Journal of Organometallic Chemistry, 363 (1989) C1–C3
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 9717PC

Preliminary communication

Silicon–carbon unsaturated compounds

XXIII *. Transition-metal-catalyzed formation of silenes from vinyldisilanes

Mitsuo Ishikawa *, **Takatoshi Ono, Yukitami Saheki,**
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724 (Japan)

Akio Minato,
Kyoto Pharmaceutical University, Yamashina, Kyoto 607 (Japan)

and Hiroshige Okinoshima
Shin-etsu Chemical Co., Ltd., Isobe, Gunma 379 (Japan)

(Received December 14th, 1988)

Abstract

Heating pentamethylvinyldisilane in the presence of a nickel(0) catalyst at 220 ° C gave a dimer, (*E*)-1-[2-(pentamethyldisilanyl)ethyl]dimethylsilyl-2-(trimethylsilyl)-ethene (**2**), via a nickel-silene complex. Similar reaction of 1-phenyl-1-vinyltetramethyldisilane and 1,1-diphenyl-1-vinyltrimethyldisilane afforded the respective dimers analogous to **2**.

During the course of our investigation concerning the transition-metal-catalyzed formation of reactive silicon unsaturated compounds [1,2], we have found that treatment of vinyldisilanes with a catalytic amount of a nickel(0) complex leads to novel dimerization products, presumably via a nickel-silene complex, arising from rearrangement of a silyl group to the terminal carbon of a vinyl group. Thus, when 0.186 g (1.2 mmol) of pentamethylvinyldisilane (**1**) was heated with 50 mg (9.4×10^{-2} mmol) of tetrakis(triethylphosphine)nickel(0) in a degassed sealed glass tube at 220 ° C for 30 h, (*E*)-1-[2-(pentamethyldisilanyl)ethyl]dimethylsilyl-2-(trimethylsilyl)ethene (**2**) was obtained in 36% yield as a single isomer. No other isomers were detected by either GLC or spectroscopic analysis. Compound **2** could readily be isolated by preparative GLC. The structure of **2** was confirmed by IR, mass, and ^{1}H and ^{13}C NMR spectroscopic analysis *. The proton coupling constants (J 22 Hz) at δ 6.54 and 6.62 ppm, due to olefinic protons for **2**, clearly indicates that **2** must have the (E)-configuration. That the nickel catalyst plays an important role for the formation of **2** can be shown by the fact that heating **1** in the absence of the nickel catalyst under the same conditions afforded no dimerization product, but the starting **1** was recovered unchanged.

It was shown that the present nickel-catalyzed dimerization is a general reaction for vinyldisilanes. Thus, treatment of 1-phenyl-1-vinyltetramethyldisilane (**3**) and 1,1-diphenyl-1-vinyltrimethyldisilane (**5**) with a nickel(0) catalyst under the same conditions gave (E)-1-[2-(1-phenyltetramethyldisilanyl)ethyl]methylphenylsilyl-2-(trimethylsilyl)ethene (**4**) and (E)-1-[2-(1,1-diphenyltrimethyldisilanyl)ethyl]diphenylsilyl-2-(trimethylsilyl)ethene (**6**) in 45 and 44% yields, respectively. The structures of **4** * and **6** ** were confirmed by mass, IR, and ^1H and ^{13}C NMR spectroscopic analysis.

In order to establish the configuration of **4** and **6**, we prepared these compounds by an independent route. Thus, addition of [2-(1-phenyltetramethyldisilanyl)ethyl]-methylphenylsilane to ethynyltrimethylsilane in the presence of a catalytic amount of chloroplatinic acid gave a hydrosilylation product in 90% yield, while similar reaction of [2-(1,1-diphenyltrimethyldisilanyl)ethyl]diphenylsilane with ethynyltrimethylsilane afforded an adduct in 50% yield. All spectral data obtained for these products were identical with those of **4** and **6**, respectively. Since the addition of an Si–H bond to a triple bond proceeds in a *cis* fashion, the resulting hydrosilylation products should have the (E)-configuration [3].

Scheme 1 illustrates a possible mechanistic interpretation for the formation of the dimerization products. The mechanism involves the nickel-catalyzed isomerization of the vinyldisilane to a silene-nickel complex (**A**), followed by C–H activation by the nickel atom leading to π-silapropenyl complex (**B**). The regiospecific addition of the nickel–hydrogen bond across the carbon–carbon double bond of the coordinated vinyldisilane, followed by reductive elimination gives the dimer. On steric grounds, the (E)-configuration is more favorable than the (Z)-configuration.

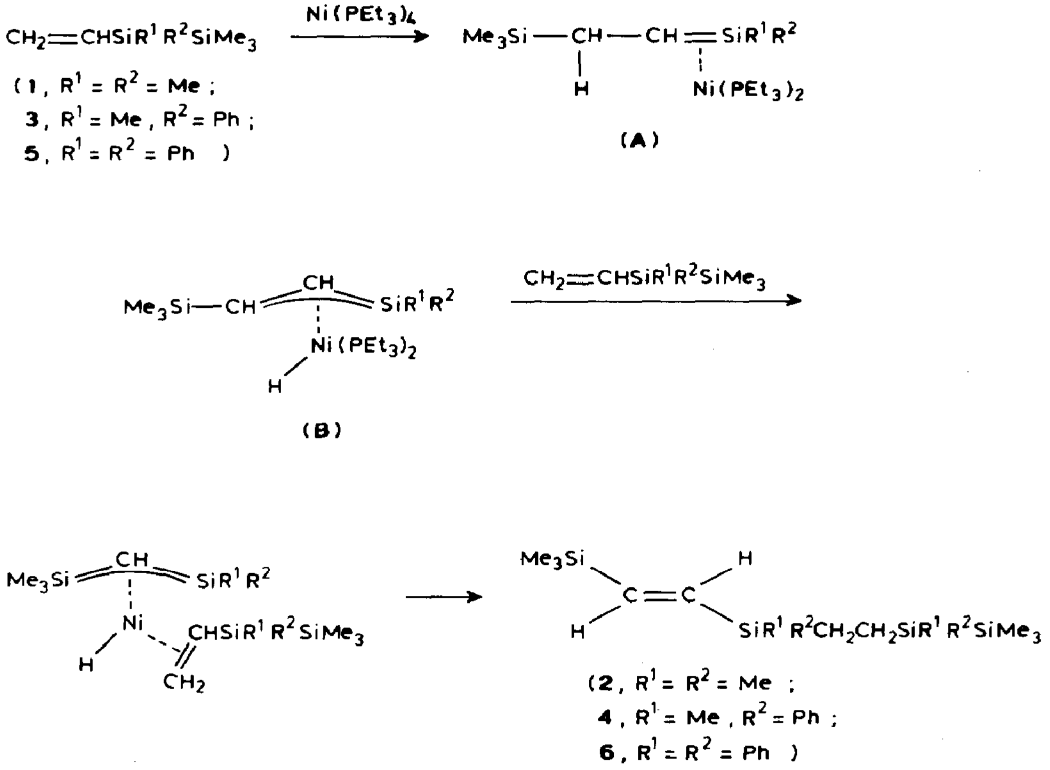
Similar reaction using vinylmonosilanes, however, afforded no dimerization products; heating a mixture of dimethylphenylvinylsilane and a 5 mole% of the

---

* Compound **2**: Mass m/e 243($M^+ - 73$); IR 1050, 1130, 1170, 1435, 1405 cm^{-1}; ^1H NMR (ppm in $CDCl_3$) 0.02(s, 6H, Me_2Si), 0.05(s, 6H, Me_2Si), 0.06(s, 9H, Me_3Si), 0.07(s, 9H, Me_3Si), 0.47(s, 4H, CH_2CH_2), 6.54(d, 1H, HC=C, J 22 Hz), 6.62(d, 1H, HC=C, J 22 Hz); ^{13}C NMR (ppm in $CDCl_3$) −4.68(Me_3Si), −4.00(Me_3Si), −1.88 (Me_2Si), −1.59(Me_2Si), 6.81(CH_2), 8.23(CH_2), 149.52, 151.50(olefinic carbons). Anal. Found: C, 52.96; H, 11.19. $C_{14}H_{36}Si_4$ calcd.: C, 53.16; H, 11.39%.

** Compound **4**: Mass m/e 440(M^+); IR 1010, 1050, 1105, 1130, 1170, 1243, 1405 cm^{-1}; ^1H NMR (ppm in $CDCl_3$) 0.06(s, 9H, Me_3Si), 0.09(s, 9H, Me_3Si), 0.33(s, 3H, MeSi), 0.34(s, 3H, MeSi), 0.80(s, 4H, CH_2CH_2), 6.70(s, 2H, olefinic protons), 7.3–7.5 (m, 10H, phenyl ring protons); ^{13}C NMR (ppm in $CDCl_3$) −6.72(MeSi), −5.57(MeSi), −1.68(Me_3Si), −1.59(Me_3Si), 5.49(CH_2), 7.04(CH_2), 127.70, 127.72, 128.28, 128.89, 134.09, 134.21, 137.73, 138.50(phenyl ring carbons), 146.58, 154.00 (olefinic carbons). Anal. Found: C, 65.39; H, 9.22. $C_{24}H_{40}Si_4$ calcd.: C, 65.45; H, 9.09%.

*** Compound **6**: Mass m/e 549($M^+ - 15$); IR 1010, 1050, 1103, 1130, 1170, 1245, 1405, 1425, 1490 cm^{-1}; ^1H NMR (ppm in $CDCl_3$) 0.11(s, 9H, Me_3Si), 0.16(s, 9H, Me_3Si), 1.17(s, 4H, CH_2CH_2), 6.69(d, 1H, HC=C, J 23 Hz), 6.98(d, 1H, HC=C, J 23 Hz), 7.2–8.0(m, 20H, phenyl ring protons); ^{13}C NMR (ppm in $CDCl_3$) −1.59(Me_3Si), −0.96 (Me_3Si), 5.14(CH_2), 6.40(CH_2), 127.80, 128.68, 129.22, 134.62, 135.31, 135.69, 136.34(phenyl ring carbons), 143.99, 156.82(olefinic carbons). Anal. Found: C, 72.25; H, 7.80. $C_{34}H_{44}Si_4$ calcd.: C, 72.34; H, 7.80%.



Scheme 1.

nickel(0) complex under the same conditions gave no product. The starting vinylsilane was recovered unchanged.

Acknowledgement. This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (Advanced Molecular Conversion) to which the authors' thanks are due. We also express our appreciation to Shin-etsu Chemical Co. Ltd., Nitto Electric Industrial Co. Ltd., and Dow Corning Japan Ltd. for financial support.

References

1 M. Ishikawa, S. Matsuzawa, T. Higuchi, S. Kamitori, K. Hirotsu, Organometallics, 4 (1985) 2040.
2 M. Ishikawa, J. Ohshita, Y. Ito, J. Iyoda, J. Am. Chem. Soc., 108 (1986) 7417.
3 J.L. Speier, Adv. Organomet. Chem., 17 (1970) 407.