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Platinum complex catalyzed double silylation of ethylene and norbornene with disilanes

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thetic transformations. Our results will be published in due course.

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Registry No. **2a**, 78-94-4; **2b**, 1629-58-9; **2c**, 814-78-8; **2d**, 2497-21-4; **2e**, 94-41-7; **2f**, 89-82-7; **2g**, 5597-27-3; **2h**, 930-68-7; **3a** (coordinated), 123992-97-2; **3a** (noncoordinated), 59586-09-3; **3b** (coordinated), 123992-98-3; **3b** (noncoordinated), 123992-87-0; **3c** (coordinated), 123992-99-4; **3c** (noncoordinated), 95244-27-2; **3d** (coordinated), 123993-00-0; **3d** (noncoordinated), 123992-88-1; **3e** (coordinated), 123993-01-1; **3e** (coordinated isomer 1), 123993-02-2; **3f** (coordinated isomer 2), 124095-67-6; **3f** (noncoordinated isomer 1), 123992-91-6; **3f** (noncoordinated isomer 2), 124095-64-3; **3g** (coordinated), 123993-03-3; **3g** (noncoordinated), 123992-90-5; **4a**, 6322-49-2; **5a**, 98746-44-2; **5b**, 123992-92-7; **5c**, 123992-93-8; **5d**, 123992-94-9; **5e**, 123992-95-0; **5f** (isomer 1), 124095-65-4; **5f** (isomer 2), 124095-66-5; **5g**, 123992-96-1; $SnCl_2 \cdot 2H_2O$, 10025-69-1; $HSnCl_3$, 20265-43-4.

Supplementary Material Available: Listings of spectroscopic and analytical data for all compounds listed in Table I (6 pages). Ordering information is given on any current masthead page.

Platinum-Complex-Catalyzed Double Silylation of Ethylene and Norbornene with Disilanes

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Summary: Double silylation of ethylene with disilanes was found to proceed in the presence of platinum phosphine complexes to give 1,2-bis(silyl)ethanes. The reactivity was enhanced by electronegative and sterically less demanding substituents on the silicon atom. The reaction of norbornene suggested cis addition of disilanes to the C=C bond.

Exploitation of silicon-containing polymers has been a subject of growing interest owing to their physical properties and chemical reactivities.[1] In this respect, double silylation of unsaturated carbon compounds with disilanes appears to be a good prospect since it provides a convenient way to synthesize α,ω-bis(silyl) compounds that are possible monomers for silicon-containing polymers. Thus, acetylenes and 1,3- and 1,2-dienes successfully undergo double silylation with disilanes to give 1,2-bis(silyl)ethenes, 1,4-bis(silyl)-2-butenes, and 2,3-bis(silyl)-1-propenes, respectively.[2] In addition, very recent publications by Ito et al. have disclosed insertion of isocyanides into Si–Si linkages, a new useful variation of double silylation.[3] In spite of the renewed interest along this line, however, successful double silylation of simple olefinic compounds has never been reported. Now, we have found that double silylation of ethylene with disilanes proceeds in the presence of platinum phosphine complexes to give 1,2-bis(silyl)ethanes.

Table I. Catalytic Double Silylation of Ethylene with $XMe_2SiSiMe_2X$ in the Presence of $Pt(PPh_3)_4$[a]

X	electroneg of X	yield/%[b]	X	electroneg of X	yield/%[b]
F	3.93	95.0	p-$CF_3C_6H_4$		16.4
CH_3O	3.70	52.6	C_6H_5	2.70	4.3
Cl	3.19	48.7	p-$CH_3C_6H_4$		3.8
CH_3	2.30	18.0			

[a] Conditions: $XMe_2SiSiMe_2X$, 1 mmol; $Pt(PPh_3)_4$, 0.04 mmol; benzene, 3 mL; ethylene, 5 atm at room temperature; 150 °C; 22 h. [b] GC yield.

In a typical experiment, a benzene (3 mL) solution of 1,2-difluoro-1,1,2,2-tetramethyldisilane (1 mmol) and $Pt(PPh_3)_4$ (0.04 mmol) was treated with ethylene (5 atm at room temperature) in an autoclave (27 mL) at 150 °C for 22 h. GC analysis showed that 1,2-bis(fluorodimethylsilyl)ethane was formed in 95.0% yield. The product was phenylated (80.0% GC yield) with phenyllithium, and 1,2-bis(dimethylphenylsilyl)ethane[4] was isolated in 68.5% yield.

$$\mathrm{XMe_2SiSiMe_2X} + \mathrm{CH_2{=}CH_2} \xrightarrow{[\mathrm{Pt}]} \mathrm{XMe_2SiCH_2CH_2SiMe_2X} \quad (1)$$

Other *sym*-tetramethyldisilanes were also subjected to the reaction. The results summarized in Table I reveal that disilanes with more electronegative groups attached to the silicon atom more readily underwent the double-silylation reaction, as was observed with palladium catalysts in the reactions of acetylenes or dienes.[2b–e,j,k] Steric factors also appear to be important, since 1,1,2,2-tetramethyl-1,2-diphenyldisilane, which should have been more reactive than hexamethyldisilane in view of the higher electronegativity of the phenyl group, in fact exhibited very low reactivity. The enhanced reactivity of 1,2-bis(p-(trifluoromethyl)phenyl)tetramethyldisilane as compared with that of the parent phenyl analogue is again associated with the trifluoromethyl group being strongly electron withdrawing.

The performance of the platinum complexes in the double silylation of ethylene with 1,1,2,2-tetramethyl-1,2-diphenyldisilane was improved when a more electron donating and sterically less demanding ligand was used; i.e.,

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(1) (a) West, R.; Maxka, J. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 2 and references therein. (b) Seyferth, D. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 3 and references therein.

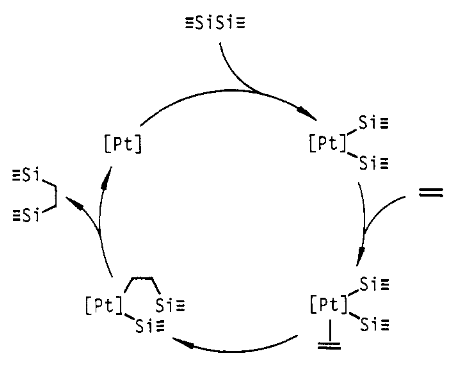
(2) (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. (b) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19. (c) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51. (d) Matsumoto, H.; Matsubara, I.; Kato, T.; Shono, K.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 43. (e) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, 149. (f) Carlson, C. W.; West, R. *Organometallics* **1983**, *2*, 1801. (g) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett.* **1975**, 887. (h) Sakurai, H.; Eriyama, Y.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1984**, *264*, 229. (i) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87. (j) Matsumoto, H.; Shono, K.; Wada, A.; Matsubara, I.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 185. (k) Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inose, J.; Nagai, Y. *J. Organomet. Chem.* **1982**, *225*, 343. (l) Seyferth, D.; Goldman, E. W.; Escudié, J. *J. Organomet. Chem.* **1984**, *271*, 337.

(3) Ito, Y.; Nishimura, S.; Ishikawa, M. *Tetrahedron Lett.* **1987**, *28*, 1293. Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692.

(4) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467.

0276-7333/90/2309-0280$02.50/0

Scheme I



the yield of 1,2-bis(dimethylphenylsilyl)ethane increased in the order $Pt(PPh_3)_4$ (yield 4.3%) < $Pt(PEt_3)_4$ (12.2%) < $Pt(PPhMe_2)_4$ (30.4%) < $Pt(PMe_3)_4$ (33.0%). Palladium complexes such as $Pd(PPh_3)_4$ and $PdCl_2(PhCN)_2$, which have been known to be active catalysts for double silylation of acetylenes and dienes, were inactive for the present reaction. Likewise, other complexes such as $PtCl_2(PPh_3)_2$, $PtCl_2(PhCN)_2$, $RhCl(PPh_3)_3$, $H_2Ru(CO)(PPh_3)_3$, and $Ru(CO)_3(PPh_3)_2$ were totally inactive.

As for the reaction mechanism, the following observations are worth noting. The Si–Si linkage in $FMe_2SiSiMe_2F$ and $ClMe_2SiSiMe_2Cl$ has been found to be readily cleaved when treated with $Pt(PEt_3)_3$ at room temperature to give *cis*-bis(silyl)bis(phosphine)platinum complexes. However, $PhMe_2SiSiMe_2Ph$ seemed unreactive.[5] Thus, the reactivities of disilanes toward $Pt(PEt_3)_3$ were in good agreement with those observed in the foregoing catalytic reactions. In addition to these, our previous paper[4] has communicated that *cis*-bis(dimethylphenylsilyl)bis(methyldiphenylphosphine)platinum readily reacts with ethylene at atmospheric pressure and room temperature to give the corresponding 1,2-bis(silyl)ethane. On the basis of all these facts combined together, the double silylation is envisaged to proceed via oxidative addition of the disilane, insertion of ethylene into one of the resulting Si–Pt bonds, and reductive elimination of 1,2-bis(silyl)ethane from the silyl(β-silylethyl)platinum intermediate as in Scheme I.

To see the stereochemistry of the addition, norbornene was allowed to react with 1,2-difluoro-1,1,2,2-tetramethyldisilane under the same conditions as above. 2,3-Bis(fluorodimethylsilyl)norbornane was formed in 26.0% yield, which was methylated with methyllithium to give 2-*exo*,3-*exo*-bis(trimethylsilyl)norbornane.[6] The result is rationalized by the cis addition of the disilane via coordination of the platinum center on the less hindered olefinic face.

In summary, this paper reports the first successful examples of double silylation of simple olefins, which offers a convenient way for the synthesis of silicon-containing polymers. For instance, 1,2-bis(chlorodimethylsilyl)ethane could be polymerized by Wurtz type condensation with sodium to give copoly(tetramethyldisilene–ethylene) with $\bar{M}_v = 192\,000$.[8] An investigation on reactivities of other types of olefins toward disilanes is now in progress.

Registry No. $FMe_2SiSiMe_2F$, 661-68-7; $(MeO)Me_2SiSiMe_2(OMe)$, 10124-62-6; $ClMe_2SiSiMe_2Cl$, 4342-61-4; $Me_3SiSiMe_3$, 1450-14-2; $(p\text{-}CF_3C_6H_4)Me_2SiSiMe_2(p\text{-}CF_3C_6H_4)$, 36112-13-7; $PhMe_2SiSiMe_2Ph$, 1145-98-8; $(p\text{-}CH_3C_6H_4)Me_2SiSiMe_2(p\text{-}CH_3C_6H_4)$, 5971-96-0; $CH_2{=}CH_2$, 74-85-1; $Pt(PPh_3)_4$, 14221-02-4; $FMe_2SiCH_2CH_2SiMe_2F$, 2251-44-7; $(MeO)Me_2SiCH_2CH_2SiMe_2(OMe)$, 76490-69-2; $ClMe_2SiCH_2CH_2SiMe_2Cl$, 13528-93-3; $Me_3SiCH_2CH_2SiMe_3$, 6231-76-1; $(p\text{-}CF_3C_6H_4)Me_2SiCH_2CH_2SiMe_2(p\text{-}CF_3C_6H_4)$, 123857-50-1; $PhMe_2SiCH_2CH_2SiMe_2Ph$, 15527-45-4; $(p\text{-}CH_3C_6H_4)Me_2SiCH_2CH_2SiMe_2(p\text{-}CH_3C_6H_4)$, 123857-51-2; $Pt(PEt_3)_4$, 33937-26-7; $Pt(PPhMe_2)_4$, 33361-89-6; $Pt(PMe_3)_4$, 33937-27-8; norbornene, 498-66-8; 2-*exo*-3-*exo*-bis(fluorodimethylsilyl)norbornane, 123857-52-3; 2-*exo*-3-*exo*-bis(trimethylsilyl)norbornane, 123857-53-4.

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[5] Details will be published elsewhere.

[6] High-resolution MS: found M^+, 240.1736; calcd for $C_{13}H_{28}Si_2$, 240.1729. MS (EI, *m/z* (relative intensity)): 240 (M^+, 2), 167 (11), 151 (3), 131 (6), 124 (5), 109 (3), 101 (2), 73 (100). ^1H NMR (200 MHz, C_6D_6): δ 0.14 (s, 18 H, $SiCH_3$), 0.89 (d, J = 1.7 Hz, 2 H, SiCH), 1.05–1.38 (m, 4 H, methylene CH_2, ethylene CH (endo)), 1.61–1.73 (m, 2 H, ethylene CH (exo)), 2.25–2.33 (m, 2 H, bridgehead CH) ppm. ^{13}C NMR (C_6D_6): δ 0.5 ($SiCH_3$), 34.3, 36.0, 38.4, 40.1 (norbornane) ppm. ^1H COSY measurement revealed that the splitting of the silyl-substituted methine proton signal into a doublet was due to the coupling with the anti proton at the bridging methylene and that its coupling with the bridgehead proton was not observed. These results combined with precedents[7] verify the 2-*exo*,3-*exo* geometry of the bis(silyl) groups.

[7] (a) Laszlo, P.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1964**, *86*, 1171 and references cited therein. (b) Kuivila, H. G.; Warner, C. R. *J. Org. Chem.* **1964**, *29*, 2845.

[8] Tverdokhlebova, I. I.; Sutkevich, O. I.; Ronova, I. A.; Polyakov, Yu. P.; Gusel'nikov, L. Ye.; Pavlova, S. A. *Vysokomol. Soedin., Ser. A* **1988**, *30*, 1070.

Formation of Cyclic Carbosilanes in the Pyrolysis of Octamethyltrisilane

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Summary: Prominent products in the pyrolysis of the title compound are cyclic carbosilanes; evidence is presented that one of these is formed in a novel and potentially useful elimination reaction.

The mechanism of breakdown of polysilanes is of interest because of their importance as photoresists[1] and as potential precursors to new polycarbosilane polymers. Accordingly, we are undertaking a study of the gas-phase pyrolysis of volatile permethylated polysilanes as model compounds and now report our initial results with octamethyltrisilane, Me_8Si_3 (**1**).

Me_8Si_3 was pyrolyzed by our stirred-flow (SFR) technique[2] between 558 and 655 °C with partial pressures of 0.25–0.9 mmHg in helium or nitrogen carrier gas. The SFR apparatus attached to a GC/mass spectrometer (HP5995C)[2] was used for identification of products. The major product was Me_3SiH, with smaller quantities of other monosilanes (Me_2SiH_2 and Me_4Si), but the main

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