Journal of Organometallic Chemistry, 134 (1977) C1—C5
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary Communication

STEREOCHEMISTRY OF THE REGIOSPECIFIC HYDROSILYLATION OF ISOPRENE CATALYZED BY A PHOSPHINE-PALLADIUM COMPLEX

IWAO OJIMA

Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara Kanagawa 229 (Japan)

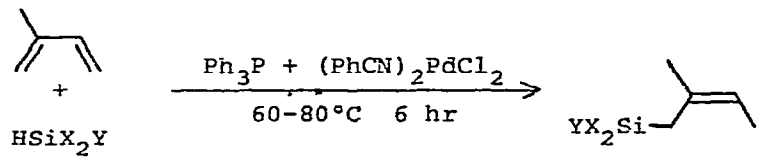
(Received March 8th, 1977)

Summary

Hydrosilylation of isoprene catalyzed by a palladium complex prepared *in situ* from triphenylphosphine and bis(benzonitrile)-palladium dichloride was studied. The reaction was found to proceed regioselectively and stereoselectively to give (Z)-2-methylbuten-2-ylsilane exclusively. The stereochemistry of the 2-methylbuten-2-ylsilane was elucidated on the basis of NMR spectroscopy, measuring the nuclear Overhauser effect. A possible mechanism of the reaction is proposed.

Recently, there have been several reports on the hydrosilylation of isoprene catalyzed by transition metal complexes [1,2]. The reaction was shown to involve formal 1,4-addition, giving 2-methylbuten-2-ylsilane as major product [1] except for the case of a platinum complex-catalyzed reaction which afforded the 1,2-adduct predominantly [2]. Although the regiospecificity of the 1,4-addition was demonstrated in these reports, less attention was given to the stereochemistry of the reaction. We describe here the stereochemistry of the regiospecific hydrosilylation of isoprene catalyzed by a phosphine-palladium complex and propose a possible mechanism of the reaction.

We have found that the hydrosilylation of isoprene catalyzed by a phosphine-palladium complex prepared *in situ* from triphenylphosphine and bis(benzonitrile)palladium dichloride, is highly regioselective and stereoselective, giving (Z)-2-methylbuten-2-ylsilane exclusively.



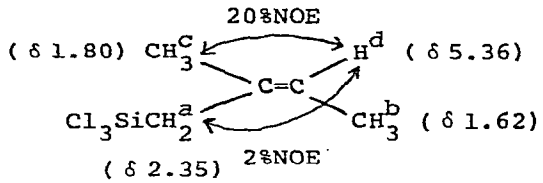
a) X = Y = Cl; b) X = Cl, Y = Me; c) X = Me, Y = Cl

Typically, dichloromethylsilane (33 mmol) was allowed to react with isoprene (30 mmol) in the presence of triphenylphosphine (40 mg, 0.15 mmol) and bis(benzonitrile)palladium dichloride (25 mg, 0.065 mmol) in a degassed sealed glass tube at 70°C for 6 hr. GLC analysis (3% OV-17) of the reaction mixture showed that the adduct was produced in quantitative yield. Distillation of the reaction mixture afforded 2-methylbuten-2-yldichloromethylsilane in 95% yield. Similarly, 2-methylbuten-2-yltrichlorosilane and 2-methylbuten-2-ylchlorodimethylsilane were obtained in excellent yield by the reaction of isoprene with trichlorosilane and chlorodimethylsilane, respectively. Other hydrosilanes such as triethoxysilane, phenyldimethylsilane and triethylsilane did not add to isoprene at all under similar conditions. GLC analysis and nmr spectra of these adducts clearly indicated that the reaction is extremely stereoselective, i.e., the adduct is not a mixture of Z and E isomer, but consists of the Z or the E isomer. The nmr data for 2-methylbuten-2-ylsilanes are listed in Table 1.

In order to elucidate the stereochemistry of 2-methylbuten-2-ylsilanes thus obtained, we measured the nuclear Overhauser effect (NOE) observed in the integration of the olefin proton H^d (quartet,‡

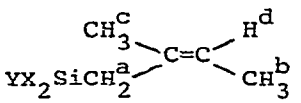
‡Small splittings arised from long range couplings are observed.

δ 5.36) by irradiating the methyl protons H^c (singlet, δ 1.80) or the methylene protons H^a (singlet, δ 2.35) of 2-methylbuten-2-yl-trichlorosilane. A relatively large NOE, 20% increase, was observed by the irradiation of H^c protons, while only a 2% NOE was observed in the case of H^a protons. Therefore, it is concluded without ambiguity that the adduct is the Z-isomer. As is seen from Table 1,



the methyl (H^b) appears as doublet at higher field than the methyl (H^c) does. This fact implies a certain shielding effect of the silylmethyl group on the methyl protons H^b.

Table 1. NMR data for (Z)-2-methylbuten-2-ylsilanes

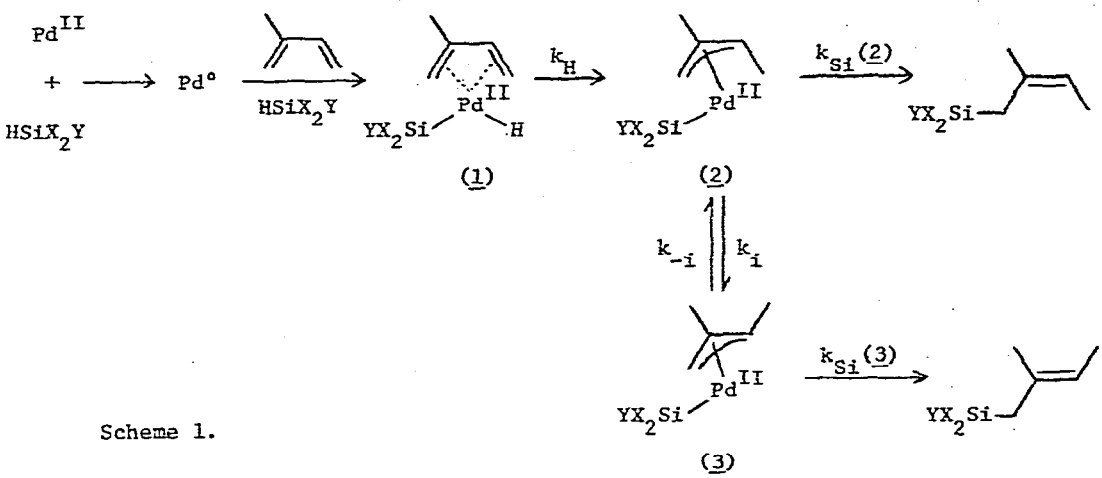


Silyl Group	Chemical Shift (δ, CCl_4)*			
	H^a	H^b	H^c	H^d
Cl_3Si	2.35	1.62	1.80	5.36
Cl_2MeSi	2.12	1.59	1.80	5.30
$ClMe_2Si$	1.82	1.53	1.72	5.18

* H^b appears as doublet (J = 7Hz) and H^d does as quartet (J = 7Hz).

A proposed mechanism of the reaction which accounts for the observed stereoselectivity is depicted in Scheme 1. It is reasonable to assume that the reaction proceeds through a π-allylic

intermediate of the type proposed previously for many catalytic reactions of dienes [3]. The results imply that the reaction involves an extremely regioselective hydride shift from an oxidative adduct (1) to the coordinated isoprene to produce the π-allylic silylpalladium complex (2). Subsequent silicon-carbon bond formation then gives (Z)-2-methylbuten-2-ylsilane as shown in Scheme 1.



Scheme 1.

If isomerization of the intermediate (2)[§] to the exo-methyl intermediate (3) is faster than the silicon migration, i.e., $k_i > k_{Si}(2)$, the adduct is a mixture of the Z and E isomers. However, our results clearly demonstrate that the silicon migration is much faster than the isomerization, i.e., $k_{Si}(2) >> k_i$, and thus the Z-isomer is formed exclusively.

[§] The occurrence of the interconversion of similar syn- and anti-forms of π-allylic silylnickel complexes was suggested by Čapka and Hetflejš [4].

REFERENCES

1. a) M. F. Lappert, J. A. Nile and S. Takahashi, J. Organometal. Chem., 72 (1974) 425; b) J. Tsuji, M. Hara and K. Ohno, Tetrahedron, 30 (1974) 2142; c) M. S. Wrighton and M. A. Schroeder, J. Amer. Chem. Soc., 96 (1974) 6235; d) Y. Kiso, M. Kumada, K. Tamao and M. Umeno, J. Organometal. Chem., 50 (1973) 297; e) V. Vaisarová, M. Čapka and J. Hetflejš, Syn. Inorg. Metal-Org. Chem., 2 (1972) 289.

2. a) K. Yamamoto, T. Hayashi and M. Kumada, J. Organometal. Chem., 28 (1971) C37; b) W. Fink, Helv. Chim. Acta, 54 (1971) 1304.

3. e.g., S. Takahashi, T. Shibano, H. Kojima and N. Hagihara, Organometal. Chem. Syn., 1 (1970/1971) 193; P. Heimbach, P. W. Jolly and G. Wilke, Advan. Organometal. Chem., 8 (1970) 29.

4. M. Čapka and J. Hetflejš, Coll. Czech. Chem. Commun., 40 (1975) 2073.