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Platinum-Catalyzed Addition of Dimethylsilylene to *β*-Methyl α,*β*-Unsaturated Ketones: *γ*-Silylation Forming 1-Oxa-2-silacyclohex-5-enes

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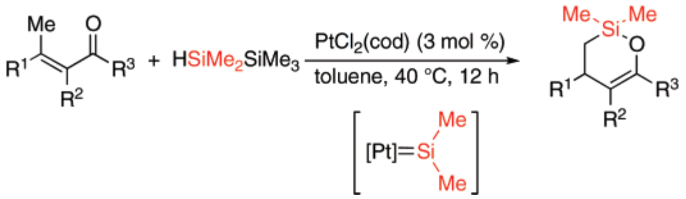
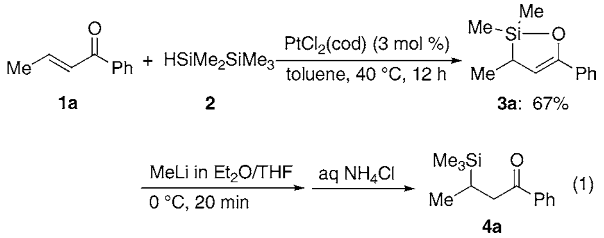
ABSTRACT



The reaction of *β*-methyl α,*β*-unsaturated ketones with pentamethyldisilane in the presence of a platinum catalyst brought about silylation on the *β*-methyl group giving high yields of oxasilacyclohexenes.

It is well-documented that silylenes (divalent silicon species, R_2Si:) are very active intermediates which react with various types of compounds giving tetravalent organosilanes.[1] However, the use of silylenes for organic synthesis had not been extensively studied before Woerpel reported a silver-catalyzed silylene transfer reaction to alkenes giving silacyclopropanes with high selectivity.[2] Among several reported methods of generating silylenes,[1] we became interested in transition-metal-catalyzed reaction of hydrodisilanes generating silylenes together with hydrosilanes because of their mild reaction conditions and the ready availability of the hydrodisilanes. Here we wish to report that dimethylsilylene generated from pentamethyldisilane under the catalysis by a platinum complex[3] is incorporated into α,*β*-unsaturated ketones giving two types of addition products depending on the substitution pattern at the *β*-position. These reactions provide oxasilacycles which are potentially useful as versatile intermediates for organic synthesis.

The reaction of (*E*)-1-phenyl-2-buten-1-one (**1a**) with pentamethyldisilane (**2**, 1.2 equiv to **1a**) in the presence of $PtCl_2$(cod) (3 mol %) in toluene at 40 °C for 12 h gave 67% yield of oxasilacyclopentene **3a** (eq 1). The formation of oxasilacyclopentene is as expected because there have been several examples of the [4 + 1] type cycloaddition of silylenes[4] including Woerpel's report[2b] where di(*tert*-butyl)silylene adds to conjugate enones and enoates. Treatment of the oxasilacyclopentene **3a** with methyllithium at 0 °C followed by hydrolysis gave *β*-trimethylsilyl ketone **4a**.



On the other hand, the reaction of *β*,*β*-dimethyl-substituted enones with the dimethylsilylene proceeded in a different manner. Thus, the platinum-catalyzed reaction of 3-methyl-1-phenyl-2-buten-1-one (**1b**) with hydrodisilane **2** (1.2 equiv

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(1) Ottosson, H.; Steel, P. G. *Chem.*−*Eur. J.* **2006**, *12*, 1576.

(2) (a) Cirakovic, J.; Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 9370. (b) Calad, S. A.; Woerpel, K. A. *J. Am. Chem. Soc.* **2005**, *127*, 2046.

(3) (a) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1970**, *23*, C7. (b) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31.

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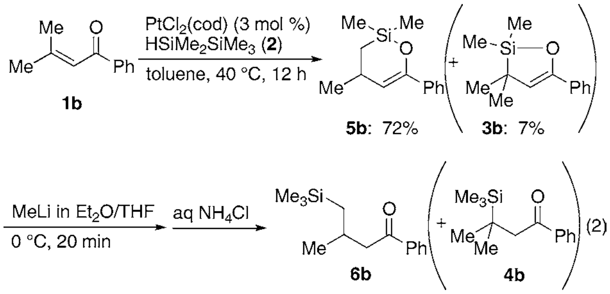
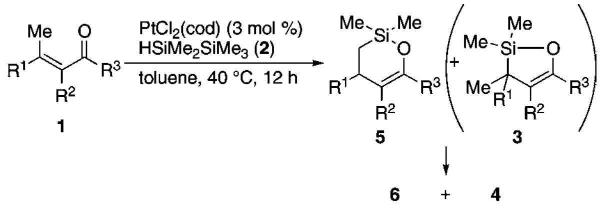
to **1b**) under the same reaction conditions gave 72% yield of oxasilacyclohexene **5b**[5] as a new type of addition product together with a minor amount (7%) of oxasilacyclopentene **3b**[4] (eq 2). Treatment of **5b** with methyllithium followed by hydrolysis gave γ-trimethylsilyl ketone **6b**, which confirms the structure of six-membered ring product **5b**.

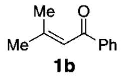
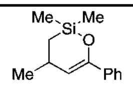
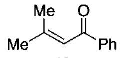
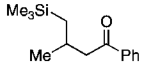
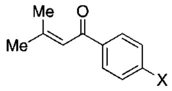
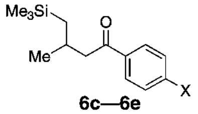
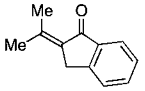
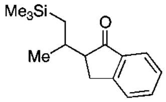
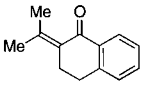
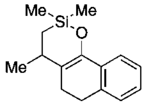
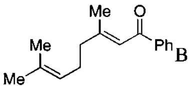
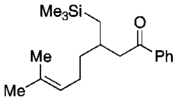
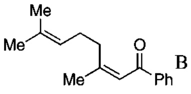
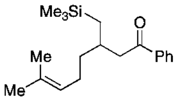


The formation of oxasilacyclohexene **5** was observed only for the β,β-disubstituted enones where at least one of the β-substituents is a methyl group. Some of the results obtained for this new type of six-membered ring formation are summarized in Table 1. Phenyl ketones containing electron-donating or -withdrawing substituents on the phenyl ring **1c**–**1e** are the substrates which gave oxasilacyclohexenes **5** as major products (entries 3–5). It is remarkable that the selectivity giving **5** over **3** is higher with a more electron-donating group at the para position. In the reaction of isopropylideneindanone **1f** and -tetralone **1g**, the selectivity in giving oxasilacyclohexene **5** is very high (entries 6 and 7). It is interesting that both *E* and *Z* isomers of enone **1h** underwent the silylene addition giving oxasilacyclohexene **5** (entries 8 and 9).[6]

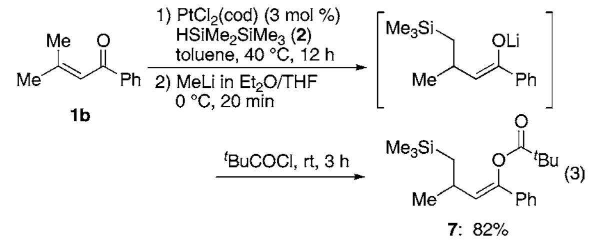
Because the oxasilacyclohexenes **5** formed by the present silylation have a cyclic structure, the lithium enolates generated by treatment with methyllithium should have exclusive *Z* geometry.[7] The (*Z*)-lithium enolates can be trapped as (*Z*)-enol esters by O-acylation with an acyl chloride. For example, the reaction mixture obtained by the platinum-catalyzed silylene reaction of enone **1b** was treated subsequently with methyllithium and pivaloyl chloride to give (*Z*)-enol pivalate **7** in 82% overall yield (eq 3). Synthetic utility of the silylation reaction is also exemplified by the oxidation of the carbon–silicon bond in oxasilacyclohexene **5b** under Tamao conditions[8] giving γ-hydroxy ketone **8** in a high yield (eq 4).

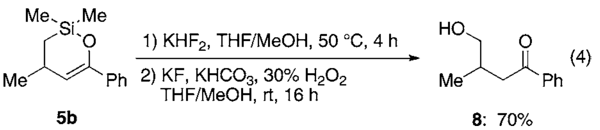
Table 1. Platinum-Catalyzed Silylene Addition to β-Methyl α,β-Unsaturated Ketones[a]



entry	enone	method[b]	product	yield (%)[c]	ratio[d]
1	 **1b**	A	 **5b**	79	10:1
2	 **1b**	B	 **6b**	81	10:1
3	 **1c—1e**	B	 **6c—6e**	78 (**c**: X = OMe)	20:1
4		B		63 (**d**: X = CF$_3$)	4:1
5		B		82 (**e**: X = Cl)	6:1
6	 **1f**	B	 **6f**	95[e]	>20:1
7	 **1g**	A	 **5g**	87	>20:1
8	 (*E*)-**1h**	B	 **6h**	76	>20:1
9	 (*Z*)-**1h**	B	 **6h**	69	>20:1

[a] Reaction conditions: enone **1** (0.20 mmol), disilane **2** (0.24 mmol), PtCl$_2$(cod) (3 mol %), toluene (0.80 mL) at 40 °C for 12 h. [b] Method A: Distillation under vacuum. Method B: MeLi in Et$_2$O/THF (1.5 equiv), 0 °C, 20 min, then aq NH$_4$Cl. [c] Isolated yield. [d] Ratio of **5**/**3** or **6**/**4**. [e] A 1:1 mixture of diastereomeric isomers.





A catalytic cycle proposed for the present silylation giving oxasilacyclohexenes **5** is shown in Scheme 1. Generation of

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(4) (a) Ishikawa, M.; Nakagawa, K.; Kumada, M. *J. Organomet. Chem.* **1977**, *135*, C45. (b) Heinicke, J.; Gehrhus, B. *J. Organomet. Chem.* **1992**, *423*, 13. (c) Heinicke, J.; Gehrhus, B.; Meinel, S. *J. Organomet. Chem.* **1994**, *474*, 71. (d) Heinicke, J. W.; Gehrhus, B. *Heteroat. Chem.* **1995**, *6*, 461. (e) Heinicke, J.; Meinel, S. *J. Organomet. Chem.* **1998**, *561*, 121.

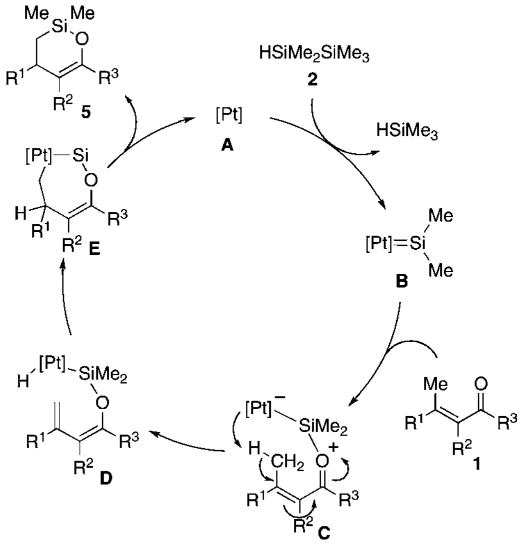
(5) Formation of 1-oxa-2-silacyclohex-5-enes by other reactions: (a) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1996**, *15*, 1524. (b) Hatanaka, Y.; Watanabe, M.; Onozawa, S.; Tanaka, M.; Sakurai, H. *J. Org. Chem.* **1998**, *63*, 422. (c) Tanaka, Y.; Yamashita, M. *Appl. Organomet. Chem.* **2002**, *16*, 51.

(6) In the reaction of (*Z*)-**1h** stopped in a shorter reaction time (30 min), a minor amount of (*E*)-**1h** (*Z*/*E* = 1/0.2) was observed, indicating the possibility of isomerization of (*Z*)-**1h** to (*E*)-**1h** before the silylene addition.

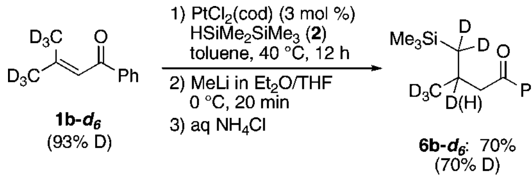
(7) For an example of the selective formation of β-silyl enolates, see: Crump, R. A. N. C.; Fleming, I.; Hill, J. H. M.; Parker, D.; Reddy, N. L.; Waterson, D. *J. Chem. Soc., Perkin Trans.* **1992**, 3277.

dialkylsilylenes from hydrodisilanes has been reported to take place on transition metal complexes including platinum.[9] It is most probable that the reaction proceeds through nucleophilic attack of the carbonyl oxygen of enone **1** onto an dimethylsilylene **B** stabilized by coordination to platinum, which is generated from pentamethyldisilane (**2**) and a low-valent platinum **A**. One of the methyl hydrogens on zwitterionic species **C**[10] is abstracted by platinum to form platinum hydride **D**. Insertion of the *exo*-methylene into the platinum hydride bond followed by reductive elimination of the carbon−silicon bond on **E** produces oxasilacyclohexene **5**.

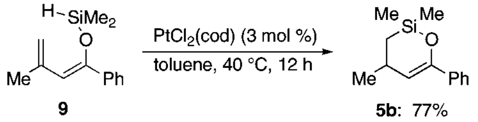
Scheme 1. A Catalytic Cycle Proposed for the Silylene Addition



This catalytic cycle is supported by the results obtained for the following two reactions (eqs 5 and 6). One is the deuterium-labeling experiment using hexadeuterated enone **1b**-d_6. The platinum-catalyzed reaction of **1b**-d_6 with hydrodisilane **2** under the standard conditions gave the silylation product **6b** where the β-position is incorporated with deuterium in 70%. The deuterium shift from γ-carbon to β-carbon is consistent with the proposed catalytic cycle which involves this hydrogen transfer from γ to β during the transformation of the intermediates from **C** to **E**. Another reaction is a platinum-catalyzed intramolecular hydrosilylation[11] of dienyloxy(hydro)silane **9**, which gave a high yield of cyclization product, oxasilacyclohexene **5b**, in the presence of platinum catalyst under similar reaction conditions to the silylene addition. This intramolecular hydrosilylation is generally accepted[11] to proceed by way of platinum hydride intermediate **D** which should be generated by oxidative addition of the hydrosilane moiety of **9**, demonstrating that the last two steps of the catalytic cycle after **D** (Scheme 1) take place once intermediate **D** is formed from **C** in the silylene addition.



(5)



(6)

In summary, we found a new type of platinum-catalyzed addition reaction of dimethylsilylene to β,β-dimethyl-substituted α,β-unsaturated ketones. A carbon−silicon bond is formed on the γ-methyl carbon to give 1-oxa-2-silacyclohex-5-enes with high selectivity. This catalytic silylene addition reaction has been studied for its synthetic utility and the catalytic cycle.

Acknowledgment. Support has been provided in part by a Grant-in-Aid for Scientific Research, the Ministry of Education, Culture, Sports, Science and Technology, Japan. K.O. thanks the Japan Society for the Promotion of Science for the award of a fellowship for graduate students.

Supporting Information Available: Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) (a) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983. (b) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. (c) Tamao, K.; Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C37.

(9) (a) Ogino, H. *Chem. Rec.* **2002**, *2*, 291 and references therein. (b) Feldman, J. D.; Mitchell, G. P.; Nolte, J.-O.; Tilley, T. D. *Can. J. Chem.* **2003**, *81*, 1127.

(10) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270.

(11) (a) Lane, T. H.; Frye, C. L. *J. Organomet. Chem.* **1979**, *172*, 213. (b) Tamao, K.; Tanaka, T.; Nakajima, T.; Sumiya, R.; Arai, H.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 3377. (c) Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712. (d) Tamao, K.; Nakagawa, Y.; Ito, Y. *J. Org. Chem.* **1990**, *55*, 3438. (e) Tamao, K.; Nakagawa, Y.; Ito, Y. *Organometallics* **1993**, *12*, 2297.