# RELATIVE REACTIVITIES OF ALKYNES IN HYDROSILYLATION REACTIONS CATALYSED BY *trans*-DI-μ-HYDRIDOBIS(TRICYCLOHEXYLPHOSPHINE)BIS-(SILYL)DIPLATINUM COMPLEXES

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## Summary

The relative rate constants ($k_{rel}$) of the addition of triethylsilane to alkynes catalysed by *trans*-di-μ-hydridobis(tricyclohexylphosphine)bis(silyl or germyl)-diplatinum complexes were determined. It was found that the reactivities of alkynes, determined by competition reactions, increase as the $\pi$-acceptor capacity of alkynes increases. Generally, alkynes bearing an electron-withdrawing substituent adjacent to an acetylenic carbon atom are more reactive than un-substituted alkynes in competition reactions. However, in simple hydrosilylation reactions these alkynes are less reactive than the unsubstituted alkynes and their reactivities decrease as the $\pi$-acceptor capacity increases. Also, in competition reactions terminal alkynes are more reactive than internal alkynes. The observed trends of the reactivities of alkynes were interpreted on the basis of the stability of the complexes formed between the alkynes and the central atom of the catalysts in the first step of the catalytic cycle.

## Introduction

Although the hydrosilylation of unsaturated substrates has been studied extensively and many effective catalytic systems were found [1—3], very little attention has been given to the kinetic study of the reaction. This is due to the fact that hydrosilylation, which is very sensitive to the reaction conditions, is characterised by an undefined induction period and poor reproducibility and, thus sufficiently reliable kinetic measurement could not be obtained.

The most extensive kinetic study of hydrosilylation has been concerned with a variety of substrates and with cobalt, rhodium and platinum catalysts [4]. From competition reactions, relative rates of the hydrosilylation of olefins were determined, and these showed that the reactivity of hydrosilanes

increased as the ionic character of the silicon—hydrogen bond decreased.

However, as far as we know, whereas there have been several studies of the reactivities of hydrosilanes and olefins in hydrosilylation [4—10], no systematic studies on the reactivity of alkynes have previously been made. We now report on the study of the reactivity of alkynes in hydrosilylation reactions catalysed by *trans*-di-$\mu$-hydridobis(tricyclohexylphosphine)bis(silyl)diplatinum complexes. Based on competition reactions the relative rate constants of the hydrosilylation of alkynes were determined and were correlated to the electronic structure of the alkynes.

## Results and discussion

Quantitative results concerning the reactivities of alkynes in hydrosilylation reactions catalysed by *trans*-di-$\mu$-hydridobis(tricyclohexylphosphine)bis(silyl)-diplatinum complexes were obtained by competition reactions. In these reactions an equimolar mixture of two alkynes is allowed to react with a deficiency of hydrosilane in the presence of the catalyst. The quantities used were chosen so that the conversion of alkynes would not exceed ~25 mol%. The results of the study of competition reactions are summarised in Table 1.

It is noteworthy that altering the reaction conditions in most of the competition experiments listed in Table 1 did not change the results. Thus, the competition experiments, where one or both of the alkynes were hydroxyalkynes, were also carried out in the presence of an excess of hydrosilane and the reaction mixtures were analysed when 10—20 mol% of the alkynes were consumed. The competition reactions of the terminal and internal alkynes were also carried out at room temperature. Finally, use of the catalyst $[(Cy_3P)(BzMe_2Si)$-$(\mu$-H)Pt$]_2$ instead of $[(Cy_3P)(Me_3Ge)(\mu$-H)Pt$]_2$, gave very similar results.

Since hydrosilylation is very sensitive to the reaction conditions, reliable absolute values of the rate constants based on kinetic studies are difficult to determine. However, using competition reactions, where the reaction conditions are the same for both alkynes, we can compare the rate constants without determining their absolute values. From the results shown in Table 1 we can calculate the ratio of the rate constants $k_1/k_2$ or the relative rate constants, $k_{rel}$, on the basis of the equation [10]:

$$\frac{k_1}{k_2} = \frac{[P][B]_0}{[Q][A]_0} \tag{1}$$

where $k_1$ is the rate constant of the reaction

$$A + C \rightarrow P$$
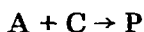
$k_2$ is the rate constant of the reaction

$$B + C \rightarrow Q$$

[P] is the concentration of the product P, [Q] is the concentration of the product Q, $[A]_0$ and $[B]_0$ are the initial concentrations of the alkyne 1, A, and alkyne 2, B, respectively and C is Et$_3$SiH.

In the case of the competition reactions studied $[A]_0 = [B]_0$ and hence equ-

TABLE 1

COMPETITION REACTIONS OF EQUIMOLAR AMOUNTS OF TWO ALKYNES FOR A DEFICIENCY
OF Et₃SiH IN THE PRESENCE OF THE CATALYST [(Cy₃P)(Me₃Ge)(μ-H)Pt]₂ [a]

| Alkyne 1 | Alkyne 2 | Products (%) | | Silylalkene 1 [b] |
|----------|----------|-------------|-------------|-------------------|
| | | Silylalkene 1 | Silylalkene 2 | Silylalkene 2 |
| n-BuC≡CH [a] | n-PrC≡CH | 58.3 | 41.7 | 1.4 |
| n-PentC≡CH | n-PrC≡CH | 60.3 | 39.7 | 1.5 |
| n-PentC≡CH | n-BuC≡CH | 51.9 | 48.1 | 1.1 |
| CyPentC≡CH [c] | n-PentC≡CH | 83.1 | 16.9 | 4.9 |
| CyPentC≡CH | n-PrC≡CH | 88.1 | 11.9 | 7.4 |
| MeEtC(OH)C≡CH | n-BuC≡CH | 82.9 | 17.1 | 4.85 |
| MeEtC(OH)C≡CH | n-PrC≡CH | 87.2 | 12.8 | 6.8 |
| Me₂C(OH)C≡CH | n-BuC≡CH | 87.2 | 12.8 | 6.8 |
| Me₂C(OH)C≡CH | MeEtC(OH)C≡CH | 58.3 | 41.7 | 1.4 |
| PhCH(OH)C≡CH | MeEtC(OH)C≡CH | 65.5 | 34.5 | 1.9 |
| PhCH(OH)C≡CH | Me₂C(OH)C≡CH | 57.4 | 42.5 | 1.35 |
| MeEtC(OH)C≡CH | (HOMe₂CC≡)₂ | 58.3 | 41.7 | 1.4 |
| Me₂C(OH)C≡CH | (HOMe₂CC≡)₂ | 66.7 | 33.3 | 2.0 |
| PhCH(OH)C≡CH | (HOMe₂CC≡)₂ | 72.2 | 27.8 | 2.6 |
| n-PrC≡CH | EtC≡CMe | ~100 | — | — |
| n-BuC≡CH | EtC≡CMe | ~100 | — | — |
| n-BuC≡CH | EtC≡CEt | ~100 | — | — |
| EtC≡CEt | EtC≡CMe | 63.6 | 36.4 | 1.75 |
| EtC≡CMe | n-PrC≡CMe | 54.6 | 45.4 | 1.2 |
| EtC≡CEt | n-PrC≡CMe | 67.7 | 32.4 | 2.1 |
| MeEtC(OH)C≡CH | n-PrC≡CMe | ~100 | — | — |
| MeEtC(OH)C≡CH | EtC≡CEt | ~100 | — | — |
| (HOMe₂CC≡)₂ | EtC≡CEt | ~100 | — | — |

[a] Reaction conditions: 60°C; [silane] = 2.5 mmol; [alkyne] = 5.0 mmol; mmol catalyst/mmol silane =
2.96 × 10⁻⁴; argon atmosphere and in the absence of solvent, except for the reactions of (HOMe₂CC≡)₂
where 3.0 ml³ of toluene were used as solvent. [b] The ratio silylalkene 1/silylalkene 2 is the same also
if the reaction mixtures are analysed in certain reaction times when 10—20% and 50—70% of the silane is
consumed. [c] CyPent = cyclopentyl ((CH₂)₄CH).

ation 1 becomes:

$$\frac{k_1}{k_2} = \frac{[P]}{[Q]} \tag{2}$$

In the case of the terminal alkynes studied the calculated values of the relative rate constants are:

Alkyne    n-PrC≡CH,    n-BuC≡CH,    n-PentC≡CH,    MeEtC(OH)C≡CH

$k_{rel}$      1           1.4          1.5             6.8

Alkyne    CyPentC≡CH,    Me₂C(OH)C≡CH,    PhCH(OH)C≡CH

$k_{rel}$      7.4          9.5              12.9

For the alkyne HOMe₂CC≡CCMe₂OH $k_{rel}$ is 4.85.

The calculated values of the relative rate constants for the internal alkynes

studied are:

Alkyne     n-PrC≡CMe,    EtC≡CMe,    EtC≡CEt

$k_{rel}$              1              1.2              2.1
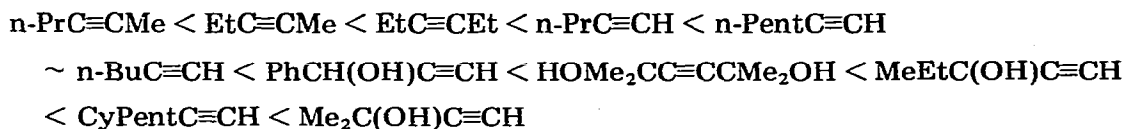
Comparison of the relative rate constants of the hydrosilylation of the internal alkynes with those of the terminal alkynes and the alkyne $HOMe_2CC≡CCMe_2OH$ was impossible. This is due to the fact that in competition reactions with terminal alkynes or the alkyne $HOMe_2CC≡CCMe_2OH$ (Table 1) the less reactive alkynes afford only traces of products (<5%), which cannot be accurately measured.

The calculated relative rate constants show clearly that the nature of the alkynes has a significant effect on the rate of the hydrosylation. Thus, the terminal alkynes and their hydroxy-derivatives are more reactive than the internal alkynes. Also, the terminal hydroxyalkynes, where an electron-withdrawing substituent is adjacent to the acetylenic bond, are more reactive than the terminally unsubstituted alkynes.

If we assume that the first step of the catalytic cycle involves coordination of the alkyne with the central atom of the catalyst, the observed relative reactivities of the alkynes can be explained on the basis of the stability of the complexes formed. It is well known [11,12] that the stability of the alkyne complexes of the group VIII metals of general formula $L_nM(RC≡CR')$ depends on the electronic structure of the alkyne. Generally, the stability of the complexes is increased as the $\pi$-acceptor capacity of the alkyne increases. This is due to the fact that the increase of the $\pi$-acceptor ability of the alkyne favors $\pi$-back bonding between the alkyne and the central atom, and this appears to be more important for the stability of the complexes than the $\sigma$-component [11,12].

In the present investigation, as a first approximation, we used as the measure of the $\pi$-acceptor capacity of the alkynes the $^{13}C$ chemical shifts of their $sp$ carbon atoms, since as it is known [13] they reflect the electron density distribution on the carbon atoms. In Table 2 are listed the $^{13}C$ chemical shifts of the $sp$ carbon atoms of the alkynes under consideration.

The $\pi$-acceptor capacities of the studied alkynes, based on the $^{13}C$ chemical shifts of the $sp$ carbon atoms, vary in the following sequence:

n-PrC≡CMe < EtC≡CMe < EtC≡CEt < n-PrC≡CH < n-PentC≡CH

~ n-BuC≡CH < PhCH(OH)C≡CH < $HOMe_2CC≡CCMe_2OH$ < MeEtC(OH)C≡CH

< CyPentC≡CH < $Me_2C(OH)C≡CH$

This sequence was based on the $^{13}C$ chemical shift of the $sp$ carbon atom with the lower electron density, since this carbon atom will be centre for the formation of the $\pi$-bond. The other $sp$ carbon atom will be the center for the formation of the $\sigma$-bond, since the higher proportion of the electron density of the $\pi$-HOMO is localised on it. This carbon atom also has a very small $\pi$-acceptor ability as the $\pi^*$-LUMO around this carbon atom is protected by the high electron density of the $\pi$-HOMO.

The above sequence agrees with that of the relative reactivity of alkynes obtained on the basis of competition reactions. The only exception is the alkyne

**TABLE 2**

$^{13}$C CHEMICAL SHIFTS ($\delta$, ppm) [a] OF THE ACETYLENIC CARBON ATOMS OF SOME TERMINAL AND INTERNAL ALKYNES

| Alkyne | C(1) | C(2) | C(3) | C(4) |
|---|---|---|---|---|
| C(1)≡C(2)—C(3)—C(4)—C(5) | 67.3 [b] | 82.7 | — | — |
| C(1)≡C(2)—C(3)—C(4)—C(5)—C(6) | 67.7 | 83.3 | — | — |
| C(1)≡C(2)—C(3)—C(4)—C(5)—C(6)—C(7) | 67.7 [b] | 83.2 | — | — |
| C(1)≡C(2)—C(OH)MeEt | 68.5 | 87.8 | — | — |
| C(1)≡C(2)—CH(CH₂)₄ | 68.6 | 88.0 | — | — |
| C(1)≡C(2)—C(OH)Me₂ | 70.0 | 89.6 | — | — |
| C(1)≡C(2)—CH(OH)Ph | 75.2 | 84.0 | — | — |
| HOMe₂C—C(3)≡C(4)—CMe₂OH | — | — | 87.3 | 87.3 |
| C(1)—C(2)≡C(3)—C(4)—C(5) | — | 73.9 | 78.8 | — |
| C(1)—C(2)≡C(3)—C(4)—C(5)—C(6) | — | 74.0 [b] | 77.2 | — |
| C(1)—C(2)—C(3)≡C(4)—C(5)—C(6) | — | — | 80.2 [b] | 80.2 |

[a] Chemical shifts are expressed relative to TMS ($\delta$(TMS) = 0). [b] Data from literature [14].

PhCH(OH)C≡CH. However, in this alkyne there is also a significant deshielding at the C(1) and possibly both carbon atoms participate in the formation of the $\pi$-back bond. Therefore, the $\pi$-acceptor capacity of PhCH(OH)C≡CH must be higher than that reflected only from the $^{13}$C chemical shift of the C(2). The anomalous behavior of PhCH(OH)C≡CH relative to the other alkynes in the above mentioned sequences may also be due to the fact that in PhCH(OH)-C≡CH the $^{13}$C chemical shifts are affected by the magnetic anisotropy effect due to the phenyl ring. This effect is absence in the other alkynes. Therefore, for PhCH(OH)C≡CH the $^{13}$C chemical shifts used as a measure of the electron density distribution on its $sp$ carbon atoms also involve a factor which is due to the magnetic anisotropy effect of the phenyl ring.

It should be noted that in the case of the terminal alkynes studied a linear relationship between $k_{rel}$ and $^{13}$C chemical shifts of the C(2) was observed (Fig. 1). The small deviation from the line of the alkyne HOMe₂CC≡CCMe₂OH may be due to steric factors. The lower relative reactivities of the internal alkynes than of the terminal alkynes can also be attributed to the steric factors.

Next, we investigated the relative reactivities of alkynes in separate hydrosilylation reactions catalysed by *trans*-di-$\mu$-hydridobis(tricyclohexylphosphine)-bis(silyl)diplatinum complexes. In this case the yield (%) of the products at certain reaction times under the same reaction conditions was used as the measure of the reactivity.

Hydrosilylations of n-PrC≡CH, n-BuC≡CH and n-PentC≡CH with Et₃SiH (reaction conditions: 65° C, 10.0 mmol of alkyne, 10.0 mmol of silane, mmol of catalyst/mmol of alkyne = $7.4 \times 10^{-5}$, argon atmosphere) after 1 h afforded products in 39%, 57% and 69% yields, respectively. Under the same conditions PhCH(OH)C≡CH gave products in 15% yield after 14 h. Thus, for these alkynes the relative reactivities are in the sequence:

PhCH(OH)C≡CH << n-PrC≡CH < n-BuC≡CH < n-PentC≡CH
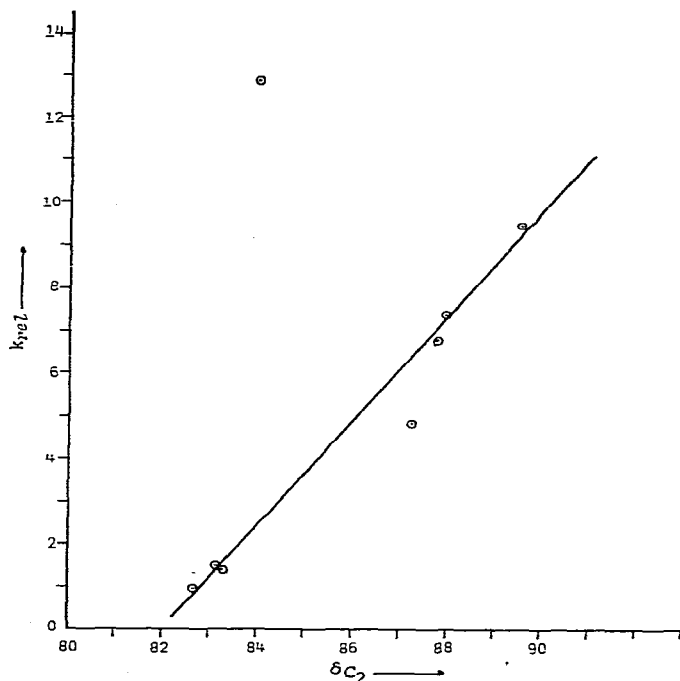
Hydrosilylations of MeEtC(OH)C≡CH, Me₂C(OH)C≡CH and PhCH(OH)-

Fig. 1. Linear dependence of the $k_{rel}$ from the $^{13}C$ chemical shifts of the C(2) carbon atom of terminal alkynes in their hydrosilylation reactions catalysed by *trans*-di-$\mu$-hydridobis(tricyclohexylphosphine)bis-(silyl)diplatinum complexes. The figure also shows the great deviation from linearity of the alkyne PhCH(OH)C≡CH.

C≡CH with Et$_3$SiH (reaction conditions: 65°C, 5.0 mmol of alkyne, 5.0 mmol of silane, mmol of catalyst/mmol of alkyne = 1.5 × 10$^{-4}$, argon atmosphere) gave products in 27%, 21% and 8% yields, respectively after 2 h, while after 14.5 h 73%, 68% and 35% yields of products were obtained. For these alkynes the relative reactivities are in the sequence:

PhCH(OH)C≡CH < Me$_2$C(OH)C≡CH < MeEtC(OH)C≡CH

Finally, hydrosilylations of EtC≡CMe, n-PrC≡CMe and EtC≡CEt with Et$_3$SiH (reaction conditions: room temperature, 5.0 mmol of alkyne, 10.0 mmol of silane, mmol of catalyst/mmol of alkyne = 3.0 × 10$^{-4}$, argon atmosphere) gave products in 83%, 75% and 10% yields, respectively after 1 h. Under the same conditions n-PrC≡CH gave a 100% yield in less than 0.25 h. For these alkynes the relative reactivities are in the sequence:

EtC≡CEt < n-PrC≡CMe < EtC≡CMe << n-PrC≡CH

Comparing the sequence of reactivities of alkynes obtained on the basis of the separate rates discussed above with that obtained by competition reactions, the following features emerge.

For terminally and internally unsubstituted alkynes the sequences of the relative reactivities obtained by the two methods are the same except for hex-

3-yne. The relative reactivity of hex-3-yne obtained from competition reactions is higher than those of the other internal alkynes, while the opposite is true for the relative reactivities determined from the reaction rate. In contrast, the hydroxyalkynes, which in competition reactions are more reactive than the unsubstituted alkynes, on the basis of the reaction rates appear to be less reactive, and the sequence of their relative reactivities is inversed.

The above observations indicate that in the unsubstituted alkynes the contribution of $\pi$-back bonding to the stability of the complexes formed is relatively small, while in the hydroxy-derivatives the contribution of $\pi$-back bonding is higher than that of $\sigma$-bonding. Thus, the hydroxyalkynes form more stable complexes with the central atom of the catalyst than the unsubstituted alkynes. This is in accordance with the observations of other workers who demonstrated that the metal—alkyne bond strength in alkyne complexes of $Pt^0$ and $Pt^{II}$ is increased when electron-withdrawing substituents are adjacent to the acetylenic bond [12,15,16].

Since hydroxyalkynes form more stable complexes with the central atom of the catalyst than the unsubstituted alkynes it is easily understood that in competition reactions hydroxyalkynes will be preferentially coordinated to the central atom compared with the unsubstituted alkynes. On the other hand, the unsubstituted alkynes will form the transition state in the hydrosilylation reactions more easily than the hydroxyalkynes, because of the instability of their complexes formed. Also, the coordinated hydroxyalkynes, because their $\pi$-acceptor capacity is greater than that of the unsubstituted alkynes, will be less susceptible to the nucleophilic attack from the hydride, since more electron density is accumulated on their $\pi^*$—LUMO.

Another fact, which further supports our interpretations of the relative reactivities of alkynes in hydrosilylation reactions, is the inability of hexafluorobut-2-yne to undergo hydrosilylation. All attempts at hydrosilylation of hexafluorobut-2-yne were unsuccessful. This is not surprising since hexafluorobut-2-yne, which is a strong $\pi$-acceptor ligand, forms very stable complexes with the central atom of the catalyst. In these complexes it would be very difficult for the coordinated alkyne to undergo nucleophilic attack by the hydride since high electron density is accumulated on its $\pi^*$-LUMO. Stable complexes of hexafluorobut-2-yne with group VIII metals have been isolated and studied [11,12], and it was observed that because of the very strong $\pi$-back bonding, the central atom and the alkyne form a metallocyclopropane ring in these complexes.

### Experimental

*Measurements*

$^1$H NMR spectra were recorded on a Varian A-60A (60 MHz) spectrometer using TMS as an internal standard. $^{13}$C NMR spectra were obtained using a Varian CFT-20 spectrometer operating in the Fourier transform mode at 20 MHz under conditions described elsewhere [17]. Analytical gas chromatography (GLC) was carried out on a Hewlett-Packard 7620A instrument fitted with a flame-ionisation detector using 3 ft × 0.25 in glass columns packed with 3% w/w OV-101 on Gas Chrom Q. The samples were introduced as

TABLE 3

RETENTION TIMES OF TRIETHYLSILYL-ALKENES

| Compound | Retention time (in min) |
|---|---|
| trans-n-PrCH=CHSiEt$_3$ | 1.58 |
| E-CH$_3$C(SiEt$_3$)=CHCH$_2$CH$_3$ }<br>E-CH$_3$CH=C(SiEt$_3$)CH$_2$CH$_3$ | 1.64 |
| E-CH$_3$C(SiEt$_3$)=CHCH$_2$CH$_2$CH$_3$ }<br>E-CH$_3$CH=C(SiEt$_3$)CH$_2$CH$_2$CH$_3$ | 2.68 |
| trans-n-BuCH=CHSiEt$_3$ | 2.76 |
| trans-Me$_2$C(OH)CH=CHSiEt$_3$ | 3.15 |
| trans-MeEtC(OH)CH=CHSiEt$_3$ | 4.73 |
| trans-PentCH=CHSiEt$_3$ | 4.80 |

~10% v/v solutions in n-hexane under the following conditions: injected quantity 1 to 3 $\mu$l, oven temperature 130°C and flow of nitrogen 20 cm$^3$/min. The retention times of the products studied are listed in Table 3. Identifications of the mixtures formed in competition reactions were made by comparison of their retention times with those of samples of authentic materials. The mixtures were quantified using the peak areas calculated by the triangulation method.

Analysis of the mixtures by $^1$H NMR spectroscopy was based on the comparison of the integrated intensities of the peaks due to the acetylenic protons of the reactants or to the olefinic protons of the products. In most systems some characteristic peaks which do not change intensity during the reactions were useful as reference peaks. In systems in which there are no such peaks toluene was added, and the peak due to the methyl protons of toluene used as the reference. The results obtained were in good agreement with those obtained by GLC.

*Materials*

The hydrosilanes and the unsaturated compounds used were commercial products. The liquid reagents were distilled in an inert atmosphere prior to use. The trans-di-$\mu$-hydridobis(tricyclohexylphosphine)bis(silyl or germyl)diplatinum complexes were prepared according to the published method [18].

*General procedures*

All reactions were carried out under pure argon in tubes (capacity ca. 100 cm$^3$) fitted with Westef stopcocks and a joint, so that the reaction vessel could be attached to a vacuum system. In some cases (non-volatile reagents) the reactions can be also carried out into Schlenk tubes (capacity ca. 80 cm$^3$). Hydrosilylations were carried out according to previously described general procedures [19,20]. Competition reactions were carried out using procedures typified by the following examples.

*(a) Competition reactions of Et$_3$SiH with Me$_2$C(OH)C≡CH and PhCH(OH)-C≡CH in the presence of the catalyst [(Cy$_3$P)(Me$_3$Ge)(μ-H)Pt]$_2$*

The reaction vessel was charged with Me$_2$C(OH)C≡CH (0.5 ml, 5.0 mmol),

PhCH(OH)C≡CH (0.625 ml, 5.0 mmol), $Et_3SiH$ (0.4 ml, 2.5 mmol) and 1.0 mg of the catalyst. The reaction temperature was kept at 60°C. After appropriate reaction times, samples of the mixture were analyzed by ^{1}H NMR and GLC. The mixture was also analysed by ^{1}H NMR and GLC at the end of the reaction, when all the $Et_3SiH$ had been consumed. The results obtained are independent of the reaction time.

*(b) Competition reactions of $Et_3SiH$ with $Me_2C(OH)C≡CH$ and hex-1-yne in the presence of the catalyst $[(Cy_3P)(Me_2BzSi)(\mu-H)Pt]_2$*

The reaction vessel was charged with $Me_2C(OH)C≡CH$ (0.25 ml, 2.5 mmol), hex-1-yne (0.3 ml, 2.5 mmol), $Et_3SiH$ (1.2 ml, 7.5 mmol), 1.0 ml of toluene as solvent and 1.0 mg of the catalyst. The mixture was kept at 60°C. After 0.5 h a ^{1}H NMR spectrum revealed 20% conversion of the hydrosilane, and after 1 h 30%. Analysis of the reaction mixture by GLC showed the formation of *trans*-$Me_2C(OH)CH≡CHSiEt_3$ (87.2%) and *trans*-n-$C_4H_9CH=CHSiEt_3$ (12.8%).

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