View Article Online
View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Zaranek, S. Witomska, V. Patroniak and P. Pawluc, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC01531C.

Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm

Chemical Communications

www.rsc.org/chemcomm

ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

Marilyn M. Olmstead, Alan L. Balch, Josep M. Poblet, Luis Echegoyen *et al.*

Reactivity differences of $Sc_3N@C_{2n}$ ($2n$ = 68 and 80). Synthesis of the first methanofullerene derivatives of $Sc_3N@D_{5h}$-C_{80}

175 YEARS

View Article Online
DOI: 10.1039/C7CC01531C

ChemComm

COMMUNICATION

Unexpected catalytic activity of simple triethylborohydride in hydrosilylation of alkenes

Received 00th January 20xx,
Accepted 00th January 20xx

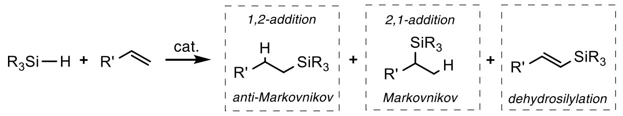
DOI: 10.1039/x0xx00000x

www.rsc.org/

M. Zaranek,†* S. Witomska,† V. Patroniak, and P. Pawluć*

The first example of sodium triethylborohydride-catalysed hydrosilylation of alkenes is reported. The hydrosilylation of certain alkenes, in particular styrenes, vinylsilanes and allyl glycidyl ether, with aromatic hydrosilanes proceeded in a highly regioselective manner to give *Markovnikov* products. It is significant that several protocols use $NaHBEt_3$ as reducing agent generating active catalysts *in situ* of other hydrosilylation reactions. An anionic mechanism of hydrosilylation is proposed.

The hydrosilylation of alkenes (Scheme 1) is one of the most widely used homogeneous catalytic processes. Thanks to its ultimate atom economy and robustness, this reaction is now successfully employed in a large-scale synthesis of various industrially-applicable chemicals, e.g. coatings and adhesives, heat transfer media, separation membranes, lubricants, surfactants, etc.[1] It can also be a step in more complex organic syntheses, e.g., as a mean of enantioselective reduction of carbonyl and imine compounds.[1]



Scheme 1. Possible products of hydrosilylation

Addition of Si-H bond to an olefin can lead to two main products of hydrosilylation – 1,2-addition yields products often referred to as *anti-Markovnikov* or *linear* ones and is facilitated by most of known catalysts, whereas 2,1-addition gives *Markovnikov* or *branched* products and has been a matter of a limited number of reports, mostly on early transition metals and lanthanides, although not only on them.[2–10] It is also possible to obtain products of formal substitution of terminal hydrogen through a process of *dehydrosilylation* which is known to occur over transition metal catalysts, especially ruthenium ones.[1,11]

Since its discovery by Sommer et al. in 1947,[12] hydrosilylation has come a long way towards its contemporary popularity. The first milestone in the development of hydrosilylation was the discovery of a platinum(IV) catalyst, known as the Speier's catalyst.[13] The second, and the truly ground-breaking one, was the discovery of the Karstedt's catalyst based on a platinum(0) complex.[14] Its use facilitated a significant decrease in the catalyst loading, down to couple dozens of ppms, thus enabling implementation in industrial synthesis. Although very active, platinum-based catalysts still make a significant component of the final product's price, mainly due to very high price of this precious metal and its complete non-recoverability. This fact combined with the invariable trends of trying to replace every platinum group metal (PGM), pushes the research towards non-precious metal and even non-metal catalysis. There has been a plenty of attempts to make a first-row transition-metal olefin hydrosilylation catalyst, of which the most successful ones were those by the groups of Chirik,[15–17] Deng,[18] Huang,[19] Holland,[20] Hu,[21], Lu,[22] Nakazawa[23,24], Nikonov,[25] and Thomas.[26] It is worth noting that many of them used sodium triethylborohydride to reduce the metal precatalyst.[8,15,22,23,25] There are even examples of main-group metals' hydrides and hydrido complexes catalysing hydrosilylation,[7,27] and a perfluorinated borane, $B(C_6F5)_3$, has been also successful.[28,29] Significantly, triethylborohydrides of lithium and sodium were found to be good catalysts for hydrosilylation of C=O and C=N bonds.[30] On the other hand, they have never been used alone as catalysts of hydrosilylation of alkenes. Only LiAlH4 has been found a catalyst of hydrosilylation of ethene and 1-hexene with SiH4,[31] and it has also been active in catalysing dehydrogenative coupling of terminal alkynes with this silane.[32]

We were trying out a cobalt catalyst which was activated by *in situ* reduction with sodium triethylborohydride.[33] In that study we followed a previously published procedure[23] that is

---

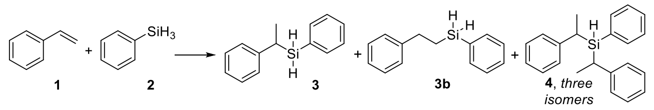
Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89C, 61-614 Poznań, Poland
† These authors contributed equally.
* piotr.pawluc@amu.edu.pl, m.zaranek@amu.edu.pl

Electronic Supplementary Information (ESI) available: experimental procedures analytical data of isolated compounds. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7CC01531C

generally accepted in examining first-row transition metal complexes needing reduction. Bearing in mind the reports on catalytic activity of $NaHBEt_3$, we decided to perform experiments without Co complex, which enabled us to state that the borohydride was not catalytically active in this transformation. In fact, the substrates used were anything but similar to those used in the literature report on hydrosilylation with $NaHBEt_3$ catalyst, as they involved imines, ketones, aldehydes, etc.[30] However, further examination of the process and change of substrates led to a conclusion that $NaHBEt_3$ can indeed convert phenylsilane and styrene. The results of preliminary catalytic reactions are presented in Table 1.

Table 1. Screening of the reaction conditions.



Entry	[**1**]/[**2**]	Catalytic system[a]	*t*/h	*T*/°C	Conv of **2**[b]	Selectivity[c]
1	2	10% $NaHBEt_3$	24	60	16%	>99% **3**
2	2	10% $NaHBEt_3$	24	80	43%	>99% **3**
3	2	10% $NaHBEt_3$	2	100	28%	>99% **3**
4	2	10% $NaHBEt_3$	8	100	52%	>99% **3**
5	2	10% $NaHBEt_3$	24	100	100%	>99% **3**
6	2	5% $NaHBEt_3$	24	100	87%	92% **3** 8% **4**
7	1	10% $NaHBEt_3$	24	100	74%	97% **3** 3% **4**
8	2	10% $LiHBEt_3$	24	100	27%	>99% **3**
9	2	10% $KHBEt_3$	24	100	100%	2% **3** 98% **4**
10	1	10% $KHBEt_3$	24	100	68%	51% **3** 49% **4**
11	2	10% BEt_3	24	100	4%	-
12	2	10% $NaHBEt_3$ *in 1,4-dioxane*	24	100	68%	92% **3** 8% **4**
13	2	10% $NaHBEt_3$ *in THF*	24	60	87%	73% **3**
14	2	10% $NaHBEt_3$ *in diglyme*	24	100	26%	18% **3**; 6% **3b** 72% **4**

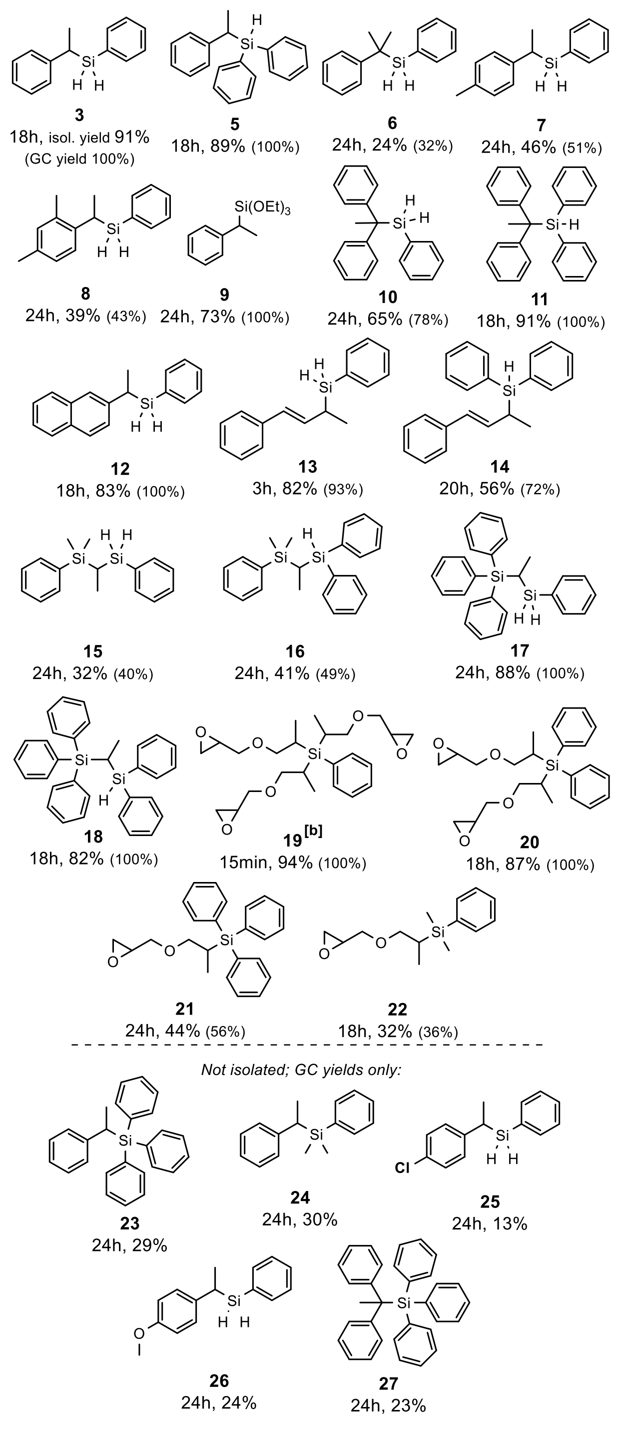
[a] Reaction as 0.5 M solution of **2** in toluene unless stated otherwise; [b] Determined by GC; [c] taking into account all actual products, determined by GC-MS and ^1H NMR of isolated **3**;

Sodium triethylborohydride occurred to be an efficient catalyst of hydrosilylation of styrene, nonetheless, it failed completely to catalyse hydrosilylation of 1-hexene, nor was it successful in a reaction of styrene with triethylsilane, in which case a complete polymerisation of the former reagent was observed. However, the positive results were encouraging to explore the capabilities of $NaHBEt_3$ further, especially as product **3** was formed quantitatively in Markovnikov manner (entry 5). To stress again, such a selectivity is not frequently observed in hydrosilylation of alkenes, being mostly a result of side reactions giving secondary products, or catalysis using sophisticated catalysts. Formation of **4** was not observed in most cases. It is worth noting that lithium triethylborohydride, while being far better in hydrosilylation of ketones and imines,[30] exhibited activity of only a quarter of that of $NaHBEt_3$ in the same conditions (entries 5 and 8). Potassium triethylborohydride led to full conversion of phenylsilane, however, with selectivity towards bis-hydrosilylation (entry 9). In the reaction of equimolar amounts of **1** and **2**, $KHBEt_3$ led to formation of both mono- and bis-hydrosilylation products in almost equal amounts (entry 10). It should be emphasised that a stochastic mixture of all three isomers of **4** was formed. A reaction tried out with triethylborane in order to exclude action similar to this of perfluorinated boranes[29] did not proceed (entry 11). Switching the solvent to 1,4-dioxane caused a drop in conversion (to 68%; entry 12) and polymerisation of styrene. No better were also THF (entry 13) and bis(2-methoxyethyl) ether (*diglyme*; entry 14), additionally giving a bunch of unidentified and higher-order side products of multiple hydrosilylation. The use of twofold excess of styrene leads to a higher $PhSiH_3$ conversion, and interestingly, the reaction proceeds almost exclusively towards the single hydrosilylation product. Apparently, the mono-hydrosilylation product is less reactive than the starting $PhSiH_3$ under these conditions, resulting in high selectivity towards monoaddition products. Then, knowing the optimal conditions for hydrosilylation of styrene with phenylsilane and some substrate scope limitations, we performed more syntheses using sodium triethylborohydride as catalyst (Table 2). We decided to use consistently 2 equivalents of olefins to provide better insight into their reactivity by excluding concentration effects. Its excess posed no threat to the reaction, as it mostly polymerised. The results depict that $NaHBEt_3$ can be applied as a catalyst to hydrosilylation of fairly various alkenes, *e.g.*, styrenes, allyl ethers, and vinylsilanes, with hydrosilanes bearing preferentially aromatic substituents. The representative products of reactions that proceeded with good yields were isolated and they were proven to be Markovnikov-type isomers. Simple styrene reacted with phenylsilane and diphenylsilane to form selectively and quantitatively **3** and **5**. Substituting the α hydrogen with a methyl group resulted in **6** obtained with only a moderate yield. What is noticeable, introduction of electron-donating groups into the phenyl ring also causes a drop in conversion, no matter if they are weak donors (products **7** and **8**) or stronger ones (products **25** and **26**). Triphenylsilane and dimethylphenylsilane were less satisfyingly efficient hydrosilylating agents either for styrene (products **23** and **24**, resp.), or allyl glycidyl ether (products **21** and **22**, resp.) than phenyl- or diphenylsilane. Similar relation was observed for 1,1-diphenylethene and vinylsilanes. Dimethylphenylvinylsilane used as an olefin led to **15** and **16** with moderate yield, whereas hydrosilylations of triphenylvinylsilane went to completion to give **17** and **18**. So did also the reaction of 2-vinylnaphthalene with phenylsilane leading to a product identified as **12**.

To our great surprise, it was possible to obtain a group of silyl derivatives of allyl glycidyl ether **19**-**22**.

View Article Online
DOI: 10.1039/C7CC01531C

Table 2. Results of alkene hydrosilylation using $NaHBEt_3$ as catalyst.[a]**2.**



3	18h, isol. yield 91% (GC yield 100%)
5	18h, 89% (100%)
6	24h, 24% (32%)
7	24h, 46% (51%)
8	24h, 39% (43%)
9	24h, 73% (100%)
10	24h, 65% (78%)
11	18h, 91% (100%)
12	18h, 83% (100%)
13	3h, 82% (93%)
14	20h, 56% (72%)
15	24h, 32% (40%)
16	24h, 41% (49%)
17	24h, 88% (100%)
18	18h, 82% (100%)
19[b]	15min, 94% (100%)
20	18h, 87% (100%)
21	24h, 44% (56%)
22	18h, 32% (36%)

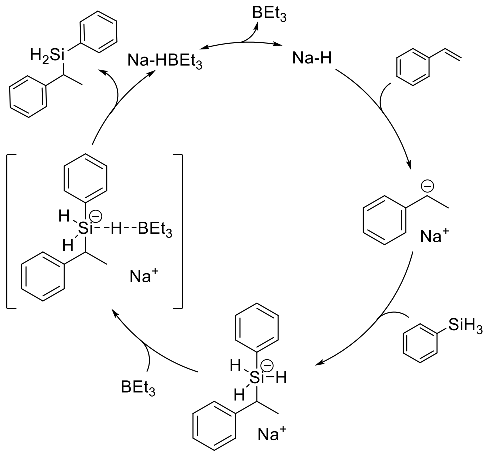
Not isolated; GC yields only:

23	24h, 29%
24	24h, 30%
25	24h, 13%
26	24h, 24%
27	24h, 23%

[a] Reaction conditions: 0.5 M silane in toluene, $[Si]:[C=C]:[NaHBEt_3] = 1:2:0.1$; 100 °C, all yields in relation to silanes, for description of GC yield determination, see *SI*; [b] $[Si]:[C=C] = 1:3$;

It turned out that products of hydrosilylation of allyl glycidyl ether are more active in hydrosilylation than starting phenylsilane. If allyl glycidyl ether was used in a stoichiometric amount relative to Si-H (*i.e.*, 3 eq relative to $PhSiH_3$), the hydrosilylation weas to completed in 15 minutes yielding quantitatively **19.** Otherwise, free phenylsilane was left unreacted and no single or double addition products were detected. Silanes with more than one Si-H bond were generally subject to only a single addition, whenever vinyl aromatics were used, which remains in a good accordance with the observation that alkyl-substituted silanes are less reactive or completely inactive in this system.A general observation is that the reactivity decreases in the sequence $PhSiH_3 \approx Ph_2SiH_2 \gg Ph_3SiH$. However, when a vinylsilane is used as alkene, triphenylvinylsilane is a better hydrosilylation substrate than dimethylphenylvinylsilane. Interestingly, product **9** of hydrosilylation of styrene with triethoxysilane was obtained with very good yield. *Trans*-1-phenylbuta-1,3-diene was subjected to hydrosilylation with phenylsilane and diphenylsilane to determine regioselectivity of the catalytic system for two potential addition sites. Product **13** was found to constitute 93% of the products mixture with a reaction completed in 3 hours, whereas product **14** was formed less selectively (73% out of mixture of isomers) over a longer time (20 h).

To examine the reactivity of other allyl ether, THP-protected 2-allyloxyethanol was prepared and reacted with triphenylsilane. Unfortunately, it gave (2-(allyloxy)ethoxy)triphenylsilane as the only silylated product, and similarly did also *tert*-butyl acrylate with diphenylsilane, giving diphenyl(*tert*-butoxy)silane. Further, it came as no surprise that a reaction of cinnamaldehyde with phenylsilane proved carbonyl reduction highly preferred over C=C hydrosilylation. An attempt to hydrosilylate styrene with 1,1,3,3-tetramethyldisiloxane led to a mixture made up mostly of undefined siloxanes containing dimethylsiloxy and dimethyl(hydro)siloxy units, and similarly failed hydrosilylation of triethoxyvinylsilane, leading to its condensation.



Scheme 2. Proposed mechanism of $NaHBEt_3$-catalysed hydrosilylation of styrene with phenylsilane

The observations made in the course of our investigation made it possible to propose a mechanism of hydrosilylation catalysed by sodium triethylborohydride (Scheme 2). It has to be stressed that there is no direct evidence for this catalytic cycle, however, some characteristic observations are backed by literature data. On the basis of the work of Brown and Kim, it is justified to assume that in the first step the addition of Na-H bond to an alkene takes place.[34] Although their work was focused on hydroboration by lithium borohydrides, they indeed mentioned

View Article Online
DOI: 10.1039/C7CC01531C

that sodium triethylborohydride was not successful in this process. The assumption on the initial step of the catalytic cycle is further supported by the fact that the addition of triethylborane slows the reaction down, which can be explained in terms of the dissociation equilibrium of triethylborohydride. It has been established that $HBEt_3^-$ has one of the lowest standard enthalpies of dissociation among many other borohydrides.[35] What is more, the observation by Brown and Kim of α-lithiation of 1,1-diphenylethylene yielding a red colour of the reaction mixture is in line with the very same observation made by us using $NaHBEt_3$.[34] This step of the reaction can also clarify the origin of its enormous selectivity as the formal benzylic carbanion is far more favourable providing essential charge stabilisation by resonance, and this approach has also been proposed by Kobayashi *et al.* in their original paper.[31] Next, it would explain a better reactivity of phenylvinylsilanes than aliphatic alkenes since silylene bridges appear to be capable of transferring electronic charge, which has been shown in spectroscopic measurements of silylene-containing polymers.[36] In a further step, it is reasonable to consider the formation of a pentacoordinate silylate species, however, a concerted mechanism involving silane-to-borane hydride transfer simultaneous to the formation of Si-C bond is also possible. Observation of the formation of a product of siloxyl substitution when using hydrosiloxane promotes rather the former possibility (see *SI*). In the final step, a hydride is abstracted from the former species by free triethylborane molecule through a transition state similar to a frustrated Lewis pair reported by Piers *et al*.[37]. The abstraction can be potentially obstructed by solvent coordination to BEt_3, which can explain worse performance of hydrosilylation in THF and other donor solvents. Overall, the anionic mechanism proposed by us is different from the one proposed by Harder *et al.*,[7] as we assumed no insertion-elimination steps.

Altogether, sodium triethylborohydride can be used as very selective, inexpensive, commercially-available catalyst of Markovnikov hydrosilylation of resonance-stabilised alkenes with aromatic silanes that does not provide pathways for dehydrogenative processes. However, the substrate scope is inherently limited to those unsusceptible to nucleophilic addition of hydrides and those without acidic protons. It is remarkable that $NaHBEt_3$, reported here as a catalyst, is widely used for *in-situ* reduction of other hydrosilylation precatalysts.

Financial support from the National Science Centre (Poland), Grant No. Opus 2011/03/B/ST5/01034 is acknowledged.

Notes and references

1 B. Marciniec, Ed., *Hydrosilylation: A Comprehensive Review on Recent Advances*, Springer, Berlin, 2009.
2 Y. Nakajima and S. Shimada, *RSC Adv.*, 2015, **5**, 20603–20616.
3 D. Troegel and J. Stohrer, *Coord. Chem. Rev.*, 2011, **255**, 1440–1459.
4 P.-F. Fu, L. Brard, Y. Li and T. J. Marks, *J. Am. Chem. Soc.*, 1995, **117**, 7157–7168.
5 Y. Ura, G. Gao, F. Bao, M. Ogasawara and T. Takahashi, *Organometallics*, 2004, **23**, 4804–4806.
6 N. Komine, M. Abe, R. Suda and M. Hirano, *Organometallics*, 2015, **34**, 432–437.
7 F. Buch, J. Brettar and S. Harder, *Angew. Chem. Int. Ed.*, 2006, **45**, 2741–2745.
8 X. Du, Y. Zhang, D. Peng and Z. Huang, *Angew. Chem. Int. Ed.*, 2016, **55**, 6671–6675.
9 L. Benítez Junquera, M. C. Puerta and P. Valerga, *Organometallics*, 2012, **31**, 2175–2183.
10 J. Li, C. Zhao, J. Liu, H. Huang, F. Wang, X. Xu and C. Cui, *Inorg. Chem.*, 2016, **55**, 9105–9111.
11 M. Zaranek, B. Marciniec and P. Pawluć, *Org. Chem. Front.*, 2016, **3**, 1337–1344.
12 L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *J. Am. Chem. Soc.*, 1947, **69**, 188–188.
13 J. C. Saam and J. L. Speier, *J. Am. Chem. Soc.*, 1958, **80**, 4104–4106.
14 US3775452 (A), 1973.
15 C. C. H. Atienza, T. Diao, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, J. L. Boyer, A. K. Roy and P. J. Chirik, *J. Am. Chem. Soc.*, 2014, **136**, 12108–12118.
16 I. Pappas, S. Treacy and P. J. Chirik, *ACS Catal.*, 2016, 4105–4109.
17 C. H. Schuster, T. Diao, I. Pappas and P. J. Chirik, *ACS Catal.*, 2016, **6**, 2632–2636.
18 Z. Mo, J. Xiao, Y. Gao and L. Deng, *J. Am. Chem. Soc.*, 2014, **136**, 17414–17417.
19 D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter and Z. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 19154–19166.
20 C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix and P. L. Holland, *J. Am. Chem. Soc.*, 2015, **137**, 13244–13247.
21 I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc and X. Hu, *Angew. Chem. Int. Ed.*, 2015, **54**, 14523–14526.
22 J. Chen, B. Cheng, M. Cao and Z. Lu, *Angew. Chem. Int. Ed.*, 2015, **54**, 4661–4664.
23 K. Kamata, A. Suzuki, Y. Nakai and H. Nakazawa, *Organometallics*, 2012, **31**, 3825–3828.
24 R. N. Naumov, M. Itazaki, M. Kamitani and H. Nakazawa, *J. Am. Chem. Soc.*, 2012, **134**, 804–807.
25 G. I. Nikonov, *ChemCatChem*, 2015, **7**, 1918–1919.
26 M. D. Greenhalgh, D. J. Frank and S. P. Thomas, *Adv. Synth. Catal.*, 2014, **356**, 584–590.
27 J. Intemann, H. Bauer, J. Pahl, L. Maron and S. Harder, *Chem. – Eur. J.*, 2015, **21**, 11452–11461.
28 M. Rubin, T. Schwier and V. Gevorgyan, *J. Org. Chem.*, 2002, **67**, 1936–1940.
29 S. Keess, A. Simonneau and M. Oestreich, *Organometallics*, 2015, **34**, 790–799.
30 M. G. Manas, L. S. Sharninghausen, D. Balcells and R. H. Crabtree, *New J. Chem.*, 2014, **38**, 1694–1700.
31 M. Kobayashi and M. Itoh, *Chem. Lett.*, 1996, 1013–1014.
32 M. Itoh, M. Kobayashi and J. Ishikawa, *Organometallics*, 1997, **16**, 3068–3070.
33 A. Gorczyński, M. Zaranek, S. Witomska, A. Bocian, A. R. Stefankiewicz, M. Kubicki, V. Patroniak and P. Pawluć, *Catal. Commun.*, 2016, **78**, 71–74.
34 H. C. Brown and S. C. Kim, *J. Org. Chem.*, 1984, **49**, 1064–1071.
35 Z. M. Heiden and A. P. Lathem, *Organometallics*, 2015, **34**, 1818–1827.
36 M. Bayda, M. Ludwiczak, G. L. Hug, M. Majchrzak, B. Marciniec and B. Marciniak, *J. Phys. Chem. A*, 2014, **118**, 4750–4758.
37 A. Y. Houghton, J. Hurmalainen, A. Mansikkamäki, W. E. Piers and H. M. Tuononen, *Nat. Chem.*, 2014, **6**, 983–988.

View Article Online
DOI: 10.1039/C7CC01531C

Highly regioselective hydrosilylation of olefins with aryl- and alkoxysilanes has been developed using a simple sodium triethylborohydride.