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(Trialkylstannyl)dimethylsilane as a New Precursor of Dimethylsilylene: A Novel Synthesis of 3,4-Disubstituted 1-Silacyclopenta-2,4-dienes

Kazutoshi Ikenaga,* Kouji Hiramatsu, Norimitsu Nasaka, and Satoshi Matsumoto

Department of Industrial Chemistry, The Kumamoto Institute of Technology, Ikeda, Kumamoto 860, Japan

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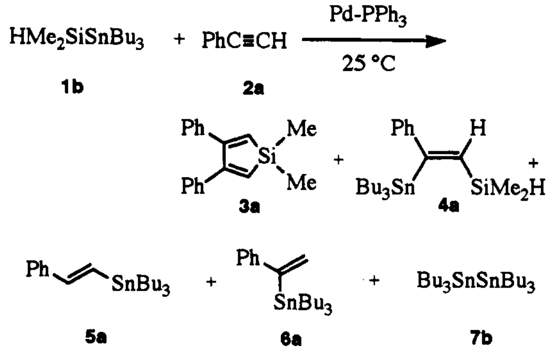
Summary: In the presence of triphenylphosphinepalladium complexes, (trialkylstannyl)dimethylsilane rapidly reacted at room temperature with terminal acetylenes to give 3,4-disubstituted 1-silacyclopenta-2,4-dienes in moderate yield. The formation of 1-silacyclopentadiene derivatives is evidence for the generation of dimethylsilylene species from (trialkylstannyl)dimethylsilane.

The chemistry of silylenes, which are carbene analogs with high reactivities, has attracted much attention in connection with the development of synthetic methodology for new silicon-containing compounds.[1] Several vigorous reactions, such as photolysis,[2] pyrolysis,[3] and transition metal-catalyzed reactions,[4] of corresponding precursors are usually employed to generate silylene species. However, few convenient room temperature methods for the generation of silylene species have been reported.[4b] We had predicted that in the presence of transition metal catalysts (trialkylstannyl)dimethylsilane ($HSiMe_2SnR_3$; **1**) would easily provide dimethylsilylene species through the elimination of an H atom and the stannyl group, since the Si–Sn bond of **1** is weaker than the Si–Si bond of 1,1,2,2-tetramethyldisilane.[4f]

We first investigated the reactivity of (tributylstannyl)dimethylsilane ($HMe_2SiSnBu_3$; **1b**)[5] toward phenylacetylene (**2a**) in the presence of transition metal catalysts at 25 °C. Actually, we found that **1b** rapidly reacted with **2a** to give 1,1-dimethyl-3,4-diphenylsilacyclopenta-2,4-diene (**3a**)[6] in good yield at 25 °C, using palladium complexes and a triphenylphosphine system. Formation of (*Z*)-1-(tributylstannyl)-2-(dimethylsilyl)styrene (**4a**),[7] (*E*)-2-(tributylstannyl)styrene (**5a**), 1-(tributylstannyl)styrene (**6a**), and hexabutyldistannane (**7b**) was also observed (eq 1). Employment of transition metal complexes with phosphine ligands afforded **3a**, and the use of $PdCl_2(PPh_3)_2$ gave the best result. In the absence of phosphine ligands, **7b** was the primary product, accompanied by a small amount of **3a**, **4a**, **5a**, and **6a**. On the other hand, the absence of **2a** resulted in **7b** only, and ^1H and ^{13}C NMR spectra of this reaction mixture indicated the formation of polysilanes containing MeSi groups. However, the formation of $HMe_2SiMe_2SiSnBu_3$[8] was not detected. A platinum complex such as $PtCl_2(PPh_3)_2$ mainly catalyzed the slow formation of **7b**. On the other hand, nickel complexes such as $NiCl_2(PPh_3)_2$, $NiCl_2[P(n\text{-}Bu)_3]_2$, and $NiCl_2(PEt_3)_2$ were not effective as catalysts for the reaction at 25 °C, and only **1b** and **2a** were recovered. With rhodium complexes such as $RhCl(PPh_3)_3$ and $RhCl(CO)(PPh_3)_2$, mainly stannyl compounds were produced. Interestingly, the addition of triphenylphosphine to inactive palladium complexes such as $PdCl_2(PhCN)_2$, $Pd(OAc)_2$, $Pd(dba)_2$, and $PdCl_2$ effectively promoted the formation of **3a**, while the addition of triphenylphosphine to $PdCl_2(PPh_3)_2$ prolonged the reaction time. The presence of diphenylphosphinoethane (dppe) or $P(OEt)_3$ in the present catalysis system tended to decrease the formation of **3a**. The presence of strong phosphine ligands significantly retarded the formation of **3a**. The results of complex and phosphine variation in the present reaction of **1b** and **2a** are summarized in Table I.



(1)

Furthermore, in varying the ratio between **1b** and **2a**, using $PdCl_2(PPh_3)_2$, the following results were obtained

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• Abstract published in *Advance ACS Abstracts*, August 15, 1993.

[1] (a) Brook, A. G. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, Chapter 15. (b) Raabe, G.; Michl, J. *Ibid.* Chapter 17; (c) Tilley, T. D. *Ibid.* Chapter 24. (d) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (e) Barton, T. J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1983; Vol. 2, Chapter 9.2. (f) Atwell, W. H.; Weyenberg, D. R. *Angew. Chem., Int. Ed. Engl.*, **1969**, *8*, 469.

[2] Gaspar, P. P.; Holten, D.; Konieczny, S.; Corey, J. Y. *Acc. Chem. Res.* **1987**, *20*, 329.

[3] (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1980**, *184*, 13. (b) Maruca, R. *J. Org. Chem.* **1971**, *36*, 1626. (c) Atwell, W. H.; Weyenberg, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 3438. (d) Gilman, H.; Cottis, S. G.; Atwell, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 1596.

[4] (a) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57. (b) Seyferth, D.; Duncan, D. P.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C5. (c) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879. (d) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27. (e) Ojima, I.; Inaba, S.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7. (f) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (g) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31. (h) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1970**, *23*, C7.

[5] (Trialkylstannyl)dimethylsilanes [$HSiMe_2SnR_3$; R = Et (**1a**), Bu (**1b**),[8] and Oc (**1c**)] were prepared by a coupling reaction of R_3SnLi, generated from R_3SnCl and Li (2 equiv to R_3SnCl) in dry THF at 5 °C, and $HSiMe_2Cl$. We thank Chisso Corp. for a gift of $HSiMe_2Cl$ and Yoshitomi Pharmaceutical Industries, Ltd. for a gift of Bu_3SnCl and Oc_3SnCl.

[6] A typical procedure follows. Under nitrogen, $Pd(PPh_3)_2Cl_2$ (0.015 mmol) was added to a mixture of (trioctylstannyl)dimethylsilane (**1c**, 0.50 mmol) and phenylacetylene (**2a**, 2.0 mmol) in dry benzene (2 mL), and the resulting solution was stirred at 25 °C for 30 min after the volatiles were removed at 25 °C/25 Torr and the catalysts were also removed by short silica gel column chromatography (hexane). The product was purified by Kugelrohr distillation (1,1-dimethyl-3,4-diphenylsilacyclopenta-2,4-diene (**3a**), 54%, isolated yield). **3a**: bp 60–100 °C/1.0 Torr; mp 97.5–98 °C; ^1H-NMR δ 0.459 (s, 6H, SiMe), 6.315 (s, 2H, vinyl H), and 7.10–7.50 (m, 10H, Ph) [lit.[4b] mp 98–99 °C; ^1H-NMR δ 0.37, 6.1, and 6.72]. The other likely structural possibility, 1,1-dimethyl-2,5-diphenylsilacyclopenta-2,4-diene, is a known compound with mp 133–134 °C and a different NMR spectrum [^1H-NMR δ 0.56 (s, 6H, SiMe), 7.32 (m, 12H)].[3b]

[7] The coupling constant (74.2 and 77.6 Hz) of SnH in the NMR spectra of **4a** was in fair agreement with that (80.1 and 83.9 Hz) of (*Z*)-1-(tributylstannyl)-2-(trimethylsilyl)styrene.[10a,b]

[8] Appler, H.; Neumann, W. *J. Organomet. Chem.* **1986**, *314*, 247.

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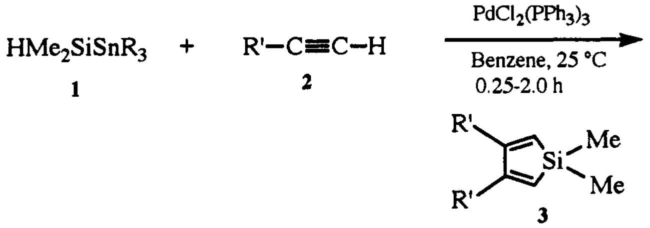
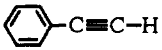
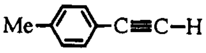
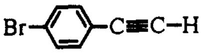
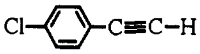
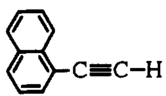
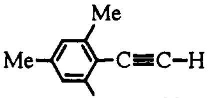
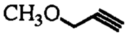
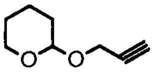
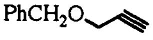
Table I. Complex and Phosphine Variation for Reactions of $HMe_2SiSnBu_3$ (1b) with Phenylaceylene (2a)[a]

		yields of products[c] (%)							yields of products[c] (%)				
complexes[b]	h	3a	4a	5a	6a	7b	complexes[b]	h	3a	4a	5a	6a	7b
$PdCl_2(PPh_3)_2$	0.2	54	9	37	31	22	$PdCl_2(PhCN)_2 + 2PPh_3$	0.17	54	9	37	31	22
$Pd(PPh_3)_4$	3.0	58	3	34	32	8	$Pd(OAc)_2 + 2PPh_3$	0.25	44	7	29	32	22
$PdCl_2(dppe)$	48	11	14	8	9	7	$Pd(dba)_2 + 2PPh_3$	0.50	39	4	17	27	14
$PdCl_2(PhCN)_2$	3.0	5	9	4	4	57	$PdCl_2 + 3LiCl + 2PPh_3$	3.0	32	8	12	20	28
$Pd(OAc)_2$	0.6	4	8	3	8	51	$PdCl_2(PPh_3)_2 + 2PPh_3$	23	50	1	10	25	5
$Pd(dba)_2$	1.0	3	10	6	5	31	$PdCl_2(PhCN)_2 + 2P(OEt)_3$	8.0	13	49	8	16	t
$NiCl_2(PEt_3)_2$	24	0	0	0	0	0	$PtCl_2(PPh_3)_2$	46	t	2	t	t	34
$NiCl_2[P(n\text{-}Bu)_3]_2$	6.5	0	0	0	0	0	$RhCl(PPh_3)_3$	4.0	t	4	18	11	18
$NiCl_2(PPh_3)_2$	24	0	0	0	0	0	$RhCl(CO)(PPh_3)_2$	2.0	1	5	23	11	14

[a] The reactions were carried out with $HMe_2SiSnBu_3$ (0.5 mmol), phenylacetylene (2.0 mmol), and complexes in benzene at 25 °C. [b] 3 mol % of complexes to 1. [c] GC yields based on 1. t = trace amount.

Table II. Palladium-Catalyzed Formation of 1,1-Dimethyl-3,4-Disubstituted-1-silacyclopentadienes[a]



	Yield of 3[b] (%)				Yield of 3[b] (%)	
	Et[c]	Bu[d]	Oc[e]		Bu[d]	Oc[e]
 **2a**	(86)	(72)	54 (66)	 **2b**	(52)	28 (43)
 **2c**		40	18	 **2d**	(76)	36 (55)
 **2e**	52	(62)		 Me **2f**		25
 **2g**		(31)	26 (27)	 **2h**	67	37
 **2i**	94	(74)		 **2j**	86	(74)

[a] The reactions were carried out with HMe_2SiSnR_3 (0.5 mmol), acetylenes (2.0 mmol), and $PdCl_2(PPh_3)_2$ (3 mol % to 1) in benzene at 25 °C for 0.25–2.0 h. [b] Isolated yields of based on 1. GC yields are in parentheses. [c] Carried out with $HMe_2SiSnEt_3$ (**1a**). [d] Carried out with $HMe_2SiSnBu_3$ (**1b**). [e] Carried out with $HMe_2SiSnOc_3$ (**1c**).

(given as **1b**/**2a**, reaction time, yield (%) of **3a**): 1/1, 3 h, 28%; 1/2, 0.25 h, 54%, 1/4, 0.25 h, 72%. By variation of the substituents on the tin atom of **1**, the following results were obtained (given as stannyl group, reaction time, yield (%) of **3a**): Et_3Sn (**1a**), 0.25 h, 86%; Bu_3Sn (**1b**), 0.25 h, 72%; Oc_3Sn (**1c**), 0.5 h, 66%. The reaction that employed **1a** gave the best result. The use of **1c** facilitated the separation of the desired 1-silacyclopentadiene **3**. The results of reactions of **1** with substituted terminal acetylene **2** are summarized in Table II. In particular, the condensation of arylacetylenes provided 3,4-bis(4′-halophenyl)-1-silacyclopentadiene **3c** and **3d**, bearing substituents on the aryl groups that could be further functionalized. Compounds **3b–j** and **4a** are new.

In contrast, internal acetylenes such as 4-octyne and 1,2-bis(trimethylsilyl)acetylene were not reactive to dimethylsilylene generated from **1b**, and these reactions only provided **7b** derived from decomposition of **1b**.

These observations suggest that the present reaction entails the generation of a palladium–dimethylsilylene species **8**[9] as an intermediate. The proposed routes of the generation of **8** and **3** are shown in Scheme I. In the first step, oxidative addition of the Si–Sn bond of **1** to the palladium complex occurs to produce a $HMe_2SiPdSnR_3$ complex.[10] The elimination of an H atom and stannyl group from this complex gives a palladium–dimethylsilylene species **8**, and the insertion of **2** into **8** proceeds

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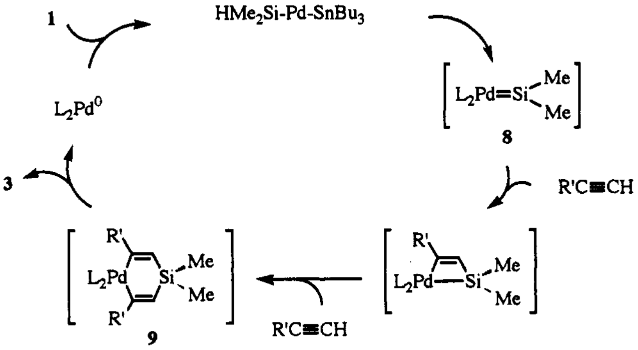
[9] Platinum,[4e,11] nickel,[4f] and Rhodium[4e] silylene complexes have been reported in recent years.

[10] (a) Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561. (b) Mitchell, T. H.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *Ibid.* **1987**, *52*, 4868. (c) Murakami, M.; Morita, Y.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 428.

Scheme I



stepwise to produce 1-palla-4-silacyclohexa-2,5-diene intermediate **9**.[11] In the final step, reductive elimination of **3** from **9** regenerates a zero-valent palladium complex. On the other hand, the formation of (tributylstannyl)styrenes (**5a** and **6a**) and hexabutyldistannane (**7b**) may be accounted for by the known palladium-catalyzed hydrostannylation[12] of acetylenes by $HSnBu_3$, generated from **1b**, and dehydrogenation[13] of $HSnBu_3$, respectively.

The present reaction provides not only a convenient method for the generation of dimethylsilylene species but also a novel synthetic approach to 3,4-disubstituted 1-silacyclopenta-2,4-dienes. Detailed studies concerning the reaction mechanism and synthetic utility of **3** are in progress.

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Supplementary Material Available: Characterization data for the compounds reported (**3a–j** and **4a**) (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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