

Mechanistic aspects of the platinum catalysed hydrosilylation of PhCH=CH_2 with Et_3SiH

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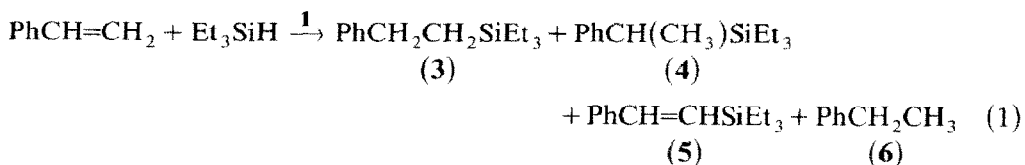
Abstract

Kinetic measurements and ^1H , ^2H and ^{195}Pt NMR studies have been carried out on the platinum catalysed hydrosilylation of styrene with triethylsilane. With *trans*- $\text{PtCl}_2(\text{PhCH=CH}_2)_2$ as catalyst precursor there is a short period during which reduction and product development take place, but with $\text{Pt}(\text{PhCH=CH}_2)_3$ the product development is linear and a plot of the yield of product against time passes through the origin. Rate measurements on reactions involving Et_3SiD reveal an overall deuterium kinetic isotope effect of ca. 3.6. ^{195}Pt NMR studies reveal a build-up of an intermediate with a $^1J(\text{Pt,H})$ value of 605 Hz, which suggests that it is a hydride-like complex. The data imply a rate-determining step in which coordinated styrene inserts into a Pt–H bond.

Introduction

The homogeneously catalysed hydrosilylation of olefins with platinum(II) and platinum(IV) precursors represents a convenient route to many useful intermediates in organic syntheses [1]. The reaction conditions are typically mild and a wide variety of substrates are tolerated [2]. Various transition metal complexes are capable of acting as catalyst precursors, with H_2PtCl_6 the most widely used [3]. In addition to platinum derivatives, rhodium [4] and palladium [5] complexes, amongst others, act as catalysts. We recently reported that *cis*- [6] and *trans*- $\text{PtCl}_2(\text{PhCH=CH}_2)_2$ [7] complexes, **1a** and **1b**, respectively, are effective catalyst precursors for the hydrosilylation of styrene, methyl vinyl ether, 1-hexene, and 1-pentyne, amongst others. The *cis* isomer is formed from the *trans* and has been characterized by NMR and crystallographic methods. Both of these complexes are reduced in situ by silane to, in the case of PhCH=CH_2 as substrate, $\text{Pt}(\text{PhCH=CH}_2)_3$ [7]. To shed further light on the subsequent reactions of this zerovalent complex we

have carried out a series of kinetic measurements on reaction 1 using either *trans*-PtCl₂(PhCH=CH₂)₂ (**1b**), or Pt(PhCH=CH₂)₃ (**2**).



(% yields of **3**, **4**, **5** and **6** are ca. 73–75, 1–2, 11–13 and 11–13, respectively)

We report here our results and their mechanistic implications.

Results and discussion

A solution of PtCl₂ in PhCH=CH₂ affords **1b** [7], which under a nitrogen atmosphere catalyses reaction 1 and comes to completion in < 2 h with a catalyst to reagent ratio of ca. 1/2300. This time scale is convenient for ¹H NMR measurements, which require ca. 15 s per measurement, thereby allowing a sufficient number of determinations for a satisfactory kinetic analysis. As all of the product components in solution have been identified separately [6], the reaction was followed by monitoring the sum of the benzyl CH₂ signals for **3** and **6**. Figure 1a shows the results for a typical run involving a catalyst/substrate ratio of 1/4349. Supplementary Fig. 1b–1d show results for the ratios 1/1305, 1/8699 and 1/21,747, and a composite of all of these runs is shown in Fig. 2. Figure 3 shows the same type of composite result based on the disappearance of the PhCH=CH₂ ¹H NMR signals. The individual traces **1a**–**1d** show two regions, an initial period with a smaller slope and a linear region with a somewhat larger slope. At the end of the reaction when almost all of the styrene has been consumed, the platinum(0) complex becomes unstable and the catalyst decomposes, in keeping with our earlier report [7].

If, instead of **1b**, the zerovalent **2** is used as precursor, the reaction is faster and the product development is linear throughout, as shown in Fig. 4. Within the

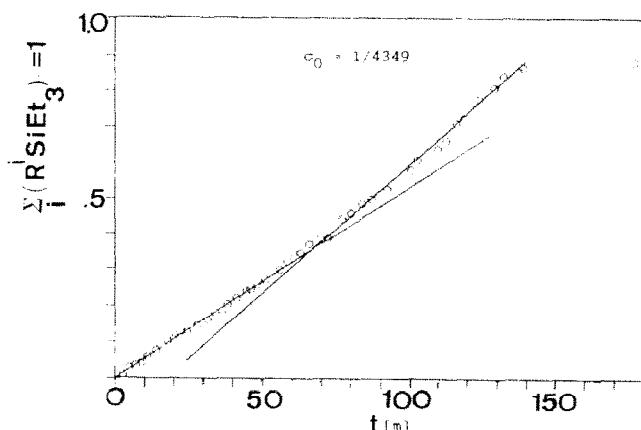


Fig. 1. Hydrosilylation using **1** as precursor. Normalized concentration for the sum of PhCH₂CH₂SiEt₃ and PhCH₂CH₃ as a function of time for a precursor-to-styrene ratio of 1/4349.

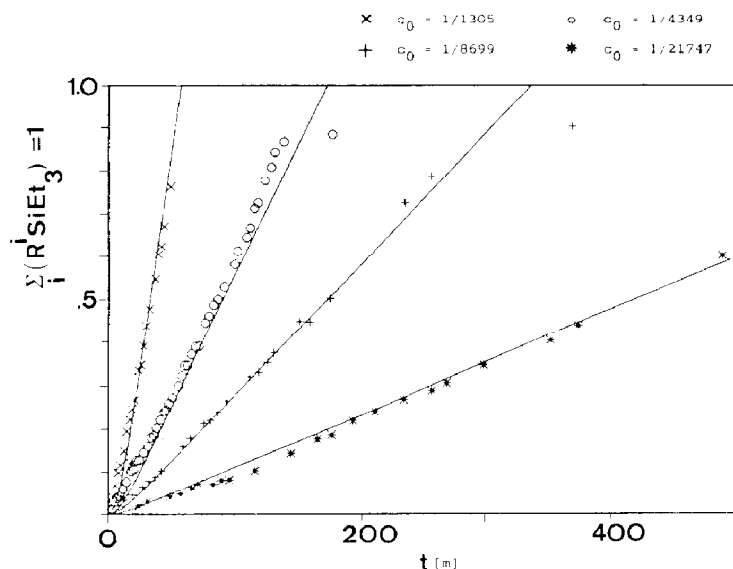


Fig. 2. Hydrosilylation using **1** as precursor. Normalized concentrations for the sum of $\text{PhCH}_2\text{CH}_2\text{SiEt}_3$ and PhCH_2CH_3 as a function of time for four different catalyst to styrene ratios: $\times = 1/1305$; $\circ = 1/4349$; $+$ $= 1/8699$ and $\star = 1/21747$.

experimental error, the curve now passes through zero. Except for the portion involving the initial rate increase, the slope of the curve is identical to that found starting from **1b**, suggesting essentially quantitative reduction of **1b** to **2** when the former is employed. From our knowledge of the time scale for the reduction of **1b** to **2** we conclude that in the early stage of the reaction the precursor **1b** is being converted into **2** which then reacts further. It is interesting that the rate in Fig. 4 does not change appreciably (once the catalyst is formed) over a substantial segment of the curve. Moreover, the product distribution is constant throughout, i.e., the

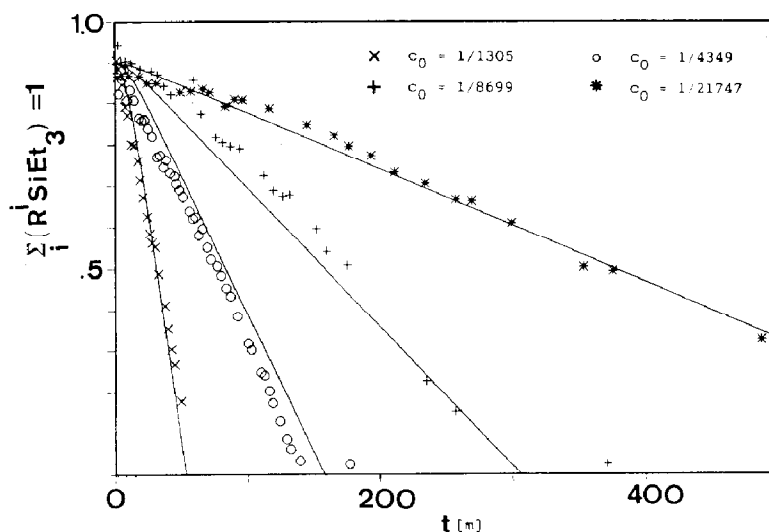


Fig. 3. Hydrosilylation using **1** as precursor. Disappearance of styrene as a function of time (minutes) for the four catalyst-to-styrene ratios, $\text{PhCH}=\text{CH}_2$ concentration normalized to **1**.

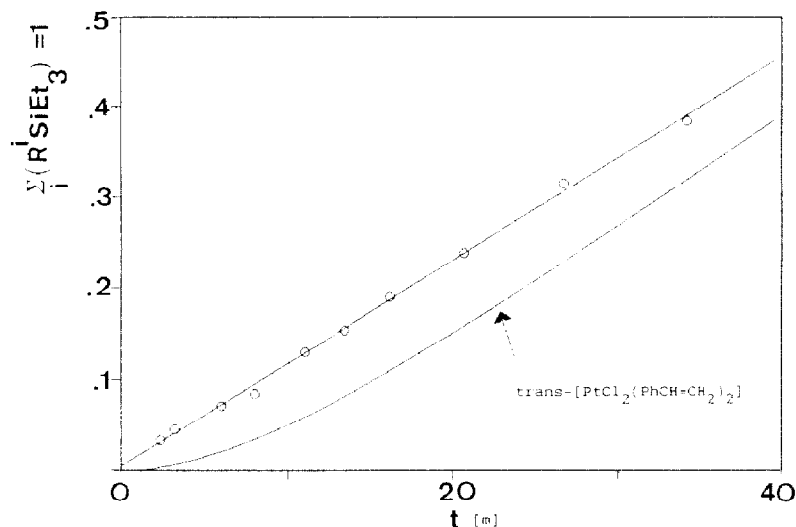


Fig. 4. Development of the sum of the products $\text{PhCH}_2\text{CH}_2\text{SiEt}_3$ and PhCH_2CH_3 (normalized) as a function of time (minutes) for the hydrosilylation reaction using **2** as precursor. The lower curve is calculated using eq. 2 with **1b** as catalyst precursor.

same ratio of products is present at both early and late stages of the reaction. It seems that the same active species is involved throughout, and consequently that the catalyst is not destroyed in a side reaction. Furthermore, as the reaction rate does not change as the reagents are consumed (an effective change in concentration of 1–2 orders of magnitude), either (a) neither reagent is involved in the rate determining step, or (b) the effective concentration of these reagents is always large enough to provide zero order conditions. There have been several earlier studies on the hydrosilylation of styrenes with (a) PhSiH_3 in presence of H_2PtCl_6 [8] and (b) MeCl_2SiH in presence of a binuclear platinum-styrene complex [9]. The studies showed that donor substituents in the silane enhance the rate, and for the latter system it has been reported [2,3,9] that the reaction is first order in catalyst precursor and zero order in reagents [9]. Consequently, it would seem that our data for $\text{PhCH}=\text{CH}_2$ and Et_3SiH confirm the more general observation.

Analysis of our results in terms of a suitable mathematical model [10] (see supplementary material available from the authors) leads to an equation expressing the appearance of the products and/or disappearance of the reactants as a function of k_1 , the rate constant for the formation of the catalyst * whatever its structure, and k_2 the rate of product development ($k_{2,1}$, for $\text{PhCH}_2\text{CH}_2\text{SiEt}_3$, $k_{2,2}$ for the sum of **5** and **6**...).

The calculated and experimental data are shown in Fig. 5 and the expression in eq. 2.

$$[\text{Product}] = k_2 c_0 (l/k_1) (k_1 t + e^{-k_1 t} - 1) \quad (2.1)$$

where k_2 is the rate for that specific product.

Starting material = SM

$$[\text{SM}] = [\text{SM}]_0 + k_2 c_0 (1/k_1) (l - k_1 t - e^{-k_1 t}) \quad (2.2)$$

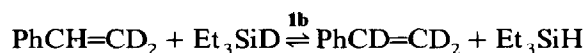
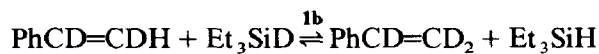
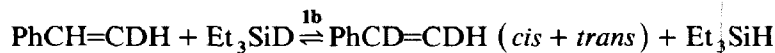
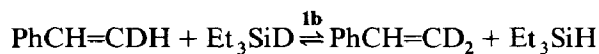
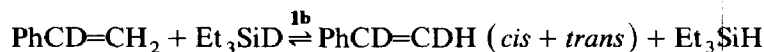
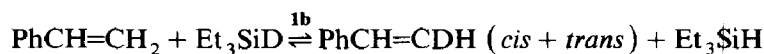
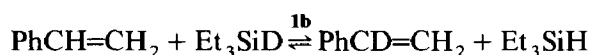
where k_2 is the rate for a specific starting material.

* **1b** and **2** are assumed to be catalyst precursors.

Solution of eq. 2 affords k_1 0.112 min^{-1} ($0.09 \text{ min}^{-1} \leq k_1 \leq 0.15 \text{ min}^{-1}$) $k_{2,1}$ $23.6 \pm 0.8 \text{ min}^{-1}$ $k_{2,2} = 2.81 \pm 0.64 \text{ min}^{-1}$, in good agreement with the experimental results.

In the supplementary material we show graphically the results for seven additional models which we considered. These gave consideration to possible catalyst destruction, a dependence on either PhCH=CH_2 or Et_3SiH in the slow step, and the possibility that $\text{trans-PtCl}_2(\text{PhCH=CH}_2)_2$ was the catalyst itself rather than a precursor. None of these fit the data.

Reaction 1 was then carried out with Et_3SiD prepared by reaction of Et_3SiCl with LiAlD_4 [11] and the reaction monitored by both ^1H and ^2H NMR spectroscopy. The relatively low field position of the Si-H resonance in the ^1H spectrum as well as the appearance of signals for free deuterated PhCH=CH_2 in the ^2H spectrum, confirm that exchange takes place, presumably via the following series of reactions:



In the absence of catalyst there was no H/D exchange after 15 h at room temperature, whereas with a $\text{PhCH=CH}_2/\text{1b}$ ratio of 2268/1 (olefin/silane = 1) 10% Et_3SiH was detected after 5 min of contact. A similar exchange starting from Cl_3SiD in the presence of H_2PtCl_6 was observed previously at room temperature [2,12]. Incorporation of ^2H into isobutylene from Cl_3SiD in presence of H_2PtCl_6 , is also known [13].

Figure 6 shows the time dependence of the concentration of Et_3SiH in a reaction starting from Et_3SiD . Of primary importance in this experiment is that the reaction requires ca. 230 min instead of the expected ca. 100 min. In the first 60 min the concentration of Et_3SiH increases owing to the various exchange reactions shown above, and then begins to fall as this hydride is consumed in the hydrosilylation. Since Et_3SiH is being produced and reacting further during the first 60 min, the overall slowing of the reaction by ca. 2.3 represents a lower limit. Indeed, if it is assumed that an equilibrium concentration is reached after ca. 60–100 min, the ratio of the slope of the “linear” section of Fig. 6 (120–220 min) to that of the analogous plot for the reaction involving the undeuterated species, corresponds to an overall

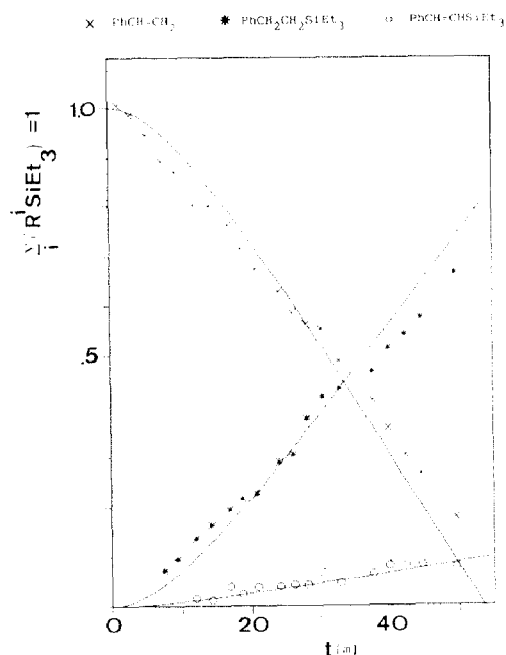


Fig. 5. Experimental and calculated (solid line) curves for the appearance and disappearance of several compounds as a function of time. Precursor/ PhCH=CH_2 = 1/1305. $\times$ = PhCH=CH_2 , $\star$ = $\text{PhCH}_2\text{CH}_2\text{SiEt}_3$, $\circ$ = PhCH=CHSiEt_3 .

^2H kinetic isotope effect of 3.6 ± 0.2 . In view of the various potential reactions within the catalyst cycle (see below) and the number of products, there are likely to be various sources of this retardation, but it is tempting to think that there is some C–H or M–H bond breaking in the rate determining step.

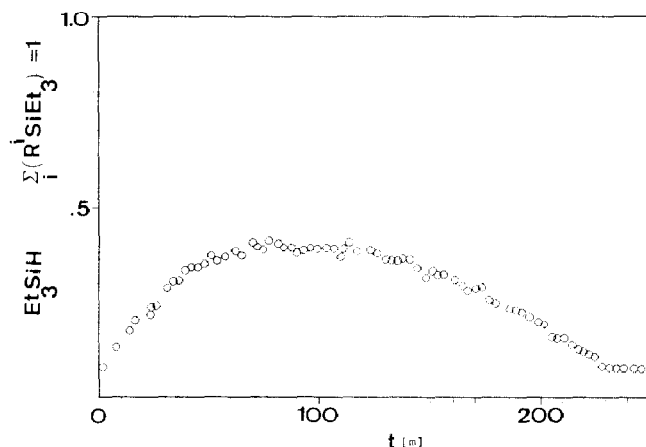


Fig. 6. Time dependence of the concentration of Et_3SiH starting from PhCH=CH_2 and Et_3SiD using 1 as catalyst precursor.

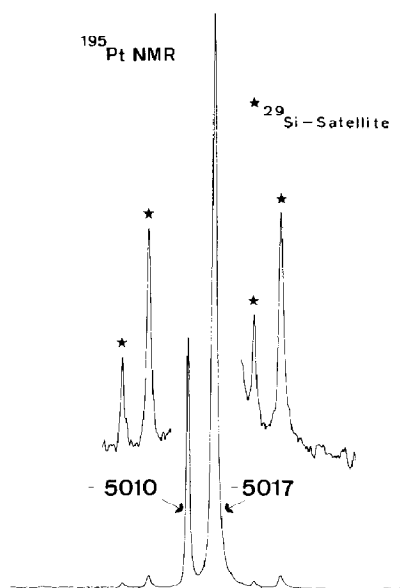
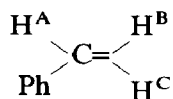


Fig. 7. $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum of the unknown intermediate. Both resonances are accompanied by ^{29}Si satellites (253 K).

We note that an analysis (via both ^1H and ^2H NMR) of the deuterium incorporation in the styrene reveals more ^2H at the CH^{A} -position as shown:



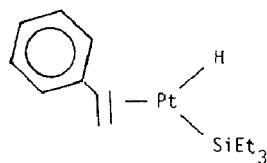
$$\text{H}_{\text{C}}/\text{B}_{\text{B}} = 1.00 \pm 0.09; \quad \text{D}_{\text{C}}/\text{D}_{\text{B}} = 1.01 \pm 0.16$$

$$\text{H}_{\text{C}}/\text{H}_{\text{A}} = 1.27 \pm 0.15; \quad \text{D}_{\text{A}}/\text{D}_{\text{B}} = 2.27 \pm 0.30$$

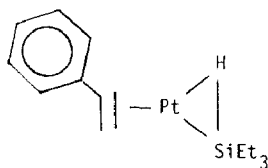
$$\text{H}_{\text{B}}/\text{H}_{\text{A}} = 1.27 \pm 0.13; \quad \text{D}_{\text{A}}/\text{D}_{\text{C}} = 2.20 \pm 0.32$$

Except for **2**, we have found no evidence for platinum intermediates at room temperature during the routine catalytic reactions. Since reduction to platinum(0) and hydrosilylation are concurrent, we chose to initially reduce **1b** to **2** with Ph_3SiH , since this does not undergo hydrosilylation with $\text{PhCH}=\text{CH}_2$ [7]. Complex **2**, in the presence of ca. 150 fold excess of styrene was then treated with between 5 and 25 equivalents of Et_3SiH at 263 K, which gave a complex which in $\text{Et}_3\text{SiH}/\text{PhCH}=\text{CH}_2/\text{C}_6\text{D}_6$ solution gives two ^{195}Pt signals at δ -5010 and -5017 ppm (see Fig. 7). Both signals are accompanied by ^{29}Si satellites, whose intensity (and integrals) confirm the presence of one coordinated ^{29}Si spin [14]. The values of the coupling constants, 1775 and 1781 Hz (both ± 12 Hz), respectively, are consistent with one-bond Pt-Si interactions [15]. In view of their similar $\delta(^{195}\text{Pt})$ values, these two components are likely to have very similar structures [16], and this is supported by their almost identical $^1J(\text{Pt},\text{Si})$ values. From measurements involving $\text{PhCH}=\text{CH}_2$, both ^{195}Pt spins can be shown to couple to one styrene molecule, $^1J(\text{Pt},\text{C})$ ca. 100–110 Hz for both isomers. There is a ^{29}Si resonance at δ 21.45 ppm

which has ^{195}Pt satellites with a separation of 1781 Hz *. In a solution composed of Et_3SiH , $\text{PhCH}=\text{CH}_2$, and a mixture of CD_2Cl_2 and CH_2Cl_2 (5/2/5/15, respectively) at 193 K, a proton-coupled ^{195}Pt spectrum reveals only one resonance at $\delta -5113$ ppm, with $^1J(\text{Pt},\text{H})$ 605 Hz. This latter value is consistent with either a terminal [17] or bridging hydride [18]. (Although it is not directly pertinent, we should mention that both Ph_3SiH and $(\text{EtO})_3\text{SiH}$ react with **2** to afford compounds showing ^{195}Pt resonances at $\delta -5127$ and -5277 ppm (both at 263 K)). Even at 193 K this molecule is dynamic on the NMR time scale. The ^{195}Pt signal is broad, $\Delta\nu_{1/2}$ ca. 80 Hz, and attempts to locate proton and carbon signals corresponding to the complex with the 605 Hz coupling have been unsuccessful. We do not know the structure of the complex, but the available data point to a species with features similar to **7** or **8** and variations thereof **.

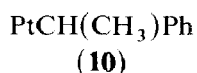
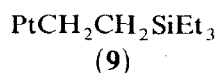


(7)

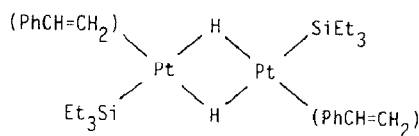


(8)

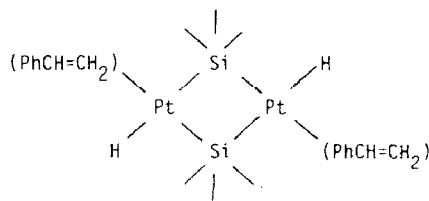
We note that an interaction such as that shown in **8** has been postulated for several different transition metals [19–21]. Whatever the exact nature of the species, the NMR studies suggest that it is a complex in which the hydride or hydride-like ligand has not yet inserted a molecule of styrene, since a molecule with a ligand such as that shown in **9** or **10**, would have a much smaller $^1J(\text{Pt},\text{H})$ value [22].



Moreover, a bridging hydride structure such as **11**, for which there is ample



(11)



(12)

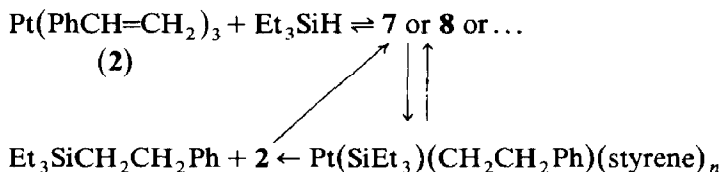
precedent [23], should show two hydride couplings to ^{195}Pt . Further, the ^{29}Si satellite intensity and integral for a structure such as **12** [24] do not fit the data.

* We observe only one ^{29}Si signal.

** The aryl moiety of the $\text{PhCH}=\text{CH}_2$ may be involved in the coordination sphere, and there are possible isomers of both **7** and **8**.

Conclusions

Taking account of the zero order conditions with respect to the reagent, we suggest the following as the simplest representation of the homogeneous hydrosilylation:



In view of the kinetic isotope effect and the constant rate of product development, we regard the insertion as the slow step, which is followed by an irreversible reductive elimination. The $^1J(\text{Pt},\text{H})$ value of 605 Hz strongly indicates the participation of a hydride intermediate i.e. **7** rather than **8**, but we cannot exclude a rate-determining oxidative addition step starting from **8**, especially as this could involve Si–H bond-breaking. We note, however, that Clark and co-workers [25] have found that oxidative addition of R_3SiH to $\text{Pt}(\text{Pcy}_3)_2$ is facile and reversible.

Although we believe we have reached a fair understanding of our reaction, we note that the literature [2,3] shows that there is a significant rate dependence on the type of silane use, so that our results may not be general.

Experimental

The ^1H and ^{195}Pt NMR spectra were determined with solutions in 5 mm and 10 mm tubes respectively, on a WM-250 NMR spectrometer. For the kinetic measurements ca. 3–4% C_6D_6 was added to stabilise the magnetic field. The ^1H (± 0.01 ppm) and ^{195}Pt (± 0.5 ppm) chemical shifts are relative to TMS and external Na_2PtCl_6 , respectively. The ^2H NMR spectra were recorded on an AM-400 MHz instrument kindly made available to us by Spectrospin AG.

Et_3SiH and $\text{PhCH}=\text{CH}_2$ were distilled immediately before the runs. PtCl_2 was obtained from Johnson-Matthey.

Kinetic experiments

PtCl_2 was dissolved in styrene to produce a stock solution of **1b**. This was diluted to provide solutions containing the various ratios of catalyst precursor to reagent. The samples were then placed under an N_2 atmosphere and treated with the appropriate quantity of Et_3SiH or Et_3SiD (flushed with N_2) so as to give a $\text{PhCH}=\text{CH}_2/\text{Et}_3\text{SiH}$ ratio of 1 (3–4% C_6D_6 injected). The progress of the reaction was then monitored directly in a 5 mm NMR tube.

Complex *cis*- $\text{PtCl}_2(\text{PhCH}=\text{CH}_2)_2$ (**1a**) is only slightly soluble in $\text{PhCH}=\text{CH}_2$, but even so its solutions catalyse the hydrosilylation at the same rate as do solutions of **1b**, and give rise to an identical product distribution.

Rate constants are regarded as accurate at the 95% certainty level.

Kinetics starting from $\text{Pt}(\text{PhCH}=\text{CH}_2)_3$

A solution of **1a** in styrene was reduced with Ph_3SiH to afford **2**, as described previously [7]. The Ph_3SiCl formed can be removed by passage of the reaction

solution through a 7 mm long, 20 mm diameter column of basic Alumina (activity I). The presence of the zerovalent complex can be demonstrated by ^{195}Pt NMR spectroscopy and confirmed by subsequent reaction with 2 equiv. of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, diphos, to yield the known $\text{Pt}(\text{diphos})_2$ [7,26]. Analysis for $\text{Pt}(\text{diphos})_2$ by ^{31}P NMR spectroscopy shows that ca. 30% ($\pm 3\%$) of **2** has been trapped. The Pt concentration of the solution was also determined after chromatography by atomic absorption spectroscopy. The two methods were in good agreement. This solution of **2** was used for the kinetic measurement.

Preparation of Et_3SiD

A mixture of chlorotriethylsilane (5.5 ml, 32.8 mmol) in 15 ml of ether in an N_2 atmosphere was treated with solid LiAlD_4 (1.10 g, 26.2 mmol). Gas bubbles were evolved. The solution was heated under reflux for 18 h and then cooled to room temperature. Treatment with 6 ml of H_2O was followed by slow addition of 40 ml of HCl (prepared from 20 ml of H_2O and 20 ml concentrated HCl). The ether was slowly distilled off (26 h) at room temperature under N_2 . The pressure was then reduced 10 Torr and the product (1.92 g, 62%) distilled into a cooled vessel. Good yields are obtained if the relatively volatile silane is maintained at the reduced pressure for as short a time as possible. ^1H NMR (CDCl_3) δ (ppm): 0.59 (g, CH_2 , $^3J(\text{H},\text{H})$ 7.9 Hz), 0.98 (t, CH_3); ^{29}Si , δ (ppm): -0.59 ($^1J(\text{Si},\text{D})$ 27.2 Hz). This material is 99.7% enriched in ^2H , as indicated by the relative integrals in the ^1H spectrum.

The ^{13}C -enriched $\text{PhCH}=\text{}^{13}\text{CH}_2$ was prepared as described previously [7].

*Generation of **7** (or **8**...) in solution*

Complex **1a** (70.0 mg, 148 μmol) was suspended in 2.5 ml of styrene and treated with triphenylsilane (76.9 mg, 295 μmol). After 30 min stirring, during which $\text{Pt}(\text{PhCH}=\text{CH}_2)_3$ was generated the solution was cooled to -20°C and 0.2 ml C_6D_6 was added (to stabilize the magnetic field). A pipette whose tip was cooled in liquid nitrogen was used to introduce 0.5 ml of Et_3SiH , 300 mg of Ph_3SiH , or 0.5 ml of $(\text{EtO})_3\text{SiH}$, previously cooled to -78°C , into the solution of **2**. Low temperature NMR measurements were then carried out on this solution.

*Preparation of **7** (or **8**...) for low temperature NMR*

Complex **1a** (50 mg, 0.105 mmol) was suspended in 2 ml of styrene and treated with 55 mg of Ph_3SiH . After 30 min stirring the solution was filtered through basic Alumina. This procedure was repeated twice and the combined solutions reduced in volume to ca. 0.2 ml then cooled to -20°C , 2 ml of cold (ca. -78°C) $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$, 3/1 (v/v) was added and the suspension shaken at room temperature until a clear solution had formed. Cooling to -78°C was followed by immediate addition of 0.5 ml of cold (ca. -78°C) Et_3SiH using a pipette previously immersed in liquid N_2 . The solution was then exposed briefly to room temperature until it became lemon-yellow and was then used for the low temperature NMR studies. (If this period at room temperature is too long the material decomposes, with formation of colloidal platinum. Our procedure involves a delicate compromise between this decomposition and the rapid consumption of the desired intermediate by hydrosilylation.

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References

- 1 E. Frainnet, *Pure and Applied Chem.*, 19 (1969) 489; T. Hayashi and K. Kabeta, *Tetrahedron Lett.*, 26 (1985) 3023; M.G. Voronkov, N.I. Ushakova, I.I. Tsykhanskaya and V.B. Pukhnarevich, *J. Organomet. Chem.*, 264 (1984) 39.
- 2 J.L. Speier in *Advances in Organometallic Chemistry*, Academic Press, London, 1979, vol. 17, p. 407.
- 3 E. Lukevics, Z. v. Belyakova, M.G. Pomerantseva and M.G. Voronkov, *J. Organomet. Chem.*, Library, Elsevier, Amsterdam, 1977, vol. 5, p. 1.
- 4 H. Brunner, R. Becker and S. Gauder, *Organometallics*, 5 (1986) 739; H. Brunner, G. Tiepl, I. Bernal and W.H. Ries, *Inorg. Chim. Acta*, 112 (1986) 65; H. Brunner and A.F.M. Mokhesur Raman, *Chem. Ber.*, 117 (1984) 719.
- 5 J. Yoshida, K. Tamao, M. Takahashi and M. Kumada, *Tetrahedron Lett.*, (1978) 2161; M. Hara, K. Ohno and J. Tsuji, *Chem. Commun.*, (1971) 247; S. Takahashi, T. Shibano and N. Hagihara, *Chem. Commun.*, (1969) 161.
- 6 A. Albinati, W.R. Caseri and P.S. Pregosin, *Organometallics*, 6 (1987) 788.
- 7 W.R. Caseri and P.S. Pregosin, *Organometallics*, in press.
- 8 M.C. Musolf and J.L. Speier, *J. Org. Chem.*, 29 (1964) 2519.
- 9 V.O. Reikhsfel'd and M.I. Astrakhanov, *Zh. Obshch. Khim.*, 40 (1970) 699.
- 10 F. Capra, "Das Tao der Physik", 8. Edition, Scherz Publisher Bern, Munich, Vienna, 1986.
- 11 C.A. Kraus and W.K. Nelson, *J. Am. Chem. Soc.*, 56 (1934) 195.
- 12 A.D. Petrov, A.F. Plate, E.A. Cheryshev and M.E. Dolgaya, *Zh. Obshch. Khim.*, 31 (1961) 1199.
- 13 J.W. Ryan and J.L. Speier, *J. Am. Chem. Soc.*, 86 (1964) 895.
- 14 $I = 1/2$, natural abundance 4.7%; see R.W. Rudolph, R.C. Taylor and C.D. Young, *Fundamental Research in Homogeneous Catalysis*, Plenum, New York, 1979, p. 987 for the problem of weak satellites surrounding an X nucleus signal.
- 15 D.W.W. Anderson, E.A.V. Ebsworth and D.W.H. Rankin, *J. Chem. Soc. Dalton*, (1973) 2370.
- 16 P.S. Pregosin in G. Webb (Ed.), *Annual Reports on NMR Spectroscopy*, Academic Press, London, 1986, vol. 17, p. 285.
- 17 T. Miyamoto, *J. Organomet. Chem.*, 134 (1977) 335; M.J. Church and M.J. Mays, *J. Chem. Soc. A*, (1968) 3074.
- 18 A. Albinati, R. Naegeli, A. Togni and L.M. Venanzi, *J. Organomet. Chem.*, 330 (1987) 85; A. Albinati, H. Lehner, L.M. Venanzi and M. Wolfer, *Inorg. Chem.*, 26 (1987) 3933; A. Albinati, T.J. Emge, T.F. Koetzle, S. Meille, A. Musco and L.M. Venanzi, *ibid.*, 25 (1986) 4821 and refs. therein.
- 19 U. Schubert, J. Müller and H.G. Alt, *Organometallics*, 6 (1987) 469.
- 20 U. Schubert, K. Bahr and J. Müller, *J. Organomet. Chem.*, 327 (1987) 357.
- 21 E. Colomer, R.J.P. Corriu, C. Marziu and A. Vioux, *Inorg. Chem.*, 21 (1982) 368.
- 22 T.G. Appleton, H.C. Clark and L.E. Manzer, *Coord. Chem. Revs.*, 10 (1973) 335.
- 23 M. Ciriano, M. Green, J.A.K. Howard, J. Proud, J.L. Spencer and F.G.A. Stone, *J. Chem. Soc. Dalton*, (1978) 801.
- 24 H.C. Clark, unpublished results. We find for $\text{Pt}(\text{diphos})_2$: ^{31}P NMR, δ (ppm) 31.20, $^1J(\text{Pt},\text{P})$ 3726 Hz, CD_2Cl_2 , 253 K.
- 25 H.C. Clark, M. Hampden-Smith and H. Rüegger, submitted for publication.