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Authors: Maren Wissing and Armido Studer

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Tuning the Selectivity of AuPd Nanoalloys towards Selective Dehydrogenative Alkyne Silylation

Maren Wissing[a] and Armido Studer*[a]

Abstract: The cross-dehydrogenative coupling of terminal alkynes and hydrosilanes catalyzed by AuPd nanoalloys is described. Metal nanoparticles are readily prepared in 15 minutes from commercially available and cheap starting materials using a photochemical approach. The ratio of Au and Pd in the alloys heavily influences their reactivity. These cooperative nanoalloy catalysts tolerate a large number of functional groups (e.g. free amines and acids), operate at room temperature under air atmosphere at low loading (2 mol%), and the cross-dehydrogenative coupling can easily be scaled up.

The cross-dehydrogenative coupling (CDC) between terminal alkynes and hydrosilanes represents the most atom economic and straightforward approach to access alkynylsilanes.[1] This versatile structural entity not only serves as protecting group,[2] but is also used in many organic transformations such as cycloisomerizations,[3] cycloadditions[4] and carbon−carbon- and carbon−heteroatom bond forming reactions.[5] Due to the mild conditions generally employed in these processes, alkynylsilanes represent highly versatile intermediates for late stage functionalization and as substrates for cyclizations to form complex molecular architectures.[6a-c] As examples, they have been successfully applied to prepare electronically, mechanically and structurally interesting materials, e.g. polymers with strong triplet emission or high thermal stability.[6d-j]

Alkynylsilanes are generally prepared by deprotonation of terminal alkynes using Grignard reagents or strong lithium bases and subsequent coupling with silyl-electrophiles.[7] However, this established route suffers some drawbacks regarding process economy, environmental impact as well as tolerance towards commonly used functional groups. As mentioned above, the direct dehydrogenative coupling of alkynes and hydrosilanes would be most appealing considering atom economy and indeed few reports along those lines have appeared. *Pukhnarevich* and coworkers disclosed the first transition metal catalyzed coupling of alkynes and hydrosilanes using H_2PtCl_6 in the presence of iodine to give the corresponding alkynylsilanes.[8a] Since this work, other homogeneous transition metal catalysts[8b-f], as well as strong bases or reducing agents such as alkoxides,[9a] Na/HMPT,[9b] MgO,[9c] NaOH,[9d] $LiAlH_4$,[9e,f] KNH_2/Al_2O_3[9g] and $NaHBEt_3$[9h] have been shown to mediate this transformation. Recently, *Hou* and *Lou* described the CDC between terminal alkynes and di- or trihydrosilanes using $B(C_6F_5)_3$/DABCO as an organic catalyst system.[9i]

In the field of heterogeneous catalysis of this reaction, only few papers have been published. Along with KNH_2/Al_2O_3 and MgO, two reports on Au based systems have appeared: *Mizuno* described a catalyst consisting of Au nanoparticles supported on manganese oxide (Au/OMS-2) [10a] while *Asao* recently studied a nanoporous gold catalyst.[10b] Both systems operate under similar conditions at 80 °C in toluene and O_2 was applied as the terminal oxidant. Despite these recent advances, there is room for improvement since exciting methods work at elevated temperatures (100°C-120 °C),[8c,d,e,9e,h] require laborious preparation of the catalyst,[9g,10a,b] lead to hydrosilylation byproducts,[8a,b,c] need high catalyst loadings[9h] and most severely show low tolerance towards functional groups.[8a-d,f,9a-c,9e-h] Therefore, new easily accessible and bench-stable catalysts that work under mild conditions are demanded.

As compared to their parent monometallic nanoparticles, bimetallic systems often show altered catalytic performance in terms of selectivity, activity and stability due to modification of their electronic and/or structural properties as a result of cooperative metal-metal interactions.[11] In recent years, AuPd nanoalloys have been shown to catalyze different transformations.[12] For example, *Shishido* and coworkers described the hydrosilylation of alkynes or *α*,*β*-unsaturated ketones to provide vinylsilanes or silyl enol ethers[13a] and also showed that the hydrosilylation of allenes to internal alkenylsilanes can be achieved with such nanoparticles.[13b] We recently studied the cooperative activity of AuPd nanoalloys in selective hydrogenation of internal alkynes to the corresponding *Z*-alkenes.[14] The incorporation of Au into the Pd nanoparticle framework led to an increase in both selectivity and activity. Herein we show that AuPd nanoalloys efficiently catalyze the cross coupling between alkynes and silanes to the corresponding alkynylsilanes. Notably, Pd-catalyzed CDC of alkynes with silanes is to the best of our knowledge currently unknown.

We commenced our studies by investigating the CDC of phenylacetylene (**1a**) and dimethylphenylsilane (**2**) to give **3a** as a function of the AuPd nanoalloy composition (Scheme 1b). The nanoparticles were readily prepared by mixing the precursor salts $HAuCl_4$ and $Pd(OAc)_2$ at defined ratio in DMF and subsequent irradiation at 254 nm for 15 minutes in the presence of the commercially available photoinitiator Irgacure D-2959 (I_{2959}, 10 equiv) and polyethylengycol (M_n=2000 g mol^{-1}, PEG2000, 10 equiv). Upon irradiation with UV-light, I_{2959} fragments to give ketyl radicals in a Norrish type 1 reaction. These radicals can act as one-electron donors to reduce Au^{3+} and Pd^{2+} to the corresponding metal atoms[15a] while PEG2000 ensures stabilization of the *in situ* generated nanoparticles (Scheme 1a).[15b] The thus obtained solution containing the nanoalloys was

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[a] M. Wissing, Prof. A. Studer
Organisch Chemisches Institut
Westfälische Wilhelms-Universität Münster
Corrensstraße 40, 48149 Münster (Germany)
E-mail: studer@uni-muenster.de

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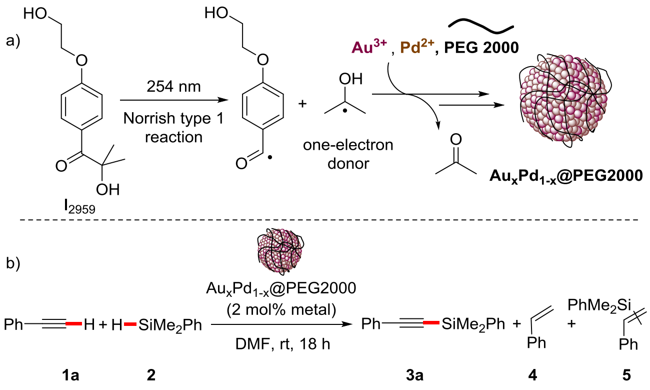
then directly used to catalyze the CDC of alkyne **1a** with hydrosilane **2**.



Scheme 1. a) Synthesis of AuPd nanoalloys by simultaneous reduction of precursor salts with ketyl radicals generated from commercially available photoinitiator I_{2959} in the presence of PEG2000. b) CDC of phenylacetylene (**1a**) and dimethylphenylsilane (**2**).

Table 1. CDC of **1a** and **2**. Variation of the AuPd nanoalloy composition and additives.

Entry	Catalyst	Conversion [%]	**3a** [%][a]	**4** [%][a]	**5** [%][a]
1	Pd	>99	33	34	13
2	$Au_{0.1}Pd_{0.9}$	>99	40	32	5
3	$Au_{0.2}Pd_{0.8}$	>99	44	33	3
4	$Au_{0.3}Pd_{0.7}$	>99	58	22	3
5	$Au_{0.4}Pd_{0.6}$	>99	58	17	3
6	$Au_{0.5}Pd_{0.5}$	>99	50	28	4
7	$Au_{0.6}Pd_{0.4}$	>99	42	27	3
8	$Au_{0.7}Pd_{0.3}$	>97	27	35	5
9[b]	$Au_{0.8}Pd_{0.2}$	>99	9	49	4
10[b]	$Au_{0.9}Pd_{0.1}$	67	6	24	3
11[b]	Au	38	-	28	-
12[c]	$Au_{0.4}Pd_{0.6}$	>99	70	9	1
13[c,d,e]	**$Au_{0.4}Pd_{0.6}$**	**>99**	**77 (78)[e]**	**10**	**2**

[a] Averaged values over 4 experiments. All reactions were carried out in DMF (1.7 mL) at rt under air with **1a** (50 µmol) and **2** (75 µmol). Conversion and selectivity were determined by GC analysis using mesitylene as internal standard. [b] Reaction was carried out only once. [c] Ethyl phenylpropiolate (1 equiv) and $HNMe_2$ in THF (0.5 equiv) were added. [d] Benzoin was used as photoinitiator for the formation of $Au_{0.4}Pd_{0.6}$@PEG2000. [e] Value in parentheses corresponds to isolated yield when the reaction was conducted in 1 mmol scale. Reaction at 0.15 mmol scale provided **3a** with 86 % yield (not shown).

The first experiment was conducted with Pd-free Au nanoparticles which showed no activity for the formation of silylalkyne **3a** and starting **1a** (62 %), dimethylphenylsilanol and styrene (28 %) were detected by GC-analysis (Table 1, entry 11). In contrast, using “bare” Pd nanoparticles the starting material was fully converted after 18 h to a mixture of targeted alkynylsilane **3a** (33 %), **5** (13 %, α- and *E*/*Z*-β-dimethylphenylsilylstyrene) and styrene **4** (34 %) (entry 1). We next switched to alloy catalysts and systematically increased the concentration of Au in the Pd-based nanoparticles.

It was found that increase of the amount of Au led to a better selectivity towards formation of the targeted **3a** with highest yields (58 %) being achieved with $Au_{0.3}Pd_{0.7}$@PEG2000 and $Au_{0.4}Pd_{0.6}$@PEG2000 as catalysts (entries 2-10). $Au_{0.4}Pd_{0.6}$@PEG2000 was selected for further optimizations. Several hydrogen scavengers were added to suppress styrene formation (see Supporting Information, SI) and best results were achieved with ethyl phenylpropiolate. The addition of amines like $HNMe_2$ (added as solution in THF) was also found to be beneficial (see SI). Upon combining both additives the yield of **3a** further increased to 70 % (entry 12). Importantly, we found that AuPd nanoalloys prepared with cheaper benzoin as photo-reducing agent in place of I_{2959} show similar activity (entry 13). Therefore, benzoin-derived nanoparticles were used in further studies. Notably, all CDC reactions were clean and we did not observe other byproducts than styrene and **5**. Since starting **1a** was fully consumed, mass loss can be understood considering that some alkyne **1a** is irreversibly adsorbed on the particle surface, as terminal alkynes are known to interact strongly with Au surfaces.[16] The robustness of the process was documented by running the CDC at 1 mmol scale in a round-bottom flask under air. After 6 h, the alkyne **1a** was fully converted and analytically pure **3a** was isolated in 78 % yield after work-up and purification by column chromatography (entry 13).

The optimized catalyst system $Au_{0.4}Pd_{0.6}$@PEG2000 was carefully analyzed by different spectroscopic techniques. Transmission electron microscopy (TEM) pictures confirmed the formation of small spherical nanoparticles with an average diameter of 2.8±1.0 nm. 2d-energy dispersive X-ray (EDX)-mapping shows no evident metal segregation within the particles, which supports the formation of alloyed AuPd nanoparticles (Figure 1 and SI). To further confirm that Au and Pd are randomly alloyed, X-ray diffraction (XRD) analysis was conducted. The XRD pattern only exhibits one set of peaks, which supports the formation of mixed AuPd particles (see SI). In addition, X-ray photoelectron spectroscopic (XPS) analysis showed that in $Au_{0.4}Pd_{0.6}$@PEG2000 both metals are fully reduced. Binding energies of Pd $3d_{5/2} = 335.4$ eV, $3d_{3/2} = 340.5$ eV and Au $4f_{7/2} = 83.7$ eV, $4f_{5/2} = 87.4$ eV fit well with previously reported values for Au^0 and Pd^0.[17a,b]

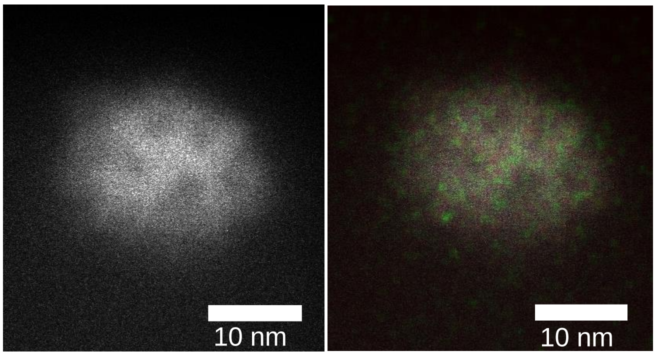
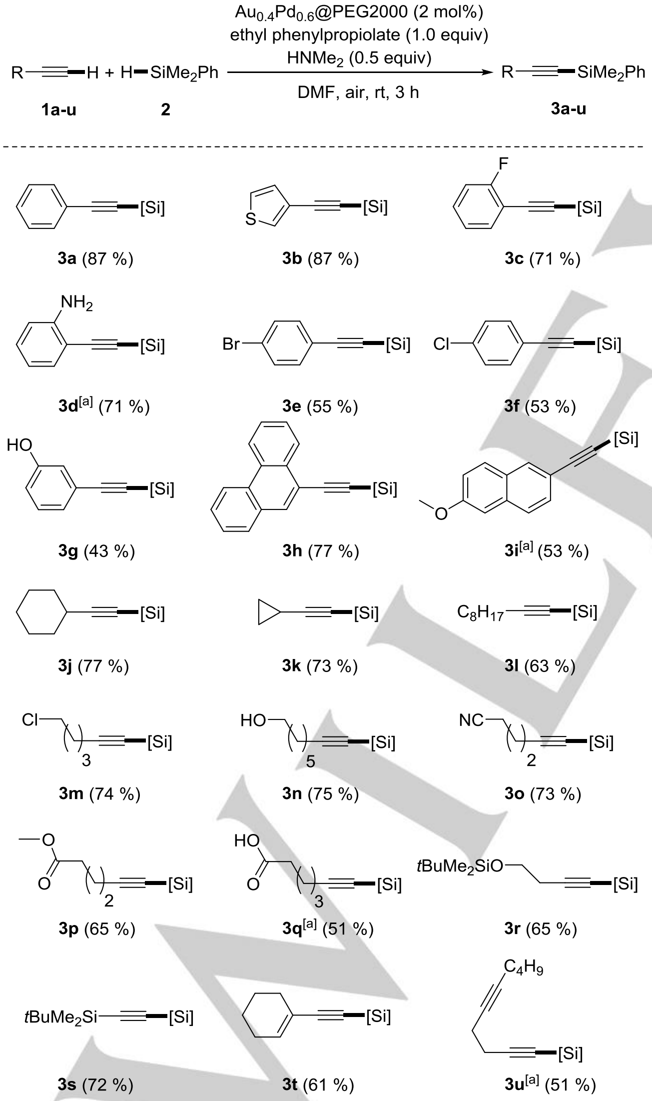


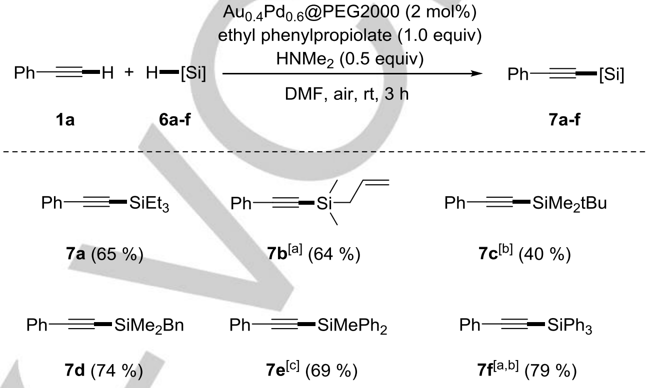
Figure 1. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and EDX-mapping for $Au_{0.4}Pd_{0.6}$@PEG2000. green: EDX signal for Pd, red: EDX signal for Au.

With the optimized reaction conditions in hand, the scope and limitations of the CDC were investigated by first testing various terminal alkynes, keeping **2** as the silyl component. The thienyl alkyne **1b**, bearing a thiophene moiety known to interact with Au nanoparticles,[18] reacted efficiently to **3b** (87 %). Aromatic alkynes bearing electron donating (**1d**,**g**) or electron withdrawing groups (**1c**,**e**,**f**) were smoothly converted to the corresponding alkynylsilanes (43 % - 71 %). Notably, substrates bearing a free alcohol (**3g, 3n**) or amino group (**3d**) are eligible for this CDC reaction. The lower yield obtained for **3g** is due to loss of material during purification. Sterically more demanding alkynes (**3h**, **3i**) also proved to be competent coupling partners and the silylation was efficient also for long chain aliphatic alkynes such as **3l** (63 %). Cyclic aliphatic alkynes **1j** and **1k** reacted well to give **3j** and **3k** in 77 % and 73 % yield, respectively. Aliphatic alkynes bearing chloro, methoxycarbonyl, siloxyl or silyl functionalities were smoothly converted to the corresponding alkynylsilanes **3m**, **3p**, **3r** and **3s**. Free acid and nitrile moieties are tolerated and **1q** and **1o** engaged in the CDC to give **3q** and **3o** in 51 % and 73 % yield. Substrates bearing internal double or triple bonds reacted to the corresponding alkene **3t** and alkyne **3u**. Hydrogenation of the π-bonds in these substrates was not observed, as checked by GC-MS.



Scheme 2. Substrate screening for the reaction between various terminal alkynes (**1a**-**u**) and **2**. [a] Reaction was conducted for 6 h.

We also evaluated the scope with respect to the hydrosilane using **1a** as the alkyne component. Trialkylsilanes **6a**, **6b** and **6c** reacted with **1a** to the corresponding CDC products **7a**-**c** in 40 - 65 % yield. The alkene moiety in **6b** remained untouched under the applied conditions. As compared to the silylation with **2**, slightly lower yields were achieved with the trialkylsilanes and hence an aryl moiety at the silane seems to be beneficial. Indeed, with silanes **6d**-**f** bearing phenyl groups higher yields were noted (69 % - 79 %). Steric effects play a role, as for the sterically demanding silanes **6c** and **6f** the reaction temperature had to be increased to 45 °C.



Scheme 3. CDC of various hydrosilanes **6a-f** and **1a**. [a] Reaction was conducted for 6 h. [b] Reaction was conducted at 45 °C. [c] Reaction was conducted for 15 h.

Finally, some mechanistic studies were conducted. CDC with the deuterium labeled $DSiMe_2Ph$ or PhCCD proceeded without any measurable change in kinetics and selectivities in both cases. The experiment with $DSiMe_2Ph$ showed that deuterium was incorporated in the hydrogen scavenger ethyl phenylpropiolate. This indicates that the hydrosilane gets activated by the particles and likely hydrogen is adsorbed on the particle surface. Notably, no evolution of hydrogen gas was observed. The thus available hydrogen is then likely transferred mainly to the internal alkyne. H-transfer to the substrate terminal alkyne cannot be fully suppressed and the corresponding alkene is observed as side product in most cases. For d1-phenylacetylene no transfer of deuterium to ethyl phenylpropiolate was found. Hence, alkyne C–H activation does likely not occur. To test whether the side products **5** arise from hydrogenation of the product silylalkyne **3a** or hydrosilylation of the alkyne **1a**, the alkynylsilane **3a** was added in a reaction of alkyne **1d** and silane **2**. Formation of the hydrogenated alkenylsilane **5** was not observed even for monometallic Pd nanoparticles. This suggests that byproducts **5** are formed through direct hydrosilylation. This is in agreement with the fact that also α-dimethylphenylsilylstyrene was identified as a side product. Considering all these results, the mechanism probably involves activation of the Si–H bond at the particle surface and that the surface bound silyl group then regioselectively inserts into the alkyne in the second step. The surface bound metal-alkenyl-species is then likely deprotonated[19] by the added base to give the product **3a**. When the reaction is carried out under Ar atmosphere, the transformation is incomplete and a larger amount of hydrosilylation side product and styrene are formed. Since H_2 formation was not observed, O_2 is the terminal oxidant regenerating the catalyst with water being formed as the byproduct (the suggested mechanism is depicted in Scheme S1). In summary, AuPd-based nanoparticle catalysts for selective dehydrogenative cross coupling between alkynes and hydrosilanes were developed. While monometallic Au nanoparticles were found to be inactive, monometallic Pd nanoparticles showed low efficiency in this CDC. Notably, this is the first report of Pd nanoparticles showing activity in the CDC of silanes with alkynes. Efficiency was significantly improved by using readily prepared AuPd nanoparticle alloys as catalysts. Reactions proceed under mild conditions and many functional groups are tolerated.

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Keywords: nanoalloys • cross-dehydrogenative coupling • photochemistry • AuPd nanoparticles • catalysis

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Layout 2:

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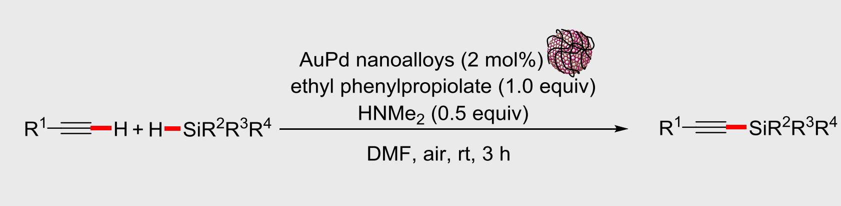

Two is better than one! Cross-dehydrogenative coupling (CDC) of terminal alkynes and hydrosilanes catalyzed by AuPd nanoalloys is reported. Au nanoparticles do not catalyze that transformation, but the alloys with cooperatively interacting Au and Pd metals show good activity. Various functional groups are tolerated and these CDC work at room temperature under air atmosphere.

M. Wissing, A. Studer[*

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Tuning the Selectivity of AuPd Nanoalloys towards Selective Dehydrogenative Alkyne Silylation