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Kinetic Studies on the Hydrosilylation of Phenylacetylene with R_3SiH (R_3 = $PhMe_2$, Ph_2Me, Ph_3, Et_3) using Bis(1,2-diphenylphosphinoethane)norbornadiene Rhodium(I) Hexafluorophosphate as Catalyst

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Product distribution and kinetic studies on the hydrosilylation of phenylacetylene by Ph_3SiH, Ph_2MeSiH, $PhMe_2SiH$ and Et_3SiH were performed using bis-[1,2-diphenylphosphinoethane]norbornadienerhodium(I) hexafluorophosphate, 1, as catalyst. Pre-equilibration of the catalyst with the acetylene produced hydrosilylations, pre-equilibration with the silane did not. The catalyst showed a pronounced selectivity for *cis*-addition to form β-products, t-PhCH=CHSiR$_3$, unlike most hydrosilylation catalysts. The kinetic studies showed a hydrosilylation reaction that is zero order with respect to both acetylene and the silane, with a dependency upon catalyst concentration. The k_{obs} value is directly influenced by the substituents on the silane: $k(PhMe_2SiH) > k$ $(Et_3SiH > k$ $(Ph_2MeSiH) > k$ (Ph_3SiH). Intercalation of the catalyst in hectorite was not useful, since either no reaction occurred in non-polar solvents, or extraction of the catalyst occurred in polar solvents to produce the same product distributions. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

The hydrosilylation reaction is catalysed by many transition-metal complexes and is often complex in nature; problems encountered in their investigation involve actors such as variable induction periods, irreproducible kinetics, radical chain processes, olefin rearrangements and the sensitivity of the resulting products to the catalyst.[1] The majority of such studies concern olefin substrates; hydrosilylation of acetylenes, an area of interest to us,[2] is less studied. Most of the transition-metal catalysts reported to be efficient for the hydrosilylation reaction involve platinum or rhodium. Early studies noted that the platinum-catalysed addition of the optically active silane NpPhMeSiH to diphenylacetylene proceeded with retention of the configuration at silicon and *cis*-addition.[3] In general *cis*-addition is the predominant mode of addition of silanes to acetylenes for platinum-based catalysts.[4–7] Relatively more *trans*-addition has been noted for rhodium systems, along with increased amounts of α-products obtained by changes in temperature and the manipulation of the catalyst by ligand substitution and/or environmental changes.[7,8]

Most hydrosilylation reactivity sequences have been based upon product yields;[1–8] however, some kinetic studies have been reported.[9–17] Marciniec and co-workers[12,15,17] reported a detailed study on a rhodium-catalysed hydrosilylation of 1-hexene by triethoxysilane and discovered that the hydrosilylation consisted of two distinct stages: an initial activation of the rhodium precursor to form an intermediate, followed by a fast catalytic cycle of hydrosilylation. In this study two intermediates involving prior coordination of either the 1-hexene

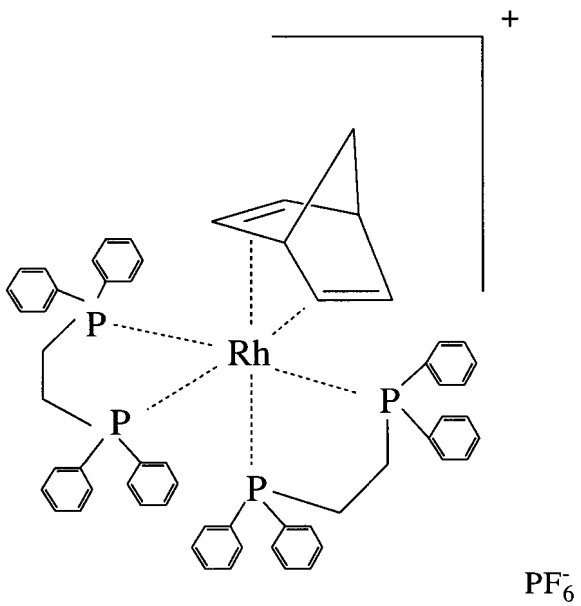

Figure 1 The catalyst (**1**): 1,2-bis(diphenylphosphinoethane)-norbornadiene rhodium(I) hexafluorophosphate.

or the silane to the rhodium centre were proposed. In the case of the former, the second reaction with silane was found to be much faster than the corresponding reaction of a silylrhodium intermediate with acetylene. Many of the kinetic studies illustrated that oxygen (O_2) played an important role in the reaction and could be crucial as an initiator. Recently, Adams and co-workers have published a kinetic analysis of the hydrosilylation of diphenylacetylene by Et_3SiH using a layer-segregated platinum–ruthenium cluster complex as an effective catalyst.[18] The kinetic analysis showed the reaction was first order in cluster and silane concentrations but zero order in alkyne.

The large range of hydrosilyation catalysts reported each have their own characteristic properties and therefore potential new catalytic systems are appropriate for study.[19,20] The relationship between hydrogenation and hydrosilylation is subtle, and many catalysts for the former process also function in the latter case. A hydrogenation catalyst of some significance is bis[1,2-diphenylphosphinoethane]norbornadienerhodium hexafluorophosphate, **1** (Fig. 1). It is also a relatively rare example of a potential cationic hydrosilylation catalyst. Since there is interest in the use of supported catalysts for hydrosilylation,[19,21] and charged species are readily intercalated in smectite clays, we decided to investigate the potential of **1** in the hydrosilylation reaction. We report a product distribution and kinetic study on the hydrosilylation of phenylacetylene using a series of silanes catalysed by **1**, and attempts to use the species intercalated in hectorite.

EXPERIMENTAL

The silanes were used as received from Petrarch Systems, Inc. (now Gelest, Inc.); phenylacetylene and $CDCl_3$ were purchased from Aldrich Chemical Co.; and the catalyst **1** was purchased from Strem Chemicals. The reactions were monitored by ^1H NMR until completion and then analysed by both ^{29}Si and ^{13}C NMR spectroscopy. Product distributions obtained are presented in Table 1.

Kinetic measurements were performed using ^1H NMR, monitoring the disappearence of the acetylenic or silane proton during the hydrosilylation reaction in NMR tubes located in the probe of a Varian M 360 spectrometer of 60 MHz. An internal reference of CH_2Cl_2 was introduced to account for instrumental variations. All data were collected at the ambient probe temperature of 28 °C. In a typical reaction, a solution of 0.0153 g (0.15 mmol) phenylacetylene in 0.3 ml $CDCl_3$ was added to a vial containing 2 mg of the rhodium catalyst, **1**. A solution of 0.8 mmol R_3SiH in 0.3 ml $CDCl_3$ was transferred to the vial and this mixture in turn was transferred to an NMR tube. The reaction was monitored and timed from 5 min after the moment the silane was added to the acetylene catalyst solution in order to equilibrate the solution inside the magnet. At this moment, an initial ^1H spectrum was obtained. A typical plot of peak height ratios as a direct function of experimental concentration *vs* time data for the catalyzed hydrosilylation of phenylacetylene by Ph_3SiH is shown in Fig. 2. Similar results were obtained from a reaction performed in a sealed tube under a nitrogen atmosphere.

RESULTS AND DISCUSSION

The use of **1** as a homogeneous hydrosilylation catalyst was totally satisfactory and provided completed reactions, reproducible product distributions and kinetic parameters, and involved no induction periods. The addition of phenylacetylene to the catalyst prior to silane addition was critical. It

Table 1 Product distributions for addition of R_3SiH to PhCCH

Catalyst	R_3Si	Product *Cis-β*	*trans-β*	α	Ref.
$[PtCl_6]$ $[Bu_4N]_2$	$PhMe_2$	0	72	28	6
	Ph_2Me	0	78	22	6
	Ph_3	0	95	5	6
	Et_3	0	70	30	6
Karsted's	Et_3	1	81	18	4
	Ph_3	15	78	7	4
H_2PtCl_6	Et_3	0	79	21	7
	$PhMe_2$	0	69	31	5
	Ph_2Me	0	78	22	5
	Ph_3	0	90	10	5
H_2PtCl_6/CO	$PhMe_2$	0	34	66	2a
	Ph_2Me	0	42	58	2a
$(PPh_3)_3RhCl$	Et_3	55	35	7	7
	$PhMe_2$	76[a]	19	5	8
	$PhMe_2$	0[b]	83	17	8
	Ph_3	26	67	6	7
$(PPh_3)_3RhCOCl$	$PhMe_2$	75	25	0	8
1	Et_3	0	>95	Trace	
	Ph_3	0	>95	Trace	
	Ph_2Me	0	>95	Trace	
	$PhMe_2$	0	70	30	

[a] 40 °C, 52 h.
[b] 80 °C, 24 h.

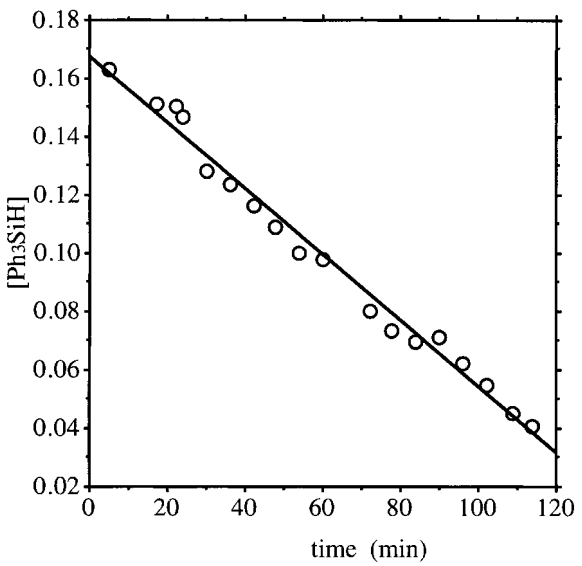

Figure 2 Relationship of $[Ph_3SiH]$ to time for the hydrosilylation of phenylacetylene.

was observed that pre-equilibration of the catalyst with the silane stops the catalytic activity; however, pre-equilibration of the catalyst with the acetylene resulted in normal hydrosilylation. Therefore it seems that a catalytically reactive complex between the acetylene and the rhodium catalyst is formed, whereas a catalytically inactive silylrhodium complex is formed in the absence of the acetylene. This result is similar to studies reported by Marciniec *et al.* noted in the Introduction, involving initial intermediates formed from the catalyst and the silane or substrate. It appears that of the two possible intermediates formed in the present study, the silyl–rhodium complex again reacts more slowly, indeed so slowly that hydrosilylation cannot be observed.

Attempts to sequester the catalyst in sodium hectorite were successful. However, the resulting material was ineffective as a catalyst when used in non-polar solvents, e.g. hexane. In chloroform hydrosilylation reactions occurred; however, there was no change in product distributions as compared to the reactions not including hectorite From the colour of the solutions it was clear that the catalyst was being extracted from the interlamellar regions

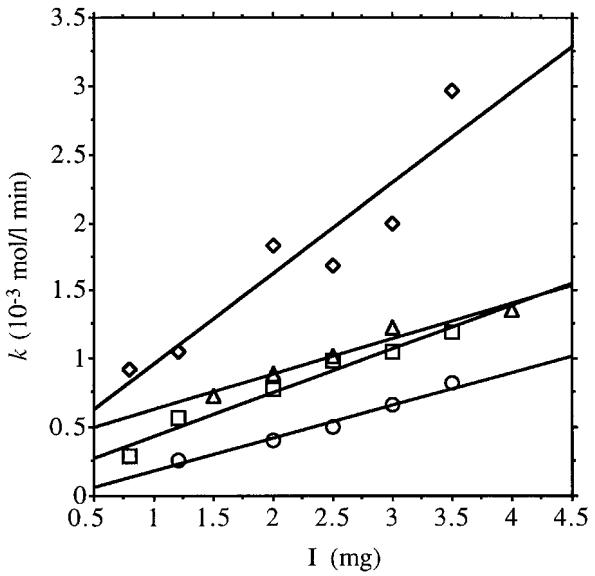

Figure 3 Variation of k_{obs} with [catalyst] for the hydrosilylation of phenylacetylene by R_3SiH: (○) Ph_3SiH; (□) Ph_2MeSiH; (△) Et_3SiH; (◊) $PhMe_2SiH$. [PhCCH] = [R_3SiH] = 0.234M, in $CDCl_3$, [catalyst] = 1.7×10^{-6} to 7.46×10^{-6} M in $CDCl_3$.

of the catalyst and hence was no longer a 'supported catalyst' system.

Product distribution

The hydrosilylations of phenylacetylene using $PhMe_2SiH$, Ph_2MeSiH, Ph_3SiH and Et_3SiH were chosen for study since the product distributions and spectroscopic analysis of these reactions using a variety of catalysts are documented. Table 1 contains a representative collection of product distributions from this reaction using a variety of catalysts. For example, when $RhCl(PPh_3)_3$ was used as a catalyst for the addition of Ph_3SiH to phenylacetylene, the presence of the *β*- (*cis*- and *trans*-) and α-isomers has been reported.[7] The addition of $PhMe_2SiH$ to phenylacetylene, also catalysed by $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$, led to both *cis*- and *trans*- *β*-addition products at low temperature, but no *cis*- products at elevated temperatures, because product isomerization occurred during the hydrosilylation.[8] Similarly the use of $[Bu_4N]_2[PtCl_6]$ as a catalyst for the same reaction led to the formation of the *trans*- *β*- and α-isomers.[6] It is clear that a wide range of activity exists.

The results obtained from the use of **1** indicated that all the reactions involved complete conversion to the hydrosilylated products. From these results, no double hydrosilylation to yield saturated disilylated products was observed. Spectroscopic data for product characterization were obtained using ^1H, ^{13}C and ^{29}Si NMR, and all data correspond to those reported elsewhere in the literature.[4,6,8,22,23] The relative product distributions are recorded in Table 1. From these data we note that the main products in the hydrosilylation of phenylacetylene by Ph_3SiH, Ph_2MeSiH and Et_3SiH were the *trans* *β*-isomers $(C_6H_5)CH{=}CHSi(C_6H_5)_3$, $(C_6H_5)CH{=}CHSiCH_3(C_6H_5)_2$ and $(C_6H_5)CH{=}CHSiEt_3$ respectively. However, the hydrosilylation products from the addition of $PhMe_2SiH$ were *trans*-$(C_6H_5)CH{=}CH(Si(CH_3)_2C_6H_5)$ and $(C_6H_5)(Si(CH_3)_2C_6H_5)C{=}CH_2$, the latter involving α-addition. The results demonstrate the utility of **1** as a catalyst for the hydrosilylation of acetylenes. The regioselectivity for addition of Et_3SiH, Ph_3SiH and Ph_2MeSiH is striking compared to the other catalysts represented in Table 1 and indicates a greater similarity to Pt catalysts than to other Rh species. The large amount of α-product obtained with $PhMe_2SiH$ also parallels results in Table 1 with other catalysts although the reasons remain unclear. Repeat experiments in which all O_2 was removed from the sample, in sealed tubes, produced identical product distributions.

Kinetic studies

The kinetic study was performed using three distinct reaction conditions. In the first set of reactions we used a constant concentration of phenylacetylene and the catalyst (6.1×10^{-6}M) while varying the silane concentration. In a second series of reactions we maintained both the silane and the catalyst concentrations constant while varying the acetylene concentration. Finally, keeping the concentrations of acetylene and silane constant we varied the concentration of the catalyst (1.69×10^{-6}–7.4×10^{-6}M).

The dependence of the rate of the hydrosilylation reaction upon the concentrations of phenylacetylene and the various silanes was determined by monitoring the disappearance of each of the respective reactants in the presence of an excess of the other. Figure 2 illustrates the results of such a study in the case of Ph_3SiH and shows the linear disappearance of the reagents with time, i.e. a zero-order dependence on phenylacetylene and silane. A plot of the rate of hydrosilylation as a function of the catalyst concentration for the four silanes used

in this study (Fig. 3) established the dependence upon catalyst as first order. In the sealed-tube experiments with removal of O_2, no different results were obtained.

This result, indicating a hydrosilylation reaction that is zero order in both acetylene and silane, but first order in catalyst, is reminiscent of studies reported by Reiksfel'd,[24] Kraus,[25] and Speier.[1b] In a series of articles Reiksfel'd and co-workers showed that the rate of hydrosilylation of styrene was independent of solvent and reagents when using a homogeneous platinum catalyst, but first order in the catalyst. Speier reached a similar conclusion from studies on platinum catalysts involving hydrosilylation of olefins, as did Kraus in a study on the hydrosilylation of acetylene using an immobilized platinum metal catalyst system.

The other conclusion derived from our study is illustrated in Fig. 3. The relative rates of hydrosilylation using the four silanes is $k(Me_2PhSiH) > k(Et_3SiH) > k(Ph_2MeSiH) > k(Ph_3SiH)$. The average k_{obs} values (mol $^{-1}$ min^{-1}) were calculated to be $k(Me_2PhSiH) = 1.95 \times 10^{-3}$; $k(Et_3SiH) = 1.06 \times 10^{-3}$; $k(Ph_2MeSiH) = 0.47 \times 10^{-3}$; and $k(Ph_3SiH) = 0.35 \times 10^{-3}$. A similar sequence of reactivity can be noted from various diverse studies in the literature using a range of catalysts and substrates. For example, the relative product distributions from H_2PtCl_6-catalysed hydrosilylation of an allylsilane illustrated a clear sequence of reactivity $Me_2PhSiH > Ph_2MeSiH > Ph_3SiH$,[26] and partial reactivity orders such as $PhMe_2SiH > Ph_2MeSiH$ have been noted.[27] The position of the Et_3SiH in our sequence is in contrast to reports suggesting the reactivity of Et_3SiH is less than that of Ph_3SiH. For example, the γ-irradiated addition of silanes to 1-hexene is reported to have a 10-fold increase in reactivity from Et_3SiH to Ph_3SiH,[28] but since the process is entirely different, involving radical processes, this does not truly apply to our study. More closely related is a study by Hazeldine *et al.*[29] on the $(Ph_3P)_3RhCl$-catalysed addition of silanes to hexene that resulted in a reactivity scale of Ph_3SiH (100) > Et_3SiH (60). However, these data were obtained from competitive product distribution studies and, as has been clearly pointed out by Speier,[1b] these do not necessarily denote the true kinetic reactivities.

Conclusions

We have investigated the potential of a cationic rhodium hydrogenation catalyst, bis-(1,2-diphenylphosphinoethane)norbornadiene rhodium(I) hexafluorophosphate, for use in hydrosilylation of phenylacetylene, from a regioselectivity and kinetic standpoint. The catalyst, which was being used for the first time (to our knowledge) in hydrosilylations has proved effective, with little or no induction period, and with reproducible regioselectivity and kinetics. The regioselectivity borders upon regiospecificity for the silanes Et_3SiH, Ph_3SiH and Ph_2MeSiH, producing trans-(β)-products, $PhCH{=}CHSiR_3$. The information obtained from this study does not permit us to detail a mechanism for its activity. However, at present we see no reason to think that a mechanism that differs significantly from the type proposed in the past,[30] involving oxidative addition of the silane to a rhodium–acetylene intermediate, migrations and reductive eliminations, should not be suggested. The availability of multi-nuclear NMR and other instrumentation and equipment in our laboratories will permit a detailed study on the chemical reactivity of the catalyst with acetylenes and silanes that, in conjunction with the data presented here, is hoped to permit such an understanding in the future.

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