

SILICON HYDRIDES AND NICKEL COMPLEXES

I. PHOSPHINE-NICKEL(II) COMPLEXES AS HYDROSILYLATION CATALYSTS

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SUMMARY

A variety of dihalodiphosphenickel(II) complexes have been found to be effective catalysts for hydrosilylation of olefins and acetylenes. Reactions with nickel(II) catalysts, at least those containing a bidentate phosphine ligand, scarcely proceed below 90°. At 120° the reaction proceeds smoothly to form, in many cases, an unexpected ("abnormal") adduct which has arisen from an interchange of hydrogen and chlorine on silicon in addition to the expected ("normal") one. Both total yields, and the ratios of the "abnormal" to the "normal" adduct increase, in general, with increasing electron-donating ability of both the phosphine ligands and the substituents on the olefins. Isomerization of olefins occurs during the course of hydrosilylation. *cis*-Addition occurs preferentially. The reactivity of the silicon hydrides decreases in the order $\text{HSiCl}_3 > \text{HSiMeCl}_2 > \text{HSiMe}_2\text{Cl} \gg \text{HSiMe}_3$.

INTRODUCTION

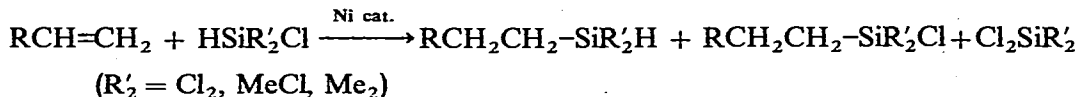
It is well-known that the addition of silicon hydrides to carbon-carbon multiple bonds is catalyzed by various transition metals, their salts and complexes^{1,2}. Chloroplatinic acid is by far the most effective and commonly used catalyst^{3,4}. Wilkinson's rhodium complexes⁵ seem to compare in efficiency with the platinum system. Dicobalt octacarbonyl⁶ and iron pentacarbonyl⁷ are also effective. Recently, platinum complexes containing tertiary phosphines proved to be active hydrosilylation catalysts⁸.

Until recently little attention has been paid to the catalytic activities of palladium and nickel derivatives in hydrosilylation, but the use of palladium-phosphine complexes as hydrosilylation catalysts has recently been reported by two research groups^{9,10}.

Only a few papers dealing with nickel catalysts had appeared before we reported the first examples of nickel-phosphine complexes as high-efficiency catalysts for hydrosilylation¹¹. Those classical nickel catalysts, including Raney nickel¹², nickel chloride-pyridine complexes¹³, nickel carbonyl¹⁴ and an iron pentacarbonyl-nickel chloride couple¹⁵, were of limited applicability, and required rather drastic condi-

tions. More recently, Bennett and Orenski¹⁶ studied the addition of trichlorosilane to styrene in the presence of a bis(phosphine)nickel halide, and Hagihara and co-workers^{9b} examined the catalytic activities of some nickel complexes for the addition of trimethylsilane to butadiene.

In order to establish the scope and limitations of hydrosilylation catalyzed by phosphine-nickel complexes, we have examined the behavior of a number of olefins and some acetylenes toward silicon hydrides in the presence of a variety of phosphine-nickel(II) complexes^{11,17}. In many cases, two types of products are obtained: one is the expected simple adduct and the other is an unexpected one, which has arisen from an interchange of hydrogen and chlorine on silicon in the course of the hydrosilylation.

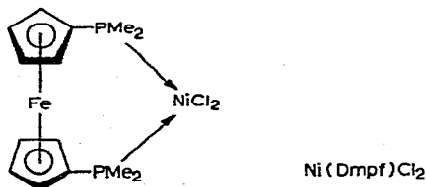


In this paper, we report the phosphine-nickel complex catalyzed hydrosilylation, focusing our attention particularly upon the SiH/SiCl interchange. The mechanistic aspects are discussed in the next paper.

RESULTS AND DISCUSSION

All experiments were carried out in degassed sealed glass tubes. In typical runs the catalyst concentration was about 10^{-3} mole per mole of olefin and about two equivalents of silicon hydride were taken for each equivalent of olefin, and the mixture was heated at 120° for 20 h. After the reaction, clear brownish solutions resulted in those cases in which the hydrosilylation had proceeded smoothly. The products were isolated by fractional distillation or by preparative GLC, and characterized by IR and NMR spectra and elementary analyses. Yields of the products were determined in almost all cases by GLC.

Of a number of phosphines used as ligands, only 1,1'-bis(dimethylphosphino)-ferrocene (hereafter, Dmpf), was a new one and prepared in 40% yield by treating dimethylchlorophosphine with dilithioferrocene*. The reaction of Dmpf and nickel chloride in acetic acid at room temperature yielded dichloro[1,1'-bis(dimethylphosphino)ferrocene]nickel(II), Ni(Dmpf)Cl₂, as a reddish brown powder. Some compounds related to Dmpf were also prepared (see Experimental).



1. Addition of silicon hydrides to 1-octene catalyzed by nickel(II) complexes containing tertiary phosphine ligands

As shown in Table 1, all the nickel(II) complexes with tertiary phosphine

* After publication of our preliminary communication¹¹, a similar preparation of 1,1'-di-substituted-ferrocenes was reported by Bishop *et al.*¹⁸.

TABLE I

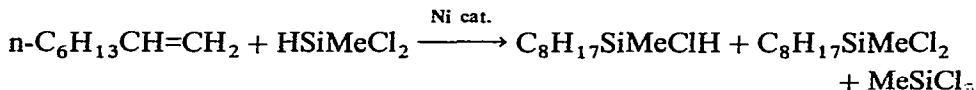
ADDITION OF METHYLDICHLOROSILANE TO 1-OCTENE CATALYZED BY NICKEL (II) COMPLEXES CONTAINING TERTIARY PHOSPHINE LIGANDS^a

Catalyst	Conditions		Products	
	Temp. (°C)	Time (h)	Total yield ^b (%)	C ₈ H ₁₇ SiMeClH/C ₈ H ₁₇ SiMeCl ₂ ratio
Ni(Ph ₃ P) ₂ Cl ₂	120	20	3-5	0/100
Ni(PhMe ₂ P) ₂ Cl ₂	120	20	77	35/65
Ni(n-Bu ₃ P) ₂ Cl ₂	120	20	44	41/59
Ni(Et ₃ P) ₂ Cl ₂	120	20	61	49/51
Ni(Et ₃ P) ₂ Br ₂	120	20	59	61/39
Ni(Me ₃ P) ₂ Cl ₂	120	20	78	50/50
Ni(Ph ₂ PCH ₂ CH ₂ PPh ₂)Cl ₂	120	40	75	7/93
	135	20	98	4/96
Ni[Ph ₂ P(CH ₂) ₃ PPh ₂]Cl ₂	135	20	94	10/90
Ni(Ph ₂ PCH=CHPPh ₂)Cl ₂ ^c	135	20	84	6/94
Ni(Me ₂ PCH ₂ CH ₂ PMe ₂)Cl ₂ ^d	120	40	87	63/37
	135	20	79	51/49
Ni(Dmpf)Cl ₂	120	20	95	83/17

^a The mixture of 1-octene (0.3 g), methyldichlorosilane (0.6 g), and Ni catalyst (catalyst/olefin 10⁻³) was heated in a sealed glass tube. ^b Yields were determined by GLC, and are based on the amount of 1-octene taken. ^c The phosphine ligand is the *cis* isomer. ^d Octyldichlorosilane, C₈H₁₇SiCl₂H, was formed as a by-product (5% yield).

ligands catalyze the addition of methyldichlorosilane to 1-octene. It will be seen that in all cases, except where triphenylphosphine was the ligand, an unexpected ("abnormal") adduct, which had arisen from an interchange of hydrogen and chlorine on silicon, was formed in addition to the expected ("normal") one.

For instance, the reaction of 1-octene (1 part) and methyldichlorosilane (2 parts) in the presence of Ni(Dmpf)Cl₂ formed octylmethylchlorosilane and octylmethyl dichlorosilane in the ratio of 83/17, together with methyltrichlorosilane. The total yield of the two adducts amounted to 95% based on the 1-octene used.



Each adduct consisted mainly of the *n*-octyl derivative, contaminated with a small amount (< 10%) of the 2-octyl derivative.

With Ni(Me₂PCH₂CH₂PMe₂)Cl₂ catalyst, a small amount of octyldichlorosilane was also formed in addition to the two adducts mentioned above, indicating that concomitant interchange of hydrogen and methyl group on silicon had occurred. The extent of the H/Cl interchange depends greatly on the nature of the phosphine ligand on nickel. With a nickel(II) chloride complexed with two molecules of triphenylphosphine, solely the normal adduct is obtained and in only 3 to 5% yield, whereas with a similar catalyst having two phenyldimethylphosphine ligands, not only is the total yield dramatically enhanced, but also a considerable amount of the abnormal adduct is produced.

From the data in Table 1, it can be seen that the extent of the H/Cl interchange decreases in the order: $\text{Dmpf} \gg \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2 > \text{PMe}_3 \approx \text{PET}_3 > \text{PBu}_3 \approx \text{PMe}_2\text{Ph} > \text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2 \approx \text{cis-Ph}_2\text{PCH}=\text{CHPPh}_2 \approx \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \gg \text{PPh}_3$. This sequence suggests that, in general, the more electron-donating the phosphine ligand on nickel, the greater the extent of the H/Cl interchange. Comparison of the results from 1,2-bis(diphenylphosphino)ethane and 1,2-bis(dimethylphosphino)ethane as ligands is especially revealing concerning the predominant role of the electron-donating phosphine ligand in the H/Cl interchange process. In these two cases, the total yields are not greatly different from each other, whereas the extent of the H/Cl interchange is much higher for the latter than for the former ligand.

The definite inductive electron-donating behavior of the ferrocenyl group has been well established¹⁹. Its inductive aromatic parameter σ_1 , being equal to -0.08 (ref. 19), is one of the largest known for electron-donating substituents²⁰. Hence, the Dmpf ligand may be expected to exhibit the largest electron-donating properties of all the ligands used and it is noteworthy that Dmpf as a ligand is markedly superior to other phosphines for the H/Cl interchange as well as in respect of the total yield.

It should be emphasized at this point that the reactions, at least those involving the bidentate phosphine-nickel(II) catalysts, scarcely proceed below 90° , since these observations would provide one of the most important pieces of information when the reaction mechanism is discussed.

The additions of other silicon hydrides to 1-octene catalyzed by $\text{Ni}(\text{PET}_3)_2\text{Cl}_2$ and $\text{Ni}(\text{Dmpf})\text{Cl}_2$ were studied (Table 2). The reactivity of the silicon hydrides is strongly dependent upon the number of chlorine atoms on silicon, and falls steadily in the sequence $\text{HSiCl}_3 > \text{HSiMeCl}_2 > \text{HSiMe}_2\text{Cl}$ for both catalysts. Dimethylchlorosilane adds to 1-octene with the former catalyst, but not with the latter. Trimethylsilane, triethoxysilane and diphenylmethylsilane did not add to 1-octene in the presence of either $\text{Ni}(\text{PET}_3)_2\text{Cl}_2$ or $\text{Ni}(\text{Dmpf})\text{Cl}_2$. The extent of the H/Cl interchange decreases in the order: $\text{HSiMeCl}_2 > \text{HSiCl}_3 > \text{HSiMe}_2\text{Cl}$, which does not parallel the reactivity order mentioned above.

Apparently, the extent of the H/Cl interchange varies with the molar ratios of silicon hydride to olefin but the variation is rather small. Thus, 5/1, 2/1, 1/1 and 1/2 mixtures of methylchlorosilane and 1-octene afforded, with $\text{Ni}(\text{Dmpf})\text{Cl}_2$ catalyst, mixtures of products in which the ratios of the abnormal adduct (resulting from H/Cl

TABLE 2

ADDITION OF SILICON HYDRIDE TO 1-OCTENE^a

Catalyst	Silicon hydride HSiX_2Cl	Products	
		Total yield (%)	$\text{C}_8\text{H}_{17}\text{SiX}_2\text{H}/\text{C}_8\text{H}_{17}\text{SiX}_2\text{Cl}$ ratio
$\text{Ni}(\text{PET}_3)_2\text{Cl}_2$	HSiCl_3	90	37/63
	HSiMeCl_2	61	49/51
	HSiMe_2Cl	44	23/77
$\text{Ni}(\text{Dmpf})\text{Cl}_2$	HSiCl_3	100	50/50
	HSiMeCl_2	95	83/17

^a See footnotes of Table 1. Conditions: 120° , 20 h.

interchange) to the normal one were 88/12, 83/17, 77/23 and 70/30, respectively. The extent of the H/Cl interchange also depends on the reaction temperature, and tends to decrease with increasing temperature, as shown for the reactions catalyzed by $\text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{Cl}_2$ in Table 1. This effect will be described in detail in the following paper.

The data described above show that $\text{Ni}(\text{Dmpf})\text{Cl}_2$ is outstanding as a catalyst in both the hydrosilylation and the H/Cl interchange. Furthermore, the largest amount of the H/Cl interchange occurred when methylchlorosilane was used as the silicon hydride, and so in the discussion that follows we concentrate on the combination of $\text{Ni}(\text{Dmpf})\text{Cl}_2$ and methylchlorosilane.

2. Addition of methylchlorosilane to various olefins catalyzed by $\text{Ni}(\text{Dmpf})\text{Cl}_2$

We find that the $\text{Ni}(\text{Dmpf})\text{Cl}_2$ complex catalyzes the addition of methylchlorosilane to a wide variety of olefins, and the extent of H/Cl interchange also depends upon the structure of olefins. The results are summarized in Tables 3, 4 and 5.

Our present interest is centered on the formation of the H/Cl interchange product, so that other features, such as the direction of addition of silicon hydride across a carbon-carbon double bond and olefin isomerization accompanying the hydrosilylation, will be only briefly described.

The addition of methylchlorosilane to simple 1-olefins examined, from ethylene to 1-octene, in the presence of $\text{Ni}(\text{Dmpf})\text{Cl}_2$ at 120° for 20 h, proceeds in substantially the same fashion in that the total yields and the ratios of the normal to the abnormal adduct vary only over a rather narrow range (Table 3). Here again, each adduct contained a small amount of the 2-alkyl derivative, indicating that in nickel complex catalyzed hydrosilylation there is a tendency to form inner adducts.

Internal olefins such as 2-pentene also underwent hydrosilylation to form a mixture of the abnormal and normal adducts, the ratio being slightly lower than that obtained from 1-pentene (Table 3); both the normal and abnormal adducts from 2-pentene contained the inner adduct (*e.g.*, 2- or 3-pentyl derivative) in a larger amount than when 1-pentene was used. This is in contrast with the platinum catalyzed hydrosilylation, in which only the terminal adduct was obtained regardless of whether 1- or 2-olefin was employed.

Cyclic olefins, such as cyclohexene and 1,5-cyclooctadiene (Table 4), formed comparable amounts of the normal and abnormal adducts. It is interesting that with 1,3-cyclooctadiene the extent of formation of the H/Cl interchange product is very small in comparison with that obtained from the 1,5-isomer. Styrene also gave a considerable amount of the H/Cl interchange product. On the other hand, 1,4-cyclohexadiene, isoprene, and so-called vinyl monomers, such as methyl acrylate, vinyl acetate, and acrylonitrile (Table 5), gave only the normal adduct.

We can now classify the olefins into two categories: those for which the hydrosilylation is accompanied by the H/Cl interchange (Class A), and those which give only the normal adduct (Class B).

Class A: 1-olefin, 2-olefin, styrene, cyclohexene, 1,5-cyclooctadiene.

Class B: acrylonitrile, methyl acrylate, vinyl acetate, 1,4-cyclohexadiene, isoprene, (1,3-cyclooctadiene).

Thus, Class B consists mainly of conjugated dienes and olefins containing the electronegative substituents. The effect of the electron-withdrawing group on the H/Cl

TABLE 3


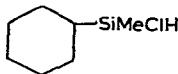
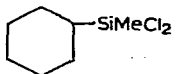

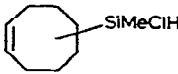
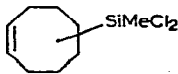

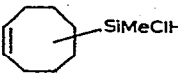
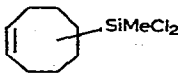
ADDITION OF METHYLDICHLOROSILANE TO 1-OLEFIN AND 2-OLEFIN CATALYZED BY Ni(Dmpf)Cl₂^a

Olefin (C _n H _{2n})	Products	
	Total yield ^b (%)	C _n H _{2n+1} SiMeClH/C _n H _{2n+1} SiMeCl ₂ ^c ratio
1-Olefin (n =): 2 ^d 100 52/48		
3	100	69/31
4	80	66/34
5	97	82/18
6	100	83/17
7	87	69/31
8	95	83/17
2-Olefin (n =): 5 90 74 ^e /26 ^e		

^a HSiMeCl₂/olefin 2; catalyst/olefin 10⁻³; 120°, 20 h. ^b See Table 1. ^c The extent of the terminal adduct (n-alkyl) formation is over 90%, unless otherwise noted. ^d The reaction was carried out in a 50 ml autoclave at 90°, 60 atm, for 6.5 days, using 19.3 g of HSiMeCl₂ and 10 mg of the catalyst. Vinylmethylchlorosilane was also formed in 16% yield. ^e n-Pentyl adduct/2-(or 3-)pentyl adduct ≈ 5/2.

TABLE 4


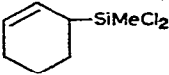
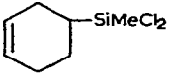
ADDITION OF METHYLDICHLOROSILANE TO OLEFINS CATALYZED BY Ni(Dmpf)Cl₂^a

Olefin	Reaction Conditions		Products (yield %)	
	Temp. (°C)	Time	"Abnormal"	"Normal"
	120	20h	 (41)	 (34)
	120	20h	 (31)	 (40)
	120	20h	 (6)	 (92)
PhCH=CH ₂	120	9 days	$\left\{ \begin{array}{l} \text{PhCH}_2\text{CH}_2(\text{SiMeClH}) \\ (17) \\ \text{PhC}(\text{Me})\text{H}(\text{SiMeClH}) \\ (3) \end{array} \right.$	$\left\{ \begin{array}{l} \text{PhCH}_2\text{CH}_2(\text{SiMeCl}_2) \\ (6) \\ \text{PhC}(\text{Me})\text{H}(\text{SiMeCl}_2) \\ (32) \end{array} \right.$

^a HSiMeCl₂/olefin 2, Ni(Dmpf)Cl₂/olefin 10⁻³-10⁻⁴.

TABLE 5

ADDITION OF METHYLDICHLOROSILANE TO OLEFINS CATALYZED BY Ni(Dmpf)Cl₂^a

Olefin	Reaction Conditions		Products	Yield (%)
	Temp. (°C)	Time		
	120	3.8 days	 -SiMeCl ₂	55
			 -SiMeCl ₂	41
CH ₂ =C(Me)-CH=CH ₂	105	8 days	Me-C(Me)=CHCH ₂ SiMeCl ₂	33
CH ₂ =CH-CO ₂ Me	120	20 h	Me-CH=C(Me)-CH ₂ SiMeCl ₂	44
CH ₂ =CHOCOMe	120	20 h	Cl ₂ MeSiC(Me)HCO ₂ Me	97
CH ₂ =CHCN ^b	100	6.5 days	Cl ₂ MeSiCH ₂ CH ₂ OCOMe	38
			MeC(CN)HSiCl ₃	51

^a HSiMeCl₂/olefin 2, Ni(Dmpf)Cl₂/olefin 10⁻³–10⁻⁴. ^b Trichlorosilane was used, since methyldichlorosilane did not add to acrylonitrile; HSiCl₃/olefin 1.2.

interchange process is in keeping with that noted for the phosphine ligands.

Isomerization of olefins also takes place during the course of hydrosilylation, but is slower than that with the platinum catalysts. Thus, *n*-pentylsilanes were formed from 2-pentene, as mentioned above (Table 3), and regardless of whether 1-pentene or 2-pentene was used the recovered pentene consisted of an isomeric mixture in which the ratio of 1- to 2-pentene reached approximately the thermodynamically determined distribution of isomers²¹ (Table 6). Furthermore, the adducts from 1,4-cyclohexadiene consisted, after methylation, of an isomeric mixture of 3- and 4-(trimethylsilyl)cyclohexene in the ratio of 57/43. This isomer distribution differs from that obtained with chloroplatinic acid as catalyst (86/14).

Although both the abnormal and normal adducts formed from 1,5-cyclooctadiene were composed of the three inseparable possible isomers, 1,3-cyclooctadiene afforded, after methylation, 3-(trimethylsilyl)cyclooctene as a sole product, indicating that 1,4-addition of silicon hydride to the 1,3-diene had occurred. The adducts from isoprene were also those from 1,4-addition. The crucial structural proof

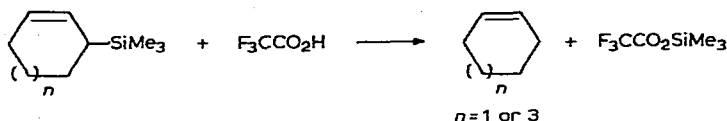
TABLE 6

ISOMERIZATION OF OLEFINS DURING THE COURSE OF HYDROSILYLATION^a

Olefin	Recovered olefin 1-pentene/2-pentene ratio ^b
1-Pentene	14/86
2-Pentene	6/94

^a The addition of HSiMeCl₂ to pentene catalyzed by Ni(Dmpf)Cl₂: HSiMeCl₂/olefin 0.5, Ni(Dmpf)Cl₂/olefin 10⁻³; 120°, 20 h. ^b Area ratio by GLC.

for 3-(trimethylsilyl)cyclohexene and 3-(trimethylsilyl)cyclooctene came from the cleavage of the silyl group by the action of trifluoroacetic acid²².



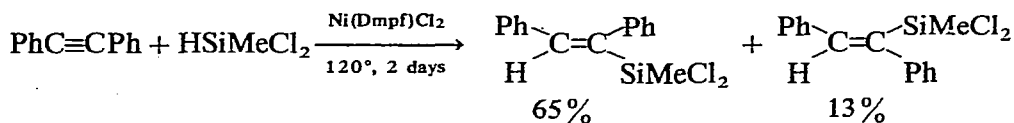
The addition to styrene proceeded in two directions, to form α - and β -adducts in the ratio of about 60/40. It seems of interest that the β -adducts contain enhanced amounts of the H/Cl interchange product while the α -adducts contain enhanced amounts of the normal products.

Furthermore, it is noteworthy that the direction of addition of silicon hydride to the so-called vinyl monomers is similar to that observed using platinum catalysts; *i.e.*, only the Markownikoff adducts are formed from acrylonitrile and methyl acrylate, while the *anti*-Markownikoff adduct is obtained from vinyl acetate.

Finally, the hydrosilylation of ethylene gave about a 16% yield of vinylmethyl-dichlorosilane, in addition to the two products, EtMeSiCl₂ and EtMeSiHCl. It is of interest that this type of reaction is characteristic of iron pentacarbonyl catalyzed hydrosilylation, for which a free radical mechanism has been proposed⁷.

3. Hydrosilylation of acetylenes catalyzed by Ni(Dmpf)Cl₂

cis-Addition occurred preferentially. The addition of methyldichlorosilane to tolan in the presence of Ni(Dmpf)Cl₂ proceeded without forming the H/Cl interchange product to give an isomeric mixture of *cis*- and *trans*- α -(methyldichlorosilyl)-stilbene in the ratio of 5/1. *cis*-Hydrosilylation usually predominates with the platinum catalysis³. The confirmation of our assignment of the geometric configuration was



based mainly on a comparison with the products obtained from the chloroplatinic acid catalyzed hydrosilylation (*cis*-addition) and from the free radical hydrosilylation (predominant *trans*-addition)^{23,24a}.

Phenylacetylene formed no adduct at all under similar conditions.

4. Catalytic activity of Pd(Dmpf)Cl₂ and Pt(Dmpf)Cl₂

Palladium(II) and platinum(II) complexes of Dmpf were also prepared and their catalytic abilities for hydrosilylation were examined. The palladium complex was prepared from Dmpf and dichlorobis(benzonitrile)palladium(II), while the platinum analogue was made from Dmpf and platinum(II) chloride. The Pt(Dmpf)Cl₂ complex catalyzed the addition of methyldichlorosilane to 1-octene under the same conditions as above to give only the normal adduct, *viz.*, *n*-octylmethyldichlorosilane, in quantitative yield, as do other platinum catalysts. On the other hand, with the Pd(Dmpf)Cl₂ complex as catalyst only traces of *n*-octylmethyldichlorosilane were formed. The low

efficiency of the $\text{Pd}(\text{Dmpf})\text{Cl}_2$ is consistent with the fact that palladium complexed with another bidentate phosphine ligand, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, exhibits little catalytic activity in hydrosilylation^{24b}.

EXPERIMENTAL

General comments

All temperatures are uncorrected. A Varian Aerograph Model 90P, equipped with a 20 ft. column packed with Apiezon-L (30% on Celite) or Silicon DC 550 (30% on Celite), was used for isolation and purification. NMR spectra were obtained on a JEOL Model C-60H spectrometer and a Varian T-60 spectrometer. Infrared spectra were measured on a Hitachi EPI G3 Grating spectrophotometer.

Phosphine-nickel(II) complexes other than $\text{Ni}(\text{Dmpf})\text{Cl}_2$ were prepared by literature methods: $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ ²⁵, $\text{Ni}(\text{PPhMe}_2)_2\text{Cl}_2$ ²⁶, $\text{Ni}(\text{PBu}_3)_2\text{Cl}_2$ ²⁷, $\text{Ni}(\text{PEt}_3)_2\text{Cl}_2$ ²⁷, $\text{Ni}(\text{PEt}_3)_2\text{Br}_2$ ²⁷, $\text{Ni}(\text{PMe}_3)_2\text{Cl}_2$ ²⁸, $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2$ ²⁹, $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2$ ²⁹, $\text{Ni}(\text{cis-Ph}_2\text{PCH}=\text{CHPPh}_2)\text{Cl}_2$ ³⁰, and $\text{Ni}(\text{Me}_2\text{-PCH}_2\text{CH}_2\text{PMe}_2)\text{Cl}_2$ ³¹. Dimethylchlorophosphine³² was prepared by treatment of tetramethyldiphosphine disulphide³³ with phenyldichlorophosphine. Monodentate tertiary phosphines were prepared by standard methods from Grignard reagents. 1,2-Bis(diphenylphosphino)ethane³⁴, 1,3-bis(diphenylphosphino)propane³⁵ and *cis*-1,2-bis(diphenylphosphino)ethylene³⁶ were prepared by established procedures. 1,2-Bis(dimethylphosphino)ethane was previously reported by Chatt and Hayter³⁷, who used a different method to make it.

Sodium chips (20 g, 0.87 g-atom) were added to a solution of dimethylchlorophosphine (17 g, 0.176 mol) in absolute dioxane (100 ml) with stirring, whereupon an exothermic reaction occurred. After 1 h of stirring, the mixture was heated at 70° for 1 h and then refluxed for 4 h. The mixture was cooled and the resulting solution of sodium dimethylphosphide was transferred to another flask by means of a syringe in order to free it from unchanged sodium. A solution of 1,2-dichloroethane (7 g, 0.07 mol) in 15 ml of dioxane was added dropwise at 0° with stirring. The mixture was allowed to stand at room temperature for 1 h. After removal of dioxane by distillation, the mixture was hydrolyzed and the product was extracted with ether, dried over calcium chloride, and concentrated. Fractional distillation gave 3.5 g (35% yield) of 1,2-bis(dimethylphosphino)ethane, boiling at 93°/40 mmHg (lit.³⁷ b.p. 81°/26 mmHg).

Preparation of 1,1'-bis(dimethylphosphino)ferrocene and its complexes

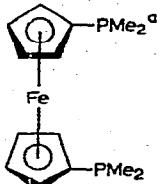
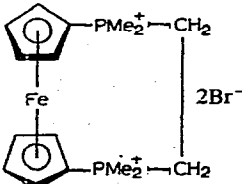
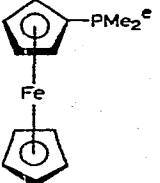
All reactions were carried out under oxygen-free, dry nitrogen. Physical constants, analytical data and IR and ¹H NMR spectral data are listed in Table 7.

(Dimethylphosphino)- and 1,1'-bis(dimethylphosphino)ferrocene. To a mixture of ferrocene (25 g, 0.134 mol) and *N,N,N',N'*-tetramethylethylenediamine (17 g, 0.147 mol) was added a solution of *n*-butyllithium in hexane (1.42 M, 218 ml, 0.309 mol). The mixture was stirred at room temperature for 50 h. Into a separate 500 ml three-necked flask, equipped with a reflux condenser, a pressure-equalizing dropping funnel, and a stirrer, 29 g (0.30 mol) of dimethylchlorophosphine was inserted from a syringe in a stream of nitrogen and the solution of lithiated ferrocene in hexane was added dropwise at 0° with stirring. After 2 h at 40°, the mixture was hydrolyzed and the resulting organic layer was separated. The solvent was evaporated and the unchanged

(continued on p. 308)

TABLE 7

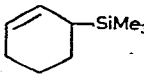
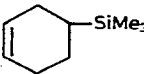



PHYSICAL CONSTANTS AND ELEMENTARY ANALYSIS OF 1,1'-BIS(DIMETHYLPHOSPHINO)FERROCENE, ITS COMPLEXES AND RELATED COMPOUNDS

Compound	Molecular formula	Decompn. at (°C) (B.p., °C/mmHg)	Analysis found (calcd.) (%)	
			C	H
	$C_{14}H_{20}FeP_2$	(140/2)	55.22 (54.93)	6.88 (6.59)
(Dmpf) $Ni(Dmpf)Cl_2^b$	$C_{14}H_{20}Cl_2FeNiP_2$	172-177	37.99 (38.59)	4.83 (4.63)
$Pd(Dmpf)Cl_2^c$	$C_{14}H_{20}Cl_2FeP_2Pd$	211-218	35.06 (34.78)	4.35 (4.17)
$Pt(Dmpf)Cl_2^d$	$C_{14}H_{20}Cl_2FeP_2Pt$	263-268	30.49 (29.39)	3.77 (3.52)
	$C_{16}H_{24}Br_2FeP_2$	156	38.90 (38.61)	4.90 (5.09)
	$C_{12}H_{15}FeP$	(106/2)	58.94 (58.57)	6.40 (6.14)

^a ¹H NMR (τ values, benzene solution); 8.62-8.82 (m, 12H), 5.62-5.85 (m, 8H). IR (cm^{-1} , liquid film); 3080 m, 2950 s, 2890 s, 2800 w, \approx 1680 w (br), 1620 w (br), 1421 s, 1412 s (sh), 1380 m, 1308 w, 1287 m, 1271 m, 1188 m, 1161 s, 1103 vw, 1050 vw, 1028 s, 1000 vw, 935 s, 902 s, 870 s, 862 w, 825 s, 815 s (sh), 702 s, 666 m, 625 w, 507 s, 448 s. ^b IR (cm^{-1} , KBr); 3075 w, 2970 vw, 2: 90 w, 1565 w, 1420 w (sh), 1410 m, 1383 m, 1310 w (sh), 1290 m, 1278 m, 1195 w, 1170 s, 1060 w, 1038 m (sh), 1030 s, 947 s, 918 s, 886 s, 870 w (sh), 833 s, 735 m, 698 m, 520 w (sh), 510 w, 490 w, 465 w, 443 m. ^c IR (cm^{-1} , KBr); 3070 w, 2970 vw, 2900 vw, 1410 s, 1382 m, 1360 w, 1305 w, 1288 m, 1278 s, 1198 w, 1172 s, 1040 s, 1030 m, 945 s (sh), 934 vs, 920 m (sh), 890 m, 838 w, 823 s, 749 m, 693 s, 630 w (br), 508 w, 492 w, 470 vs, 418 w. ^d IR (cm^{-1} , KBr); 3085 w, 3070 w, 2970 vw, 2900 w, 1415 m (sh), 1408 m, 1381 w, 1360 w, 1305 w, 1289 m, 1280 s, 1196 w, 1080 m (sh), 1073 s, 1040 m, 1030 m, 1027 m (sh), 945 m (sh), 933 vs, 915 m (sh), 885 w (br), 822 s, 815 w (sh), 747 w (sh), 741 m, 695 s, 630 w, 510 w, 496 w, 476 vs, 448 w, 420 m. ^e ¹H NMR (τ , benzene solution); 8.55-8.77 (deformed doublet, 6H), 5.65-5.94 (m, 9H).

TABLE 8

SILICON-HYDROGEN STRETCHING FREQUENCIES, ¹H NMR SPECTRA AND ELEMENTAL ANALYSES OF HYDROSILYLATION PRODUCTS

Compound	$\nu(\text{Si-H})$ (cm^{-1})	¹ H NMR (τ^a)			Analysis found (calcd.) (%)		
		Si-CH ₃ ^b	Si-H ^{b,c}	Others	C	H	Cl
C ₂ H ₅ SiMeClH	2150	9.55 (d) ^f	5.25	8.9-9.3 (m, 5H)			
C ₃ H ₇ SiMeClH	2150	9.52 (d) ^f	5.20 (sext.)	8.15-9.35 (m, 7H)			
C ₄ H ₉ SiMeClH	2150	9.57 (d) ^f	5.23 (sext.)	8.35-8.85 (m, 4H)	44.91	9.92	25.40
				8.85-9.35 (m, 5H)	(43.93)	(9.59)	(25.94)
C ₅ H ₁₁ SiMeClH	2150	9.57 (d) ^f	5.22 (sext.)	8.15-8.9 (m, 6H)	47.52	9.79	23.37
				8.9-9.3 (m, 5H)	(47.81)	(10.03)	(23.52)
n-C ₅ H ₁₁ SiMe ₂ H	2100	9.95 (d) ^f	6.14 (m)	8.35-8.9 (m, 6H)	64.46	13.95	
				8.9-9.7 (m, 5H)	(64.52)	(13.92)	
2,3-C ₅ H ₁₁ SiMe ₂ H	2150	9.97 (d) ^f	6.23 (m)	8.3-8.85 (m, 4H)	64.55	13.91	
				8.85-9.35 (m, 7H)	(64.52)	(13.92)	
C ₆ H ₁₃ SiMeClH	2150	9.53 (d) ^f	5.22 (sext.)	8.65 (bs, 8H)	51.08	10.39	21.72
				8.93-9.35 (m, 5H)	(51.06)	(10.41)	(21.53)
C ₇ H ₁₅ SiMeClH	2150	9.57 (d) ^f	5.23 (sext.)	8.69 (bs, 10H)	53.61	10.70	19.97
				8.90-9.35 (m, 5H)	(53.74)	(10.71)	(19.83)
C ₈ H ₁₇ SiMeClH ^d	2150	9.52 (d) ^f	5.20 (sext.)	8.67 (bs, 12H)	55.81	10.90	18.21
				8.90-9.30 (m, 5H)	(56.06)	(10.98)	(18.39)
C ₈ H ₁₇ SiCl ₂ H ^e	2200		4.50 (t)	8.70 (bs, 12H)	44.88	8.40	33.73
				8.95-9.30 (m, 5H)	(45.06)	(8.51)	(33.26)
n-C ₈ H ₁₇ SiMe ₂ H	2100	9.97 (d) ^f	6.15 (n)	8.71 (bs, 12H)	69.62	13.59	
				8.95-9.70 (m, 5H)	(69.67)	(14.03)	
2-C ₈ H ₁₇ SiMe ₂ H	2100	9.96 (dd) ^f	6.20 (m)	8.65 (bs, 10H)	69.91	14.29	
				8.90-9.35 (m, 7H)	(69.67)	(14.03)	
c-C ₆ H ₁₁ SiMeClH	2150	9.58 (d) ^f	5.40 (m)	7.85-9.1 (m, 11H)	52.23	9.66	21.23
					(51.66)	(9.29)	(21.79)
c-C ₆ H ₁₁ SiMeCl ₂		9.29 (s)		7.9-9.1 (m, 11H)			35.75
							(35.96)
		10.01 (s)		4.27-4.5 (m, 2H)	69.85	11.65	
				7.75-8.75 (m, 7H)	(70.04)	(11.76)	
		10.04 (s)		4.35 (bs, 2H)			
				7.85-8.50 (m, 7H)			
	2150				57.36	9.15	18.38
					(57.26)	(9.08)	(18.78)
					48.64	7.52	31.26
					(48.42)	(7.22)	(31.77)
	2100	9.94 (d) ^f 9.99 (d) ^f	6.22 (m)	4.25-4.55 (m, 2H)	71.35	11.75	
				7.5-9.35 (m, 11H)	(71.34)	(11.97)	
PhCHMeSiMe ₂ H	2110	10.03 (dd) ^f	6.13 (m)	2.6-3.15 (m, 5H)	73.14	10.05	
				7.6-8.05 (m, 1H)	(73.09)	(9.82)	
				8.65 (d, 3H) ^j			

(continued)

TABLE 8 (contd.)

Compound	$\nu(\text{Si-H})$ (cm^{-1})	$^1\text{H NMR} (\tau)^a$			Analysis found (calcd.) (%)		
		Si-CH ₃ ^b	Si-H ^{b,c}	Others	C	H	Cl
PhCH ₂ CH ₂ SiMeClH	2150	9.57 (d) ^f	5.20 (m)	2.87 (m, 2H) 7.05-7.45 (m, 2H) 8.35-9.15 (m, 2H)	59.07 (58.51)	7.31 (7.09)	
Me ₂ C=CHCH ₂ SiMeCl ₂ ^k		9.23 (s)		4.6-5.4 (m, 1H) 7.97 (bd, 2H) ⁱ 8.1-8.25 (m, 3H) 8.25-8.35 (m, 3H)	39.14 (39.34)	6.89 (6.60)	
MeCH=CMeCH ₂ SiMeCl ₂ ^k		9.17 (s)		4.45-4.9 (m, 1H) 7.85 (bs, 2H) 8.17 (m, 3H) 8.36 (bd, 3H) ^m	39.48 (39.34)	6.53 (6.60)	

^a Carbon tetrachloride solution with benzene as an internal standard (60 MHz); s singlet, bs broad singlet, d doublet, bd broad doublet, dd double doublet, t triplet, sext sextet, n nine line, m multiplet. ^b $J(\text{H-SiCH}_n)$ 3.0-3.5 Hz. ^c Centre of a multiplet. ^d B.p. 96°/20 mmHg. ^e B.p. 97°/13 mmHg. ^f Consists of three isomers. ^g B.p. 117°/33.5 mmHg. ^h B.p. 130°/31.5 mmHg. ⁱ B.p. 93.5°/25 mmHg. ^j $J(\text{HCCH}_3)$ 7.5 Hz. ^k B.p. 62°/19 mmHg (mixture of these two isomers). ^l $J(=\text{CH}-\text{CH}_2-)$ 6.9 Hz. ^m $J(=\text{CH}-\text{CH}_3)$ 6.4 Hz.

ferrocene was removed by sublimation under the reduced pressure. Fractional distillation of the remaining reddish brown liquid gave 6 g (17% yield) of (dimethylphosphino)ferrocene, and 17 g (40.5% yield) of 1,1'-bis(dimethylphosphino)ferrocene (Dmpf), as an air-unstable, reddish brown liquid.

A diquaternary salt with 1,2-dibromoethane was obtained as light orange crystals in 50% yield by refluxing Dmpf (1 g) with 1,2-dibromoethane (0.6 g) in benzene and subsequently washing with tetrahydrofuran.

Dichloro[1,1'-bis(dimethylphosphino)ferrocene]nickel(II), $\text{Ni}(\text{Dmpf})\text{Cl}_2$. To a stirred mixture of anhydrous nickel(II) chloride (0.13 g, 1 mmol) and Dmpf (0.31 g, 1 mmol) was added 30 ml of glacial acetic acid at room temperature. Immediately, the color changed to dark purple. After heating for 20 h, the mixture was filtered to leave, after drying *in vacuo*, 0.22 g (50% yield) of brown powder.

Dichloro[1,1'-bis(dimethylphosphino)ferrocene]palladium(II), $\text{Pd}(\text{Dmpf})\text{Cl}_2$. A mixture of dichlorobis(benzonitrile)palladium(II) (0.375 g, 1 mmol) and Dmpf (0.31 g, 1 mmol) in 30 ml of dry benzene was stirred at room temperature for 20 h. A light brown powder separated, and this was filtered off, washed with benzene, and dried *in vacuo*. The product weighed 0.39 g (80% yield).

Dichloro[1,1'-bis(dimethylphosphino)ferrocene]platinum(II), $\text{Pt}(\text{Dmpf})\text{Cl}_2$. A mixture of platinum(II) chloride (0.266 g, 1 mmol) and Dmpf (0.31 g, 1 mmol) in 30 ml of benzene was heated to reflux for 20 h with stirring. Filtration and recrystallization of the precipitate from ethanol gave 0.53 g (93% yield) of light yellow needles.

Hydrosilylation

All reactions, except for that involving ethylene, were carried out in glass ampoules. Olefin (1 part), hydrosilane (2 parts), and nickel catalyst (10^{-3} part) were placed in a glass ampoule and degassed at -196° , and the ampoule was then sealed.

After heating for a given period of time, the ampoule was again cooled to -78° before opening. Products were isolated by fractional distillation where possible, or by preparative GLC after flash distillation. Infrared [$\nu(\text{Si-H})$], ^1H NMR, and analytical data for the abnormal adducts resulting from the concomitant H/Cl interchange are listed in Table 8, together with the NMR and analytical data for some of the normal adducts. Most of the normal adducts were characterized by comparison of their physical properties, spectral data, and GLC retention times with those of authentic samples obtained from the chloroplatinic acid catalyzed hydrosilylation, and also by chlorine analysis.

The reaction involving ethylene was performed in a 50 ml autoclave containing a glass tube. Ethylene was introduced under pressure into a mixture of a silicon hydride and the catalyst contained in the autoclave. The progress of the reaction was monitored by the change in pressure. Characterization and estimation of yield of ethylmethylchlorosilane were based on the NMR spectrum, because the product could not be separated from the methyltrichlorosilane produced by H/Cl interchange. Vinylmethylchlorosilane, formed as a by-product, was characterized by comparison with a authentic sample.

The cleavage reactions of 3-(trimethylsilyl)cyclohexene and 3-(trimethylsilyl)cyclooctene were carried out as previously described^{2,2}.

ACKNOWLEDGEMENTS

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