Organometallics **2004,** *23,* 169−171

Palladium-Catalyzed Dehydrogenative Double Silylation of Acetylenes with Bis- and Tris(dichlorosilyl)methanes: One-Step Synthesis of 1,1,3,3-Tetrachloro-1,3-disilacyclopent-4-ene Compounds

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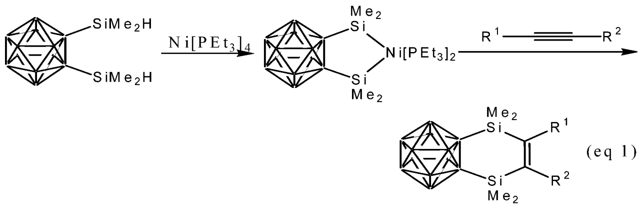
Received September 16, 2003

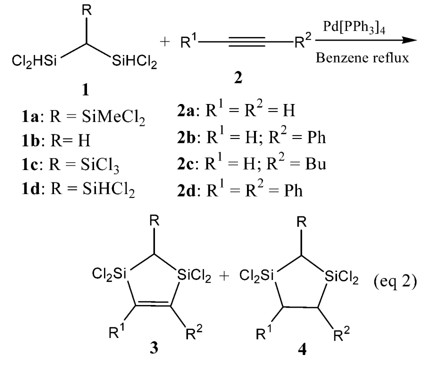
Summary: In situ tetrakis(triphenylphosphine)palladium appeared to be a very efficient catalyst for dehydrogenative double silylation of bis- and tris(dichlorosilyl)methanes with acetylenes to produce 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-enes in fair to excellent yields (32.7−92.6%), depending upon the substituents R^1 and R^2 at alkynes or R at silanes.

Although the hydrosilylation reaction is one of the most important Si−C bond forming reactions and has been widely investigated,[1] dehydrogenative double-silylation reactions of unsaturated organic compounds with hydridosilanes are relatively unexplored. The dehydrogenative double silylation of acetylenes with chlorosilanes was first reported by Kumada et al. in 1975.[2] The reaction gave stereospecific cis silylation products in good yields, but the nickel complex catalyst was unstable and high reaction temperatures of 250−300 °C were required. Tanaka et al. later reported the double-silylation reactions of acetylenes, alkenes, and dienes with *o*-bis(dimethylsilyl)benzene to give the corresponding disilacyclohexadiene derivatives.[3] Several nickel, palladium, and platinum compounds were found to be active catalysts for the reaction.[4] In the reaction mechanism, a five-membered intermediate derived from the oxidative addition of two Si−H bonds to the catalyst metal, followed by the evolution of hydrogen, was proposed.[5] The five-membered intermediate containing two Si−metal bonds interacted with acetylene to afford the disilacyclic double-silylation products.

Kang et al. recently reported the double silylation of alkynes, olefins, conjugated dienes, conjugated enones, and cyanides with *o*-bis(dimethylsilyl)carborane as a silylating agent.[6] They were able to isolate the nickel-, palladium-, or platinum-containing five-membered silacarborane intermediates and reported the X-ray structures (eq 1). From these results, metal-containing five-membered silacarboranes were proved to be the key intermediates in the dehydrogenative double-silylation reactions and the mechanism was clarified.



Recently, we reported the successful preparations of bis(dichlorosilyl)methane and tris(silyl)methanes by reacting elemental silicon directly with a mixture of methylene chloride,[7] (dichloromethyl)silanes, or chloroform and hydrogen chloride, respectively.[8] Considering that bis- and tris(silyl)methanes have two Si−H bonds, we attempted to react them with acetylenes by hydrosilylation to prepare 1,3-disilacyclopentanes. Surprisingly, 1,3-disilacyclopent-4-enes were obtained as the major products in fair to excellent yields, depending upon the reactants, when tetrakis(triphenylphosphine)palladium was used as a catalyst. Herein we wish to communicate the one-step synthesis of 1,3-disilacyclopent-4-enes having four Si−Cl functional groups by the dehydrogenative double-silylation reaction (eq 2).



As shown in Table 1, acetylene was bubbled into a solution of **1a** (4.91 g) and 0.087 g of tetrakis(triphen-

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[1] For reviews, see: (a) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, pp 1687−1792. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 1, pp 1479−1526. (c) Marciniec, B.; Gulinky, J.; Urbaniak, W.; Kornetka, Z. W. In *Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Pergamon: Oxford, U.K., 1992.

[2] Tamao, K.; Miyake, N.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5603.

[3] (a) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H. J. *Organometallics* **1991**, *10*, 16−18. (b) *J. Organomet. Chem.* **1992**, *428*, 1.

[4] (a) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467. (b) Naka, A.; Ishikawa, M.; Cha, S. H.; Lee, K. K.; Kwak, Y. W. *J. Organomet. Chem.* **2002**, *645*, 47. (c) Yoshida, H.; Ikadai, J.; Shudo, M.; Ohshita, J.; Kunai, A. *J. Am. Chem. Soc.* **2003**, *125*, 6638.

[5] (a) Belluco, U.; Bertani, R.; Michelin, R. A.; Mozzon, M. *J. Organomet. Chem.* **2000**, *600*, 37. (b) Ozawa, F.; Hikida, T. *Organometallics* **1996**, *15*, 4501. (c) Marciniec, B. *Appl. Organomet. Chem.* **2000**, *14*, 527.

10.1021/om034171z CCC: $27.50

Table 1. Dehydrogenative Double Silylations of Acetylenes with Bis- and Tris(silyl)methanes[a]

	reactant[b]						yield (%)[c]		
entry		R		R^1	R^2	time (h)	3		4
1			**2a**	H	H	8	**3aa**	92.6	trace
2	**1a**	SiMeCl$_2$	**2b**	H	Ph	3	**3ab**	83.3	
3			**2c**	H	Bu	2	**3ac**	72.3[d]	
4			**2d**	Ph	Ph	15	**3ad**	4.5[d]	
5			**2a**	H	H	5	**3ba**	38.9	2.1[d]
6	**1b**	H	**2b**	H	Ph	2	**3bb**	32.7	1.5[d]
7			**2d**	Ph	Ph	12	**3bd**	trace	
8	**1c**	SiCl$_3$	**2a**	H	H	6	**3ca**	45.3	
9	**1d**	SiHCl$_2$	**2a**	H	H	4	**3da**	47.8	
10			**2b**	H	Ph	2	**3db**	72.6	

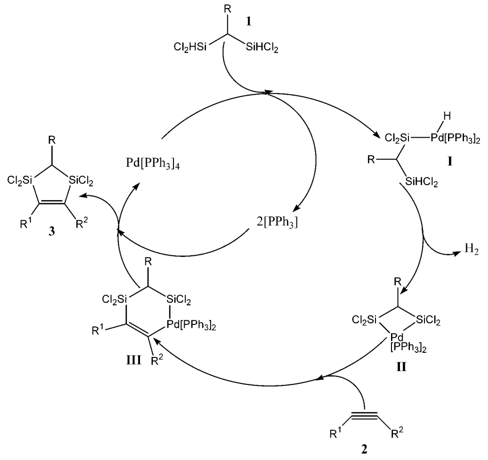
[a] (Methyldichlorosilyl)bis(dichlorosilyl)methane (**1a**), bis(dichlorosilyl)methane (**1b**), (trichlorosilyl)bis(dichlorosilyl)methane (**1c**), and tris(dichlorosilyl)methane (**1d**) were synthesized according to refs 7 and 8. [b] Reactions were carried out in benzene solvent at reflux temperature, in the presence of 0.5 mol % of palladium complex based on **1** used. Acetylene was blown into the reaction solution at a rate of 50 mL/min. [c] Isolated yields were based on reacted **1a** unless otherwise noted. [d] Yields were determined by GLC using *n*-dodecane as an internal standard.

ylphosphine)palladium in 75 mL of benzene at reflux temperature for 8 h. The reaction products were vacuum-distilled at 0.5 Torr to give 4.88 g of 2-(methyldichlorosilyl)-1,1,3,3-tetrachloro-1,3-disilacyclopent-4-ene (**3aa**)-in 92.7% isolated yield, based on reacted **1a**.[9]

The same reaction with **2b**,**c** also gave the double-silylation products in slightly lower yields than the reaction with **2a**, presumably due to the increased steric bulk of the acetylenes. The reaction of **1a** with diphenylacetylene **2d** gave only 4.5% yield of product while the reaction of **1b** with **2d** did not proceed. Similarly, only a small amount of dehydrogenative double-silylation product was obtained from the reaction of 3-hexyne with **1a**.[10] Lower reactivities of acetylenes having substituents at both sides of the triple bond might be explained by the higher steric interactions between the reacting acetylenes and silanes. This is in contrast to previously reported results for other systems, where steric hindrance was not a factor.[3a,6]

Although metal complexes of nickel, palladium, and platinum are known to be good catalysts for dehydrogenative double silylation,[3−6] reactions using Karstedt's platinum catalyst and tetrakis(triphenylphosphine)nickel instead of tetrakis(triphenylphosphine)palladium did not give the same double-silylation products. Reactions using chloroplatinic acid as a catalyst gave the double-silylation products in lower yields than the reactions using the palladium catalyst. Interestingly, the reaction of **1a** with **2d** in the presence of chloroplatinic acid gave the double-hydrosilylation product **4ad** in excellent yield instead of the dehydrogenative double-silylation product.[10] This indicates that dehydrogenative double-silylation and double-hydrosilylation reactions are competing and that the platinum catalyst is less sensitive to steric effects compared to the palladium catalyst. The results also indicate that double hydrosilylation is more favored when acetylenes having electron-withdrawing groups are used. Hydrosilylation is also more favored in the presence of platinum catalyst than palladium, likely due to easy complexation of platinum with carbon−carbon multiple bonds.[11]

Scheme 1



Reactions of **1b** with **2a**,**b** yielded **3ba**−**b** in moderate yields, along with a small amount of the open-chain hydrosilylation products. Besides the dehydrogenative 1,2-double-silylation products, 1,1-double-silylation products were also reported as byproducts in reactions with terminal acetylenes.[3] However, the 1,1-double-silylation products were not detected in the reactions of terminal alkynes **2b**,**c** with **1a**, probably due to the high ring strain of the four-membered-ring products. The dehydrogenative 1,2-double silylation was also extended to alkenes and conjugated dienes. The reaction of **1b** with alkenes at refluxing temperature in the presence of palladium complex for 20 h did not give any product but gave open-chain hydrosilylation products in the presence of chloroplatinic acid. The analogous palladium-catalyzed reaction of **1b** with conjugated dienes gave open-chain hydrosilylation products.[12] This indicates that the reactivity of alkynes in the double-silylation reaction to afford **3** and **4** is higher than those of alkenes and alkanedienes in the presence of palladium or platinum catalyst. In general, trisilyl compounds give cyclized products in higher yields than dissilyl compounds. The favorable intramolecular cyclization reaction of trisilyl compounds may be explained by the closer interaction of the two dichlorosilyl groups due to steric repulsion between the silyl substituents on the α-carbon and the two dichlorosilyl groups.

On the basis of our results and previous reports, a plausible catalytic cycle is proposed, as shown in Scheme

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(6) (a) Kang, Y. J.; Lee, J. H.; Kong, Y. K.; Kang, S. O.; Ko, J. J. *Organometallics* **2000**, *19*, 1722. (b) Kang, S. O.; Lee, J. H.; Ko, J. J. *Coord. Chem.* **2002**, *231*, 47.

(7) (a) Jung, I. N.; Yeon, S. H.; Han, J. S. *Organometallics* **1993**, *12*, 2360. (b) Yeon, S. H.; Han, J. S.; Yoo, B. R.; Jung, I. N. *J. Organomet. Chem.* **1996**, *516*, 91.

(8) (a) Han, J. S.; Yeon, S. H.; Yoo, B. R.; Jung, I. N. *Organometallics* **1997**, *16*, 93. (b) Lee, C. Y.; Han, J. S.; Oh, H. S.; Yoo, B. R.; Jung, I. N. *Bull. Korean Chem. Soc.* **2000**, *21*, 1020.

(9) As a representative reaction for a liquid acetylene, the reaction of **1a** with **2b** is described as follows: a 100 mL, round-bottomed, flame-dried, two-necked flask equipped with a magnetic stir bar, condenser, and N$_2$ inlet was charged with **1a** (4.91 g, 15 mmol), 0.087 g of Pd-[PPh$_3$]$_4$, and 75 mL of dried benzene. The flask was then heated to reflux temperature. **2b** (2.30 g, 22.5 mmol) was added to the flask at 0.02 mL/min using a syringe pump. After they were maintained at reflux temperature for 3 h, the reaction products were distilled under vacuum to give 5.34 g of 2-(methyldichlorosilyl)-1,1,3,3-tetrachloro-4-phenyl-1,3-disilacyclopent-4-ene (**3ab**) in 83.3% isolated yield. This yield drastically decreased to 31.2% and a larger amount of polymeric material was obtained when **2b** was added in one portion at the beginning stage of the reaction.

(10) Details will be published elsewhere.

(11) (a) Sakaki, S.; Ogawa, M.; Musashi, Y.; Arai, T. *J. Am. Chem. Soc.* **1994**, *116*, 7258. (b) Albinati, A. *Organometallics* **1987**, *6*, 788.

(12) See the Supporting Information.

1. First, an oxidative addition of the Si−H bond of **1** to palladium presumably takes place to form intermediate **I**, and subsequently the second Si−H bond adds to palladium to liberate hydrogen and form disilacyclic intermediate **II**. The formation of intermediate **II** is reasonable and consistent with the five-membered silacarborane intermediates reported by Kang et al.[6] Although the ring strain of intermediate **II** should be higher than that of the five-membered silacarborane intermediates,[6] its existence is not unreasonable; a three-membered palladacyclopropane intermediate has been reported and characterized by X-ray spectroscopy in the bis-silylation of acetylenes catalyzed by a palladium complex.[13] The insertion of an in situ alkyne into a silicon−palladium bond to produce **III**, followed by reductive elimination, provides the dehydrogenative double-silylation products **3**.

In summary, the dehydrogenative double-silylation reactions of alkynes with bis- and tris(dichlorosilyl)methanes **1a**−**d** were effectively catalyzed by a palladium complex to afford 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-enes. Details of the extension of this chemistry to other substituted bis- and tris(dichlorosilyl)methane compounds will be reported shortly.

Acknowledgment. Financial support from Dow Corning Co. for this research is gratefully acknowledged. We thank Prof. D. Son of Southern Methodist University, Dallas TX, for his help and discussions in the preparation of this paper.

Supporting Information Available: Text giving experimental procedures and characterization data for the products obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034171Z

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[13] Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237.