CHEMISTRY LETTERS, pp. 1663-1666, 1982. © The Chemical Society of Japan 1982

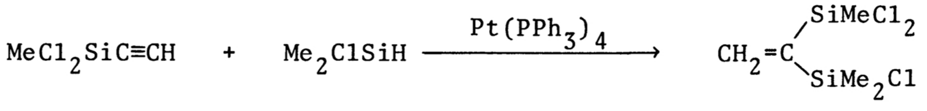
UNUSUAL REGIOSELECTIVE HYDROSILYLATION OF ETHYNYLMETHYLDICHLOROSILANE WITH DIMETHYLCHLOROSILANE CATALYZED BY TETRAKIS(TRIPHENYLPHOSPHINE)-PLATINUM(0)

Hideyuki MATSUMOTO*, Yoshikazu HOSHINO, and Yoichiro NAGAI*
Department of Chemistry, Gunma University, Kiryu, Gunma 376

The hydrosilylation of ethynylmethyldichlorosilane with dimethylchlorosilane catalyzed by tetrakis(triphenylphosphine)-platinum(0) was found to show quite an unusual regioselectivity to afford the geminal product, 1-(methyldichlorosilyl)-1-(dimethylchlorosilyl)ethene, almost exclusively.

Regioselective hydrosilylation of ethynylsilanes are one of the most attractive routes to bis(silyl)ethenes which have recently found much synthetic application.[1)] Previous workers demonstrated that the chloroplatinic acid-catalyzed reaction generally involved <u>cis</u>-vicinal addition to give (E)-1,2-bis(silyl)ethenes.[2)] For instance, Birkofer and Khün reported that the reaction of ethynyltrimethylsilane with dimethylchlorosilane in the presence of the platinum(IV) catalyst afforded (E)-1-(dimethylchlorosilyl)-2-(trimethylsilyl)ethene in 66% yield.[2f)] Regioselective formation of 1,1-bis(silyl)ethenes by the corresponding hydrosilylation, however, has not yet been reported, although Yarosh and coworkers showed that the reaction of ethynylalkoxysilanes with trialkylsilanes catalyzed by chloroplatinic acid gave 47:53-58:42 mixtures of 1,1- and 1,2-bis(silyl)ethenes.[3)]

It occurred to us that such a regioselective hydrosilylation can be achieved by the careful selection of both the silicon-substituents on the reactants and the transition-metal catalyst. We report here our finding that the reaction of ethynylmethyldichlorosilane with dimethylchlorosilane in the presence of tetrakis-(triphenylphosphine)platinum(0) showed quite an unusual regioselectivity to afford the geminal product, 1-(methyldichlorosilyl)-1-(dimethylchlorosilyl)ethene, almost exclusively.



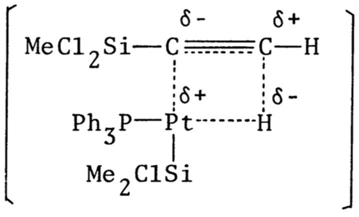
$$\mathrm{MeCl_2SiC{\equiv}CH} + \mathrm{Me_2ClSiH} \xrightarrow{\mathrm{Pt(PPh_3)_4}} \mathrm{CH_2{=}C}\begin{matrix}\diagup \mathrm{SiMeCl_2} \\ \diagdown \mathrm{SiMe_2Cl}\end{matrix} \qquad (1)$$

(96% regioselectivity)

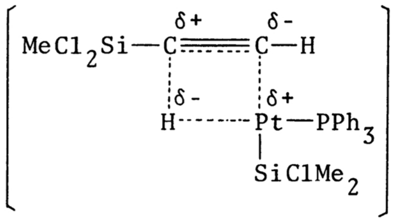
Thus, a toluene solution of ethynylmethyldichlorosilane[4)] (1.43 g, 10.2 mmol) and dimethylchlorosilane (1.30 g, 13.7 mmol) was heated with the platinum(0) complex (0.12 g, 0.11 mmol) at 120°C for 10 h in a sealed stainless steel reaction vessel. GLC analysis of the resulting mixture disclosed that the reaction had given the 1:1 addition products (95% yield) which was found to consist of 96% 1-(methyldichlorosilyl)-1-(dimethylchlorosilyl)ethene $\underline{1}$ and 4% (E)-1-(methyldichlorosilyl)-2-(dimethylchlorosilyl)ethene $\underline{2}$. Compound $\underline{1}$: NMR (CCl_4) δ 0.61 (s, 6H, $SiMe_2Cl$), 0.92 (s, 3H, $SiMeCl_2$), 6.75 (d, 1H, J = 3 Hz, C=C$\underline{H}$H), and 6.80 (d, 1H, J = 3 Hz, C=CH$\underline{H}$); IR (neat) 3025 (w, $C=CH_2$), 1565 (w, C=C), and 1265 cm^{-1} (s, SiMe); SiMe); Mass (15 eV) m/e 232 (M^+). Compound $\underline{2}$: NMR (CCl_4) δ 0.55 (s, 6H, $SiMe_2Cl$), 0.88 (s, 3H, $SiMeCl_2$), 6.58 (d, 1H, J = 22 Hz, C$\underline{H}$=CH), and 7.01 (d, 1H, J = 22 Hz, CH=C$\underline{H}$); IR (neat) 1262 (s, SiMe) and 998 cm^{-1} (m, (E)-CH=CH); Mass (15 eV) m/e 232 (M^+). The structure of each regioisomer was further confirmed on a basis of a comparison of its physical properties with those of an authentic sample prepared according to literatures[2f, 5)] after treatment with methylmagnesium bromide.

For comparison purposes, ethynylmethyldichlorosilane was allowed to react with dimethylchlorosilane in the presence of chloroplatinic acid. It was thus found that the reaction had afforded (E)-1,2-bis(silyl)ethene $\underline{2}$ in 94% yield. Further, the reaction in the presence of chlorotris(triphenylphosphine)rhodium(I), which have received much interest as a selective hydrosilylation catalyst,[6)] resulted in the formation of a 40:60 mixture of the geminal product $\underline{1}$ and the vicinal product $\underline{2}$ (85% combined yield).

In view of the mechanism proposed for the hydrosilylation of alkynes catalyzed by low-valent platinum complexes,[7)] it is reasonable to assume that the product determining step of the present reaction involves the hydride-shift from the silylplatinum(II) hydride complex to the coordinated ethynylmethylchlorosilane, for which two regioisomeric transition states can be depicted, depending upon the orientation of the platinum-hydrogen bond relative to the carbon-carbon triple bond, as follows.



(A)



(B)

It is thus suggested that the regioselectivity of this step should strongly depend upon the electronic nature of the ethynylsilane. The ^{13}C NMR chemical shifts of the ethynylsilanes, $Me_{3-n}Cl_nSiC{\equiv}CH$, measured in the present study (see Table 1) diclose that chlorine atom on the silicon significantly decreases the electron density on the C(2) carbon, perhaps due to the strong pπ-dπ interaction.[8)]

$$\mathrm{MeCl_2Si{-}C{\equiv}CH \longleftrightarrow MeCl_2\overset{-}{Si}{=}C{=}\overset{+}{C}H}$$

Thus, nucleophilic attack by the hydride favors transition state A leading to the geminal product <u>1</u> rather than another one, B.

Table 1. ^{13}C NMR Chemical Shifts for Ethynylsilanes $\mathrm{Me_{3-n}Cl_nSiC^1{\equiv}C^2H}$ ^{a}

n	δ, ppm C(1)	 C(2)	Δδ[C(2)-C(1)]
0	90.0	93.0	3.0
1	85.8	95.3	9.5
2	83.0	96.5	13.5

^{a}Recorded in CCl_4 solution with Me_4Si as an internal standard.

This explanation may be supported by the fact that the successive substitution of the electron-donating group, e.g., methyl, for chlorine atom in the ethynylsilane led to the decrease of the geminal selectivity. For instance, the reaction of ethynyldimethylchlorosilane or ethynyltrimethylsilane with dimethylchlorosilane in the presence of the platinum(0) complex afforded a 57:43 or 20:80 mixture of the 1,1- and (E)-1,2-bis(silyl)ethenes, respectively.

Further, dependency of regioselectivity on the structure of the hydrosilane was also observed. The reaction of ethynylmethyldichlorosilane with methyldichlorosilane catalyzed by the platinum(0) complex produced a 43:57 mixture of 1,1- and (E)-1,2-bis(methyldichlorosilyl)ethenes, whereas the hydrosilylation with dimethylchlorosilane showed 96% geminal selectivity (cf. eqn. 1). The result again emphasizes the prominent role of the electronic effect in determining the regioselectivity.

Finally, it is noted that the regioselective hydrosilylation of ethynylmethyldichlorosilane with dimethylchlorosilane can be also performed in a preparative-scale experiment. Thus, a 94:6 mixture of the geminal product <u>1</u> and the vicinal product <u>2</u> was obtained in 70% isolated yield, using 0.1 mole quantity of the reactants. The result indicates that the present system may open a direct and quick route to 1,1-bis(silyl)ethenes, which were hitherto obtained only with methods involving multi-step sequences.[5,9)]

References

1) E. W. Colvin, "Silicon in Organic Synthesis," Butterworhts, London (1981), pp. 44.

2) (a) V. F. Mironov and V. V. Nepmnina, Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk, <u>1960</u>, 1419; Chem. Abstr., <u>55</u>, 358 (1961); (b) M. F. Shostakovskii,

N. V. Kamarov, O. G. Yarosh, and L. V. Balashenko, Izv. Akad. Nauk SSSR, Ser. Khim., 1971, 1478; Chem. Abstr., 75, 98618 (1971); (c) M. G. Voronkov, O. G. Yarosh, L. V. Tsvetaeva, M. V. Sigalov, and R. A. Gromkova, Zh. Obshch. Khim., 44, 1747 (1974); Chem. Abstr., 82, 4353 (1975); (d) M. G. Voronkov, O. G. Yarosh, V. A. Pestunovich, M. V. Sigalov, and L. V. Tsvetaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 1974, 2066; Chem. Abstr., 82, 43502 (1975); (e) M. G. Voronkov, L. V. Shchukina, O. G. Yarosh, and E. O. Tsetlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 1874; Chem. Abstr., 86, 55511 (1977); (f) L. Birkofer and Th. Khün, Chem. Ber., 111, 3119 (1978).

3) O. G. Yarosh, N. V. Komarov, and Z. G. Ivanova, Izv. Akad. Nauk SSSR, Ser. Khim., 1972, 2751; Chem. Abstr., 78, 111420 (1973).

4) H. Matsumoto, T. Kato, I. Matsubara, Y. Hoshino, and Y. Nagai, Chem. Lett., 1979, 1287.

5) J. Cudlín and V. Chvalovský, Coll. Czech. Chem. Comm., 27, 974 (1962).

6) For reviews, see (a) J. L. Speier, Adv. Organometal. Chem., 17, 407 (1979); (b) I. Ojima and T. Kogure, Rev. Silicon, Germanium, Tin, and Lead Compd., 5, 8 (1981).

7) (a) A. J. Chalk and J. F. Harrod, J. Am. Chem. Soc., 87, 16 (1965); (b) M. Green, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, J. Chem. Soc. Dalton, 1977, 1519, 1525; (c) C. A. Tsipis, J. Organometal. Chem., 187, 427 (1980).

8) (a) A. G. Proidakov, A. G. Kalabin, R. G. Mirskov, N. P. Ivanova, and A. L. Kuznetsov, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 94; Chem. Abstr., 89, 23297 (1978); (b) K. Kamienska-Trela, J. Organometal. Chem., 159, 15 (1978).

9) (a) A. D. Petrov, V. F. Mironov, and V. G. Glukhovtsev, Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1956, 461; Chem. Abstr., 50, 16663 (1956); (b) G. Fritz and J. Grobe, Z. anorg. allg. Chem., 309, 98 (1961); (c) H. Bock and H. Seidl, J. Organometal. Chem., 13, 87 (1968); (d) B.-Th. Grobel and D. Seebach, Chem. Ber., 110, 852 (1977).

(Received August 5, 1982)