

ORGANIC SYNTHESIS BY MEANS OF NOBLE METAL COMPLEXES—XCII¹

PALLADIUM CATALYZED HYDROSILYLATION OF MONOENES AND CONJUGATED DIENES

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Abstract—Palladium compounds and metallic palladium combined with phosphine are active catalysts of selective hydrosilylation of terminal olefins. Butadiene and trichlorosilane give a 1:1 adduct and trimethylsilane affords a 1:2 adduct. Special features of the palladium catalyzed hydrosilylation reactions are presented.

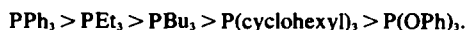
It is well known that hydrosilylation of olefinic bonds can be carried out in the presence of a radical generator or some transition metal compounds as a catalyst. Several transition metal compounds are known to catalyze the hydrosilylation reactions of olefins. The best established is a platinum catalyst, such as chloroplatinic acid. Although palladium is somewhat related to platinum in chemical properties, palladium is not regarded as a good catalyst for hydrosilylation,² and there has been no report on the palladium catalyzed hydrosilylation of olefins. Recently Hagihara and coworkers reported that zerovalent palladium complexes are efficient catalysts of the hydrosilylation of butadiene.^{3,4} During our studies of palladium-catalyzed reactions of olefins, we have independently found that palladium can be a good hydrosilylation catalyst of various olefinic bonds in the presence of proper ligands, and that palladium-catalyzed hydrosilylation is somewhat different from the platinum catalyzed reactions. Preliminary account of the work has already been given⁵ and details of the reaction are presented in this paper.

RESULTS AND DISCUSSION

At first hydrosilylation of simple olefins was tried by using tetrakis(triphenylphosphine)palladium as a catalyst. Terminal olefins were silylated easily at about 100° in high yields, but almost no reaction took place with inner olefins. Unlike the catalysis by chloroplatinic acid, which gives terminally-hydrosilylated products from both terminal and inner olefins, palladium catalyst has no ability to transform an inner olefin to a terminal position and also the hydrosilylation of inner olefins is very slow. In addition, the platinum catalyst is active even in the absence of proper ligands. On the other hand, it was found that palladium catalyst is active only when phosphine is present. In other words,

palladium and phosphine are two essential components of the catalysis, and any palladium compound can be used as the catalyst by combining with phosphine. As the most easily available one, palladium chloride and triphenylphosphine can be used as the catalyst. Furthermore, it was found that even metallic palladium can be used as the catalyst in the presence of phosphine. Usually after the reaction, metallic palladium precipitates in a reaction vessel, and the precipitated palladium can be used again as the active catalyst by adding fresh phosphine. Thus the palladium catalyst can be used for hydrosilylation repeatedly by adding a certain amount of phosphine each time. The palladium catalyst is very active at low concentration. For example, tetrakis(triphenylphosphine)palladium showed satisfactory activity at a concentration as low as 10⁻⁵ mole for one mole of olefin.

One component is phosphine and it was found that triphenylphosphine is the most active one. Alkylphosphines can be used but their activity is lower than that of triarylphosphines. The following rough order of activity was observed:

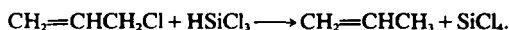


Thus it is concluded that triphenylphosphine is most suitable for efficient catalysis.

As described above, terminal olefins are hydrosilylated preferentially and selective reaction is possible. For example, by the hydrosilylation of cis-1,4-hexadiene, only the terminal double bond was hydrosilylated leaving the inner olefin intact to give cis and trans-1-trichlorosilyl-4-hexene as a main product.

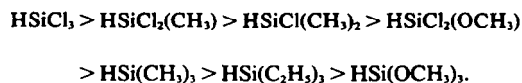


As expected, cyclohexene was not hydrosilylated, but cyclooctene was hydrosilylated in a poor yield. Only the side chain reacted by the reaction of 4-vinylcyclohexene and trichlorosilane. 2-Trichlorosilylpropionitrile was obtained from acrylonitrile and trichlorosilane. A 1:1 mixture of trichlorosilane and allyl chloride was converted to tetrachlorosilane and propylene quantitatively in the presence of tetrakis(triphenylphosphine)palladium.



Rate of hydrosilylation is also markedly dependent on the kind of silanes used. The most reactive one is trichlorosilane. The reactivity decreased by

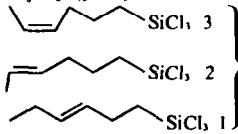
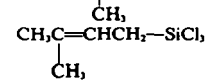
displacement of the chlorine of trichlorosilane with an alkyl group. The following order of reactivity of various silanes was observed.



The results of the hydrosilylation reactions of various olefins catalyzed by several palladium catalysts are shown in Tables 1 and 2.

Palladium-catalyzed hydrosilylation of butadiene proceeds smoothly, but the products of the reaction are different crucially depending on the silanes used. For example, addition of trichlorosilane affords 1-trichlorosilyl-2-butene as a sole product.

Table 1. Hydrosilylation of various olefins catalyzed by Pd(PPh₃)₄*

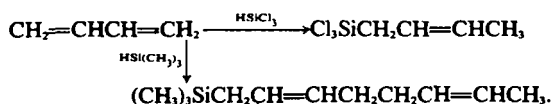
Silane	Olefin	Pd(PPh ₃) ₄ g	Reaction temp (°C)	time (h)	Product	Yield
HSiCl ₃	ethylene (50 atm)	0.1	110	6	EtSiCl ₂	90.5
HSiCl ₃	propylene	0.1	120	5	PrSiCl ₂	92.5
HSiCl ₃	1-hexene	0.1	110	6	n-C ₆ H ₁₃ SiCl ₂	90.0
HSiCl ₃	1-octene	0.1	100	5	n-C ₈ H ₁₇ SiCl ₂	85.3
HSiCl ₃	cyclooctene	0.1	120	15	cy-C ₈ H ₁₅ SiCl ₂	30.0
HSiCl ₃	1,4-hexadiene	0.2	110	8		91.8
HSiCl ₃	acrylonitrile	0.1	120	8	CH ₂ CH(CN) SiCl ₃	40.0
HSiCl ₃	styrene	0.1	100	5	C ₆ H ₅ -CH(SiCl ₃) CH ₃	95.0
HSiCl ₂ Me	1-octene	0.1	120	6	n-C ₈ H ₁₇ SiMeCl ₂	90.5
HSiClMe ₂	1-octene	0.1	120	6	n-C ₈ H ₁₇ SiMe ₂ Cl	85.6
HSiMe ₃	1-octene	0.1	120	6	n-C ₈ H ₁₇ SiMe ₃	45.3
HSiEt ₃	1-octene	0.1	120	6	n-C ₈ H ₁₇ SiEt ₃	17.3
HSi(OMe) ₂ Cl	1-octene	0.1	120	6	n-C ₈ H ₁₇ Si(OMe) ₂ Cl	75.3
HSi(OMe) ₂ Cl	1-octene	0.1	120	6	n-C ₈ H ₁₇ Si(OMe) ₂ Cl	30.5
HSi(OMe) ₃	1-octene	0.1	120	6	n-C ₈ H ₁₇ Si(OMe) ₃	trace
HSiCl ₃	allene	0.1	120	5	CH ₂ =C(CH ₂) ₂ -SiCl ₃	70.6
HSiCl ₃	butadiene	0.1	100	5	CH ₃ SiCH ₂ CH ₂ CH ₂ SiCl ₃	10.5
HSiCl ₃	isoprene	0.1	110	6	CH ₃ CH=C(CH ₃)CH ₂ SiCl ₃	85
					Cl ₃ SiCH ₂ C(CH ₃)=CH-CH ₃	82.5
						3.5
HSiCl ₃	1,3-pentadiene	0.1	110	6	CH ₃ CH=CHCH(SiCl ₃) CH ₃	80.6
HSiCl ₃	1,3,7-octadiene	0.1	110	5	CH ₃ CH=CHCH(CH ₃)CH ₂ CH=CH ₂	82.3
HSiMeCl ₂	butadiene	0.1	110	6	CH ₃ CH=CHCH ₂ SiMeCl ₂	83.5
					CH ₃ CH=CHCH ₂ CH ₂ CH=CHCH ₂	5.2
HSiEt ₃	butadiene (excess)	0.1	120	6	CH ₃ CH=CHCH ₂ SiEt ₃	1.2
					CH ₃ CH=CHCH ₂ CH ₂ CH=CHCH ₂	95.3

*0.1 mol of olefin and 0.1 mol of silanes are used.

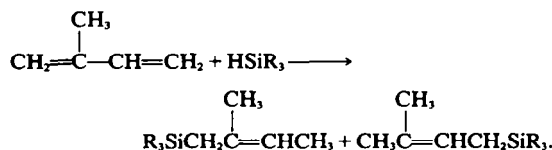
Table 2. Hydrosilylation of 1-octene (0.1 mol) with trichlorosilane (0.1 mol) catalyzed by various palladium catalysts

Catalyst (g)	Reaction temperature	time (h)	Yield (%)
PdCl ₂ (PPh ₃) ₂ (0.1)	120	5	90
PdBr ₂ (PEt ₃) ₂ (0.3)	80	10	65
PdI ₂ (PEt ₃) ₂ (0.1)	100	10	60.6
PdCl ₂ [P(OBu) ₃] ₂ (0.2)	120	10	20.5
PdCl ₂ [P(OPh) ₃] ₂ (0.2)	120	15	15.9
Pd(0.1) + PPh ₃ (1.0)	120	5	88.1
Pd(OAc) ₂ (0.1) + PBu ₃ (1.0)	120	10	75.6
Pd(0.1) + PBu ₃ (1.0)	120	10	53.5

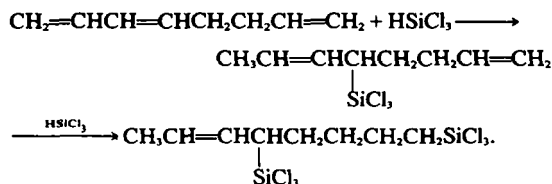
On the other hand, dimerization and hydrosilylation occurred simultaneously to give 1-trimethylsilyl-2,6-octadiene by the reaction of trimethylsilane.



A mixture of the 1:1 adduct (83.5%) and 1:2 adduct (5.2%) was obtained when dichloromethylsilane was used. It is well known that butadiene dimerizes with incorporation of nucleophiles to give 1-substituted 2,7-octadiene by using palladium triphenylphosphine complex as a catalyst.⁶ It should be noted that 2,6-octadiene, rather than 2,7-octadiene, was obtained with trimethylsilane and butadiene. Reaction of other conjugated dienes such as isoprene, 1,3,7-octatriene, 1,3-pentadiene with trimethylsilane gave the 1:1 adducts and no 1:2 adduct was formed. For example, isoprene gave 1-silylated 2-methyl-2-butene as a main product, accompanied by 3-methyl-2-butene.



1,3-Pentadiene afforded 2-silylated 3-pentene. The reactivity of conjugated dienes is higher than that of non-conjugated terminal olefins. For example, by the reaction of the 1:1 mixture of 1,3,7-octatriene and trichlorosilane, 4-trichlorosilyl-2,7-octadiene was obtained selectively. Further reaction with trichlorosilane gave the terminally silylated product.



A competitive reaction of an equimolar mixture of butadiene, 1-hexene and trichlorosilane gave 1-trichlorosilyl-2-butene almost exclusively. Higher reactivity of the conjugated diene is also apparent by catalytic species. Even in the absence of phosphine, hydrosilylation of butadiene proceeds. Palladium alone is moderately active, but addition of certain ligands activates the palladium catalyst. For this purpose ligands such as glyoxime, benzonitrile, 1,5-cyclooctadiene, norbornadiene can be used as the effective ligands of the palladium catalyst for the hydrosilylation of butadiene.

Reaction of allene with trichlorosilane at 120° for 5 h gave 1-trichlorosilyl-2-propene in 70% yield. Further reaction for 10 h afforded 1,3-di(trichlorosilyl)propane.

Mechanism of the hydrosilylation catalyzed by transition metal complexes has been proposed by Chalk and Harrod.² It is likely that the palladium-catalyzed hydrosilylation reactions reported in this paper also proceeds through the same mechanism by oxidative addition of hydrosilane to a low valent palladium phosphine complex, followed by the insertion of olefin. Divalent palladium compounds used in this reaction seem to be reduced to the low valent, catalytically active state by the action of hydrosilane. Active species formed from metallic palladium should be the same phosphine complex. We have confirmed that the reaction of metallic palladium, phosphine and excess trichlorosilane at 120° gave yellow crystals of bis(triphenylphosphine)palladium.⁷ The same complex was obtained also by the reaction of tetrakis(triphenylphosphine)palladium with trichlorosilane at 120°.

EXPERIMENTAL

Commercially available trichlorosilane and dichloromethylsilane were used after distillation. Chlorodimethylsilane and trimethylsilane were prepared by the reduction of dichlorodimethylsilane and chlorotrimethylsilane with lithium aluminium hydride.⁸ Triethylsilane was prepared by the Grignard reaction of trichlorosilane.⁹ Triethoxysilane was prepared by the reaction of trichlorosilane and ethanol.¹⁰ Trimethoxysilane, chlorodimethoxysilane and dichloromethoxysilane were synthesized by the reaction of trichlorosilane with methyl nitrite.¹¹

Only typical examples of the hydrosilylation are shown below. Structure determination, not shown specifically in the following, was carried out by comparing NMR and IR spectra with those of authentic samples. NMR spectra were taken on a Varian HA 100 spectrometer.

Reaction of 1-hexene with trichlorosilane. Trichlorosilane (6.77 g, 0.05 mole), 1-hexene (4.2 g, 0.05 mole) and Pd(PPh₃)₄ (0.1 g) were charged in a glass made pressure bottle and heated at 120° for 5 h. After the reaction, the mixture was distilled to give 9.9 g of 1-(trichlorosilyl)hexane at 87–89°/30 mm Hg. Identification was made by comparing its NMR and IR spectra with those of an authentic sample.

Reaction of cis-1,4-hexadiene with trichlorosilane. Reaction of trichlorosilane (13.5 g, 0.1 mole), cis-1,4-hexadiene (8.2 g, 0.1 mole) and Pd(PPh₃)₄ (0.2 g) was carried out at 110° for 8 h. Distillation of the reaction mixture gave 19.5 g of liquid at 85–90°/30 mm Hg. (Found; C, 33.08; H, 5.07; Cl, 48.96; C₆H₁₁SiCl₃ requires: C, 33.12; H, 5.10; Cl, 48.88). Gas chromatographic analysis showed that the product is composed of 3 components. IR bands at 1600, 966, 730 cm⁻¹ show the presence of cis and trans double bonds. Ozonization afforded acetaldehyde and propionaldehyde (confirmed by gas chromatography as dimethylacetal) in a ratio of 5:1. Also the treatment with methyl Grignard, followed by hydrogenation gave 1-(trimethylsilyl)hexane. From these data, it was concluded that the products were cis-1-(trichlorosilyl)-4-hexene, trans-1-(trichlorosilyl)-4-hexene and trans-1-(trichlorosilyl)-3-hexene.

Properties of other products are: 1-(trichlorosilyl)-2-butene—b.p. 140–142°. NMR: 8.92 (d, 3H), 8.03 (d, 2H), 3.2–4.2 (m, 2H); 1-(trichlorosilyl)-2-methyl-2-butene.

NMR: 8.36 (d, 3H), 8.15 (s, 3H), 7.63 (s, 2H), 4.54 (q, 1H); 5-(trichlorosilyl)-1,6-octadiene. b.p. 85–92°/10 mm Hg. (Found: C, 39.12; H, 5.15; Cl, 43.86; C₈H₁₃SiCl₃ requires: C, 39.44; H, 5.38; Cl, 43.66). NMR: 4.6 (m, 3H), 5.03 (d, 2H), 7.27 (m, 1H), 7.85 (m, 2H), 8.34 (q, 2H), 8.69 (d, 3H), 1-(triethylsilyl)-1,6-octadiene. b.p. 130–132°. (Found: C, 74.90; H, 12.49; mol. wt. 223 (benzene). C₁₄H₂₈Si requires: C, 74.91; H, 12.57; mol. wt., 224.5). NMR: 4.65 (m, 4H), 7.96 (m, 4H), 8.41 (d, 3H), 8.56 (d, 2H), 8.9–9.6 (m, 15H). IR: 3000, 2940, 1665, 965, 770, 735 cm⁻¹.

REFERENCES

- ¹T. Mitsuyasu and J. Tsuji, *Tetrahedron*, **7**, 831 (1974)
- ²A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.* **87**, 16 (1965)
- ³S. Takahashi, T. Shibano and N. Hagihara, *Chem. Commun.* 161 (1969)
- ⁴S. Takahashi, T. Shibano, H. Kojima and N. Hagihara, *Organometal. Chem. Synthesis*, **1**, 193 (1970)
- ⁵M. Hara, K. Ohno and J. Tsuji, *Chem. Commun.* 247 (1971)
- ⁶For a review of the palladium-catalyzed dimerization of butadiene; J. Tsuji, *Accounts Chem. Res.* **6**, 8 (1973)
- ⁷P. Fitton and J. E. McKeon, *Chem. Commun.* **4**, (1968); and J. A. Osborn, *Ibid.* 1231 (1968)
- ⁸S. Tannenbaum, S. Kaye and G. F. Lewenz, *J. Am. Chem. Soc.* **75**, 3753 (1953)
- ⁹F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, *Ibid.* **69**, 2108 (1947)
- ¹⁰M. Kumada and K. Tarama, *Kogyo Kagaku Zasshi* **54**, 769 (1951)
- ¹¹O. J. Klejnot, *Inorg. Chem.* **2**, 825 (1963)