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Hydrosilylation of Internal Alkynes Catalyzed by Tris-Imidazolium Salt-Stabilized Palladium Nanoparticles

Marc Planellas,[a] Wusheng Guo,[a] Francisco Alonso,[b] Miguel Yus,[b]
Alexandr Shafir,[a,]* Roser Pleixats,[a,]* and Teodor Parella[a,c]

[a] Departament de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193 Barcelona, Spain
Fax: (+34)-93-581-2477; phone: (+34)-93-581-2067; e-mail: Alexandr.Shafir@uab.cat or Roser.Pleixats@uab.cat
[b] Departamento de Química Orgánica, Facultad de Ciencias and Instituto de Síntesis Orgánica (ISO), Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain
[c] Servei de Ressonància Magnètica Nuclear, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193-Barcelona, Spain

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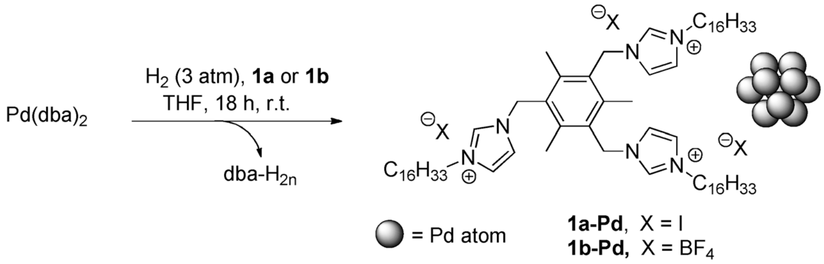
Abstract: Palladium nanoparticles stabilized with tris-imidazolium tetrafluoroborates catalyze the stereoselective hydrosilylation of internal alkynes in a dry inert atmosphere to give (*E*)-vinylsilanes in excellent yields. In the presence of controlled amounts of water a transfer hydrogenation reaction takes place with the formation of (*Z*)-alkenes or the corresponding alkanes.

Keywords: alkynes; hydrosilylation; imidazolium salts; nanoparticles; palladium; transfer hydrogenation

Introduction

The transition metal-catalyzed hydrosilylation of alkynes represents the most straightforward and convenient route for the preparation of vinylsilanes. This transformation proceeds with 100% atom efficiency,[1] and the resulting organosilicon reagents are versatile building blocks in a number of synthetic processes. Some examples of reactions involving vinylsilanes include protodesilylation[2] to produce the corresponding alkene, the Hiyama cross-coupling[3] with vinyl and aryl halides, as well as the Tamao–Fleming oxidation[4] to generate the carbonyl derivatives. In general, vinylsilanes exhibit reactivity similar to that of certain organometallic vinyl derivatives, but may offer advantages in terms of cost, low molecular weight, low toxicity, functionality tolerance and high chemical stability. Platinum-based catalysis is the most usual choice for the addition of silanes to unsaturated C–C bonds,[5] most famously chloroplatinic acid (Speier's catalyst),[5a,b] and olefin-stabilized Karstedt's catalyst.[5c,d] More recently, ruthenium complexes, despite being generally less reactive, have also become popular in alkyne hydrosilylation due to their high levels of stereoselectivity.[6] Thus, the regio- and stereochemistry of the metal-catalyzed alkyne hydrosilylation is known to be controlled by the nature of the catalyst. Terminal acetylenes tend to be far more reactive in this process, although certain systems, including Trost's ruthenium catalyst,[6g] do perform well with the more challenging internal alkynes.

Our own work on C–C bond formation catalyzed by Pd nanoparticles led us to explore the preparation of vinylsilanes using the same class of catalyst. We found only few reports dealing with the addition of silanes to acetylenic compounds catalyzed by metal nanoparticles. In one instance, the regioselective hydrosilylation of terminal alkynes was recently achieved[7] with supported rhodium,[7a] rhodium-platinum[7a] and gold nanoparticles;[7b] in addition, the hydrosilylation of internal alkynes and diynes has been described with platinum deposited on titania[8a,b] and on magnetite.[8c] Although palladium nanoparticles (Pd_{np}) have found widespread applications as catalysts, mainly in hydrogenation, oxidation and cross-coupling reactions,[9] little attention has been paid to their use in the hydrosilylation reactions of unsaturated hydrocarbons. Thus, while there are few examples describing their use in the hydrosilylation of enals, enones,[10] and styrene,[11] to the best of our knowledge they have never been reported as catalysts in the hydrosilylation of alkynes. In fact, even discrete Pd complexes are quite uncommon in this process, with some examples appearing in the past years.[12]



Scheme 1. Preparation of Pd$_{np}$ *via* hydrogenation of Pd(dba)$_2$.

Recently, our group reported[13] a family of palladium nanoparticles (Pd$_{np}$) stabilized by tris-imidazolium salts that were active as catalysts in Suzuki–Miyaura cross couplings. We describe herein our results on the hitherto unreported hydrosilylation of internal alkynes catalyzed by this family of palladium catalysts. We also report a competitive process of transfer hydrogenation of alkynes achieved by replacing the neat silane with a silane/water mixture.

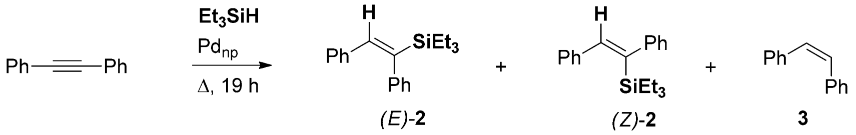
Results and Discussion

Full details on catalyst preparation are reported in our earlier publication (Scheme 1).[13] Briefly, the tris-imidazolium-stabilized nanoparticles were prepared following the organometallic approach developed by Chaudret and co-workers,[14] consisting in the reduction and subsequent displacement of a ligand from a zerovalent organometallic precursor. In our case, a THF solution of Pd(dba)$_2$[15] was stirred overnight under 3 atm of hydrogen in the presence of the corresponding stabilizer (**1a** or **1b**, Pd:L = 1:1), affording palladium nanoparticles **1a-Pd** and **1b-Pd** with a mean diameter of 2.9–4.2 nm in good yields.

Hydrosilylation of diphenylacetylene with Et$_3$SiH was chosen as the model substrate combination, and both **1a-Pd** and **1b-Pd** were tested as catalyst under a range of conditions (Table 1).

After an extensive testing, it was found that neat silane (4 equiv.) was the best reaction medium. Thus, treatment of the model symmetrical alkyne with neat triethylsilane in the presence of 5 mol% of the iodide salt **1a-Pd** at 90 °C under an inert atmosphere for 19 h gave complete conversion of the alkyne with good selectivity for the *syn* addition product (*E*)-**2** (entry 1,

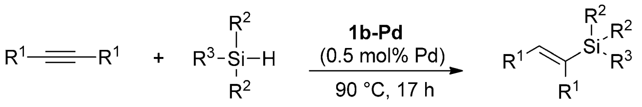
Table 1. Optimization of the reaction conditions for the hydrosilylation of diphenylacetylene with triethylsilane under Pd$_{np}$ catalysis.[a]

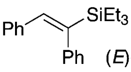
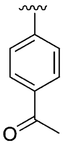
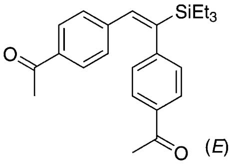
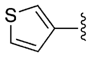
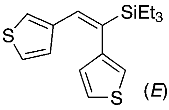
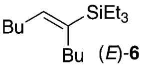
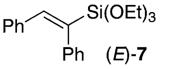
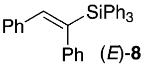
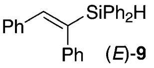


Entry	Catalyst	mol% Pd	Equiv. Silane[b]	Temperature [°C]	Conversion [%][c]	Yield of (*E*)-**2** [%][c]	Ratio (*E*)-**2**:(*Z*)-**2**:**3**
1	**1a-Pd**	5	4	90	100	95	93:7:0
2	**1a-Pd**	1	4	90	72	67	67:21:12
3	**1a-Pd**	0.5	4	90	67	64	75:17:8
4	**1b-Pd**	5	4	90	100	99	100:0:0
5	**1b-Pd**	1	4	90	100	97	100:0:0
6	**1b-Pd**	0.5	4	90	100	97	**100:0:0**
7	**1b-Pd**	0.25	4	90	100	98	**100:0:0**
8[d]	**1b-Pd**	0.5	4	90	100	56	51:0:49
9	**1b-Pd**	0.5	4	25	30	18	100:0:0
10	**1b-Pd**	0.5	2	90	79	66	96:0:4
11[e]	**1b-Pd**	0.5	1	90	4	1	–
12	–	–	4	90	0	0	–

[a] Performed in closed vessels (45 mL) in a multireactor, with 0.5 mmol of alkyne under dry N$_2$ atmosphere.
[b] Used as solvent.
[c] % Yield/conversion determined by GC (n-C$_{11}$H$_{24}$ as internal standard).
[d] Reaction under air atmosphere.
[e] THF was added (0.25 mL).

Table 2. Hydrosilylation of symmetric alkynes by **1b-Pd$_{np}$**.[a]



Entry	R^1	R^2, R^3	Product	Yield (%)[b]
1	Ph	Et, Et	 (*E*)-**2**	97
2		Et, Et	 (*E*)-**4**	97
3		Et, Et	 (*E*)-**5**	99
4	Bu	Et, Et	 (*E*)-**6**	60[c]
5	Ph	OEt,OEt	 (*E*)-**7**	99
6	Ph	Ph, Ph	 (*E*)-**8**	86
7[d]	Ph	Ph, H	 (*E*)-**9**	78

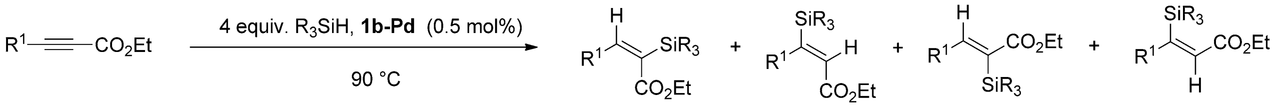
[a] In closed vessels (45 mL) with 1 mmol alkyne, 4 mmol triethylsilane under dry nitrogen.
[b] Isolated yield. The conversion was complete in all entries.
[c] Lower yield due to evaporation.
[d] 1 mmol of alkyne and 2 mmol of silane, reaction time = 170 h.

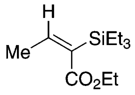
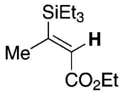
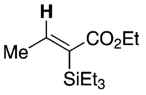
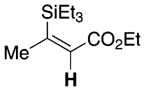
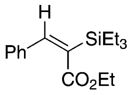
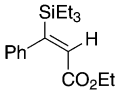
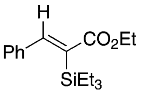
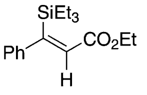
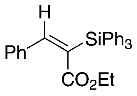
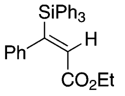
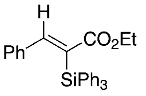
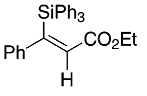
Table 1). However, incomplete conversions and lower selectivities were achieved upon decreasing the catalyst loading, with the stereoisomeric vinylsilane (*Z*)-**2** (*anti* addition) and (*Z*)-stilbene (**3**) formed as by-products (entries 2 and 3, Table 1). To our delight, analogous experiments with the tetrafluoroborate catalyst **1b-Pd** gave full conversion and complete selectivity for the vinylsilane (*E*)-**2** with catalyst loading down to 0.25 mol% Pd (entries 4–7, Table 1). When the reaction with 0.5 mol% of **1b-Pd** took place under air, the chemoselectivity dropped to about 50% in favor of the semihydrogenation product **3** (entry 8, Table 1). These experiments established **1b-Pd** as the best catalyst for the hydrosilylation, and showed that an inert atmosphere was crucial for achieving high chemoselectivity. A lower yield of (*E*)-**2** was obtained at 25 °C (entry 9, Table 1). Using less silane resulted in incomplete conversion and the formation of traces of **3** (entry 10, Table 1). An experiment with a stoichiometric amount of silane in THF as solvent was unsuccessful (entry 11, Table 1). Control experiments showed that the reaction did not occur in the absence of catalyst (entry 12). For comparison, other palladium sources, such as Pd(dba)$_2$, Pd(OAc)$_2$ and Pd(PPh$_3$)$_4$, were tested as catalysts and poorer results were achieved in terms of conversion and selectivity.

Having established nanoparticles **1b-Pd** as the best catalyst, the optimized conditions (0.5 mol% Pd, 4 equiv. of silane, 90 °C) were then applied to the hydrosilylation of some symmetrical internal alkynes with triethylsilane (entries 1–4, Table 2). This catalyst proved to be highly efficient and selective, furnishing the corresponding (*E*)-alkenylsilanes (entries 1–3, Table 2) in excellent yields, with the carbonyl groups of (*E*)-**4** unaltered under the reaction conditions. For the non-aromatic substrate (entry 4), the reduced yield was attributed to some loss in the isolation process due to higher volatility. For the reactions involving volatile silanes, the work-up consisted in filtering the reaction mixture through a short plug of silica gel with hexane as eluent and evaporating the solvent and excess reagent under an air flow, to afford a product that did not require any further purification.

Next, the hydrosilylation of diphenylacetylene with other silanes was examined under the same conditions. The reactions with triethoxysilane and triphenylsilane (entries 5 and 6, Table 2) proceded with high stereoselectivity, affording the corresponding (*E*)-vi-

Table 3. Hydrosilylation of differentiated unsymmetric alkynes.[a]



Entry	Yield [%][b]	Products and % selectivity[c]			
1	85	 (*E*)-**10**, 85%	 (*E*)-**11**, 4%	 (*Z*)-**10**, 11%	 ---
2	95	 (*E*)-**12**, 70%	 (*E*)-**13**, 16%	 (*Z*)-**12**, 9%	 (*Z*)-**13**, 5%
3	99	 (*E*)-**14**, 55%	 (*E*)-**15**, 45%	 ---	 ---

[a] Reactions performed in closed vessels (45 mL) with 0.72 mmol alkyne, 2.88 mmol triethylsilane under N_2 for 15–22 h.
[b] Isolated yield of the mixture of vinylsilanes; complete conversion in all entries.
[c] Determined by GC.

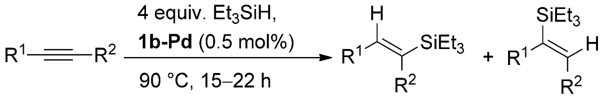
nylsilanes **7** and **8** in good isolated yields. In the case of the diphenylsilane (Ph_2SiH_2, entry 7), 2 mmol of this reagent were used for 1 mmol of alkyne and a longer reaction time was required for the full consumption of the starting alkyne. Under these conditions, the monoaddition product (*E*)-**9** was isolated in 78% yield (entry 7, Table 2). Once again, in all cases the only product detected arose from the *syn* addition of the Si–H bond across the carbon-carbon triple bond, as determined by the selective NOE experiments.

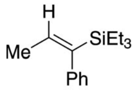
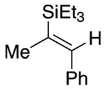
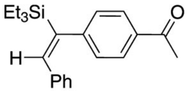
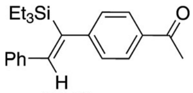
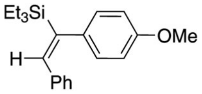
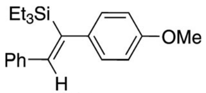
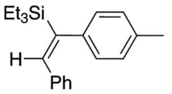
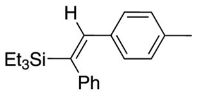
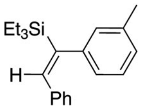
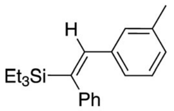
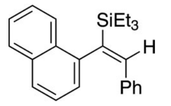
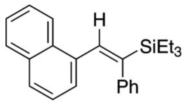
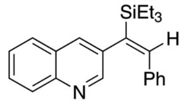
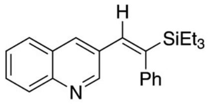
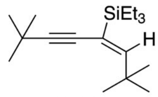
Next, the nanocatalyst **1b-Pd** was used in the hydrosilylation of asymmetrical internal alkynes (Table 3). In this case, four different vinylsilanes could be envisaged, with two stereoisomers (*syn* and *anti* addition) possible for each of the two regioisomeric forms. Although the expected *syn* preference might reduce this number to two, a reasonable degree of regioselectivity would only be possible for substrates with the two sides clearly differentiated.

Indeed, the reaction between ethyl 2-butynoate and triethylsilane was highly regio- and stereoselective, with the major product (*E*)-**10** arising from the *syn* addition that placed the triethylsilyl moiety *gem* to the electron-withdrawing ester group; only minor amounts of the *anti* addition compound (*Z*)-**10** and traces of the regioisomer (*E*)-**11** were observed by ^{1}H NMR (entry 1, Table 3). A similar α-directing effect of the electron-withdrawing groups in the addition of silanes to internal triple bonds has been previously reported by other groups.[12b,16] The selectivity decreased somewhat in the case of the ethyl 3-phenylpropiolate, although the *syn* addition and α regioselectivity were nevertheless predominant [product (*E*)-**12**, entry 2, Table 3]. However, the use of triphenylsilane with the latter alkyne substrate led to a lower regioselectivity, giving a 55:45 mixture of the two *syn* regioisomers (*E*)-**14** and (*E*)-**15** (entry 3, Table 3). In substrates lacking such a directing group (Table 4), differentiation could be observed for an alkyne bearing one alkyl and one aryl substituents. Thus, selective *syn* addition with high regioselectivity took place in the reaction of triethylsilane with prop-1-yn-1-ylbenzene, giving an 88:12 mixture of (*E*)-**16** and (*E*)-**17** (entry 1, Table 4). In general, unsymmetrical diarylalkynes gave mixtures of the two *syn* regioisomeric vinylsilanes (entries 3–7, Table 4), although the selectivity could be improved by introducing 1-naphthyl or 3-quinolyl substituents (entries 6 and 7). However, in entry 2, a 76:24 mixture of the two stereoisomers (*E*)-**18** and (*Z*)-**18** was obtained, and only a trace amount of the *syn* regioisomeric compound (*E*)-**19** was detected by ^{1}H NMR (see the Supporting Information). The high regioselectivity can be attributed to the electron-withdrawing effect of the acetyl group. In addition, we were able to prepare enyne (*E*)-**30** in 95% isolated yield from the *syn* monohydrosilylation of the corresponding symmetric diyne (entry 8, Table 4).

Interestingly, terminal alkynes, such as phenylacetylene, proved unreactive under the reaction conditions. We traced this lack of reactivity to a poisoning effect exerted by this substrate on the catalyst. In fact, addition of phenylacetylene was found to halt the otherwise efficient hydrosilylation of diphenylacetylene.

Table 4. Hydrosilylation of unsymmetric alkynes.[a]



Entry	Products		Ratio[b]	Yield [%][c]
1	 (*E*)-**16**	 (*E*)-**17**	88:12	96
2	 (*E*)-**18**	 (*Z*)-**18**	76:24	98[d]
3[e]	 (*E*)-**20**	 (*E*)-**21**	33:67	90
4	 (*E*)-**22**	 (*E*)-**23**	42:58	99
5	 (*E*)-**24**	 (*E*)-**25**	46:54	99
6	 (*E*)-**26**	 (*E*)-**27**	94:6	96
7	 (*E*)-**28**	 (*E*)-**29**	75:25	99
8	 (*E*)-**30**		–	95

[a] Performed in closed vessels (45 mL) with 0.72 mmol alkyne, 2.88 mmol Et_3SiH and 0.5 mol% of Pd under N_2.

[b] Determined by GC.

[c] Isolated yield of the mixture of vinylsilanes. Complete conversion in all entries.

[d] Trace amount of regioisomeric *syn* addition product (*E*)-**19** was detected by GC and ^1H NMR.

[e] Reaction time = 40 h.

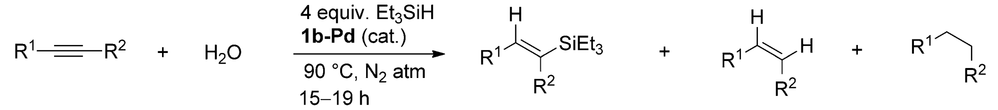
Although no further experiments were conducted, it is possible that the formation of Pd σ-alkynyl species is responsible for catalyst deactivation.

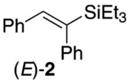
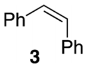
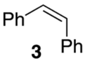
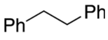
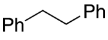
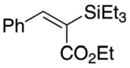
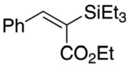
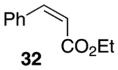
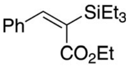
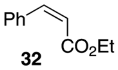
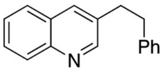
Structural characterization of all compounds included two-dimensional NMR techniques (COSY, HSQC, HMBC and NOESY experiments). The stereoselectivity of the reaction was studied by determining the relative (*E*)/(*Z*) configuration of the corresponding trisubstituted double bonds. This assignment was further confirmed by measuring the long-range proton-carbon and proton-silicon coupling constants using the selHSQMBC method[17] and determining the through-space NOE effects mainly on the olefinic proton. For instance, in the case of the (*E*)-**14** isomer, a large coupling of 15.4 Hz was measured between the olefinic proton and the carbonyl carbon, confirming their relative *trans* disposition. On the other hand, a large value of 11.1 Hz was measured between the olefinic proton and the *ipso* aromatic carbon resonating at 140.9 ppm in (*E*)-**15**, also confirming the *trans* relationship between phenyl group and the olefinic proton. The three-bond $^1H,^{29}Si$ coupling constant was also used for unambiguous determination of double bond configuration. As a general trend, values around 7–8 Hz were measured when the olefinic proton and the silicon atom are in a relative *cis* configuration, whereas larger values around 11 Hz were measured in *trans* dispositions. The regioselectivity of the process was studied by using chemical shift assignments and NOE contacts obtained from HMBC and NOESY spectra, respectively. The deshielding effects observed for the chemical shifts of olefinic carbons in the β position with respect to the ester group in isomers of entries 1–3 of Table 3, allow us a tentative determination of the α or β position of the silane group. For instance, whereas the olefinic carbon (=C–H) resonates at 147.5 ppm in (*E*)-**14**, this carbon appears at higher field (133.1 ppm) in the corresponding regioisomer (*E*)-**15**. In other isomers from entries 1–7 of Table 4, chemical shift differences of olefinic carbons are not so evident and the concerted use of HMBC and NOE data was successfully applied to elucidate the structure of each regioisomer (see the Supporting Information).

As mentioned above, the failure to employ an inert atmosphere (dry N_2) led to a decrease in the selectivity, giving a vinylsilane/alkene mixture (entry 8, Table 1). After some experimentation, we found that this was a general trend and that the formation of the semihydrogenated products was due to the moisture present in the air atmosphere. We thought we could take advantage of this observation and to perform the selective transfer hydrogenation of alkynes by the addition of controlled amounts of water to the alkyne-silane reaction mixture

The preliminary experiments with added water confirmed this assumption (*vide infra*). Presumably, dihydrogen is formed *in situ* from the reaction of the silane with water, which would also give rise to the corresponding silanol. Indeed, silanol and disiloxane (from the co-condensation of silanol) were the main side products in the hydrosilylation reactions performed under an air atmosphere. The related hydrogen production by the hydrolytic or alcoholytic oxida-

Table 5. Hydrogenation of internal alkynes using triethylsilane/water under Pd_{np} catalysis.[a]



Entry	R^1, R^2	Alkyne:H_2O[b]	Products		Ratio[c]	Conversion (yield [%])[d]
1	Ph, Ph	1:1	 (*E*)-**2**	 **3**	83:17	100
2	Ph, Ph	1:3	 **3**	 **31**	–	100
3	Ph, Ph	1:4	 **31**		–	100 (94)
4	Ph, CO_2Et	1:3	 (*E*)-**12**		–	100
5	Ph, CO_2Et	1:4	 (*E*)-**12**	 **32**	29:71	100
6	Ph, CO_2Et	1:8	 (*E*)-**12**	 **32**	6:94	100 (62)
7	3-quinolyl, Ph	1:8	 **33**		–	100 (78)

[a] *Reaction conditions:* 1 (or 0.5) mmol alkyne, 4 (or 2) mmol triethylsilane, 0.005 (or 0.025) mmol Pd (and the corresponding amount of water) in a closed vessel (45 mL) under dry nitrogen atmosphere at 90 °C.

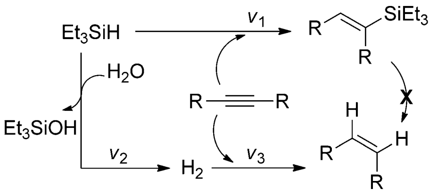
[b] Mmol alkyne/mmol water.

[c] Ratio of products determined by GC.

[d] GC conversion. Isolated yield in parentheses.

tion of silanes is a hot topic that has received considerable attention in the recent literature.[18] Thus, the reaction has been reported to take place in the presence of catalysts such as metal NPs (silver,[18a] gold,[18b–e] Pd,[18f,g] Ni[18h]) as well as transition metal complexes (rhenium,[18i] iridium,[18j,k] ruthenium,[18l–o] and zinc[18p]). Hydrogenation of unsaturated carbon-carbon bonds with the system silane-water under palladium(II) acetate catalysis had also been previously described.[19] Oxidative cycloaddition of 1,1,3,3-tetramethyldisiloxane to terminal alkynes[20] and oxidative hydrolysis of 1,2-disilanes,[21] both under catalysis by Au/TiO_2 NP, also proceed with concomitant evolution of hydrogen gas. Selective semireduction of alkynes has also been recently accomplished with silane/alcohol under copper catalysis.[22] Although Pd/C-induced catalytic transfer hydrogenation of several types of substrates with triethylsilane has also been reported,[23] no discussion about the origin of the hydrogen atoms was included.

Our preliminary results for the transfer hydrogenation of internal alkynes with triethylsilane/water catalyzed by **1b-Pd** are summarized in Table 5. The amount of water required for the semi to full hydrogenation was highly dependent on the nature of the alkyne substrate. Thus, in the case of the diphenylacetylene, the addition of 1 mmol of water per mmol of alkyne gave a mixture of vinylsilane (*E*)-**2** and *cis*-stilbene **3**, with the hydrosilylation still predominating (entry 1, Table 5). Increasing the amount of water to 3 mmol water/mmol alkyne led to the suppression of the formation of the silylated product, but afforded a mixture of alkene **3** and 1,2-diphenylethane, **31** (entry 2, Table 5). Finally, a quantitative yield of the same fully hydrogenated alkane (**31**) was isolated when a 4:1 water/alkyne ratio was employed (entry 3, Table 5). In contrast, for ethyl phenylpropynoate the addition of three equivalents of water still produced an almost exclusive formation of the hydrosilylated product (*E*)-**12**. Selective hydrogenation in this case required eight mmol of water/mmol of alkyne to give the corresponding *cis*-alkene **32**, whereas with four equivalents of water a mixture of both products was observed (entries 4–6, Table 5). Finally, while we were unable to selectively semihydrogenate the 3-(phenylethynyl)quinoline, the fully hydrogenated compound **33** was isolated when using 8 mmol of water per mmol of alkyne (entry 7, Table 5).



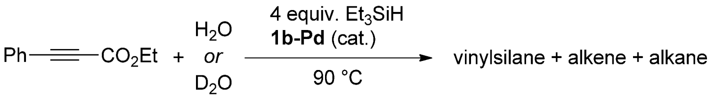
Scheme 2. Competitive hydrosilylation and transfer hydrogenation of internal alkynes.

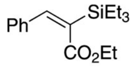
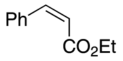
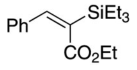
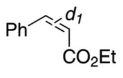
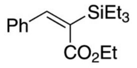
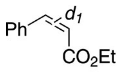
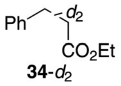
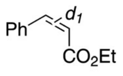
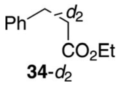
The hypothesis of formation of semi-hydrogenated products through protodesilylation of the intermediate vinylsilanes was discarded as compound (*E*)-**2** was recovered unaffected after being subjected to the conditions of entry 2 of Table 5. This indicates that the hydrosilylation (rate v_1) and transfer hydrogenation processes (rates v_2 and v_3) occur in a competing fashion, with the relative rates (and thus the outcome) dependent on the amount of water added (Scheme 2).

The origin of each of the two hydrogen atoms of the *in situ* formed dihydrogen molecule[24] was probed using D_2O. For this purpose, the reaction corresponding to entry 6 of Table 5 was repeated with D_2O (Table 6, entries 1 and 2). Under these conditions, the use of D_2O caused the reaction to proceed more slowly and to give a mixture with the vinylsilane as the major product. Since the rate of the hydrosilylation v_1 would be unaffected by the change, this outcome indicates a strong kinetic isotope effect in the putative hydrogenation rates v_2 or v_3 (or both), diminished with respect to v_1. A partial selectivity towards the hydrogenated product could be achieved by further increasing the amount of D_2O (entries 3 and 4, Table 6). Thus, for a molar ratio alkyne:D_2O of 1:15, a mixture of the vinylsilane (*E*)-**12**, the *cis*-alkene **32** and alkane **34** was achieved (entry 3), whereas with a ratio of 1:20 the alkane **34** was the major product isolated (Table 6, entry 4). The ^1H NMR spectrum of the fully reduced compound **34** obtained with D_2O (see the Supporting Information) showed two methylene resonances at 2.6 and 2.9 ppm, but with an integrated intensity of 1 H each, instead of the 2 H expected for the fully *protio* species. This observation indicates that: a) about 50% of the newly incorporated H atoms proceed from water; and b) the deuterium incorporation takes place indiscriminately at both ends of the unsaturated bond. This was confirmed by recording the corresponding ^2H NMR spectrum (see the Supporting Information).

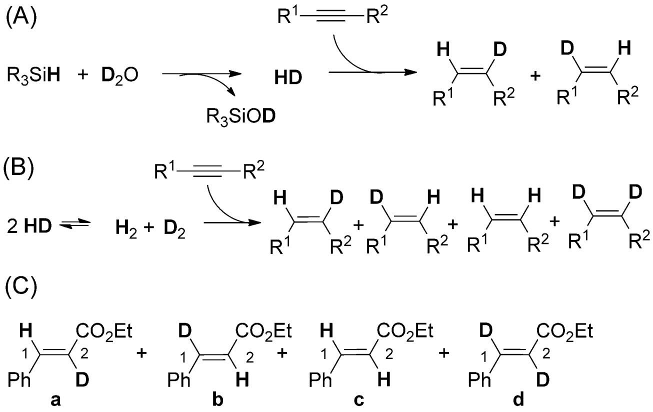
One possibility for the statistical 50% deuterium incorporation into **34** is the hydrogenation with two HD molecules to give exactly 2 D/molecule. However, bulk **34** could also simply consist of a mixture of isotopomers arising from indiscriminate hydrogenation with a fully (or partially) scrambled HH/HD/DD mixture. Focusing on the initial addition of dihydrogen to the alkyne, the reaction with the pure HD would give two monodeuterated regioisomers (Scheme 3, A). On

Table 6. The effect of using D_2O in the hydrosilylation/hydrogenation manifold with **1b-Pd**.[a,b]



Entry	Water (equiv.)[c]	Products			Ratio	Conversion (yield [%])[d]
1[e]	H_2O (8)	 (*E*)-**12**	 **32**		6:94	100 (62)
2	D_2O (8)	 (*E*)-**12**	 **32**-*d*1		>95:5	75[f]
3	D_2O (15)	 (*E*)-**12**	 **32**-*d*1	 **34**-*d*2	43:45:12	100
4	D_2O (20)		 **32**-*d*1	 **34**-*d*2	10:90	100 (80)

[a] Conditions are the same as in Table 5.
[b] Product ratio determined by GC.
[c] This refers to mmol water per mmol alkyne.
[d] GC conversion. Isolated yield in parentheses.
[e] Entry taken from Table 5.
[f] Approximate value.



Scheme 3. Products of the transfer hydrogenation of internal asymmetric alkynes using D_2O. (A): without HD scrambling; (B): with HD scrambling; (C): the four *trans* olefins obtained as side-products for the case of ethyl phenylpropiolate.

the other hand, hydrogenation with a scrambled isotope mixture would yield four isotopomers (Scheme 3, B).

Here, our analysis was aided by the fact that some of the semihydrogenated *cis* alkene **32**-d_1 (minor product, entry 4, Table 6) had partially isomerized to its *trans* isomer during work-up, and that the olefinic ^{1}H NMR resonances (two H in *trans*) for this new species were well discernible from the rest of the signals in the mixture containing **34**-d_2 as major product. Characteristically, each olefinic resonance appeared as a combination of a triplet with a small $J_{H,D}$ (2.4 Hz) nestled within a large J doublet (16 Hz) for the *trans* H,H coupling (see Figure 1). Thus, the two large doublets correspond to the H,H product, while each of the triplets (coupling to D, $S=1$) belongs respectively to each of the two H,D isotopomers; the presence of the fully deuterated form is deduced from the missing integral intensities. Based on the signal pattern and integration (Figure 1, see also the Supporting Information), the product was confirmed as a statistical mixture of isomers (a, b and c, 25% each, Scheme 3, C), with the "invisible" dideuterated isotopomer d accounting for the remaining 25%. This was confirmed by recording the corresponding ^{2}H NMR spectrum (see the Supporting Information).

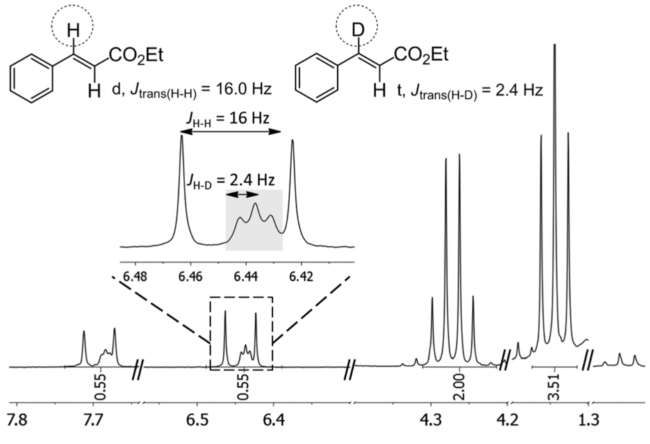


Figure 1. A fragment of the ^{1}H NMR spectrum of *trans*-**32**-d_1 (minor component; major component not shown for clarity).

Conclusions

We have developed an efficient and stereoselective *syn* addition of silanes to internal alkynes, providing (*E*)-vinylsilanes in excellent yields, by the use of palladium nanoparticles stabilized by tris-imidazolium tetrafluoroborates as catalyst under a dry inert atmosphere. Fair to good regioselectivities have been achieved in the case of asymmetric alkynes. To the best of our knowledge, this is the first report of palladium nanoparticles involved in hydrosilylation reactions of internal alkynes, substrates that are much less reactive than the terminal acetylenes and which have received less attention in the literature. The addition of controlled amounts of water to the silylation mixture promotes the oxidative hydrolysis of silanes with the concomitant formation of dihydrogen, leading to a competitive process of transfer hydrogenation of the alkynes to the (*Z*)-alkenes or the corresponding alkanes depending on the amount of water and the nature of the acetylenic substrates.

Experimental Section

Hydrosilylation of Diphenylacetylene with Triethylsilane by Pd_{np} (Entry 1, Table 2); Typical Procedure

Diphenylacetylene (178 mg, 1 mmol) and catalyst **1b-Pd** (0.5 mol% Pd) were weighed into a screw-top sealable tube. The system was subjected to three evacuate-refill cycles with dry nitrogen. Triethylsilane (640 μL, $\rho = 0.73\ \mathrm{g\,mL^{-1}}$, 4 mmol) was added under nitrogen atmosphere. The reaction was left under stirring at 90 °C until total conversion of the alkyne (GC monitoring). The mixture was filtered through a plug of silica-gel eluting with hexane and the solvent was removed under air to afford the (*E*)-(1,2-diphenylvinyl)triethylsilane, (*E*)-**2**, as a yellowish liquid; yield: 287 mg (97%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.30$ (t, $J = 7.2$ Hz, 2H, Ph-*H*), 7.20 (t, $J = 7.2$ Hz, 1H, Ph-*H*), 7.12–7.07 (m, 3H, Ph-*H*), 7.03–7.01 (m, 1H, Ph-*H*), 7.00–6.94 (m, 3H, Ph-*H*), 6.78 (s, 1H, SiC=C*H*), 0.97 (t, $J = 7.8$ Hz, 9H, $-CH_2CH_3$), 0.65 (q, $J = 8$ Hz, 6H, $-CH_2CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 144.2$, 143.3, 138.9, 137.6, 129.7, 128.7, 128.0, 127.4, 127.1, 125.7, 7.5, 2.9; MS: *m/z* = 294.1 (M^+).

Supporting Information

The Supporting Information contains details of the experimental procedures and characterization of compounds along with copies of all ^{1}H and ^{13}C NMR spectra.

Acknowledgements

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References

[1] a) I. Ojima, Z. Li, J. Zhu, in: *The Chemistry of Organosilicon Compounds*; (Eds.: Z. Rappoport, Y. Apeloig), Wiley-VCH, Weinheim, **1998**, Vol. 2, pp 1687–1792; b) B. Marciniec; H. Maciejewski, C. Pietraszuk, P. Pawluc, in: *Hydrosilylation: A Comprehensive Review on Recent Advances*, *Advances in Silicon Science Series*, (Ed.: B. Marciniec), Springer Verlag, Berlin, Heidelberg, **2009**, Vol. 1, Chapter 2.

[2] B. M. Trost, Z. T. Ball, T. Jöge, *J. Am. Chem. Soc.* **2002**, *124*, 7922–7923.

[3] For some recent reviews on the palladium-catalyzed cross-coupling of organosilicon reagents, see: a) Y. Nakao, T. Hiyama, *Chem. Soc. Rev.* **2011**, *40*, 4893–4901; b) H. F. Sore, W. R. J. D. Galloway, D. R. Spring, *Chem. Soc. Rev.* **2012**, *41*, 1845–1866.

[4] a) K. Tamao, N. Ishida, T. Tanaka, M. Kumada, *Organometallics* **1983**, *2*, 1694–1696; b) I. Fleming, R. Henning, H. Plaut, *J. Chem. Soc. Chem. Commun.* **1984**, 29–31.

[5] a) J. L. Speier, J. A. Webster, H. H. Barnes, *J. Am. Chem. Soc.* **1957**, *79*, 974–979; b) G. Chandra, P. Y. Lo, P. B. Hitchcock, M. F. Lappert, *Organometallics* **1987**, *6*, 191–192; c) B. D. Karstedt, U.S. Patent 3,775,452, **1973**; d) J. Stein, L. N. Lewis, Y. Gao, R. A. Scott, *J. Am. Chem. Soc.* **1999**, *121*, 3693–3703.

[6] For the early work, see: a) M. A. Esteruelas, J. Herrero, L. A. Oro, *Organometallics* **1993**, *12*, 2377–2379. For later work, see: b) Y. Na, S. Chang, *Org. Lett.* **2000**, *2*, 1887–1889; c) S. V. Maifeld, M. T. Tran, D. Lee, *Tetrahedron Lett.* **2005**, *46*, 105–108; d) C. Menozzi, P. I. Dalko, J. Cossy, *J. Org. Chem.* **2005**, *70*, 10717–10719; e) C. S. Aricó, L. R. Cox, *Org. Biomol. Chem.* **2004**, *2*, 2558–2562; f) B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2001**, *123*, 12726–12727; g) B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2005**, *127*, 17644–17655.

[7] a) W. A. Solomonsz, G. A. Rance, M. Suyetin, A. La Torre, E. Bichoutskaia, A. N. Khlobystov, *Chem. Eur. J.* **2012**, *18*, 13180–13187; b) A. Psyllaki, I. N. Lykakis, M. Stratakis, *Tetrahedron* **2012**, *68*, 8724–8731.

[8] a) F. Alonso, R. Buitrago, Y. Moglie, J. Ruiz-Martínez, A. Sepúlveda-Escribano, M. Yus, *J. Organomet. Chem.* **2011**, *696*, 368–372; b) F. Alonso, R. Buitrago, Y. Moglie, A. Sepúlveda-Escribano, M. Yus, *Organometallics* **2012**, *31*, 2336–2342; c) R. Cano, M. Yus, D. J. Ramón, *ACS Catal.* **2012**, *2*, 1070–1078.

[9] a) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757–3778; b) M. Moreno-Mañas, R. Pleixats, *Acc. Chem. Res.* **2003**, *36*, 638–643; c) A. Balanta, C. Godard, C. Claver, *Chem. Soc. Rev.* **2011**, *40*, 4973–4985; d) *Nanoparticles and Catalysis*, (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2008**.

[10] M. Benohoud, S. Tuokko, P. M. Pihko, *Chem. Eur. J.* **2011**, *17*, 8404–8413.

[11] M. Tamura, H. Fujihara, *J. Am. Chem. Soc.* **2003**, *125*, 15742–15743.

[12] a) D. Motoda, H. Shinokubo, K. Oshima, *Synlett* **2002**, 1529–1531; b) Y. Sumida, T. Kato, S. Yoshida, T. Hosoya, *Org. Lett.* **2012**, *14*, 1552–1555; c) H. Zhou, C. Moberg, *Org. Lett.* **2013**, *15*, 1444–1447.

[13] M. Planellas, R. Pleixats, A. Shafir, *Adv. Synth. Catal.* **2012**, *354*, 651–662.

[14] K. Philippot, B. Chaudret, *Organometallic Derived Metals, Colloids and Nanoparticles*, in: *Comprehensive Organometallic Chemistry III*, (Eds.: R. H. Crabtree, M. P. Mingos), Elsevier, **2007**, Vol. 12, Chapter 12–03, pp 71–99.

[15] a) M. F. Rettig, P. M. Maitlis, *Inorg. Synth.* **1990**, *28*, 110–113.

[16] D. A. Rooke, E. M. Ferreira, *Angew. Chem.* **2012**, *124*, 3279–3284; *Angew. Chem. Int. Ed.* **2012**, *51*, 3225–3230.

[17] S. Gil, J. F. Espinosa, T. Parella, *J. Magn. Reson.* **2011**, *213*, 145–150.

[18] a) T. Mitsudome, S. Arita, H. Mori, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem.* **2008**, *120*, 8056–8058; *Angew. Chem. Int. Ed.* **2008**, *47*, 7938–7940; b) T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Commun.* **2009**, 5302–5304; c) N. Asao, Y. Ishikawa, N. Hatakeyama, Menggenbateer, Y. Yamamoto, M. Chen, W. Zhang, A. Inoue, *Angew. Chem.* **2010**, *122*, 10291–10293; *Angew. Chem. Int. Ed.* **2010**, *49*, 10093–10095; d) W. Li, A. Wang, X. Yang, Y. Huang, T. Zhang, *Chem. Commun.* **2012**, *48*, 9183–9185; e) M. Yan, T. Jin, Y. Ishikawa, T. Minato, T. Fujita, L.-Y. Chen, M. Bao, N. Asao, M.-W. Chen, Y. Yamamoto, *J. Am. Chem. Soc.* **2012**, *134*, 17536–17542; f) K. Shimizu, T. Kubo, A. Satsuma, *Chem. Eur. J.* **2012**, *18*, 2226–2229; g) M. Jeon, J. Han, J. Park, *ChemCatChem* **2012**, *4*, 521–524; h) K. Shimizu, K. Shimura, N. Imaiida, A. Satsuma, *J. Mol. Catal. A: Chem.* **2012**, *365*, 50–54; i) E. A. Ison, R. A. Corbin, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2005**, *127*, 11938–11939; j) Y. Lee, D. Seomoon, S. Kim, H. Han, S. Chang, P. H. Lee, *J. Org. Chem.* **2004**, *69*, 1741–1743; k) D.-W. Wang, D-Sh. Wang, Q.-A. Chen, Y.-G. Zhou, *Chem. Eur. J.* **2010**, *16*, 1133–1136; l) M. Lee, S. Ko, S. Chang, *J. Am. Chem. Soc.* **2000**, *122*, 12011–12012; m) E. Choi, C. Lee, Y. Na, S. Chang, *Org. Lett.* **2002**, *4*, 2369–2371; n) K. Mori, M. Tano, T. Mizugaki, K. Ebitani, K. Kaneda, *New. J. Chem.* **2002**, *26*, 1536–1538; o) S. T. Tan, J. W. Kee, W. Y. Fan, *Organometallics* **2011**, *30*, 4008–4013; p) W. Sattler, G. Parkin, *J. Am. Chem. Soc.* **2012**, *134*, 17462–17465; q) M. Jeon, J. Han, J. Park, *ACS Catal.* **2012**, *2*, 1539–1549.

[19] J. M. Tour, J. P. Cooper, S. L. Pendalwar, *J. Org. Chem.* **1990**, *55*, 3452–3453.
[20] I. N. Lykakis, A. Psyllaki, M. Stratakis, *J. Am. Chem. Soc.* **2011**, *133*, 10426–10429.
[21] C. Gryparis, M. Stratakis, *Chem. Commun.* **2012**, *48*, 10751–10753.
[22] A. M. Whittaker, G. Lalic, *Org. Lett.* **2013**, *15*, 1112–1115.
[23] P. K. Mandal, J. S. McMurray, *J. Org. Chem.* **2007**, *72*, 6599–6601.
[24] Formation of HD from a mixture of Et_3SiH, D_2O and **1b-Pd** in C_6D_6 at 333 K was detected by ^1H NMR as a 1:1:1 signal at 4.43 ppm ($J_{H,D}=42.7$ Hz) (see the Supporting Information). The chemical shift and coupling constant are in agreement with the reported values for HD in toluene-d_8, see: J. Y.-C. Chen, A. A. Martí, N. J. Turro, K. Komatsu, Y. Murata, R. G. Lawler, *J. Phys. Chem. B* **2010**, *114*, 14689–14695.