only obtained as oily deposits containing significant amounts of impurities and all efforts to obtain a pure sample of Int-2 failed. The ²⁹Si NMR spectrum of the reaction mixture is not very conclusive as it shows two new resonances at δ -70.87 and -74.21 ppm indicating the formation of Int-2 along with an undesired penta-coordinate silicon compound.



Figure 2. Molecular structure of Int-1. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms (except H1 bonded to Si1) are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Si1–H1 1.50(5), Si1–C16 1.960(8), Si1–C17 1.845(7), Si1–N1 1.970(5), Si1–N2 1.802(5), C16–N3 1.15(1); N2–Si1–C16 99.3(3), N2–Si1–N1 69.2(2), N2–Si1–C17 119.6(3), C17–Si1–C16 94.8(3), C17–Si1–N1 97.0(3), C16–Si1–N1 166.6(3), Si1–C16–N3 168.5(7).

In summary, we have developed cyanosilylation of aldehydes promoted by a simple amidinato silane, **1**. The first step of the catalytic cycle is the nucleophilic substitution at the silicon center in **1** leading to the formation of $(PhC(NtBu)_2SiH(CH_3)CN)$ (Int-1). Both **1** and Int-1 were structurally characterized. As the elimination of halosilane kicks start the catalytic cycle, this approach will motivate to use halogenated silicon compounds as catalysts for other organic transformations. Additional notable features of the reaction are the utilization of simple neutral silicon(IV) compound as a catalyst, mild and convenient experimental procedure.

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