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Nucleophile induced ligand rearrangement reactions of alkoxy- and arylsilanes

Jamie H. Docherty [a, **], Andrew P. Dominey [b], Stephen P. Thomas [a, *]

[a] EaStCHEM School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh EH9 3FJ, UK
[b] GSK Medicines Research Centre, Gunnels Wood Road, Stevenage, Hertfordshire SG1 2NY, UK

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ABSTRACT

The ligand-redistribution reactions of aryl- and alkoxy-hydrosilanes can potentially cause the formation of gaseous hydrosilanes, which are flammable and pyrophoric. The ability of generic nucleophiles to initiate the ligand-redistribution reaction of commonly used hydrosilane reagents was investigated, alongside methods to hinder and halt the formation of hazardous hydrosilanes. Our results show that the ligand-redistribution reaction can be completely inhibited by common electrophiles and first-row transition metal pre-catalysts.

1. Introduction

Hydrosilanes are a highly important class of reagent used in widespread applications from organic synthesis to polymer production [1,2]. The formation of carbon-silicon bonds by olefin hydrosilylation constitutes one of the largest applications of homogeneous catalysis with the silicones industry forecast to be worth $18 billion per annum by 2021 (Scheme 1, **a**) [3]. Predominantly these reactions have been achieved using platinum-based catalysts, however Earth-abundant alternatives have emerged [4]. The utility of hydrosilane reagents has been further exemplified by their use in other reductive transformations; such as the hydrogen-atom transfer mediated reductive functionalisation of alkenes (Scheme 1, **b**) [5], carbonyl reduction [6] and nitro-group reduction [7].

While hydrosilane reagents show a wide breadth of reactivity in reductive transformations, they have often been observed to undergo ligand-redistribution reactions (Scheme 1, **c**) [8]. Most commonly ligand-redistribution reactions of arylsilanes have been observed using metal complexes as catalysts; including: Ir [9], Pd [10], Sm [11], Mo [12], Co [13], Ti [14], Yb [15] and Ru [16]. Similarly, a number of hydride sources, including $LiAlH_4$, KH and NaH, have proven effective towards ligand-redistribution [17]. The common feature in all ligand-redistribution reactions of phenylsilane is the formation of a mixture of products containing: diphenylsilane, silane (SiH_4) and triphenylsilane.

Hu has shown that stable alkoxy-hydrosilane reagents can be used as surrogates to access volatile and challenging to handle alkyl-hydrosilanes (Scheme 1, **d**) [18]. Using this method, olefin hydrosilylation could be used to access primary hydrosilane products that would have normally required the use of gaseous hydrosilane reactants.

Given that silane (SiH_4, b.p. $\rightarrow$112 °C) [19], methylsilane ($MeSiH_3$, b.p $\rightarrow$57 °C) [20] and dimethylsilane (Me_2SiH_2, $\rightarrow$20 °C) [21] are hazardous, flammable and pyrophoric gases, the use and generation of these reagents presents a safety concern [22]. Importantly Hu has shown that while ligand-redistribution occurs when using alkoxy-hydrosilanes in the presence of NaO^tBu, there was no build-up of hazardous gaseous alkyl-hydrosilanes in the presence of the nickel-catalyst [18]. Similarly, Thomas, and others, have made use of alkoxide salts to enable pre-catalyst activation for a range of reductive functionalisation reactions using Earth-abundant metals with no build-up or formation of hazardous gases under the catalytic reaction conditions [23].

* Corresponding author.
** Corresponding author.
E-mail addresses: jdocher5@ed.ac.uk (J.H. Docherty), stephen.thomas@ed.ac.uk (S.P. Thomas).

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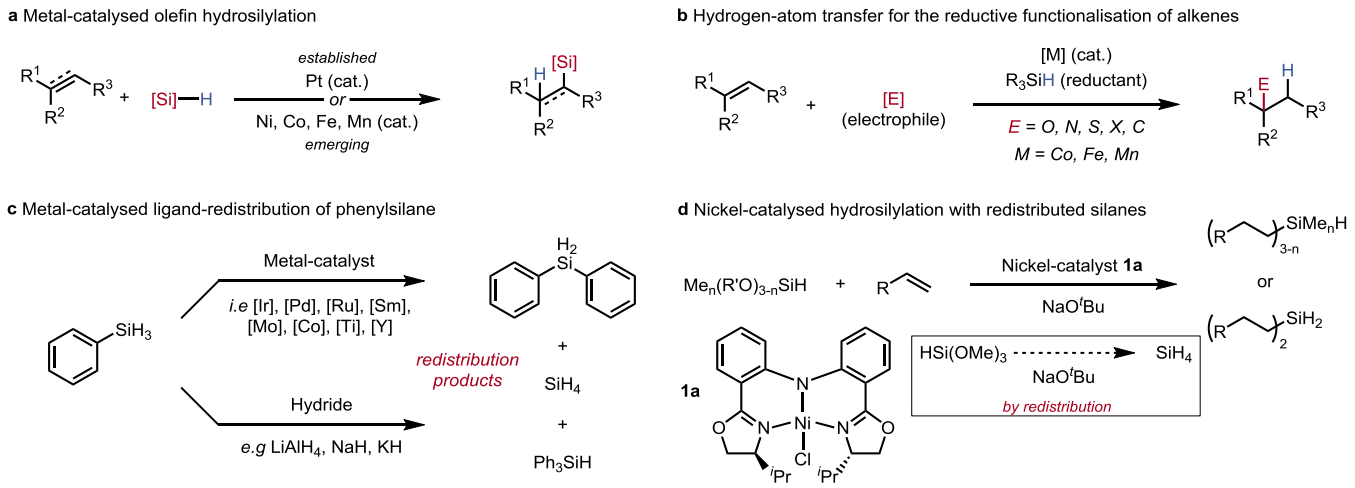


Scheme 1. Utility of silane reagents in modern synthetic chemistry. **a** Metal-catalysed hydrosilylation of alkene or alkynes. **b** Reductive functionalisation of alkenes by hydrogen atom transfer. **c** Ligand-redistribution reaction of phenylsilane to diphenylsilane, silane and triphenylsilane. **d** Use of ligand-redistribution as *masked* hazardous silanes.

2. Results and discussion

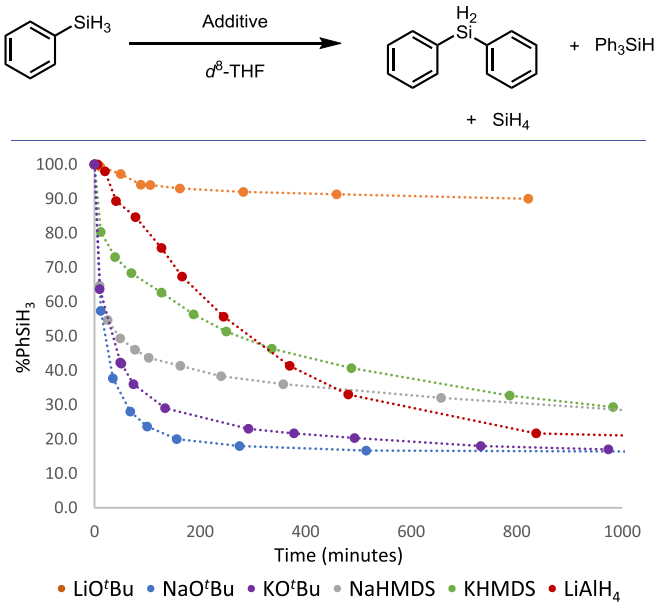
These precedents prompted us to consider the factors important to hydrosilane ligand-redistribution reactions. One important question was whether any generic nucleophile could be used to initiate ligand-redistribution. In answering this possibility we selected phenylsilane as a test substrate in combination with various nucleophiles (Fig. 1). Using ^{1}H NMR, the reaction progress of the ligand-redistribution reaction could be directly monitored. Lithium *tert*-butoxide proved to be a slow initiator for the reaction, only achieving 10% conversion after 13 h. Lithium aluminium hydride displayed significantly better reactivity, and steadily converted phenylsilane to a mixture of diphenylsilane, silane and triphenylsilane over the course of *ca.* 17 h to 80% total conversion. Hexamethyldisilazide (HMDS) anions of both sodium and potassium reacted faster than both previous reagents, but achieved less overall conversion, plateauing at *ca.* 70%. Sodium- and potassium *tert*-butoxide demonstrated the best reactivity towards the ligand-redistribution reaction, both showing the fastest rate of reaction and highest conversion. Reaction profiling of all components of the reaction mixture containing phenylsilane and sodium *tert*-butoxide (5 mol%) showed concomitant consumption of phenylsilane and formation of silane and diphenylsilane. The latter is subsequently consumed as triphenylsilane is formed (Fig. 1, bottom).

Additionally we tested a range of alkoxy-hydrosilane reagents in combination with sodium *tert*-butoxide to both assess the rate of ligand-redistribution and identify the products of these reactions (Scheme 2). Methyldiethoxysilane underwent ligand-redistribution to quickly generate methylsilane and methyltriethoxysilane. The analogous dimethylethoxysilane reacted to form dimethylsilane and dimethyldiethoxysilane. Triethoxysilane rapidly underwent redistribution to form silane and tetraethoxysilane. Tetramethyldisiloxane (TMDS) reacted significantly slower to give a complex mixture of products, as observed by ^{1}H and ^{29}Si NMR, with dimethylsilane being one component of the mixture. 1,1,1,3,5,5,5-Heptamethyltrisiloxane (MD'M) slowly decomposed to an unidentifiable mixture of silicon containing products. The prevailing reactivity across all alkoxy-hydrosilanes examined is suggestive of a general pathway towards the entropically favoured gaseous alkyl-hydrosilanes (or silane). The general reactivity trend observed was: $(EtO)_3SiH > Me(EtO)_2SiH > Me_2(EtO)SiH > PhSiH_3 > Me_2SiHOSiHMe_2 > (Me_3SiO)_2MeSiH$.

The absence of a build-up of alkyl-hydrosilane gases in metal-catalysed hydrosilylation suggested that the presence of an electrophile, or electrophilic metal complex, may hinder, or retard, the formation of these hazardous species. We therefore investigated whether common electrophiles could inhibit the ligand-redistribution reaction (Fig. 2). By adding the electrophile after the nucleophile, the initiator of hydrosilane redistribution, any subsequent reactivity could be monitored to assess whether ligand-redistribution had stalled. In separate reactions, the ligand-redistribution of phenylsilane initiated by NaO^{t}Bu was monitored by ^{1}H NMR to which an electrophile was added after 10 min. The standard reaction, without any added electrophile, displayed *ca.* 40% conversion after 10 min and continued to a plateau at *ca.* 84% conversion after 7 h. However, when benzaldehyde was added, 10 min after initiation, the ligand-redistribution reaction was completely retarded and the conversion of phenylsilane at each subsequent time point was equivalent to that observed at 10 min (Fig. 2, •).

The addition of ethyl benzoate produced the same observation, with complete cessation of ligand-redistribution (Fig. 2, •). The addition of either a cobalt(II) dichloride complex (^{Et}BIPCoCl$_2$) or iron(II) dichloride complex (^{Et}BIPFeCl$_2$) proved similarly effective at inhibiting the ligand-redistribution reaction (Fig. 2,•,•) [24]. Addition of acetonitrile showed some retardation activity, with a significantly lower observed rate of reaction when compared to the control reaction with no added acceptor (Fig. 2, •).

To gain insight into these processes we opted to assess the effect of the nucleophile on the rate of the reaction. Specifically we questioned if a variation of the nucleophile loading showed any rate change in the ligand-redistribution reaction of phenylsilane. Using sodium *tert*-butoxide as the nucleophile we monitored the reaction progress using different loadings (2.5, 3.75 and 5 mol%, Fig. 3, **a**). The kinetic data obtained showed similar patterns of reactivity to that obtained when using other nucleophiles (Fig. 1). On changing the loading, or concentration, of sodium *tert*-butoxide there was a slight but noticeable change in the rate of reactions whereby increased loading of sodium *tert*-butoxide led to increased rates of ligand-redistribution. Taking these results we could use the graphical variable time normalisation analysis method (VTNA) reported by Burés to determine the reaction order in [NaO^{t}Bu] [25]. The normalized time scale directly uses reaction profile kinetics adjusted for t[NaO^{t}Bu]^n on the x-axis, where t represents time and n is the order in sodium *tert*-butoxide. When $n = 0.5$, overlay between all reaction profiles was found suggesting that the order with



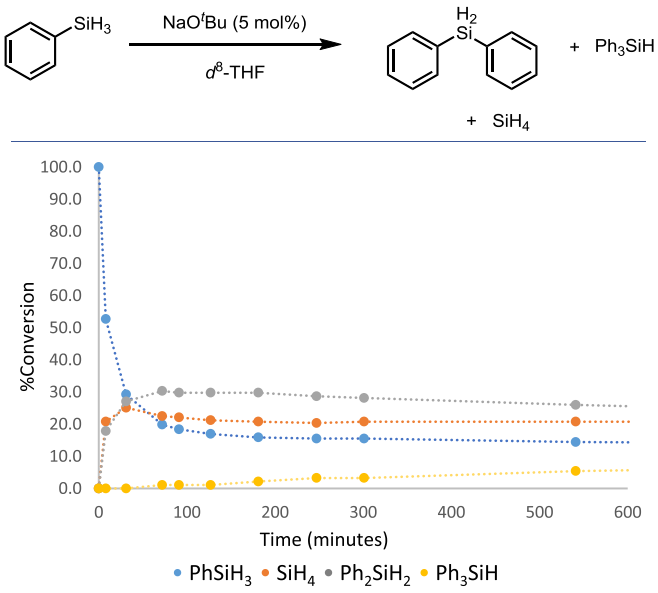
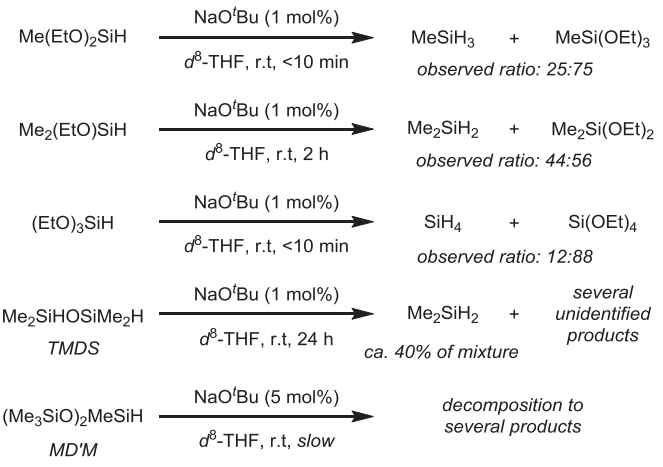


Fig. 1. Ligand-redistribution reaction of phenylsilane with various nucleophiles, monitoring consumption of $PhSiH_3$ (top). Reaction conditions: $PhSiH_3$ (0.4 mmol), additive (2.5 mol%) in d^8-THF (0.8 M). Monitoring formation of distribution products over time (bottom). Reaction conditions: $PhSiH_3$ (0.4 mmol), NaO^tBu (5 mol%) in d^8-THF (0.8 M). Mass balance <100% due to gas loss. Conversions are relative to $PhSiH_3$.



Scheme 2. Redistribution of various alkoxysilanes with NaO^tBu. General reaction conditions: alkoxysilane (0.4 mmol), NaO^tBu (1–5 mol%) in d^8-THF (0.8 M). Products identified by ^1H and ^{29}Si NMR. Observed ratios of products in solution, not accounting for gas dissolution.

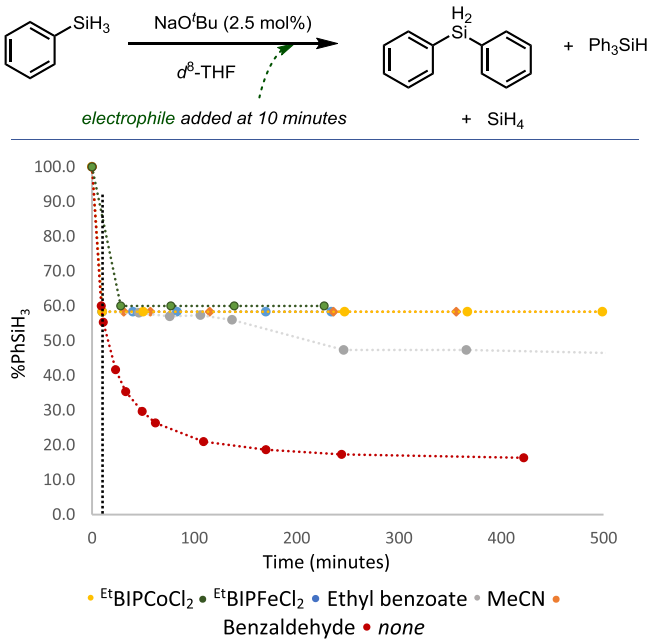


Fig. 2. Ligand-redistribution reaction of phenylsilane with NaO^tBu retarded by added hydride acceptors. Reaction conditions: $PhSiH_3$ (0.4 mmol), NaO^tBu (2.5 mol%) in d^8-THF (0.8 M) and hydride acceptor added at 10 min, denoted by dashed black line.

respect to sodium *tert*-butoxide is 0.5 (Fig. 3, **b**). The same process suggested an order with respect to the concentration of phenylsilane of 2 (Fig. 3, **c**, **d**).

3. Conclusions

In summary, nucleophiles such as alkoxides, hydrides and nitrogen-based anions serve as good initiators of the ligand-redistribution reaction of hydrosilane reagents. Phenylsilane readily underwent ligand-redistribution to form silane, diphenylsilane and triphenylsilane, with the latter formed at a significantly slower rate. Alkoxy-hydrosilanes favoured ligand-redistribution to the corresponding alkyl-hydrosilanes. Significantly, the addition of electrophiles or metal pre-catalysts to these reactions resulted in the cessation of ligand-redistribution. These strategies may hold promise for use in the safe application and handling of hazardous hydrosilane reagents from more stable surrogate hydrosilanes.

4. Experimental section

4.1. General

Reaction setup: All reactions were performed in oven (185 °C) and/or flame dried J-Youngs NMR tubes under an atmosphere of anhydrous argon. All glassware was cleaned using base (KOH, ^{i}PrOH) and acid (HCl_{aq}) baths. All reported reaction temperatures correspond to ambient room temperature, which was

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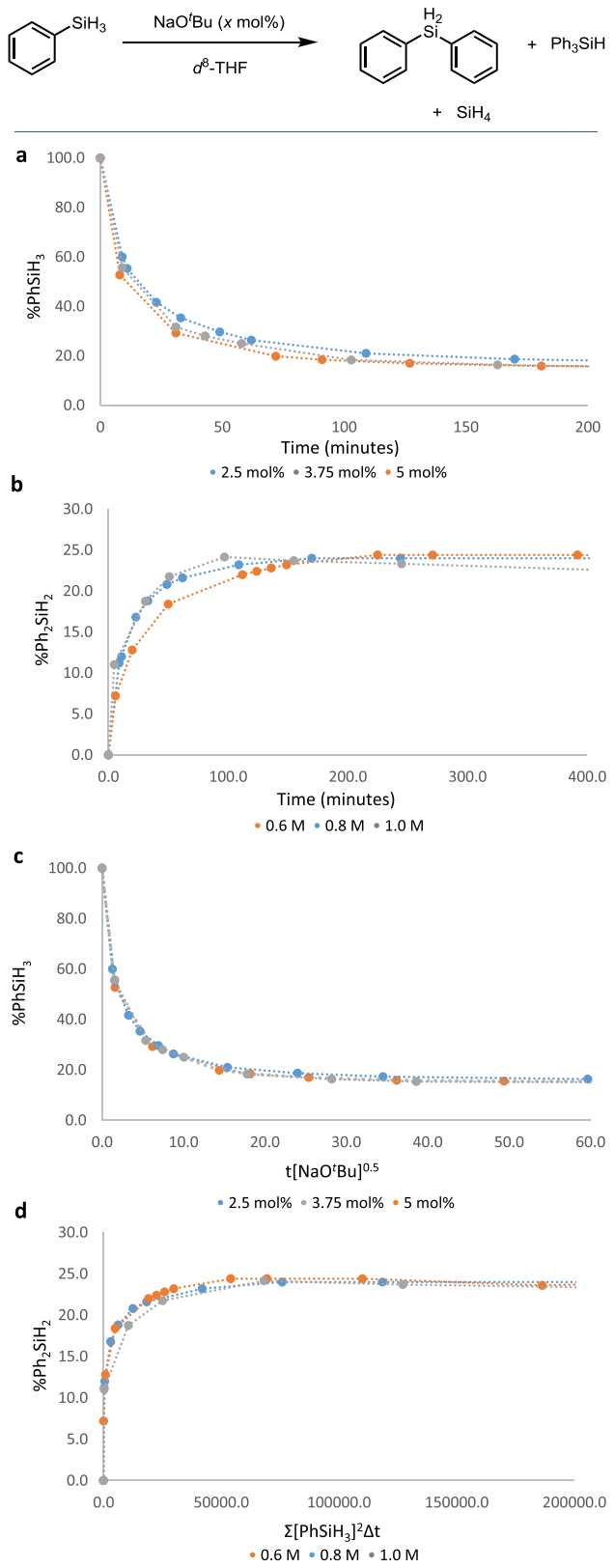

Fig. 3. Ligand-redistribution reaction of phenylsilane with NaO^{t}Bu. **a** Monitoring consumption of $PhSiH_3$ over time with varied loadings of NaO^{t}Bu. Reaction conditions: $PhSiH_3$ (0.4 mmol), NaO^{t}Bu (*n* mol%) in d^8-THF (0.8 M). **b** VTNA *x*-axis normalisation for [NaO^{t}Bu]. **c** Monitoring the formation of Ph_2SiH_2 over time at varied concentration of $PhSiH_3$. Reaction conditions: $PhSiH_3$ (0.4 mmol), NaO^{t}Bu (2.5 mol%) in d^8-THF (*n* M) **d** VTNA x-axis normalisation for [$PhSiH_3$]. Conversions and $\%Ph_2SiH_2$ observed are relative to $PhSiH_3$.

approximately 20 °C.

NMR spectroscopy: ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on Bruker Avance III 400 and 500 MHz; Bruker AVI 400 MHz; and Bruker Avance I 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C NMR spectra were referenced to the residual deuterated solvent peak (d^8-THF: 1.73 ppm). Multiplicities are indicated by s (singlet), t (triplet), q (quartet), sept. (septet). Coupling constants, *J*, are reported in Hertz and rounded to the nearest 0.1 Hz. Integration is provided and assignments are indicated.

The spin-lattice relaxation value (T_1) for $PhSiH_3$ (Si-**H**) in d^8-THF was measured by the standard inversion recovery method with a variable delay (d_1) and found to be 5 s at room temperature [26]. A 50 s delay between acquisitions was used to allow for reliable integrations when monitoring consumption of $PhSiH_3$.

Chemicals: All reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros organics, Tokyo Chemical Industries UK, Fluorochem and Apollo Scientific or synthesised within the laboratory. Sodium *tert*-butoxide (97%) was purchased from Sigma Aldrich (UK).

4.2. Procedures for ligand-redistribution reactions

Reaction monitoring: Ligand-redistribution reactions of phenylsilane were monitored by combination of ^{1}H and ^{29}Si NMR spectroscopy. Relative conversions of phenylsilane were determined by comparison of the overall integration of aromatic protons (7.73–7.27 ppm) to that of phenylsilane ($PhSi\mathbf{H_3}$, 4.21 ppm, s, 3H), diphenylsilane ($Ph_2Si\mathbf{H_2}$, 4.95 ppm, s, 2H) and silane ($Si\mathbf{H_4}$, 3.23 ppm, s, 4H).

General procedure: Hydrosilane (0.4 mmol) was added to d^8-THF (0.5 mL) in a dried J-Youngs NMR tube. Following a vigorous shake, nucleophile (2.5 mol%, 0.01 mmol) was added and the tube sealed, shaken and the NMR spectra quickly recorded. The NMR spectra were subsequently recorded at further time points to obtain overall reaction progress plots.

Safety note: Given the hazardous nature of the gaseous products often formed in these reactions, precautions should be taken when using any hydrosilane reagent, particularly in the absence of electrophile or metal-catalyst or if conducted on a large scale. J-Youngs NMR tubes containing hazardous product hydrosilanes were carefully opened and diluted with ^{i}PrOH (0.5 mL), then NaOH (2 M, 0.5 mL) to destroy remaining hydrosilanes. See also reference [18].

Characterisation: Ligand-redistribution reaction of phenylsilane by NaO^{t}Bu.^{1}H NMR (500 MHz, d^8-THF): 7.73–7.27 (m, 5H, Ar-**H**), 4.95 (s, 2H, $Ph_2Si\mathbf{H_2}$), 4.21 (s, 3H, $PhSi\mathbf{H_3}$), 3.23 (s, 4H, SiH_4). ^{29}Si NMR (99 MHz, d^8-THF): →33.9 ($Ph_2\mathbf{Si}H_2$), →60.6 ($Ph\mathbf{Si}H_3$), →96.2 ($\mathbf{Si}H_4$).

$MeSiH_3$ ^{1}H NMR (500 MHz, d^8-THF): 3.54 (q, $J = 4.6$ Hz, 3H), 0.21 (q, $J = 4.7$ Hz, 3H). ^{29}Si NMR (99 MHz, d^8-THF): →65.7.

Me_2SiH_2 ^{1}H NMR (500 MHz, d^8-THF): 3.80 (sept., $J = 4.0$ Hz, 2H), 0.17 (t, $J = 4.0$ Hz, 6H). ^{29}Si NMR (99 MHz, d^8-THF): →38.5.

SiH_4 ^{1}H NMR (500 MHz, d^8-THF): 3.23 (s, 4H). ^{29}Si NMR (99 MHz, d^8-THF): →96.2.

Values are in good agreement with those previously reported [27].

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