

NEW STARTING MATERIALS FOR SILICONES AND CARBOSILANES: DIRECT SYNTHESIS OF ORGANOCHLOROSILANES CONTAINING Si-C-Si AND Si-H BONDS

By Il Nam Jung
Organometallic Chemistry Lab.
Korea Institute of Science & Technology
P.O. Box 131 Cheongryang,
Seoul 130-650, Korea

Introduction

Organosilicon polymers, known as silicones are compounds in which the elements silicon and oxygen alternate in the molecular skeleton. Organosiloxanes containing Si-O-Si bonds can be considered to be structurally derived from silica. Polycarbosilanes are compounds in which the elements silicon and carbon alternate in the molecular skeleton. They are similar to silicones except that the oxygen bridges of silicones are replaced by methylene units. Polycarbosilanes have been reported to be useful as precursors for the silicon carbide continuous fiber.¹ When carbosilanes having the alternating Si-C-Si arrangements in the molecular skeleton are used for the modification of silicones, interesting properties of the silicones are expected from the molecular arrangements.

Since the early 1940's, the direct synthesis of organochlorosilanes from elemental silicon and organic chlorides has been intensively studied.² Recently, the direct synthesis of organochlorosilanes containing Si-C-Si bonds from elemental silicon and organic polychloride or chloromethyl group containing silicon compounds appeared. These new monomeric compounds open numerous routes to other organosilicon derivatives and find a number of industrial applications. This review provides a summary on the direct synthesis of organochlorosilanes, particularly emphasizing compounds containing the Si-C-Si bond.

The Direct Synthesis of Methylchlorosilanes

The direct synthesis of methylchlorosilanes, known as the Rochow reaction is the reaction of methyl chloride with elemental silicon in the presence of copper catalyst. The direct process is the most widely used basic technique in the silicone industry.³ The reaction gives dimethyldichlorosilane, methyltrichlorosilane, trimethylchlorosilane, tetrachlorosilane and small quantities of a number of high boiling compounds.

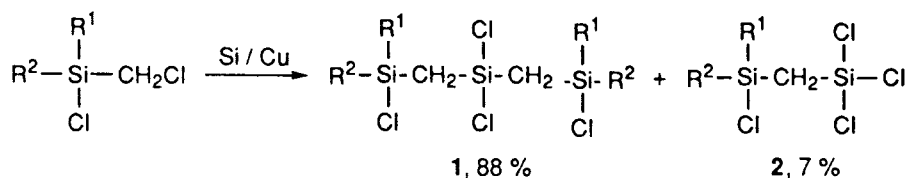
		bp (°C)	composition(%)	
CH ₃ Cl	$\xrightarrow{\text{Si / Cu}}$	(CH ₃) ₂ SiCl ₂	70	75
		(CH ₃) ₃ SiCl	66	10
		CH ₃ SiCl ₃	58	4
		CH ₃ HSiCl ₂	41	6
		Others		

The composition of products and reaction rate depend on a large number of factors such as the nature of the starting materials, the catalyst, the reaction temperature, the reaction pressure, the type of reactor used, and the degree of conversion of silicon and methyl chloride. The catalyst for the direct process is always copper, in some cases co-catalysts such as zinc, aluminum, cadmium etc. are added. The co-catalysts enhance the reactivity of elemental silicon and shorten the induction period and increase the selectivity of dimethyldichlorosilane production. The reaction is carried out at 250-350°C, and the yield of dimethyldichlorosilane decreases at temperatures above 300°C. In the absence of a catalyst, the reaction is sluggish and gives irreproducible results.³

The Direct Reactions with Chloromethyl-containing Organosilanes

The reaction of α -chloromethylsilanes with elemental silicon is very similar to that of methyl chloride and was first reported by Mironov et al in 1956.⁴ α -Chloromethylsilanes are readily prepared by the chlorination of corresponding methylsilanes under UV irradiation in refluxing carbon tetrachloride.⁵ When (chloromethyl)methyldichlorosilane was directly reacted with silicon, 1,1,1,3,3-pentachloro-1,3-disilabutane and 2,2,4,4,6,6-hexachloro-2,4,6-trisilaheptane were obtained in 28.7% and 16.7% yields respectively. They obtained only a small amount of 1,1,1,3-tetrachloro-1,3-disilabutane and 2,4,4,6-tetrachloro-2,4,6-trisilaheptane from the reaction of (chloromethyl)-dimethylchlorosilane with silicon at 370-390°C.⁶ They also claimed that the yields of the reaction between α -chloromethylsilanes and elemental silicon in the presence of copper catalyst were improved by adding zinc and cadmium as promoters at 400-500°C.⁷ In all cases above, the yields were relatively poor and the major products were trichlorosilyl group terminated compounds. This indicates that the dechlorination or decomposition of the starting silane was involved. Although the direct reaction of α -chloromethylsilanes with elemental silicon gives Si-C-Si bond containing chlorosilanes, the decompositions of the starting material or the products easily deactivate the elemental silicon and make the process economically less feasible.

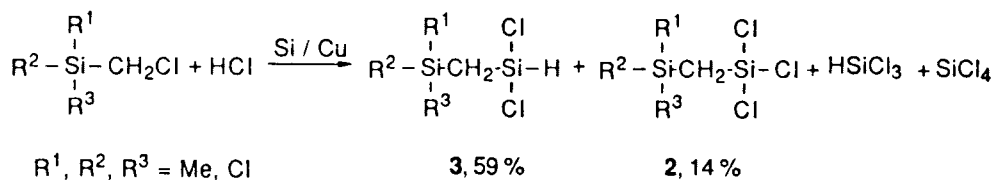
We investigated direct reaction of a series of α -chloromethylsilanes with elemental silicon in the presence of copper catalyst using a stirred reactor equipped with a spiral band agitator at carefully controlled temperatures between 250 and 350°C.⁸ Trisilaalkanes were obtained as the major products and bis(silyl)methanes as the minor products. The selectivity for the trisilaalkanes was as high as 88%. This result indicates that the success of the direct synthesis depends on an accurately specified reaction temperature.



The Si-H bonds containing organochlorosilanes are very important starting materials for silicones, because it undergoes hydrosilylation reaction to the unsaturated organic compounds. Methyldichlorosilane is a minor product of commercial direct process reaction. The addition of hydrogen chloride to methyl chloride increases the yield of methyldichlorosilane up to 9.5% at the maximum.⁹ The reactivity difference between the two chlorides prevents higher yield of methyldichlorosilane.

We attempted the synthesis of Si-H containing bis(silyl)methanes by reacting elemental silicon with a mixture of α -chloromethylsilanes and hydrogen chloride.¹⁰ In the reaction, Si-H containing bis(silyl)methanes were obtained as the major products and the yields were around 50% for all the cases. The major products were presumably derived from the reaction in which one mole of each α -chloromethylsilanes and hydrogen chloride reacted with the same silicon atom. The two minor byproducts were identified as trichlorosilane and tetrachlorosilane. The production ratio of trichlorosilane and tetrachlorosilane was about 3:1, which would be normally obtained from the direct reaction of silicon with hydrogen chloride.¹¹

The success in the direct synthesis of Si-H containing bis(silyl)methanes suggested that this hydrogen chloride incorporating method could be applied to the direct reaction of polychlorinated alkanes.

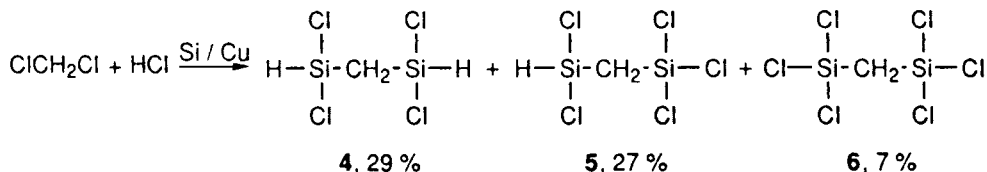


The Direct Reactions with Polychlorinated Alkanes

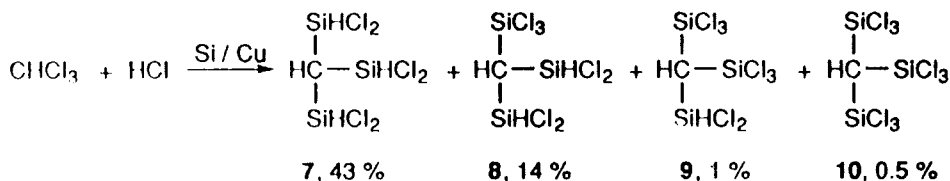
The direct reactions of elemental silicon with polychlorinated alkanes, such as methylene chloride and chloroform were investigated as early as 1947.¹² In general, methylene chloride reacts with silicon at lower temperature than methyl chloride. The products obtained from the reaction with methylene chloride were linear compounds of formula $\text{Cl}_3\text{Si}(\text{SiCl}_2\text{CH}_2)_n\text{Si}_2\text{Y}$ ($\text{Y} = \text{H}$ or Cl , $n = 1 - 4$) as well as cyclic organosilicon compounds of formula $(\text{SiCl}_2\text{CH}_2)_x$ ($x = 3$). Later, Fritz et al reported the same reaction and isolated from a similar reaction mixture the crystalline compound 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane $(\text{Cl}_2\text{Si-CH}_2)_3$ as well as the eight-membered ring compound $(\text{Cl}_2\text{Si-CH}_2)_4$.¹³

However, many of these reactions are accompanied by dehydrochlorination and dechlorination under the conditions of the direct synthesis. This is the reason that the reactions give many products.¹⁴ Fritz and his coworker first reported that Si-H containing (trichlorosilyl)(dichlorosilyl)methane, **5** was obtained in about 3% as a by-product from the direct reaction of metallic silicon with methylene chloride in the presence of copper catalyst at 280 °C.¹⁵ This indicates that hydrogen chloride generated from the decomposition of methylene chloride simultaneously reacts with elemental silicon as methylene chloride reacts. In this case, the yield was not very high and the decomposition of methylene chloride easily deactivated the elemental silicon and copper catalyst and made the process economically less feasible.

The influence of hydrogen chloride addition to direct reactions of elemental silicon with methylene chloride has been reinvestigated.¹⁶ The decomposition of methylene chloride and production of polymeric carbosilanes were greatly reduced by simultaneously reacting hydrogen chloride and methylene chloride. The major products were bis(chlorosilyl)methanes such as bis(dichlorosilyl)methane, **4**, (dichlorosilyl)(trichlorosilyl)methane, **5**, and bis(trichlorosilyl)methane, **6**, along with a number of high boiling compounds in a small quantity. The deactivation problem of the contact mass due to decomposition of methylene chloride and polycarbosilanes was eliminated. Cadmium was a good promoter for the reaction, while zinc was found to be an inhibitor for this particular reaction.

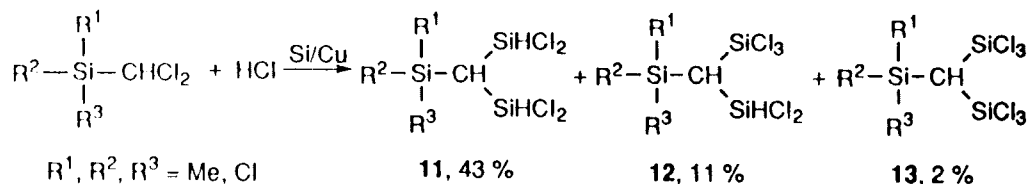


The effect of hydrogen chloride addition to direct reactions of elemental silicon with chloroform has been also reinvestigated in the presence of copper catalyst using a stirred reactor equipped with a spiral band agitator at the carefully controlled temperature between 220 °C and 320 °C.¹⁷ Tris(silyl)methanes with Si-H bonds was obtained as the major products along with trichlorosilane and tetrachlorosilane derived from the reaction between elemental silicon and hydrogen chloride. Besides these products, bis(silyl)methanes such as **4**, **5** and **6** derived from the reaction between elemental silicon and methylene chloride were also obtained in a small quantity. This indicates that methylene chloride is generated during the direct reaction presumably by the decomposition of chloroform.

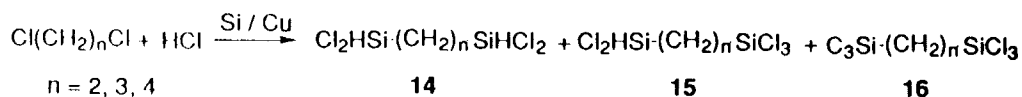


When a mixture of carbon tetrachloride and hydrogen chloride was reacted with elemental silicon, tetrakis(silyl)methanes were not obtained, but bis(silyl)methanes(**4-6**) and tris(silyl)methane(**7-10**) derived from the reaction of methylene chloride and chloroform respectively were also obtained. This indicates that methylene chloride and chloroform is generated during the direct reaction presumably by the decomposition of carbon tetrachloride.

Mixtures of hydrogen chloride and α, α -dichloromethylsilanes react with elemental silicon to give Si-H bonds containing tris(silyl)methanes (**11-13**) as represented in the following equation.¹⁸ α, α -Dichloromethylsilanes are easily obtained as byproducts from the chlorination of corresponding methylsilanes under UV irradiation in refluxing carbon tetrachloride.⁵



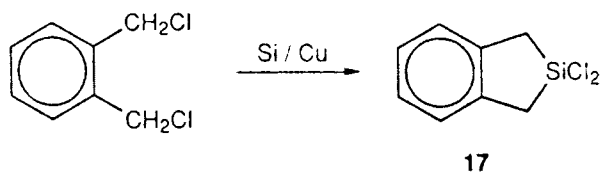
Similarly the direct reaction of elemental silicon with a mixture of α, ω -dichloroalkanes and hydrogen chloride give α, ω -bis(silyl)alkanes in good yields.¹⁶



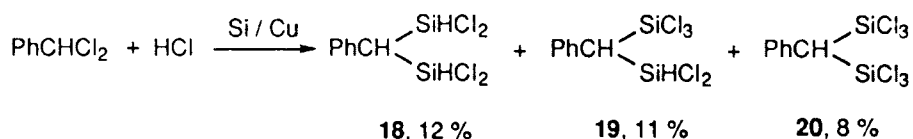
The Direct Reactions with Benzyl Chlorides

Although direct reactions of elemental silicon with various alkyl chlorides have been reported, the direct reaction with benzyl chlorides has never been reported. The reason is that benzyl chloride decomposes rapidly when contacted with Si-Cu contact mixture at temperatures above 150°C.¹⁹ Even if a mixture of hydrogen chloride and benzyl chloride is reacted with silicon, benzylchlorosilanes are not obtained. The following two cases are the first examples for the direct reactions of benzyl chlorides with silicon.

When α, α' -dichloro-*o*-xylene was reacted with elemental silicon, 2,2-dichloro-2-silaindan was obtained in 51% yield.²⁰



When hydrogen chloride was added to a reaction of α, α -dichlorotoluene with silicon, α, α -bis(silyl)toulenes were obtained as shown in the following equation.¹⁶



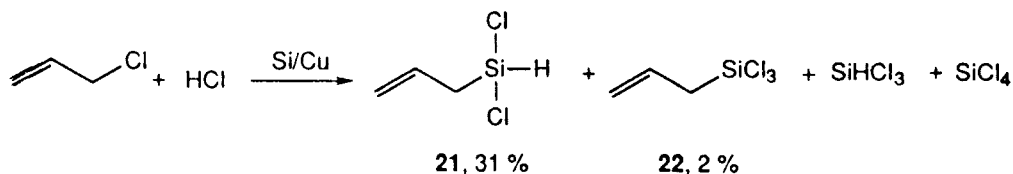
The Direct Synthesis of Allylchlorosilanes

Direct synthesis of allylchlorosilanes was first reported by Hurd as early as in 1945.²¹ When allyl chloride was reacted with a 9:1 Si-Cu alloy, a vigorous exothermic reaction occurred even at 250°C. The yield based on allyl chloride used was not reported, but the condensate in an ice cooled condenser obtained 60% allyl containing chlorosilane products with allyltrichlorosilane predominating due to the decomposition of allyl chloride during the reaction.

A more detailed investigation on the direct reaction was reported by Mironov and Zelinskii.⁸ The yield of all the allylchlorosilanes was only 18% based on allyl chloride used. A mixture of allylchlorosilanes amounting to 50% of the products was obtained from the reaction of allyl chloride with a 4:1 Si-Cu alloy at 300°C. Allyldichlorosilane, allyltrichlorosilane, and diallyldichlorosilane were presented in the product

mixture in a ratio of 1:0.5:0.3. Allyldichlorosilane was presumably produced from the reaction of silicon atom with one mole of each allyl chloride and hydrogen chloride generated from allyl chloride decomposition. The decomposition of allyl chloride and the easy polymerization of diallyldichlorosilane at high temperatures above 130 °C were the major problems involved in the direct synthesis of allylchlorosilanes.²¹ This is why this direct reaction has never been used on a large scale in industry.

We reinvestigated the direct synthesis of allyldichlorosilane by reacting elemental silicon simultaneously with allyl chloride and hydrogen chloride in the presence of copper catalyst.²² Allyldichlorosilane, **21** was obtained as the major product and allyltrichlorosilane was a minor product. The decomposition of allyl chloride was suppressed and the production of diallyldichlorosilane reduced by adding hydrogen chloride to the allyl chloride reactant. The polymerization problem in the distillation process of the products due to diallyldichlorosilane was eliminated.

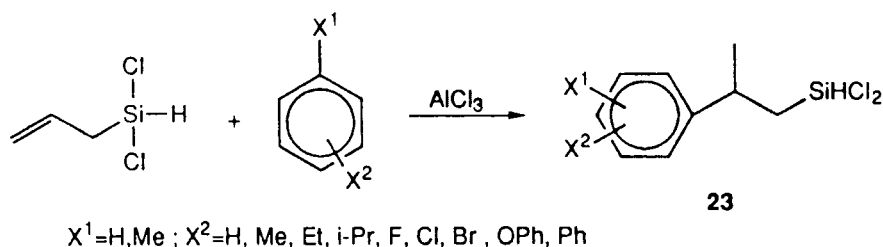


The success of this direct synthesis made allyldichlorosilane, a useful reagent for further reactions such as Friedel-Crafts type alkylation and hydrosilylation, readily available.

Friedel-Crafts Type Alkylation with Allylchlorosilanes

The alkylation of benzene systems with allylsilanes was firstly reported by the Nametkin group.²³ (2-Arylpropyl)silanes were obtained on reaction of allylchlorosilanes, such as allyldichlorosilane and allyltrichlorosilane with substituted benzenes. The yields ranged from 34% to 66% depending upon the benzene ring substituents, but information concerning reaction rates and product isomer distribution was not reported.

We studied the alkylation of substituted benzenes with allyldichlorosilane and reported substituent effects of benzene ring systems, relative reaction rates, and isomer distributions of the products.

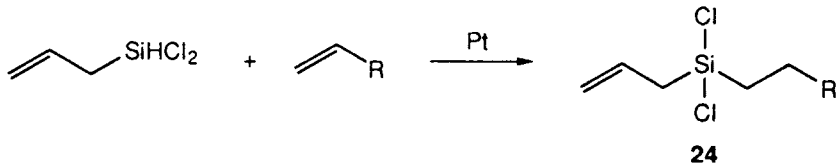


Friedel-Crafts type reaction of substituted benzenes with allyldichlorosilane in the presence of aluminum chloride as a catalyst resulted in alkylation giving 3-aryl-1,1-dichloro-1-silabutanes in good yields (60-85%).²⁴ The alkylation of substituted benzenes with allyldichlorosilane at temperatures below 0 °C gave *ortho*- and *para*-directing products at an early stage, but the products isomerized to *meta*-isomer as the reaction proceeded for prolonged times or at moderately higher reaction temperature. The competitive alkylation rates of substituted benzenes having a various substituents (X) decreased in the following order; X = Ph > PhO > i-Pr > Et > Me > H > F > Cl > Br.²⁵ When the alkylation rates of substituted benzenes with respect to benzene (log *kx/kh*) were plotted against the substituent coefficients (σ), a linear relationship was observed. The results showed that electron-donating groups on benzene ring generally facilitate the alkylation, while electron-withdrawing groups are deactivating. This alkylation method is a good route to (2-arylpropyl)dichlorosilanes having Si-H functionality which can be used for subsequent hydrosilylation reactions designed to introduce various organic functional groups into the silanes.

(2-Arylpropyl)dichlorosilane containing Si-H bond obtained from the alkylation of substituted benzenes with allyldichlorosilane could find industrial applications as starting materials for new silicones.

Hydrosilylation Using Allyldichlorosilane

The hydrosilylation of olefins with allyldichlorosilane in the presence of chloroplatinic acid diluted with iso-propanol gave allylalkyldichlorosilanes retaining the allyl group. When the olefin was used in five-fold excess or more relative to allyldichlorosilane, allylalkyldichlorosilanes were obtained in good yields (63-89%) and the formation of double hydrosilylation products was reduced to less than 6%. The isomerization of allylsilane to 1-propenylsilane was suppressed by lowering reaction temperatures below 100 °C.²⁵ This hydrosilylation of olefins with allyldichlorosilane is a good synthetic route to allyl group containing organodichlorosilanes.



Summary

A number of organochlorosilanes containing Si-C-Si and Si-H bonds have been successfully prepared by reacting elemental silicon with chloromethyl-containing silanes or polychlorinated alkanes. The success of this direct synthesis makes new class of organochlorosilanes readily available, which will find many industrial applications as starting materials for silicones and as precursors for silicon containing ceramic materials.

References

1. (a) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M.T. *J. Mater. Sci.* **1978**, *13*, 2659. (b) Hasegawa, Y.; Iimura, M.T.; Yajima, S. *J. Mater. Sci.* **1980**, *15*, 720. (c) Yajima, S. *Am. Ceram. Soc. Bull.* **1983**, *62*, 893.
2. (a) Voorhoeve, R.J.H. *Organochlorosilanes: Precursors to Silicones*, Elsevier Publishing Co., New York, 1967. (b) Noll, W. *Chemistry and Technology of Silicones*, Academic Press, New York, 1968. (c) Rochow, E. *Chemistry of Silicones*, Wiley, New York, 1951. (d) K. M. Lewis, D.G. Rethwisch, "Catalyzed Direct Relations of Silicon", Elsevier, Amsterdam, 1993.
3. (a) E.G. Rochow, *J. Am. Chem. Soc.* **1945**, *67*, 963 (1945). (b) E.G. Rochow in *Inorganic Synthesis*, Vol. III. McGraw-Hill, New York 1950, p56. (c) E.G. Rochow, US Patent 2,380,995; *Chem Abstr.* **1945**, *39*, 4889.
4. Mironov, V.M.; Zelinski, D.N. *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk.* **1957**, 383.
5. Krieble, R.H.; Elliott, J.R. *J. Am. Chem. Soc.* **1945**, *67*, 1810.
6. Mironov, V.F.; Gar, T.K.; Buyakov, A.A. *Zh. Obshch. Khim.* **1972**, *42* 1361.
7. Mironov, V.F.; Gar, T.K.; V.D. Sheludyakov, V.D.; Buyakov, A.A.; Andreev, V.I.; Petrova, I.N. U.S.S.R. Patent 394, 378.; *Chem. Abstr.* **1974**, *80*, 37274v.
8. (a) Jung, I.N.; Lee, G.H.; Yeon, S.H.; Suk, M.Y. *Bull. Korean Chem. Soc.* **1991**, *12*, 445. (b) Jung, I.N.; Lee, G.H.; Yeon, S.H.; Suk, M.Y. U.S. Patent 5,075,477.; *Chem. Abstr.* **1992**, *116*, 174424v.
9. Halm, R.L.; Zapp, R.H. U.S. Patent 4,966,986; *Chem. Abstr.* **1991**, *114*, 102385u.
10. (a) Jung, I.N.; Yeon, S.H.; Han, J.S. *Organometallics* **1993**, *12*, 2360. (b) Jung, I.N.; Yeon, S.H.; Han, J.S. U.S. Patent 5,233,069; *Chem. Abstr.* **1993**, *119*, p226189f.
11. Friedel, C.; Ladenburg, A. *Justus Liebigs Ann. Chem.* **1867**, *143*, 118.
12. Padnode and Schiessler, U.S. Patent 2,381,000; *Chem. Abstr.* **1945**, *39*, 4889.
13. (a) Fritz, G.; Thielking, H.Z. *Anorg. Allg. Chem.* **1960**, *306*, 39. (b) Fritz, G.; Worsching, A.Z. *Anorg. Allg. Chem.* **1984**, *512*, 131.
14. Fritz, G.; Matern, E. *Carbosilanes-Synthesis and Reactions*, Spring-Verlag, New York, 1986.
15. Fritz, G.; Thielking, H.Z. *Anorg. Allgem. Chem.* **1960**, *306*, 39.
16. Jung, I.N.; Yeon, S.H.; Lee, B.W. U.S. Patent 5,235,083; *Chem. Abstr.* **1993**, *119*, p226190z.
17. Jung, I.N.; Yeon, S.H.; Han, J.S. U.S. Patent 5,332,849; *Chem. Abstr.* **1994**, *121*, 231048e.
18. Jung, I.N.; Yeon, S.H.; Han, J.S. U.S. Patent Application#08/164,944 ('93. 12. 10).
19. Jung, I.N.; Yeon, S.H. unpublished results.
20. Jung, I.N.; Yeon, S.H.; Han, J.S. *Bull. Korean Chem. Soc.* **1993**, *14*, 315.
21. Hurd, D.T., *J. Am. Chem. Soc.* **1945**, *67*, 1813.
22. Yeon, S.H.; Lee, B.W.; Kim, S.-I.; Jung, I.N. *Organometallics* **1993**, *12*, 4887.
23. Nametkin, N.S.; Vdovin, V.M.; Finkel-shtein, E.S.; Oppengeim, V.D.; Chekalina, N.A. *Izv. Akad. Nauk. S.S.S.R., Ser. Khim.* **1966**, *11*, 1998.
24. Lee, B.W.; Yoo, B.R.; Kim, S.-I.; Jung, I.N., *Organometallics* **1994**, *13*, 1312.
25. Lee, B.W.; Yoo, B.R.; Yeon, S.H.; Lee, K.-B.; Jung, I.N., *Main Group Chemistry*, **1995**, in press.