Direct Reactions of Zirconacyclopentadienes with Halosilanes as a Convenient Synthetic Method for Siloles

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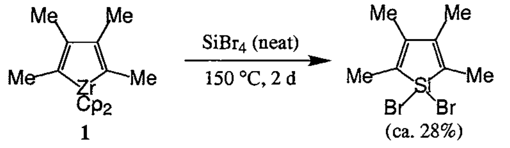
Direct reactions of 1,1-bis(cyclopentadienyl)zirconacyclopentadienes with various halosilanes afford the corresponding siloles in excellent yields. The reactions are very sensitive to the steric bulkiness of both zirconacyclopentadienes and halosilanes.

Although much attention has been focused on the unique electronic properties of siloles (silacyclopentadienes) and their applicability toward materials, synthetic methods for siloles are rather limited.[1,2] Among recent advances in the silole synthesis,[3] zirconacyclopentadiene route[3a-c] is unique and widely applicable. However, in this route, zirconacyclopentadienes are required to be converted first to the corresponding 1,4-diiodobutadienes, which are dilithiated and then treated with halo- or alkoxysilanes. As a simpler method, direct reactions of zirconacyclopentadienes with halosilanes have been reported to give rather disappointed results,[4] whereas zirconacyclopentadienes react with various main-group elements like germanium, tin, etc. to produce the corresponding heteroles in high yields.[4,5] The reaction of zirconacyclopentadiene **1** with silicon tetrabromide affords the corresponding 1,1-dibromosilole in only low yield under rather drastic reaction conditions (Eq. 1); **1** does not react with neat silicon tetrachloride.[4] We report herein that the direct reactions afford a convenient and useful method for the synthesis of siloles, if proper selection of reactants and solvents is made.

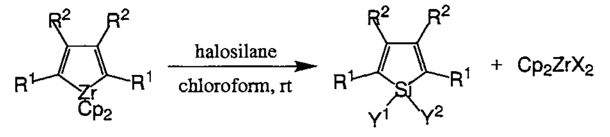


(1)

The results of the reactions of zirconacyclopentadienes **1** – **3** with a series of halosilanes are summarized in Table 1. Typically, to a solution of **1** in chloroform, dichloromethylsilane (2 equiv.) was added and the reaction mixture was stirred for 24 h at rt; a colorless precipitate of zirconocene dichloride was formed gradually. Complete consumption of **1** and the formation of 1,2,3,4,5-pentamethylsilole[6] as a sole product were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the reaction mixture. Filtration of the precipitate followed by Kugel-rohr distillation gave the silole in 88% yield. Similarly, reactions of **1** with dichlorophenylsilane and silicon tetrafluoride in chloroform at rt gave 1-phenyl-[7] (89% yield) and 1,1-difluoro-2,3,4,5-tetramethylsiloles[8] (96% yield), respectively. Compared to the reaction of **1** with silicon tetrabromide (Eq. 1), these reactions proceed smoothly under much milder conditions with high product yields.

Remarkable solvent effects were found for the reaction of **1** with dichloromethylsilane. While the reaction in dichloromethane-d_2 proceeds with a similar rate to that in chloroform-d, the reaction in benzene-d_6 is very sluggish; heating at 50 °C for 2 days is required for the complete consumption of **1**. The reaction in THF-d_8 is extremely slow and not completed even after heating at 50 °C for 6 days. Among investigated solvents, chloroform and dichloromethane are the most suitable solvents for the reaction. The reaction rates do not depend monotonously on the solvent polarity which is estimated by the dielectric constant (ε).[9] While the ε values are in the order of dichloromethane (8.93) > THF (7.52) > chloroform (4.81) > benzene (2.28), the order of the reaction rates is dichloromethane ≈ chloroform > benzene >> THF. The observed solvent effects suggest that the reaction is accelerated by a polar solvent but a highly coordinating solvent like THF stabilizes **1** to render the reactivity toward halosilanes.

Table 1. Reactions of zirconacyclopentadienes with several halosilanes in chloroform at rt



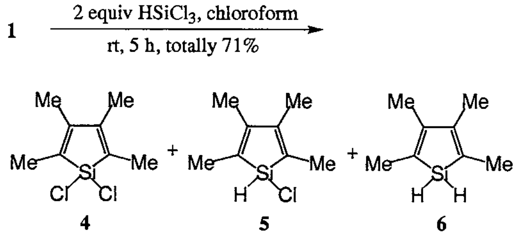
1 ($R^1 = R^2 = Me$)
2 ($R^1 = R^2 = Et$)
3 ($R^1 = SiMe_3$, $R^2 = Me$)

entry	Zr cycle	silane	time	silole Y^1	silole Y^2	yield/%[a]
1	**1**	$MeHSiCl_2$	24 h	Me	H	88
2	**1**	$PhHSiCl_2$	24 h	Ph	H	89
3	**1**	SiF_4	24 h	F	F	96[b]
4	**2**	H_2SiCl_2	5 min	H	H	92
5	**3**	H_2SiCl_2	24 h	H	H	97

[a]Isolated yield. [b]Determined by ^{1}H NMR.

The reaction of **1** with trichlorosilane is much faster than that with dichloromethylsilane but gives a 1 : 2 : 1 mixture of three siloles, 1,1-dichloro- (**4**),[3a] 1-chloro-1-hydro- (**5**),[10] and 1,1-dihydro-2,3,4,5-tetramethylsiloles (**6**)[10] in 72% total yield (Eq. 2). Similarly, the reaction of **1** with dichlorosilane in chloroform or benzene is completed within a minute to afford a 1:3 mixture of **5** and **6** in 97% total yield (Eq. 3). These products were identified by MS and NMR spectroscopy. While the detailed mechanism of the present silole formation remains open, the reaction may proceed via stepwise σ-bond metathesis mechanisms,[4a,11] where both hydrides and chlorides serve as leaving groups on silicon. The formation of **6** in the reaction of **1** with trichlorosilane (Eq. 2) may be explained by the formation of dichlorosilane through the chlorine-hydrogen exchange reaction between trichlorosilane and zirconocene chloride hydride.

The existence of hydrides in silanes is not essential to promote the reaction; **1** reacts smoothly with silicon tetrafluoride to give the corresponding difluorosilole in high yield as



4 5 6
(1 : 2 : 1) (2)

$$1 \xrightarrow[\text{rt, 5 s, totally 97\%}]{\text{excess } H_2SiCl_2\text{, chloroform}} \underset{(1}{5} + \underset{:}{} \underset{3)}{6} \qquad (3)$$

mentioned above. Zirconacyclopentadiene **1** does not react with silicon tetrachloride, 1,1-dichlorosilacyclobutane, chlorodimethylsilane, or diphenylsilane in chloroform even at 60 °C for several days. Although the addition of CuCl has been reported to promote the reactions of zirconacyclopentadienes toward halostannanes in THF,[5] no significant effect of CuCl as an additive was observed for the reaction of **1** with silicon tetrachloride in THF.

In contrast with the reaction of **1** in Eq. 3, the reactions of **2** and **3** having more crowded zirconacyclopentadiene rings with dichlorosilane produce the corresponding siloles as single products, 1,1-dihydro-2,3,4,5-tetraethylsilole[12] and 1,1-dihydro-2,5-bis(trimethylsilyl)-3,4-dimethylsilole,[3c] in 92 and 97% yield, respectively (Table 1). It is suggested that because the Si-H bond metathesis requires a more congested transition state than the Si-Cl bond metathesis, the former reaction is more sensitive to the steric bulkiness of a zirconacycle. Zirconacycle **2** does not react with dichloromethylsilane in chloroform even at 50 °C. The reaction of **2** with trichlorosilane as well as the reaction of **3** with dichloromethylsilane produces a complex mixture.

In conclusion, the direct reactions of zirconacyclopentadienes with halosilanes provide a convenient and useful method for synthesis of various siloles, while the reactions are affected critically by the steric factors of the zirconacycles and halosilanes and by solvents.

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References and Notes

1 For recent reviews of siloles, see: J. Dubac, A. Laporterie, and G. Manuel, *Chem. Rev.*, **90**, 215 (1990); E. Colomer, R. J. P. Corriu, and M. Lheureux, *Chem. Rev.*, **90**, 265 (1990); K. Tamao and S. Yamaguchi, *Pure & Appl. Chem.*, **68**, 139 (1996); J. Dubac, C. Guérin, and P. Meunier, in "The Chemistry of Organic Silicon Compounds", ed by Z. Rappoport and Y. Apeloig, J. Wiley & Sons, Chichester (1998), Vol. 2, Chap. 34, p 1961-2036; S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans.*, **1998**, 3693; J. Hermanns and B. Schmidt, *J. Chem. Soc., Perkin Trans. 1*, **1998**, 2209; J. Hermanns and B. Schmidt, *J. Chem. Soc., Perkin Trans. 1*, **1999**, 81.

2 A number of silole-containing oligomers and polymers have recently been reported. Inter alia: K. Tamao, S. Yamaguchi, Y. Ito, Y. Matsuzaki, T. Yamabe, M. Fukushima, and S. Mori, *Macromolecules*, **28**, 8668 (1995); S. Yamaguchi, R.-Z. Jin, and K. Tamao, *Organometallics*, **16**, 2486 (1997); B. P. S. Chauhan, T. Shimizu, and M. Tanaka, *Chem. Lett.*, **1997**, 785; K. Kanno, M. Ichinohe, C. Kabuto, and M. Kira, *Chem. Lett.*, **1998**, 99; T. Sanji, T. Sakai, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **120**, 4552 (1998); H. Sohn, R. R. Huddleston, D. R. Powell, and R. West, *J. Am. Chem. Soc.*, **121**, 2935 (1999); S. Yamaguchi, R.-Z. Jin, and K. Tamao, *J. Am. Chem. Soc.*, **121**, 2937 (1999); J. Ohshita, T. Hamaguchi, E. Toyoda, A. Kunai, K. Komaguchi, M. Shiotani, M. Ishikawa, and A. Naka, *Organometallics*, **18**, 1717 (1999).

3 Zirconacyclopentadiene routes: a) U. Bankwitz, H. Sohn, D. R. Powell, and R. West, *J. Organomet. Chem.*, **499**, C7 (1995). b) W. P. Freeman, T. D. Tilley, L. M. Liable-Sands, and A. L. Rheingold, *J. Am. Chem. Soc.*, **118**, 10457 (1996). c) S. Yamaguchi, R.-Z. Jin, and K. Tamao, *J. Organomet. Chem.*, **559**, 73 (1998). A titanacyclopentadiene route: d) S. Yamaguchi, R.-Z. Jin, K. Tamao, and F. Sato, *J. Org. Chem.*, **63**, 10060 (1998). Dialkynylsilane routes: e) K. Tamao, S. Yamaguchi, and M. Shiro, *J. Am. Chem. Soc.*, **116**, 11715 (1994). f) B. Wrackmeyer, G. Kehr, J. Süß, and E. Molla, *J. Organomet. Chem.*, **577**, 82 (1999). See also ref 1 and references cited therein. A tellurophene route: g) M. Katkevics, S. Yamaguchi, A. Toshimitsu, and K. Tamao, *Organometallics*, **17**, 5796 (1998).

4 a) P. J. Fagan, W. A. Nugent, and J. C. Calabrese, *J. Am. Chem. Soc.*, **116**, 1880 (1994). b) P. J. Fagan and W. A. Nugent, *J. Am. Chem. Soc.*, **110**, 2310 (1988).

5 Y. Ura, Y. Li, Z. Xi, and T. Takahashi, *Tetrahedron Lett.*, **39**, 2787 (1998).

6 1,2,3,4,5-Pentamethylsilole: a colorless oil; bp 60-90 °C/23 mmHg (Kugel-rohr distillation); ^{1}H NMR ($CDCl_3$, δ) 4.16 (q, 1 H, J = 4 Hz), 1.83 (s, 12 H), 0.17 (d, 3 H, J = 4 Hz); ^{13}C NMR ($CDCl_3$, δ) 150.6, 128.0, 14.1, 13.5, -8.6; ^{29}Si NMR ($CDCl_3$, δ) -15.3; MS (70 eV) *m/z* (%) 152 (M$^+$, 32), 137 (81), 109 (36), 97 (62), 73 (68), 59 (81), 43 (100); HRMS *m/z* Calcd for $C_9H_{16}Si$: 152.1021, Found: 152.1019.

7 1-Phenyl-2,3,4,5-tetramethylsilole: a colorless oil; bp 60-70 °C/0.01 mmHg (Kuger-rohr distillation); ^{1}H NMR ($CDCl_3$, δ) 7.60-7.55 (m, 2 H), 7.45 – 7.33 (m, 3 H), 4.77 (s, 1 H), 1.94 (s, 6 H), 1.90 (s, 6 H); ^{13}C NMR ($CDCl_3$, δ) 152.2, 135.1, 132.4, 129.6, 128.0, 126.7, 14.4, 13.7; ^{29}Si NMR ($CDCl_3$, δ) -15.7; MS (70 eV) *m/z* (%) 214 (M$^+$, 94), 199 (79), 159 (38), 135 (43), 121 (64), 105 (100), 53 (51); HRMS *m/z* Calcd for $C_{14}H_{18}Si$: 214.1178, Found: 214.1178.

8 1,1-Difluoro-2,3,4,5-tetramethylsilole: a colorless oil; bp 70–90 °C/50 mmHg (Kuger-rohr distillation); ^{1}H NMR ($CDCl_3$, δ) 1.84 (s, 6 H), 1.72 (s, 6 H); ^{13}C NMR ($CDCl_3$, δ) 153.8 (t, $^3J_{C\text{-}F}$ = 8 Hz), 117.2 (t, $^2J_{C\text{-}F}$ = 18 Hz), 13.8 (t, $^3J_{C\text{-}F}$ = 2 Hz), 11.9 (s); ^{29}Si NMR ($CDCl_3$, δ) -21.1 (t, $^1J_{Si\text{-}F}$ = 320 Hz); ^{19}F NMR ($CDCl_3$, δ) -158.9; MS (70 eV) *m/z* (%) 174 (M$^+$, 41), 108 (50), 93 (100), 91 (33); HRMS *m/z* Calcd for $C_8H_{12}F_2Si$: 174.0676, Found: 174.0676.

9 Dielectric constants were taken from : "CRC Handbook of Chemistry and Physics", ed by D. R. Lide and H. P. R. Frederikse, CRC Press, Inc., Boca Raton (1996), 77th ed.

10 1-Chloro-1-hydro-2,3,4,5-tetramethylsilole (**5**): ^{1}H NMR (C_6D_6, δ) 4.14 (s, 1 H), 1.72 (s, 6 H), 1.49 (s, 6 H); ^{13}C NMR (C_6D_6, δ) 152.7, 124.8, 14.0, 12.4; ^{29}Si NMR (C_6D_6, δ) -4.8; MS (70 eV) *m/z* (%) 174 (M$^+$+2, 38), 172 (M$^+$, 78), 159 (25), 157 (44), 94 (92), 93 (100), 79 (54). 1,1-Dihydro-2,3,4,5-tetramethylsilole (**6**): ^{1}H NMR (C_6D_6, δ) 4.34 (s, 2 H), 1.82 (s, 6 H), 1.64 (s, 6 H); ^{13}C NMR (C_6D_6, δ) 153.1, 124.4, 14.4, 14.0; ^{29}Si NMR (C_6D_6, δ) -38.1; MS (70 eV) *m/z* (%) 138 (M$^+$, 67), 123 (100), 95 (53).

11 T. Takahashi, M. Hasegawa, N. Suzuki, M. Saburi, C. J. Rousset, P. E. Fanwick, and E. Negishi, *J. Am. Chem. Soc.*, **113**, 8564 (1991); Y. Ura, R. Hara, and T. Takahashi, *Chem. Lett.*, **1998**, 195; J. Terao, K. Torii, K. Sato, N. Kambe, A. Baba, and N. Sonoda, *Angew. Chem. Int. Ed.*, **37**, 2653 (1998).

12 1,1-Dihydro-2,3,4,5-tetraethylsilole: a colorless oil; bp 25-40 °C/0.01 mmHg (Kuger-rohr distillation); ^{1}H NMR ($CDCl_3$, δ) 4.18 (s, 2 H), 2.33 (q, 4 H, J = 7.5 Hz), 2.28 (q, 4 H, J = 7.5 Hz), 1.09 (t, 6 H, J = 7.5 Hz), 0.98 (t, 6 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, δ) 157.1, 133.7, 22.3, 21.2, 16.3, 14.3; ^{29}Si NMR ($CDCl_3$, δ) -44.8; MS (70 eV) *m/z* (%) 194 (M$^+$, 74), 165 (91), 137 (100), 123 (46), 109 (34), 95 (24); HRMS *m/z* Calcd for 194.1491, Found: 194.1488.