

# Reduction of 1-chloro-1,2,3,4,5-pentaphenylsilole: formation of silole monoanion and dianion

Honglae Sohn \*

Department of Chemistry, Chosun University, 375 Seosuk-dong, Dong-gu, Gwangju 501759, Republic of Korea

Received 28 May 2003; accepted 29 September 2003

## Abstract

The reduction of 1-chloro-1,2,3,4,5-pentaphenylsilole, ( $C_4Ph_4SiPhCl$ , **1**) with 2 equiv lithium gave the pentaphenylsilole anion [ $C_4Ph_4SiPh$ ]<sup>-</sup> (**2**), silole dianion [ $C_4Ph_4Si$ ]<sup>2-</sup> (**3**), and hexaphenylsilole  $C_4Ph_4SiPh_2$  (**4**). **2**, **3**, and **4** from the reaction mixture were characterized by <sup>29</sup>Si NMR spectroscopy. The <sup>29</sup>Si chemical shift of 3.7 ppm for **2** is shifted upfield as compared to that of previously reported *t*-butyltetraphenylsilole anion  $Li[C_4Ph_4Si^tBu]$ , but shifted downfield compared to that of the other silole monoanion such as  $Li[C_4Me_4SiSiMe_3]$ , indicating the delocalization of silole anion through the 5-membered ring. Derivatization of the reaction mixture with iodomethane gave  $C_4Ph_4SiPh_2$  (**4**),  $C_4Ph_4SiMePh$  (**5**), and  $C_4Ph_4SiMe_2$  (**6**), which were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy. The silole dianion **3** could be either from the continuous reduction of **1** with lithium or from the disproportionation of **2**. The reduction of **1** with excess lithium in THF gave the silole dianion [ $C_4Ph_4Si$ ]<sup>2-</sup> in about 70% yield. © 2003 Elsevier B.V. All rights reserved.

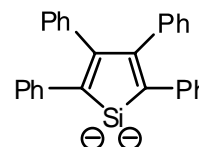
**Keywords:** Reduction; Delocalization; Silole monoanion; Silole dianion

## 1. Introduction

In recent times, a considerable amount of interest has developed with regard to anions of siloles and their structure, bonding, reaction, and possible aromaticity leading to novel optical properties for a variety of applications [1–14]. Analogous of cyclopentadiene, siloles are  $\pi$ -electron systems containing a single silicon atom as part of a cyclic 5-membered ring. Characteristic features of siloles include a low reduction potential and a low-lying LUMO due to  $\sigma^*-\pi^*$  conjugation arising from the interaction between the  $\sigma^*$  orbital of silicon, and the  $\pi^*$  orbital of the butadiene moiety of the five membered ring [15,16]. Since silole and germole dianions  $(RC)_4Si^{2-}$  and  $(RC)_4Ge^{2-}$ , R = Ph and Me, were initially studied by X-ray crystallography [3–6], siloles and germoles have received growing attention, both because of their unusual electronic and optical properties [17,18] and because of their possible application as electron trans-

porting materials in devices [19] such as light-emitting diodes (LEDs) [20–22] or in chemical sensors [23,24].

X-ray crystal structures of  $[Li_2^+(THF)_5][C_4Ph_4Si^{2-}]$  [3] and  $[K(18-crown-6)^+]_2[C_4Me_4Si^{2-}]$  [5] indicate that the silole dianions are highly delocalized and aromatic. In contrast, several crystal structures of silole monoanion have been published and showed the localization of 5-membered ring. For example,  $[K(18-crown-6)][C_4Me_4SiSiMe_3]$  [6] has a localized structure. Only one silole monoanion  $Li[C_4Ph_4Si^tBu]$  has been published as a delocalized structure by the interpretation of <sup>13</sup>C and <sup>29</sup>Si NMR data [7a], however its crystal structure has not been reported to date.

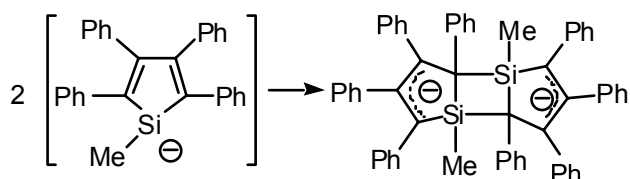


Recently, it has been reported that the methylsilole anion [ $C_4Ph_4SiMe$ ]<sup>-</sup> dimerized to the tricyclic diallylic dianion [ $C_4Ph_4SiMe$ ]<sub>2</sub><sup>2-</sup> by head-to-tail, 2 + 2 cycload-

\* Tel.: +82-622307372; fax: +82-622344326.

E-mail address: hsohn@chosun.ac.kr (H. Sohn).

dition [25]. The possible mechanism for the tricyclic diallylic dianion could take place in the mesomeric forms having Si=C double bond character of methylsilole monoanion. In addition, the reduction of methylsilole [C<sub>4</sub>Ph<sub>4</sub>SiMeH] would involve the presence of the equilibrium between carboanion and silyl anion [26]. Therefore, it seems of interest to investigate the pentaphenylsilole monoanion.



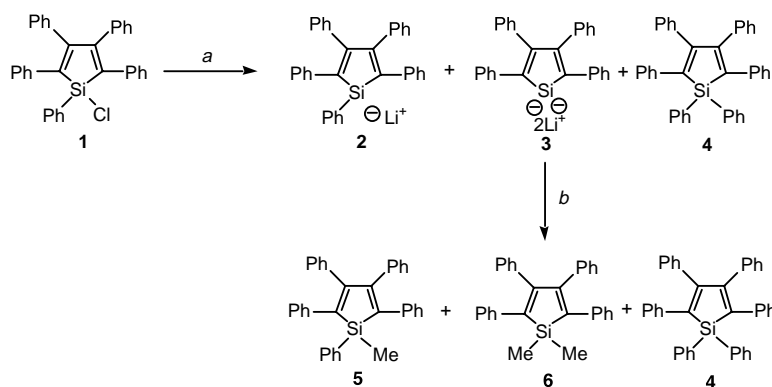
## 2. Results and discussion

Herein the reduction of 1-chloro-1,2,3,4,5-pentaphenylsilole, (C<sub>4</sub>Ph<sub>4</sub>SiPhCl, **1**) to the pentaphenylsilole anion [C<sub>4</sub>Ph<sub>4</sub>SiPh]<sup>−</sup> (**2**), and the derivatization products; C<sub>4</sub>Ph<sub>4</sub>SiPh<sub>2</sub> (**4**), C<sub>4</sub>Ph<sub>4</sub>SiMePh (**5**), and C<sub>4</sub>Ph<sub>4</sub>SiMe<sub>2</sub> (**6**) is reported. The reduction of **1** with 2 equiv of lithium in THF at −78 °C gave a dark red solution. The addition of excess iodomethane to the solution produced mixture products of **4**, **5**, and **6**. (Scheme 1) The derivatization

products **4**, **5**, and **6** were separated by preparative scale size exclusion chromatography and characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy.

The isolated yield of the products **4**, **5**, and **6** is 25%, 13%, and 25%, respectively. The ratio of isolated product distribution of **4**:**5**:**6** is 2:1:2, showing that the formation quantity of silole dianion **3** and hexaphenylsilole **4** is equal. The silole dianion **3** could be either from the continuous reduction of **1** with lithium or from the disproportionation of **2**. Fig. 1 shows two possible mechanisms, over-reduction and disproportionation. Disproportionation exhibits the equal formation of silole **3** and **4**. However, the formation of the diphenylsilole **4** may result from the reaction of **1** with phenyllithium, which is produced during the over-reduction of **2** to the silole dianion **3**. This mechanism would also produce **3** and **4** in equal amounts. We are not able to observe the phenyl derivative. Therefore, any mechanisms are not ruled out at this stage.

While silole **5** forms after quenching, indicating the presence of the pentaphenylsilole anion **2**, the silole **6** is expected from the silole dianion [C<sub>4</sub>Ph<sub>4</sub>Si]<sup>2−</sup> (**3**). Using a 10 mm NMR tube containing **1** (0.248 g, 0.50 mmol) and lithium (0.007 mg, 1.0 mmol) in THF-d<sub>8</sub>, <sup>29</sup>Si NMR study was carried out for the dark red solution. <sup>29</sup>Si NMR spectrum of dark red solution showed three <sup>29</sup>Si resonance signals at 67.0, 3.7, and −6.0 ppm which shows the presence of silole dianion **3**, silole anion **2**, and



Scheme 1. Reduction of C<sub>4</sub>Ph<sub>4</sub>SiPhCl, **1**, with 2 equiv lithium. Reagents and conditions: (a) 2Li/THF/−78 °C – RT/2 h; (b) excess MeI/THF/−78 °C – RT/3 h.

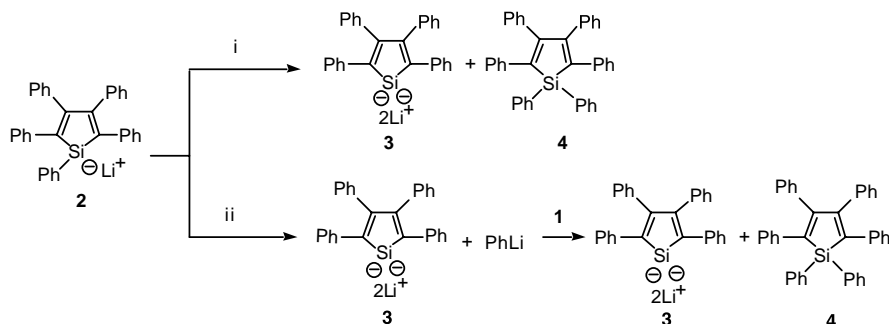
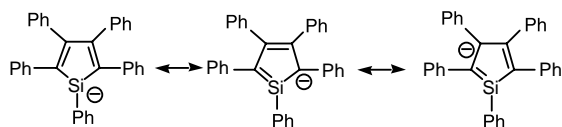


Fig. 1. Two possible mechanisms for the equal formation of **3** and **4**: (i) disproportionation; (ii) over-reduction.

hexaphenylsilole  $C_4Ph_4SiPh_2$  (**4**), respectively. Silole dianion **3** and hexaphenylsilole **4** were independently synthesized and characterized by  $^{29}Si$  NMR spectroscopy, and gave the two  $^{29}Si$  chemical shifts of 67.0 and  $-6.0$  ppm for silole dianion **3** and hexaphenylsilole **4**, respectively. The  $^{29}Si$  chemical shift of 3.7 ppm for **2** is shifted upfield as compared to that of previously reported *t*-butyltetraphenylsilole anion  $Li[C_4Ph_4Si^tBu]$  (25.1 ppm) [7], but shifted downfield compared to that of the other silole monoanion such as  $Li[C_4Me_4SiSiMe_3]$  ( $-45.38$  ppm) [6]. It is believed that this is caused by the delocalization of silole anion through the 5-membered ring. It should be noted that one of the products observed after quenching is the silole dianion **3** that is formed as a result of cleavage of Si–C bond of the phenyl-silicon moiety.



Methylsilole anion  $[C_4Ph_4SiMe]^-$  (**8**) dimerized to the tricyclic diallylic dianion  $[C_4Ph_4SiMe]_2^{2-}$  (**9**) by head-to-tail, 2 + 2 cycloaddition [25], which means that the anion of **8** is delocalized over the silicon-containing cyclic 5-membered ring. However, the dimerization of pentaphenylsilole anion,  $[C_4Ph_4SiPh]^-$  (**2**), did not take place. Possible reasons for this are that **2** is less nucleophilic than  $[C_4Ph_4SiMe]^-$  and that the steric hindrance of phenyl group at silicon in **2** is too large to allow dimerization. Unfortunately, attempts to obtain crystals of **2** for the X-ray analysis were not successful.

The reduction of **1** with excess lithium in THF also gave dark red solution. (Scheme 2) However, after removal of unreacted lithium, the derivatization of reaction mixture with iodomethane gave **6** in about 70% yield, respectively. The  $^{29}Si$  NMR spectrum of latter solution gave only single resonance at 67 ppm that is the silole dianion **3**. The pentaphenylsilole anion **2** and hexaphenylsilole **4** can be further reduced to give silole dianion **3** in latter reaction, due to the good leaving group of phenyl moiety in pentaphenylsilole anion **2**.

Although the standard synthetic route for the formation of silole dianion is via the dehalogenation of dihalosiloles, the observation that monohalogenated silole also results in the formation of a silole dianion

represents a new synthetic route to the silole dianion via slightly more air stable monohalogenated silole starting materials.

### 3. Experimental

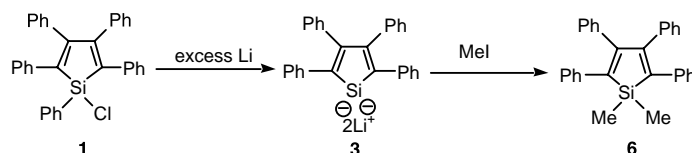
#### 3.1. General

All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard vacuum-line Schlenk techniques. All solvents were degassed and purified before use according to standard literature methods: diethyl ether, hexanes, tetrahydrofuran, and toluene were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone. All other reagents (Aldrich, Gelest) were used as received or distilled before use. NMR data were collected with Bruker AC-300, 400, or 500 MHz spectrometers (300.1 MHz for  $^1H$  NMR, 75.5 MHz for  $^{13}C$  NMR and 99.2 MHz for  $^{29}Si$  NMR). The NMR solvent THF- $d_8$  was purified by vacuum distillation from Na/K alloy. Chloroform- $d$  was stirred over  $CaH_2$  for 1 day, transferred by vacuum distillation onto  $P_2O_5$ , stirred for 2 h, and then vacuum-distilled for purification. Chemical shifts are reported in parts per million ( $\delta$  ppm); downfield shifts are reported as positive values from tetramethylsilane (TMS) standard at 0.00 ppm. The  $^1H$  and  $^{13}C$  chemical shifts were referenced relative to  $CHCl_3$  ( $\delta = 77.0$  ppm) as an internal standard, and the  $^{29}Si$  chemical shifts were referenced to an external TMS standard.  $^{13}C$  NMR were recorded as proton decoupled spectra, and  $^{29}Si$  NMR spectra were acquired using an inverse gate pulse sequence with a relaxation delay of 30 s. High-resolution electron-impact ionization mass spectrometry was performed on an MS80 Kratos spectrometer.

#### 3.2. Preparation of 1-chloro-1,2,3,4,5-pentaphenylsilole

1-Chloro-1,2,3,4,5-pentaphenylsilole (**1**) and 1,1,2,3,4,5-hexaphenylsilole (**4**), were prepared as described in the literature [12], by adding the corresponding phenyltrichlorosilane and diphenyldichlorosilane, respectively. 1,1-dilithio-2,3,4,5-tetraphenylsilole (**3**) was prepared as described in the literature [3]. The NMR spectra of **6** agreed with those reported earlier [27].

Selected data for **1**.  $^1H$  NMR (300.133 MHz,  $CDCl_3$ ):  $\delta = 6.80$ – $7.10$  (m, 20H, Ph), 7.35– $7.50$  and 7.75– $7.85$



Scheme 2. Reduction of **1** with excess Li.

(m, 5H, Ph);  $^{13}\text{C}\{\text{H}\}$  NMR (75.403 MHz,  $\text{CDCl}_3$  ( $\delta = 77.00$ )):  $\delta = 126.36$  (C), 126.91 (C), 127.67 (C), 127.95 (C), 128.48 (C), 129.19 (C), 129.68 (C), 130.22 (C), 131.15 (C), 134.37 (C), 135.64 (C), 137.15 (C), 137.74 (C), 156.26 (C);  $^{29}\text{Si}$  NMR (INEPT, 99.363 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.00$ . MS(EI):  $m/z$  (%): 496 (24) [ $\text{M}^+$ ], High-resolution MS: calcd. for  $\text{C}_{34}\text{H}_{25}\text{SiCl}$  496.1414 found 496.1432.

### 3.3. Reduction of 1-chloro-1,2,3,4,5-pentaphenylsilole with 2 equiv Li

**1** (2.48 g, 5.0 mmol) and lithium (69 mg, 10 mmol) was stirred in 50 ml of THF at  $-78^\circ\text{C}$ , then the solution was allowed to warm up slowly to room temperature and stirred for an additional 2 h to give a dark red solution. The solution was kept at  $-78^\circ\text{C}$ . Excess iodomethane (ca. 20 mmol) was added by a syringe in one portion at  $-78^\circ\text{C}$ . The mixture was kept at  $-78^\circ\text{C}$  for 5 min before the cooling bath was removed, then the solution was allowed to warm up slowly to room temperature and stirred for 3 h to give a yellow solution. Then the volatiles were removed under reduced pressure. The residue was extracted with small portions of toluene (a total of 50 ml) and filtered. The products **4**, **5**, and **6** were separated by preparative size exclusion chromatography. Each solution was concentrated and cooled to  $-20^\circ\text{C}$  for the crystallization.

*1,1,2,3,4,5-hexaphenylsilole (4)*. Greenish-yellow crystals (isolated yield = 25%). Selected data; M.p.  $190$ – $191^\circ\text{C}$  (lit.  $186$ – $187$ ) [9].  $^1\text{H}$  NMR spectra of **4** agreed with those reported earlier [9];  $^{13}\text{C}\{\text{H}\}$  NMR (75.403 MHz,  $\text{CDCl}_3$  ( $\delta = 77.00$ )):  $\delta = 125.61$  (C), 126.35 (C), 127.42 (C), 127.74 (C), 128.23 (C), 128.32 (C), 129.19 (C), 129.96 (C), 130.11 (C), 131.59 (C), 136.08 (C), 138.76 (C), 139.49 (C), 156.72 (C);  $^{29}\text{Si}$  NMR (INEPT, 99.363 MHz,  $\text{CDCl}_3$ ):  $\delta = -5.30$ . High-resolution MS: calcd. for  $\text{C}_{40}\text{H}_{30}\text{Si}$  538.2116 found 538.2112.

*1-methyl-1,2,3,4,5-pentaphenylsilole (5)*. Greenish-yellow crystals (isolated yield = 13%). Selected data; M.p.  $172$ – $173^\circ\text{C}$  (lit.  $170$ – $171$ ) [9].  $^1\text{H}$  NMR spectra of **5** agreed with those reported earlier [9];  $^{13}\text{C}\{\text{H}\}$  NMR (75.403 MHz,  $\text{CDCl}_3$  ( $\delta = 77.00$ )):  $\delta = 6.51$  ( $\text{CH}_3$ ), 125.55 (C), 126.29 (C), 127.44 (C), 127.79 (C), 128.20 (C), 128.94 (C), 129.79 (C), 129.94 (C), 133.44 (C), 134.59 (C), 138.81 (C), 139.35 (C), 140.53 (C), 155.51 (C);  $^{29}\text{Si}$  NMR (INEPT, 99.363 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.25$ . High-resolution MS: calcd. for  $\text{C}_{35}\text{H}_{28}\text{Si}$  476.1960 found 476.1966.

### 3.4. Reduction of 1-chloro-1,2,3,4,5-pentaphenylsilole with excess Li

**1** (2.48 g, 5.0 mmol) and lithium (276 mg, 40 mmol) was stirred in 50 ml of THF at room temperature for 2 h to give a dark red solution. The solution was cannulated

to remove the residual lithium metal. The solution was kept at  $-78^\circ\text{C}$ . Excess iodomethane was added by a syringe in one portion at  $-78^\circ\text{C}$ . The mixture was kept at  $-78^\circ\text{C}$  for 5 min before the cooling bath was removed, then the solution was allowed to warm up slowly to room temperature and stirred for 3 h to give a yellow solution. Then the volatiles were removed under reduced pressure. The residue was extracted with hexane and filtered. The solution was concentrated and cooled to  $-20^\circ\text{C}$  for the crystallization. The product **6** was isolated in about 70 % yield.

### 3.5. NMR study of 2

To a 10 mm NMR tube containing **1** (0.248 g, 0.50 mmol) in  $\text{THF-d}_8$  was added lithium (0.007 mg, 1.0 mmol), then the NMR tube was sealed under vacuum. The solution was kept at  $-78^\circ\text{C}$ , then the solution was allowed to warm up to room temperature and stirred for an additional 2 h to give a dark red solution.  $^{13}\text{C}$  NMR spectrum was measured, however it was not clear to analyze the products, respectively.  $^{29}\text{Si}$  NMR (inversed gated decoupling, 99.36 MHz,  $\text{THF-d}_8$ /reference; external TMS):  $\delta = -6.0$ , 3.7, 67.0.

### Acknowledgements

The author greatly acknowledges the advice and useful discussions provided by Professor Robert West (University of Wisconsin-Madison).

### References

- [1] (a) M.S. Gordon, P. Boudjouk, F. Anvari, *J. Am. Chem. Soc.* 105 (1983) 4972–4976;  
(b) J.R. Damewood, *J. Org. Chem.* 51 (1986) 5028–5029.
- [2] K. Tamao, A. Kawachi, *Adv. Organomet. Chem.* 38 (1995) 1–58.
- [3] R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apelog, T. Mueller, *J. Am. Chem. Soc.* 117 (1995) 11608–11609.
- [4] R. West, H. Sohn, D.R. Powell, T. Mueller, Y. Apeloig, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 1002–1004.
- [5] W.P. Freeman, T.D. Tilley, G.P.A. Yap, A.L. Rheingold, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 882–884.
- [6] W.P. Freeman, T.D. Tilley, L.M. Liable-Sands, A.L. Rheingold, *J. Am. Chem. Soc.* 118 (1996) 10457–10468.
- [7] (a) J.-H. Hong, P. Boudjouk, *J. Am. Chem. Soc.* 115 (1993) 5883–5884;  
(b) J.-H. Hong, P. Boudjouk, S. Castellino, *Organometallics* 13 (1994) 3387–3389.
- [8] B. Goldfuss, P.v.R. Schleyer, *Organometallics* 14 (1995) 1553–1555.
- [9] B.Z. Tang, X.W. Zhan, G. Yu, P.P.S. Lee, Y.Q. Liu, D.B. Zhu, *J. Mater. Chem.* 11 (2001) 2878–2974.
- [10] W.-C. Joo, J.-H. Hong, S.-B. Choi, H.-E. Son, *J. Organomet. Chem.* 391 (1990) 27–36.
- [11] (a) U. Bankwitz, H. Sohn, D.R. Powell, R. West, *J. Organomet. Chem.* 499 (1995) C7–C9;

- (b) T. Mueller, Y. Apeloig, H. Sohn, R. West, in: N. Auner, J. Weis (Eds.), *Organosilicon Chemistry III*, Wiley-VCH, New York, 1998, pp. 144–151.
- [12] (a) H. Sohn, J. Merritt, D.R. Powell, R. West, *Organometallics* 16 (1997) 5133–5134;  
(b) H. Sohn, H.-G. Woo, D.R. Powell, *Chem. Commun.* 6 (2000) 697–698.
- [13] S.-B. Choi, P. Boudjouk, P. Wei, *J. Am. Chem. Soc.* 120 (1998) 5814–5815.
- [14] Y.X. Liu, T.C. Stringfellow, D. Ballweg, I.A. Guzei, R. West, *J. Am. Chem. Soc.* 124 (2002) 49–57.
- [15] Y. Yamaguchi, *Synth. Met.* 82 (1996) 149–153.
- [16] S. Yamaguchi, K. Tamao, *Bull. Chem. Soc. Jpn.* 69 (1996) 2327–2334.
- [17] S. Yamaguchi, K. Tamao, *J. Chem. Soc., Dalton Trans.* (1998) 3693–3702.
- [18] S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa, K. Tamao, *Chem. Eur. J.* 6 (2000) 1683–1692.
- [19] K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, S. Yamaguchi, *J. Am. Chem. Soc.* 118 (1996) 11974–11975.
- [20] H. Sohn, R.R. Huddleston, D.R. Powell, R. West, K. Oka, X. Yonghua, *J. Am. Chem. Soc.* 121 (1999) 2935–2936.
- [21] Y. Xu, T. Fujino, H. Naito, T. Dohmaru, K. Oka, H. Sohn, R. West, *Jpn. J. Appl. Phys.* 38 (1999) 6915–6918.
- [22] T. Sanji, T. Sakai, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* 120 (1998) 4552–4553.
- [23] H. Sohn, R.M. Calhoun, M.J. Sailor, W.C. Trogler, *Angew. Chem. Int. Ed.* 11 (2001) 2104–2105.
- [24] H. Sohn, M.J. Sailor, D. Magde, W.C. Trogler, *J. Am. Chem. Soc.* 125 (2003) 3821–3830.
- [25] H. Sohn, D.R. Powell, R. West, J.-H. Hong, W.-C. Joo, *Organometallics* 16 (1997) 2770–2772.
- [26] T. Wakahara, W. Ando, *Chem. Lett.* 11 (1997) 1179–1180.
- [27] G.K. Henry, R. Shinimoto, Q. Zhou, W.P. Weber, *J. Organomet. Chem.* 350 (1988) 3–8.