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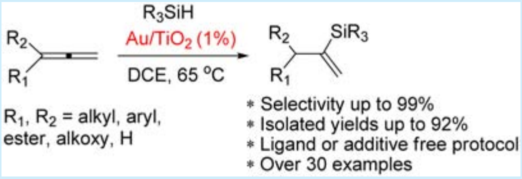
Ligandless Regioselective Hydrosilylation of Allenes Catalyzed by Gold Nanoparticles

Marios Kidonakis and Manolis Stratakis*

Department of Chemistry, University of Crete, Voutes, 71003 Iraklion, Greece

Supporting Information

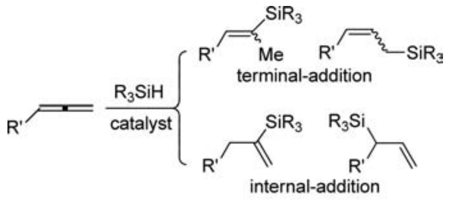
ABSTRACT: The first example of Au-catalyzed hydrosilylation of allenes is presented using recyclable gold nanoparticles as catalyst, without the requirement of any external ligands or additives. The hydrosilane addition takes place on the more substituted double bond of terminal allenes in a highly regioselective manner. The observed regioselectivity/reactivity modes are attributed to steric and electronic factors.



Among the various organic transformations catalyzed by nanoparticulated gold under heterogeneous conditions,[1] the hydrosilylation of π systems has been limited to alkynes. Thus, the Au nanoparticle-,[2] gold film-,[3] or nanoporous[4] gold-catalyzed addition of hydrosilanes to alkynes provides β-(E) adducts regioselectively. Notably, no efficient hydrosilylation protocol has been reported so far under homogeneous ionic gold catalysis conditions. Our continuous interest in the catalytic activation of silanes by supported gold nanoparticles (Au NPs)[2c,5] toward addition reactions urged us to examine the reaction among hydrosilanes and allenes. To the best of our knowledge, there are no examples in the literature regarding any addition reactions on allenes (including hydrosilylation) in the presence of Au NPs as catalysts. In contrast, allenes are readily activated under homogeneous ionic gold conditions through coordination on Au(I),[6] which triggers intra or intermolecular addition reactions by a variety of nucleophiles.[7] In the same context, there are two literature reports presenting the regioselective insertion of a Au(III)−H pincer complex,[8] as well as the gold−silicon bond of the $Ph_3PAu(I)-SiMe_2Ph$ complex[9] on the less substituted double bond of terminal allenes. In both cases, the metal (Au) is bonded to the central sp-C atom of the allene.

The so far reported protocols of hydrosilylation of allenes (Scheme 1) are rather scarce and include catalysis by Lewis acid,[10] the requirement of stoichiometric amounts of $Co_2(CO)_8$,[11] and catalysis by in situ generated Ni(0) or Pd(0) complexes bearing suitable N-heterocyclic carbene ligands.[12] The latter conditions as reported by Montgomery's group have the advantage that depending on the bulkiness of ligand, switchable regioselectivity can be observed. More recently, a highly efficient cationic [(3IP)Pd(allyl)]OTf-catalyzed protocol was reported,[13] which provides mechanistically different regioselective internal or terminal-addition modes, depending on the substitution of hydrosilane (tertiary or secondary). Indirect hydrosilylation of allenes can also be achieved via their Cu(I)-catalyzed reaction with silylboranes[14] at the expense of the boronate moiety, or with silylzincation followed by quenching with acid.[15]

Scheme 1. Possible Hydrosilylation Adducts in the Case of a Terminal Monosubstituted Allene



While all attempts to achieve allene hydrosilylation using a series of ionic gold catalysts under homogeneous conditions failed,[16] we were pleased to find that, in the presence of catalytic amounts of supported gold nanoparticles on the surface of metal oxides, hydrosilanes react smoothly with terminal allenes affording addition products (α-vinylsilanes)[17] in good to excellent yields (Table 1). Optimizing the conditions, Au/TiO_2 or Au/Al_2O_3 (1 mol %)[18] were proven as the catalysts of choice and dry 1,2-dichloroethane (DCE) or benzene the most suitable solvents. The reactants are mixed in an almost equimolar ratio and the reaction time varies from 30 min to 12 h at 65 °C depending on the substrate or hydrosilane.[19] In the absence of catalyst or in the presence of the support alone (TiO_2 or Al_2O_3), the reaction does not take place. Nondried solvent can also be used, yet an excess of hydrosilane (typically 1.5−2 molar equiv) must be added to compensate its hydrolytic destruction to the corresponding 1,3-disiloxanes. A variety of hydrosilanes are compatible ($PhMe_2SiH$, Ph_2MeSiH, Et_3SiH, $Me_3SiOSiMe_2H$, $HMe_2SiOSiMe_2H$) with the exception of triethoxysilane.

The current hydrosilylation protocol tolerates a variety of functional groups and the product selectivity is in general high. For the case of monosubstituted allenes, the addition takes place regioselectively on the more substituted internal double bond (80−98% selectivity depending on substituents). On both

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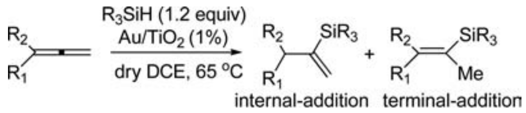
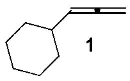
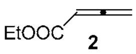
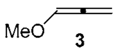
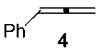
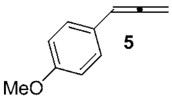
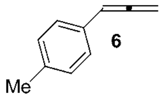
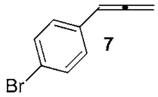
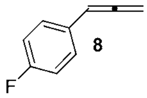
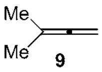
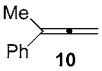
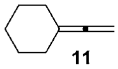
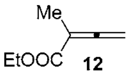
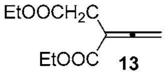
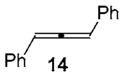
Table 1. Hydrosilylation of Allenes Catalyzed by Au/TiO_2



allene	hydrosilane	relative ratio internal/terminal	yield[a], %/time, h
 **1**	$PhMe_2SiH$	97/3	88/2
	Et_3SiH	95/5	87/2
	Ph_2MeSiH	98/2	84/12
	$Me_3SiOSiMe_2H$	97/3	89/2
	$(HMe_2Si)_2O$	97/3	80/2
 **2**	$PhMe_2SiH$	83/17	87/3
	Et_3SiH	82/18	83/3
	Ph_2MeSiH	80/20	90/18
 **3**	$PhMe_2SiH$	97/3	88/0.5
	Et_3SiH	98/2	88/0.5
	Ph_2MeSiH	98/2	88/4
 **4**	$PhMe_2SiH$	93/7	87/2
	Et_3SiH	97/3	89/2
 **5**	$PhMe_2SiH$	97/3	92/2
	Et_3SiH	97/3	89/2
 **6**	$PhMe_2SiH$	97/3	90/2
	Et_3SiH	98/2	91/2
 **7**	$PhMe_2SiH$	93/7	84/2
	Et_3SiH	94/6	83/2
 **8**	$PhMe_2SiH$	97/3	88/2
	Et_3SiH	95/5	88/2
 **9**	$PhMe_2SiH$	>99/1	92/6
	Et_3SiH	>99/1	90/6
	Ph_2MeSiH	>99/1	85/12
 **10**	$PhMe_2SiH$	>99/1	83/6
	Et_3SiH	>99/1	81/6
 **11**	$PhMe_2SiH$	>99/1	92/6
	Et_3SiH	>99/1	87/6[b]
	$Me_3SiOSiMe_2H$	>99/1	88/6[c]
 **12**	$PhMe_2SiH$	>99/1	90/8
	Et_3SiH	>99/1	87/8
 **13**	$PhMe_2SiH$	>99/1	91/8
	Et_3SiH	>99/1	90/8

unreactive allenes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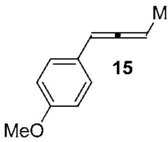
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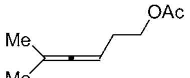
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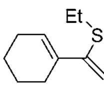
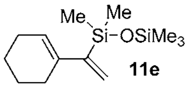

11c


11e

side products in the hydrosilylation of **11**

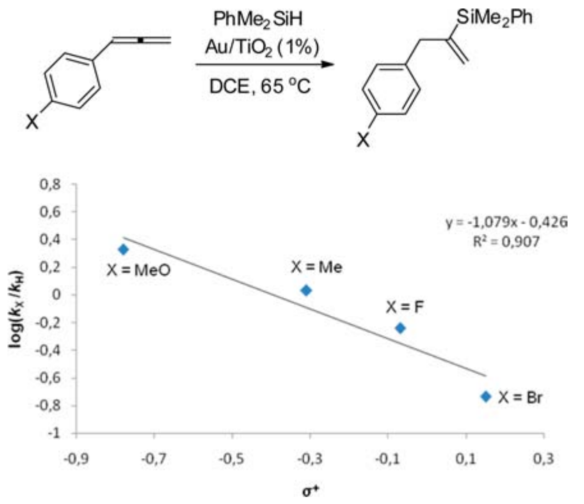
[a]Isolated yield. [b]Relative ratio **11b** (hydrosilylation product)/**11c** = 45/55. [c]Relative ratio **11d** (hydrosilylation product)/**11e** = 65/35.

regioisomers (terminal or internal-adducts), the new C−Si bond occurs on the former sp-C atom of the allene. The minor terminal-regioisomer has always the *E* stereochemistry as proven by NOE experiments, indicative of a highly diastereoselective facial hydrosilylation. To our delight, 1,1-disubstituted allenes form a single regioisomer by addition on the more substituted internal double bond in excellent yields. The reaction has limitations, however; 1,3-disubstituted or trisubstituted allenes are unreactive and the possible reasons are analyzed in the accompanying mechanistic discussion. As per product selectivity, only in the case of ester bearing monosubstituted allene **2** is the side product arising from terminal double bond hydrosilylation formed in 17−20% relative ratio. Alkyl, alkoxy, or aryl monosubstituted allenes form this minor addition side product in 2−5% relative yield, while in the case of 1,1-disubstituted allenes as commented above, the terminal double bond addition product is completely absent. A sound example of this trend is the case of allenes **12** and **13** where an extra substituent (methyl or $-CH_2COOEt$) relative to **2** has a profound effect in selectivity, with **12** and **13** affording a single product. An interesting reactivity was observed with vinylidenecyclohexane (**11**), as substantial amounts of oxidative hydrosilylation products (**11c** and **11e**, respectively) were seen with Et_3SiH and $Me_3SiOSiMe_2H$, but not with $PhMe_2SiH$. Their formation is attributed to elimination of H_2 in the proposed π-allyl intermediate (see proposed mechanism in Scheme 3).[20] In those specific examples, a possible mechanism involving isomerization of allene to 1,3-diene followed by an oxidative hydrosilylation is excluded, as a series of 1,3-dienes do not undergo any reaction with hydrosilanes in the presence of Au nanoparticles. Another interesting aspect is the reaction of **1** with 1,1,3,3-tetramethyldisiloxane (TMDS), which is known to cycloadd to alkynes in a dehydrogenative manner.[5a] We found that no cycloadduct is formed, and the hydrosilylation pathway solely operates (product **1e**), in contrast to the Pt(0)-catalyzed reaction between *o*-bis(dimethylsilyl)benzene, an analogue to TMDS tethered dihydrodisilane, which provides the 1,2-disilylation cycloadduct on the terminal double bond of an allene with elimination of H_2.[21]

We also wish to point out that the supported gold catalysts used in our hydrosilylation protocol are recyclable and reusable in three consecutive experiments without loss of activity and deterioration of conversion yields. The recycling was performed by filtration of catalyst after each run, washing with solvent and drying in the oven at 100 °C for 1 h.

The kinetics of hydrosilylation as studied in a series of *p*-substituted phenylallenes reveal that electron donating substituents accelerate the reaction rate. This trend is also apparent with methoxyallene (**3**) which reacts much faster than allene **2** which bears an electron withdrawing substituent. A Hammett plot of the relative reaction rates among *p*-X-substituted phenylallenes and parent phenylallene ($\log k_X/k_H$) against the σ^+ values of substituents shown in Scheme 2 has a fair linear fit and a negative slope ($\rho = -1.08$) which indicates the development of a partial positive charge on the benzylic position in the transition state of the rate-determining step of reaction. The same plot against σ values shows inferior results in terms of linearity (Supporting Information, p S19), an observation that once more supports the partial carbocationic character in the transition state. Note that the kinetic profile of hydrosilylation of arylallenes is in contrast to the Au/TiO_2-

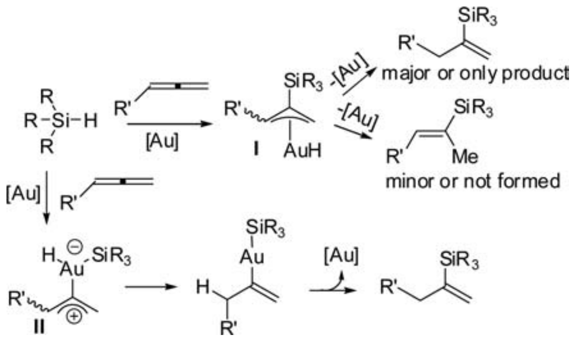
Scheme 2. Hammett Plot in the Competing Hydrosilylation of 1-Arylallenes



catalyzed hydrosilylation of arylalkynes,[2c] where the reaction rate is retarded by electron donating substituents.

Regarding the proposed mechanism (Scheme 3), two possible scenarios are suggested as working hypotheses. In the first, the π-allyl gold intermediate **I** is postulated, reminiscent of an analogous intermediate during the hydrosilylation of allenes catalyzed by a Pd(0) complex in the presence of bulky NHC ligands.[12a] The silylmetalation pathway may be driven in our case due to the bulkiness of the Au NP itself, just as in the case of Pd(0) catalysis, where bulky ligands favor silylmetalation while nonbulky ligands favor the hydrometalation pathway instead. In intermediate **I**, the hydride is selectively delivered on the more substituted sp^2-carbon atom for electronic reasons forming the major or only product. Formation of a σ bonded intermediate η-1 complex **II** may also explain the product selectivity and cannot be excluded. As per the nature of the active catalytic sites on Au NPs, since our so far experience in addition reactions to alkynes via σ bond activation of disilanes,[5d] hydrosilanes[5a] and silylboranes[22] resembles redox catalysis by Pd(0), we suggest once again ionic gold(I) species at the interface between nanoparticle and the support[23] as the reacting sites. The oxidative insertion of σ bonds on Au(I) by analogy to Pd(0) is well established.[24]

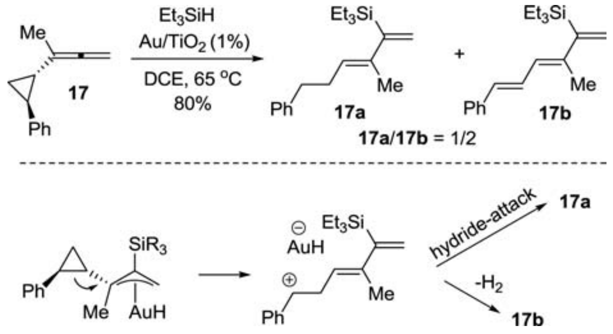
Scheme 3. Possible Mechanisms of Hydrosilylation of a Monosubstituted Allene Catalyzed by Au NP



1,3-Disubstituted or trisubstituted allenes (**14**–**16**) are completely unreactive. In those substrates, any possible product-forming transition state is destabilized by nonbonded interactions either invoking a π-allyl complex (**I**) or an η-1 (**II**). We have shown in a recent publication studying the Au NP-catalyzed silaboration of alkynes[22] how steric interactions among Au NP and the alkyne substituents in intermediate addition products affect not only the regiochemistry of addition, but also the reactivity of internal alkynes.

Another evidence of the carbocationic character of the reaction intermediate was provided upon studying the hydrosilylation of allene **17** bearing as side chain the sensitive phenylcyclopropyl moiety. The reaction among **17** and Et$_3$SiH in the presence of Au NPs proceeded smoothly affording an inseparable mixture of acyclic **17a** along its dehydrogenation analogue **17b** in a relative ratio 1/2 (Scheme 4). In none of the products did the cyclopropyl group of reactant remained intact. Either a π-allyl gold intermediate of type **I** or an η-1 σ complex of type **II** may reasonably undergo ring opening isomerization to the final products (**17a** via hydride attack or **17b** via H$_2$ elimination). Note that in a blank experiment, allene **17** does not undergo any reaction or rearrangement in the presence of Au NPs.

Scheme 4. Hydrosilylation of Cyclopropyl Allene 17 and a Possible Mechanism of Product Formation



In conclusion, we have presented herein the first example of gold-catalyzed allene hydrosilylation using as catalysts supported gold nanoparticles on TiO$_2$ or Al$_2$O$_3$ in low loading level (1 mol %). The reaction is regioselective, favoring the addition of hydrosilane on the more substituted double bond of terminal allenes. We emphasize that the protocol is extremely simple, the catalyst is recyclable and reusable, and, most importantly, no external additives or ligands are required as in the so far known homogeneous metal-catalyzed analogous protocols.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02236.

Copies of ^{1}H, ^{13}C NMR of all products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: stratakis@uoc.gr

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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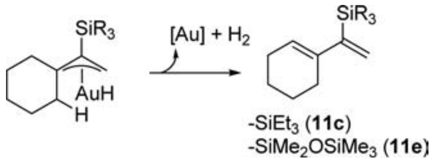
(16) We have tested the following homogeneous gold(I) or (III) catalysts under various conditions (temperature, catalyst loading) and different solvents: $Ph_3PAuNTf_2$, Ph_3PAuCl + Ag(I) salts, [(2-biphenyl)di-*tert*-butylphosphine]$AuSbF_6$ and $AuCl_3$.

(17) Recent examples for the synthesis of α-vinylsilanes via catalytic hydrosilylation of terminal alkynes: (a) Wang, P.; Yeo, X.-L.; Loh, T.-P. *J. Am. Chem. Soc.* **2011**, *133*, 1254. (b) Menozzi, C.; Dalko, P. I.; Cossy, J. *J. Org. Chem.* **2005**, *70*, 10717.

(18) Au/TiO_2 and Au/Al_2O_3 (~1 wt % in Au) with an average gold crystallite size of ~ 2–3 nm are commercially available.

(19) General procedure for the Au/TiO_2 or Au/Al_2O_3-catalyzed hydrosilylation of allenes: To a vial containing the allene (0.2 mmol) hydrosilane (0.24 mmol) and 1 mL of dry DCE or benzene are added 40 mg of Au/TiO_2 or Au/Al_2O_3 (1.0 mol % in Au). After a certain period of time (see Table 1) at 65 °C, the reaction is complete (TLC, GC–MS). The slurry is filtered with the aid of solvent under a low pressure through a short pad of silica gel or celite, and the filtrate is evaporated to afford the hydrosilylation products which can be further purified by column chromatography.

(20) The formation of oxidative hydrosilylation side products (**11c** and **11e**) in the hydrosilylation of vinylidenecyclohexane (**11**) is attributed to elimination of H_2 via a six-membered ring transition state. Hydrogen elimination is more likely favored in this system due to the rigidity of reacting C-H bond on the cyclohexyl ring.



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