

CHEMISTRY

A European Journal

A Journal of



www.chemeurj.org



Reprint

ACES
Asian Chemical
Editorial Society

WILEY-VCH

Catalysis

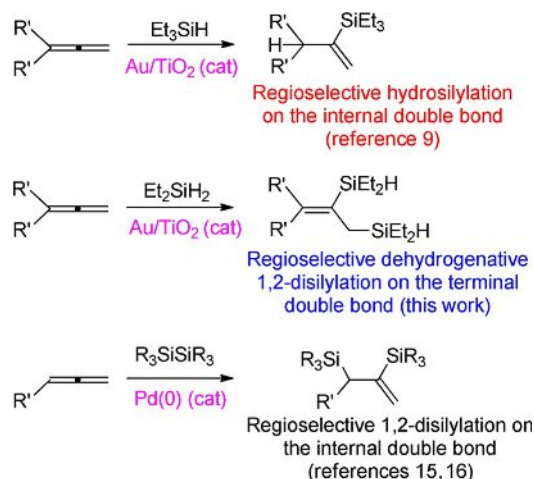
Supported Au Nanoparticles-Catalyzed Regioselective Dehydrogenative Disilylation of Allenes by Dihydrosilane

Marios Kidonakis, Vasiliki Kotzabasaki, Eleni Vasilikogiannaki, and Manolis Stratakis*^[a]

Abstract: Supported Au nanoparticles on TiO₂ catalyze the unprecedented dehydrogenative disilylation of mono-substituted and 1,1-disubstituted allenes by Et₂SiH₂ exclusively on the terminal double bond in a stereoselective manner. Treatment of the disilylation products with H₂O, in a one-pot operation also catalyzed by Au/TiO₂, leads to 3-alkylidene-1,2,5-oxadisilolanes, an unknown class of heterocyclic compounds, which are excellent scaffolds for the stereoselective synthesis of alkenes under Hiyama-type cross-coupling conditions.

The unexpected catalytic ability of Au nanoparticles and other nano-Au⁰ materials to activate interelement σ linkages such as Si–H, Si–Si, B–B or B–Si, as well as their subsequent addition on several functional groups has been documented in recent years.^[1] Among them, the activation of hydrosilanes has gained the most attention. Thus, in the presence of nano-Au⁰ catalysts, hydrosilanes react with H₂O or alcohols,^[2] alkynes,^[3] carbonyl compounds or imines,^[4] α -diazo carbonyl compounds,^[5] and can be used as reductants on several occasions.^[6] Dihydrosilanes (R₂SiH₂), on the other hand, exhibit a different mode of reactivity as compared to simple monohydrosilanes (R₃SiH). For example, we have recently reported^[7] the predominant Au/TiO₂-catalyzed *cis*-dehydrogenative disilylation of alkynes by dihydrosilanes, instead of the anticipated hydrosilylation. Immediately after, Li and co-workers^[8] observed that certain cyclic ethers may undergo AuNPore-catalyzed dehydrogenative disilylation by a dihydrosilane.

Continuing our exploration on the unconventional reactivity of dihydrosilanes in Au⁰-catalyzed transformations, we explored their reactivity against allenes. Previously we had shown that simple monohydrosilanes react smoothly with allenes in the presence of Au/TiO₂ yielding hydrosilylation products, primarily or exclusively on the more substituted double bond of terminal allenes (Scheme 1).^[9] In this paper we report that the reaction between a dihydrosilane (Et₂SiH₂) and a series of allenes mainly yields products of dehydrogenative disilyl-



Scheme 1. Au/TiO₂-catalyzed reaction motifs between a monohydrosilane or a dihydrosilane with allenes, and the Pd⁰-catalyzed regioselectivity pattern of disilylation of allenes with disilanes.

ation exclusively on the terminal double bond, in contrast to regioselectivity pattern of the analogous hydrosilylation reaction (Scheme 1). Thus, mixing Et₂SiH₂ (2.5 equiv) with a mono-substituted or an 1,1-disubstituted allene and Au/TiO₂ (1% mol) as catalyst, in anhydrous benzene at 25 °C, results to the predominant formation of the dehydrogenated disilylation adducts with concomitant H₂ elimination (Table 1). The reaction time is 1–4 h depending on the substitution of the substrate. In other solvents, and by using Au/Al₂O₃ or Au/ZnO as catalysts, the selectivity in favor of the disilylation pathway, and the reaction rate as well were lower (Table S1, Supporting Information). Note that when using 1 equiv of dihydrosilane, the consumption of the allene was approximately 35–40%, but the relative ratio of dehydrogenative 1,2-disilylation versus hydrosilylation was unchanged, which basically implies that the side hydrosilylation product is not a precursor of the major disilylation adduct. If the solvent is not appropriately dry, excess of Et₂SiH₂ is required to compensate its partial destruction from the Au/TiO₂-catalyzed reaction of its Si–H functionality with H₂O. For monosubstituted allenes, which react faster, the product selectivity dehydrogenative disilylation versus hydrosilylation varies between 65–79%, while for 1,1-disubstituted the same relative selectivity is higher (> 80%). The regioselectivity pattern of the current disilylation protocol on the terminal double bond of allenes is analogous to the corresponding Au/TiO₂-catalyzed direct diboration or silaboration.^[10] As proved by nOe experiments, the disilylation in the case of monosubstituted allenes is highly *E*-stereoselective, and the diastereoselectiv-

[a] Dr. M. Kidonakis, Dr. V. Kotzabasaki, Dr. E. Vasilikogiannaki, Prof. Dr. M. Stratakis
Department of Chemistry, University of Crete
Voutes 71003 Heraklion (Greece)
E-mail: stratakis@uoc.gr

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/chem.201901408>.

Table 1. Reaction of terminal allenes with Et₂SiH₂ catalyzed by Au/TiO₂.

allene	a/b	E/Z in a	yield of a ^a /time
	69/31	>97/3	51%/1 h
	73/27	>97/3	57%/1 h
	70/30	94/6	50%/1 h
	72/28	90/10	54%/1 h
	73/27	>97/3	58%/1 h
	70/30	>97/3	55%/1 h
	79/21	93/7	53%/4 h
	71/29	87/13	53%/2 h
	65/35	96/4	50%/3 h
	88/12	-	68%/4 h
	87/13	-	72%/4 h
	83/17	-	68%/4 h

[a] Isolated yield of the disilyl adducts after chromatography.

ity varies from 87 to >97%. The reaction does not occur in the absence of the catalyst or in the presence of the support only (TiO₂), therefore, the catalytic involvement of Au nanoparticles is beyond doubt.

To the best of our knowledge, all known reported examples regarding the reaction between a dihydrosilane and an allene afford the typical hydrosilylation products, such as using as catalysts Pd^{II},^[11] Mo(CO)₆^[12] or Co^{II}.^[13] The direct 1,2-disilylation of allenes by disilanes is a long known transformation, yet not

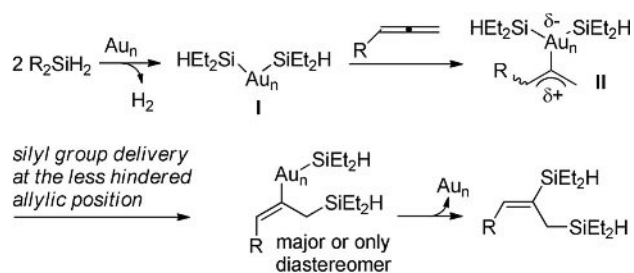
extensively studied.^[14] The first example appeared in 1981 using acyclic disilanes and Pd(PPh₃)₄ as catalyst,^[15] and then the transformation was expanded to cyclic disilanes.^[16] In all reports however, the addition occurs exclusively on the internal double bond of a monosubstituted allene (Scheme 1), in sharp contrast to our results. A single example of a Pt⁰-catalyzed dehydrogenative disilylation of an allene by *o*-bis(dimethylsilyl)-benzene has been also reported,^[17] a process that is similar to what we have previously observed with this specific hydrosilane and alkynes in the presence of Au/TiO₂.^[18] Moreover, non-catalyzed 1,2-disilylation of cyclic allenes has been achieved upon treatment with Li metal and Me₃SiCl.^[19]

Treatment of the crude reaction mixture in each case with 2 equiv of H₂O into the same flask, resulted to the quantitative dehydrogenative oxidation of the two Si–H functionalities, in a well-established^[2,20] process that is also catalyzed by Au nanoparticles. The resulting disilanol undergo intramolecular cyclization to form 3-alkylidene-1,2,5-oxadisilolanes, a new unknown class of 5-membered ring heterocyclic compounds (Table 2). Note that the yield of these cyclic products is typically higher than their original disilyl precursors, because the

Table 2. One pot synthesis of 3-alkylidene-1,2,5-oxadisilolanes from the Au/TiO₂-catalyzed reaction between allenes and Et₂SiH₂ followed by addition of H₂O.

1c (54%)	2c (58%)	3c (53%)^a
4c (60%)^a	5c (61%)	6c (59%)
7c (55%)^a	8c (54%)^a	9c (50%)
10c (72%)	11c (73%)	12c (70%)

[a] Products **3c**, **4c**, **7c** and **8c** contain minor amounts of their Z isomers in relative ratios as appear in products **3a**, **4a**, **7a** and **8a** of Table 1.



Scheme 2. A possible mechanism for the regioselective dehydrogenative disilylation of a monosubstituted allene on the surface of a Au_n nanoparticle.

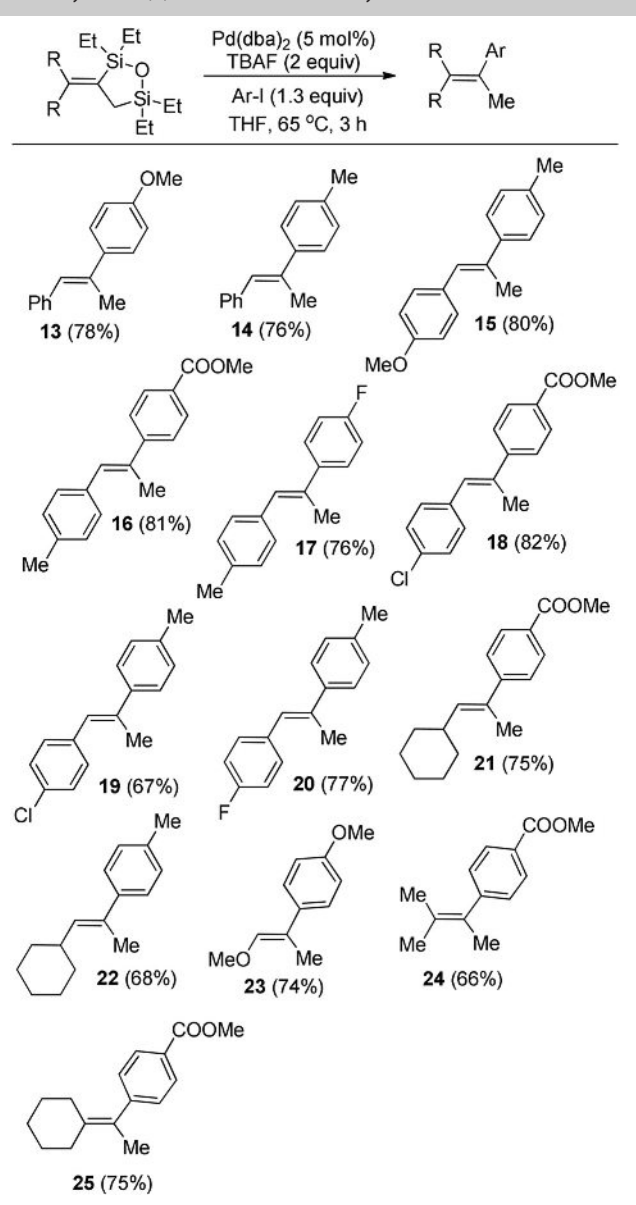
complete separation of disilyl adducts from those of hydrosilylation during their purification was often difficult due to their similar polarities.

From a mechanistic point of view (Scheme 2), we invoke the same arguments regarding the Au/TiO_2 -catalyzed dehydrogenative disilylation of alkynes,^[7] as well as the regioselective Au/TiO_2 -catalyzed diboration or silaboration of allenes.^[10] Thus, the disilyl $\text{HEt}_2\text{Si-Au}_n\text{-SiEt}_2\text{H}$ species (I)^[7] generated from the dehydrogenative coupling between two molecules of Et_2SiH_2 on the surface of Au nanoparticle (Au_n) react with the allene forming intermediate II, which then collapses into the final products. The regioselectivity of addition of the two silyl units on the terminal double bond is attributed to steric reasons, just as in the corresponding diboration or silaboration. Moreover, the high degree of stereoselectivity is attributed to the more favorable proximity of addition on the terminal double bond from the less hindered face.

The 3-alkylidene-1,2,5-oxadisilolanes (Table 2) possess two types of C–Si bonds and we attempted the C–C cross-coupling reaction of this class of compounds under Hiyama-type conditions.^[21] Given the known suitability of siloxanes^[22] in cross-coupling reactions, we examined the 3-alkylidene-1,2,5-oxadisilolanes as scaffolds with a series of Pd catalysts such as $\text{Pd}(\text{dba})_2$, $[(\text{allyl})\text{PdCl}]_2$ or $\text{Pd}_2(\text{dba})_3$. It was found that $\text{Pd}(\text{dba})_2$ is the most suitable in terms of product yields and reaction rates. Thus, in the presence of $\text{Pd}(\text{dba})_2$ (5 mol%), TBAF (2 equiv) and an aryl iodide (1.3 equiv), the 3-alkylidene-1,2,5-oxadisilolanes underwent C–C coupling at the $\text{Csp}^2\text{-Si}$ bond, while the $\text{Csp}^3\text{-Si}$ bond was unmasked generating a methyl group. Given that the majority of the silylated precursors appear as a single isomer, the produced trisubstituted alkenes were isolated as the *E*-geometrical isomers in good yields. The only byproducts of this transformation were the symmetrical biphenyls from the homocoupling of aryl iodides.

In conclusion, we have uncovered a novel mode of reactivity of a dihydrosilane (Et_2SiH_2) with allenes catalyzed by Au/TiO_2 leading to products of dehydrogenative 1,2-disilylation regioselectively on the terminal double bond. These products were further functionalized in the same flask by adding H_2O and were transformed into 3-alkylidene-1,2,5-oxadisilolanes, an unknown class of heterocyclic compounds. 3-Alkylidene-1,2,5-oxadisilolanes were found to be excellent synthons in C–C cross-coupling reaction under Hiyama-type conditions leading to stereodefined aryl alkenes.

Table 3. Synthesis of aryl alkenes using the Pd-catalyzed cross coupling of 3-alkylidene-1,2,5-oxadisilolanes with aryl iodides.



Experimental Section

Typical procedure of the Au/TiO_2 -catalyzed disilylation of alkenes with Et_2SiH_2

To a flame-dried vial containing phenylallene, **1** (23 mg, 0.2 mmol), Au/TiO_2 (39 mg, 1.0 mol%) and 0.5 mL dry benzene was added 65 μL (0.5 mmol) of Et_2SiH_2 via syringe at room temperature. The Au content in catalyst is ≈ 1 wt%. The reaction was monitored by TLC and GC, and after 1 h (100% consumption of the allene) the slurry was filtered under reduced pressure through a short pad of silica gel with the aid of dichloromethane (≈ 2 mL) to withhold the supported catalyst. The filtrate was evaporated under vacuum and the residue was carefully chromatographed with hexane as eluent to afford **1a** (51% yield). Alternatively, the crude reaction was treated with 2 equiv of H_2O (7 μL) for 1 h. After workup and sol-

vent evaporation as described above, the residue was chromatographed with hexane. The 3-alkylidene-1,2,5-oxadisilolane **1c** was isolated in 55% yield (37 mg).

Additional experimental details and product characterization can be found in the Supporting Information.

Acknowledgements

This research has been co-financed by the Operational Program "Human Resources Development, Education and Lifelong Learning" and is co-financed by the European Union (European Social Fund) and Greek national funds (program MIS 5005942). ProFI (FORTH, Heraklion, Greece) is also acknowledged for obtaining the HRMS spectra of the unknown compounds. We thank I. Saridakis for preliminary work in this project.

Conflict of interest

The authors declare no conflict of interest.

Keywords: allenes · Au nanoparticles · catalysis · disilylation · Hiyama coupling

- [1] a) M. Stratakis, H. Garcia, *Chem. Rev.* **2012**, *112*, 4469; b) B. S. Takale, M. Bao, Y. Yamamoto, *Org. Biomol. Chem.* **2014**, *12*, 2005; c) L. Liu, A. Corma, *Chem. Rev.* **2018**, *118*, 4981; d) M. Stratakis, I. N. Lykakis, *Synthesis* **2019**, *51*, 2435–2454.
- [2] a) T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Commun.* **2009**, 5302; b) T. Mitsudome, Y. Yamamoto, A. Noujima, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Eur. J.* **2013**, *19*, 14398.
- [3] a) A. Corma, C. Gonzalez-Arellano, M. Iglesias, F. Sanchez, *Angew. Chem. Int. Ed.* **2007**, *46*, 7820; *Angew. Chem.* **2007**, *119*, 7966; b) I. N. Lykakis, A. Psyllaki, M. Stratakis, *J. Am. Chem. Soc.* **2011**, *133*, 10426; c) A. Psyllaki, I. N. Lykakis, M. Stratakis, *Tetrahedron* **2012**, *68*, 8724.
- [4] a) E. Vasilikogiannaki, I. Titilas, C. Gryparis, A. Louka, I. N. Lykakis, M. Stratakis, *Tetrahedron* **2014**, *70*, 6106; b) B. S. Takale, S. M. Tao, X. Q. Yu, X. J. Feng, T. Jin, M. Bao, Y. Yamamoto, *Org. Lett.* **2014**, *16*, 2558.
- [5] M. Kidonakis, M. Stratakis, *Org. Lett.* **2018**, *20*, 4086.
- [6] a) S. Park, I. S. Lee, J. Park, *Org. Biomol. Chem.* **2013**, *11*, 395; b) M. Yan, T. Jin, Q. Chen, H. E. Ho, T. Fujita, L.-Y. Chen, M. Bao, M.-W. Chen, N. Asao, Y. Yamamoto, *Org. Lett.* **2013**, *15*, 1484; Chen, N. Asao, Y. Yamamoto, *Org. Lett.* **2013**, *15*, 1484; c) 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.
- [7] I. Saridakis, M. Kidonakis, M. Stratakis, *ChemCatChem* **2018**, *10*, 980.
- [8] H. Li, H. Guo, Z. Li, C. Wu, J. Li, C. Zhao, S. Guo, Y. Ding, W. He, Y. Li, *Chem. Sci.* **2018**, *9*, 4808.
- [9] M. Kidonakis, M. Stratakis, *Org. Lett.* **2015**, *17*, 4538.
- [10] M. Kidonakis, M. Stratakis, *ACS Catal.* **2018**, *8*, 1227.
- [11] H. Tafazolian, J. A. R. Schmidt, *Chem. Commun.* **2015**, *51*, 5943.
- [12] S. Asako, S. Ishikawa, K. Takai, *ACS Catal.* **2016**, *6*, 3387.
- [13] C. Wang, W. J. Teo, S. Ge, *Nat. Commun.* **2017**, *8*, 2258.
- [14] a) I. Beletskaya, C. Moberg, *Chem. Rev.* **2006**, *106*, 2320; b) M. Suginoe, Y. Ito, *Chem. Rev.* **2000**, *100*, 3221.
- [15] H. Watanabe, M. Saito, N. Sutou, Y. Nagai, *J. Chem. Soc. Chem. Commun.* **1981**, 617.
- [16] a) D. Seyferth, E. W. Goldman, J. Escudie, *J. Organomet. Chem.* **1984**, *271*, 337; b) T. Kusukawa, Y. Kabe, B. Nestler, W. Ando, *Organometallics* **1995**, *14*, 2556.
- [17] M. Tanaka, Y. Uchimar, H.-J. Lautenschlager, *J. Organomet. Chem.* **1992**, *428*, 1.
- [18] V. Kotzabasaki, I. N. Lykakis, C. Gryparis, A. Psyllaki, E. Vasilikogiannaki, M. Stratakis, *Organometallics* **2013**, *32*, 665.
- [19] K. Kwetkat, B. H. Riches, J.-M. Rosset, D. J. Brecknell, K. Byriel, C. H. L. Kennard, D. J. Young, U. Schneider, T. N. Mitchell, W. Kitching, *Chem. Commun.* **1996**, 773.
- [20] Y. Sawama, M. Masuda, N. Yasukawa, R. Nakatani, S. Nishimura, K. Shibata, T. Yamada, Y. Monguchi, H. Suzuka, Y. Takagi, H. Sajiki, *J. Org. Chem.* **2016**, *81*, 4190.
- [21] a) Y. Nakao, T. Hiyama, *Chem. Soc. Rev.* **2011**, *40*, 4893; b) H. F. Sore, W. R. J. D. Galloway, D. R. Spring, *Chem. Soc. Rev.* **2012**, *41*, 1845.
- [22] a) K. Shibata, K. Miyazawa, Y. Goto, *Chem. Commun.* **1997**, 1309; b) S. E. Denmark, C. R. Butler, *J. Am. Chem. Soc.* **2008**, *130*, 3690.

Manuscript received: March 26, 2019

Revised manuscript received: May 16, 2019

Accepted manuscript online: May 20, 2019

Version of record online: July 3, 2019