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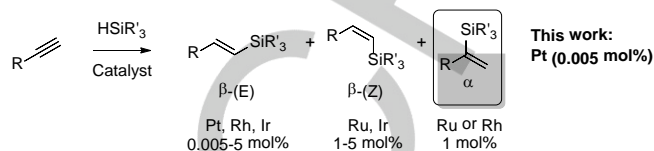
# A Ligand-Free Pt<sub>3</sub> Cluster Catalyses the Markovnikov Hydrosilylation of Alkynes with up to 10<sup>6</sup> Turnover Frequencies

Miguel A. Rivero-Crespo,<sup>[a]</sup> Antonio Leyva-Pérez<sup>\*[a]</sup> and Avelino Corma.<sup>\*[a]</sup>

**Abstract:** The Pt-catalysed hydrosilylation of alkynes is the procedure of choice to obtain vinylsilanes, and this is claimed to be the most relevant application of Pt in organic synthesis. More than half a century after its discovery, only  $\beta$ -vinylsilanes (anti-Markovnikov addition) are obtained with simple Pt catalysts, while  $\alpha$ -vinylsilanes (Markovnikov addition) remain elusive compounds. Here we report that Pt<sub>3</sub> clusters, in part-per-million (ppm) amounts, catalyse the Markovnikov hydrosilylation of terminal alkynes to give a wide variety of  $\alpha$ -vinylsilanes in reasonable isolated yields and with turnover frequencies that can reach up to one million per hour. We also show that these  $\alpha$ -vinylsilanes are reactive in well-established C–C bond forming reactions, in cascade, where the corresponding  $\beta$ -isomers are not. Besides efficient and synthetically useful, this catalytic system is an excellent example of how the atom-by-atom aggregation of a catalytic metal leads to a different selectivity for a given reaction

## Introduction

Alkenyl- or vinylsilanes are useful intermediates in organic chemistry due to their unique reactivity, which includes very important transformations such as Hiyama C–C couplings,<sup>[1]</sup> Friedel-Crafts reactions,<sup>[2]</sup> Diels-Alder transformation as dienophiles,<sup>[3]</sup> reduction of the double bond,<sup>[4]</sup> Heck couplings,<sup>[5]</sup> etc. to give a wide variety of chemical functionalities and structures. Alkenylsilanes are ideally obtained by hydrosilylation of alkynes, since this is the simplest transformation from the point of view of atom economy. Figure 1 shows the three possible products one can obtain during the hydrosilylation of terminal alkynes:  $\beta$ -(E)-vinylsilane (the most thermodynamically stable),  $\beta$ -(Z)-vinylsilane, and  $\alpha$ -vinylsilane.<sup>[6]</sup> Extensive research have been carried out to obtain and functionalize the  $\beta$ -products (anti-Markovnikov addition) which can be formed in high yield and selectivity with ppm amounts of Pt catalysts, and with other metal catalysts including, among others, Ir,<sup>[7]</sup> Ru,<sup>[8]</sup> Rh<sup>[8a, 9]</sup> and Co<sup>[9e, 10]</sup> In contrast,  $\alpha$ -vinylsilanes (Markovnikov addition) are only accessible by a few methods so far, involving Ru<sup>[3, 11]</sup> Cu,<sup>[12]</sup> Rh<sup>[13]</sup> and Co complexes<sup>[14]</sup> as catalysts in ~1 mol% amounts and the development of methodologies to access them in a simple and cheap way would open the door to the preparation of new compounds and to simplify existing synthetic procedures for other molecules.



**Figure 1.** Possible products in the hydrosilylation of terminal alkynes.

It has been observed that unexpected amounts of  $\alpha$ -vinylsilanes can be obtained when working at low concentrations of Pt-complex solutions and at temperatures  $>80$  °C, regardless of the steric factors in the alkyne or silane.<sup>[15]</sup> These results were not discussed since the objective of that work was to evaluate the effect of a new ligand on the transformation. However, this result made us to think that different Pt species are formed when working under diluted and heating conditions, and that some of these Pt species could be more active for the  $\alpha$ -isomer than others. If this was so, the speciation of the Pt catalyst during the hydrosilylation of alkynes should allow improving the Markovnikov selectivity.

Catalysis by metallic clusters is a quite recent field of research that has attracted the attention from the chemical community during the past decade.<sup>[16]</sup> It has been reported that clusters can be significantly more active than conventional catalyst in a number of transformations presenting higher TON and TOF than metal salts and complexes.<sup>[16c]</sup> Indeed, clusters are often formed from these compounds *in-situ* under reaction conditions.<sup>[16c, 16e, 16h]</sup> The increased reactivity can be explained for their molecular-like electronic states that interact with the orbitals of organic molecules allowing the transformation to proceed faster. While increased activity is an accepted feature of cluster catalysts, studies have been mostly done on straightforward reactions with only one possible product. However, to our knowledge, the effect of cluster catalysts on the selectivity of more complex reactions with different possible isomers as products has not been studied yet. For these reasons we chose hydrosilylation of alkynes as a model reaction to evaluate the effect that clusters can have on the selectivity of organic reactions.

Here, we report that ppm of simple Pt compounds catalyse the chemo- and regioselective Markovnikov hydrosilylation of alkynes in good yields and with a broad scope, when Pt<sub>3</sub> clusters are generated. Turnover frequencies approach 1 million per hour for some substrates, and the new  $\alpha$ -vinylsilanes give access to undeveloped carbon-carbon bond forming reactions such as the coupling of vinylsilanes to carbonyls to give protected allyl alcohols, or to ring-closing alkene metatheses to give cyclic alkenyl silanes, in clear contrast to  $\beta$ -vinylsilanes.

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Supporting information for this article including experimental  
procedures, additional figures, and compound characterization with  
NMR copies, is given via a link at the end of the document.

## Results and Discussion

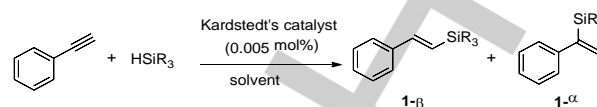
### Markovnikov hydrosilylation of alkynes

Table 1 shows the results obtained for the hydrosilylation of phenylacetylene with different silanes in the presence of 0.005 mol% (50 ppm) of some representative Pt compounds as catalysts. An increase of the temperature from 25 to 110 °C produces a significant change in the selectivity of the reaction, from the  $\beta$  to  $\alpha$  isomer, to give the corresponding geminal 1,1-vinylsilane in >65% yield regardless of the solvent (entries 1–6, a complete screening of solvents can be found in the Supplementary Information, Figure S1), silane (entries 7–8) or Pt catalyst (entries 9–11). Similar results were found with 1-octyne as the alkyne (Figure S2). Among all the solvents tested, cyclohexanone was the best one in terms of both activity and selectivity to the Markovnikov hydrosilylation, however it was not used in further experiments since toluene and 1,4-dioxane gave fairly similar results being much cheaper and purification far easier. The only tested solvent where the  $\alpha$  isomer is not formed preferentially under heating is *N,N*-dimethylformamide (DMF, entry 12). Considering that DMF is a well-known reducing agent for Pt to give nanoparticles,<sup>[17]</sup> it could very well occur that Pt nanoparticles does not catalyse the Markovnikov hydrosilylation. Indeed, preformed Pt nanoparticles supported on carbon (Pt/C, entry 13) poorly catalyze the reaction when toluene was used as a solvent, and products are only formed after a long induction period (more than 2 hours) indicating that the  $\alpha$  isomer does not form with Pt nanoparticles. Likely Pt species detached from nanoparticles are the real catalysts for the little activity shown under these conditions. This correlates well with the observation that Pt nanoparticles are generally formed during classical Pt-catalysed hydrosilylation reaction conditions, where only the  $\beta$  isomer is formed.<sup>[18]</sup>

### Active species elucidation

Given that selectivity to Markovnikov hydrosilylation is constant under similar conditions for Pt compounds with different aggregation and oxidation state (Table 1, entries 4, 9–11, 13 and Figure S2) being the only difference the induction period after which reaction started, we hypothesized that Pt species evolved to form *in-situ* in the reaction media the real catalyst responsible for the observed selectivity. Analysis by electrospray ionization/mass spectrometry with a quadrupole time-of-flight analyzer (ESI-QTOF) of the hydrosilylation reaction in a solution of 50 ppm of Karstedt's catalyst (Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane) in toluene or 1,4-dioxane at 110 °C (Figure S3) detected the presence of small Pt clusters of 3–4 atoms (Pt<sub>3–4</sub>) during reaction, together with minor amounts of Pt<sub>2</sub> clusters. The atomicity for each cluster is unequivocally assigned with the isotopic pattern for Pt. According to the jellium model, these Pt<sub>3–4</sub> clusters should, unlike nanoparticles, absorb and emit (fluorescence) in UV-vis between 300–360 nm.<sup>[19]</sup> Indeed, UV-visible absorption spectroscopy (UV-Vis)

measurements during reaction at 110 °C, when the  $\alpha$ -isomer is formed (Figure S4),



**Table 1.** Screening of reaction conditions for the hydrosilylation of phenylacetylene (0.5 mmol) with trialkylsilane (0.6 mmol) in 1 ml of solvent. Yield to  $\beta$ -(*Z*) product was <1% unless otherwise specified. Percentages indicate GC yields using dodecane as internal standard.

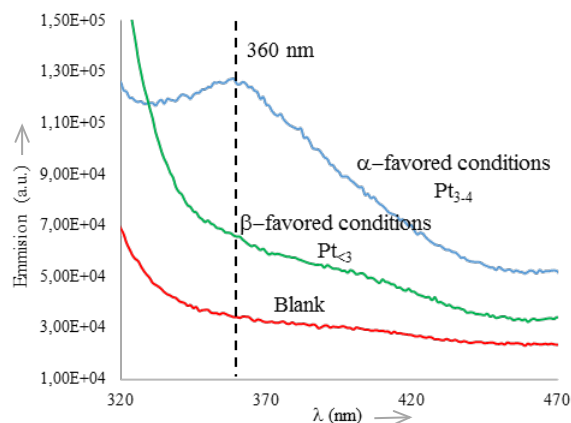
Entry	Pt catalyst	R <sub>3</sub>	Solvent	T (°C)	t (h)	$\beta$ <sup>[a]</sup> (%)	$\alpha$ (%)
1 <sup>[b]</sup>	Karstedt	Et <sub>3</sub>	toluene	25	1	76	15
2	Karstedt	Et <sub>3</sub>	toluene	60	17	43	5
3	Karstedt	Et <sub>3</sub>	toluene	80	7	17	47
<b>4</b>	<b>Karstedt</b>	<b>Et<sub>3</sub></b>	<b>toluene</b>	<b>110</b>	<b>0.5</b>	<b>26</b>	<b>72</b>
<b>5</b>	<b>Karstedt</b>	<b>Et<sub>3</sub></b>	<b>1,4-dioxane</b>	<b>110</b>	<b>0.7</b>	<b>21</b>	<b>78</b>
6	Karstedt	Et <sub>3</sub>	c-hexanone	110	0.3	18	81
7	Karstedt	Me <sub>2</sub> Ph	toluene	110	1	24	66
8	Karstedt	Me <sub>2</sub> Bn	toluene	110	5	26	73
9 <sup>[c]</sup>	Pt/SiO <sub>2</sub>	Et <sub>3</sub>	toluene	110	1	25	73
10	H <sub>2</sub> PtCl <sub>6</sub>	Et <sub>3</sub>	toluene	110	6	25	74
11 <sup>[d]</sup>	PtO <sub>2</sub>	Et <sub>3</sub>	toluene	110	0.7	25	74
12	Karstedt	Et <sub>3</sub>	DMF	110	17	5	8
13 <sup>[e]</sup>	Pt/C	Et <sub>3</sub>	toluene	110	24	16	25

[a] *E* isomer. [b] 0.5 mol% Pt, 6%  $\beta$ -(*Z*). [c] Pt/SiO<sub>2</sub> 1 wt%. [d] 0.05 mol% Pt. [e] Pt/C 10 wt% was used, 2 h induction time., Et = ethyl, Me = methyl, Ph = phenyl, Bn = benzyl, Karstedt = Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane, c-hexanone = cyclohexanone, DMF = *N,N*-dimethylformamide.

show the appearance of new bands at ~300 nm, and the fluorescence spectrum in Figure 2 confirmed the expected emission band for Pt<sub>3–4</sub> (~360 nm) when the  $\alpha$  product is predominant. In contrast, only the plasmonic band of Pt nanoparticles was observed when working under  $\beta$ -favored reaction conditions, i.e. reaction temperatures <70 °C, without any absorption or emission band corresponding to sub-nanometric clusters. These results strongly support the formation of Pt<sub>3–4</sub> clusters during the hydrosilylation reaction at 110 °C with 0.005 mol% of Karstedt's catalyst, without nanoparticle formation, in good agreement with the reported decomposition of some Pt complexes to Pt<sub>3–4</sub> clusters in refluxing benzene or acetone, and point out that Pt clusters could be the active species for formation of the  $\alpha$  isomer.<sup>[20]</sup> Zeta potential measurements (Figure S5) at 110 °C showed a value of -3 mV for the new Pt cluster species, much higher than for Pt nanoparticles (from -20 to -50 mV<sup>[21]</sup>), which would support the presence of quasi-neutral Pt clusters.

To confirm that the Pt<sub>3</sub> clusters, and no other Pt species, are catalytically active for the formation of  $\alpha$ -vinylsilanes, Pt<sub>3</sub> clusters

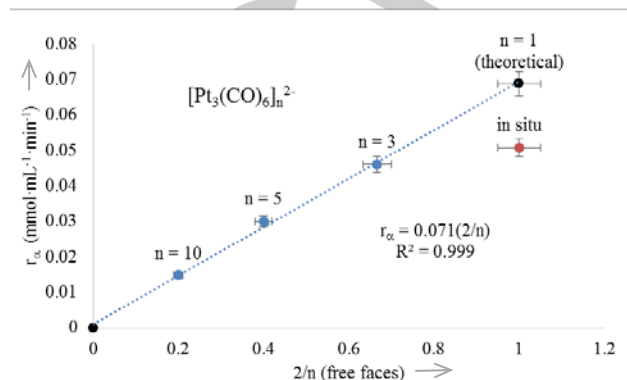
were synthesized in the form of Chini clusters, including:  $[\text{NEt}_4]_2[\text{Pt}_3(\text{CO})_6]_3$ ,<sup>[19]</sup>  $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_5$ <sup>[22]</sup> and  $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ .<sup>[19]</sup> These clusters have a layered structure that only exposes the two ending  $\text{Pt}_3$  units to the reactants, where the CO ligands can



**Figure 2.** Fluorescence emission spectra (excitation at 250 nm) of the reaction mixture (0.5 mmol of 1-octyne, 0.6 mmol of  $\text{HSiEt}_3$  in 1 ml of 1,4-dioxane) catalysed by 0.005 mol% of Kardstedt's catalyst in  $\alpha$ -favored (at 110 °C) or  $\beta$ -favored reaction conditions (60 °C). Blank experiment is performed with no reagents.

exchange with alkynes in <1 min in solution (Figure S6).<sup>[23]</sup> When the reaction of 1-octyne with triethylsilane was carried out with the different Chini clusters under anti-Markovnikov reaction conditions (25 °C, 0.1 mol% of Pt, >95% of  $\beta$ -vinylsilane with Pt salts and complexes) the  $\alpha$ -vinylsilane was the major product without any induction time observed and also when the reaction was carried out under Markovnikov reaction conditions (110 °C, <100 ppm Pt) (Figure S7), in clear contrast with the Kardstedt's catalyst that start to show induction period when concentration is lower than 50 ppm. UV-vis measurements confirmed that the Chini clusters are not decomposed during reaction (Figure S8). Indeed, clusters are stable enough to be active for the reaction using DMF as solvent as was demonstrated by using preformed  $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_5$  clusters (0.005 mol% Pt) to obtain preferentially the  $\alpha$  isomer for both 1-octyne and phenylacetylene at 110 °C. While Kardstedt's catalyst aggregates in DMF and therefore is not active for hydrosilylation (Table 1, entry 12), with preformed Pt clusters further aggregation to nanoparticles is prevented and the selectivity for the hydrosilylation is equal to that of the clusters formed in-situ from Kardstedt's catalyst. The initial hydrosilylation rate of the different Chini clusters plotted vs. the number of exposed layers shows a direct correlation between catalytic activity and  $\text{Pt}_3$  exposed, and also nicely extrapolates the value for free  $\text{Pt}_{3-4}$  clusters formed from the Kardstedt's catalyst (Figure 3). Notice that the experimental value found for the in-situ generated free  $\text{Pt}_{3-4}$  clusters is ~20% lower than predicted if one assumes a quantitative formation of clusters. However, this deviation correlates well with the minor amounts of  $\beta$ -selective Pt catalyst present in the mixture under reaction

conditions, according to  $\beta$ -vinylsilane yields (~20%). An alternative scenario would involve that the  $\alpha$ -selectivity of the  $\text{Pt}_3$  species is not complete and that the observed selectivity is just an average of the selectivity for each Pt species present, within their respective



**Figure 3.** Rate of formation of the  $\alpha$ -alkenylsilane of 1-octyne with triethylsilane, catalyzed by  $[\text{Pt}_3(\text{CO})_6]_n^{2-}$  clusters (0.005 mol% of Pt). Rate values are average of three measurements. Error bars account for 5% uncertainty.

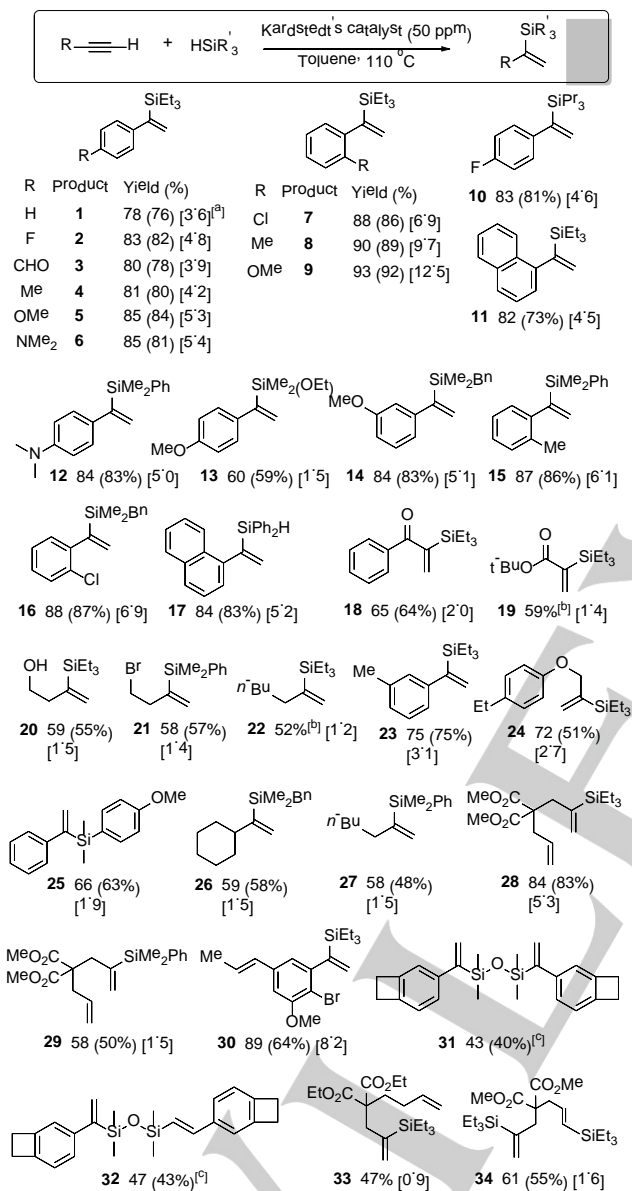
levels of speciation. In any case, we can conclude that  $\text{Pt}_3$  clusters are very active catalysts for the Markovnikov hydrosilylation of terminal alkynes, and that these  $\text{Pt}_3$  clusters can be introduced by working with  $[\text{NEt}_4]_2[\text{Pt}_3(\text{CO})_6]_3$ ,  $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_5$  and  $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ . An example of the exceptional activity of the clusters is the TOF  $1.0 \cdot 10^6 \text{ h}^{-1}$  for the hydrosilylation of 1-octyne with 4 equivalents of triethylsilane.

### Scope of the Markovnikov hydrosilylation

Figure 4 shows that a wide diversity of  $\alpha$ -vinylsilanes in reasonable isolated yields are obtained when using 0.005 mol% (50 ppm) of the Kardstedt's catalyst under optimized reaction conditions, in up to 5-gram scale (product 1). The  $\text{Pt}_3$ -catalysed reaction has tolerance to many functional groups including halides (products 2, 7, 10, 16, 21, 30), aldehydes (product 3), ethers (products 5, 9, 13–14, 24–25), amines (products 6, 12), esters (product 19), alcohols (product 20) and, remarkably, alkenes (products 28–30, 33). Aromatic alkynes give better yields than aliphatic alkynes, and *ortho*-substituted alkynes are particularly selective (compare products 4–5 with 8–9). Silanes bearing either aliphatic, aromatic, alkoxy or hydride functionalities are all reactive, and disilanes and bis-alkynes also work well (products 31–34). The selective formation of vinylsilane 30 illustrates the generality of the method shown here and its potential use in advanced intermediates for synthesis (see Figure S9 for the preparation of the starting alkyne in 7 steps and the structure of a related natural product),<sup>[24]</sup> since the bromide and the alkene functionalities are both preserved during

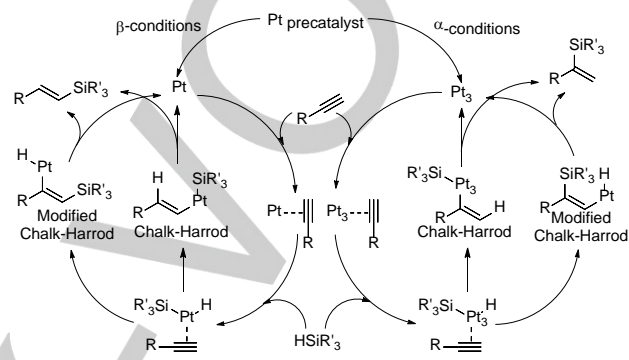


the Pt<sub>3</sub>-catalysed hydrosilylation reaction. Taking into account that pharmaceutical companies are starting to focus their attention on Si functionalized drugs which, in some cases, give better activity and lower side effects than traditional drugs,<sup>[25]</sup> the procedure shown here can help organic chemists in Pharma to prepare new biologically active compounds. Moreover, with the procedure



**Figure 4.** Scope for the hydrosilylation of terminal alkynes with different silanes with 0.005 mol% (50 ppm) of Kardstedt's catalyst (with respect to the alkyne) at 110 °C in toluene (0.5 M). GC yields, isolated yields of  $\alpha$  isomer between parenthesis,  $\alpha/\beta$  ratio of the mixture, before isolation and calculated by GC-MS and <sup>1</sup>H-NMR, between brackets. [a] 5-gram scale. [b] NMR yield. [c] Ratio ( $\alpha\alpha$ )/( $\alpha\beta$ )/( $\beta\beta$ ) = 43/47/10.

presented here, the synthesis of  $\alpha$ -vinylsilanes with industrial interest that are hardly accessible by other synthetic methodologies it is now possible. For instance, the  $\alpha$  isomers of polymer for advanced electronics (divinylsilanes **31** and **32**). Compared to the methods reported so far for the Markovnikov hydrosilylation of terminal alkynes,<sup>[3,9-12]</sup> the ligand-free Pt<sub>3</sub> cluster catalyst is more efficient and readily amenable for scaling-up.



**Figure 5.** Possible pathways for hydrosilylation of alkynes to obtain the  $\beta$ - (left) and  $\alpha$ -alkenylsilanes (right) through both Chalk-Harrod and modified Chalk-Harrod mechanism.

#### Origin of the Markovnikov selectivity in Pt<sub>3</sub> clusters

Considering the reactivity trends of the Pt<sub>3</sub> clusters presented in Figure 4 we can discuss about the origin of the inverse selectivity towards the hydrosilylation with respect to the traditional Pt compounds. Chalk-Harrod and modified Chalk-Harrod mechanism is presented in Figure 5 and is the most accepted mechanism for hydrosilylation of alkynes and alkenes catalyzed by Pt.<sup>[6b, 26]</sup> Based on this mechanism, the key step that determines the regioselectivity of the reaction is the migratory insertion, which proceeds through hydro-platination for the former and silyl-platination for the latter. If we take the alkynes 2- and 4-ethynyltoluene (Figure 4, compounds **4** and **8**) that have the same electronic properties and considering that chelating effect cannot occur as in compound **9**, their only difference is the sterical bulkiness. Markovnikov selectivity is considerably higher for the hindered ortho-substituted phenylacetylene ( $\alpha/\beta$  9.7 for compound **8** vs 4.2 for compound **4**) this can be explained if hydrosilylation goes through silylplatination (i.e. modified Chalk-Harrod mechanism) because hydroplatination would be completely for bulkier reagents. Therefore, the origin of the inverse selectivity of the cluster catalyst would arise from its bulkiness with respect to the Pt single atom. However, Markovnikov selectivity of arenes with respect to alkenes with similar sterical bulkiness is higher (Figure 4, compounds **1** and **26**) so an electronic effect must play also a role in the reaction selectivity. Further mechanistic studies will be carried out to get a deep understanding on how Markovnikov hydrosilylation of alkynes work.

## One-pot hydrosilylation and subsequent reactions

The difficulties to synthesize  $\alpha$ -vinylsilanes translates into few uses of these compounds in organic synthesis and, therefore, their potential applications can be further exploited.<sup>[27]</sup> However, Figure 6 shows that  $\alpha$ -vinylsilanes perform well in a variety of representative organic reactions,

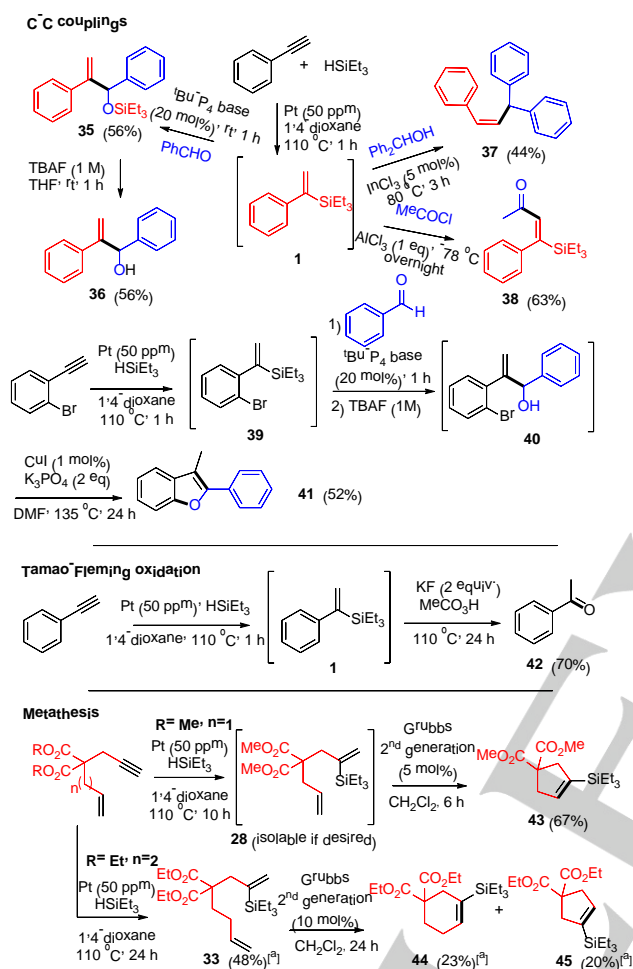


Figure 6. Different reactions with  $\alpha$ -vinylsilanes. Isolated yields. [a] GC yields.

including nucleophilic additions, and oxidation and metathesis reactions, where the corresponding  $\beta$ -(*E*)-vinylsilanes show a dramatically different reactivity. For instance,  $\alpha$ -triethylphenylsilane **1** reacts in an unexpected regioselective manner during Friedel–Crafts type additions to aldehydes (products **35**<sup>[28]</sup> and **40**), alcohols (product **37**) or acyl chlorides (product **38**), to give stereodefined alkenes otherwise difficult to prepare,<sup>[29]</sup> in reasonable yields and with 100% atom economy in some cases, as confirmed by later desilylation reactions (product **36**). In contrast,  $\beta$ -(*E*)-triethylphenylsilane does not react at all under the conditions tested.<sup>[30]</sup>

Notice that the reactions are carried out directly from the alkyne and silane without purifying the intermediate  $\alpha$ -

vinylsilane. This one-pot strategy can be implemented by the small amount of Pt catalyst employed during the Markovnikov hydrosilylation and by the tolerance of the catalytic system to a wide range of solvents. For instance, benzofuran **41** was obtained in one-pot in 52% yield after three consecutive reactions, with a different catalyst required for each reaction: 1) Pt<sub>3</sub>-catalysed hydrosilylation reaction, 2) phosphazene-catalysed nucleophilic addition, and 3) Cu-catalysed intramolecular Ullmann-type coupling.

The different reactivity of  $\alpha$ -vinylsilanes respect to the corresponding  $\beta$ -isomers is clearly seen in the classical Tamao–Fleming oxidation reaction,<sup>[31]</sup> which transforms  $\beta$ -vinylsilanes to the corresponding ketones at room temperature, but not  $\alpha$ -vinylsilanes. For instance,  $\alpha$ -vinylsilane **1** only forms ketone **42** under forcing conditions (110 °C). Indeed, a consecutive one-pot hydrosilylation–Tamao oxidation at room temperature was used here to purify  $\alpha$  from  $\beta$ -isomers, since only the former transform to ketones which easily separate by chromatography on silica. Vinylsilanes could in principle react in alkene metathesis and maintain the silane moiety, in contrast to their  $\beta$ -counterparts. Figure 6 shows that the five- and six-membered ring vinylsilanes **43** and **44+45** are obtained by one-pot intramolecular metathesis reaction of the corresponding  $\alpha$ -vinylsilanes **28** and **33**, respectively, catalysed by the 2<sup>nd</sup> generation Grubbs' complex catalyst under standard conditions. Compound **45** forms after isomerization of the terminal double bond in **33**. The synthesis of heteroatom-substituted alkenes by metathesis is a topic of interest with wide potential applications.<sup>[32]</sup>

## Conclusions

In summary, Pt<sub>3</sub> clusters, either formed in-situ with <100 ppm of simple Pt compounds or added externally in the form of Chini clusters, catalyse the Markovnikov hydrosilylation of terminal alkynes to give a wide variety of new  $\alpha$ -vinylsilanes in good isolated yields. Turnover frequencies approach 1 million per hour in some cases. This work sheds light on some anomalous artifacts found in previous Pt-catalysed hydrosilylation reactions, and the reversal of selectivity using the same catalyst precursor but forming Pt<sub>3</sub> clusters instead of in situ formed Pt nanoparticles represents a paradigm shift in the understanding of this transformation.  $\alpha$ -Vinylsilanes behave as valuable intermediates for well-established C–C bond forming reactions, with a dramatically different reactivity than the  $\beta$ -isomers. This efficient preparation method of  $\alpha$ -vinylsilanes expands the toolkit in organic synthesis and becomes a beautiful example in which the atom-by-atom aggregation of a catalytic metal leads to a different and unprecedented selectivity.

## Experimental Section

Reagents were obtained from commercial sources and were used without further purification unless otherwise indicated.

Anhydrous solvents were obtained from a resin-exchanger apparatus. Reactions were performed in conventional round-bottomed flasks or sealed vials equipped with a magnetic stirrer. All the products were characterized by GC-MS, <sup>1</sup>H-, <sup>13</sup>C-NMR and DEPT. TLCs and flash chromatography were performed on silica and silica plates, respectively; one-pot Tamao oxidation, after the hydrosilylation, can be used to easily separate trace amounts of β-isomers. Gas chromatographic analyses were performed in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone. GC/MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions. <sup>1</sup>H-, <sup>13</sup>C and DEPT were recorded in a 300 MHz instrument using CDCl<sub>3</sub> as solvent unless otherwise indicated, containing TMS as internal standard. IR spectra of the compounds were recorded with a spectrophotometer by impregnating the windows with a dichloromethane solution of the compound and leaving evaporate before analysis. HRMS were performed using the electrospray ionization technique in an UPLC (ultra-pressure) equipment.

Pt species were analyzed by UV-Vis spectroscopy (UV0811M209, Varian). Fluorescence spectra were obtained with a LP S-220B (Photon Technology International) equipped with a 75 W Xe lamp. The photophysical measurements were performed under air at room temperature in a quartz cell of 1.0 cm optical path length. ESI-TOF-Mass Spectrometry measurements were performed with a Shimadzu MALDI-TOF (Matrix-Assisted Laser Desorption and Ionization Time-Of-Flight) mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm using cyanohydroxycinnamic acid or dithranol as a matrix. Zeta potential measurements were carried out in a Malvern Zetasizer equipment.

#### Typical reaction procedure for the Markovnikov hydrosilylation reaction.

A solution of the corresponding alkyne (0.5 M), HSiEt<sub>3</sub> (0.6 M) and dodecane (50 μl, internal standard) in toluene or 1,4-dioxane (1.0 ml) was placed in a vial equipped capped with a septum and magnetically stirred in an oil bath at 110 °C for 5 minutes. Then, the corresponding amount of Pt catalyst (dissolved or not in toluene) was added to the reaction mixture and aliquots (25 μl) were taken periodically for GC analysis after diluting in dichloromethane (1.0 ml). At the end of the reaction, solvent was removed through rotary evaporation and products were purified by flash column chromatography or preparative TLC on silica.

#### Procedures for the one-pot couplings.

After performing the hydrosilylation reactions, the one-pot reactions were carried out as follow. Compound **35**: The hydrosilylation solution was cooled down to room temperature, 1.5 equivalents of benzaldehyde and <sup>t</sup>Bu-P<sub>4</sub> base (20 mol%) were added, and the reaction was stirred for 1 h. The mixture was diluted in ethyl acetate, washed three times with ammonium

chloride concentrated solution, the organic fraction was dried over MgSO<sub>4</sub> and concentrated by rotary evaporation, and the residue was purified by silica column chromatography. This work-up, when needed, is typical for the compounds described below. Otherwise, direct silica column chromatography is performed. Compound **36**: 1 equivalent of TBAF was added to the reaction mixture with **35** and stirred for 1 h. Compound **37**: The solution was placed in a pre-heated oil bath at 80 °C and was transferred to a vial with InCl<sub>3</sub> (5 mol%) and benzohydrol (1 equivalent) and stirred for 3 hours. Compound **38**: After hydrosilylation, the solvent was removed with rotary evaporation and dichloromethane (1 mL) was added. The resulting mixture was cooled down to -78 °C and transferred to a vial with a magnetic bar and AlCl<sub>3</sub> (1 equivalent). Then the corresponding acyl chloride was added (1 equivalent) and the reaction was allowed to warm up to room temperature overnight. Compound **41**: After obtaining **39** and **40** (not isolated) the solvent was removed through rotary evaporation and the crude was transferred to a vial with CuI (1 mol%), K<sub>3</sub>PO<sub>4</sub> (2 equivalents) and DMF (1 mL) and heated at 135 °C while stirring for 24 h. Compound **42**: KF (2 equivalents) and an excess of CH<sub>3</sub>CO<sub>3</sub>H were added to the hydrosilylation solution and stirred at 110 °C for 24 h. Compounds **43**, **44** and **45**: The hydrosilylation solution was allowed to cool down to room temperature and then 2nd generation Grubbs catalyst (5 to 10 mol%) was added to the mixture and stirred from 6 to 24 hours.

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**Keywords:** alkynes • clusters • hydrosilylation • parts-per-million • platinum

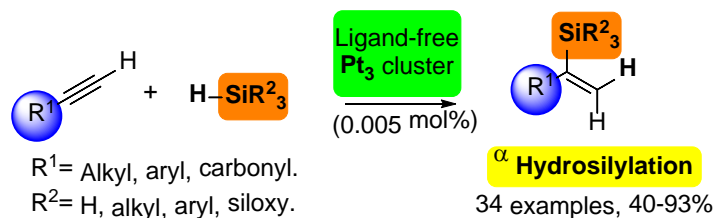
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## Entry for the Table of Contents

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Pt<sub>3</sub> clusters reverse the classical selectivity of the Pt-catalysed hydrosilylation of terminal alkynes and give  $\alpha$ -vinylsilanes with turnover frequencies up to one million per hour. The synthetic utility of these new  $\alpha$ -vinylsilanes in one-pot reactions is also showed.

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Page No. – Page No.

**A Ligand-Free Pt<sub>3</sub> Cluster Catalyses the Markovnikov Hydrosilylation of Alkynes with up to 10<sup>6</sup> Turnover Frequencies**