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Electron-transfer reactions of 1,2-dimetallacyclohexa-3,5-dienes with TCNE

Kunio Mochida [a],*, Hiromi Shimizu [a], Tsuyoshi Kugita [b], Masato Nanjo [a]

[a] Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan
[b] Department of Material Science, Teikyo University of Science and Technology, 2525 Yatsuzawa, Uenohara-machi, Yamanashi 409-0193, Japan

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Abstract

Thermal reactions of 1,2-dimetallacyclohexa-3,5-dienes (**1**–**3**) with tetracyanoethylene (TCNE) were investigated. The reaction of 1,2-disilacyclohexa-3,5-diene (**1**) with TCNE mainly gave 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-2,11-disilatricyclo[6.2.1.0^{3,7}]undeca-4,6,9-triene through a charge-transfer complex. The reaction of 1,2-digermacyclohexa-3,5-diene (**2**) with TCNE afforded 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-2,11-digermatricyclo[6.2.1.0^{3,7}]undeca-4,6,9-triene. 2,2,3,3-Tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabicyclo[2.2.1]hept-5-ene was also detected. On the other hand, 1-germa-2-silacyclohexa-3,5-diene (**3**) reacted with TCNE to give 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-11-germa-2-silatricyclo[6.2.1.0^{3,7}]undeca-4,6,9-triene, 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-11-germa-2-silatricyclo[6.3.0^{1,8}.0^{3,7}]undeca-4,6,9-triene, and 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabicyclo[2.2.1]hept-5-ene as main products. The mechanism of the formation of new heterocyclic compounds through electron-transfer reactions of 1,2-dimetallacyclohexa-3,5-dienes with TCNE is discussed.

Keywords: 1,2-Dimetallacyclohexa-3,5-diene; TCNE; Electron-transfer

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1. Introduction

Group 14 elements (silicon, germanium)–Group 14 elements σ bonds with rather low oxidation potentials in solutions are excellent electron donors. As electron-rich species, these Group 14 elements 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 elements catenates σ bonds and common electron acceptors such as tetracyanoethylene (TCNE) have been amply investigated [2–8]. However, a large portion of studies on their CT interactions are limited to CT spectra between Group 14 catenates and electron acceptors such as TCNE and their ion radicals by means of UV, ESR, and other spectroscopies. A few reports on ring contraction through CT interactions between cyclic Group 14 elements catenate compounds and TCNE have been reported [4]. We describe herein the formation of new heterocyclic compounds through electron-transfer reactions of 1,2-dimetallacyclohexa-3,5-dienes having Group 14 elements–Group 14 elements σ bonds with TCNE.

2. Results

2.1. Reactions of 1,2-dimetallacyclohexa-3,5-dienes with TCNE

Reactions of Group 14 elements–Group 14 elements σ bonds of 1,2-disila-, 1,2-digerma-, and 1-germa-2-sila-

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* Corresponding author. Tel.: +81-3-3986-0221; fax: 81-3-5992-1029.

E-mail address: kunio.mochida@gakushuin.ac.jp (K. Mochida).

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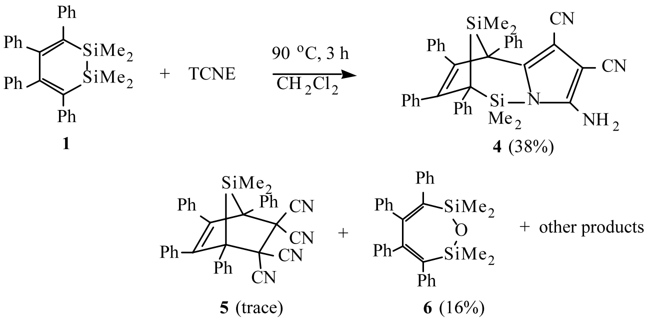
cyclohexa-3,5-dienes (**1-3**) with TCNE at 90 °C were examined.

A solution of 1,1,2,2-tetramethyl-1,2-disila-3,4,5,6-tetraphenylcyclohexa-3,5-diene [9] (**1**) (0.4 mmol) and TCNE (0.4 mmol) in dichloromethane (CH_2Cl_2) 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 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-2,11-disilatricyclo[6.2.1.0^{3,7}]undeca-4,6,9-triene (**4**, 38%) and 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hept-5-ene (**5**, trace). 1,1,3,3-Tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1,3-disilacyclohepta-4,6-diene (**6**, 16%) and some unidentified products were also formed (Eq. (1)). The rest of **1** (40%) was recovered unchanged from the CH_2Cl_2 solution. The yields of products (**4**, **5**, **6**) were based on the amounts of initial amount of **1** and were determined by NMR spectra. Concentration of the reaction mixture by evaporation of CH_2Cl_2 followed by both preparative GPC and TLC (silica gel) gave pure **4**. The structure of **4** was determined by NMR and MS spectra. 7-Silabicyclo[2.2.1]hept-5-ene **5** and 2-oxa-1,3-disilacyclohepta-4,6-diene **6** could not be isolated. Compounds **5** and **6** were characterized by NMR and MS spectra in comparison with those of authentic samples. In spite of every efforts of minimizing moisture and air, **6** was obtained in substantial amounts.



(1)

The molecular structures of **4** and **5** were fully established by spectroscopic and X-ray diffraction methods. The molecular structure of **4** is shown in Fig. 1, and crystallographic data are summarized in Table 1. Selected bond lengths and angles in compound **4** are summarized in Table 2. The pyrrole ring and the C(5)–C(4)–N(1)–Si(2)–C(8) plane are nearly 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. Fig. 2 shows the molecular structure of **5**. The crystallographic data are included in Table 1. Selected bond lengths and bond angles are summarized in Table 3. The 7-silabicyclo[2.2.1]hept-5-ene **5** shown in Fig. 2 has a distorted geometry, with bond lengths of C(3) or C(3)*–Si(1) (1.9310(13) Å) and bond angle of C(3)–Si(1)–C(3)*(82.08(8)°). The bond lengths of C(3)–Si(1) and C(3)*–Si(1) are longer than those of Si–Me (1.852(2) and 1.8597(19) Å) in **5**. The bond angles of Si(1)–C(8)–C(4), Si(1)–C(3)–C(5), and C(4)–C(3)–C(5) are 123.9, 122.0, and 114.1°, respectively.

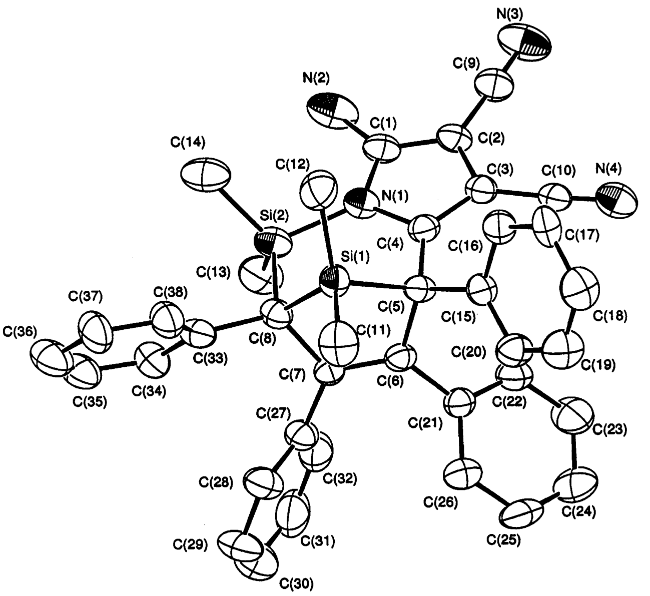


Fig. 1. Molecular structure of the 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-2,11-disilatricyclo[6.2.1.0^{3,7}]undeca-4,6,9-triene (**4**). (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

The colored solution of **1** and TCNE in CH_2Cl_2 at 70 °C was examined by ESR spectroscopy. The observed ESR spectrum showed a weak broad signal with $g = 2.0031$. The g value suggests the presence of the TCNE radical anion [3].

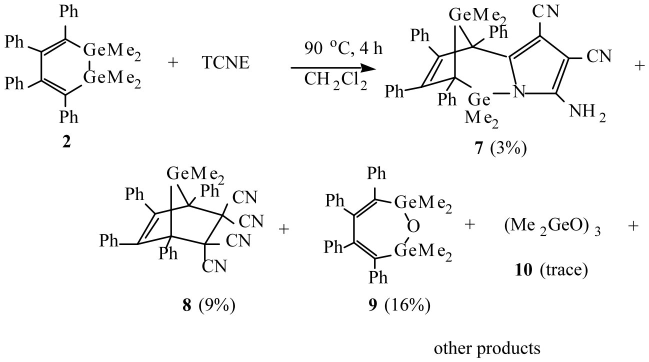
A Pyrex tube containing CH_2Cl_2 solution of 1,1,2,2-tetramethyl-1,2-digerma-3,4,5,6-tetraphenylcyclohexa-3,5-diene [10] (**2**) (0.01 mmol) and TCNE (0.01 mmol) was placed in argon and sealed. The tube was heated at 90 °C for 4 h to give 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-2,11-digermatricyclo[6.2.1.0^{3,7}]undeca-4,6,9-triene (**7**, 3%) together with 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabicyclo[2.2.1]hept-5-ene (**8**, 9%). 1,1,3,3-Tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1,3-digermacyclohepta-4,6-diene (**9**, 16%), 2,2,4,4,6,6-hexamethyl-1,3,5-trioxa-2,4,6-trigermacyclohexane (**10**, trace), and some unidentified products were also detected (Eq. (2)). The rest of **2** (45%) remained unreacted and was recovered from the CH_2Cl_2 solution. The color of the solution of **2** and TCNE changed from yellow to green. The yields of products (**7**–**10**) were based on the amounts of initial amount of **2** and were determined by NMR spectra.

Table 1
Crystallographic data for **4**, **5**, **7**, **8**, **11** and **12**

	4	**5**	**7**	**8**	**11**	**12**
Chemical formula	$C_{38}H_{32}N_4Si_2$	$C_{36}H_{26}N_4Si$	$C_{39}H_{36}Ge_2N_4$	$C_{36}H_{26}GeN_4$	$C_{38}H_{32}GeN_4Si$	$C_{38}H_{34}GeN_4Si$
Formula weight	685.78	542.70	776.80	587.20	730.28	647.37
Temperature (K)	295(2)	200(0)	293(2)	293(2)	200(0)	295(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/m$	$P2_1/c$	$P2_1/m$	$P2_1/c$	$P2_1/n$
a (Å)	9.7060(6)	8.8570(5)	9.7410(8)	8.8680(3)	9.6500(5)	10.4920(4)
b (Å)	15.7580(10)	20.1310(10)	15.6950(5)	20.1090(9)	15.6930(5)	16.8670(11)
c (Å)	23.6360(8)	8.7790(5)	23.3660(14)	8.9420(3)	23.5020(13)	18.8150(10)
α (°)	90	90	90	90	90	90
β (°)	98.928(4)	111.823(3)	98.207(3)	111.797(2)	98.446(3)	94.920(3)
γ (°)	90	90	90	90	90	90
V (Å^3)	3571.3(3)	1453.07(17)	3535.7(4)	1480.59(10)	3520.5(3)	3317.4(3)
Z	4	2	4	2	4	4
D_{calc} (g cm^{-3})	1.275	1.240	1.459	1.317	1.378	1.296
Crystal dimensions (mm)	0.45 × 0.45 × 0.40	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2	0.4 × 0.3 × 0.2	0.3 × 0.3 × 0.2	0.50 × × 0.45 × 0.20
Reflections (hkl) limits	$0 \le h \le 10$, $0 \le k \le 17$, $-26 \le l \le 25$	$0 \le h \le 9$, $0 \le k \le 22$, $-9 \le l \le 9$	$0 \le h \le 10$, $0 \le k \le 17$, $-26 \le l \le 25$	$0 \le h \le 11$, $0 \le k \le 26$, $-11 \le l \le 10$	$0 \le h \le 10$, $0 \le k \le 17$, $-26 \le l \le 25$	$0 \le h \le 11$, $0 \le k \le 18$, $-20 \le l \le 20$
Unique reflections	5114	2168	4907	3492	5094	4546
R [$I > 2\sigma(I)$]	0.0691	0.0391	0.0487	0.0360	0.0441	0.0403
(All data)	0.0794	0.0407	0.0558	0.0382	0.0510	0.0463
Rw [$I > 2\sigma(I)$]	0.2192	0.1521	0.1566	0.1105	0.1417	0.1279
(All data)	0.2306	0.1521	0.1566	0.1105	0.1489	0.1345
Goodness-of-fit	1.831	1.480	1.356	1.040	1.238	1.161

Table 2
Selected bond distances (Å) and angles (°) for **4**

Si(1)–C(11)	1.847(4)	Si(1)–C(12)	1.859(4)
Si(1)–C(8)	1.902(4)	Si(1)–C(5)	1.927(3)
Si(2)–N(1)	1.811(3)	Si(2)–C(14)	1.843(4)
Si(2)–C(13)	1.858(4)	Si(2)–C(8)	1.888(3)
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)–C(6)	1.553(4)	C(6)–C(7)	1.358(5)
C(7)–C(8)	1.556(4)		
C(11)–Si(1)–C(12)	110.7(2)	C(11)–Si(1)–C(8)	112.29(18)
C(12)–Si(1)–C(8)	118.38(18)	C(11)–Si(1)–C(5)	109.76(17)
C(12)–Si(1)–C(5)	113.06(17)	C(8)–Si(1)–C(5)	91.08(14)
N(1)–Si(2)–C(14)	108.71(17)	C(14)–Si(2)–C(13)	111.3(2)
N(1)–Si(2)–C(8)	105.29(14)	C(14)–Si(2)–C(8)	111.69(18)
C(1)–N(1)–C(4)	107.8(3)	C(1)–N(1)–Si(2)	124.2(2)
C(4)–N(1)–Si(2)	127.4(2)		



2

7 (3%)

8 (9%)

9 (16%)

10 (trace)

(2)

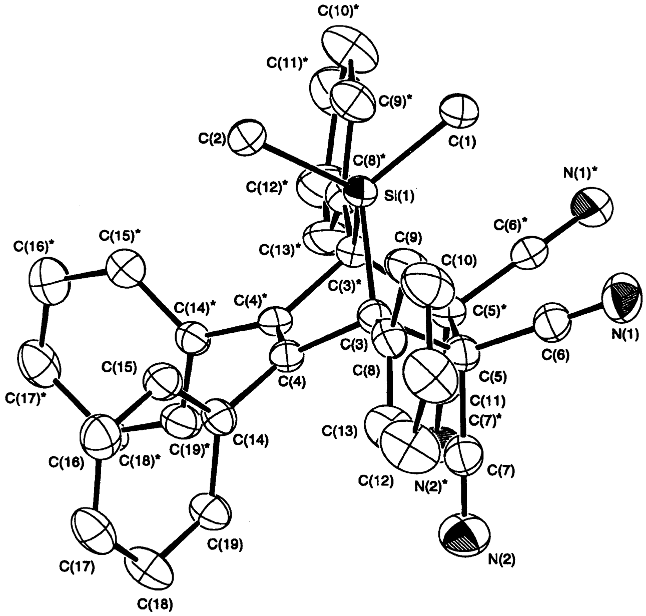


Fig. 2. Molecular structure of the 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hept-5-ene (**5**). (50% probability thermal ellipsoids.) Hydrogen atoms are omitted for clarity.

Concentration of the CH_2Cl_2 solvent by evaporation followed by both preparative GPC and the TLC (silica gel) gave pure **7**, which showed satisfactory NMR and MS data. Products **8**–**10** were characterized by NMR and GC–MS spectra in comparison with those of authentic samples [11,12]. In spite of every efforts of

Table 3
Selected bond distances (Å) and angles (°) for **5**

Si(1)–C(1)	1.852(2)	Si(1)–C(2)[a]	1.8597(19)
Si(1)–C(3)	1.9311(13)	Si(1)–C(3)[a]	1.9310(13)
C(3)–C(4)	1.5427(17)	C(3)–C(5)	1.6055(19)
C(4)–C(4)[a]	1.350(3)	C(5)–C(5)[a]	1.616(3)
C(1)–Si(1)–C(2)	109.85(9)	C(1)–Si(1)–C(3)[a]	117.93(6)
C(2)–Si(1)–C(3)[a]	113.39(6)	C(1)–Si(1)–C(3)	117.93(6)
C(2)–Si(1)–C(3)	113.39(6)	C(3)[a]–Si(1)–C(3)	82.08(8)

[a] $x, -y^{3/2}, z$.

minimizing moisture and air, **9** and **10** were obtained in an appreciable amount.

The molecular structures of **7** and **8** were fully established by spectroscopic methods and X-ray diffraction analysis. The molecular structures of **7** and **8** are shown in Figs. 3 and 4, respectively, and crystallographic data are included in Table 1. Selected bond lengths and angles in compounds **7** and **8** are summarized in Tables 4 and 5, respectively. The pyrrole ring and the C(5)–C(4)–N(1)–Ge(2)–C(8) plane are nearly planar. The bond angles of Ge(1)–C(8)–C(7) and Ge(1)–C(8)–Ge(2) are 99.0(3) and 105.57 (19)°, respectively. The 7-germabicyclo[2.2.1]hept-5-ene **8** shown in Fig. 4 has a distorted geometry, with bond lengths of C(3) or C(3)*–Ge(1) (2.0269(15) Å) and bond angle of C(3)–Ge(1)–C(3)* (78.72(8)°). The bond lengths of C(3) or C(3)*–Ge(1) are longer than those of Ge–Me (1.939(2) and 1.952(2) Å) in **8**. The bond angles of Ge(1)–C(8)–C(4), Ge(1)–C(3)–C(5), and C(4)–C(3)–C(5) are 123.3, 122.2, and 115.6°, respectively.

ESR studies of the colored CH_2Cl_2 solution containing **2** and TCNE revealed a well resolved radical anion of TCNE ($g = 2.0031$, $a_N = 1.56$ G) [3].

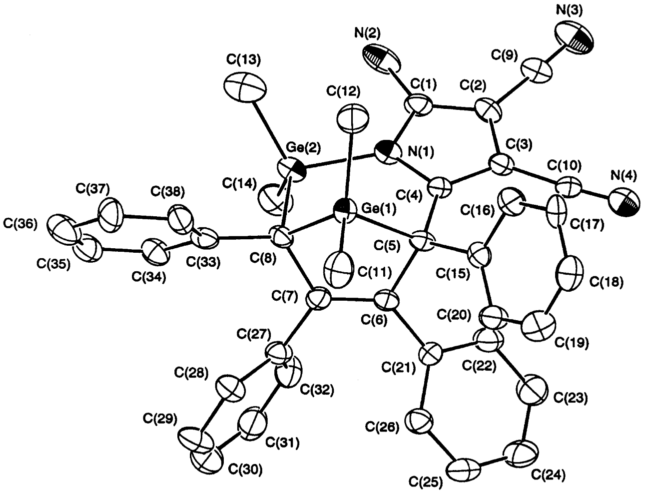


Fig. 3. Molecular structure of the 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-2,11-digermatricyclo[6.2.1.0^{3,7}]undeca-4,6,9-triene (**7**). (30% probability thermal ellipsoids.) Hydrogen atoms are omitted for clarity.

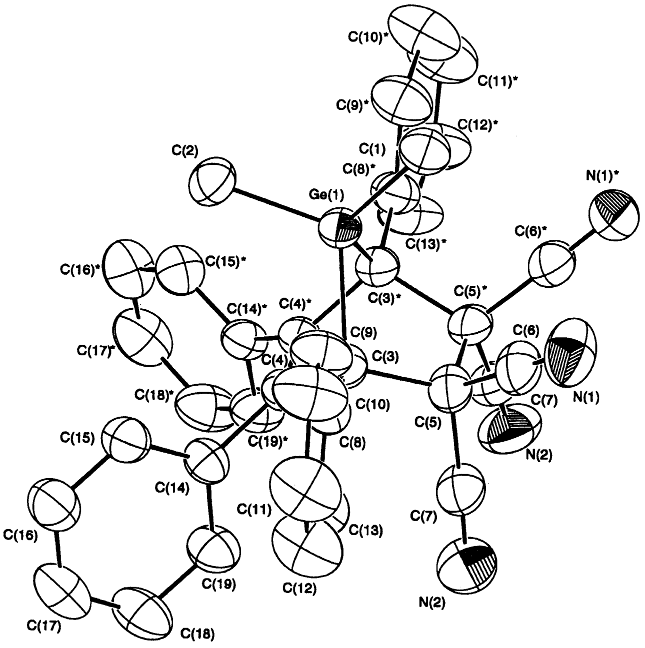


Fig. 4. Molecular structure of the 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabicyclo[2.2.1]hept-5-ene (**8**). (50% probability thermal ellipsoids.) Hydrogen atoms are omitted for clarity.

A CH_2Cl_2 solution of 1,1,2,2-tetramethyl-1-germa-2-sila-3,4,5,6-tetraphenylcyclohexa-3,5-diene (**3**) (0.4 mmol) and TCNE (0.4 mmol) was placed in a Pyrex tube under argon and sealed. Heating of the reaction mixture of **3** at 90 °C for 3 h afforded 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-11-germa-2-silatricyclo[6.2.1.0^{3,7}]undeca-4,6,9-triene (**11**, 5%), 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-11-germa-2-silatricyclo[6.3.0^{1,8}.0^{3,7}]undeca-4,6,9-triene (**12**, 4%), and 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabicyclo[2.2.1]hept-5-ene (**8**, 15%). 1,1,3,3-Tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1-germa-3-silacyclohepta-4,6-diene (**13**, 23%) and some unidentified products were

Table 4
Selected bond distances (Å) and angles (°) for **7**

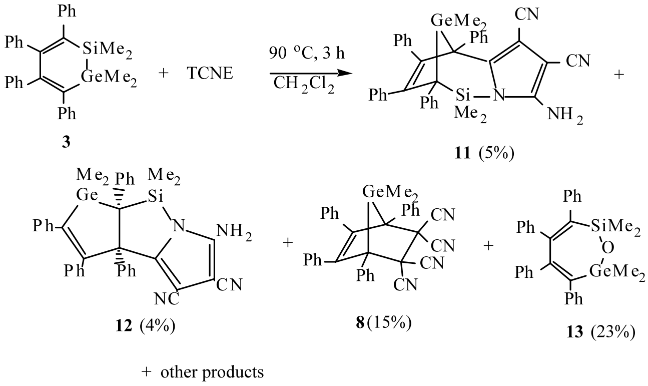
Ge(1)–C(11)	1.934(4)	Ge(1)–C(12)	1.938(4)
Ge(1)–C(8)	1.987(3)	Ge(1)–C(5)	2.012(3)
Ge(2)–N(1)	1.927(4)	Ge(2)–C(13)	1.935(5)
Ge(2)–C(14)	1.945(5)	Ge(2)–C(8)	1.972(4)
C(1)–C(2)	1.372(6)	C(2)–C(3)	1.450(6)
C(3)–C(4)	1.371(7)	C(4)–C(5)	1.515(6)
C(5)–C(6)	1.559(6)	C(6)–C(7)	1.339(6)
C(7)–C(8)	1.541(6)		
C(11)–Ge(1)–C(12)	113.2(2)	C(11)–Ge(1)–C(8)	111.7(2)
C(12)–Ge(1)–C(8)	119.5(2)	C(11)–G(1)–C(5)	108.7(2)
C(12)–Ge(1)–C(5)	112.3(2)	C(8)–Ge(1)–C(5)	88.63(17)
N(1)–Ge(2)–C(14)	103.4(2)	C(14)–Ge(2)–C(13)	113.8(2)
N(1)–Ge(2)–C(8)	102.86(16)	C(14)–Ge(2)–C(8)	115.2(2)
C(1)–N(1)–C(4)	108.2(4)	C(1)–N(1)–Ge(2)	122.9(3)
C(4)–N(1)–Ge(2)	128.2(3)		

Table 5
Selected bond distances (Å) and angles (°) for **8**

Ge(1)–C(1)	1.952(2)	Ge(1)–C(2)	1.939(2)
Ge(1)–C(3)	2.0269(1)	Ge(1)–C(3)[a]	2.0269(15)
C(3)–C(4)	1.5314(19)	C(3)–C(5)	1.593(2)
C(4)–C(4)[a]	1.355(3)	C(5)–C(5)[a]	1.629(3)
C(1)–Ge(1)–C(2)	111.02(11)	C(1)–Ge(1)–C(3)[a]	119.56(7)
C(2)–Ge(1)–C(3)[a]	112.26(7)	C(1)–Ge(1)–C(3)	119.55(7)
C(2)–Ge(1)–C(3)	112.26(7)	C(3)[a]–Ge(1)–C(3)	78.72(8)

[a] $x, -y^{3/2}, z$.

also formed (Eq. (3)). The color of the solution changed from yellowish-green to reddish-brown. The rest of **3** (46%) was recovered unchanged from the CH_2Cl_2 solution. Concentration of the reaction mixture by evaporation of CH_2Cl_2 followed by both preparative GPC and TLC (silica gel) gave pure **11** and **12**, which showed satisfactory NMR and MS data. In spite of every efforts of minimizing moisture and air, **13** was obtained in substantial amounts. The yields of products (**8**, **11**–**13**) were based on the amounts of initial amount of **3** and were determined by NMR.



(3)

Products **8**, **13** were characterized by NMR and GC–MS spectra in comparison with those of authentic samples.

The molecular structures of **11** and **12** were fully established by spectroscopic methods and X-ray diffraction analysis. The molecular structures of **11** and **12** are shown in Figs. 5 and 6, respectively, and crystallographic data are included in Table 1. Selected bond lengths and angles of **11** and **12** are summarized in Tables 6 and 7, respectively. The pyrrole ring and the C(5)–C(4)–N(1)–Ge(2)–C(8) plane in **11** are nearly planar. The bond angles of Ge(1)–C(8)–C(7) and Ge(1)–C(8)–Ge(2) are 99.0(3) and 105.57(19)°, respectively.

The TCNE anion radical generated by a CT complex between **3** and TCNE in CH_2Cl_2 at 70 °C is evidenced by ESR signals [3].

2.2. Electrochemical properties of 1,2-dimetallacyclohexa-3,5-dienes

The one-electron oxidation potentials of 1,2-dimetallacyclohexa-3,5-dienes, **1**–**3**, in solutions are one of important characters in the electron-transfer reactions. Electrochemical measurements were carried out in a three-electrode system. The working and counter electrodes were platinum disk and platinum wire, respectively. The reference was $Ag\,|\,Ag^+$. 1,2-Dimetallacyclohexa-3,5-dienes, **1**–**3** were dissolved in dry acetonitrile (CH_3CN) containing 0.1 M of tetrabutylammonium tetrafluoroborate. The cyclic voltammogram (CV) of **1**–**3** is shown in Fig. 7. The scan was started around 0 V vs. $Ag\,|\,Ag^+$. The CV of **1**–**3** are characterized by anodic waves, but no cathodic waves were observed on the reverse scan, even at high scan rates. The irreversible behavior suggests that the one-electron oxidation species are unstable and the easiness of oxidation processes for **1**–**3** is fast on the time scale of the CV measurements. It has several oxidation peaks. The half peak potentials ($E_{p/2}$) of peak 1 for **1**–**3** are involved in Table 8 together with containing $(Me_2Ge)_6$ as reference sample [13]. The $E_{p/2}$ values increase in order **2** < **1** < **3** as shown in Table 8.

3. Discussion

In order to obtain information on the reaction intermediates, 1-sila- and 1-germacyclopenta-2,4-dienes reacted with TCNE at room temperature to give the corresponding 7-sila- and 7-germabicyclo[2.2.1]hept-5-enes (**5** and **8**), respectively [14].

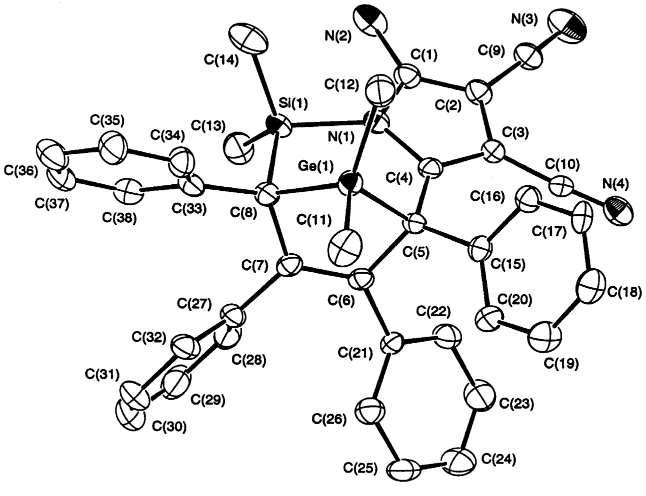


Fig. 5. Molecular structure of the 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-11-germa-2-silatricyclo[6.2.1.$0^{3,7}$]undeca-4,6,9-triene (**11**). (30% probability thermal ellipsoids.) Hydrogen atoms are omitted for clarity.

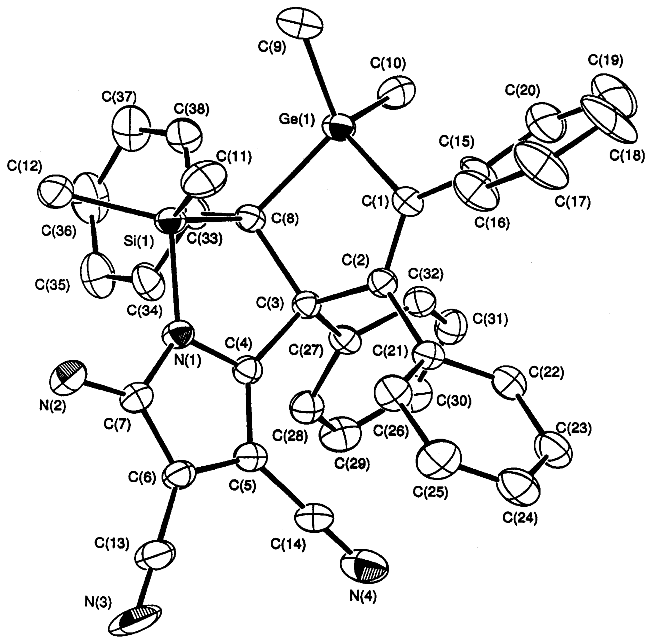


Fig. 6. Molecular structure of the 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-2,11-digermatricyclo[6.3.$0^{1,8}$.$0^{3,7}$]undeca-4,6,9-triene (**12**). (30% probability thermal ellipsoids.) Hydrogen atoms are omitted for clarity.

Table 6
Selected bond distances (Å) and angles (°) for **11**

Ge(1)–C(11)	1.934(4)	Ge(1)–C(12)	1.938(4)
Ge(1)–C(8)	1.987(3)	Ge(1)–C(5)	2.012(3)
Si(1)–N(1)	1.823(3)	Si(1)–C(13)	1.856(4)
Si(2)–C(14)	1.847(4)	Si(1)–C(8)	1.882(3)
C(1)–C(2)	1.371(5)	C(2)–C(3)	1.444(4)
C(3)–C(4)	1.373(5)	C(4)–C(5)	1.500(5)
C(5)–C(6)	1.554(4)	C(6)–C(7)	1.349(4)
C(7)–C(8)	1.545(4)		
C(11)–Ge(1)–C(12)	112.85(18)	C(11)–Ge(1)–C(8)	111.86(15)
C(12)–Ge(1)–C(8)	119.69(15)	C(11)–G(1)–C(5)	109.06(15)
C(12)–Ge(1)–C(5)	112.50(15)	C(8)–Ge(1)–C(5)	88.09(12)
N(1)–Si(1)–C(14)	108.27(15)	C(14)–Si(1)–C(13)	111.95(19)
N(1)–Si(1)–C(8)	105.38(13)	C(14)–Si(1)–C(8)	111.66(17)
C(1)–N(1)–C(4)	108.2(3)	C(1)–N(1)–Si(1)	123.1(2)
C(4)–N(1)–Si(1)	128.1(2)		

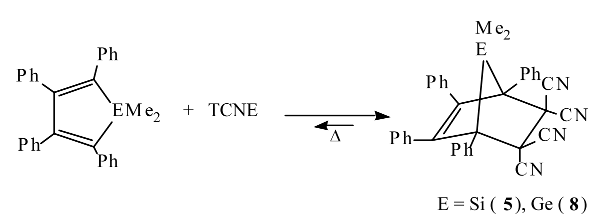


Table 7
Selected bond distances (Å) and angles (°) for **12**

Ge(1)–C(1)	1.942(3)	Ge(1)–C(9)	1.945(3)
Ge(1)–C(10)	1.943(3)	Ge(1)–C(8)	1.998(3)
Si(1)–N(1)	1.787(2)	Si(1)–C(8)	1.911(3)
N(1)–C(7)	1.371(3)	N(1)–C(4)	1.390(3)
C(1)–C(2)	1.335(4)	C(2)–C(3)	1.566(4)
C(3)–C(4)	1.522(3)	C(4)–C(5)	1.374(4)
C(5)–C(6)	1.443(4)	C(6)–C(7)	1.386(4)
C(1)–Ge(1)–C(9)	113.50(12)	C(1)–Ge(1)–C(10)	115.27(13)
C(9)–Ge(1)–C(10)	106.71(14)	C(1)–G(1)–C(8)	88.77(10)
C(9)–Ge(1)–C(8)	116.37(14)	C(10)–Ge(1)–C(8)	115.82(12)
N(1)–Si(1)–C(11)	105.89(15)	N(1)–Si(1)–C(112)	108.93(14)
N(1)–Si(1)–C(8)	91.88(11)	C(11)–Si(1)–C(8)	120.66(14)
C(7)–N(1)–C(4)	109.6(2)	C(7)–N(1)–Si(1)	136.09(19)
C(4)–N(1)–Si(1)	114.14(17)	C(2)–C(1)–Ge(1)	111.74(19)

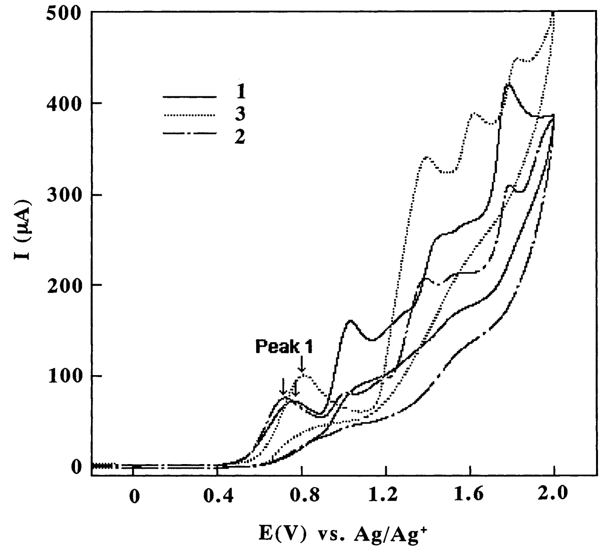


Fig. 7. CVs for 1,2-dimetallacyclohexa-3,5-diene (**1**–**3**) in 0.1 M TBAP CH_3CN solution at the scan rate of 100 mV s^{-1}.

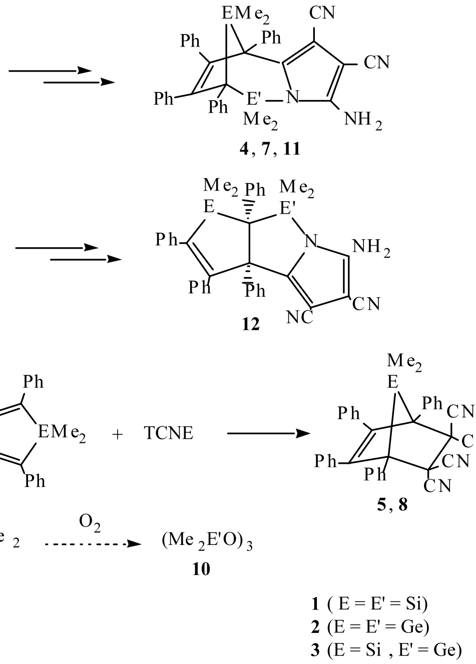
Table 8
One-electron oxidation potentials of 1,2-dimetallacyclohexa-3,5-dienes, **1**–**3** and $(Me_2Ge)_6$

Compound	$E_{p/2}$ (V) vs. Ag | Ag^+
1	0.61
2	0.56
3	0.65
$(Me_2Ge)_6$	0.53

The 7-sila- and 7-germabicyclo[2.2.1]hept-5-ene **5**, **8** were stable at room temperature for at least 72 h, but very slowly decomposed at above 70 °C. Thus, compound **5** in CH_2Cl_2 was heated at 70 °C for 6 h to give 1-silacyclopenta-2,4-diene in 41% and unidentified products derived from TCNE with the decomposition of **5** (60%). The yield of unidentified products from TCNE could not be determined by NMR and GC spectra. The generation of dimethylsilylene from thermolysis of **5** was also expected. However, no formation of products derived from dimethylsilylene was detected. On the other hand, heating of **8** in CH_2Cl_2 solution at 70 °C for 6 h led to the decomposition of **8** (13%) with the formation of 1-germacyclopenta-2,4-diene (6%), cyclic germoxane **10** (4%), and unidentified products. The presence of **10** is explained by the oligomerization of germanones, which formed by the reaction of dimethylgermylene with included oxygen [15].

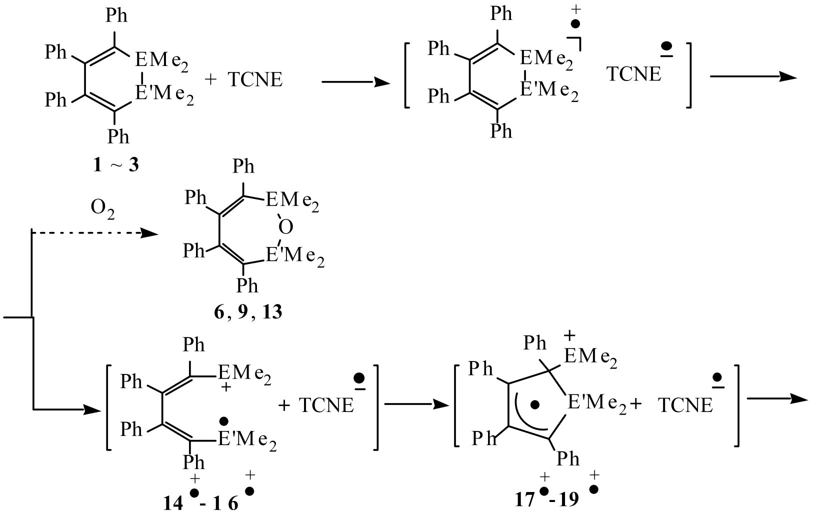
From these results, we propose the following scheme as one possible reaction pathway of the formation of heterocyclic compounds. Since Group 14 elements–Group 14 elements σ bonds of 1,2-dimetallacyclohexa-3,5-dienes, **1**–**3**, with low oxidation potentials (0.56–0.65 V vs. Ag | Ag$^+$) are excellent electron donors, electron-transfer from compounds **1**–**3** to TCNE generates the geminate radical ions composed of the radical cation of **1**–**3** and the radical anion of TCNE. For obtaining their radical ions we attempted the detection of an intermediate species by ESR spectroscopy. The radical anion of TCNE was observed in all reactions, but the radical cation of the compounds **1**–**3** could not be detected due to their instability at even low temperature [16]. In the radical cation of **1**–**3** the Group 14 elements–Group 14 elements bonds are possibly cleaved to give the corresponding open intermediates **14**$^{+\bullet}$–**16**$^{+\bullet}$, respectively. Then, subsequent intramolecular addition of one of the silyl or germyl radicals to the diene moiety gives **17**$^{+\bullet}$–**19**$^{+\bullet}$, respectively, depicted in Scheme 1.

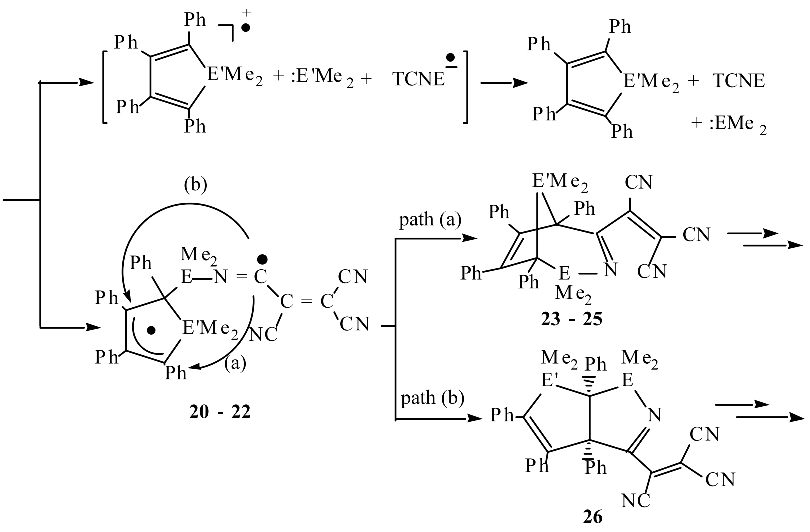
The intermediates **17**$^{+\bullet}$–**19**$^{+\bullet}$ undergo spontaneous scission to cation radicals of 1-sila- and 1-germacyclopenta-2,4-dienes with extrusion of silylene and germylene units. The cation radicals of 1-metallacyclopenta-2,4-dienes are reduced by the anion radical of TCNE to give 1-metallacyclopenta-2,4-dienes. However, we failed to detect the silylene and germylene with trapping reagents such as 2,3-dimethylbuta-1,3-diene and triethylsilane (Et_3SiH) [17]. The silylene and germylene generated are easily converted into silicon- and germanium-containing oligomers. On the other hand, the



Scheme 1.

intermediates **17**$^{+\bullet}$–**19**$^{+\bullet}$ react with the anion radical of TCNE (TCNE$^{-\bullet}$) to give the corresponding biradical species **20**–**22**, respectively. The carbon-centered radical in the biradical intermediates **20**–**22** intramolecularly adds to one of the two allylic position to give tricyanovinyl substituted 3-aza-2,8-disilabicyclo[3.2.1]octa-3,6-diene derivatives **23**–**25**, respectively (path a). Compounds **4**, **7**, **11** may be considered to be derived from the intermediates **23**–**25** after several steps. On the other hand, the carbon-centered radical in the biradical intermediate **22** intramolecularly adds to the another of the two allylic position to give tricyanovinyl substituted 3-aza-2-germa-8-silabicyclo[3.3.0]oct-3,6-diene deriva-





tives **26** (path b). Compounds **12** may be derived from the intermediates **26** after several steps.

Some parts of the radical cations of 1,2-dimetallacyclohexa-3,5-dienes react with included oxygen to give 1,3-dimetalla-2-oxacyclohepta-4,6-dienes **6**, **9**, **13** [10]. 1,2-Dimetallacyclohexa-3,5-dienes (**1**–**3**) do not react with oxygen.

4. Experimental

4.1. General methods

The NMR spectra were obtained on a Varian Unity Inova 400 MHz spectrometer. The GC–MS spectra were measured on a JEOL JMS-DX 303 mass spectrometer. The UV and UV–vis spectra were recorded with a Shimadzu UV 2000 spectrometer. The infrared spectra were recorded with a Shimadzu FT IR 4200 spectrometer. Gas chromatography was performed on a Shimadzu GC 8A with a 1 m 20% SE30 column. GPC was performed on a Twincle with an Asahipak GS 310 column. X-ray crystallographic data and diffraction intensities were collected on a MacScienec DIP2030 diffractometer utilizing graphite-monochromated Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods using SIR-92 [18] and refined with all data on F^2 by means of SHELXL-97 [19]. A refinement was performed by a SILICON Graphics O$_2$ with maXus. CH_2Cl_2 and other solvents were purified and dried as reported in the literature.

4.2. Materials

1,1,2,2-Tetramethyl-1,2-disila-3,4,5,6-tetraphenylcyclohexa-3,5-diene [9], 1,1,2,2-tetramethyl-1,2-digerma-3,4,5,6 - tetraphenylcyclohexa - 3,5 - diene [10], 1,1 - dimethyl-1-sila-2,3,4,5-tetraphenylcyclopenta-2,4-diene [20], 1,1 - dimethyl - 1 - germa - 2,3,4,5 - tetraphenylcyclopenta-2,4-diene [21], 1,1,3,3-tetramethyl-4,5,6,7-tetraphenyl - 2 - oxa - 1,3 - digermacyclohepta - 4,6 - diene [10], 2,2,4,4,6,6-hexamethyl-1,3,5-trioxa-2,4,6-trigermacyclohexane [12], triethylsilane [22], dimethyldichlorogermane [23] were prepared as reported in the literature. TCNE, CCl_4, 2,3-dimethylbuta-1,3-diene, and *m*-chloroperoxybenzoic acid were commerically available.

*4.3. Preparation of 1,1,2,2-tetramethyl-1-germa-2-sila-3,4,5,6-tetraphenylcyclohexa-3,5-diene (**3**)*

A mixture of lithium metal (0.25 g, 3.6 mmol) and diphenylacetylene (6.3 g, 35 mmol) in anhydrous diethyl ether (40 ml) was stirred for 1 d at room temperature. To this solution was added anhydrous THF (50 ml) and then (dimethylchlorogermyl)dimethylchlorosilane 4.11 g (18 mmol). After it was stirred for 51 h for 35–40 °C, the mixture was hydrolyzed with water. The organic layer was extracted with diethyl ether and dried over Na_2SO_4. After the solvent had been evaporated, the residue was diluted with aetone to cause crystallization of pure 1,1,2,2-tetramethyl-1-germa-2-sila-3,4,5,6-tetraphenylcyclohexa-3,5-diene (4.23 g, 8.2 mmol, 70%): m.p.: 172–173 °C. ^{1}H-NMR (δ, $CDCl_3$) 0.28 (s, 6H), 0.32 (s, 6H), 6.72–6.84 (m, 14H), 6.94–7.01 (m, 2H), 7.08–7.14 (m, 4H); ^{13}C-NMR (δ, $CDCl_3$) −4.7, −3.7, 124.3, 124.5, 125.1, 125.2, 126.6, 127.5, 127.8, 128.3, 129.6, 141.0, 141.6, 141.9, 142.9, 143.6, 145.8, 149.0, 152.4; MS *m/z* 518 (^{74}Ge); UV (cyclohexane) $\lambda_{\max}$ 352 nm (log ε 3.88). Anal. Calc. for $C_{32}H_{32}GeSi$: C, 73.05; H, 6.54. Found: C, 73.37; H, 6.21.

4.4. Preparation of 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hept-5-ene (5)

A mixture of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene (0.41 g, 0.1 mol) and TCNE (0.13 g, 0.1 mmol) in CH_2Cl_2 (30 ml) was stirred for 3 d at room temperature. After the solvent had been evaporated, the residue was diluted with CH_2Cl_2 to cause crystallization of pure 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hept-5-ene (0.42 g, 0.75 mmol, 75.1%): dec. 170 °C. ^{1}H-NMR (δ, $CDCl_3$) 1.00 (s, 3H), 1.10 (s, 3H), 6.78–7.30 (m, 20H); ^{13}C-NMR (δ, $CDCl_3$) −3.0, 3.9, 54.4, 59.3, 11.3, 113.5, 127.4, 127.5, 128.6, 128.9, 129.7, 130.0, 132.4, 134.2, 144.4; MS *m/z* 416 (-TCNE); UV (CH_2Cl_2) $\lambda_{\max}$ 264 nm (log ε 4.43). Anal. Calc. for $C_{36}H_{26}N_4Si$: C, 79.67; H, 4.83; N, 10.32. Found: C, 79.46; H, 4.94; N, 10.27.

4.5. Preparation of 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabicyclo[2.2.1]hept-5-ene (**8**)

A mixture of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (0.23 g, 0.5 mol) and TCNE (0.063 g, 0.5 mmol) in CH_2Cl_2 (30 ml) was stirred for 3 h at room temperature. After the solvent had been evaporated, the residue was diluted with CH_2Cl_2 to cause crystallization of pure 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabicyclo[2.2.1]hept-5-ene (0.26 g, 0.43 mol, 87.4%): dec. 150 °C. ^{1}H-NMR (δ, $CDCl_3$) 1.17 (s, 3H), 1.36 (s, 3H), 6.79–7.31 (m, 20H); ^{13}C-NMR (δ, $CDCl_3$) −1.56, −1.51, 8.25, 8.33, 55.4, 62.1, 107.2, 11.3, 113.5, 127.3, 129.8, 130.1, 130.3, 133.0, 134.6, 144.2; MS *m/z* 460 (-TCNE) (^{74}Ge); UV (CH_2Cl_2) $\lambda_{\max}$ 266 nm (log ε 3.96). Anal. Calc. for $C_{36}H_{26}N_4Ge$: C, 73.63; H, 4.46; N, 4.46. Found: C, 73.53; H, 4.44; N, 4.44.

4.6. Preparation of 1,1,3,3-tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1,3-disilacyclohepta-4,6-diene (6)

A mixture of 1,1,2,2-tetramethyl-1,2-disila-3,4,5,6-tetraphenylcyclohexa-3,5-diene (0.33 g, 0.7 mmol) and *m*-chloroperoxybenzoic acid (0.24 g, 1.0 mmol) in diethyl ether (30 ml) was stirred for 4 h at room temperature. After the solvent had been evaporated, the residue was diluted with CH_2Cl_2 to cause crystallization of pure 1,1,3,3-tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1,3-disilacyclohepta-4,6-diene (0.26 g, 0.38 mmol, 76.1%): ^{1}H-NMR (δ, $CDCl_3$) −0.02 (broad, s, 3H), 0.70 (broad s, 3H), 6.79–7.14 (m, 20H); ^{13}C-NMR (δ, $CDCl_3$) 1.56, 125.0, 125.8, 126.8, 127.5, 129.6, 140.5, 143.0, 144.8, 154.3; MS *m/z* 488; UV (cyclohexane) $\lambda_{\max}$ 274 nm (log ε 4.16). Anal. Calc. for $C_{32}H_{32}OSi_2$: C, 78.64; H, 6.60. Found: C, 78.70; H, 6.46.

4.7. Preparation of 1,1,3,3-tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1-germa-3-silacyclohepta-4,6-diene (13)

A mixture of 1,1,2,2-tetramethyl-1-germa-2-sila-3,4,5,6-tetraphynycyclo-hexa-3,5-diene (0.26 g, 0.5 mmol) and *m*-chloroperoxybenzoic acid (0.17 g, 1.0 mmol) in diethyl ether (20 ml) was stirred for 4 h at room temperature. After the solvent had been evaporated, the residue was diluted with CH_2Cl_2 to cause crystallization of pure 1,1,3,3-tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1-germa-3-silacyclohepta-4,6-diene (0.19 g, 0.35 mmol, 69.8%): ^{1}H-NMR (δ, $CDCl_3$) −0.02 (broad, s, 3H), 0.70 (broad s, 3H), 6.69–7.20 (m, 20H); ^{13}C-NMR (δ, $CDCl_3$) 1.56, 125.0, 125.8, 126.8, 127.5, 129.6, 140.5, 143.0, 144.8, 154.3; MS *m/z* 534; UV (cyclohexane) $\lambda_{\max}$ 275 nm (log ε 4.09). Anal. Calc. for $C_{32}H_{32}OGeSi$: C, 72.07; H, 6.05. Found: C, 72.38; H, 6.29.

4.8. Reaction of 1,2-disilacyclohexa-3,5-diene (1) with TCNE

A solution of 1,1,2,2-tetramethyl-1,2-disila-3,4,5,6-tetraphenylcyclohexa-3,5-diene (**1**) (0.18 g, 0.4 mmol) and TCNE (0.4 mmol) in CH_2Cl_2 (6 ml) was placed in a Pyrex tube ($\phi = 1$ cm) 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 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-2,11-disilatricyclo[6.2.1.0^{3,7}]undeca-4,6,9-triene (**4**, 38%), 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hept-5-ene (**5**, trace), 1,1,3,3-tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1,3-disilacyclohepta-4,6-diene (**6**, 16%), and some unidentified products. The rest of **1** (40%) was recovered unchanged from the CH_2Cl_2 solution. Concentration of the reaction mixture by evaporation of CH_2Cl_2 followed by both preparative GPC and TLC (silica gel) gave pure **4**. **4**: m.p.: < 220 °C; ^{1}H-NMR (δ, $CDCl_3$) 0.10 (s, 3H), 0.17 (s, 3H), 0.61 (s, 3H), 0.65 (s, 3H), 4.03 (broad s, 2H), 6.45–7.16 (m, 20 H); ^{13}C-NMR (δ, $CDCl_3$) −5.7, −2.3, −1.4, −0.9, 15.2, 18.4, 93.6, 103.7, 125.5, 126.1, 126.3, 126.6, 127.1, 128.0, 129.4, 130.6, 131.4, 136.5, 137.5, 137.7, 139.0, 146.3, 148.7; MS *m/z* 602; UV (CH_2Cl_2) $\lambda_{\max}$ 277 nm (log ε 3.43).

4.9. Reaction of 1,2-digermacyclohexa-3,5-diene (2) with TCNE

A solution of 1,1,2,2-tetramethyl-1,2-digerma-3,4,5,6-tetraphenylcyclohexa-3,5-diene (**2**) (0.22 g, 0.4 mmol) and TCNE (0.4 mmol) in CH_2Cl_2 (6 ml) was placed in a Pyrex tube under argon and sealed. The color of the solution changed from yellow to green. The Pyrex tube was heated at 90 °C for 4 h to give 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-2,11-digermatricyclo[6.2.1.$0^{3,7}$]undeca-4,6,9-triene (**7**, 3%), 2,2,3,3-tetracyano-7,7,dimethyl-1,4,5,6-tetraphenyl-7-germabicyclo[2,2,1]hepta-5-ene (**8**, 9%), 1,1,3,3-tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1,3-digermacyclohepta-4,6-diene (**9**, 16%), 2,2,4,4,6,6-hexamethyl-1,3,5-trioxa-2,4,6-trigermacyclohexane (**10**, trace), and some unidentified products. The rest of **2** (45%) was recovered unchanged from the CH_2Cl_2 solution. Concentration of the reaction mixture by evaporation of CH_2Cl_2 followed by both preparative GPC and TLC (silica gel) gave pure **7**. **7**: ^{1}H-NMR (δ, $CDCl_3$) 0.33 (s, 3H), 0.71 (s, 3H), 0.72 (s, 3H), 1.10 (s, 3H), 3.86 (broad s, 2H), 6.76–7.65 (m, 20H); ^{13}C-NMR (δ, $CDCl_3$) −0.5, 0.8, 1.7, 1.9, 56.2, 76.6, 93.2, 94.6, 113.1, 114.2, 126.3, 126.3, 127.1, 127.3, 128.1, 128.2, 128.3, 130.4, 130.6, 130.8, 135.1, 137.7, 138.8, 139.2, 144.6, 145.0, 146.5, 155.0; MS m/z 692; UV (CH_2Cl_2) λ_{max} 287 nm (log ε 3.49).

4.10. Reaction of 1-germa-2-silacyclohexa-3,5-diene (3) with TCNE

A solution of 1,1,2,2-tetramethyl-1-germa-2-sila-3,4,5,6-tetraphenylcyclohexa-3,5-diene (**3**) (0.207 g, 0.4 mmol) and TCNE (0.4 mmol) in CH_2Cl_2 (6 ml) was placed in a Pyrex tube ($\phi = 1$ cm) under argon and sealed. The color of the solution changed from yellowish-green to reddish-brown. The Pyrex tube was heated at 90 °C for 3 h to give 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-tetraphenyl-3-aza-11-germa-2-silatricyclo[6.2.1.$0^{3,7}$]undeca-4,6,9-triene (**11**, 5%), 4-amino-5,6-dicyano-2,2,11,11-tetramethyl-1,8,9,10-3-aza-11-germa-2-silatricyclo[6.3.$0^{1,8}$.$0^{3,7}$]undeca-4,6,9-triene (**12**, 4%), 2,2,3,3-tetracyano-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germabicyclo[2.2.1]hept-5-ene (**8**, 15%), 1,1,3,3-tetramethyl-4,5,6,7-tetraphenyl-2-oxa-1-germa-3-silacyclohepta-4,6-diene (**13**, 23%), and some unidentified products. The color of the solution changed from yellowish-green to reddish (**10**, trace), and some unidentified products were also detected. The rest of **3** (46%) was recovered unchanged from the CH_2Cl_2 solution. Concentration of the reaction mixture by evaporation of CH_2Cl_2 followed by both preparative GPC and TLC (silica gel) gave pure **11** and **12**. **11**: ^{1}H-NMR (δ, $CDCl_3$) 0.19 (s, 3H), 0.27 (s, 3H), 0.65 (s, 3H), 0.76 (s, 3H), 3.98 (broad s, 2H), 6.45–7.16 (m, 20H); ^{13}C-NMR (δ, $CDCl_3$) −5.0, −1.2, −0.8, 0.8, 42.9, 48.5, 93.5, 99.9, 113.3, 114.1, 125.1, 126.1, 126.2, 126.4, 127.1, 127.5, 128.1, 129.4, 130.8, 131.4, 137.1, 138.0, 138.2, 139.0, 139.6, 143.8, 146.0, 146.4, 148.8; MS m/z 648; UV (CH_2Cl_2) λ_{max} 345 nm (log ε 3.27). **12**: ^{1}H-NMR (δ, $CDCl_3$) 0.19 (s, 3H), 0.27 (s, 3H), 0.65 (s, 3H), 0.78 (s, 3H), 3.98 (broad s, 2H), 6.45–7.16 (m, 20H); ^{13}C-NMR (δ, $CDCl_3$) −1.8, 0.9, 2.0, 2.2, 3.9, 12.7, 71.6, 106.3, 112.7, 113.9, 125.8, 126.3, 127.1, 127.4, 127.9, 128.1, 128.2, 129.1, 130.5, 130.7, 134.8, 137.5, 138.8, 139.2, 145.4, 146.3, 154.7; MS m/z 646; UV (CH_2Cl_2) λ_{max} 269 nm (log ε 4.48).

4.11. Reactions of 1,2-dimetallacyclohexa-3,5-dienes with TCNE in the presence of trapping reagents

As a representative example, the reaction of 1,1,2,2-tetramethyl-1,2-disila-3,4,5,6-tetraphenylcyclohexa-3,5-diene (**1**) with TCNE in the presence of 2,3-dimethyl-1,3-butadiene is described. A solution of 1,1,2,2-tetramethyl-1,2-disila-3,4,5,6-tetraphenylcyclohexa-3,5-diene (**1**) (0.01 mmol), TCNE (0.01 mmol), and 2,3-dimethylbuta-1,3-diene (0.08 mmol) in CD_2Cl_2 (0.6 ml) was placed in a NMR tube under argon and sealed. The color of the solution changed from yellowish-green to reddish-brown. The reaction products were examined by NMR and GC–MS spectra analysis.

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