

Note

Photoactivated hydrosilylation reaction of alkynes

Fei Wang, Douglas C. Neckers*

 Center for Photochemical Sciences¹, Bowling Green State University, Bowling Green, OH 43403, USA

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Abstract

The photoactivated (350 nm) hydrosilylation of alkynes by silanes catalyzed by platinum(II) bis(acetylacetonato) has been studied. Platinum(II) bis(acetylacetonato) is an efficient catalyst. High yields of adducts (>98% for terminal alkynes) can be obtained in 2–3 h after a short induction period with a catalyst–reactant molar ratio of $10^{-3}/1$. The reaction rate depends on the choice of silane, irradiation time and the concentration of catalyst. The major product is the β -*trans* adduct. Minor products are the α isomer with a trace of β -*cis* isomer. Comparisons of hydrosilylation reactions of alkynes with hydrosilylation reactions of alkenes are reported.

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1. Introduction

Platinum complexes are reported to be among the most active catalysts for hydrosilylation reactions [1–12]. The thermal hydrosilylation of alkynes catalyzed by transition-metal complexes such as $\text{Rh}_4(\text{CO})_{12}$, $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ [13,14] Kartstedt's catalyst, [15] the diplatinum complex $\{\text{Pt}(\text{SiR}_3)(\mu\text{-H})[(\text{C}_6\text{H}_{11})_3\text{P}]\}_2$, [16,17] and H_2PtCl_6 , [18] has been studied in detail and yields three kinds of products: the β -*trans* adduct, as well as the α and β -*cis* isomers (Scheme 1). The products are predominantly *cis* [19] from the rhodium complex catalyzed reaction. The platinum-catalyzed hydrosilylation with alkynes forms mainly the *trans* product via a stereospecific *cis* addition [20].

Platinum(II) bis(acetylacetonato) complexes have been found to be excellent catalysts for the photoactivated hydrosilylation of alkenes [6,7]. In this note, we report the photoactivated (350 nm) $\text{Pt}(\text{acac})_2$ catalyzed hydrosilylation of alkynes. The reaction is proposed to occur via a similar mechanism to that of the photo-

activated (350 nm) hydrosilylation of alkenes also catalyzed by $\text{Pt}(\text{acac})_2$. Control experiments showed the thermal reaction much slower than the photoactivated reaction and reaction mixtures were unchanged after 5 h in the absence of irradiation.

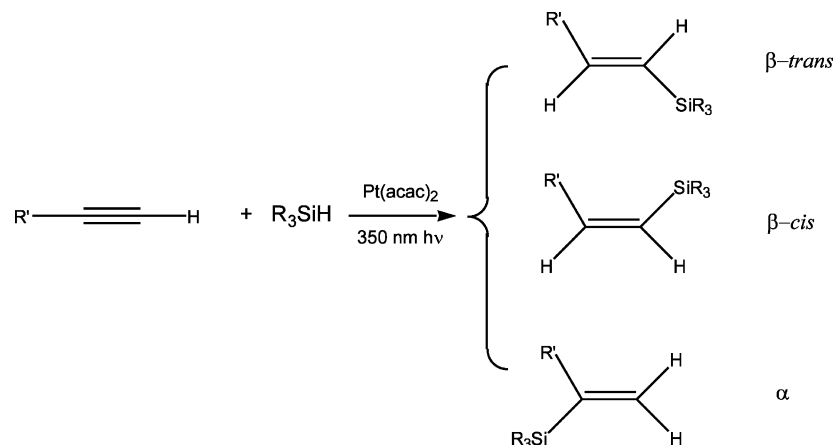
The alkynes studied were 1-, 2-, 3-hexyne, phenylacetylene and diphenylacetylene. The silanes investigated were Ph_3SiH , Et_3SiH , $(\text{EtO})_3\text{SiH}$, Et_2SiH_2 , ClMe_2SiH and triisopropylsilane. The initial photoreaction rate increases with an increase in the concentration of alkyne if the concentrations of silane and $\text{Pt}(\text{acac})_2$ are kept constant. An increase in either irradiation time or concentration of catalyst results in an increase in the initial rate (Fig. 1). However, if the concentration of $\text{Pt}(\text{acac})_2$ exceeds $5 \times 10^{-4} \text{ M}$ ($\epsilon_{350} = 3763 \text{ M}^{-1} \text{ cm}^{-1}$) such it absorbs more than 98% of the light at 350 nm, the initial reaction rate is unchanged with irradiation time. This is similar to what was observed in the hydrosilylation of alkene [7].

The subsequent dark reaction is much slower than the photoreaction. What is more, if after a 10 min irradiation, and a 1 h dark reaction, the reaction mixture was irradiated for another 10 min, the reaction rate increased (Fig. 2). Thus we submit that irradiation enhances formation of an active species, and it is this species that catalyzes the hydrosilylation reaction in the absence of irradiation.

* Corresponding author. Fax: +1-419-372-2034

 E-mail address: neckers@photo.bgsu.edu (D.C. Neckers).

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Scheme 1.

Mercury, an inhibitor for heterogeneous catalysis [21] because it forms an amalgam with bulk platinum metal, is known to have little effect on the homogeneous catalytic reaction [7]. We find that the addition of two drops of mercury to a reaction mixture containing $\text{Pt}(\text{acac})_2$, 1-hexyne and Et_3SiH has no effect on the reaction rate. This implies the reaction is a homogeneous catalytic reaction. Oxygen has a minor effect on both the reaction rate and the final yield of the hydrosilylation of alkynes. Thus the reaction rate is little effected if the reaction mixture is degassed for 10 min or if the reaction is carried out in the presence of air. This is in contrast to the $\text{Pt}(\text{acac})_2$ catalyzed photoactivated hydrosilylation reaction of alkenes which is quite sensitive to oxygen [7]. In this case the reaction yield is reduced from 85 to 15% if the reaction mixture is not degassed [7]. Oxygen inhibition of hydrosilylation of alkene but not hydrosilylation of alkyne might result from oxygen quenching of the photogenerated catalyst of hydrosilylation of an alkene but not that formed during the hydrosilylation of alkyne.

Photoactivated hydrosilylations of Et_3SiH with various alkynes and of 1-hexyne with different silanes were also studied. In reactions of Et_3SiH with 1-, 2- and 3-hexyne, phenylacetylene, diphenylacetylene, the terminal alkynes 1-hexyne and phenylacetylene react much more rapidly than do the internal alkynes, 2- and 3-hexyne. Aromatic alkynes also have a greater reactivity. Phenylacetylene reacts much more rapidly than does 1-hexyne with Et_3SiH . Diphenylacetylene reacts with Et_3SiH completely within 2 h. In contrast, reaction of 3-hexyne with Et_3SiH is much slower and the conversion is low. This result is consistent with the observation that electronic-donating aromatic substituents on olefins increase the rate of the hydrosilylation [8,9]. In the previous study, electron-withdrawing substituents increased the reactivity of the silane [22,23].

The reactivity of different silanes with 1-hexyne immediately after 20 min irradiation is shown in Table 1. Triphenylsilane and chlorodimethylsilane are the most reactive. For example, immediately after 15 min irradiation, the reactions of these two silanes with 1-

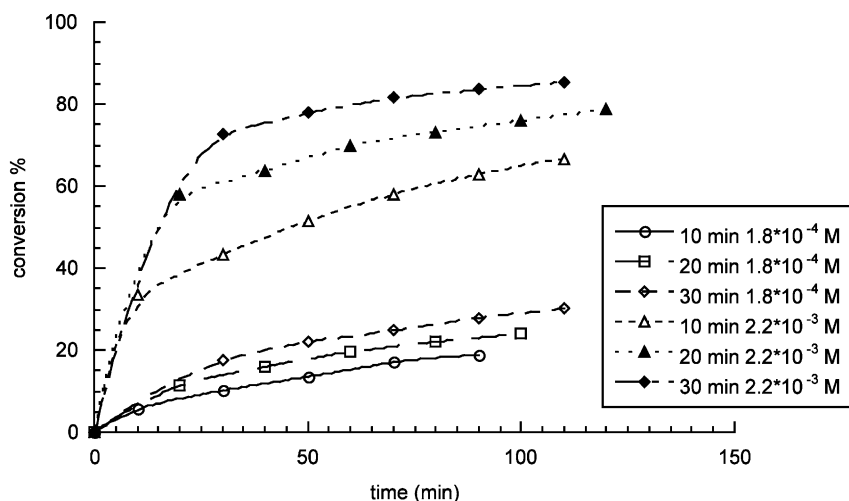


Fig. 1. Effect of irradiation time and concentration of $\text{Pt}(\text{acac})_2$ on the conversion of photoactivated hydrosilylation reaction of 1-hexyne and Et_3SiH (2.2 M). Time 0 is the starting time of irradiation.

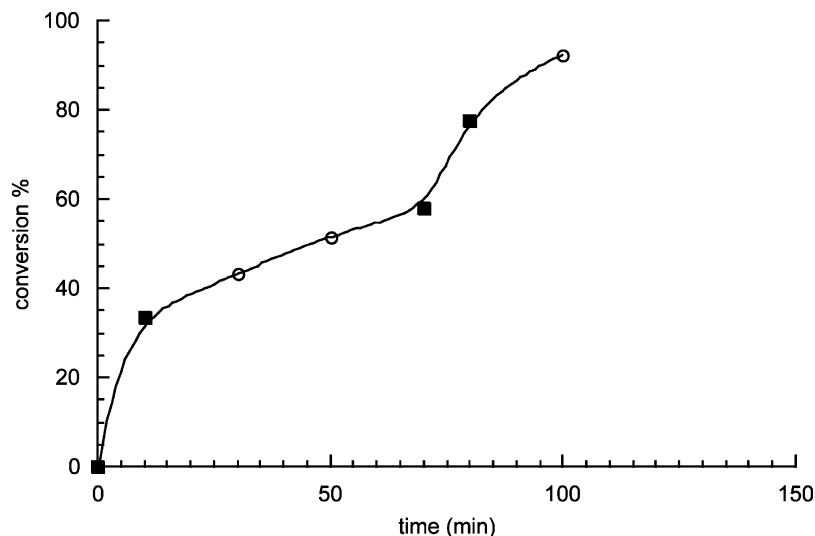


Fig. 2. Conversion from the photoactivated hydrosilylation reaction of 1-hexyne and Et_3SiH . Procedure, 10 min irradiation followed by 1 h dark reaction, then a subsequent irradiation of the reaction mixture for another 10 min (molar ratio of 1-hexyne:silane: $\text{Pt}(\text{acac})_2$ is $1:1:10^{-3}$; the irradiation period is indicated by the dark squares).

Table 1

Conversion 1-hexyne with different silanes immediately after 20 min irradiation at 350 nm (molar ratio of 1-hexyne:silane: $\text{Pt}(\text{acac})_2$ is $1:1:10^{-4}$)

Silane	Ph_3SiH	ClMe_2SiH	$(\text{EtO})_3\text{SiH}$	Et_3SiH
Conversion (%)	97.25	98.41	33.42	13.44

hexyne and diphenylacetylene are complete. The relative reactivity of the silanes that follow is $\text{Ph}_3\text{SiH} > \text{ClMe}_2\text{SiH} > (\text{EtO})_3\text{SiH} > \text{Et}_3\text{SiH} > \text{Et}_2\text{SiH}_2$. PhSiH_3 and triisopropylsilane are unreactive. This is consistent with the trend for the hydrosilylation reaction of alkenes except for the case of Ph_3SiH [7]. Triphenylsilane is the least reactive silane in the hydrosilylation of alkenes [7].

In the thermal process, the rate of addition of silane to alkynes has been reported to be much faster than that with alkenes [24]. Likewise we found that the rate of the photoactivated hydrosilylation of alkynes is faster than that of the photoactivated hydrosilylation of alkenes. The competition between the hydrosilylation of an alkyne with the hydrosilylation of an alkene was studied by irradiating a degassed mixture of Et_3SiH [one part] with 1-hexyne [one part] and styrene [one part] for 10 min. The hydrosilylation of 1-hexyne occurs with the same rate as it does in the absence of styrene, but no hydrosilylation of styrene was observed.

Product distributions after 98% conversion of reactant are summarized in Table 2. The ratio of the β -*trans* isomer to the α isomer is decreased for the internal alkynes in comparison with terminal alkynes. Concentrations of alkyne or silane do not significantly effect product distribution. Upon increasing the ratio of triethylsilane to 2-hexyne to 2:1, the ratio of products, β -*trans*: α also increased.

Product distribution from the photoactivated reaction of Et_3SiH and 1-hexyne catalyzed by $\text{Pt}(\text{acac})_2$ is the same as in the thermal reactions catalyzed by Karstedt catalyst or CODPtCl_2 β : α = 89:11 [15]. If the concentration of catalyst in the reaction mixture is increased or irradiation time increased, product distribution does not change. In every case, the β -*trans* isomer is the major product. This is consistent with results from other platinum complex catalyzed hydrosilylation reactions though it is different from the rhodium complex catalyzed reactions.

We found that if we increased the molar ratio of silane to alkyne to 2:1 but kept the concentration of $\text{Pt}(\text{acac})_2$ the same, no further hydrosilylation of the products occurred. However, isomerization of *trans*-1-(triethylsilyl)-1-hexene formed in the reaction of 1-hexyne with Et_3SiH with $\text{Pt}(\text{acac})_2$ (molar ratio $1:2:10^{-4}$) after irradiation of 20 min is shown in Fig. 3. Studies of these isomerization reactions will be reported elsewhere.

We propose that the mechanism of the $\text{Pt}(\text{acac})_2$ catalyzed photoactivated hydrosilylation of an alkyne is similar to that of the photoactivated hydrosilylation of an alkene [1]. Irradiation of $\text{Pt}(\text{acac})_2$ either with Et_3SiH or with 1-hexyne for 10 min followed by immediate addition of the other reactant gave the same result in the subsequent dark reaction as did the irradiation of Et_3SiH , 1-hexyne and $\text{Pt}(\text{acac})_2$ in the same flask at the same time though the reaction rate is slower (Fig. 4). This can be explained were the reactive species formed upon irradiation composed of both alkyne and silane coordinated to platinum.

In a previous study of the photoactivated hydrosilylation of ethylene, we isolated the five-coordinated platinum complex $\text{Pt}(\text{hfac})_2(\eta^2\text{-C}_2\text{H}_4)$ [hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato] [25]. This

Table 2

Product distribution from the photoactivated hydrosilylation catalyzed by $\text{Pt}(\text{acac})_2$

Reaction (molar ratio)	β - <i>trans</i> Adduct	α -Adduct	β - <i>cis</i> Adduct
Phenyl acetylene + Et_3SiH (1:1)	<i>trans</i> -1-(triethylsilyl)-2-phenylethene 79.85	α -(triethylsilyl)styrene 20.15	2-(triethylsilyl)-2-phenylethene Trace
(2:1)	82.37	17.63	/
Phenyl acetylene + Ph_3SiH (1:1)	<i>trans</i> -1-(triphenylsilyl)-2-phenylethene most	/	/
1-hexyne + ClMe_2SiH (1:1)	<i>trans</i> -1-(chlorodimethylsilyl)-1-hexene 83.73	2-(chlorodimethylsilyl)-1-hexene 16.27	/
1-hexyne + Et_3SiH (1:1)	<i>trans</i> -1-(triethylsilyl)-1-hexene 89.16	2-(triethylsilyl)-1-hexene 10.84	<i>cis</i> -1-(triethylsilyl)-1-hexene Trace
(2:1)	90.56	9.43	Trace
1-hexyne + $(\text{EtO})_3\text{SiH}$ (1:1)	<i>trans</i> -1-(triethoxysilyl)-1-hexene 72.85	2-(triethoxysilyl)-1-hexene 20.88	<i>cis</i> -1-(triethoxysilyl)-1-hexene 6.26
1-hexyne + Ph_3SiH (1:1)	<i>trans</i> -2-(triphenylsilyl)-1-hexene 89.11	2-(triphenylsilyl)-1-hexene 10.89	/
(2:1)	90.93	9.07	/
2-hexyne + Et_3SiH (1:1)	<i>trans</i> -2-(triethylsilyl)-2-hexene 59.09	<i>trans</i> -3-(triethylsilyl)-2-hexene 40.91	/
(2:1)	58.37	41.63	/
(1:2)	63.12	36.87	/
2-hexyne + Ph_3SiH (1:1)	<i>trans</i> -2-(triphenylsilyl)-2-hexene 70.25	<i>trans</i> -3-(triphenylsilyl)-2-hexene 29.75	/
3-hexyne + Et_3SiH (1:1)	<i>cis</i> -3-(triethylsilyl)-3-hexene 100	/	/
3-hexyne + Ph_3SiH (1:1)	<i>cis</i> -3-(triphenylsilyl)-3-hexene 100	/	/
Diphenylacetylene + Et_3SiH (1:1)	<i>cis</i> -(triethylsilyl)-diphenylacetylene 100	/	/

complex catalyzes hydrosilylation without irradiation. In a recent paper Roy and Taylor synthesized, characterized and explored the chemistry of two classes of alkene–platinum–silyl complexes. They suggested that

dimeric complexes $[\text{R}_3\text{Si}(\mu\text{-Cl})(\eta^2\text{-COD})\text{Pt}]_2$ are precatalysts for hydrosilylation and bis-silyl complexes $(\eta^4\text{-COD})\text{Pt}(\text{SiR}_3)_2$ are the active catalysts for the hydrosilylation reaction by means of a Chalk–Harrod me-

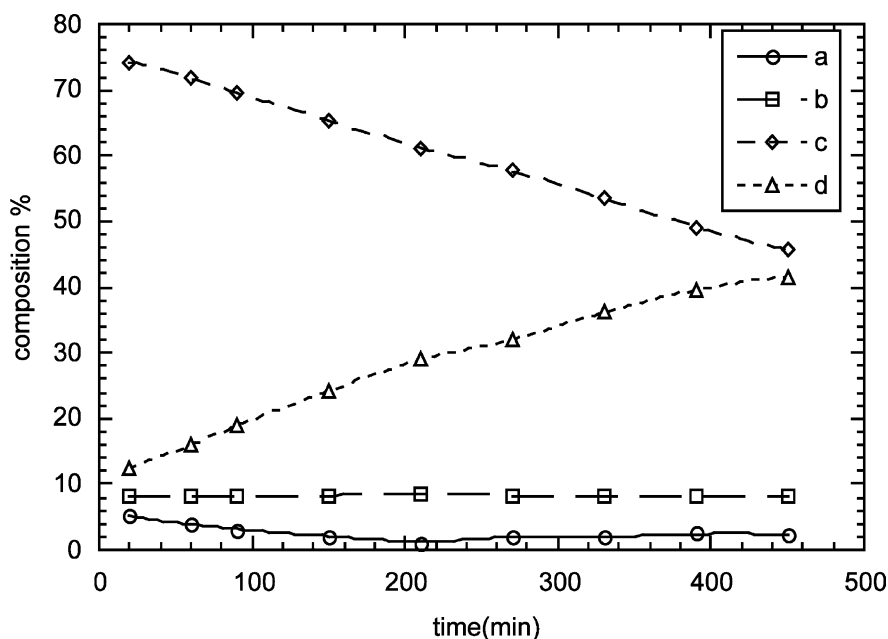


Fig. 3. Product composition vs. the dark reaction time for the reaction of 1-hexyne and Et_3SiH with $\text{Pt}(\text{acac})_2$ (molar ratio of 1-hexyne: Et_3SiH : $\text{Pt}(\text{acac})_2$ is 1:2:10⁻³) after irradiation for 20 min. Products (a) *cis*-1-(triethylsilyl)-1-hexene; (b) 2-(triethylsilyl)-1-hexene; (c) *trans*-1-(triethylsilyl)-1-hexene; (d) *trans*-1-(triethylsilyl)-2-hexene.

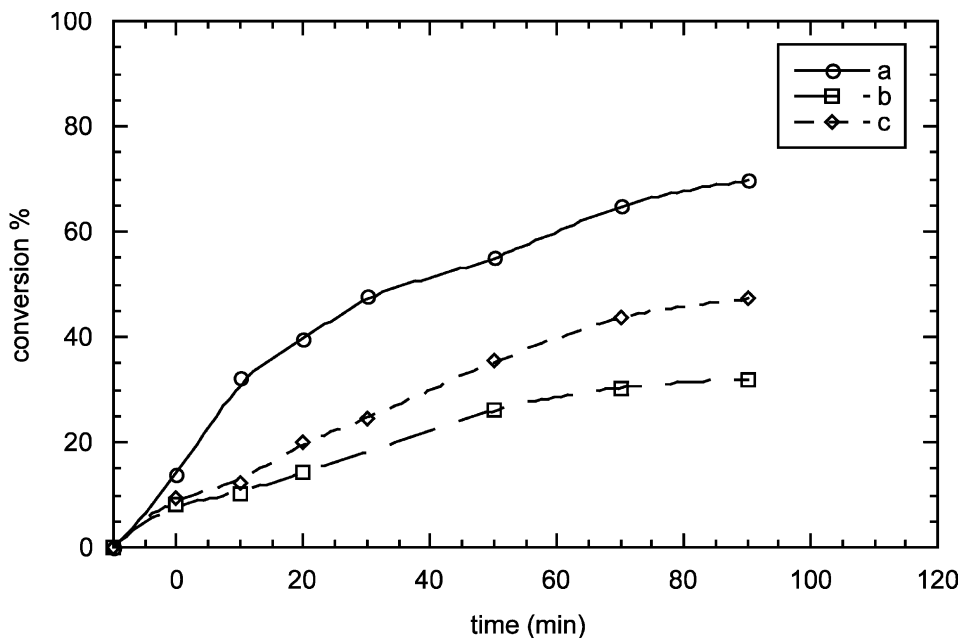


Fig. 4. Conversion vs. irradiation time at 350 nm for 10 min (a) irradiation of Et_3SiH $\text{Pt}(\text{acac})_2$ and 1-hexyne at same time; (b) irradiation 1-hexyne with $\text{Pt}(\text{acac})_2$ first followed by the addition of Et_3SiH ; (c) irradiation Et_3SiH with $\text{Pt}(\text{acac})_2$ first, followed by the addition of 1-hexyne. Time 0 min is the starting time of dark reaction (molar ratio of 1-hexyne: Et_3SiH : $\text{Pt}(\text{acac})_2$ is 1:1:10⁻³).

chanism [26]. Steady state studies (UV) showed that upon irradiation at 350 nm, the behavior of $\text{Pt}(\text{acac})_2$ in the presence of alkyne is the same as that of $\text{Pt}(\text{acac})_2$ in the presence of alkene [27]. The photoactivated hydrosilylation of an alkyne, however, as a result of the stronger coordination of alkyne to platinum. The reason that there is no further hydrosilylation of the products formed from an alkyne with a silane is believed to result from steric effects.

The photoactivated hydrosilylation of alkynes by silanes catalyzed by platinum(II) bis(acetylacetonato) at 350 nm irradiation has been studied. The β -*trans* adduct is the major product. The mechanism proposed is similar to the mechanism of platinum(II) bis(acetylacetonato) catalyzed hydrosilylation reaction of alkenes.

2. Experimental

^1H spectra were recorded in CDCl_3 solution with a Varian Gemini 200 MHz. Chemical shift values are expressed in ppm relative to tetramethylsilane. GC–MS spectra were obtained on a Shimadzu GC–MS–QP5050 mass spectrometer coupled to a GC-17A (Restek ST1-5 column 30 m $\times$ 0.25 mm $\times$ 0.25 μm). Irradiations were carried out on solutions in a borosilicate glass container in a Rayonet PRP-100 photochemical reactor equipped with a jacketed beaker (Pyrex). Lamps (8 W $\times$ 16 RPR–3500 Å) from Southern NE Ultraviolet Co. were used.

Typically an equimolar solution of silane and alkyne containing a catalytic amount of $\text{Pt}(\text{acac})_2$ (molar ratio

of $\text{Pt}(\text{acac})_2$ to reactant is 10⁻³:1) was irradiated under air at 350 nm in a Rayonet photochemical reactor for 10–20 min. After the reaction is complete, the products are separated from starting materials by passing columns. The products were characterized using GC–MS and ^1H -NMR and identified by comparison with authentic materials or compared with literature data. Conversions and product ratios were determined by GC analysis using octane as the internal standard. The disappearance of silane was used to determine conversion.

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