Ga-As bond lengths of 2.432 (2)-2.464 (1) Å. The long Ga-As bond lengths in the dimers are primarily the result of ring strain due to endocyclic bond angles of 83-96° and steric repulsion. In $[Br_2GaAs(CH_2SiMe_3)_2]_3$, the Ga-As bond length is short since the ring strain is minimal, with endocyclic bond angles ranging from 103 to 121°. The Ga-As bond length is also reduced by electronic effects due to the electronegative bromide on the gallium. Electronic effects leading to bond shortening can be seen in the Ga-As and Ga-Sb bond lengths in $[Br_2GaAs(CH_2SiMe_3)_2]_3$ and $[Cl_2GaSb(t\text{-}Bu)_2]_3$,[20] which are consistent with the sum of their covalent radii. In contrast, the In-As bond length in $[Me_2InAsMe_2]_3$[20] of 2.669 (3)-2.679 (2) Å is slightly longer than the sum of their covalent radii (2.64 Å). A more dramatic shortening of the Ga-As bond is seen in $[(THF)Br_2Ga]_3As$,[21] which has the shortest known Ga-As distance of 2.404 (4) Å.

The Newman projection (Figure 2) of 1 down the Ga-As bond clearly shows that the lone pair on arsenic must be orthogonal to the unoccupied p orbital on gallium, which precludes the possibility of Ga-As double-bond character. The stabilization of the monomeric unit is due to the fact that the Ga and As atoms are effectively shielded from intermolecular association by the bulky *tert*-butyl substituents on both gallium and arsenic. Therefore, the yellow to yellow-orange color observed in these monomeric arsinogallanes must originate from charge-transfer processes. In contrast, associated compounds in which charge transfer cannot occur, containing tetracoordinated gallium and arsenic, are colorless solids.

$(t\text{-}Bu)_2GaAs(t\text{-}Bu)_2$ was heated to 150 °C for 10 min without decomposition but decomposed to red oligomers and/or polymers at 188-190 °C. Pyrolysis of 1 under a He atmosphere with a cool yellow flame (~400 °C) resulted in crystalline GaAs and an approximately 1:1 mole ratio of 2-methylpropane and 2-methylpropene.[22] The decomposition can be rationalized by a β-elimination followed by alkane elimination (Scheme I), a free-radical mechanism (Scheme II), or both.

β-Elimination in group III-V chemistry is not new. The thermal decomposition[23] of Et_3Ga occurs by this route to give Et_2GaH and ethylene, and $t\text{-}BuPH_2$ decomposes to give PH_3, 2-methylpropene, and 2-methylpropane.[24] In a recent pyrolysis study of diorganotellurium compounds, it was demonstrated that $(t\text{-}Bu)_2Te$ decomposes by both β-elimination and free-radical mechanisms to give 2-methylpropene and 2-methylpropane.[25] Both mechanisms may also be involved in the pyrolytic decomposition of 1.

Single-source organometallic precursors have been utilized to prepare epitaxial films of GaP,[26] GaAs,[27] and InP.[27,28] Volatile monomeric mono(arsino)gallanes, such as $(t\text{-}Bu)_2GaAs(t\text{-}Bu)_2$, may be better source compounds for the metal-organic chemical vapor deposition of GaAs. The expected advantages of $(t\text{-}Bu)_2GaAs(t\text{-}Bu)_2$ are as follows: (1) the lower vapor pressure and reduced air sensitivity[14] reduces the toxicity (AsH_3) and safety hazards (flammability of Me_3Ga) in GaAs film deposition; (2) the incorporation of *tert*-butyl groups, which can undergo β-elimination reactions, could result in lower carbon incorporation into the GaAs film; (3) highly crystalline GaAs films can be prepared at less than 550 °C; (4) high-purity source compounds can be achieved through multiple sublimations; (5) the correct stoichiometry of Ga to As is always maintained.

Acknowledgment. The financial support of the Office of Naval Research is gratefully acknowledged. We thank Drs. R. A. Nissan, M. P. Nadler, and T. A. Vanderah for their assistance in obtaining ^{13}C NMR and infrared spectra and Gandolfi data. We also thank R. Woolever for SEM X-ray analysis.

Supplementary Material Available: Atomic coordinates and isothermal displacement coefficients (Table S-I), bond lengths (Table S-II), bond angles (Table S-III), anisotropic displacement coefficients (Table S-IV), hydrogen atom coordinates and isotropic displacement coefficients (Table S-V), structure determination summary (Table S-VI), data collection summary (Table S-VII), and solution refinement summary (Table S-VIII) (6 pages); observed and calculated structure factors (Table S-IX) (5 pages). Ordering information is given on any masthead page.

(20) Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M.; Westmoreland, D. L. *J. Organomet. Chem.* **1988**, *341*, C1.
(21) Wells, R. L.; Shafieezad, S.; McPhail, A. T.; Pitt, C. G. *J. Chem. Soc., Chem. Commun.* **1987**, 1823.
(22) A sealed flask equipped with a Teflon valve containing 0.1 g of $(t\text{-}Bu)_2GaAs(t\text{-}Bu)_2$ under He was heated with a cool yellow flame for 10 min. The volatile products and 0.5 mL of deuterated toluene were condensed into an NMR tube at 10^{-4} Torr, and the tube was sealed. The molar ratio of 2-methylpropene to 2-methylpropane was 0.74, but this does not account for the products in the gas phase of the NMR sample. Energy-dispersive X-ray analysis of the GaAs powder showed a 53:47 Ga:As atom ratio. The error associated with SEM-EDX analysis is 5-6%. The sample was confirmed to be highly crystalline GaAs by the X-ray diffraction powder pattern (Gandolfi method).
(23) Yoshida, M.; Watanabe, H.; Uesugi, F. *J. Electrochem. Soc.* **1985**, *132*, 677.
(24) Chen, C. H.; Larsen, C. A.; Stringfellow, G. B.; Brown, D. W.; Robertson, A. J. *J. Cryst. Growth* **1986**, *77*, 11.
(25) Kirss, R.; Brown, D. *Abstracts of Papers*, 198th National Meeting of the American Chemical Society, Miami, FL, Sept 1989; American Chemical Society: Washington, DC, 1989; INOR 285.
(26) Maury, F.; Combes, M.; Constant, G.; Renucci, J. B. *J. Phys., Colloq.* **1982**, C1, 347.
(27) Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 624.
(28) Andrews, D. A.; Davies, G. J.; Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; White, E. A. D. *Semicond. Sci. Technol.* **1988**, *3*, 1053.

Convenient Synthesis of β-Trichlorostannyl Ketones from α,β-Unsaturated Ketones and Their Facile Conversion to β-Trialkylstannyl Ketones

Hiroyuki Nakahira, Ilhyong Ryu,* Akiya Ogawa, Nobuaki Kambe, and Noboru Sonoda*

Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565, Japan

Received August 16, 1989

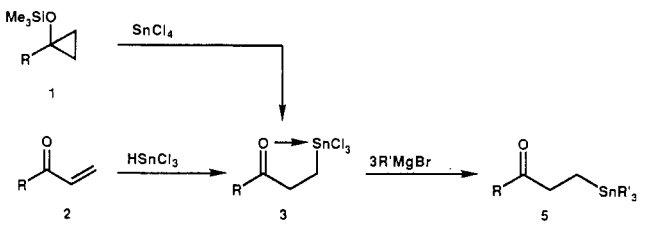
Summary: Reaction of α,β-unsaturated ketones with tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) and chlorotrimethylsilane in ether afforded β-trichlorostannyl ketones in good yields. These underwent chemoselective alkylation at Sn to give the corresponding β-trialkylstannyl ketones by the reaction with 3 equiv of Grignard reagents at −78 °C.

In the course of our study on the utilization of β-metallo ketones as synthetic intermediates,[1] we required a variety of β-trichlorostannyl ketones. While the ring-opening reaction of siloxycyclopropanes 1 with tin(IV) chloride ($SnCl_4$), which we have recently reported,[2] gives the β-

(1) For recent work, see: (a) Ryu, I.; Suzuki, H.; Ogawa, A.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1988**, *29*, 6137. (b) Ikura, K.; Ryu, I.; Ogawa, A.; Kambe, N.; Sonoda, N. *Ibid.*, in press.
(2) Ryu, I.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 2389.

0276-7333/90/2309-0277$02.50/0

Scheme I



trichlorostannyl ketones **3** having an unsubstituted methylene group next to the Sn atom, this method cannot be applied to the synthesis of those ketones with an alkyl substituent at the α-carbon. In this context we have also been interested in another method, the *hydrotrichlorostannation* of α,β-unsaturated ketones **2** (Scheme I). This reaction, first demonstrated in 1976,[3,4] however, has not been tested thoroughly, and only limited examples are available. Furthermore, we felt that the procedure for "$HSnCl_3$", which involved bubbling an excess of HCl gas into a mixture of tin(II) chloride ($SnCl_2$) and the enone, should be altered. We have found that the combination of $SnCl_2{\cdot}2H_2O$ with Me_3SiCl affords "$HSnCl_3$" efficiently and that this makes the overall procedure quite facile. We report herein a convenient preparation of β-trichlorostannyl ketones **3** according to this *one-pot* procedure and the conversion of **3** to the corresponding β-trialkylstannyl ketones **5**, which was achieved by chemoselective alkylation with 3 equiv of a Grignard reagent at −78 °C.

Hydrotrichlorostannation of α,β-unsaturated ketones **2** was carried out according to the following typical procedure. To a stirred suspension of $SnCl_2{\cdot}2H_2O$ (2.26 g, 10 mmol) in ether (10 mL) was added chlorotrimethylsilane (1.52 mL, 12 mmol) at 25 °C. On the addition of Me_3SiCl an exothermic reaction took place, and the mixture separated into two layers. After 10 min, methyl vinyl ketone (**2a**) (0.701 g, 10 mmol) was added to the mixture in one portion, which caused a slight exotherm. The resulting mixture was stirred at 25 °C for 1 h. After removal of the solvent and the hexamethylsiloxane formed as a byproduct, the residual oil was dried under reduced pressure and recrystallized from *n*-pentane/chloroform to give **3a** (2.55 g, 86%).

As one can see in Table I, the procedure can be applied to a variety of enones with the exception of cyclic enone **2h**. Yields of **3** are generally high. Lower frequency shifts in IR spectroscopy indicated strong coordination of the carbonyl group to the Sn atom in **3**. Hydrotrichlorostannation of (*R*)-(+)-pulegone (**2f**) gave the β-trichlorostannyl ketone **3f** in 90% yield (entry 6).[6] 3-Methylene-2-norbornanone (**2g**) was converted to the exo form **3g** in 79% yield (by ^1H NMR spectroscopy).

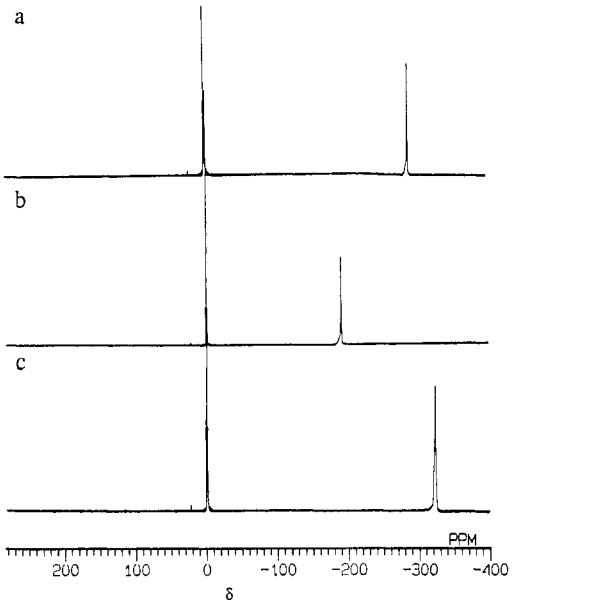
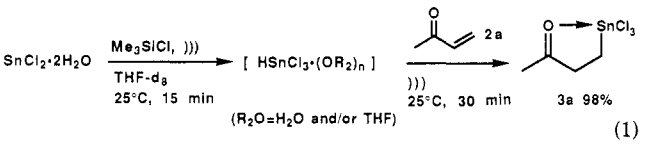


Figure 1. ^{119}Sn NMR spectra at 25 °C (100 MHz, Me_4Sn as an external standard) of (a) $SnCl_2{\cdot}2H_2O$ in THF, (b) $HSnCl_3{\cdot}nOR_2$ prepared from $SnCl_2{\cdot}2H_2O$ and Me_3SiCl in THF, and (c) β-trichlorostannyl ketone **3a** by further treatment with methyl vinyl ketone (**2a**).

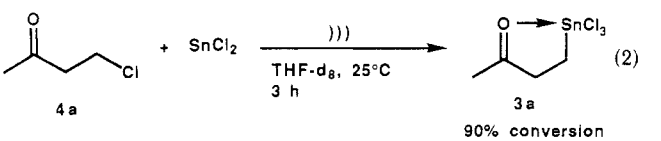
To clarify the reaction path, the reaction of **2a** with $SnCl_2{\cdot}2H_2O/Me_3SiCl$ was monitored by ^1H and ^{119}Sn NMR spectroscopy (eq 1). Treatment of $SnCl_2{\cdot}2H_2O$ (64 mg,



(1)

0.29 mmol) with Me_3SiCl (36 μL, 0.29 mmol) in THF-d_8 at 25 °C under ultrasonic irradiation gave a two-layer mixture instantly. The ^1H NMR spectrum of the lower layer showed two peaks at δ 0.06 (s) and 9.04 (br s) ppm with a 9:4 intensity ratio.[7] On the addition of **2a** (20 mg, 0.29 mmol) to this solution, the reaction ended within 30 min to give **3a**. In ^{119}Sn NMR measurements,[8] three signals (δ −284.9, −190.1, and −322.3 ppm) that were ascribed to $SnCl_2{\cdot}2H_2O$, $HSnCl_3{\cdot}nOR_2$, and β-trichlorostannyl ketone **3a** were observed (Figure 1).

A possible competitive reaction path, which involves the initial formation of 1-chlorobutan-3-one (**4a**) from **2a** and HCl and a subsequent reaction with $SnCl_2$, proved to be less important since the reaction of **4a** with $SnCl_2$ in THF-d_8 proceeded fairly sluggishly (3 h for 90% conversion as determined by ^1H NMR spectroscopy) (eq 2).[9]



(2)

We also examined the conversion of **3** to the β-trialkylstannyl ketones **5**, which are useful intermediates in

(3) For the synthesis of β-substituted monoalkyltin trihalides by the use of $SnCl_2$ and HCl, see: (a) Burley, J. W.; Hutton, R. E.; Oakes, V. *J. Chem. Soc., Chem. Commun.* **1976**, 803. (b) Hutton, R. E.; Burley, J. W.; Oakes, V. *J. Organomet. Chem.* **1978**, *156*, 369. The related method involving Sn and HCl suffers from the formation of dialkyltin dichloride; see: (c) Burley, J. W.; Hope, P.; Mack, A. G. *Ibid.* **1984**, *277*, 37.

(4) For other related work on β-substituted alkyltin halides, see: (a) Matsuda, S.; Kikkawa, S.; Kashiwa, N. *Kogyo Kagaku Zasshi* **1966**, *69*, 1036. (b) Matsuda, S.; Nomura, M. *J. Organomet. Chem.* **1970**, *25*, 101. (c) Bulten, E. J.; Hurk, J. W. G. *Ibid.* **1978**, *162*, 161. (d) Burley, J. W.; Hope, P.; Hutton, R. E. *Ibid.* **1979**, *170*, 21. (e) Howie, R. A.; Paterson, E. S.; Wardell, J. L. *Ibid.* **1983**, *259*, 71.

(5) For $HSnCl_3$ and related species, see ref 4c and references cited therein.

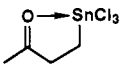
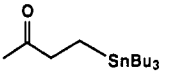
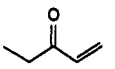
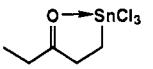
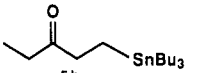
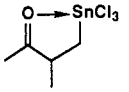
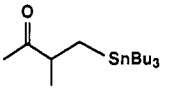
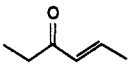
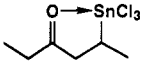
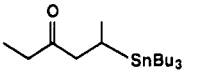
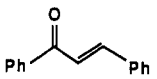
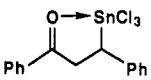
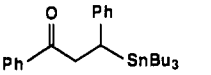
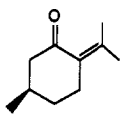
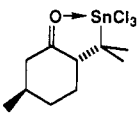
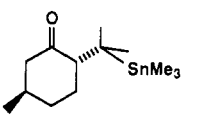
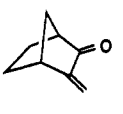
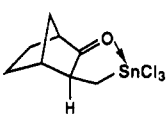
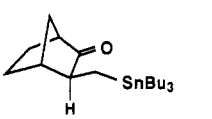
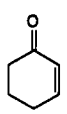
(6) Obtained as a mixture of two diastereoisomers (two doublets of methyl protons at δ 1.00 (d, J = 7.3 Hz, *Z* form) and 1.12 (d, J = 6.4 Hz, *E* form) ppm by 270-MHz ^1H NMR spectroscopy). During recrystallization from *n*-pentane and chloroform, isomerization to the *E* isomer took place.

(7) Previous work indicated that $HSnCl_3{\cdot}nOEt_2$, prepared by treating $SnCl_2$ with HCl gas in Et_2O, is not a pure form because of the contamination of $H_2SnCl_4{\cdot}nOEt_2$, and as a result observed chemical shifts of ^1H NMR spectra varied in the range δ 10.9–12.8 ppm.[4c] In the present case we were unable to discern the proton signal of H–Sn from the signals of coordinated H_2O, suggesting rapid exchange between these protons.

(8) The intermediacy of $HSnCl_3{\cdot}nOR_2$ is also supported by its trapping with *n*-BuMgBr, affording *n*-Bu_3SnH, although the yield was modest.

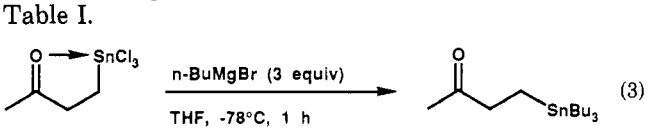
(9) Bulten and Hurk indicated that hydrotrichlorostannation of methyl acrylate proceeded much faster than hydrochlorination.[4c]

Table I. Preparation of β-Trichlorostannyl Ketones[a] and β-Trialkylstannyl Ketones[b]

entry	substrate 2	β-trichlorostannyl ketone 3	mp, °C IR(νC=O), cm^{-1}	yield[c] %	β-trialkylstannyl ketone 5	yield[d] %
1	 2a	 3a	76-77 1663	86	 5a	88
2	 2b	 3b	82-83 1660	87	 5b	86
3	 2c	 3c	95-96 1654	81	 5c	85
4	 2d	 3d	96-97 1660	70	 5d	81
5	 2e	 3e	145-147 1621	75	 5e	81
6	 2f	 3f	118-119[e] 1673	90[f]	 5f	84[g]
7	 2g	 3g	205-206 1680	86[h]	 5g	79[h]
8	 2h	[i]				

[a] Generally reactions were carried out on a 10-mmol scale; see text. [b] Each reaction is carried out by treating **3** with 3 equiv of *n*-BuMgBr or MeMgBr at −78 °C for 1 h in THF followed by the standard workup with 1 N HCl, $NaHCO_3$, and water. [c] Isolated yields after purification by recrystallization or reprecipitation. [d] Isolated yields after purification by column chromatography. [e] Measured for 92/8 (*E*/*Z*) isomers obtained by repeated recrystallization from $CHCl_3$/*n*-pentane. [f] *E*/*Z* = 75/25 for the sample obtained by reprecipitation in *n*-pentane (determined by 270-MHz ^1H NMR spectroscopy). [g] *E*/*Z* = 75/25 (determined by GLC). [h] Characterized as the exo form by ^1H NMR spectroscopy. [i] Examined in THF-d_8 as a solvent. After 12 h the measurement of ^1H NMR spectra showed 98% recovery of **2h**.

organic synthesis.[10,11] We envisioned that chemoselective reaction of the β-trichlorostannyl ketone **3** with organometallic reagents at Sn would afford **5**. Although attempted alkylation of **3a** with use of alkyllithiums afforded a mixture of the γ-trialkylstannyl alcohol and the β-trialkylstannyl ketone, selective alkylation of **3a** leading to **5a** could be effected by using Grignard reagents (3 equiv) at −78 °C (eq 3). Some other results are also shown in Table I.



3a 5a 88% (3)

In summary, hydrotrichlorostannation of α,β-unsaturated ketones **2** with $HSnCl_3$ generated in situ from $SnCl_2 \cdot 2H_2O$ and Me_3SiCl in ether provides a convenient procedure for the preparation of the β-trichlorostannyl ketones **3**, which can be further elaborated to the β-trialkylstannyl ketones **5**. This method for **3** complements the method involving siloxycyclopropane cleavage. We are presently studying applications of **3** and **5** to useful syn-

(10) (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. Also see recent reports: (b) Johnson, C. R.; Kadow, J. F. *J. Org. Chem.* **1987**, *52*, 1493. (c) Posner, G. H.; Webb, K. S.; Asirvatham, E.; Jew, S.; Degl'Innocenti, A. *J. Am. Chem. Soc.* **1988**, *110*, 4754.

(11) For the preparation of these compounds, the conjugate addition of (trialkylstannyl)metals to **2** has been most widely used. R_3SnLi: (a) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836. (b) Fleming, I.; Urch, C. J. *J. Organomet. Chem.* **1985**, *285*, 173. (c) Sato, T.; Watanabe, M.; Watanabe, T.; Onoda, Y.; Murayama, E. *J. Org. Chem.* **1988**, *53*, 1894. R_3SnNa: (d) Kuivila, H. G.; Lein, G. H., Jr. *Ibid.* **1978**, *43*, 750. R_3SnK: (e) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *197*, C19. $R_3SnMgBr$: (f) Lahournere, J. C.; Valade, J. *Ibid.* **1971**, *33*, C7. $[Me_3SnCuI]Li$: (g) Hudec, J. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1020. $[Me_3SnCuSPh]Li$: (h) Piers, E.; Morton, H. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1034. (i) Piers, E.; Morton, H. E.; Chong, J. M. *Can. J. Chem.* **1987**, *78*, 65. $Me_3SnCu(2\text{-Th})(CN)Li_2$: (j) Piers, E.; Tillyer, R. D. *J. Org. Chem.* **1988**, *53*, 5366. Also see a synthesis of **5** by the oxidation of a γ-stannyl alcohol: (k) Kuivila, H. G.; Dixon, J. E.; Maxfield, P. L.; Scarpa, N. M.; Topka, T. M.; Tsai, K.-H.; Wursthorn, K. R. *J. Organomet. Chem.* **1975**, *86*, 89. (l) Ueno, Y.; Ohta, M.; Okawara, M. *Tetrahedron Lett.* **1982**, *23*, 2577.

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

Acknowledgment. Support of this work by a Grant-in-Aid from the Ministry of Education, Science and Culture of Japan is gratefully acknowledged. We also thank Shin-Etsu Chemical Co. Ltd. for a gift of trimethylchlorosilane.

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

Teruyuki Hayashi, Toshi-aki Kobayashi, Aparecida M. Kawamoto, Hiroshi Yamashita, and Masato Tanaka*

National Chemical Laboratory for Industry
Tsukuba, Ibaraki 305, Japan

Received September 26, 1989

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.

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

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.,

(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