Cyclization of 1,2-Disilacyclohexa-3,5-dienes Initiated by Electron Transfer Reactions with TCNE

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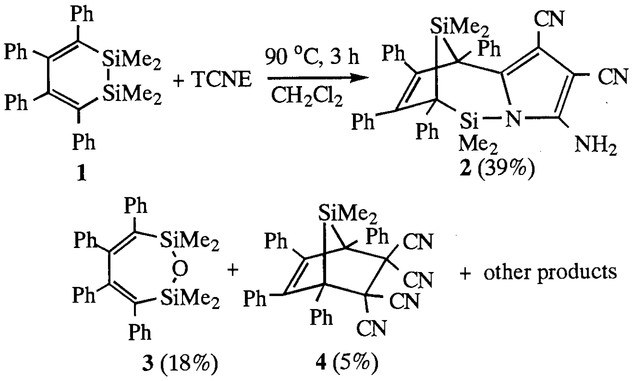
Thermal reaction of 1,2-disilacyclohexa-3,5-dienes with tetracyanoethylene (TCNE) gave 8-amino-6,6,11,11-tetramethyl-2,3,4,5-tetraphenyl-7-aza-6,11-disilatricyclo[5,3,0,$1^{2,5}$]undeca-3,8,10(1)-triene-9,10-dicarbonitrile through a charge-transfer complex.

Group 14 element (silicon, germanium)–group 14 element σ bonds with rather low ionization potential are excellent electron donors. As electron-rich species, these group 14 element catenates are subject to cleavage by various organic electrophiles as well as transition metal complexes through a charge-transfer (CT) complex.[1] During the past two decades, the CT interactions between group 14 element–group 14 element σ bonds and common electron acceptors such as tetracyanoethylene (TCNE) have been amply investigated.[2–8] In a previous paper,[9] we reported a ring-contraction reaction of 1,2-digermacyclohexa-3,5-dienes initiated by CT with TCNE. We describe herein the cyclization reaction of 1,2-disilacyclohexa-3,5-dienes through a CT complex with TCNE.

A solution of 1,1,2,2-tetramethyl-1,2-disila-3,4,5,6-tetraphenylcyclohexa-3,5-diene[10] (**1**) (0.4 mmol) and TCNE (0.4 mmol) in dichloromethane was placed in a Pyrex tube under argon and sealed. The color of the solution changed from yellowish-green to reddish-brown. The reaction mixture was heated at 90 °C for 3 h to give 8-amino-6,6,11,11-tetramethyl-2,3,4,5-tetraphenyl-7-aza-6,11-disilatricyclo[5,3,0,$1^{2,5}$]undeca-3,8,10(1)-triene-9,10-dicarbonitrile (**2**, 39%), 1,1,3,3-tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1,3-disilacyclohepta-4,6-diene (**3**, 18%), and 5,5,6,6-tetracyano-7,7-dimethyl-1,2,3,4-tetraphenyl-7-silanorbornene (**4**, 5%). The rest of **1** remained unreacted. Concentration of the reaction mixture by evaporation of dichloromethane followed by preparative GPC gave pure **2** and **3**, which showed satisfactory NMR and MS data.[11] 7-Silanorbornene **4** could not be isolated owing to its small amount. The silanorbornene **4** was characterized by NMR spectra in comparison with those of authentic sample.[12] Several unidentified by-products in minor amounts were also formed. In spite of all efforts to minimize moisture and air, **3** was obtained in substantial amounts.



The effect of reaction conditions on the yield of **2** in the present CT reaction was examined. The ratio of **1**/TCNE on the yield of **2** at 90 °C for 3 h was examined. Increase in the concentration of TCNE relative to **1** did not influence the yields of **2**. Lowering the reaction temperature from 90 to 70 °C resulted in lower yields of **2** (39 to 15%). Extending the reaction time scarcely improved the yield of **2**.

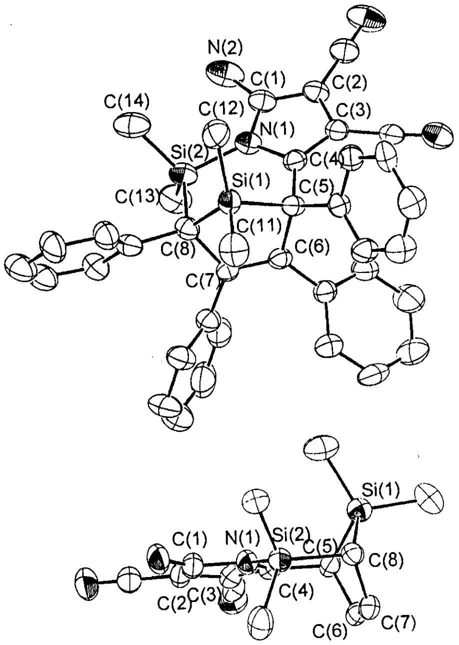


Figure 1. Top and side* views of the molecular structure of **2**. Selected bond lengths (Å) and angles (°): Si(1)-C(5) 1.927(3), Si(1)-C(8) 1.902(4), Si(2)-C(8) 1.888(3), Si(2)-N(1) 1.811(3), C(1)-N(1) 1.380(4), C(1)-N(2) 1.377(5), C(1)-C(2) 1.367(5), C(2)-C(3) 1.451(4), C(3)-C(4) 1.368(5), C(4)-C(5) 1.515(5), C(5)-Si(1)-C(8) 91.08(14), C(12)-Si(1)-C(11) 110.7(2), N(1)-Si(2)-C(8) 105.29(14), C(13)-Si(2)-C(14) 111.3(2), Si(2)-N(1)-C(1) 124.2(2), C(1)-N(1)-C(4) 107.8(3), C(4)-N(1)-Si(2) 127.4(2), C(2)-C(3)-C(4) 108.1(3), C(6)-C(7)-C(8) 116.7(3), C(7)-C(8)-Si(2) 107.2(2), Si(1)-C(8)-Si(2) 107.65(16), Si(1)-C(8)-C(7) 97.2(2). *Phenyl groups have been omitted to clarity.

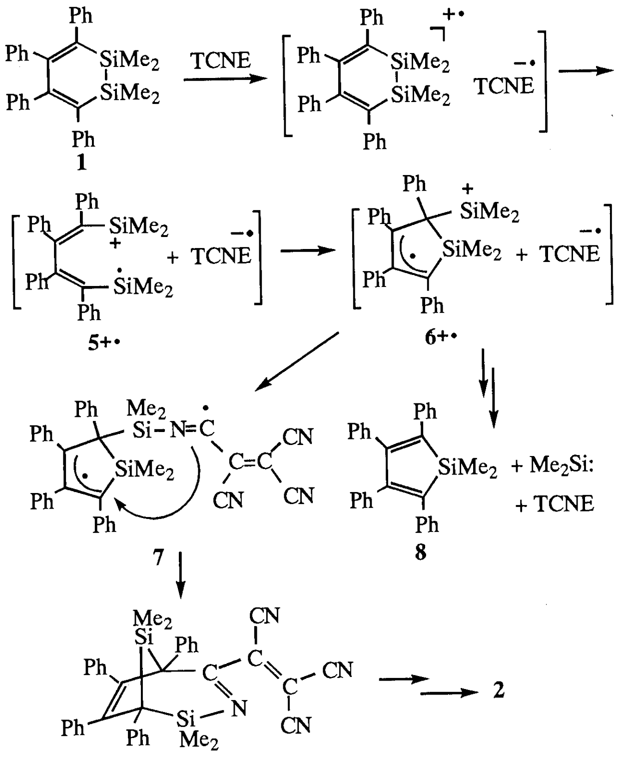
The molecular structure of $\mathbf{2}^{13}$ is shown in Figure 1, together with selected bond distances and angles. The 1-azacyclopentadiene ring and the C(5)–C(4)–N(1)–Si(2)–C(8) plane are almost planar. The bond angles of Si(1)–C(8)–C(7) and

Si(1)–C(8)–Si(2) are 97.2 (2) and 107.65 (16)°, respectively.

The color of the solution of **1** and TCNE in dichloromethane strongly suggests the CT interaction between **1** and TCNE. The formation of a CT complex is evidenced by the ESR spectrum of the TCNE radical anion (g = 2.0031, a_N = 1.56 G) at room temperature.[3]

From these results, we propose a possible mechanism for the formation of products **2**–**4** by CT of **1** with TCNE as depicted in Scheme 1. Initially, **1** is readily oxidized by TCNE to give radical cation $\mathbf{1}^{+\bullet}$, in which the Si–Si bond possibly gives an open intermediate $\mathbf{5}^{+\bullet}$. Then, subsequent intramolecular addition of one of the silyl groups to the diene moiety gives to $\mathbf{6}^{+\bullet}$. The intermediate $\mathbf{6}^{+\bullet}$ reacts with TCNE$^{-\bullet}$ to give biradical **7**. Compound **2** is derived from **7** after several steps. On the other hand, the intermediate $\mathbf{6}^{+\bullet}$ undergoes spontaneous scission to a radical cation of 1-silacyclopenta-2,4-diene (silole) and dimethylsilyene (Me_2Si:). The radical cation of silole is reduced with TCNE$^{-\bullet}$ to afford silole **8** and TCNE. The silole **8** thus formed reacts with TCNE to give 7-silanorbornene **4**. Some parts of $\mathbf{5}^{+\bullet}$ react with oxygen to give 2,3-disila-1-oxacyclohepta-4,6-diene **3**. None of the eliminated Me_2Si: part could be detected. Further mechanistic studies of **2** are in progress to verify these speculations.

The present results are in marked difference to those of the formation of siloles in photo-induced electron transfer of 1,2-disilacyclohexadienes with methylene blue[14] and dibenzosilole in the photoexcitation of the CT complex between dibenzodisilacyclohexadiene and TCNE.[15]



Scheme 1.

We thank Prof. Yasuhiro Nakadaira of The University of Electro-Communications for valuable discussion of reaction mechanism.

References and Notes

1 J. K. Kochi, "Organometallic Mechanisms and Catalysis," Academic Press, New York (1978).

2 V. F. Traven and R. West, *J. Am. Chem. Soc.*, **95**, 6824 (1973).

3 H. Sakurai, M. Kira, and T. Uchida, *J. Am. Chem. Soc.*, **95**, 6826 (1973).

4 M. Kira, K. Sakamoto, and H. Sakurai, *J. Am. Chem. Soc.*, **105**, 7496 (1983); H. Sakurai, K. Sakamoto, and M. Kira, *Chem. Lett.*, **1984**, 1213; M. Kira, K. Takeuchi, and H. Sakurai, "Studies in Organic Chemistry," ed. by M. Kobayashi, Elsevier, Amsterdam (1987), Vol. 31, p. 407; M. Kira, K. Takeuchi, C. Kabuto, and H. Sakurai, *Chem. Lett.*, **1988**, 353.

5 Y. Nakadaira, N. Komatsu, and H. Sakurai, *Chem. Lett.*, **1985**, 1781; H. Watanabe, M. Kato, E. Tabei, H. Kawabara, N. Hirai, T. Sato, and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, **1986**, 1662.

6 S. Kyushin, Y. Ehara, Y. Nakadaira, and M. Ohashi, *J. Chem. Soc., Chem. Commun.*, **1989**, 279; Y. Nakadaira, A. Sekiguchi, Y. Funada, and H. Sakurai, *Chem. Lett.*, **1991**, 327; Y. Nakadaira, S. Otani, S. Kyushin, M. Ohashi, H. Sakurai, Y. Funada, K. Sakamoto, and A. Sekiguchi, *Chem. Lett.*, **1991**, 601.

7 Y. Nakadaira, S. Kyushin, and M. Ohashi, *Yuki Gosei Kagaku Kyokai Shi*, **48**, 331 (1990) and references cited therein.

8 K. Mochida, C. Hodota, R. Hata, and S. Fukuzumi, *Organometallics*, **12**, 586 (1993).

9 K. Mochida, H. Shimizu, and M. Nanjo, *Chem. Lett.*, **2000**, 1226.

10 Y. Nakadaira, S. Kanouchi, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 5623 (1974).

11 **2**: ^{1}H NMR (δ in $CDCl_3$) 0.10 (s, 3H), 0.17 (s, 3H), 0.61 (s, 3H), 4.03 (s, 2H), 6.45–7.16 (m, 20H). ^{13}C NMR (δ in $CDCl_3$) –6.1, –2.7, –1.9, –1.4, 39.4, 46.4, 93.1, 112.9, 113.7, 125.0, 125.7, 125.9, 126.2, 126.7, 127.2, 127.6, 127.7, 129.0, 130.2, 131.0, 136.1, 137.1, 137.3, 137.9, 138.6, 145.0, 145.9, 148.4. MS *m/z* 602 (M^+). **3**: ^{1}H NMR (δ in $CDCl_3$) –0.04 (s, 6H), 0.47 (s, 6H), 6.78–7.11 (m, 20H). ^{13}C NMR (δ in $CDCl_3$) 11.13, 105.8, 124.6, 125.4, 126.4, 127.1, 129.2, 140.1, 142.6, 144.4, 153.9; MS m/z 488 (M^+–Me).

12 **4**: ^{1}H NMR (δ in $CDCl_3$) 1.00 (s, 3H), 1.10 (s, 3H), 6.78–7.30 (m, 20H). ^{13}C NMR (δ in $CDCl_3$) –3.03, 3.87, 54.4, 59.3, 111.3, 113.5, 127.4, 127.5, 128.6, 128.9, 129.7, 130.0, 132.4, 134.2 ; MS m/z 413 (M^+–TCNE).

13 Crystal data for **2**: $C_{38}H_{32}N_4Si_2$; fw = 600.87; crystal size 0.2 × 0.2 × 0.2 mm; monoclinic, space group $P2_1/c$, Z = 4; a = 9.7060(6) Å, b = 15.7580(10) Å, c = 23.6360(8) Å, β = 98.928(4)°; V = 3571.3(3) Å^3, D = 1.275 g/cm^3; Goodness of fit = 1.831, R = 0.0691, R_w = 0.2192, 5114 reflections measured.

14 M. Kako, H. Takada, and Y. Nakadaira, *Tetrahedron Lett.*, **38**, 3525 (1997).

15 H. Sakurai, K. Sakamoto, and M. Kira, *Chem. Lett.*, **1984**, 1213.