REACTIONS OF ORGANOSILYLHYDRIDES WITH ORGANIC COMPOUNDS CONTAINING AN ACIDIC HYDROGEN CATALYZED BY GROUP VIII METAL COMPLEXES

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#### ABSTRACT

# REACTIONS OF ORGANOSILYLHYDRIDES WITH ORGANIC COMPOUNDS CONTAINING AN ACIDIC HYDROGEN CATALYZED BY GROUP VIII METAL COMPLEXES

#### By

Irvin David Crossan

A study was made to determine if the homogeneous catalysts tris-(triphenylphosphine)chlororhodium (I), bis-(triphenylphosphine)carbonylchloroiridium (I) and (triethylphosphite)bromocopper (I) would catalyze the addition of alcohols to organosilylhydrides. It was found that the catalysts tris-(triphenylphosphine)chlororhodium (I) and bis-(triphenylphosphine)carbonylchloroiridium (I) provide a convenient way to prepare the corresponding organoalkoxysilanes. A number of organoalkoxysilanes were synthesized. It was also discovered that tris-(triphenylphosphine)chlororhodium (I) catalyzed the addition of amines, water and ketones to the organosilylhydride.

A relative rate study of different alcohols added to triethylsilane showed that the rate was  $1^{2}2^{3}3^{2}$  phenol and that the longer the aliphatic portion of the alcohol, the faster the rate. It was also found that the relative rates of different silanes reacted with an alcohol were as follows:  $(CH_{3})_{2}(C_{6}H_{5})SiH>(C_{2}H_{5})_{3}SiH>HSi(OC_{2}H_{5})_{3}$ .

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By

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# TABLE OF CONTENTS

Lis	t of	Tab	les	vi
I.	Int	rodu	ction	1
II.	Res	ults	and Discussion	4
	A.	Syn	thetic Utility	4
	в.	Eff the	ect of Organosilane and Alcohol on Reaction Rate	10
	C.	Dis	cussion of Proposed Mechanism	15
III.	Exp	erim	ental	19
	A.	Mat	erials	19
	в.	Rea chl	ctions using Tris-(triphenylphosphine)- ororhodium (I) as Catalyst	19
		1.	Preparation of Triethylsilane	19
		2.	Preparation of Tris-(triphenyl- phosphine)chlororhodium (I)	20
		3.	Preparation of Triethylethoxysilane	20
		4.	Preparation of Dimethylphenylethoxy- silane	22
		5.	Preparation of Triethyl(sec-butoxy)- silane	23
		6.	Preparation of Triethyl(4-methyl- cyclohexanoxy)silane	24
		7.	Preparation of Triethylcyclohexan- oxysilane	25
		8.	Preparation of Tetraethoxysilane	26
		9.	Preparation of Triethyl( <u>n</u> -butoxy)silane	27

C.	Rea car	ctions Using Bis-(triphenylphosphine)- bonylchloroiridium (I) as Catalyst	28
	1.	Preparation of Triethylethoxysilane	28
	2.	Preparation of Dimethylphenylethoxy- silane	28
D.	Rea cop	ctions Using Triethylphosphitebromo- per (I) as Catalyst	29
	1.	Attempted Preparation of Triethyl- ( <u>n</u> -butoxy)silane	29
	2.	Preparation of Dimethylphenyl( <u>n</u> - butoxy)silane	29
E.	Oth pho	er Reactions Using Tris-(triphenyl- sphine)chlororhodium (I) as Catalyst	30
	1.	Preparation of Dimethylphenyl( <u>n</u> - butylamino)silane	30
	2.	Preparation of Dimethylphenylsilanol	31
	3.	Preparation of Dimethylcyclohexanoxy- silane	32
	4.	Reaction of Cyclohexanone with Tri- ethylsilane Using Triethylamine as a Catalyst	3 <b>3</b>
F.	Rea Alc	ctions of an Organosilane with an ohol Catalyzed by an Acid	34
	1.	Reaction of Triethylsilane with Ethanol Catalyzed by Dimethylchloro- silane	34
G.	Com for	petition Reactions of Triethylsilane Various Alcohols	34
	1.	<b>Competitive Reactions of Triethylsilane</b> for Ethanol and 2-Butanol	34
	2.	Competitive Reaction of Triethylsilane for Ethanol and tert-Butanol	35
	3.	Competitive Reaction of Triethylsilane for Methanol and <u>n</u> -Butanol	36

		4.	Competitive Reaction of Triethylsilane for Ethanol and Phenol	36
		5.	Competitive Reaction of Triethylsilane for 1-Butanol and 2-Butanol	37
	H.	Com sil	petition Reactions of Various Organo- anes for a Single Alcohol	37
		1.	Competition Reaction of <u>n</u> -Butanol for Dimethylphenylsilane and Triethylsilane	37
		2.	Competition Reaction of Ethanol for Triethylsilane and Triethoxysilane	38
		3.	Competition Reaction of Butanol for Triethylchlorosilane and Dimethyl- phenylchlorosilane	39
	I.	Alk	oxy Exchange on Silicon	40
		1.	Reaction of Triethyl(sec-butoxy)silane with Ethanol	40
		2.	Reaction of Triethyl(sec-butoxy)silane with Triethylethoxysilane	40
IV.	Bib	liog	raphy	42
۷.	App	endi	xes	46
	A.	Inf	rared Spectra	46
	в.	Pro	ton NMR Spectra	59

# LIST OF TABLES

I.	Compounds Prepared Using Tris-(triphenyl- phosphine)chlororhodium (I) as Catalyst	5
II.	Compounds Prepared Using Bis-(triphenyl- phosphine)carbonylchloroiridium (I) as Catalyst	7
III.	Competitive Reactions of Triethylsilane for Various Alcohols	12
IV.	Competitive Reactions of Organosilanes for a Single Alcohol	14

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#### I. INTRODUCTION

In organic chemistry the element most commonly associated with carbon is hydrogen. This is not true in organosilicon chemistry. This is due to the higher reactivity of the silicon-hydrogen bond in comparison to the carbon-hydrogen bond. Thus, for example, the  $\equiv$ Si-H bond is readily cleaved by water<sup>1-6</sup>, alcohols<sup>7-18</sup>, ammonia<sup>19-21</sup>, and amines<sup>19,20,22-24</sup> in the presence of suitable bases such as hydroxides, alcoholates and amides of alkali metals. By contrast, the  $\equiv$ Si-H bond exhibits adequate stability towards dilute mineral acids and is completely inert to pure water and alcohols. All of these reactions of substitution of the hydrogen atom linked to silicon have no analogy in organic chemistry.

What physical properties of the bonds can explain the difference in reactivity? The silicon-hydrogen bond is weaker than the carbon-hydrogen bond<sup>25</sup>. This energy difference is much too small to account for the reactivity difference<sup>26</sup>. The bonds also have about the same amount of ionic character<sup>25</sup>, but the great difference lies in the direction of polarization. The relative electronegitivities of carbon, hydrogen and silicon are 2.5, 2.1 and 1.8 respectively. This means that the hydrogen atom has the positive end of the dipole in the carbon-hydrogen bond and in the silicon-hydrogen bond the negative end.

This suggests that the chemistry of the  $\equiv$ Si-H bond should be compared not to the  $\equiv$ C-H bond but with the

similarly polarized carbon-halogen bond.

It has also been demonstrated that the silicon-hydrogen bond is extremely labile in the presence of catalytic amounts of transition metals<sup>27,28</sup>. As a result, a large number of reactions involving the cleavage of this bond have been studied<sup>29,30-32</sup>.

The metals of Group VIII and some of their salts are known to catalyze the addition and substitution reactions of silanes with various organic functionalities. The reaction of hydrosilation, the addition of silicon hydrides for unsaturated organic compounds (I), has been the most widely studied reaction<sup>33</sup>.

(I)  $R_1R_2R_3SIH + RCH=CHR \cdot Cat$   $R_1R_2R_3SICHRCH_2R^{\circ}$ The catalysts used to promote the hydrosilation reaction above are: platinum on carbon or alumina supports and chloroplatinic acid. The catalysts palladium, nickel, cobalt, ruthenium, rhodium or iridium on supports, as well as some of their salts, have shown some success<sup>29</sup>.

It has also been demonstrated<sup>34</sup> that the class of Group VIII metals catalyzes the addition of various organic compounds containing hydroxy<sup>35-45</sup> or amino<sup>44,46</sup> functions to an organosilicon hydride. Reactions of this type provide a convenient method for the preparation of silanols<sup>36,38</sup>, siloxanes<sup>35,36</sup>, alkoxy or aryloxysilanes<sup>37, 39-42</sup>, silyl esters<sup>43-45</sup> and aminosilanes<sup>44,46</sup>.

In the majority of instances the reactions are believed to be examples of heterogeneous catalysis<sup>29</sup>. Despite

the numerous studies dealing with synthetic utility, little has been related about their mechanism35-46. Very little work has been reported concerning the homogeneous catalysis of these reactions. Lukevits and Voronkov37 have studied the rates of chloroplatinic acid catalyzed alcoholysis of triethylsilane. These authors found (a) second order kinetics, (b) dependence of rate on catalyst concentrations. (c) large rate dependence on steric hindrance in the alcohol, (d) faster rates in non-polar than in polar solvents and (e) reduction of chloroplatinic acid to platinum metal during the course of the reaction. This thesis deals with the use of homogeneous transition metal complexes which might promote these types of reactions under more controlled conditions. The variables affecting the reactions will also be studied since results obtained from homogeneous catalysts are more amenable to mechanistic interpretation than those obtained from heterogeneous catalysts.

#### **II. RESULTS AND DISCUSSION**

#### A. Synthetic Utility

The transition metal complex tris-(triphenylphosphine) chlororhodium (I) has been found to catalyze the addition of various alcohols to various organosilicon compounds possessing a silicon-hydride bond. The transition metal complex bis-(triphenylphosphine)carbonylchloroiridium (I) was also found to catalyze the addition of ethanol to triethylsilane and dimethylphenylsilane but was not studied as extensively as the rhodium complex. The reaction scheme is:

ROH +  $R_1R_2R_3SiH$  <u>Cat</u>; ROSi $R_1R_2R_3$  +  $H_2$ . The proposed mechanism will be discussed in a later section.

Table 1 gives the compounds synthesized and the yields obtained by the use of a catalytic amount of the rhodium complex (2.2 x  $10^{-6}$  moles to 0.01 moles of silane). The reactions proceed to completion in 8 to 36 hours when the reactions are run at a temperature between  $40^{\circ}$  and  $70^{\circ}$  C. The reactions were conveniently followed by gas chromatography. No observable side products were produced in any of the reactions. All of the pure products were isolated by flash distillation of the product from the catalyst under reduced pressure after removal of the solvent. The structures of the compounds were confirmed by infrared and nmr spectroscopy. The reaction is a convenient way to prepare silylether compounds from the silyl hydride and alcohol.

# Table I

# Compounds Prepared Using

# Tris-(triphenylphosphine)chlororhodium (I)

# <u>As</u> <u>Catalyst</u>

Compound	Solvent	Time	Temp	<u>Yield</u>
(C2H5)3S10C2H5	Benzene	24 hours	60 <sup>0</sup>	92 <b>%</b>
Ø(CH3)2SIOCH2CH3	Benzene	8 hours	80 <sup>0</sup>	100%
(c <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> sioch(cH <sub>3</sub> )(c <sub>2</sub> H <sub>5</sub> )	Benzene	24 hours	50 <sup>0</sup>	80 <b>%</b>
$H_3C \longrightarrow OS1(C_2H_5)_3$	Benzene	48 hours	70 <sup>0</sup>	75%
$\bigcirc$ -OS1(C <sub>2H5</sub> );	Benzene	72 hours	70 <sup>0</sup>	100%*
si(oc <sub>2</sub> H <sub>5</sub> )4	Benzene	60 hours	70 <sup>0</sup>	80%
(C2H5)3S10(CH2)3CH3	Benzene	24 hours	60 <sup>0</sup>	85 <b>%</b>

\* All starting alcohol consumed during this period; products identified by g.l.c. In the absence of a catalyst the trialkylsilanes do not react with  $alcohols^{47}$ .

Table 2 gives the compounds synthesized and the yields obtained when the complex bis-(triphenylphosphine)carbonylchloroiridium (I) was substituted for the rhodium complex. It should be noted that the reaction would not proceed at room temperature but proceeded at a moderate rate at slightly elevated temperatures. No further reactions were run using the iridium complex since the reactions proceeded at a rate comparable to the rhodium complex reactions. No side products were seen by gas chromatography in these reactions.

Miller, Peake and Nabergall<sup>48</sup> have reported that copper powder catalyzes the addition of a  $\equiv$ Si-H to an H-OR when the silicon atom possesses more than one hydrogen. Thus, the complex (triethylphosphite)bromocopper (I) was prepared and used as a catalyst in the reaction of butanol with triethylsilane. At reflux in a benzene solvent in 24 hours, no reaction was observed. When dimethylphenylsilane was substituted for the triethylsilane, the reaction went to completion in 48 hours. No further experiments were run using homogeneous copper catalysts since the reaction was relatively slow and proved to be limited in scope in comparison with the rhodium complex.

Sommer and Citron<sup>33</sup> have reported that heterogeneous catalysts, such as Pd/C and Pd/Al<sub>2</sub>O<sub>3</sub>, catalyze the reaction of primary and secondary amines with a silylhydride to give

# Table 2

# Compounds Prepared Using

# Bis-(triphenylphosphine)carbonylchloroiridium (I)

# <u>As</u> <u>Catalyst</u>

Compound	Solvent	Time	Temp	<u>Yield</u>
(c <sub>2H5</sub> ) <sub>3</sub> s10c <sub>2H5</sub>	Benzene	20 hours	40 <sup>0</sup>	71%
Ø(CH <sub>3</sub> ) <sub>2</sub> S10C <sub>2</sub> H <sub>5</sub>	Benzene	12 hours	60 <sup>0</sup>	91 <b>%</b>

the corresponding silylamine. It was found that the transition metal complex tris-(triphenylphosphine)chlororhodium (I) also catalyzes this reaction. The compound dimethylphenyl(n-butylamino)silane was prepared by reacting dimethylphenylsilane with n-butylamine using the transition metal complex tris-(triphenylphosphine)chlororhodium (I). The reaction did not proceed at room temperature but did proceed at a moderate rate at  $80^{\circ}$  C. The reaction was followed by gas chromatography. In 36 hours the reaction was complete, and no side products were detected. An H nmr spectrum of the product confirmed its structure. In the nmr absorptions due to  $\left[(CH_3)_2(C_6H_5)Si\right]_20$  which comes from hydrolysis of the silylamine were observed. No further work was done on changing the alkyl group on the amine or silane to see just how much synthetic utility this reaction would have. It could be assumed that it would possess quite broad synthetic utility since the reaction is only slightly slower in rate than the reaction of dimethylphenylsilane with a primary alcohol.

It was found also that the transition metal complex tris-(triphenylphosphine)chlororhodium (I) would also catalyze the reaction of dimethylphenylsilane with water to form the corresponding silanol. The reaction proceeded at room temperature and was complete in 8 hours. The reaction progress again was followed by gas chromatography. Two products resulted from the reaction. These were dimethylphenylsilanoland 1,1,3,3-tetramethyldiphenyldisiloxane. The

second product resulted from the side reaction (II) which is known to be catalyzed by transition metals $^{35,36}$ .

(II) 
$$(CH_3)_2(C_6H_5)S1OH + (CH_3)_2(C_6H_5)S1H \longrightarrow$$
  
 $[(CH_3)_2(C_6H_5)S1]_2O + H_2$ 

This side reaction could be minimized by changing the reaction parameters.

A reaction was run to see if the enol form of a ketone would react with silicon hydride in the presence of a transition metal catalyst to form the unsaturated silylether. The ketone used was cyclohexanone. A catalytic amount of tris-(triphenylphosphine)chlororhodium (I) and triethylamine was used. The amine was expected to facilitate the formation of the enol form of the ketone. A reaction did take place, but no hydrogen was evolved. The isolated product was triethylcyclohexanoxysilane instead of the expected product triethyl(l-cyclohexenoxy)silane (a). It is widely known that transition metals catalyze the addition of a silylhydride across a carbon-carbon double bond<sup>9</sup>. In this case the silylhydride has added across a carbon-oxygen double bond. It is possible that compound (a) was formed but then hydrogenated. The catalyst tris-(triphenylphosphine)chlororhodium (I) has proved to be an excellent hydrogenation catalyst. It seems more likely, however, that there was addition across the carbon-oxygen double bond. It has been reported that under the influence of ultraviolet light addition of silylhydrides across carbonoxygen double bond does occur. Also, Calas, Frainnet and

Bonastre<sup>49</sup> have reported that aliphatic ketones and cyclohexanone react with triethylsilane in the presence of the catalyst zinc chloride to give the addition product, i.e. the alkoxysilane. It also has been reported that trialkylsilanes have been added to furfural, 5-methylfurfural and thiophenaldehyde on prolonged heating in the presence of chloroplatinic acid<sup>50</sup>.

It might be postulated that the catalyst is triethylamine and not tris-(triphenylphosphine)chlororhodium (I). A mixture of cyclohexanone, triethylsilane and a catalytic amount of triethylamine gave no observable reaction (g.l.c.) after refluxing together for 24 hours. This indicates that the catalyst for the reaction is indeed tris-(triphenylphosphine)chlororhodium (I).

This reaction could have synthetic utility as a means of conveniently reducing ketones to their corresponding alcohols under mild conditions. Also, this is another way of preparing silylethers from ketones instead of alcohols. The reaction needs to be explored much more deeply than was possible here to determine its synthetic utility.

#### B. Effect of Organosilane and Alcohol on the Reaction Rate

In the reaction of an organosilane with an alcohol using a transition metal catalyst, such as tris-(triphenylphosphine)chlororhodium (I), different reaction rates should be observed depending on the silane and alcohol used. Differences in rate were determined. Another parameter to be considered is solvent. The solvent used should also have

some effect on the rates of reaction<sup>51</sup>. The solvent used in the rate studies was benzene. This may not necessarily be the optimum solvent. Although other solvents were not studied, it is likely that changing the solvent could give different results.

A way to determine relative rates is to competitively react equal molar ratios of two different alcohols with a limited amount of triethylsilane and to determine the amounts of the two silylethers obtained. This was the route taken. The molar ratios used were 1:1:1 (silane: alcohol:alcohol). The reaction was followed by gas chromatography and hydrogen gas evolution. The final molar ratios of the two resulting alkoxysilanes were determined by gas chromatography using standard samples of the alkoxysilanes to determine relative response factors. The data obtained is given in Table 3. As one can see, the tris-(triphenylphosphine)chlororhodium (I) catalyzed reactions of triethylsilane are affected by the bulk and basicity of the hydrocarbon portion of the alcohol. The order of reactivity is in general  $1^{\circ}$   $2^{\circ}$   $3^{\circ}$   $\approx$  phenol. It was found that chain lengthening of the hydrocarbon portion of the alcohol resulted in an increase in the rates. Similar effects have been reported for the reaction of silanes with alcohols using copper powder<sup>48</sup> and chloroplatinic acid<sup>37</sup> as catalysts.

In the base or acid catalyzed reactions of alcohols with a silylhydride the opposite effect is seen, i.e. the longer the organic radical, the slower the reaction rate<sup>47</sup>.

# Table 3

# $\frac{\text{Competitive Reactions of Triethylsilane}}{\text{For Various Alcohols}}$ $(C_{2}H_{5})_{3}SIH + ROH + R'OH \frac{Rh(\emptyset_{3}P)_{3}Cl}{benzene}$ $\frac{R}{(C_{2}H_{5})_{3}SIH + ROH + R'OH \frac{Rh(\emptyset_{3}P)_{3}Cl}{(C_{2}H_{5})_{3}SIOR:(C_{2}H_{5})_{3}SIOR'}$ $C_{2}H_{5}^{-} CH_{3}CC_{2}H_{5} 1.57:1$ $C_{2}H_{5}^{-} (CH_{3})_{3}C- only (C_{2}H_{5})_{3}SIOR formed (1:0)$ $C_{2}H_{5}^{-} Only (C_{2}H_{5})_{3}SIOR formed (1:0)$ $C_{2}H_{5}^{-} CH_{3}^{-}CC_{2}H_{5} 3.36:1$

сн <sub>3</sub> (сн <sub>2</sub> )3 <sup>-</sup>	сн3_	1 <b>.</b> 25 <b>:1</b>
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This has been accounted for by steric factors. The lack of reaction of t-butyl alcohol could be due to both the steric bulk and electronic effects. It has also been found that t-butyl alcohol does not react with trialkylsilanes using a base catalyst<sup>47</sup>. The reason phenol does not react must be attributed entirely to electronic effects since triethylsilane and cyclohexanol do react to give the alkoxysilane. It was reported that phenol did not react with trialkylsilanes when metallic potassium was used as a catalyst<sup>52</sup>.

Reactions were also carried out to determine competition between an equal molar ratio of silanes possessing different alkyl or aryl groups for a limited amount of the same alcohol. The results of these competition reactions are given in Table 4. It was observed that dimethylphenylsilane reacts much more rapidly than triethylsilane. This can be attributed more to electronic than steric differences. In the reaction of triethoxysilane and triethylsilane, triethylsilane reacts more rapidly. The rate difference can also be accounted for by electronic rather than steric effects. Haszeldine, Parrish and Parry<sup>53</sup> have shown that the  $(Ph_3P)_2RhCl(H)$  [Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>] complex is much more stable than the  $(Ph_3P)_2RhCl(H)[Si(C_2H_5)_3]$  complex which they found dissociated in all solvents tried. This relative stability is opposite to what is expected and is attributed to a  $d_{\pi}-d_{\pi}$ bonding between the silicon and metal atoms. If the bonding is that much stronger, then one would expect that the complex  $(Ph_3P)_2RhCl(H)[Si(OC_2H_5)]$  would be less able to react with a

<u>For a Single Alcohol</u>						
	RlR	2 <sub>R</sub> 3 <sub>S1H</sub>	+ R <sup>l</sup>	1 <sub>R</sub> 12 <sub>R</sub> 13	Sih + F	ROH $\frac{\operatorname{Rh}(\emptyset_{3}P)_{3}C1}{\operatorname{benzene}}$
Rl	<u>R<sup>2</sup></u>	<u>R</u> 3	<u>R11</u>	<u>R</u> 12	<u>R13</u>	<u>Mole Ratio</u> of Silylether Product R <sup>1</sup> R <sup>2</sup> R <sup>3</sup> SiOR:R <sup>11</sup> R <sup>12</sup> R <sup>13</sup> SiOR
C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C2H5	CH3	СНЗ	$\bigcirc$	.208:1
C <sub>2</sub> H <sub>5</sub>	С <sub>2</sub> Н5	C <sub>2</sub> H <sub>5</sub>	С <sub>2</sub> Н <sub>5</sub> О	C <sub>2</sub> H <sub>5</sub> O	C <sub>2</sub> H <sub>5</sub> O	1.65:1

# <u>Competitive Reactions of Organosilanes</u>

Table 4

molecule of alcohol.

A comparison of the relative rate differences of dimethylphenylsilane and triethylsilane to an alcohol catalyzed by tris-(triphenylphosphine)chlororhodium (I) and dimethylphenylchlorosilane and triethylchlorosilane with the same limited quantity of the same alcohol was made. The chlorosilanes were prepared by reacting the silylhydrides with chlorine gas in carbon tetrachloride and then distilling out the carbon tetrachloride and adding back benzene. Then a 1-mole ratio of alcohol was reacted with a 1:1 molar mixture of  $(C_2H_5)_3SiCl:(C_6H_5)(CH_3)_2SiCl$ . The relative product ratios obtained from gas chromatography were .1112 (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiO(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>:(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>SiO(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>. There is a difference in relative rates between an acid catalyzed reaction and the transition metal catalyzed reaction (.202 ratio). However, in both cases the dimethylphenyl(n-butoxy)silane is favored. The relative rates would be expected to be different unless it is assumed that the mechanism is an ionic one rather than a transition metal catalyzed reaction.

The question could be raised whether the relative rate data presented here is kinetically or thermodynamically controlled. Two experiments were run to prove that the data presented is kinetically controlled. In one experiment triethyl(sec-butoxy)silane was heated with ethanol using tris-(triphenylphosphine)chlororhodium (I) as catalyst at 70°C for 48 hours with no alcohol exchange (by glc) detected.

In the second experiment triethylethoxysilane and triethyl(sec-butoxy)silane were heated together in the presence of tris-(triphenylphosphine)chlororhodium (I) for 48 hours with no alkoxy exchange detected by gas chromatography.

#### C. Discussion of Proposed Mechanism

Many mechanisms have been published for the catalysis of olefin hydrosilylation reactions by homogeneous catalysts. No such mechanism has been proposed for the reaction of a silane with an alcohol catalyzed by a homogeneous catalyst. The following mechanism is proposed for the reaction:

The rhodium complexes (c) have already been prepared  $^{53,54}$ . The complexes are co-ordinatively unsaturated, and they would be expected to take up a further ligand. The formation of the complex (c) is reversible, and the equilibrium is markedly affected by the electronegativity of the groups on silicon. Thus,  $k_1$  would depend on the strength of the silyl-metal bond that is formed. It is interesting that the predicted order of M-Si<sup>®</sup> bond strength is  $(C_{2H_5})_3Si > (CH_3)_2C_6H_5Si > (C_{2H_5}O)_3Si^{53,60}$ . The next step is the addition of a molecule to the transition

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metal complex to form (d). The  $k_2$  would thus depend on the basicity and also steric effects of the alcohol. The third step is the rate determining step and involves the loss of  $H_2$  and the producing of the transition metal complex (e). The complex (e) can then lose  $R_1R_2R_3SiOR$  to produce the active rhodium complex (b) back. Therefore, the rate equation could be written as follows:

rate =  $k_{rd}k_1k_2 [L_3MX] [R_1R_2R_3SiH] [ROH]$ where  $k_1$  would depend on the  $\equiv$ Si-M bond strength and where  $k_2$  would depend on the basicity of the alcohol.

This reaction scheme seems to adequately describe the trends that have been seen in the rate studies of Part B., i.e. the reaction seems to depend more on electronic rather than steric effects. Also, in the reactions using the catalyst tris-(triphenylphosphine)chlororhodium (I) the color of the reaction mixture changes from red to yellow on addition of the silane to a mixture of the catalyst, benzene and the alcohol. At the end of the reaction the original red color of the catalyst returned. This color change is indicative of a reaction involving an oxidative addition. This would also seem to indicate that the equilibrium  $k_1$  is completely to the product (c).

One could postulate that traces of HCl could be formed in the reaction of either the alcohol or silane with the catalyst tris-(triphenylphosphine)chlororhodium (I) and that this could be the real catalyst. An experiment was run where triethylsilane and anhydrous ethanol were refluxed

in a benzene solution for 36 hours with a catalytic amount of trimethylchlorosilane present. Less than a 5% theoretical yield of the product triethylethoxysilane was obtained. This clearly indicates that the HCl is not the acid catalyst for the reaction. Thus, all data collected seems to confirm the proposed mechanism presented above. A. <u>Materials</u>

All solvents and reagents were dried over 4 Å molecular sieves before use. The starting organosilicon compounds were obtained from Dow Corning Corporation and used without further purification. The gas chromatographs were run on a Varian Areograph 90-P equipped with a six-foot column packed with 10% SE-30 on chromosorb W. The starting temperature was 80°C and was programed up to 200°C. The infrared spectra were run on a Perkin Elmer 239B grating spectrophotometer. The nmr spectra were obtained on a Varian T-60 spectrometer.

#### B. <u>Reactions Using Tris-(triphenylphosphine)chlororhodium (I)</u> as Catalyst

#### 1. Preparation of Triethylsilane

In a 5 liter three-necked flask fitted with a stirrer, dropping funnel, large bulb condensor and Nitrogen atmosphere was prepared 12.6 moles of ethylmagnesium bromide. Then a solution of 406.5 g (3.0 mols) of trichlorosilane in 1200 ml of anhydrous diethylether was added over an 8 hour period with external cooling and vigorous stirring. The mixture was allowed to stir at room temperature for 12 hours and then was refluxed for 8 hours. Ether was then distilled away from the reaction mixture through a two-foot vigreux column until the pot temperature reached 100°C. After cooling, the solid residue was slowly hydrolyzed with 1800 ml of water followed by 372 ml of concentrated hydrochloric acid. The aqueous layer was then separated and extracted twice with 500 ml portions of diethylether. The ether extracts and

product were combined, washed with water until neutral and then dried over 300 g of anhydrous potassium carbonate for two hours. Fractional distillation through a two-foot vigreux column gave 212.1 g (46% yield) of pure triethylsilane (bp 108° at 760 mm). The ir and nmr spectra were in agreement with known standards.

The ir spectrum showed bands at 2100 cm<sup>-1</sup> (Si-H), at 1240 cm<sup>-1</sup> (CH<sub>2</sub> wag), at 1380 cm<sup>-1</sup> (symmetric CH<sub>3</sub> deformation), at 1420 cm<sup>-1</sup> (CH<sub>2</sub> deformation), at 1460 cm<sup>-1</sup> (asymmetric CH<sub>3</sub> deformation) and at 980 cm<sup>-1</sup> and 1020 cm<sup>-1</sup> (Si-CH<sub>2</sub>).<sup>61</sup> The nmr spectrum showed absorptions at  $\delta$ .

d values
$\approx$ 3.65 (septet J=3H <sub>z</sub> )
$\approx$ 0.65 (quartet)
$\approx$ 0.9 (triplet)

#### 2. <u>Preparation of Tris-(triphenylphosphine)chloro-</u> <u>rhodium (1)</u><sup>59</sup>

To a solution of freshly recrystallized triphenylphosphine (12.0 g, 6 mols excess) in hot ethanol (350 ml) was added a solution of rhodium trichloride trihydrate (2.0g) in hot ethanol (70 ml), and the solution was heated under reflux (30 min). The hot solution was filtered and the burgundy-red crystals of the complex were washed with degassed, anhydrous ether (50 ml) and dried in vacuum. Yield 6.0 g (80% based on rh) mp 157-58°C.

#### 3. Preparation of Triethylethoxysilane

To a 10 ml single-necked flask was added 1.16 g



(0.01 mols) of triethylsilane, 0.46 g (0.01 mols) of anhydrous ethanol and 5 ml of anhydrous benzene. The mixture was heated to reflux for one hour under nitrogen to remove all dissolved oxygen present. Then the mixture was cooled and 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) was added. The mixture was heated to  $60^{\circ}$ C. Hydrogen evolution was at a moderate rate. The solution was yellow in color. The reaction was kept at 60°C and followed by gas chromatography and hydrogen evolution for 24 hours. At this time hydrogen evolution had stopped. No starting materials were seen by gas chromatography, and the solution had turned red in color. The solvent was then distilled away from the product and the product flash-distilled away from the catalyst. A total of 1.4697 g (92% yield) of pure product was obtained. The structure of the compound was confirmed by infrared and nmr spectroscopy.

The ir spectrum showed bands at 1130 cm<sup>-1</sup> and 1070 cm<sup>-1</sup> (due to  $\exists$ Si-O-Et), at 1150 cm<sup>-1</sup> ( $\exists$ Si-O-Et), at 930 cm<sup>-1</sup> ( $\exists$ Si-O-Et), at 1380 cm<sup>-1</sup> (symmetric CH<sub>3</sub> deformation), at 1240 cm<sup>-1</sup> (CH<sub>2</sub> wag), at 1420 cm<sup>-1</sup> (CH<sub>2</sub> deformation), at 1460 cm<sup>-1</sup> (asymmetric CH<sub>3</sub> deformation), at 980 cm<sup>-1</sup> and 1020 cm<sup>-1</sup> (Si-CH<sub>2</sub>) and no band at 2100 cm<sup>-1</sup> (due to  $\exists$ Si-H). The nmr spectrum showed absorptions at  $\delta$ .

	<b>S</b> values
≡S1-OCH2	$\sim$ 3.5 (quartet)
≡Si-CH2 <sup>+</sup>	$\sim$ 0.7 (quartet)
≡sicH2-CH3	∼0.9 (triplet)
≡s1-och2ch3	~1.1

#### 4. Preparation of Dimethylphenylethoxysilane

To a 10 ml single-necked flask was added 1.36 g (0.01 mols) of dimethylphenylsilane, 0.46 g (0.01 mols) of absolute ethanol and 5 ml of anhydrous benzene. The mixture was refluxed under nitrogen for one-half hour to remove dissolved oxygen in the mixture. Then the mixture was cooled and 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) was added. The mixture was heated to  $60^{\circ}$ C. At this temperature the evolution of hydrogen was slow. The mixture was heated to reflux. In less than 8 hours the reaction had gone to completion. The solvent was removed and the pure product flash-distilled away from the catalyst. A total of 1.8224 g (100% yield) of dimethylphenylethoxysilane was obtained.

The ir spectrum showed bands at 1590 cm<sup>-1</sup> (phenyl), at 1430 cm<sup>-1</sup> (phenyl), at 1250 cm<sup>-1</sup> (Si-CH<sub>3</sub>), at 1100 cm<sup>-1</sup> (Si-OCH<sub>2</sub>), at 1000 cm<sup>-1</sup> (phenyl), at 940 cm<sup>-1</sup> (Si-OCH<sub>2</sub>), at 790 cm<sup>-1</sup> (Si-CH<sub>3</sub>) and a very small band at 2100 cm<sup>-1</sup> (due to a trace of Si-H). The nmr spectrum gave the following absorptions.
	<u>Proton ratio</u>	<b>d</b> values
C6H5S1≡	6	~7.4 (broad - trace of benzene present)
≡S1-0CH2	2	$\sim$ 3.7 (quartet)
≡s1-och2ch3	2.8	$\sim$ 1.2 (triplet)
CH3-S13	6	$\sim$ 0.4 (singlet)

## 5. Preparation of Triethyl(Sec-butoxy)silane

To a single-necked 10 ml flask was added 1.16 g (0.01 mols) of triethylsilane, 1.48 g (0.02 mols) of dried butan-2-ol and 5 ml of anhydrous benzene. The mixture was refluxed under nitrogen for one hour to remove any dissolved oxygen present. The mixture was cooled to room temperature and a catalytic amount, 0.002 g (2.2 x  $10^{-6}$  mols), of tris-(triphenylphosphine)chlororhodium (I) was added. The reaction mixture was kept at a temperature between 40-50°C and was yellow in color. Hydrogen evolution was at a slow rate. In 24 hours the reaction had not gone to completion. The mixture was cooled to room temperature and allowed to proceed to completion in an additional 14 hours. The solvent was removed and the pure product flash-distilled away from the catalyst. A total of 1.5132 g (80% yield) of pure triethyl-(sec-butoxy)silane was obtained. An nmr and ir confirmed the structure.

The ir spectrum showed bands at 1380 cm<sup>-1</sup> (symmetric CH<sub>3</sub> deformation), 1460 cm<sup>-1</sup> (asymmetric CH<sub>3</sub> deformation), 1420 cm<sup>-1</sup> (CH<sub>2</sub> deformation), 1050 cm<sup>-1</sup> (Si-O-C), 1020 and 980 cm<sup>-1</sup> (Si-CH<sub>2</sub>), 1110 cm<sup>-1</sup> (Si-O-C) and no band at 2100 cm<sup>-1</sup> (due to Si-H). The nmr gave the following absorptions.

<u>Proton ratio</u>	J values	
1	$\sim$ 3.6 (sextet)	
9	~1.1	
6	~ 0.7	
8.7	~ 0.9	
	<u>Proton ratio</u> 1 9 6 8.7	

6. <u>Preparation of Triethyl(4-methylcyclohexanoxy)</u> <u>silane</u>

To a 10 ml single-necked flask was added 1.16 g (0.01 mols) of triethylsilane, 1.14 g (0.01 mols) of 4methylcyclohexanol and 5 ml of anhydrous benzene. The mixture was refluxed under nitrogen for one-half hour to remove any dissolved oxygen present. Then 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) was added. No reaction was seen at room temperature. Upon heating, gas evolution started at 70°C. The reaction mixture temperature was kept at 70° for 24 hours. A gas chromatograph at this time showed the reaction was not completed (i.e. there were still starting materials present). At this time a few drops of triethylsilane were added to insure complete reaction of the alcohol. The reaction mixture was kept at 70°C for an additional 24 hours. After this time, the solvent was distilled off and the product flash-distilled away from the catalyst. A gas chromatograph of the product showed that both the cis and trans isomers were present. An nmr of the product confirmed the structure.

24

The nmr gave the following absorptions.



#### 7. Preparation of Triethylcyclohexanoxysilane

To a 10 ml single-necked flask was added 1.16 g (0.01 mols) of triethylsilane, 1.00 g (0.01 mols) of dried cyclohexanol and 5 ml of anhydrous benzene. The mixture was refluxed for one hour under nitrogen to remove any dissolved oxygen present. Then a catalytic amount, 0.002 g  $(2.2 \times 10^{-6} \text{ mols})$ , of tris-(triphenylphosphine)chlororhodium (I) was added. The mixture was kept at a temperature of 70-80°C. The hydrogen evolution proceeded at a slow rate. After 48 hours, the reaction had only gone 50% (by glc) to completion. The mixture was kept at 70-80°C for an additional 24 hours. The reaction was still not completely finished. The solvent was removed by distillation, and the product and residual cyclohexanol was flash-distilled from the catalyst. The cyclohexanol was then distilled from the pure product. An ir and nmr confirmed the structure.

The ir spectrum gave the following bands: at 1380 cm<sup>-1</sup>

(symmetric CH<sub>3</sub> deformation, at 1420 cm<sup>-1</sup> (CH<sub>2</sub> deformation), at 1460 cm<sup>-1</sup> (asymmetric CH<sub>3</sub> deformation, at 1100 cm<sup>-1</sup> (Si-O-CH), at 1020 and 980 cm<sup>-1</sup> (Si-CH<sub>2</sub>), at 1240 cm<sup>-1</sup> (CH<sub>2</sub> wag), at 1070 cm<sup>-1</sup> (Si-O-CH), and no band at 2100 cm<sup>-1</sup> (due to (Si-H). The nmr spectrum showed the following absorptions.

<b>TT</b> _	<u>Proton ratio</u>	Svalues
	1	~3.6
-CH2-S1Ξ	<pre>{ 12</pre>	~0.7
CH <sub>3</sub> CH <sub>2</sub> S1Ξ	( 17	~0.9
<u></u> s1-0-	10	~1.1-2.0

## 8. Preparation of tetraethoxysilane

To a single-necked 10 ml flask was added 1.64 g (0.01 mols) of triethoxysilane, 0.46 g (0.01 mols) of absolute ethanol and 5 ml of anhydrous benzene. The mixture was refluxed under nitrogen for one-half hour to remove any dissolved oxygen present. Then the mixture was cooled and 0.002 g  $(2.2 \times 10^{-6} \text{mols})$  of tris-(triphenylphosphine)chloro-rhodium (I) was added. The hydrogen evolution at room temperature was very slow. At  $70^{\circ}$ C the evolution of hydrogen was somewhat faster. The reaction was kept at  $70^{\circ}$ C and followed by gas chromatography. The reaction was complete in 60 hours. The benzene solvent was removed by distillation, and the pure tetraethoxysilane was flash-distilled from the catalyst. An nmr confirmed the structure.

The nmr spectrum gave the following absorption data.

	Proton ratio	J values	
≡s1-och2 <sup>-</sup>	6	$\sim$ 3.4 (triplet)	
≡s1-och2ch3	9.2	$\sim$ 0.8 (quartet)	

9. Preparation of Triethyl(n-butoxy)silane

To a 10 ml single-necked flask was added 0.88 g (0.005 mols) of triethylsilane, 0.37 g (0.005 mols) of dried n-butanol and 3 g of anhydrous benzene. The mixture was refluxed for one-half hour under nitrogen. Then 0.002 g  $(2.2 \times 10^{-6} \text{ mols})$  of tris-(triphenylphosphine)chlororhodium (I) was added. The reaction was run at  $60^{\circ}$ C. In 24 hours all the triethylsilane had disappeared (by glc). The benzene was distilled away and the product flash-distilled from the catalyst. A total of 0.80 g (85% yield) of pure product was obtained.

The ir spectrum shows bands at 1240 cm<sup>-1</sup> (CH<sub>2</sub> wag), at 1380 cm<sup>-1</sup> (symmetric CH<sub>3</sub> deformation, at 1420 cm<sup>-1</sup> (CH<sub>2</sub> deformation), 1460 cm<sup>-1</sup> (asymmetric CH<sub>3</sub> deformation), at 980 and 1020 cm<sup>-1</sup> (Si-CH<sub>2</sub>), 1100 cm<sup>-1</sup> (Si-O-CH<sub>2</sub>), 1120 cm<sup>-1</sup> (Si-O-CH<sub>2</sub>) and no band at 2100 cm<sup>-1</sup> (Si-H). The nmr spectrum showed the following absorptions.

	<u>Proton ratio</u>	5 values
ΞS1-CH2-	6.0	~0.65 (quartet)
$\equiv$ S1-CH <sub>2</sub> CH <sub>3</sub>	9.0	$\sim$ 0.9 (triplet)
-och <sub>2</sub> -	1.9	~3.58 (triplet)
-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	7.0	~1.0-1.5

# C. <u>Reactions Using Bis-(triphenylphosphine)carbonyl-</u> <u>chloroiridium (I) as catalyst</u>

#### 1. Preparation of Triethylethoxysilane

To a single-necked 10 ml flask was added 1.16 g (0.01 mols) of triethylsilane, 0.46 g (0.01 mols) of absolute ethanol and 4 ml of anhydrous benzene. Then 0.002 g  $(2.6 \text{ x} 10^{-6} \text{ mols})$  of bis-(triphenylphosphine)carbonylchloroiridium (I) was added. There was no reaction. The catalyst did not seem to go into solution. The mixture was heated to  $\sim 50^{\circ}$ C. Hydrogen gas started to evolve at a moderate rate at this temperature. The heating was stopped. The hydrogen evolution kept up at room temperature. In 18 hours the reaction had gone almost to completion. The volatiles were distilled off and the pure product flash-distilled away from the catalyst. A total of 1.15 g (71% yield) of triethylethoxysilane was obtained. Ir and nmr spectra confirmed the structure of the compound. Spectra were in agreement with compound triethylethoxysilane prepared previously.

#### 2. Preparation of Dimethylphenylethoxysilane

To a single-necked 10 ml flask was added 1.36 g (0.01 mols) of dimethylphenylsilane, 0.46 g (0.01 mols) of absolute ethanol and 5 ml of anhydrous benzene. Then 0.002 g (2.6 x  $10^{-6}$  mols) of bis-(triphenylphosphine)carbonylchloroiridium (I) was added. The mixture was heated to  $60^{\circ}$ C. Hydrogen evolution was at a moderate rate. The reaction was complete in ~10 hours. The solvent was removed by distillations from the mixture and the product flash-distilled from the catalyst. The amount of dimethylphenylethoxysilane obtained was 1.6533 g (91% yield). An nmr confirmed the structure. The spectrum was in agreement with compound dimethylphenylethoxysilane prepared previously.

## D. <u>Reactions Using Triethylphosphitebromocopper (I) as</u> <u>Catalyst</u>

## 1. Attempted Preparation of Triethyl(n-butoxy)silane

To a 10 ml single-necked flask was added 1.16 g (0.01 mols) of triethylsilane, 0.74 g (0.01 mols) of dried <u>n</u>-butanol and 3 ml of anhydrous benzene. Then 0.5 g of a benzene solution of the complex triethylphosphitebromocopper (I) (0.67 x  $10^{-3}$  mols) was added. No gas evolution was seen. The mixture was heated to reflux for one hour. Again there was no gas evolution. At this time a gas chromatograph was run. No products were detected. The mixture was allowed to stand at room temperature under a nitrogen atmosphere over night. A gas chromatograph run after this time showed no reaction had taken place.

#### 2. Preparation of Dimethylphenyl(n-butoxy)silane

To a single-necked 10 ml flask was added 1.36 g (0.01 mols) of dimethylphenylsilane, 0.74 g (0.01 mols) of dried <u>n</u>-butanol and 5 ml of anhydrous benzene. Then 0.5 g of a benzene solution of triethylphosphitebromocopper (0.67  $x 10^{-3}$  mols) was added. A very slow evolution of hydrogen was observed at room temperature. The mixture was heated to 70°C. At this temperature the evolution of hydrogen was slow. The reaction took 48 hours to go to completion. During this time some of the catalyst had plated-out as metallic copper along the sides of the flask. The solvent was removed by distillation and the product flash-distilled from the catalyst. An ir and nmr confirmed the structure.

The ir spectrum showed bands at 3080 cm<sup>-1</sup> (phenyl), 1590 cm<sup>-1</sup> (phenyl), at 1430 cm<sup>-1</sup> (phenyl), at 1250 cm<sup>-1</sup> (Si-CH<sub>3</sub>), at 1090 cm<sup>-1</sup> (Si-O-CH<sub>2</sub>), at 1120 cm<sup>-1</sup> (Si-O-CH<sub>2</sub>), at 790 cm<sup>-1</sup> (Si-CH<sub>3</sub>), and no band present at 2100 cm<sup>-1</sup> (Si-H). Ir spectrum also showed bands at 3480 cm<sup>-1</sup> and 3640 cm<sup>-1</sup> (due to small amounts of free alcohol present). The nmr spectrum showed the following absorptions.

	Proton ratio	S values	
C6H5-S1≣	5.2	~2.4-2.8 (broad)	
-0-CH2-	2.5*	~3.6	
-CH2CH2CH3	9•3*		
ES1-CH3	5.9	~0.32	

\*High proton ratio due to small amount of free alcohol present

- E. Other Reactions Using Tris-(triphenylphosphine)chlororhodium (I) as Catalyst
  - 1. <u>Preparation of Dimethylphenyl(n-butylamino)silane</u>

To a 10 ml single-necked flask was added 1.36 g (0.01 mols) of dimethylphenylsilane, 1.46 g (0.02 mols) of dried <u>n</u>-butylamine and 3 ml of anhydrous benzene. The mixture was refluxed under nitrogen for one hour to remove any dissolved oxygen present. Then 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) was added. The mixture was kept at  $80^{\circ}$ C. The evolution of hydrogen was

slow at this temperature. The reaction was complete in 36 hours. There were two product peaks present on the gas chromatograph. The small peak is probably 1,1,3,3tetramethyldiphenyldisiloxane which was formed by traces of water present. The benzene and excess butylamine were removed by distillation. The product and disiloxane component were flash-distilled from the catalyst. A gas chromatograph of the product showed that more of the aminosilane had hydrolyzed to the disiloxane during the distillation. An nmr showed the product to be a mixture of the dimethylphenyl(n-butylamino)silane and 1,1,3,3-tetramethyldiphenyldisiloxane.

The nmr gave the following absorption data.

	<u>Proton ratio</u>	S values	
C6H5S1≡	5	~7.2-7.6	(broad)
CH <sub>3</sub> S1≡	6	~0.4	(singlet)
H ≡S1-N-CH <sub>2</sub> -	2.5	~2.8	(broad)
$\equiv \text{S1-N-CH}_2-\text{CH}_2-\text{CH}_2$	5	~1.4	(septet)
$\equiv \text{S1-N-(CH}_2)_3 - \text{CH}_3$	3.3	~1.0	(quartet)

#### 2. Preparation of Dimethylphenylsilanol

To a small vial (3 ml) was added 0.5 g of dimethylphenylsilane, 2 ml of benzene, 2 drops of water and 0.002 g of tris-(triphenylphosphine)chlororhodium (I). Hydrogen gas evolution started immediately. The color of the solution was yellow. In ~8 hours two more drops of water were added. In 24 hours the reaction was complete. A gas chromatograph of the reaction mixture showed two product peaks. These peaks were believed to be dimethylphenylsilanol and 1,1,3,3-tetramethyldiphenyldisiloxane. The benzene was distilled off and the products flash-distilled from the catalyst. An ir and nmr confirmed that the products were dimethylphenylsilanol and 1,1,3,3-tetramethyldiphenyldisiloxane.

The ir spectrum showed the bands at  $3600 \text{ cm}^{-1}$  (OH), at  $3280 \text{ cm}^{-1}$  (OH), at  $1600 \text{ cm}^{-1}$  (phenyl), at  $1490 \text{ cm}^{-1}$  (phenyl), at  $1430 \text{ cm}^{-1}$  (phenyl), at  $1250 \text{ cm}^{-1}$  (Si-CH<sub>3</sub>), at  $1050 \text{ cm}^{-1}$  (Si-O-Si), at  $1000 \text{ cm}^{-1}$  (Si-phenyl), at  $860 \text{ cm}^{-1}$  (OH), at  $790 \text{ cm}^{-1}$  (Si-CH<sub>3</sub>) and no band at  $2100 \text{ cm}^{-1}$  (due to Si-H). The nmr spectrum showed the following absorptions.

 Stalues

 CH3-Sim
 ~0.5 (singlet

 C6H5
 ~7.4 (broad)

 ES1-OH
 ~3.2 (broad)

3. Preparation of Triethylcyclohexanoxysilane

To a 15 ml single-necked flask was added 1.16 g (0.01 mols) of triethylsilane, 1.00 g (0.01 mols) of dried cyclohexanone and 5 ml of anhydrous benzene. The mixture was refluxed under nitrogen for one-half hour to remove any dissolved oxygen present. Then 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) and one drop of triethylamine were added. The mixture was kept at  $70^{\circ}$ C for 24 hours. There was a product peak seen by gas chromatography

32

during this time. There was, however, very little gas evolution. The solvent was removed by distillation and the product flash-distilled away from the catalyst. A gas chromatograph of the product showed it to be pure. An nmr and ir showed that the product was a mixture of hexaethyldisiloxane and triethylcyclohexanoxysilane. A gas chromatograph of the mixture of pure hexaethyldisiloxane and the compounds prepared showed that they had exactly the same retention times. A mass spectrum of the sample could only be explained if both compounds were present. Hydrolysis of the prepared compound produced one new peak in the gas chromatograph which had the same retention time as cyclohexanol.

The nmr spectrum showed the following absorption data.

	<u>Proton ratio</u>	<b>d</b> values
	1	~3.5 (broad)
Esi-0-€	10	~1.0-2.0 (very broad)
ch₃ch₂s1Ξ	20.8	~0.4-1.0 (due to hexa- ethyldisiloxano present)

#### 4. <u>Reaction of Cyclohexanone with Triethylsilane</u> <u>Using Triethylamine as a Catalyst</u>

To a 10 ml single-necked flask was added 1.00 g (0.01 mols) of dry cyclohexanone, 1.16 g (0.01 mols) of triethylsilane, 3 drops of triethylamine and 5 ml of anhydrous benzene. The mixture was heated for 24 hours between 80-90°C. A gas chromatograph after this time showed only starting materials present. There was no triethylcyclohexanoxysilane detected.

## F. <u>Reactions of an Organosilane with an Alcohol Catalyzed</u> by an Acid

1. <u>Reaction of Triethylsilane with Ethanol Catalyzed</u> by Dimethylchlorosilane

To a 10 ml single-necked flask was added 1.16 g (0.01 mols) of triethylsilane, 0.46 g (0.01 mols) of absolute ethanol and 5 ml of anhydrous benzene. Then 0.1 g of dimethylchlorosilane was added. The mixture was kept at  $60^{\circ}$ C under a nitrogen atmosphere for two days. After this time a gas chromatograph of the reaction mixture showed a very small amount of triethylethoxysilane present. The starting materials were distilled from the product. A total of 0.12 g of triethylethoxysilane was obtained. This amounts to a 7.5% yield.

- G. <u>Competitive Reactions of Triethylsilane for Various</u> <u>Alcohols</u>
  - 1. <u>Competitive Reactions of Triethylsilane for</u> <u>Ethanol and 2-Butanol</u>

To a 10 ml single-necked flask was added 1.16 g (0.01 mols) of triethylsilane, 0.46 g (0.01 mols) of absolute ethanol, 0.74 g (0.01 mols) of dry 2-butanol and 5 g of anhydrous benzene. The mixture was refluxed for one hour under nitrogen to remove any dissolved oxygen present. Then 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) was added. The mixture was heated at  $60^{\circ}$ C for 24 hours. At this time the reaction was complete (i.e. no starting materials were seen by glc and no hydrogen evolution). A gas chromatograph of the mixture was run three times and the ratio of areas determined and averaged. The areas under the curves were determined by height times width at half height. The response factors for the two products were determined from standard solutions of the two pure components. The response factors for the two components were equal to 1. The following was determined: Area  $[(C_2H_5)_3SiOC_2H_5]/Area [(C_2H_5)_3SiOCH(CH_3))$  $(C_2H_5)] = 4.50/2.84 = 1.595.$ 

## 2. <u>Competitive Reaction of Triethylsilane for</u> <u>Ethanol and tert-Butanol</u>

To a 10 ml single-necked flask was added 1.16 g (0.01 mols) of triethylsilane, 0.46 g (0.01 mols) of absolute ethanol, 0.74 g (0.01 mols) of dried tert-butanol and 5 ml of anhydrous benzene. The mixture was refluxed under nitrogen to remove any dissolved oxygen. Then 0.002 g  $(2.2 \times 10^{-6} \text{ mols})$  of tris-(triphenylphosphine)chloro-rhodium (I) was added. The mixture was kept at  $60^{\circ}$ C for 24 hours. A gas chromatograph at this time showed very little triethylsilane present. There was also much tert-butanol present and no ethanol. A product peak was seen for triethylethoxysilane, but no further product peaks were seen. The conclusion is that the ethanol reacts at a much greater rate than tert-butanol.

### 3. <u>Competitive Reaction of Triethylsilane for</u> <u>Methanol and n-Butanol</u>

To a 10 ml single-necked flask was added 1.16 g (0.01 mols) of triethylsilane, 0.32 g (0.01 mols) of anhydrous methanol, 0.74 g (0.01 mols) of dried n-butanol and 5 g of anhydrous benzene. The mixture was refluxed for one hour under nitrogen to remove any dissolved oxygen present. The mixture was then cooled and 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) was added. The mixture was kept at 50°C for 10 hours. At this time the reaction had gone to completion. A gas chromatograph of the mixture was run three times, and the areas of the two products averaged. The average areas obtained were: Area [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiOCH<sub>3</sub>]/Area [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiOC<sub>4</sub>H<sub>9</sub>]= 3.169/3.974 = 0.798. The response factors are again found to be 1 for the two pure components.

## 4. <u>Competitive Reaction of Triethylsilane for Ethanol</u> and Phenol

To a 10 ml single-necked flask was added 1.16 g (0.01 mols) of triethylsilane, 0.46 g (0.01 mols) of absolute ethanol, 0.94 g (0.01 mols) of phenol and 5 g of anhydrous benzene. The mixture was heated at reflux for one hour under nitrogen to remove any dissolved oxygen. Then the mixture was cooled and 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) was added. The mixture was kept at  $60^{\circ}$ C for 24 hours. A gas chromatograph after this time showed complete reaction of the triethylsilane. The only product peak seen was triethylethoxysilane.

36

The peak due to phenol was still present, and the peak due to ethanol had completely disappeared. The conclusion drawn was that ethanol reacts at a much faster rate than phenol.

#### 5. <u>Competition Reaction of Triethylsilane for</u> <u>1-Butanol and 2-Butanol</u>

To a 10 ml single-necked flask was added 1.16 g (0.01 mols) of triethylsilane, 0.74 g (0.01 mols) of dried 1-butanol, 0.74 g of dried 2-butanol and 5 ml of anhydrous benzene. The mixture was refluxed for one hour under nitrogen to remove any dissolved oxygen present. Then the mixture was cooled, and 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) was added. The reaction was kept at 50°C for 24 hours and then at room temperature for another 24 hours. At this time the reaction was complete (by glc). Three gas chromatographs were run. The average areas obtained were: Area  $\left[ (C_2H_5)_3 SiOCH(CH_3) \right]$  $(C_2H_5)$  /Area  $[(C_2H_5)_3S10CH_2CH_2CH_2CH_3] = 1.499/4.275 =$ 0.351. The response factor for this system was determined to be 0.85. Therefore, the true ratio is 0.298.

# H. <u>Competition Reactions of Various Organosilanes</u> for a Single Alcohol

#### 1. <u>Competition Reaction of n-Butanol for</u> <u>Dimethylphenylsilane and Triethylsilane</u>

To a 10 ml single-necked flask was added 0.58 g (0.005 mols) of triethylsilane, 0.68 g (0.005 mols) of dimethylphenylsilane, 0.37 g (0.005 mols) of n-butanol and 5 ml anhydrous benzene. The mixture was refluxed under nitrogen for one hour to remove any dissolved oxygen present. Then 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) was added. The mixture was heated at  $60^{\circ}$ C for one hour, then cooled to room temperature and followed by gas chromatography. When the reaction was complete, the mixture was run three times on the gas chromatograph. The average areas determined are as follows: Area [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiOC<sub>4</sub>H<sub>9</sub>]/Area [(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>SiOC<sub>4</sub>H<sub>9</sub>]= .669/ 2.700 = 0.248. The response factor determined for the two pure components is 0.810. Therefore, the true ratio becomes 0.201.

## 2. <u>Competition Reaction of Ethanol for Triethylsilane</u> and Triethoxysilane

To a single-necked 10 ml flask was added 1.64 g (0.01 mols) of triethoxysilane, 1.16 g (0.01 mols) of triethylsilane. 0.46 g (0.01 mols) of absolute ethanol and 5 ml of anhydrous benzene. The mixture was refluxed under nitrogen for one hour to remove any dissolved oxygen pre-Then the mixture was cooled and 0.002 g (2.2 x  $10^{-6}$ sent. mols) of tris-(triphenylphosphine)chlororhodium (I) was added. The reaction was kept at 60°C and followed by gas The reaction had not progressed to any chromatography. extent in 36 hours. One drop of triethylamine was added at this time to rid the system of any residual hydrogen chloride present which could have come from the triethoxysilane since it was prepared from trichlorosilane and ethanol without a hydrogen chloride acceptor present. A

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precipitate did form and hydrogen evolution started. It is known that hydrogen chloride will inhibit the activity of the catalyst in hydrogenation reactions. When the reaction had reached completion, three gas chromatographs were run, and the average areas were determined as follows: Area  $[(C_{2H_5})_{3}SiOC_{2H_5}]/Area [(C_{2H_5}O)_{3}SiOC_{2H_5}] = 2.2942/2.5338 =$ 0.905. The response factor determined for the two pure compounds was determined to be 1.82. The true ratio is 1.65.

#### 3. <u>Competition Reaction of Butanol for Triethylchloro-</u> and Dimethylphenylchlorosilane

To a 50 ml three-necked flask equipped with a condensor, drying tube, magnetic stirrer, ice bath and gas tube was added 2.72 g (0.02 mols) of dimethylphenylsilane, 2.32 g (0.02 mols) of triethylsilane and 35 ml of dry carbon tetrachloride. The mixture was cooled to 0°C and then chlorine gas was slowly bubbled through the stirring mix-The chlorine gas was added until the stirring mixture. ture stayed a green color. The reaction was then allowed to stir at room temperature for one-half hour. A gas chromatograph at this time confirmed that no starting materials remained. The carbon tetrachloride was then distilled off at room temperature under reduced pressure. Then 10 ml of anhydrous benzene was added to the residue followed by 1.48 g (0.02 mols) of dried n-butanol. The mixture was allowed to stir for one hour. A gas chromatograph showed that the n-butanol had been consumed. Then  $\sim 5$  ml of benzene was removed under reduced pressure. Three gas chromatographs of the mixture were run and the areas averaged to give the following data: Area  $[(C_2H_5)_3SiOC_4H_9]/Area [(C_6H_5)(CH_3)_2 SiOC_4H_9] = .49/3.73 = .132$ . The response factor determined for the pure components is 0.810. Therefore, the true ratio is 0.107.

## I. Alkoxy Exchange on Silicon

# 1. Reaction of Triethyl(sec-butoxy)silane with Ethanol

To a 10 ml, single-necked flask was added 2.0 g of anhydrous benzene, 0.2 g (l.1 x  $10^{-3}$  mols) of triethyl(secbutoxy)silane and 0.1 g (2.2 x  $10^{-3}$  mols) of absolute ethanol. The mixture was then refluxed under nitrogen for one hour to remove any dissolved oxygen. Then 0.002 g (2.2 x  $10^{-6}$  mols) of tris-(triphenylphosphine)chlororhodium (I) was added. The mixture was kept at  $70^{\circ}$ C for 24 hours. A gas chromatograph at this time showed no triethylethoxysilane had formed. An additional 0.1 g of absolute ethanol was added. The mixture was kept at  $70^{\circ}$ C for an additional 24 hours. After this time a gas chromatograph of the mixture showed no triethylethoxysilane had formed.

# 2. <u>Reaction of Triethyl(sec-butoxy)silane with Tri-</u> ethylethoxysilane

To a 10 ml, single-necked flask was added 2.0 g of anhydrous benzene, 0.1 g  $(5.3 \times 10^{-4} \text{ mols})$  of triethyl(secbutoxy)silane and 0.1 g  $(6.25 \times 10^{-4} \text{ mols})$  of triethylethoxysilane. A gas chromatograph of the mixture was run. The mixture was then heated at reflux for one hour under nitrogen to remove any dissolved oxygen. Then 0.002 g  $(2.2 \times 10^{-6} \text{ mols})$ of tris-(triphenylphosphine)chlororhodium (I) was added. The mixture was kept at 65°C for 48 hours. At this time a gas chromatograph showed the same area ratio of triethylethoxysilane to triethyl(sec-butoxy)silane as when initially mixed.

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# APPENDIX A

Infrared Spectra

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## APPENDIX B

## Proton NMR Spectra

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