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# Organopotassium-Catalyzed Silylation of Benzylic C(sp<sup>3</sup>)–H Bonds

Baptiste Neil, Lamine Saadi, Louis Fensterbank, and Clément Chauvier\*

**Abstract:** Benzylsilanes have found increasing applications in organic synthesis as bench-stable synthetic intermediates, yet are mostly produced by stoichiometric procedures. Catalytic alternatives based on the atom-economical silylation of benzylic C(sp<sup>3</sup>)–H bonds remain scarcely available as specialized directing groups and catalytic systems are needed to outcompete the kinetically-favored silylation of C(sp<sup>2</sup>)–H bonds. Herein, we describe the first general and catalytic-in-metal undirected silylation of benzylic C(sp<sup>3</sup>)–H bonds under ambient, transition metal-free conditions using stable *tert*-butyl-substituted silyldiazenes (tBu–N=N–SiR<sub>3</sub>) as silicon source. The high activity and selectivity of the catalytic system, exemplified by the preparation of various mono- or *gem*-bis benzyl(di)silanes, originates from the facile generation of organopotassium reagents, including *tert*-butylpotassium.

silylmethane, R<sub>3</sub>SiCH<sub>2</sub>–M),<sup>[3]</sup> all these approaches require extensive pre-functionalization of the coupling partners. Such functional group manipulations could in principle be obviated by the direct and atom-economical C(sp<sup>3</sup>)–H silylation of widely available alkylarenes. However, its practical implementation poses considerable challenge because of the weak acidity of this bond that usually gets activated at a much slower rate than arene C(sp<sup>2</sup>)–H bonds. As a consequence, though innovative catalytic silylation of C(sp<sup>3</sup>)–H bonds have been reported,<sup>[4]</sup> they remain generally limited compared to their C(sp<sup>2</sup>)–H silylation counterparts.<sup>[5]</sup>

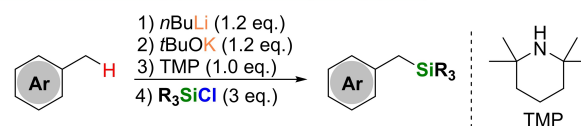
In the stoichiometric realm, selective metalation/silylation at the benzylic position has recently been achieved with strong Brønsted bases and chlorosilanes.<sup>[6]</sup> In this regard, the bimetallic mixed Li/K amide (Scheme 1A) reported by O’Shea and co-workers still constitute the state-of-the-art system for the selective realization of challenging lateral metalations. Catalytic alternatives, which benefit from enhanced atom-economy compared to the s-block metal-based approaches, lack generality as benzylic silylation only occurs selectively when proper directing groups (DG) are installed on the arene core. To date, only alkyipyridines<sup>[7]</sup> or methylarenes bearing *ortho*-pyridyl,<sup>[8]</sup> amino<sup>[9]</sup> and phosphino<sup>[10]</sup> groups have been silylated with hydrosilanes as silicon source and Ir or Ru-based catalysts (Scheme 1B.a). In fact, a catalytic undirected C(sp<sup>3</sup>)–H silylation of methylarenes has yet to be developed, though isolated examples

## Introduction

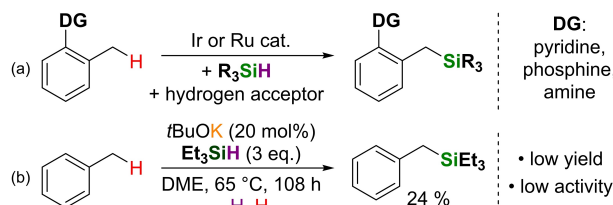
The advent of catalytic hydrosilylation over the last fifty years has arguably revolutionized the field of organosilicon chemistry by providing a direct and scalable entry to alkylsilanes through the insertion of unsaturated compounds (e.g. alkenes) into the Si–H bond of hydrosilanes.<sup>[1]</sup> Since then, numerous applications have emerged both in organic synthesis and in material science, including the manufacture of hybrid organic–inorganic silicone polymers. However, the preparation of some valuable alkylsilanes such as primary benzylsilanes, which are important synthetic intermediates,<sup>[2]</sup> is precluded by hydrosilylation and therefore requires other strategies to be devised.

To date, benzylsilanes have mainly been prepared by stoichiometric C(sp<sup>3</sup>)–Si bond formation upon coupling benzyllithium or benzylic Grignard reagents and chlorosilanes. Although various catalytic cross-coupling technologies have also emerged to assemble benzylsilanes through C–C bond formation (e.g. between arylhalides and  $\alpha$ -metalated

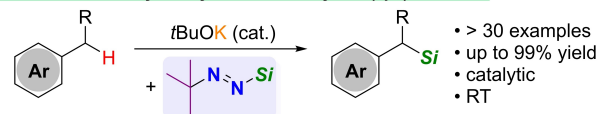
### A. State-of-the-art stoichiometric benzylic silylation



### B. Reported catalytic strategies



### C. This work: catalytic silylation of benzylic C(sp<sup>3</sup>)–H bonds



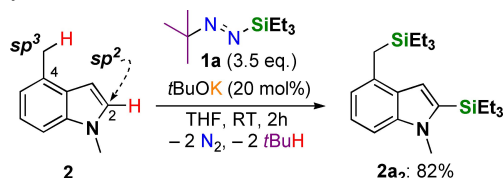
**Scheme 1.** Benzylic C(sp<sup>3</sup>)–H bond silylation reactions.

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have been reported using a homogeneous (Scheme 1B.b)<sup>[11]</sup> or a heterogeneous<sup>[12]</sup> transition metal-free catalytic system.

Herein, we describe for the first time a transition metal-free catalytic protocol for the undirected silylation of benzylic C(sp<sup>3</sup>)-H bonds with easy-to-access and thermally stable *tert*-butyl-substituted silyldiazenes (*t*Bu-N=N-SiR<sub>3</sub>, Scheme 1C). We have shown previously that the latter reagents promote the C(sp<sup>2</sup>)-H bond silylation of weakly acidic (hetero)aryl compounds such as indoles or fluoroarenes upon treatment with a catalytic amount of Brønsted bases.<sup>[13]</sup> In particular, we noticed that when 1,4-dimethylindole **2** was reacted with diazene **1a** (1.2 equiv) and *t*BuOK (10 mol %), the expected C<sub>2</sub>-silylated products was produced in good yields along with minor amounts of a C(sp<sup>3</sup>)-SiEt<sub>3</sub> containing byproduct. The latter was unambiguously identified through the marginal modification of these reaction conditions (3.5 equiv **1a** and 20 mol % *t*BuOK) that allowed to cleanly isolate the benzylsilane **2a<sub>2</sub>** in 82 % yield (Equation (1) below). **2a<sub>2</sub>** arises from the innate silylation of the methyl C(sp<sup>3</sup>)-H bond, which in this case is slower than the C<sub>2</sub>-silylation event yet kinetically accessible without any directing group. This observation prompted us to study such an unprecedented silylation pathway with unactivated methylarenes.



## Results and Discussion

We began our investigations by selecting 4-methylanisole **3** as a model substrate because the selective functionalization of the benzylic  $\alpha$ -position by conventional stoichiometric metalation approaches has only been met with little success despite tremendous research effort.<sup>[14]</sup> For example, metalation with *n*BuLi/TMEDA followed by anion-trapping with Me<sub>3</sub>SiCl afforded almost exclusively the silylated product arising from the directed *ortho* metalation (*DoM*) rather

than the  $\alpha$ -silylated (laterally-silylated) one.<sup>[15]</sup> With this in mind, we reacted **3** with triethylsilyl-substituted diazene **1a** (1.2 equiv) and *t*BuOK (10 mol %) as a catalytic promoter (entry 2, Table 1) in THF (0.14 M). While these conditions proved successful for the silylation of C(sp<sup>2</sup>)-H bonds,<sup>[13]</sup> only modest yield and selectivity were observed as benzylsilane **3a** was formed in 36 % yield alongside the *ortho*-silylated anisole **3a'** (24 %) and the bis-silylated product **3a<sub>2</sub>** (ca. 8 %) formed by both lateral and *ortho* silylation.

Subsequent optimization of the reaction parameters (see Table 1 and Table S1 in the Supporting Information for details) revealed that both productive (>95 % conversion) and selective (>81 % **3a**) lateral silylation could be achieved by dropping neat more than 2 equiv of diazene **1a** while using THF as solvent and a potassium salt as catalyst (entries 1 and 3–4 in Table 1). Under the optimal conditions (2 equiv **1a** and 10 mol % *t*BuOK), the benzylsilane **3a** could be isolated in 84 % yield after chromatography. This result is striking as **3** had thus far resisted selective lateral silylation. For example, when hydrosilanes were used as silicon sources in conjunction with catalytic amount of *t*BuOK<sup>[11]</sup> or a calcium benzyl complex,<sup>[16]</sup> only the arylsilane **3a'** was obtained. Similarly, using O'Shea's benzylic silylation protocol that we carried out for the sake of comparison, **3a'** was still the major product formed at the expense of **3a** (7 % yield, entry 5 in Table 1), though this strategy constitutes one of the best option available for challenging lateral metalation/functionalization. With diazene **1a** as silicon source, such a selectivity reversal could be achieved simply by replacing *t*BuOK with its sodium counterpart (entry 6, Table 1). As an illustration, the *ortho*-silylated anisole **3a'** was formed in 64 % yield along with only 7 % of **3a** after 30 h of reaction with 20 mol % *t*BuONa. The previously elusive C(sp<sup>3</sup>)-H silylation of **3** or its *ortho*-silylation may therefore be selectively selected by changing the nature of the cationic part of the catalytic system.

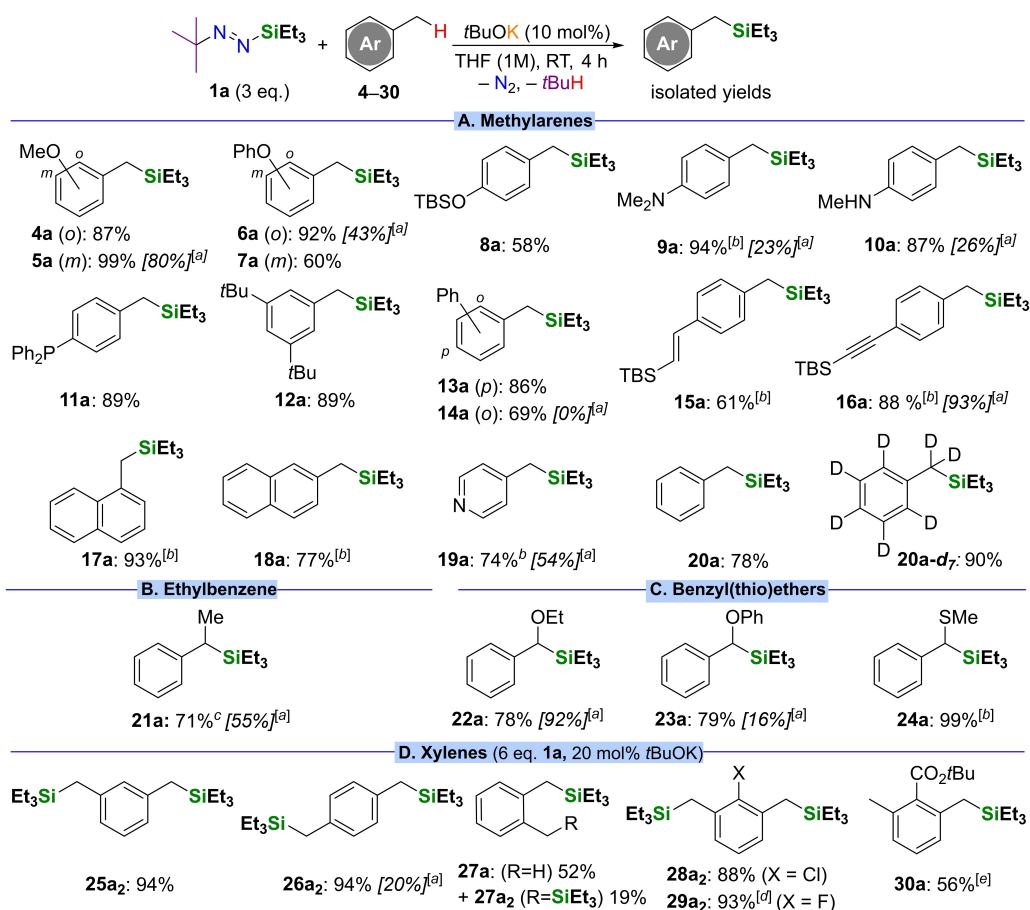
The generality of the **1a**/KO*t*Bu<sub>cat</sub> system to achieve undirected benzylic C(sp<sup>3</sup>)-H silylation selectively was further probed with various methylarenes. The *meta* and *ortho* isomers of **3** reacted smoothly (99 % and 87 % isolated yield, respectively) with nearly complete selectivity for lateral silylation. The latter site selectivity contrasts sharply with the reported rhodium-catalyzed dehydrogenative silyla-

**Table 1:** Optimization of the silylation of 4-methylanisole.

Entry	Deviation	$\rho$	Yield <b>3a</b>	<b>3a</b> / <b>3a'</b> / <b>3a<sub>2</sub></b>
1	none	98	81 (84) <sup>[a]</sup>	81/5/14
2	1.2 equiv <b>1a</b> , <sup>[b]</sup> THF (0.14 M)	77	36	53/35/12
3	KOH (10 mol %), 30 h	44	28	75/21/4
4	Me <sub>3</sub> SiOK (10 mol %)	97	82	83/5/12
5 <sup>[c]</sup>	<i>n</i> BuLi (1.2 eq), <i>t</i> BuOK (1.2 equiv), TMP (1.0 equiv) 15 min, then Et <sub>3</sub> SiCl (3.0 equiv)	88	7	10/77/13
6	<i>t</i> BuONa (20 mol %), 30 h	80	64 ( <b>3a'</b> )	9/81/10

Conversion ( $\rho$ ), yield and selectivity [all %] determined by calibrated GC (gas chromatography) using *n*-tetracosane as an internal standard.

[a] Isolated yield. [b] **1a** added dropwise in solution. [c] O'Shea's protocol<sup>[6b]</sup> conducted on 1.0 mmol scale of **3**. TMP=2,2,6,6-tetramethylpiperidine.



**Scheme 2.** C( $sp^3$ )–H silylation of methylarenes. Reaction conditions: alkylarene (0.5 mmol), **1a** (3.0 equiv),  $t\text{BuOK}$  (10 mol%) and THF (0.5 mL, 1 M) at RT. Yields refer to those of purified isolated products. [a] NMR yield of product obtained following O'Shea's stoichiometric protocol (c.f. entry 5 in Table 1). [b] 20 mol%  $t\text{BuOK}$ . [c] 20 mol%  $t\text{BuOK}$ , 0.14 M. [d] 10 mol%  $t\text{BuOK}$  and 3.0 equiv **1a**.<sup>[e]</sup> 40 mol%  $t\text{BuOK}$ , 3.0 equiv **1a**, 0.01 M, 1.5 h. TBS = *tert*-butyldimethylsilyl.

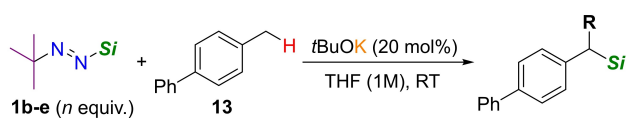
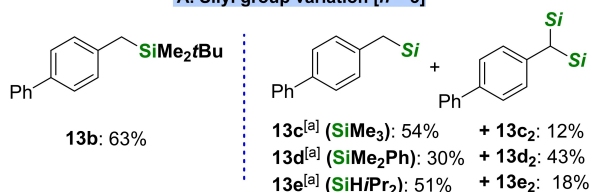
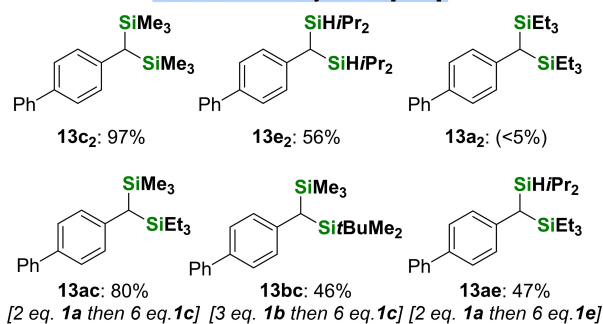
tion reactions that exclusively take place on the arene ring of these substrates.<sup>[17]</sup> Beyond the methoxy group, other electron-releasing groups were well-tolerated in the reaction, such as potentially directing phenoxy (**6–7**), TBS-protected hydroxyl (**8**), amino (**9–10**) and diphenylphosphino (**11**) substituents or two *meta*-located bulky *tert*-butyl groups (**12**). Importantly, the N–H bond in **10** was well-tolerated as it was first *in situ* silylated before being deprotected upon purification to afford **10a** in 87% yield. In all instances, the mono-silylated benzylsilanes arising from the *undirected* C( $sp^3$ )–H silylation were largely major over the potentially competing arylsilanes or the mixed  $sp^2/sp^3$  bis-silylated products. As an illustration, while the 2-phenoxybenzylsilane **6a** was isolated in 92% yield with nearly complete lateral selectivity, the *meta* isomer **7a** (60% yield) was accompanied by ca. 14% of separable  $sp^2/sp^3$  bis-silylated product.

Slightly electron-withdrawing substituents (Ph, vinyl and alkynyl) were also tolerated, even when the benzylic position is hindered by a rigid Ph group in the ortho position as in product **14a** (69% yield). Importantly, the benzylsilanes **15a** and **16a** bearing TBS-substituted vinyl and alkynyl moieties were isolated in 61% and 88% yield with

untouched  $\pi$ -bonds that would readily undergo hydrosilylation with hydrosilanes. In contrast, the reaction of methylarenes bearing strongly electron-withdrawing cyano or nitro groups in the *para* position gave almost no desired benzylsilanes. Nonetheless, less aromatic methylarenes such as 1- and 2-methylnaphthalene (**17–18**) and electron-deficient 4-methylpyridine (**19**) afforded good to excellent yields of the desired silanes **17–19a**.

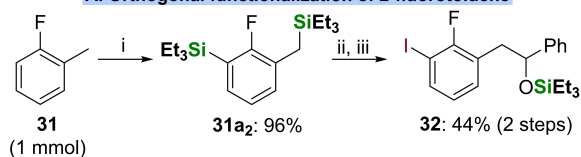
Toluene or its perdeuterated congener that display no electronic nor steric bias reacted in a very efficient manner with diazene **1a** affording **20a** and **20a-d<sub>7</sub>** in 78% and 90% isolated yield, respectively. This result contrasts sharply with the 24% yield of **20a** obtained with the Grubbs-Stoltz reagent ( $\text{Et}_3\text{SiH}/\text{KO}t\text{Bu}_{\text{cat}}$ ) after 108 h at 65 °C.<sup>[11]</sup> The enhanced productivity of the **1a**/ $\text{KO}t\text{Bu}_{\text{cat}}$  pair was further established with substrates displaying comparatively higher steric bulk at the benzylic position, such as ethylbenzene **21** and some benzyl(thio)ethers. In all cases, the benzylsilanes **21–24a** were isolated in good to excellent yields, with only marginal change of the reaction conditions needed in the case of ethylbenzene (dilute reaction medium).

To put the above-described reaction scope into perspective, we further set out to compare it with O'Shea's

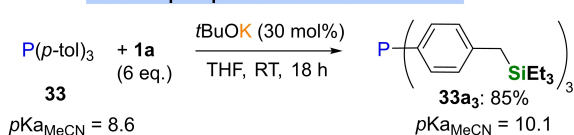
A. Silyl group variation [*n* = 3]B. Gem-disilanes synthesis [*n* = 8]

**Scheme 3.** Silyl group influence (A) and gem-disilanes synthesis (B). [a] Yields refer to those of purified isolated products but those for **13c–e** were determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

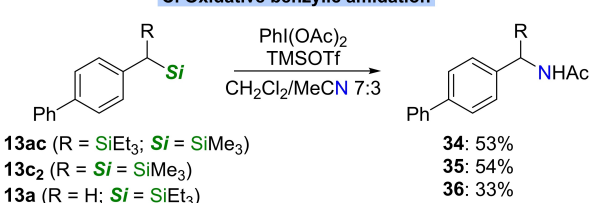
## A. Orthogonal functionalization of 2-fluorotoluene



## B. Facile phosphine electronic modification



## C. Oxidative benzylic amidation



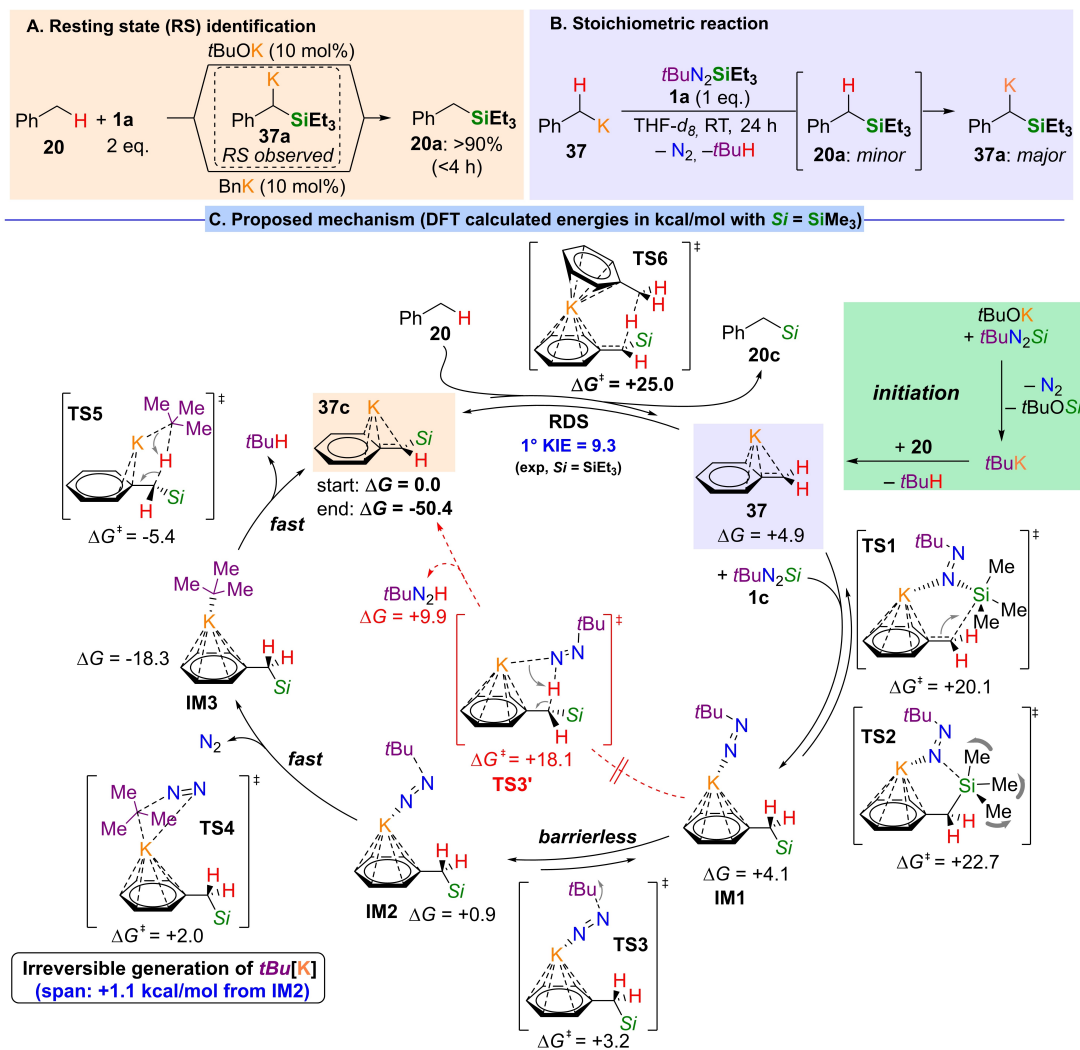
**Scheme 4.** Applications. A. i: **1a** (6 equiv), tBuOK (20 mol%), RT, 4 h. ii: ICl (1.1 equiv), RT, 13 h, 78% iii: PhCHO (1.2 equiv), Me<sub>3</sub>SiOK (20 mol%), NBu<sub>4</sub>Cl (20 mol%), RT, 21 h, 56%. B:  $pK_a$ 's in MeCN were determined by DFT calculations and relate to the Ar<sub>3</sub>PH<sup>+</sup>/Ar<sub>3</sub>P couples.

stoichiometric benzylic silylation protocol<sup>[6b]</sup> for a handful of previously-unreported examples (yields within square brackets on Scheme 2). Specifically, the **1a**/KOtBu<sub>cat</sub> system not only allows catalytic-in-metal benzylic silylations under non-cryogenic conditions, but also performs clearly better in terms of activity and/or selectivity on substrates such as

methylarenes with an electron releasing group in the *para* position (e.g. **3**, **9** & **10**), those bearing a hindered benzylic position (e.g. in **6** & **14**) or arylbenzylethers (**23**). In the same vein, one-step silylation of multiple benzylic positions in substrates such as dimethylbenzene (xylene) derivatives remains largely out of reach of stoichiometric metalation/silylation sequences because of the instability of the corresponding poly-benzylanions. In contrast, the exhaustive silylation of the *meta* (**25**) and *para* (**26**) isomers of xylene was easily achieved using **1a** (6 equiv) and 20 mol % tBuOK, though *o*-xylene mostly afforded the mono-silylated product **27a** (Scheme 2D). Importantly, the bis-silylation process tolerates a chloride, a fluoride or an ester substituent at the 2-position of *m*-xylene that were barely compatible in the corresponding mono-methylarenes for reactivity (Cl, CO<sub>2</sub>tBu) or selectivity (F, *vide infra*) reasons. In the case of the benzoate **30**, the steric hindrance favored the mono-silylation product (**30a**, 56% yield) and the reaction conditions had to be slightly modified to avoid its decomposition in the reaction medium.

Beyond the Et<sub>3</sub>Si group, we also studied the transfer of other silyl groups from the corresponding diazenes **1b–e** to 4-methylbiphenyl **13** (Scheme 3A). The bulky Me<sub>2</sub>tBuSi group was transferred cleanly albeit more slowly (63% isolated after 16 h). In contrast, the benzylsilanes **13c–e** bearing Me<sub>3</sub>Si, Me<sub>2</sub>PhSi and *i*Pr<sub>2</sub>HSi groups were rapidly formed yet were all contaminated with the corresponding homoleptic gem-disilanes that could be isolated in the case of **13c**<sub>2</sub> and **13e**<sub>2</sub> simply by increasing the amount of **1c** or **1e**. Because such disilanes were not formed with excess **1a** or **1b**, we also showed that the heteroleptic gem-disilanes bearing Me<sub>3</sub>Si/Et<sub>3</sub>Si (**13ac**), Me<sub>3</sub>Si/Me<sub>2</sub>tBuSi (**13bc**) and *i*Pr<sub>2</sub>Si/Et<sub>3</sub>Si (**13ae**) groups can be prepared with one-pot procedures by adding first the bulkier diazene followed by the less hindered one (see the Supporting Information for details). Such a control over the mono vs. bis-silylation pathways that arises from the fine tuning of the steric hindrance of the silyl group contrasts sharply with the related benzylic C–H borylation protocols that exclusively deliver unstable bis-boronate species.<sup>[18]</sup> Hence, the present methodology offers an alternative synthesis of benzylic geminal bis-silane compounds that were pioneered by Snieckus<sup>[19]</sup> and that have recently been prepared by repeated metalation/silylation sequences<sup>[2a]</sup> or by Pd-catalyzed cross-coupling<sup>[20]</sup> and carbene insertion into Si–Si bond.<sup>[21]</sup>

We next sought to illustrate one aspect of the synthetic potential of the present methodology in that it allows to easily produce polysilylated compounds on both *sp*<sup>2</sup> and/or *sp*<sup>3</sup> centers so as to readily increase molecular complexity from cheap and widely available starting materials. At the outset, we reacted 2-fluorotoluene **31** with excess diazene **1a**. As expected, we deliberately obtained the bis-silylated compound **31a**<sub>2</sub> in 96% yield that contains two C–SiEt<sub>3</sub> bonds displaying different reactivity that can be exploited in orthogonal synthetic downstream functionalization (Scheme 4A). In this respect, the arylsilane moiety of **31a**<sub>2</sub> was first converted into the corresponding iodide by *ipso* substitution and the resulting benzylsilane was reacted with



**Scheme 5.** Experimental (A and B) as well as computational (C) mechanistic investigations. Gibbs free energies (kcal mol<sup>-1</sup>) were calculated at the B3LYP-D3 (PCM = THF)/Def2TZVP//B3LYP-D3 (PCM = THF)/6-31 + G(d) level of theory. RDS = rate determining step; KIE = kinetic isotope effect.

benzaldehyde to afford the Et<sub>3</sub>Si-protected secondary alcohol **32** in 56% isolated yield.<sup>[6b]</sup> Beyond organic synthesis, the polysilylation strategy also enables the facile modification of tri(*p*-tolyl)phosphine **33** widely used as ligand in homogeneous catalysis (Scheme 4B). The three-fold silylation of **33** afforded the novel triarylphosphine **33a<sub>3</sub>** (85% yield within 18 h) in which the three -CH<sub>2</sub>SiEt<sub>3</sub> group greatly enrich the P atom as a result of strong  $\sigma$ - $\pi$  hyperconjugation. As a consequence, **33a<sub>3</sub>** displays  $\sigma$ -donating properties similar to those of tri(*p*-anisyl)phosphine as witnessed by the relative pK<sub>a</sub>'s of the corresponding phosphoniums (10.1 vs. 10.2 for (4-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PH<sup>+</sup> in MeCN) that correlate to the Tolman's electronic parameters.<sup>[22]</sup>

The last illustration involves electron rich homo- and heteroleptic *gem*-disilanes, which we surmised could undergo oxidative functionalization, though tetraalkylsilanes (including benzyltrialkylsilanes) are generally considered unreactive towards common oxidants (Scheme 4C).<sup>[23]</sup> Inspired by a recent report from Shafir and Cuenca,<sup>[24]</sup> we reacted

**13ac** and **13c<sub>2</sub>** with TMSOTf-activated PhI(OAc)<sub>2</sub> at low temperature and obtained the new  $\alpha$ -silylated benzylacetamides **34** and **35** that still contain a potentially reactive C-Si bond in 53% and 54% yield respectively. In the case of **13ac**, the C-SiMe<sub>3</sub> bond was preferentially cleaved over the C-SiEt<sub>3</sub>, though the latter was not deemed oxidatively unbreakable (**13a**–**36**).

Finally, we investigated the mechanism of the reaction between toluene **20** and diazene **1a** with the goal in mind to delineate the fate of the potassium cation initially bound to the *tert*-butoxide anion. At the outset, a careful monitoring of the catalytic silylation of **20** with **1a** triggered by 10 mol% *t*BuOK revealed that all the potassium is stored in the  $\alpha$ -silylated benzylpotassium **37a** that acts as the resting state of the catalysis (Scheme 5A). **37a** was the only intermediate observed by NMR spectroscopy irrespective of the reaction conversion. Importantly, independently synthesized benzylpotassium (BnK, **37**, 10 mol%) also catalyzes the silylation of **20** (and of 4-methylanisole **3**) with similar activity, selectivity and resting state identity (**37a**) than the

much less basic *t*BuOK. As a consequence, the latter alkoxide likely plays the role of *anionic initiator* that ultimately generates catalytically-competent BnK upon reaction with diazene **1a** in the presence of toluene. In fact, trapping experiments with electrophilic carbanion scavengers strongly suggests that *tert*-butylpotassium (*t*BuK) is rapidly formed upon reaction of *tert*-butyl-substituted silyldiazene with *t*BuOK (see section 4.6 in the Supporting Information).<sup>[25]</sup> As such, the initiation step furnishes BnK through the metalation of toluene **20** with *t*BuK (top right corner in Scheme 5C).

Fully in line with the catalytic observations, the stoichiometric reaction of the thus-generated BnK with **1a** (1 equiv) in THF-*d*<sub>8</sub> at room temperature rapidly afforded **37a** (Scheme 5B), structure of which was ultimately confirmed by its independent preparation from BnK and benzyltriethylsilane **20a**. This result demonstrates that (i) **37** preferentially reacts with the silyl group of diazene **1a** to afford BnSiEt<sub>3</sub> **20a** and that (ii) the latter species was the most acidic present in the reaction medium as most of the potassium is “stored” in the conjugate base **37a**. It also indicates that the diazene decomposition upon reaction with BnK generates highly basic species well poised to metalate **20a**.

To shed light on the experimentally-elusive intermediates generated by the decomposition of *tert*-butyl-substituted silyldiazene with catalytically-competent BnK **37**, we conducted DFT calculations (B3LYP-D3(PCM=THF)/Def2TZVP//B3LYP-D3(PCM=THF)/6-31+G(d)) with **1c** as a model diazene (Scheme 5C and Figure S6 in the Supporting Information). First, the initiation pathway furnishes **37** from *t*BuOK, **20** and **1c**. The catalytic cycle then begins with the facile formation of the C–Si bond from **37** and **1c** through **TS1** followed by the collapse of the silicate (not shown) into the potassium diazenyl intermediate **IM1** upon Berry-pseudorotation and N–Si dissociation (**TS2**). The singly-bent diazenyl moiety in **IM1** further evolves by denitrogenation through a rapid two-step process (**IM1**→**IM3**). First, a barrierless elongation of the C–N bond between the *t*Bu and N=N units leads to the weakly bound diazenyl complex **IM2** (*d*<sub>N=N</sub> = 1.18 Å vs. 1.21 Å in **IM1** and 1.10 Å in N<sub>2</sub>) through **TS3**. **IM2** then undergoes an irreversible denitrogenative β-carbon elimination to generate the η<sup>6</sup>-arene *tert*-butylpotassium complex **IM3**. The extremely low barrier (+1.1 kcal mol<sup>-1</sup> for **TS4** from **IM2**) that needs to be overcome to obtain such a reactive intermediate is remarkable, yet fully intelligible owing to the high stability of N<sub>2</sub>. A concerted metalation deprotonation (CMD) of one of the benzylic C–H bonds with *t*Bu<sup>-</sup> as base subsequently takes place via **TS5** (+12.9 kcal mol<sup>-1</sup> from **IM3**) to yield the α-silylated benzylpotassium **37c**. An alternative pathway for the generation of the latter species directly from **IM1** was uncovered, in which the CMD occurs with the *t*BuN<sub>2</sub><sup>-</sup> unit. However, not only is this step endergonic but the associated computed barrier (**TS3'**, 14.0 kcal mol<sup>-1</sup> from **IM1**) is also much higher than the ones obtained for the irreversible denitrogenative pathway (**IM1**→**IM3**). As a consequence, the *tert*-butylpotassium complex **IM3** is the true metalating agent involved in the

formation of **37c** from **37** and **1c** that overall proceeds rapidly with a barrier of 17.9 kcal mol<sup>-1</sup> (**TS<sub>2</sub>**) and quantitatively ( $\Delta G = -55.2$  kcal mol<sup>-1</sup> for **37** + **1c**→**37c** + N<sub>2</sub> + *t*BuH).

In agreement with the experimentally verified resting state identity, **37c** is the lowest-in-energy intermediate on the potential energy surface (and thus the origin of all relative energies in Scheme 5C). Under the catalytic conditions, it is also the direct precursor of the desired benzylsilane through protonation with toluene. In line with the accumulation of **37a** in the reaction medium, this step is rate limiting (**TS6**, 25 kcal mol<sup>-1</sup>) and regenerates BnK that further sustains catalytic turnovers upon reaction with **1c**. As far as Et<sub>3</sub>Si-substituted diazene **1a** is concerned, the observation of a strong primary kinetic isotope effect (KIE) of 9.3 by evaluating the relative rate of reaction of toluene and toluene-*d*<sub>8</sub> further supports such a view.<sup>[26]</sup>

## Conclusion

To conclude, we have disclosed the first general, catalytic-in-metal and undirected silylation of benzylic C(*sp*<sup>3</sup>)–H bonds that allows to selectively prepare both mono- or *gem*-bis benzyl(di)silanes under ambient, transition metal-free conditions. The high activity and selectivity of the **1a**/KO*t*Bu<sub>cat</sub> combination towards benzylic silylation originates from the facile generation of organopotassium reagents that proved highly selective for lateral metalation compared to their lighter congeners (Na or Li). Both experimental and computational mechanistic studies point to the facile, steady-state generation of *tert*-butylpotassium that further sustains an anionic chain reaction in a tamed way. As such, the anionic decomposition of *tert*-butyl-substituted silyldiazene brings a new solution to the metalation of weakly acidic benzylic C–H bonds with s-block-based polar organometallics.<sup>[27]</sup>

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

**Keywords:** C–H Functionalization · Diazene · Metalation · Organopotassium · Silylation

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