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Formal SiH_4 chemistry using stable and easy-to-handle surrogates

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Monosilane (SiH_4) is far less well behaved than its carbon analogue methane (CH_4). It is a colourless gas that is industrially relevant as a source of elemental silicon, but its pyrophoric and explosive nature makes its handling and use challenging. Consequently, synthetic applications of SiH_4 in academic laboratories are extremely rare and methodologies based on SiH_4 are underdeveloped. Safe and controlled alternatives to the substituent redistribution approaches of hydrosilanes are desirable and cyclohexa-2,5-dien-1-ylsilanes where the cyclohexa-1,4-diene units serve as placeholders for the hydrogen atoms have been identified as potent surrogates of SiH_4. We disclose here that the commercially available Lewis acid tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, is able to promote the release of the Si–H bond catalytically while subsequently enabling the hydrosilylation of C–C multiple bonds in the same pot. The net reactions are transition-metal-free transfer hydrosilylations with SiH_4 as a building block for the preparation of various hydrosilanes.

Our laboratory recently established ionic transfer hydrosilylation as a new strategy in silicon chemistry[1–4]. Cyclohexa-2,5-dien-1-yl-substituted silanes **I** were found to serve as hydrosilane precursors when treated with fluoroarylboron Lewis acids, for example, $B(C_6F_5)_3$ (**1a**, Fig. 1a)[5,6]. This reaction involves two interdependent catalytic cycles. First, borane-mediated hydride abstraction in the bisallylic position[7,8] of **I** releases the silicon-stabilized Wheland complex or benzene-stabilized silicon cation **III** (**I**→**II**→**III**) that eventually collapses to liberate hydrosilane **IV** and one molecule of benzene (**III**→**IV**). The borane Lewis acid then activates the thus-formed hydrosilane **IV**[9] to perform C=X bond hydrosilylation[10–12] through ion pair **VI** (**IV**→**V**→**VI**)[13]. We have already shown that reagents **I** are generally applicable to the hydrosilylation of σ- and π-basic substrates[1,3] and Si–O dehydrogenative couplings[2]. One obvious advantage of this method is the possibility to generate *in situ* the highly flammable Me_3SiH gas from an easy-to-handle liquid.

To assess the limits of this strategy, we became interested in its implementation for the release of monosilane (SiH_4) gas. This smallest member of the hydrosilane family raises particular safety issues because of its highly pyrophoric, explosive and toxic nature[14]. The semiconductor industry has faced several incidents, sometimes fatal, linked to this chemical[15–17], which is intensively used for the growth of silicon thin films and nanowires via various deposition methods[18–23]. Indeed, other than in the semiconductor research field, the danger of handling SiH_4 often results in its banishment from laboratories. The reactivity of SiH_4 in alkene hydrosilylation[24–26], another industrially relevant process, has been poorly investigated. In the 1990s, Itoh and co-workers from the Mitsui Toatsu Chemicals Company developed methods for the transition-metal-catalysed hydrosilylation of alkenes and conjugated dienes with SiH_4[27–31] and, to the best of our knowledge, these few articles and patents are the only experimental work related to hydrosilylation reactions with monosilane (Fig. 1b). Spurred by the intuition that safe and practical alternatives to the direct use of SiH_4 or its generation by disproportionation of hydrosilanes[32,33] would be highly desirable and relevant to several areas of silicon chemistry, we now report our efforts towards achieving this goal. In this Article, we describe the preparation of novel silanes exclusively bearing hydride and/or cyclohexa-2,5-dien-1-yl substituents as potent SiH_4 surrogates. Their manifold use in transition-metal-free catalytic as well as transition-metal-catalysed hydrosilylation is demonstrated (Fig. 1c).

Results and discussion

Synthesis of SiH_4 surrogates. We began by targeting the potential SiH_4 surrogates tetra(cyclohexa-2,5-dien-1-yl)silane (**2a**) and tri(cyclohexa-2,5-dien-1-yl)silane (**2b**) (Fig. 2a). We envisioned their synthesis by reacting $SiCl_4$ or $HSiCl_3$ with a cyclohexa-2,5-dien-1-yllithium reagent[34]. Standard reaction conditions in THF (~1 M) allowed us to obtain **2a** in decent yield, but the same setup was not suitable for the preparation of **2b** in reasonable yield and purity. We were nonetheless able to establish an improved procedure for its synthesis by switching to a nonpolar solvent (*n*-hexane) and lower concentration (0.4 M). Single crystals of **2b** suitable for X-ray diffraction analysis were obtained (see Supplementary Fig. 17 for its molecular structure). We then turned our attention to the preparation of di(cyclohexa-2,5-dien-1-yl)silane (**2c**) (Fig. 2a). We initially applied the procedures elaborated for the syntheses of **2a** and **2b** using dihalosilanes as electrophiles. However, these approaches led to inseparable mixtures of several silicon-containing compounds, including **2c**. This forced us to explore a two-step sequence starting with the reaction of cyclohexa-2,5-dien-1-yllithium with $(EtO)_2SiCl_2$ to afford **3** quantitatively; reductive Si–O cleavage in **3** with diisobutylaluminium hydride (DIBAL-H) furnished **2c** in good yield. It is worth noting that it is possible to handle compounds **2a**–**c** under air, but rearomatization of one of the cyclohexa-1,4-diene moieties occurs if exposed to ambient atmosphere for prolonged periods of time, yielding the corresponding phenyl-substituted surrogates.

To verify whether silanes **2a**–**c** could actually be ‘decomposed’ to SiH_4, their behaviour in the presence of catalytic amounts of $B(C_6F_5)_3$ (**1a**) was monitored by ^1H NMR spectroscopy. Fully substituted **2a** released a hardly discernible amount of SiH_4 and decomposed to an unidentified material instead (Supplementary Fig. 2). However, we found that **2b** reacted smoothly with catalyst **1a** to successively give **2c**, cyclohexa-2,5-dien-1-ylsilane (**2d**) and eventually

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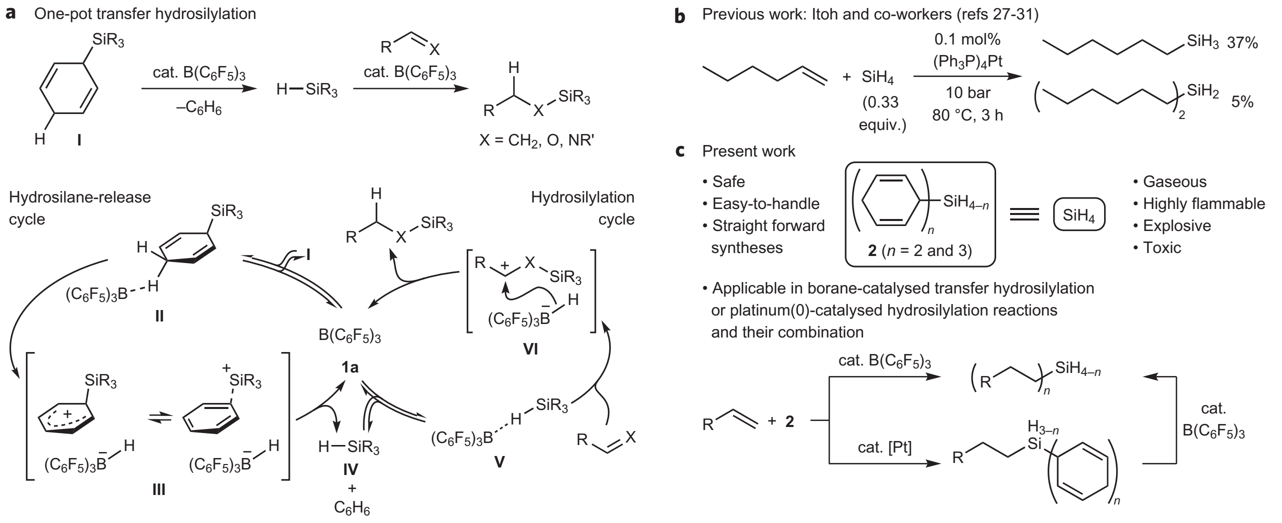


Figure 1 | Transfer hydrosilylation: mechanism and implementation for the release of SiH_4. **a**, The concept of transfer hydrosilylation and its mechanism with R = alkyl, aryl, alkoxy and H. **b**, Direct hydrosilylation with SiH_4. **c**, Cyclohexa-2,5-dien-1-ylsilanes as safe SiH_4 surrogates in metal-free and transition-metal-catalysed hydrosilylations.

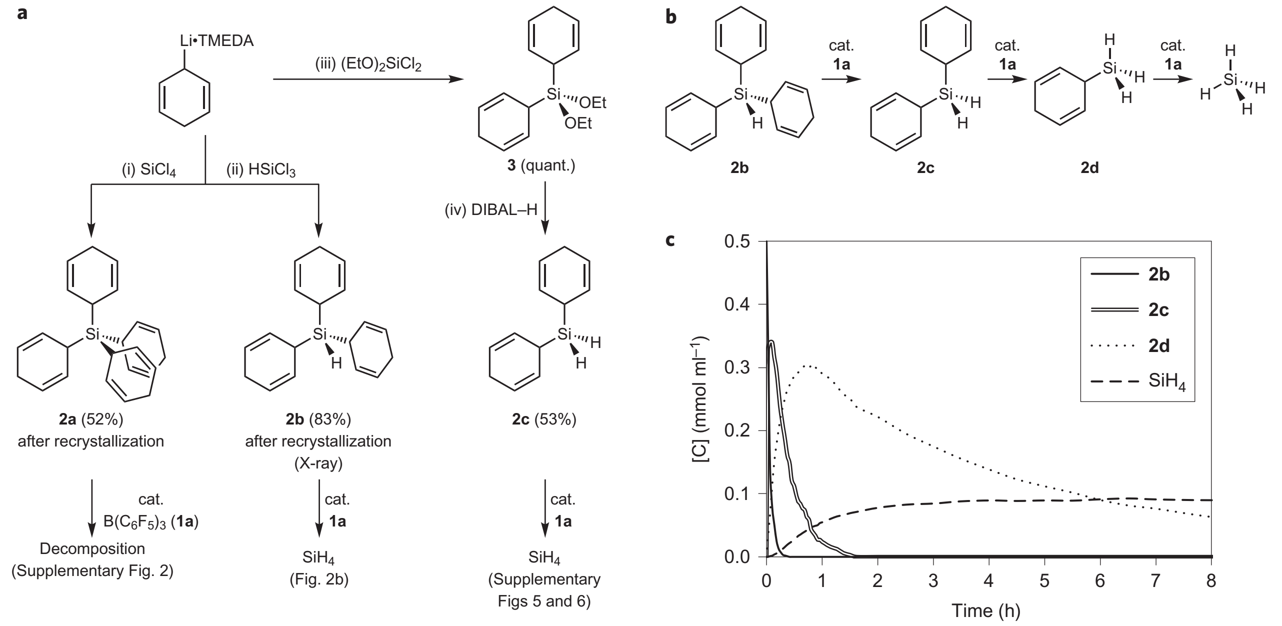
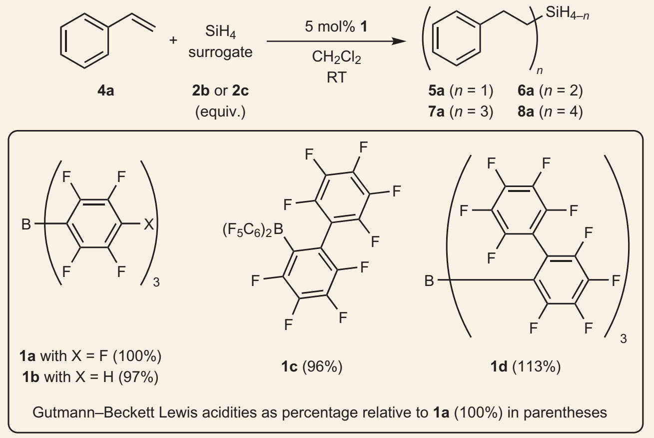


Figure 2 | Syntheses and evaluation of cyclohexa-2,5-dien-1-ylsilanes 2a–c as potential SiH_4 surrogates. **a**, Reactions of lithiated cyclohexa-1,4-diene with various silicon electrophiles allow the preparation of cyclohexa-2,5-dien-1-ylsilanes 2a–c. (i) $SiCl_4$ (0.24 equiv.), THF, −78 °C to room temperature, 3 days. (ii) $HSiCl_3$ (0.33 equiv.), *n*-hexane, −78 °C to room temperature, overnight. (iii) $(EtO)_2SiCl_2$ (0.5 equiv.), THF, −78 °C to room temperature, overnight. (iv) DIBAL-H (3.8 equiv.), *n*-hexane, −78 °C to room temperature, 1 h. **b**, $B(C_6F_5)_3$-catalysed stepwise release of SiH_4. **c**, Plot of concentrations of hydrosilanes 2b–d and SiH_4 against time in the reaction of 2b with catalytic amounts of 1a. TMEDA, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

SiH_4 (Fig. 2b,c as well as Supplementary Figs 3 and 4). A plot of the concentration of the various species formed during this experiment against time is presented in Fig. 2c. Silane 2b was almost immediately converted into 2c and was no longer detectable after a few minutes. 2c reached its maximum concentration at the early stage of the reaction and was consumed within 2 h. After 1 h, 2d was the major species in the reaction mixture and its concentration slowly diminished over hours. SiH_4 was formed over the course of hours and its concentration reached a plateau after 4 h at a concentration as low as 0.1 mmol ml^{-1}, indicating the solubility limit of this gas in CD_2Cl_2 (monosilane is insoluble in most organic solvents). When the same experiment was repeated with 2c, a similar trend was observed (Supplementary Figs 5 and 6). The lower rate of consumption of 2d compared to 2c or 2b is likely to originate from a more stable η^1-Si–H/$B(C_6F_5)_3$ complex of 2d as a result of negligible steric repulsion. Conversely, steric bulk around the Si-H bond in 2b hampers that adduct formation (see its molecular structure, Supplementary Fig. 17), thereby steering the boron Lewis acid towards a bisallylic C–H bond and hence accelerating the transformation of 2b into 2c. To clarify whether SiH_4 inhibits the decomposition of compounds 2b–d, we monitored the degradation of 2b in an open system over a period of 7 h. The SiH_4 concentration remained constant at ~0.05 mmol ml^{-1} (vs. ~0.1 mmol ml^{-1} in a closed system), and no significant acceleration was observed (Supplementary Fig. 3).

Table 1 | Transfer hydrosilylation of styrene (4a).



Entry	SiH_4 surrogate (equiv.)	Catalyst	Time (h)	Conversion of 4a (%)*	Product distribution 5a:6a:7a:8a[†]
1	2b (0.35)	1a	20	100	0:0:100:0
2	2c (0.35)	1a	20	100	0:0:100:0
3	2b (0.55)	1a	20	100	0:23:77:0
4	2c (0.55)	1a	20	100	18:25:57:0
5	2b (1.10)	1a	20	100	39:36:25:0
6	2c (1.10)	1a	20	100	49:31:20:0
7[‡]	2b (0.35)	1b	40	72	0:0:100:0
8[§]	2b (0.35)	1d	20	0	0:0:0:0
9[‖]	2c (0.35)	1d	20	100	0:0:0:0
10	2b (0.35)	1c	120	72	0:6:94:0
11	2c (0.35)	1c	120	90	0:18:82:0
12	2c (0.55)	1c	80	94	0:52:48:0
13	2b (0.55)	1c	80	82	0:35:65:0

Conditions: 4a (0.2 mmol), 2 (0.07–0.22 mmol), 1 (0.01 mmol), CH_2Cl_2 (1.0 M), room temperature, 20–120 h. Unless otherwise noted, conversion of 2 was always 100%; *measured by gas chromatography with mesitylene as an internal standard; [†]determined by integration of chromatograms, uncorrected; [‡]no further conversion of 4a was observed after this period of time; [§]no conversion of 2b; [‖]a gel was obtained.

Optimization of the transfer hydrosilylation. Validated silanes 2b,c were next evaluated as SiH_4 precursors in the transfer hydrosilylation of styrene (4a) with catalyst 1a (Table 1) and we found that both participated in this process. These reactions went to full conversion of the starting material 4a with perfect selectivity in favour of the formation of monohydrosilane 7a (entries 1 and 2). Notably, and despite the poor solubility of SiH_4 in CH_2Cl_2 (Fig. 2b), only a slight excess of the required stoichiometry of 2 (0.35 instead of 0.33 equiv.) and no dilute reaction medium were required to secure complete consumption of the substrate. Chemoselectivity is an issue frequently encountered with substitution processes at the silicon atom decorated with identical leaving groups. The kinetics are similar for single, double or even triple displacements, and it is usually steric effects and not the stoichiometry of the reactants that make the reaction stop at a certain stage[35]. Accordingly, an increase in the amount of 2b (0.55 equiv.) also led to dihydrosilane 6a, but the formation of monohydrosilane 7a still prevails (entry 3). Essentially the same result was obtained with 0.55 equiv. of 2c, yielding trihydrosilane 5a along with 6a and 7a (entry 4). Even the use of over-stoichiometric amounts of the SiH_4 surrogate (1.1 equiv.) did not override the lack of chemoselectivity (entries 5 and 6).

Apart from benchmark catalyst 1a, we also investigated the performance of other electron-deficient arylboranes in this reaction. We chose partially fluorinated tris(2,3,5,6-tetrafluorophenyl) borane (1b)[36] to probe the effect of decreased Lewis acidity and bis(pentafluorophenyl)(nonafluorobiphenyl)borane (1c)[37] and tris-(nonafluorobiphenyl)borane (1d)[38] were selected because their augmented steric hindrance could perhaps bias the chemoselectivities observed with tris(pentafluorophenyl)borane (1a). Estimation of their Lewis acidities relative to archetypical $B(C_6F_5)_3$ (1a, 100%) are given according to the established Gutmann–Beckett method[39,40] (percentage values[3] in parentheses below catalysts **1** in Table 1; for the determination of the value for 1d, see Supplementary Table 1). As expected, partially fluorinated 1b showed reduced reactivity (entry 7). No reaction occurred when highly sterically encumbered, perfluorinated borane 1d was tested in combination with 2b (entry 8). Conversely, the reaction mixture turned into a gel when using less hindered surrogate 2c (entry 9). The steric situation between 2c and 1d allows for hydride abstraction (see Fig. 1a, **I**→**II**→**III**), but the resulting borohydride is too congested to rapidly react with the benzene-stabilized silicon cation intermediate (**III**→**IV**). As a result, the silicon cation/Wheland intermediate might potentially serve as an initiator of cationic polymerization. Borane 1c, exhibiting intermediate steric properties, was indeed able to bias the product distribution to a limited extent. However, 1c was far less reactive than 1a. With 0.35 equiv. of 2b or 2c, di-adduct 6a is now formed together with tri-adduct 7a (6:94 with 2b or 18:82 with 2c, entries 10 and 11 vs. 0:100 with catalyst 1a, entries 1 and 2). Better conversion and improved selectivity for 6a were noticed when 2c was used. Increasing its amount to 0.55 equiv. allowed us to obtain a 52:48 mixture of 6a and 7a, again improving the chemoselectivity obtained with 1a (entry 12). Changing the SiH_4 surrogate to 2b resulted in a diminished conversion of 4a over the same reaction time (entry 13).

The results in Table 1 show no significant chemoselectivity differences between 2b and 2c when full conversion of styrene (4a) was reached, implying degradation of 2b and 2c to a common reagent prior to the hydrosilylation event. Time-dependent ^1H NMR measurements of the degradation of 2b and 2c (Fig. 2c and Supplementary Figs 3–6) clearly support this assumption as the half-lives of 2b and 2c were in the range of minutes and less than 1 h, respectively. Hence, 2d or SiH_4 are presumably the actual hydrosilylating agents. To verify this, we monitored the reaction of 4a and 0.35 equiv. of 2b by means of time-dependent, multinuclear ^1H and ^{29}Si NMR experiments (see Table 1, entry 1, Fig. 3 and Supplementary Figs 7–11). In line with what we have previously observed, SiH_4 surrogate 2b is completely degraded by $B(C_6F_5)_3$ (1a) within a few minutes into its di- and trihydro-substituted congeners 2c and 2d, respectively. 2c is also rapidly consumed (~1 h), while 2d remains detectable for 4 h. Notably, SiH_4 was also detected, and its concentration reaches a plateau after 1 h (Fig. 3b). Half of the styrene (4a) is consumed after 1 h, and the intermediate mono- and di-adducts 5a and 6a are formed during this time. These, as well as unreacted 4a, are then slowly converted to tri-adduct 7a (Fig. 3c). We did not detect any silanes with 'mixed' substitution patterns, that is, homobenzyl and cyclohexa-2,5-dien-1-yl groups. It is therefore reasonable to assume that homobenzyl-substituted hydrosilanes 5a and 6a are the actual hydrosilylating agents leading to 6a and 7a, respectively. However, we cannot fully exclude the participation of cyclohexa-2,5-dien-1-yl-substituted 2d in the initial hydrosilylation event, leading to a short-lived intermediate that eventually releases 5a. Comparison of the observed initial rates of formation of 5a, 6a and 7a reveals that hydrosilylation of 4a by 5a is faster than with SiH_4 or 6a. While in the latter case this kinetic difference might merely be the result of different steric situations (monoalkylation in 5a versus dialkylation in 6a), we believe that conversion of 4a into 5a is impeded by the poor availability of monosilane at the early stage of the reaction, resulting in substantial accumulation of 6a. In another time-dependent NMR experiment run with 2b in excess (1.35 equiv., Supplementary Figs 12–16), this rate difference became even more apparent. The solubility limit of SiH_4 was also well demonstrated by a significant decline in its concentration during the third hour.

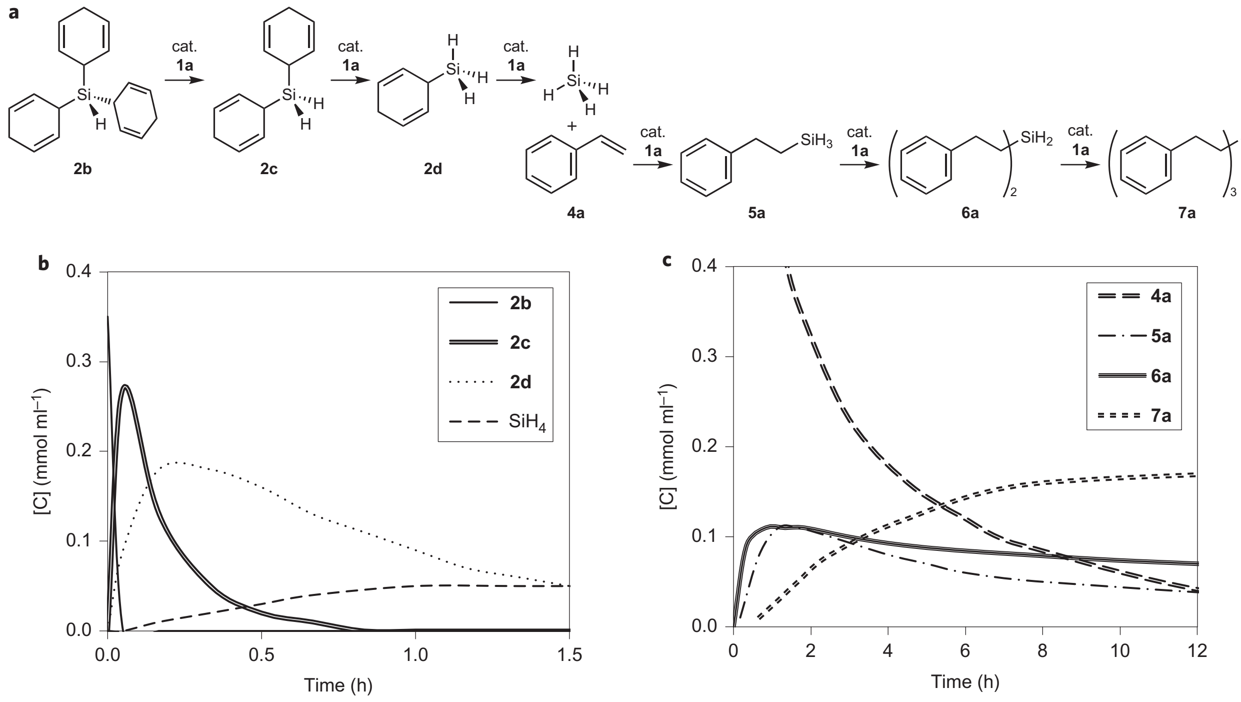


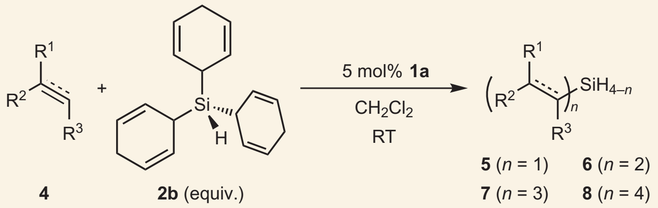
Figure 3 | Time-dependent NMR study of the transfer hydrosilylation of 4a with 2b catalysed by 1a. a, Stepwise B(C_6F_5)$_3$-catalysed release of SiH_4 followed by multiple alkene hydrosilylation. **b**, Plot of concentrations of hydrosilanes **2b–d** and SiH_4 in the presence of styrene (**4a**) against time at the early stage of the reaction. **c**, Plot of concentrations of starting material **4a** and hydrosilylation products **5a**, **6a** and **7a** against time.

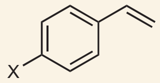
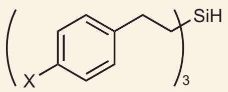
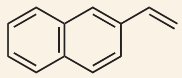
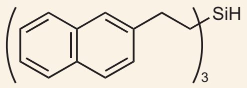
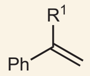
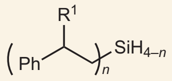
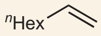
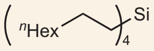
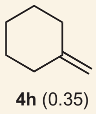
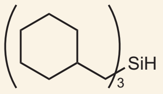
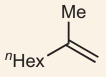
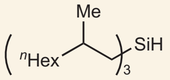
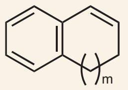
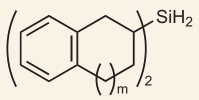
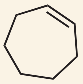
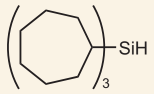
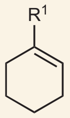
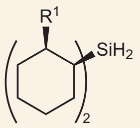
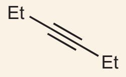
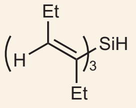
Scope and limitations. Encouraged by the results compiled in Table 1, we subjected differently substituted alkenes to these protocols. As solid **2b** is readily accessible in large quantities, we used it for the substrate scope study (Table 2). Electronically modified styrenes **4a**–**4c** showed the expected reactivity trends (entries 1–3). An electron-donating methyl group led to a higher yield and an electron-withdrawing fluorine group to a lower yield than the parent styrene. This illustrates well the need for sufficient π basicity of C=C double bond in the nucleophilic attack at the silicon atom in **V** and the stabilization of the positive charge developed in **VI** (see Fig. 1a with X=CR_2). To demonstrate practicality, we performed the preparation of **7a** from **2b** in good yield outside the glovebox, using Schlenk techniques with wet and non-degassed CH_2Cl_2 and catalyst **1a** briefly exposed to air (footnote † in Table 2). The reaction of the corresponding naphthalene **4d** gave moderate yield, presumably due to its ease of polymerization (entry 4). The transfer hydrosilylations of α-substituted styrenes held a few surprises. The reaction of α-methylstyrene (**4e**) was plagued by substantial decomposition, yielding 26% of the di-adduct **6e** rather than the typical tri-adduct **7e** (entry 5). According to ^{1}H and ^{29}Si NMR data, **6e** is formed as a mixture of *meso* and C_2-symmetric compounds, attesting to the absence of any diastereoinduction in the hydrosilylation of **4e** by the chiral trihydrosilane intermediate, that is, mono-adduct **5e**. In turn, 1,1-diphenylethylene (**4f**) participated in the transfer hydrosilylation with excellent 84% yield of the tri-adduct **7f** (entry 6). Moreover, it was possible to almost completely reverse the chemoselectivity with this substrate by using 0.55 equiv. of **2b**, furnishing the di-adduct **6f** in 79% yield (entry 7). This example corroborates that an adjustment of the stoichiometry will allow for the control of the chemoselectivity in selected cases. The absence of positive-charge-stabilizing alkene substituents was detrimental, and α-olefins such as **4g** were not fully converted into hydrosilylation products. With no branching in the carbon chain, the tetra-adduct **8g** formed chemoselectively in moderate yield (entry 8). Conversely, 1,1-dialkyl-substituted alkenes **4h** and **4i** reacted smoothly to the tri-adducts **7h** and **7i**, respectively (entries 9 and 10). Internal alkenes such as indene (**4j**) and less reactive 1,2-dihydronaphthalene (**4k**) afforded di- rather than tri-adducts, and **6j** and **6k** were obtained in good to moderate yields (entries 11 and 12). 1,2-Dialkyl-substituted alkene **4l** exhibited poor reactivity and converted into tri-adduct **7l** in low yield after a long reaction time (entry 13). Unlike previous studies[1,12], this type of substrate as well as terminal olefins (for example, **4g**) proved to be poorly reactive. This difference might stem from the attenuated ability of the SiH_3 relative to SiR_3 groups to effect stabilization of the β carbocation developed after transfer of the silicon atom onto the C=C bond (**V**→**VI**, Fig. 1a with X=CR_2)[41]. Finally, we examined a small panel of trisubstituted double bonds. 1-Methylcyclohex-1-ene (**4m**) provided di-adduct **6m** in good yield with complete *cis* selectivity at the cyclohexyl backbone, but more sterically demanding 1-phenylcyclohex-1-ene (**4n**) and also 2-methylindene (not shown) did not react at all (entries 14 and 15). As discussed for transfer hydrosilylation of prochiral **4e** (entry 5), there is generally no diastereoinduction in multiple additions, and statistical mixtures of stereoisomers are obtained with **4i**, **4k** and **4m** (entries 10, 12, and 14).

We also attempted the transfer hydrosilylation of alkynes[3,42]. Terminal alkynes, for example, phenylacetylene and hex-1-yne, inhibited the reaction completely (not shown), but hex-3-yne (**4o**) fully converted into trivinylmonohydrosilane **7o** (entry 16) with double bonds of *Z* geometry. The sensitivity of the method to steric hindrance was further exemplified by the lack of reactivity for diphenylacetylene (not shown).

Cyclohexa-2,5-dien-1-yl substituents as masked Si–H bonds in transition-metal-catalysed hydrosilylation. Although di- and monohydrosilanes **6** and **7** could be selectively prepared using the above methods, trihydrosilanes **5** remained occasionally observed, but not accessible chemoselectively. Moreover, α-olefins were too unreactive and were processed to the tetra-adduct **8** after the initial hydrosilylation with SiH_4 had occurred. We asked

Table 2 | Transfer hydrosilylation of C–C multiple bonds with SiH_4 surrogate 2b.



Entry	Substrate (equiv.)	Time (h)	Product (Yield, %)*
			
1	**4a**, X = H (0.35)	20	**7a** (91)[†]
2	**4b**, X = Me (0.35)	20	**7b** (99)
3	**4c**, X = F (0.35)	40	**7c** (85)[‡]
			
4	**4d** (0.35)	40	**7d** (63)[§]
			
5	**4e**, R^1 = Me (0.35)	20	**6e**, *n* = 2 (26)[‖,¶]
6	**4f**, R^1 = Ph (0.35)	70	**7f**, *n* = 3, (84)[‡,#]
7	**4f**, R^1 = Ph (0.55)	20	**6f**, *n* = 2 (79)[**]
			
8	**4g** (0.25)	100	**8g** (50)[‡,††]
			
9	**4h** (0.35)	20	**7h** (99)
			
10	**4i** (0.35)	20	**7i** (99)[‡‡]
			
11	**4j**, *m* = 0 (0.55)	20	**6j** (83)
12	**4k**, *m* = 1 (0.55)	40	**6k** (55)[‡,¶]
			
13	**4l** (0.35)	120	**7l** (42)[‡,††,§§]
			
14	**4m**, R^1 = Me (0.55)	80	**6m** (76)[¶]
15	**4n**, R^1 = Ph (0.55)	70	No reaction
			
16	**4o** (0.35)	20	**7o** (81)

Conditions: **4** (0.2 mmol), **2** (0.07–0.11 mmol), **1** (0.01 mmol), CH_2Cl_2 (1.0 M), room temperature, 20–120 h; *isolated yields; [†]75% yield was obtained at a 0.3 mmol scale in wet, non-degassed CH_2Cl_2 with **1a** handled in air; [‡]full conversion of **4** was not reached; [§]trace amounts of **6d** were also detected by ^1H NMR analysis of the crude reaction mixture but could not be isolated; [‖]decomposition. **5e** was also detected in the crude reaction mixture but could not be isolated; [¶]obtained as a 1:1 mixture of *meso* and C_2-symmetric compounds; [#]**2c** was used instead of **2b**; [**]trace amounts of **7f** were also detected by ^1H NMR analysis of the crude reaction mixture but could not be isolated; [††]reaction run on a 0.4 mmol scale; [‡‡]obtained as a 3:1 mixture of C_1- and C_3-symmetric compounds; [§§]isolated along with trace amounts of **6l**.

ourselves whether it would be possible to close these gaps by combining the borane catalysis with transition-metal-catalysed hydrosilylation (Fig. 1c). The strategy would be to hydrosilylate, for example, oct-1-ene (**4g**) with surrogate **2b** or **2c** with transition-metal catalysis. If such a reaction were compatible with the cyclohexa-2,5-dien-1-yl groups, the Si–H bonds could be 'deprotected' with catalytic amounts of $B(C_6F_5)_3$ (**1a**) in a subsequent step to release the trihydrosilane **5g** relevant to material sciences[43–47]. As a starting point to illustrate this idea, we treated surrogate **2b** with Karstedt's catalyst, tris(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)diplatinum, in the presence of excess **4g** and were pleased to obtain hydrosilylation adduct **9** in good yield (Fig. 4a). The same procedure applied to **2c** containing two Si–H bonds furnished monohydrosilane **10** in low yield (24%, not shown). This was substantially improved with dichloro(cycloocta-1,5-diene)platinum as catalyst (Fig. 4a). The potential of adducts **9** and **10** to serve as precursors of trihydrosilane **5g** was verified by catalytic 'deprotection' with $B(C_6F_5)_3$ (**1a**) in CD_2Cl_2 (Fig. 4b). Merely 30% NMR yield of **5g** accompanied by significant decomposition to unidentified compounds were recorded for the reaction of **9**. Conversely, the same conditions applied to **10** resulted in clean release of the Si–H bonds, affording **5g** in quantitative NMR yield.

Conclusion

This work shows that cyclohexa-2,5-dien-1-yl-substituted hydrosilanes **2b** and **2c** serve as safe and easy-to-handle precursors for the extremely dangerous monosilane (SiH_4) gas. The method uses their ability to release SiH_4 *in situ* upon treatment with catalytic amounts of $B(C_6F_5)_3$ (**1a**) and makes use of the hydrosilylation of C–C multiple bonds promoted by the same catalyst. All this happens in the same pot. This allowed us to perform, for the first time, a comprehensive experimental investigation of alkene hydrosilylation with SiH_4 in an academic laboratory. The syntheses of hydrosilanes that would be difficult to prepare by known methods (of the 15 silanes prepared in Table 2, only four had been synthesized previously) were made possible through practical, metal-free and room-temperature protocols. Moreover, we have also shown here that **2b** and **2c** are compatible with transition-metal-catalysed processes such as platinum(0)-catalysed alkene hydrosilylation leaving the cyclohexa-2,5-dien-1-yl substituents untouched. Subsequent 'deprotection' of the Si–H bonds catalysed by B

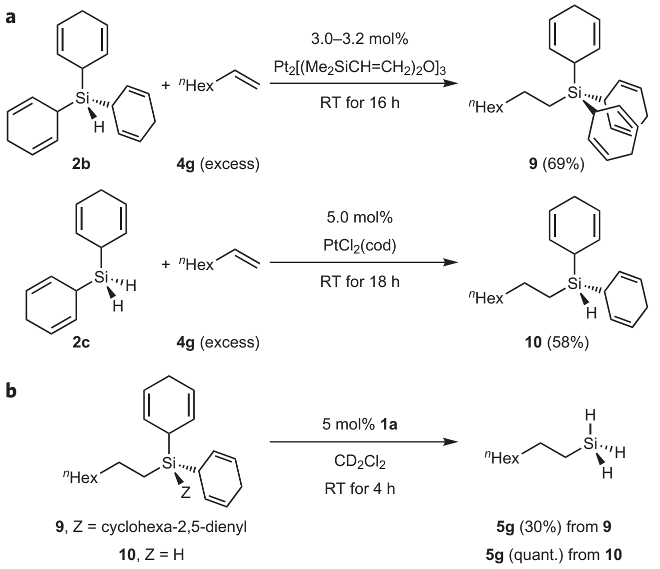


Figure 4 | The cyclohexa-2,5-dien-1-yl substituent as a SiH protecting group in transition-metal-catalysed reactions. **a**, Platinum(0)-catalysed hydrosilylation of an α-olefin with SiH_4 surrogates leaving the cyclohexa-2,5-dien-1-yl groups intact. **b**, $B(C_6F_5)_3$-catalysed 'deprotection' of the Si–H bonds.

$(C_6F_5)_3$ (**1a**) allowed for the preparation of a trihydrosilane derived from an α-olefin with perfect chemoselectivity compared to the hydrosilylation of terminal alkenes with SiH_4 (Fig. 1b)[28]. These results pave the way for the use of cyclohexa-2,5-dien-1-yl substituents as protecting groups for Si–H bonds in other transition-metal-catalysed reactions.

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Author contributions

A.S. and M.O. conceived and designed the experiments. A.S. performed the experiments and analysed the data. A.S. and M.O. discussed the results and co-wrote the paper.

Additional information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.O.

Competing financial interests

The authors declare no competing financial interests.