

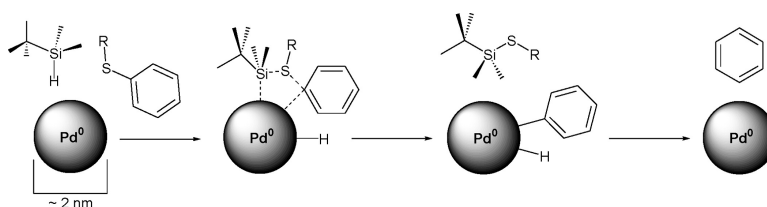
Article

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A Catalytic Synthesis of Thiosilanes and Silthianes: Palladium Nanoparticle-Mediated Cross-Coupling of Silanes with Thio Phenyl and Thio Vinyl Ethers through Selective Carbon–Sulfur Bond Activation

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Abstract: Palladium nanoparticles generated in situ from *N,N*-dimethyl-acetamide (DMA) solutions of PdX₂ (X = Cl⁻, OAc⁻, OCOCF₃⁻) or Pd₂(dba)₃ by reduction with alkyl silanes R₃SiH (R = Me, Et, *i*-Pr, *t*-Bu) are selective catalysts for the cross-coupling of the silanes R₃SiH with phenyl and vinyl thioethers forming the corresponding thiosilanes and silthianes in high yields and under mild conditions. The method is applicable to phenyl thioglycosides, giving access to thiosilyl glycosides a new class of sugar derivatives.

Introduction

Thiosilanes are a distinct class of organosulfur compounds characterized by the high reactivity of the relatively weak silicon–sulfur bond (estimated at ~300 kJ/mol)¹ and the oxophilicity of silicon, which result in interesting applications in organic synthesis. For example, they have been used as selective masking reagents of carbonyl groups to generate *O*-silylhemithioacetals and ketals, which are precursors for the preparation of unsymmetrical sulfides.^{2,3} They also react with acid halides to produce thio carboxylic esters (thiol esters),⁴ which upon sulfur activation act as synthons for carboxyl in esterification reactions.⁵ In addition, thiosilanes have been employed for oxirane ring-opening through C–O bond cleavage, which is a useful starting point for the synthesis of multifunctionalized organic compounds⁶ and in the synthesis of vinyl sulfides.⁷

Thiosilanes are normally prepared from the chlorosilane and metal thiolate.¹ The silylation of thiols with trialkyl/aryl silanes or alkyl/aryl disilane catalyzed by transition-metal complexes such as Wilkinson's catalyst also provides a convenient route to thiosilanes.⁸ At elevated temperatures, the reaction can also be carried out without catalyst.⁹ The reductive cleavage of disulfides with metallic sodium in the presence of trimethyl-

chlorosilane generates the corresponding alkylthio trimethylsilane. With dimethyl disulfides and dibenzyl disulfides, hexamethyldisilthiane is produced.¹⁰ Hexamethyldisilthiane, widely used as a sulfur transfer agent, can also be prepared by a reaction of chlorosilanes and Na/S/naphthalene or Li₂S in THF^{11,12} and by the silylation of hydrogen sulfide with 1-(trimethylsilyl)imidazole.¹³ An interesting class of cyclic silthianes is formed by reaction of organochlorosilanes with hydrogen sulfide and base.^{14,15} Here we wish to report on the serendipitous discovery of a new chemoselective palladium nanoparticle-catalyzed route to thio silanes and silthianes starting from phenyl or vinyl sulfides.

Discovery and Context. Recently, we reported a new method for the regioselective silylation of simple alkyl and phenyl glycosides using a palladium nanoparticle colloid-catalyzed silane alcoholysis reaction in which the catalyst is formed in situ by reduction of a Pd²⁺ precursor.¹⁶ Palladium nanoparticles formed in situ from Pd(OAc)₂ have also been shown to be the active catalyst in the silaesterification reaction of polyhydrosiloxanes with carboxylic acids.¹⁷ Analogous to the role of the silane in the silane alcoholysis reaction described by us, in this reaction the polyhydrosiloxanes also act as the reductant, reactant, and nanocolloid stabilizer at the same time.

To further test the scope and limitations of the silane alcoholysis method for the synthesis of sugar silyl ethers, we sub-

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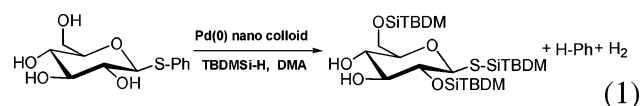
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Table 1. Survey of the Cross-Coupling Reaction of Various Alkyl and Aryl Sulfides with Excess Silane *t*-BuMe₂SiH (TBDMSiH) and Various Palladium Catalyst Precursors at 298 K in DMA

entry	sulfide	products	yields (%) of products with various catalyst precursors by quantitative GC (reaction time in hours) ^a					
			PdCl ₂ ^b	Pd(OAc) ₂ ^b	Pd(OCOCF ₃) ₂ ^b	Pd ₂ (dba) ₃ ^b	Pd ⁰	Pd(PPh ₃) ₄
1	HOCH ₂ CH ₂ SPh ^c	TBDMSi-OCH ₂ CH ₂ S-SiTBDM	quant. (3)	quant. (2)	quant. (2)	quant. (2)	14 (19)	0 (2)
2	EtSPh ^d	EtS-SiTBDM	quant. (4)	quant. (5)	quant. (3)	quant. (4)	0 (5)	0 (1)
3	EtSEt ^e	EtS-SiTBDM/(TBDMSi) ₂ S	0/0 (24)	0/0 (24)	0/0 (24)	0/0 (24)	0/0 (24)	0/0 (24)
4	PhSPh ^c	PhS-SiTBDM/(TBDMSi) ₂ S	68/32 (4)	71/29 (4)	73/27 (4)	57/43 (7)	19/2 (9)	0/0 (12)
5	PhSSPh ^e	PhS-SiTBDM/(TBDMSi) ₂ S ₂	0/0 (24)	1/0 (24)	0/0 (24)	3/0 (24)	0/0 (24)	0/0 (24)
6	PhSCH ₂ SPh ^c	PhSCH ₂ S-SiTBDM/ TBDMSi-SCH ₂ S-SiTBDM	0/quant. (11)	0/quant. (11)	0/quant. (11)	0/quant. (11)	0/0 (11)	0/0 (11)
7	EtSCH=CH ₂ ^d	EtS-SiTBDM/EtSEt	22/71 (24)	45/54 (24)	38/62 (24)	35/65 (24)	0/0 (24)	0/0 (24)
8	PhSCH=CH ₂ ^e	PhS-SiTBDM/ TBDMSi-SEt/PhSEt/ (TBDMSi) ₂ S	37/6/30/7 (12)	48/21/6/21 (12)	47/12/18/8 (12)	46/23/6/10 (12)	0/0/2/0 (12)	0/0/0/0 (12)
9	MeSPh- <i>p</i> -OMe ^d	MeS-SiTBDM	quant. (12)	quant. (12)	quant. (12)	quant. (12)	0 (12)	0 (12)
10	MeSPh- <i>p</i> -Cl ^{d,f}	MeS-SiTBDM	quant. (12)	quant. (12)	quant. (12)	quant. (12)	0 (12)	0 (12)

^a Catalysts load 3 mol % with respect to thioether in all reactions. ^b TEM analysis shows that Pd⁰ nanoparticles are generated in situ. ^c Amount of TBDMSiH = 3.5 equiv. ^d Amount of TBDMSiH = 1.3 equiv. ^e Amount of TBDMSiH = 2.3 equiv. ^f Byproducts are chlorobenzene and benzene (~21–30%).

sequently extended our study to sugars containing other functional groups. With phenyl 1-thio- β -D-glucopyranoside as the substrate, we observed the following surprising reaction (eq 1) confirmed by elemental analysis of the product for sulfur and loss of the signals for phenyl in the ¹H and ¹³C NMR spectra.



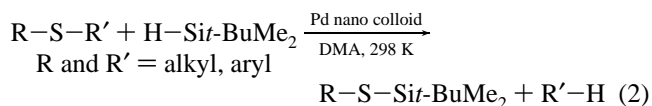
In addition to the anticipated normal silane alcoholysis of the hydroxyl functions at C-2 and C-6,¹⁶ the reaction produces the sugar thiosilane, *t*-BuMe₂Si-1-thio-2,6-*O*-bis(*t*-BuMe₂Si)- β -D-glucopyranoside, as the major product through phenyl C(sp²)-S bond cleavage and subsequent Si-S bond formation at the anomeric position (C-1) with the concomitant formation of benzene, whose presence was confirmed by GC-MS. This result is unique both from the point of view of C(sp²)-S bond activation as well as S-Si bond formation to produce a sugar thiosilane, an entirely new class of anomerically functionalized sugars.

The transition-metal-mediated activation of C(sp³)-S and C(sp²)-S bonds for both synthetic purposes^{18–29} and petrochemical hydrodesulfurization^{30–34} as well as in bioinorganic related systems³⁵ has been extensively studied. In many cases, transition-metal-catalyzed C-S bond scissions are followed by carbon-carbon bond formation through a cross-coupling reaction with Grignard or other organometallic reagents. However,

to date a silicon-sulfur bond formation by the corresponding reaction via C(sp²)-S bond cleavage is, to our knowledge, unknown.

Results

To establish the scope and limitation of the generalized reaction (eq 2), we investigated a series of simple sulfides with *t*-BuMe₂SiH (TBDMSiH) as the silane and various palladium catalyst precursors in *N,N*-dimethyl-acetamide (DMA). The results of this survey with individual yields as determined by quantitative GC analysis calibrated against authentic samples are summarized in Table 1.



Comparison of the reactions of entries 2–4 and 6 shows that C(sp²)-S bonds are cleaved selectively by the palladium

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Table 2. Isolated Yields of Silylated Products Obtained from Representative Sulfides with PdCl₂ and Excess Silane TBDMSiH (2.3 equiv) at 298 K

entry	sulfides	silylated products	isolated yields (%)	
			vacuum distillation	column chromatography ^a
1	HOCH ₂ CH ₂ SPh	TBDMSi-OCH ₂ CH ₂ S-SiTBDM	95	42
2	AcOCH ₂ CH ₂ SPh	AcOCH ₂ CH ₂ S-SiTBDM	60	45
3	TBDMSi-OCH ₂ CH ₂ SPh	TBDMSi-OCH ₂ CH ₂ S-SiTBDM	89	33
4	PhSCH ₂ Ph	TBDMSi-SCH ₂ Ph	56	57
5	PhSCH ₂ SPh	TBDMSi-SCH ₂ S-SiTBDM	85	54

^a Balance of products decomposed during column chromatography.

nanoparticles generated from a variety of PdX₂ salts or Pd₂(dba)₃, while C(sp³)-S bonds do not react under the reaction conditions. In all reactions, the nano structure of the catalyst obtained by reaction of the precursor with the silane before addition of the thioether is a necessary prerequisite for catalytic activity (vide infra). Bulk Pd⁰ (palladium black) and the homogeneous molecularly dispersed Pd⁰ precursor Pd(PPh₃)₄, which does not result in nanoparticle formation, give only marginal or no catalytic activity at all. The reaction of entry 4 also shows that even with the sterically demanding silane TBDMSiH repeated activation of C(sp²)-S bonds on the same sulfur atom are possible, leading to a mixture of the thiosilane and silthiane.

In contrast, PhSSPh (entry 5 in Table 1) either reacts not at all or at best stoichiometrically with the silane (using Pd₂(dba)₃ as the nanoparticle precursor). Poisoning of heterogeneous precious metal catalysts by sulfur or thiols is a well-established phenomenon³⁶ and probably operates here as well, i.e., the catalysts are poisoned by interaction between the surface of Pd(0) nanoparticles and the sulfur atoms of S-Ph fragments formed through the cleavage of relatively weak S-S bonds in the disulfides. Thermodynamically S-S bond cleavage in PhSSPh (~230 kJ/mol) is substantially easier than that of C(sp²)-S bonds (~370 kJ/mol), and it has been reported that the disulfide bond can be cleaved by a nucleophilic substitution reaction through the combined catalytic action of both an electrophile and a nucleophile.^{37,38} To promote electrophilic S-S bond cleavage, metal ions with a high affinity for sulfur, such as palladium, silver, and mercury, are commonly used.

To test the hypothesis of catalyst deactivation by Ph-S fragments resulting from the cleavage of PhSSPh, we carried out a series of control reactions, in which various phenyl sulfides including HOCH₂CH₂SPh (cf. entry 1 of Table 1) were added to DMA solutions containing PhSSPh, excess amounts of TBDMSiH, and Pd(0) nanoparticles pregenerated from PdCl₂. Except for a trace amount of silane alcoholysis product of HOCH₂CH₂SPh, only the starting sulfides and PhSSPh were detected in all cases. The control reactions thus assert that an irreversible reaction occurs between PhSSPh and the palladium surface, which poisons the catalyst as subsequently added phenyl sulfides were not converted to the corresponding thiosilanes and only marginal catalytic activity for silane alcoholysis is observed.

When the two sulfur atoms are separated by a methylene unit as in PhSCH₂SPh (entry 6, Table 1) the selective activation of the C(sp²)-S bond is again achieved, but under conditions identical to those of the reaction of diphenyl sulfide (2.3 equiv

of silane present), and both C(sp²)-S bonds present are activated quantitatively, leading to TBDMSi-SCH₂S-SiSiTBDM as the sole product. Compared to PhSPh (entry 4), this is likely the result of the better steric accessibility of the second sulfur once the first has been functionalized by the bulky silane.

The reactions of entries 7 and 8 in Table 1 demonstrate that the reaction can be extended to vinyl rather than aryl sulfides, but the hydrogenation of the carbon-carbon double bond becomes the dominant reaction with ethyl vinyl sulfide. With vinyl phenyl sulfide (entry 8), the displacement of the vinyl group is the more favorable process; however, activation of the phenyl-sulfur bond as well as double activation of both the phenyl and vinyl carbon sulfur bond also take place. The theoretically possible product TBDMSi-S-CH=CH₂ is not observed, i.e., in all cases the vinyl group is either cleaved off or hydrogenated. The overall product distributions depend somewhat on the nature of the counterion in the catalyst precursor, but they elude obvious interpretation. The hydrogen required for the hydrogenation of the vinyl group can only originate from the silane, either by activation of the silicon-hydrogen bond by the nanoparticles or through the reaction of the silane with trace amounts of water in the highly polar DMA solvent leading to the formation of molecular hydrogen and silanols. In either case, active hydrogen must be present on the surface of the nanoparticles, effecting a heterogeneous hydrogenation of the carbon-carbon double bond as previously described for this type of system.^{39,40} Comparison of the reactions of entries 2, 9, and 10 in Table 1 also shows that the presence of an electron withdrawing or donating substituent in the para position of the phenyl sulfide has no influence on the reaction yield.

To evaluate the actual synthetic utility of the new method, some thiosilanes were isolated by solvent removal in vacuo followed by flash column chromatography or vacuum distillation (Table 2). Thiosilanes are thermally stable, but the Si-S bond is readily cleaved by many protic reagents, particularly those containing the O-H group, in part because the formation of relatively stronger Si-O single bonds (~800 kJ/mol)⁴¹ compared to the Si-S single bonds (300-330 kJ/mol).¹ Silica gel adsorbent for column chromatography contains Si(OSi≡)₄, Si(OSi≡)₃(OH), and Si(OSi≡)₂(OH)₂ groups, which explains the substantially lower yields obtained by chromatography and makes either distillation or crystallization the isolation method of choice for this class of compounds.

The effect of the nature of the silane on the C(sp²)-S bond cleavage and silicon-sulfur cross-coupling reaction was ex-

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Table 3. Effect of Various Silanes on the Palladium Nanoparticle-Mediated Cross-Coupling Reaction with Ethyl Phenyl Sulfide at 298 K^a

entry	silane (2.3 equiv)	yields(%) of EIS-SiR ₃ ^a
1	Et ₃ SiH	quant.
2	<i>t</i> -BuMe ₂ SiH	quant.
3	<i>i</i> -Pr ₃ SiH	quant.
4	PhMe ₂ SiH	42
5	Ph ₃ SiH	0

^a Compound identity determined by comparative GC-MS with authentic samples. Yields are determined by quantitative GC.

aminated with ethyl phenyl sulfide as the substrate and PdCl₂ as the palladium nanoparticle precursor. Reactions were monitored by GC and analyzed for compound identity by GC-MS (Table 3).

From the results in Table 3, it is apparent that the C(sp²)-S bond cleavage is not influenced by the steric properties of the silane employed, as *i*-Pr₃SiH having the most sterically demanding environment activates C(sp²)-S bonds quantitatively, while Ph₃SiH bearing the less bulky phenyl substituents does not. Instead, the yields of the cross-coupling reaction appear to be dependent on the electronic properties of the substituents present on silicon: silanes bearing only alkyl substituents (entries 1-3 in Table 3) lead to a quantitative conversion, while the exchange of one alkyl for a phenyl substituent leads to the much lower yield of 42% or no conversion at all for triphenyl silane. This is in contrast to the high reactivity of all these silanes in nanoparticle-catalyzed silane alcoholysis reactions. For example, both Et₃SiH and Ph₃SiH are quantitatively consumed in reactions with ethylene glycol⁴² and sugars,¹⁶ respectively, giving the corresponding silyl ethers in very high yields. Quantum mechanical calculations on the free silanes (see Supporting Information for details) show that the HOMO energies of the silanes monotonously increase in the order Et₃SiH < *i*-Pr₃SiH < TBDMSiH < PhMe₂SiH < Ph₃SiH and that the LUMO energies as well as ΔE_{LUMO-HOMO} monotonously decrease in the same order. While the absolute orbital energies of any silyl species involved will change relative to those of the free silanes during the reaction (see Discussion section for a possible mechanism), their relative energetic ordering should remain the same. Extrapolating from the relative orbital energies of the free silanes, the absolute hardness^{43,44} of a surface-adsorbed Ph₃Si fragment should then be lower compared to that of any R₃Si (R = alkyl) fragments. This results in more synergistic bonding, i.e., a larger amount of back-bonding from the palladium into an energetically more accessible LUMO and hence stronger adsorption of Ph₃Si to the surface, potentially explaining its low reactivity.⁴⁵

Nature of the Catalysts. We and others have previously shown that PdCl₂, Pd(OAc)₂, and Pd(hfacac)₂ give nanoparticles when treated with a silane in DMA or less polar organic solvents.^{16,46} The nanoparticle formation is complete within seconds of silane addition to a solution of the palladium precursor. Under the same conditions, Pd(OCOCF₃)₂ also results

Table 4. Results of the Characterization of the Palladium Colloids by TEM

	catalyst precursor			
	PdCl ₂	Pd(OAc) ₂	Pd(OCOCF ₃) ₂	Pd ₂ (dba) ₃
no. of particles sampled	100	213	100	100
temp (°C)	25	25	25	25
mean size (nm)	2.04	62.21	1.52	1.49
ESD	0.57	33.74	0.30	0.31
min. size (nm)	1.03	21.83	0.91	0.86
max. size (nm)	3.40	207.71	2.61	2.15

in the rapid formation of nanoparticles, while with the Pd(0) precursor Pd₂(dba)₃ and silane alone, clear purple homogeneous solutions—the original color of Pd₂(dba)₃—initially result. However, upon addition of sulfides or methanol, the solution turns dark black within ~30 min, and TEM reveals the presence of nanoparticles, which are catalytically active. Pd(PPh₃)₄ does not give nanoparticles under any of the reaction conditions investigated. The Pd(0) nanoparticles obtained from all usable precursors have been characterized by transmission electron microscopy (TEM) with size distributions of the nanoparticles determined over an ensemble of at least 100 individually measured particles. The particle size distribution was reproducible. Table 4 summarizes the results of the TEM analyses of all four nanoparticle colloids obtained in DMA from PdCl₂, Pd(OAc)₂, Pd₂(dba)₃, and Pd(OCOCF₃)₂ at 25 °C in the presence of a 40-fold excess of *t*-BuMe₂SiH. The nanoparticle nature of the catalysts is a necessary condition for the sulfur-silicon cross-coupling reaction to occur because neither bulk Pd(0) black nor Pd(PPh₃)₄ are catalytically active. From the combined results in Table 1 and Table 4, the actual particle size is, however, not critical for the catalytic activity since relatively smaller particles derived from PdCl₂ (~2 nm) show similar catalytic activity as much larger Pd(OAc)₂ (~60 nm) derived particles.

Application to Sugar Model System. Returning to our original objective of expanding the scope of our previously described method for the silylation of sugars,¹⁶ we further investigated the influence of the nanoparticle precursor and the amount of silane on the reaction and product distribution with phenyl-1-thio-β-D-glucopyranoside as the model substrate. Entries 1-7 of Table 5 list the results of these reactions, and Figure 1 shows the structures and silylation patterns (**1,2**; **1**; **1,2,6**; **6**; or **3,6**) of some of the products. Mixtures of chromatographically separable products originating from cross-coupling and silane alcoholysis or silane alcoholysis are always obtained, but in no case was exclusive thiosilyl glycoside formation without silane alcoholysis observed.

Silane alcoholysis is precluded when the fully protected sugars phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside and phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside are reacted with PdCl₂ and 1.3 equiv of silane (entries 9 and 10, Table 5); however, the cross-coupling product is only generated for the perbenzylated phenyl thio-β-D-glucopyranoside, but not with the peracetylated phenyl thio-β-D-glucopyranoside. This is in contrast to the result of a simple acetylated sulfide (Entry 2, Table 2), which is formed in at least 60% yield. This renders improbable a direct reactivity of the silane with the acetyl group

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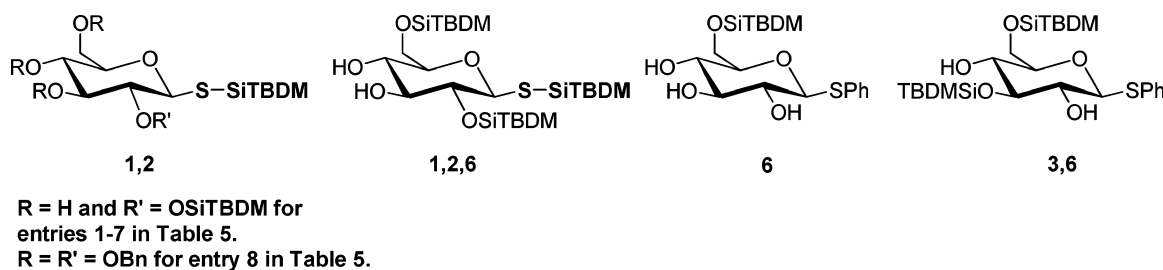
(45) A more complete computational study modelling the relative orbital energies of surface-adsorbed silyl species on actual and well-defined palladium nano clusters may be able to explain the observed reactivity differences more rigorously but is at present beyond our capabilities.

(46) Fowley, L. A.; Michos, D.; Luo, X.-L.; Crabtree, R. H. *Tetrahedron Lett.* **1993**, *34*, 3075.

Table 5. Results of Silylation Reactions of Phenyl Thio Glucopyranosides with in Situ Generated Pd⁰ Nanoparticles and *t*-BuMe₂SiH at 298 K in DMA

entry	thioglycosides	nanoparticle precursor	amount of silane (equiv)	yields (%) of cross-coupling products		yields (%) of O-silylated derivatives		total yields (%) of silylated derivatives
				1,2 or 1	1,2,6	6	3,6	
1	phenyl-1-thio-β-D-glucopyranoside	PdCl ₂	1.3	— ^a	17	47	8	72 ^b
2			2.5	—	45	—	19	64 ^{b,c}
3			3.5	—	61	—	19	80 ^b
4	phenyl-2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside	Pd(OAc) ₂	1.3	31	7	12	—	50
5			2.3	31	18	16	—	65
6			3.5	22	35	14	—	71
7			1.3	—	21	61	6	87
8	phenyl-2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside	PdCl ₂	1.3	70 ^{d,e}	—	—	—	70
9			phenyl-2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside ^f	PdCl ₂	1.3	n.r.	n.r.	n.r.

^a Traces of other cross-coupling products (<3%) were produced, but could not be identified because of decomposition during workup. ^b 4,6-Disilylated derivatives (<2%) were generated. ^c Trisilylated derivatives (<10%) were also produced. ^d Cross-coupling product at anomeric position (C-1). ^e Reaction carried out at 1/3 experimental scale. ^f No reaction.

**Figure 1.** Structures and silylation patterns of the reaction products listed in Table 5.

as the origin of this effect. The adsorption of one or several acetyl groups on the surface of the palladium catalyst may explain the lack of reactivity of the peracetylated sugar.

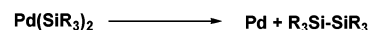
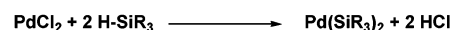
Discussion

Possible Nanoparticle Surface Composition and Mechanistic Considerations. The fact that the nanoparticle catalyst is only stable against agglomeration and precipitation of bulk palladium as long as excess silane is present in solution¹⁶ has to date prevented us from gaining further insights into the actual surface structure of the nanoparticles, a common problem with this type of system.⁴⁷ In the absence of such structural information, any statements about a possible mechanism of the C(sp²)-S bond activation are speculative. However, the necessary presence of excess silane for colloid stability along with several other pieces of ancillary information derived from the macroscopically observed reaction outcomes and GC-MS analysis of the reaction solution give some clues about the surface structure of the nanoparticles and also allow the exclusion of certain reaction pathways.

GC-MS analysis of nanoparticle colloids obtained from the reaction of PdCl₂ and excess TBDMSi-H reveals the presence of (TBDMSi)₂, whose formation is a possible consequence of the reduction of Pd²⁺ to Pd⁰ by the silane. Starting from PdCl₂, Scheme 1 suggests plausible pathways for the initial nucleation and subsequent Pd⁰-possibly autocatalytic-particle growth, generating (TBDMSi)₂ and HCl. Previous experiments with added base,¹⁶ as well as the fact that Pd(OAc)₂, Pd(OCOFCF₃)₂,

Scheme 1

Nucleation:



Particle Growth:



and Pd₂(dba)₃ result in active catalysts for silane alcoholysis and the cross-coupling reaction (Table 1), preclude any role of HCl or other acids in the catalytic reaction and also make a role for the corresponding anion in the stabilization of the colloid unlikely.

The fact that excess silane is necessary to stabilize the nanoparticles against agglomeration and precipitation demands that, once all palladium has been reduced, the resulting particles are stabilized through silane adsorbed on the surface, whose steric bulk then prevents agglomeration as has also been proposed for other systems with bulky polymeric or surfactant-type stabilizers.^{40,47} Since the observed reactivity requires a breaking of the silicon hydrogen bond, we propose a dissociative adsorption of the silane on the palladium nanoparticle surface as illustrated in Figure 2 as the first reaction step. Reductive elimination of two adjacent trialkyl silyl fragments then constitutes a plausible pathway for the formation of (TBDMSi)₂ and the presence of hydrogen adsorbed on the particle surface accounting for the observed hydrogenation of vinyl sulfides.

The proposed dissociative adsorption of the silane mirrors the behavior of the molecularly disperse Pd(0) complex [(μ-dcpe)Pd]₂, dcpe = 1,2-bis(dicyclohexylphosphino)ethane, that has recently been shown to activate silanes R₃SiH (R = phenyl,

(47) Finke, R. G. In *Transition-Metal Nanoclusters: Solution-Phase Synthesis, Then Characterization and Mechanism of Formation, of Polyoxoanion- and Tetrabutylammonium-Stabilized Nanoclusters*; Feldheim, D. L., Foss, C. A., Jr., Eds.; Marcel Dekker: New York, 2002; pp 17–54.

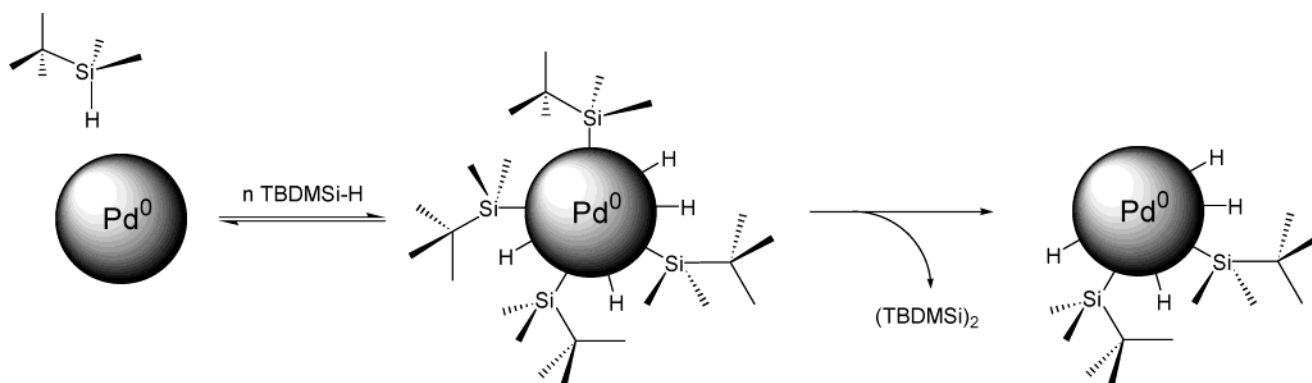


Figure 2. Proposed silane activation pathway and nanoparticle surface structure.

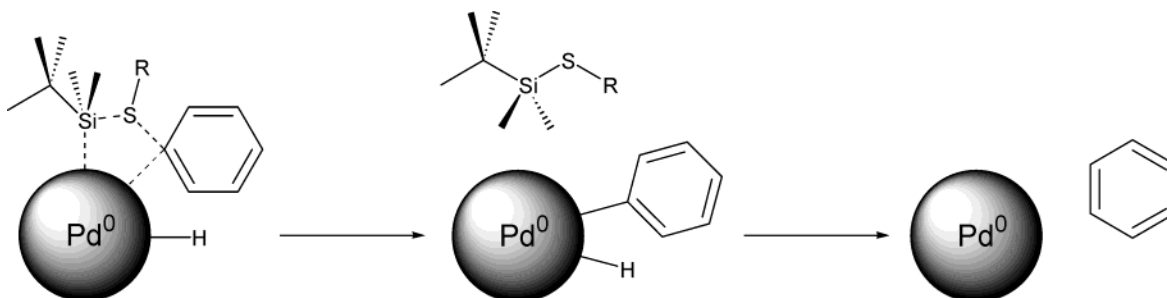


Figure 3. Proposed C(sp²)-S bond activation pathway. (Only the reacting adsorbed silane is shown.)

alkyl) through oxidative addition, yielding the mononuclear silyl palladium hydrides (dcpe)Pd(H)SiR₃.⁴⁸ From a comparison of the activation barrier for this process, the relative reactivity of the silanes in this reaction directly parallels that in the nanoparticle-catalyzed reaction (Table 3): the greater the number of phenyl groups on the silane, the greater its tendency to bind (and remain bound) to the palladium and the lower its subsequent reactivity. The dissociative adsorption pathway is also congruent with the mechanism of silane alcoholysis on bulk palladium metal derived by Sommer and Lyons on the basis of stereochemical studies that showed an inversion of stereochemistry of chiral silanes in this reaction, which is best explained by a “backside attack” of an alcohol onto a SiR₃ fragment adsorbed on the metal surface.⁴⁹

In analogy, we postulate a “backside attack” of a thioether on a surface-adsorbed silicon center as the second reaction step in the nanoparticle-catalyzed formation of the thiosilanes. This scenario is also consistent with the poisoning of the catalyst by PhS fragments generated from the disulfide PhSSPh, as it excludes an actual adsorption of sulfur to the nanoparticle surface, which should equally lead to catalyst poisoning and therefore seems unlikely. Instead, an activation of the C(sp²)-S bond must occur, in which the carbon rather than the sulfur atom is adsorbed to the nanoparticle surface. A reductive elimination of the resulting surface-bound phenyl or ethyl groups (resulting from the hydrogenation of vinyl by insertion into a palladium hydrogen bond) and surface bound hydrogen then leads to the formation of benzene or ethane. Figure 3 summarizes this proposed pathway.

Experimental Section

All synthetic experiments were performed under a dry argon atmosphere by standard Schlenk-tube techniques. Sample solutions for TEM were prepared inside an inert-gas drybox under argon atmosphere.

Electron microscopy was carried out on a LEO 912AB operating at 100 kV with a liquid nitrogen anticontaminator in place. Digital images were collected using a 1 K × 1 K PROSCAN CCD camera and processed using the measurement software in the SIS EsiVision program. Both negatively stained (using 2% w/v uranyl acetate) and unstained samples were imaged for measurement comparison. GC quantitative analyses were carried out using naphthalene as the internal standard. GC-MS spectra were obtained in EI mode. Isomer assignments of the silylated sugar species were made on the basis of 2D COSY and HSQC spectra (see Supporting Information for details). Sugar substrates, solvents, silanes, and metal salts were purchased from commercial sources and used as received. DMA was dried by vacuum distillation from BaO and subsequently stored over activated 4 Å molecular sieves. Flash column chromatography was performed on wet-packed silica gel (60 μm) at 1 psi static pressure set by a breakthrough valve at the column head. Details for the chromatographic separations of the individual sugars are given in the Supporting Information.

General Procedure for the Silylation of Sulfide or Sugar Substrates Using Pd Catalyst Precursors. A DMA (3 mL) solution of the substrate (1.0 mmol) was prepared in a one-necked round-bottom flask fitted with a Schlenk stopcock. *t*-BuMe₂SiH (1.3–3.5 equiv depending on the experiment performed) was added to a second Schlenk flask containing the catalyst precursors (3 mol % with respect to substrate) in 3 mL DMA and stirred for 1 min to give a black colloidal solution. Subsequently the substrate solution was added, the apparatus connected to a gas bubbler, and the reaction stirred until hydrogen gas evolution stopped (2–24 h) and TLC indicated completion of the reaction. DMA was removed by rotary evaporation at 45 °C under full oil-pump vacuum. Flash column chromatography of the residue with ethyl acetate and hexane in various ratios removes the catalyst and yields the silylated substrates and also separated isomers. For simple sulfides, Kugelrohr vacuum distillations using a vacuum controller were

(48) Boyle, R. C.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 3228–3229.

(49) Sommer, L. H.; Lyons, J. E. *J. Am. Chem. Soc.* **1969**, *91*, 7061–7066.

carried out for compound isolation. See Supporting Information for detailed spectral and other data on individual compounds.

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Supporting Information Available: Comprehensive collection of 400 MHz ^1H and ^{13}C NMR data (COSY, HSQC) for sugar and (new) thiosilane products with images of all spectra and peak assignments; conditions for chromatographic or distillation isolation; images of GC–MS spectra for thiosilanes and silthianes; and HOMO/LUMO energies of free silanes as determined by HF 6-311g(d,p) calculations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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