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THE REACTION OF VINYLSILANES WITH DICHLOROBIS(BENZONITRILE)PALLADIUM(II)

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It has been reported that allylsilane or -stannane readily reacts with certain transition metal compounds containing a halogen ligand to undergo cleavage of the silicon (or tin)-allyl bond, forming π-allylic-metal complexes (metal = Pd[1] and Mn[2]). We have independently been engaged in the same subject of research in which reactions of allyl and vinyl compounds of Group IV elements with dichlorobis(benzonitrile)palladium(II)[3] (1) in benzene solution are examined. Thus, allyltrimethylsilane was found to react with 1 in three days to give known bis($\underline{h}^3$-allyl)-μ-dichlorodipalladium(II) in 87% yield along with trimethylchlorosilane. Germanium and tin analogs similarly underwent cleavage in the presence of 1, and relative rates of the reaction decreased in the order of Sn > Ge > Si[4].

Vinylsilane or -stannane may coordinate to copper(I) chloride[5] or to Zeise's salt[6] to form fairly stable complexes, and a reaction of β-trimethylsilylstyrene with palladium(II) chloride has also been reported[7]. These studies prompted us to report our own results on the reaction of a variety of vinyl derivatives of Group IV elements with 1.

To a red-brown solution of 1 (0.24 g, 0.63 mmol) in 5 ml of dry benzene was added under argon atmosphere 2.0 ml (ca. 13 mmol) of trimethylvinylsilane. The mixture immediately turned dark-brown, and was allowed to stand at room temperature for 20 h. Then, the palladium metal precipitates (43 mg; 64% recovery from 1) were filtered off and the yellow filtrate was concentrated to a minimum volume. To the residual oil was added 5 ml of light petroleum ether to precipitate fine yellow solid, the latter being washed with three 5 ml-portions of petroleum ether and dried under vacuum. The product (43.5 mg) was characterized as follows: Mp 184°

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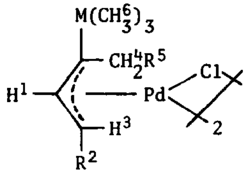
(decomp.); Anal. Calcd. as $C_7H_{15}ClPdSi$: C, 31.24; H, 5.62; Cl, 13.17. Found: C, 31.31; H, 5.74; Cl, 13.11%; NMR ($CDCl_3$, TMS as an internal standard) δ 0.22[*s*, $(CH_3)_3Si$], 1.10[*s*, CH_3], 3.43[*d*, *J* 12.6 Hz, H^3], 4.06[*d*, *J* 7.2 Hz, H^2], and 5.23ppm[double *d*, *J* 12.6 and 7.2 Hz, H^1]. All data indicate that the sole product (26% yield) is bis[*h*^{3}-1-(trimethylsilyl)-1-methylallyl]-μ-dichlorodipalladium(II) (**2a**), in which the trimethylsilyl group is tentatively assigned to the *syn*-position (see Scheme 1).

Trimethylvinylgermane also afforded the same type of π-allylic-palladium complex **2b**. Furthermore, trimethylpropenylsilane and β-trimethylsilylstyrene were found to undergo the reaction to give similar complexes, **3** and **4**, while an isopropenyl- or α-phenylvinylsilane derivative did not yield any isolable complex but resulted in complicated decomposition. Melting points and NMR data of these π-allylic-palladium complexes are given in Table 1.

Table 1.

NMR Data for New π-Allylic Palladium Complexes (60 MHz, $CDCl_3$).

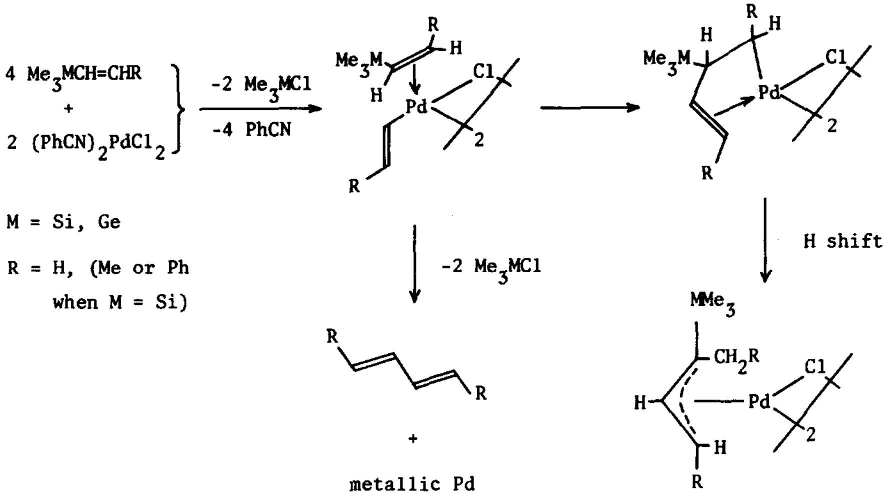


Olefin	Complex[a]	Yield[b] (%)	Mp (°C)	Chemical Shifts: (multiplicity), H^1	R^2	H^3	H^4	R^5	H^6
$Me_3SiCH{=}CH_2$	**2a** ($R^2{=}R^5{=}H$, M=Si)	26	183	5.29(q)	4.06(q)	3.43(q)	1.10(s)	1.10(s)	0.22(s)
$Me_3GeCH{=}CH_2$	**2b** ($R^2{=}R^5{=}H$, M=Ge)	30	181	5.60(q)	3.80(q)	2.93(q)	1.41(s)	1.41(s)	0.42(s)
$Me_3SiCH{=}CHMe$ (*cis*)	**3** ($R^2{=}R^5{=}Me$, M=Si)	21	135	5.05(d)	1.33(d)	4.06 ∿ 4.58(m)	1.4 ∿ 1.8(m)	0.8 ∿ 1.1(b.t)	0.25(s)
$Me_3SiCH{=}CHPh$ (*trans*)	**4** ($R^2{=}Ph$, $R^5{=}H$, Ph instead of MMe_3)	19	187	5.47(d)	7.2 ∿ 7.3(m)	4.47(d)	1.49(s)	1.49(s)	7.2 ∿ 7.3(m)[c]

[a] All complexes gave correct elemental analyses. [b] Based on 1 used. [c] Phenyl protons.

Although yields of the new π-allylic palladium complexes were generally low owing to much deposition of palladium metal, their structure assigned reveals some interesting feature of the reaction, which may be outlined as Scheme 1, except for β-trimethylsilylstyrene[8].

It is likely to assume that the addition of palladium chloride across the double bond takes place in such a direction as to leave a transient σ-vinyl palladium complex, as a result of known facile β-elimination of Me_3MCl from β-chloroethyl derivative of Group IV elements in the resultant adduct. The insertion of the olefinic function of the second vinylic compound into the palladium-



Scheme 1

carbon σ-bond[8] has ample precedents as a key step in the homogeneously catalyzed dimerization reactions of unsaturated hydrocarbons[9].

In the present case, a hydrogen shift would follow the insertion to give the final π-allylic-palladium complexes, because α-substituted vinylsilane derivatives could not form any isolable complex. Related reactions involving coupling of α-olefins and disubstituted acetylenes to form a β-chlorovinyl-palladium bond have been reported[10].

Finally, Felix et al.[7] have reported that β-trimethylsilylstyrene reacts with palladium chloride in methanol to give trans,trans-1,4-diphenyl-1,3-butadiene in a 52% yield, assuming a consecutive chloropalladation of the vinyl compound with $PdCl_2$ to form bis(σ-vinyl)palladium intermediate. Therefore, the extensive deposition of metallic palladium in the present reaction may be indicative of the butadiene formation, though we have not pursued such product but the π-allylic-palladium complexes. The latter may have only been observable in non-polar solvent as a result of olefin-insertion into a carbon-palladium σ-bond competing with that into a chlorine-palladium linkage.

References and Notes

1) J. M. Kliegman, J. Organometal. Chem., 29, 73 (1971).

2) E. W. Ebel and S. Moorhouse, Angew. Chem., 83, 360 (1971); J. Chem. Soc. Dalton, 1706 (1973).

3) The complex 1 can be conveniently regarded as simply a source of soluble $PdCl_2$.

4) It is very likely that coordination of the allylic moiety to palladium is essential for the nucleophilic attack of the chloro-ligand on the silicon (germanium and tin) atom. The observed rate order is of interest in this respect.

5) J. W. Fiter, D. P. Flores, and J. E. George, *J. Organometal. Chem.*, **29**, 263 (1971).

6) E. M. Haschke and J. W. Fitch, *J. Organometal. Chem.*, **57**, C93 (1973).

7) W. P. Weber, R. A. Felix, A. K. Willard, and K. E. Koenig, *Tetrahedron Lett.*, 4701 (1971).

8) In the case of β-trimethylsilylstyrene, the insertion reaction took place with inverse direction to that indicated in the Scheme, resulting in the formation of π-[1,3-diphenyl-1-(trimethylsilylmethyl)allyl] complex, which in turn be very sensitive to miosture to give bis(h^3-1,3-diphenyl-1-methylallyl)-μ-dichlorodipalladium(II) (**4**).

9) P. N. Maitlis, "The Organic Chemistry of Palladium", Vol. 2, Academic Press, New York, 1971.

10) (a) T. Hosokawa, I. Moritani, and S. Nishioka, *Tetrahedron Lett.*, 3833 (1969).
(b) P. Mushak and M. A. Battiste, *Chem. Commun.*, 1146 (1969).