

5. Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1984**, *5*, 129.
6. Woods, R. J.; Khalil, M.; Pell, W.; Moffat, S. H.; Smith, Jr. V. H. *J. Comput. Chem.* **1990**, *11*, 297.
7. Chirlian, L. E.; Francl, M. M. *J. Comput. Chem.* **1987**, *8*, 894.
8. (a) Williams, D. E. *J. Comput. Chem.* **1988**, *9*, 745. (b) Stouch, T. R.; Williams, D. E. *J. Comput. Chem.* **1993**, *14*, 858.
9. Poland, D.; Scheraga, H. A. *Biochemistry* **1967**, *6*, 3791.
10. Abraham, R. J.; Hudson, B. J. *Comput. Chem.* **1985**, *6*, 173.
11. Mortier, W. J.; Ghosh, S. K.; Shankar, S. *J. Am. Chem. Soc.* **1986**, *108*, 4315.
12. (a) Stone, A. J. *Chem. Phys. Lett.* **1981**, *83*, 233. (b) Stone, A. J.; Alderton, M. *Mol. Phys.* **1985**, *56*, 1047.
13. Momany, F. A.; McGuire, R. F.; Burgess, A. W.; Scheraga, H. A. *J. Phys. Chem.* **1975**, *79*, 2361.
14. Matsuoka, O.; Clementi, E.; Yoshimine, M. *J. Chem. Phys.* **1976**, *64*, 1351.
15. Sanderson, R. T. *Chemical Bonds and Bond Energy*; Academic Press, New York, 1976, 15.
16. Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.
17. Hinze, J.; Jaffé, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540.
18. Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284.
19. (a) Gasteiger, J.; Marsili, M. *Tetrahedron* **1980**, *36*, 3219. (b) Guillen, M. D.; Gasteiger, J. *Tetrahedron* **1983**, *39*, 1331. (c) Gasteiger, J.; Saller, H. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 687.
20. (a) Mortier, W. J.; Van Genechten, K.; Gasteiger, J. *J. Am. Chem. Soc.* **1985**, *107*, 829. (b) Mortier, W. J.; Ghosh, S. K.; Shankar, S. *J. Am. Chem. Soc.* **1986**, *108*, 4315. (c) Van Genechten, K. A.; Mortier, W. J.; Geerlings, P. *J. Chem. Phys.* **1987**, *86*, 5063 (d) Baekelandt, B. G.; Mortier, W. J.; Lievens, J. L.; Schoonheydt, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6730.
21. (a) Nalewajski, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 944. (b) Nalewajski, R. F.; Parr, R. G. *J. Chem. Phys.* **1982**, *77*, 399.
22. Mullay, J. *J. Am. Chem. Soc.* **1984**, *106*, 5842.
23. Hammarström, L.-G.; Liljefors, T.; Gasteiger, J. *J. Comput. Chem.* **1988**, *9*, 424.
24. (a) No, K. T.; Grant, J. A.; Scheraga, H. A. *J. Phys. Chem.* **1990**, *94*, 4732. (b) No, K. T.; Grant, J. A.; Jhon, M. S.; Scheraga, H. A. *J. Phys. Chem.* **1990**, *94*, 4740. (c) Park, J. M.; No, K. T.; Jhon, M. S.; Scheraga, H. A. *J. Comput. Chem.* **1993**, *14*, 1482.

Redistribution of Bis- and Tris(silyl)methanes Catalyzed by Red-Al

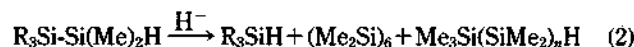
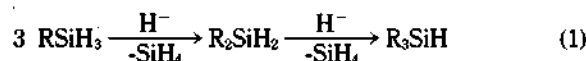
Hee-Gweon Woo*, Sun-Jung Song, Eun Jeong Cho†, and Il Nam Jung†

Department of Chemistry, Chonnam National University, Kwangju 500-757, Korea

†Organometallic Chemistry Laboratory, Korea Institute of Science & Technology, P.O. Box 131 Cheongryang, Seoul 130-650, Korea

Received November 15, 1995

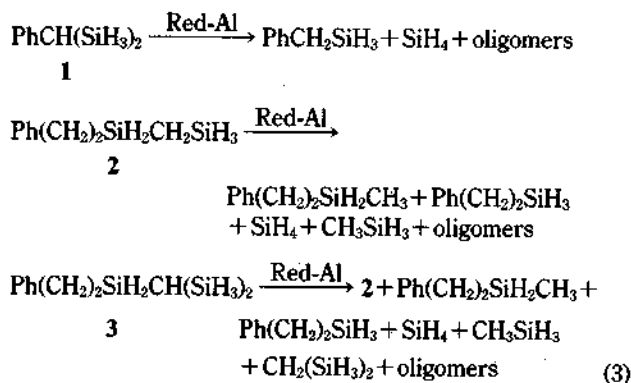
Red-Al (or Vitride; sodium bis(2-methoxyethoxy)aluminum hydride) is known to catalyze the polymerization of lactams and olefins and the trimerization of isocyanates.¹ Corriu and coworkers reported the exchange reactions of di- and trihydrosilanes^{2a} (eq. 1) and the oligomerization of disilanes^{2b} (eq. 2), catalyzed by inorganic hydrides (e.g., NaH, KH, etc.). They suggested a mechanism *via* the intermediacy of a pentacoordinated hydrosilyl anion,^{2c} which is formed by addition of hydride (H⁻) on the silanes.



Riviere *et al.* described the preparation of oligogermane (PhHGe)_n by redistribution of PhH₂GeGeH₂Ph with PhH₂GeLi.³ The Lewis acid AlCl₃ is well known to catalyze redistribution reaction of hydroarylsilane to afford quaternary arylsilane and SiH₄.⁴ We recently reported the dehydropolymerization of bis(silyl)alkylbenzenes catalyzed by group 4 metallocene complexes, generated *in situ* from Cp₂MCl₂/Red-Al, to produce highly cross-linked polysilanes.⁵ During the study we found an intriguing redistribution of bis- and tris(silyl)methanes, catalyzed by Red-Al.

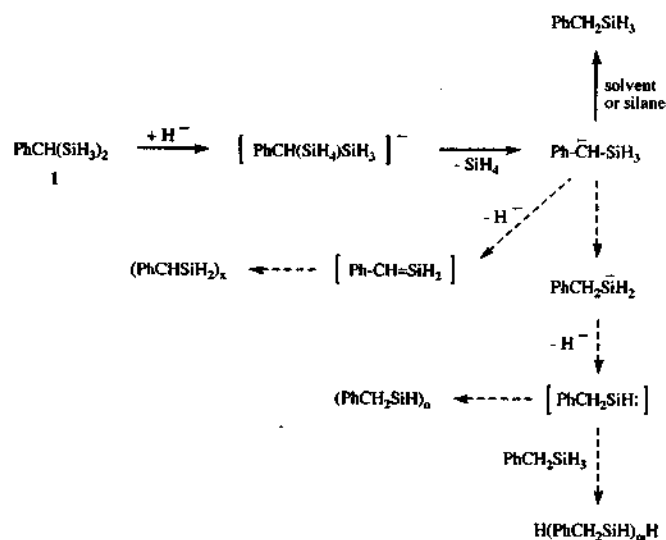
2-Phenyl-1,3-disilapropane **1**,⁵ 1-phenyl-3,5-disilapentane **2**,⁶ and 1-phenyl-4-silyl-3,5-disilapentane **3**⁶ were prepared by reaction of corresponding chlorosilane with LiAlH₄. In a typical experiment, **1** (0.18 g, 1.18 mmol) was slowly added to a Schlenk flask charged with Red-Al (17 μL, 0.058 mmol; 3.4 M solution in toluene) and toluene (5 mL). (*Warning! In the absence of toluene solvent, rapid addition of 1 to Red-Al resulted in a violent explosion with fire due to the drastic production of SiH₄, which is an explosive gas upon contact with air. Therefore, the reaction should be performed in the dilute condition with suitable precaution. We recommend you not to exceed the reaction scale employed here.*) The reaction started immediately, as monitored by the immediate release of SiH₄ gas. After being stirred for 1 h, GC/MS analysis and ¹H NMR spectroscopy showed that **1** was quantitatively converted to benzylsilane as major and as yet uncharacterized high-boiling oligomers as minor. The starting silane **1** was completely disappeared. However, it was difficult to assign the exact composition and yields of the products because the minor product could be a mixture of high-boiling oligomers, and the amount of evolved gases is difficult to measure. Similarly, the bis(silyl)methane **2** was quantitati-

vely transformed to methylphenethylsilane and phenethylsilane (7 : 3 ratio, identified by GC/MS analysis) as major and as yet uncharacterized high-boiling oligomers as minor with SiH_4 and MeSiH_3 gases. The tris(silyl)methane **3** was quantitatively changed to **2**, methylphenethylsilane, and phenethylsilane (3 : 12 : 4 ratio, identified by GC/MS analysis⁷) as major and as yet uncharacterized high-boiling oligomers as minor with SiH_4 , MeSiH_3 , and $\text{CH}_2(\text{SiH}_3)_2$ gases (eq. 3).



The benzylsilane seemed not to undergo appreciably a further redistribution in the redistribution reaction of **1**. The methylphenethylsilane can be obtained *via* Si-C bond cleavage of **2**, giving off SiH_4 gas in the redistribution reaction of **2**. However, the phenethylsilane cannot be obtained *via* the direct Si-C bond cleavage of methylphenethylsilane, but *via* the direct Si-C bond cleavage of **2** with CH_3SiH_3 gas evolution. These facts were confirmed by the control experiments: the independently prepared benzylsilane, methylphenethylsilane and phenethylsilane were apparently inert toward Red-Al catalyzed redistribution (1 h, room temperature). The methylphenethylsilane was obtained in higher yield than the phenethylsilane, implying that SiH_4 formation is easier than CH_3SiH_3 formation due to different steric hindrance in the addition of hydride on the silanes. On the other hand, the methylphenethylsilane can be formed *via* consecutive Si-C bond scissions of **3**, discharging SiH_4 gas in the redistribution reaction of **3**. However, the phenethylsilane cannot be obtained by the direct Si-C bond cleavage of methylphenethylsilane, but either by the direct Si-C bond cleavage of **2** with CH_3SiH_3 gas release or by the direct Si-C bond cleavage of **3** with $\text{CH}_2(\text{SiH}_3)_2$ gas evolution. The yield for methylphenethylsilane was higher than for phenethylsilane, suggesting that SiH_4 formation is easier than $\text{CH}_2(\text{SiH}_3)_2$ formation due to their different steric hindrance in the addition of hydride on the silane. The as yet uncharacterized high-boiling oligomers are believed to be obtained only during the redistribution because the reaction of benzylsilane, methylphenethylsilane, and phenethylsilane with Red-Al did not yield the oligomeric mixture of silanes.

It is known that methylene bridges between two silicon atoms are more readily deprotonated by strong organometallic bases than are methyl groups bonded to a single silicon atom,⁸ but cleavage of the Si-C bond occurs normally under extremely vigorous conditions.⁹ No appreciable redistribution of **1-3** with AlCl_3 for 24 h at ambient temperature was observed. Experiments for trapping silylene or silene using 2,3-dimethyl-1,3-butadiene, cyclohexene, and trimethylmethoxysilane were unsuccessful due probably to the hydrosilane



Scheme 1. Postulated mechanism for redistribution of **1**, catalyzed by Red-Al.

species possessing active Si-H bonds existed in the reaction mixture. It is apparently essential to occur the rapid Si-C bond cleavage at room temperature that a silane should have at least one Si-C-Si connection. The more Si-C-Si connection apparently accelerates the redistribution reaction (judged by ¹H NMR spectroscopy and GC analyses).

Although enough experimental data are not currently available, some comments on the redistribution mechanism seem appropriate. We propose a mechanism involving the preferential attack of the hydride on the less hindered silicon with formation of a pentacoordinated anionic species which collapses to give an α -silyl carbanion intermediate and a silane gas. The α -silyl carbanion may then pick up a hydrogen from the hydrogen source (e.g., silane or solvent) to yield a silane, may lose a hydride to produce a silene associating to produce some oligo(carbosilanes), or may be isomerized to a silyl anion. The silyl anion may lose a hydride to give an unstable silylene which will add to silane or associate, producing some cyclic or linear oligosilanes. The regenerated hydride may participate again in the catalytic cycle (Scheme 1).

We tentatively assign the as yet uncharacterized high-boiling oligomers as a mixture of oligo(carbosilanes) and oligosilane. We are making our effort to elucidate the structure of the oligomeric mixture with ²⁹Si NMR, GPC, and TGA analytical techniques.⁶

The silanes **1-3** might be used along with Red-Al as a potent α -silyl carbanion synthon in the organic synthesis. The redistribution reaction might be further employed for modifying polycarbosilanes $(\text{Si}(\text{H})\text{R}(\text{CH}_2)_n)_m$ with Red-Al. The detailed studies on the full characterization of the oligosilanes and on the application of these redistribution reactions are in progress and will be reported in the near future.

In conclusion, the redistribution of bis- and tris(silyl)methanes with Si-C-Si connection, catalyzed by Red-Al, produces new silanes *via* cleavage of the Si-C bonds, which could be attributed to the stability of resulting α -silyl carbanion intermediate.

Acknowledgment. This research was supported by the Non-directed Research Fund, Korea Research Foundation

(1995).

References

- (a) Kralicek, J.; Kubanek, V.; Kondelikova, J. *German Patent* 1973, 2,301,784; (b) Kralicek, J.; Kubanek, V.; Kondelikova, J.; Casensky, B.; Machacek, J. *German Patent* 1976, 2,445,647; (c) Bukac, Z.; Sebenda, J. *U.S. Patent* 1976, 3, 962,239.
- (a) Becker, B.; Corriu, R. J. P.; Guérin, C.; Henner, B. *J. L. J. Organomet. Chem.* 1989, 369, 147. (b) Becker, B.; Corriu, R.; Guérin, C.; Henner, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1987, 28(1),409. (c) Corriu, R. J. P. *J. Organomet. Chem.* 1990, 400, 81.
- Riviere, P.; Satge, J.; Soula, D. *J. Organomet. Chem.* 1974, 72, 329.
- Speier, J. L.; Zimmerman, R. E. *J. Am. Chem. Soc.* 1955, 77, 6395.
- Woo, H.-G.; Kim, S.-Y.; Kim, W.-G.; Yeon, S. H.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* 1995, 16(11), 1109.
- Woo, H.-G.; Song, S.-J.; Cho, E. J.; Jung, I. N. Unpublished results.
- 2-Phenyl-1,3-disilapropane (1): GC/MS (m/e (relative intensity)): 152 (40) (M⁺), 121 (53), 120 (100), 119 (38), 105 (33), 93 (19), 91 (15), 53 (12).
Benzylsilane: GC/MS (m/e (relative intensity)): 122 (30) (M⁺), 121 (45), 119 (10), 105 (100), 93 (50), 91 (20), 53 (10).
1-Phenyl-3,5-disilapentane (2): GC/MS (m/e (relative intensity)): 180 (20) (M⁺), 163 (1), 152 (19), 149 (31), 135 (41), 119 (2), 102 (100), 91 (45), 77 (20), 74 (80), 71 (20), 53 (81), 51 (10).
1-Phenyl-4-silyl-3,5-disilapentane (3): GC/MS (m/e (relative intensity)): 210 (20) (M⁺), 179 (35), 154 (10), 147 (12), 130 (80), 105 (100), 91 (50), 77 (25), 73 (60), 71 (50), 65 (20), 51 (12).
Phenethylsilane: GC/MS (m/e (relative intensity)): 136 (62) (M⁺), 133 (18), 119 (1), 108 (80), 105 (75), 91 (100), 77 (30), 65 (20), 58 (21), 51 (20).
- Seyferth, D.; Lang, H. *Organometallics* 1991, 10, 551.
- Armitage, A. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, Ch. 1.

Synthesis and Characterization of Dicationic Diammine Complex of Palladium(II) Chelating with DPPE

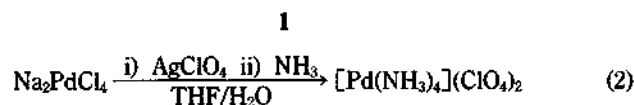
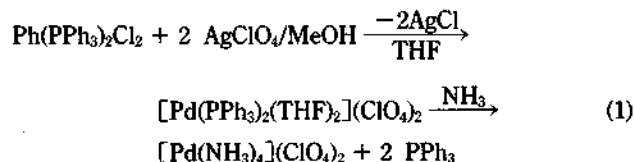
Soonheum Park

Department of Chemistry, College of Natural Science,
Dongguk University,
Kyong-Ju 780-714, Korea

Received November 15, 1995

Although ammine complexes of transition metals have been known since the early history in the classical coordination chemistry, such complexes containing tertiary phosphines or organic moieties are relatively rare.¹ Recently there has been an increasing interest in the amido complexes of transition metals because of their potential applications for catalysis.² One class in this category is such complexes of late transition metals having unsubstituted amide ligand NH₂.³ Ammine complexes having tertiary phosphines are useful synthetic precursors for unsubstituted amido complexes in which the coordinated tertiary phosphines can stabilize electronically and sterically with a variety of substituents.⁴ Ammonia is a very weak acid (*pK_a*=33) and the N-H bond dissociation energy in ammonia is very high (107 kcal/mol).⁵ Ammonia upon coordination to cationic metal center, however, becomes considerably acidic to be deprotonated by appropriate base.

Reported here is the synthesis and characterization of a novel dicationic palladium(II) diammine complex containing 1,2-bis(diphenylphosphino)ethane as a supporting ligand. Our initial attempt to synthesize dicationic diammine complex having monodentate bis-triphenylphosphine has been proven not successful. When gaseous ammonia was added to a THF solution of [Pd(PPh₃)₂(THF)](ClO₄)₂ prepared *in situ* by the reaction of PdCl₂(PPh₃)₂ and 2 equivalents of AgClO₄, dicationic tetraammine complex [Pd(NH₃)₄](ClO₄)₂ (1) was obtained (eq. 1). The formation of 1 can be explained by a sequence of reactions involving the initial formation of [Pd(PPh₃)₂(NH₃)₂](ClO₄)₂, and then further substitution of coordinated triphenylphosphines with excess ammonia. We can not observe the intermediate complex [Pd(PPh₃)₂(NH₃)₂](ClO₄)₂. The formulation of 1 has been confirmed by its independent synthesis from the reaction of aqueous THF solution of [PdCl₄]²⁻, 4 equivalents of AgClO₄ and ammonia (eq. 2).⁶



Targeting diammine complex of bis-phosphine palladium (II) has been successfully prepared by employing 1,2-bis(diphenylphosphino)ethane as chelating ligand in the displace-