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Journal of Organometallic Chemistry 690 (2005) 731–741
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Non-degenerate 1,2-silyl shift in silyl substituted alkyltrimethylcyclopentadienes

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Received 23 June 2004; accepted 14 September 2004

Abstract

The five new silanes $C_5Me_3RSiMe_nCl_{3-n}$ ($n = 3$, R = *i*-Pr (**5**); $n = 2$, R = *i*-Pr (**6**); $n = 2$, R = *s*-Bu (**7**); $n = 2$, R = cyclohexyl (**8**); and $n = 3$, R = *t*-Bu (**9**)) were synthesized by reaction of 1-alkyl-2,3,4-trimethylcyclopentadienyl lithium salts with appropriate chlorosilane and characterized by NMR, MS, and IR spectra. At elevated temperatures (250–360 K), all the silanes undergo a non-degenerate sigmatropic silyl rearrangement, which generates non-equivalent structures **a** and **b**. The presence of minor structure **c** was observed in compounds **5** and **7** only. The Diels–Alder cycloaddition of **5** with strong dienophiles tetracyanoethylene (TCNE), and dimethylacetylenedicarboxylate (DMAD) provides compounds **10** and **11**, which confirmed isomers **a** and **b**, respectively. The free energy of activation of **b** → **a** isomerization for compounds **5**–**8** evaluated from variable temperature NMR spectra show only marginal influence of group R on the 1,2-silyl shift rate. Moreover, in compounds **5** and **7**, the process **b** → **a** was found significantly faster than **b** → **c** process in the above-mentioned temperature range.

Keywords: Substituted cyclopentadienes; Silatropic shift; Dynamic NMR spectroscopy; Diels–Alder cycloaddition; X-ray crystallography

1. Introduction

Fluxional behaviour of cyclopentadienyl-like frameworks with σ-bonded main group elements [1] is induced by two main processes: 1,2-metallotropic and 1,2-prototropic shift. The rate of both depends on the nature of main group element, substituents bonded to this element, and on the effect of other groups substituted on cyclopentadienyl [2], isodicyclopentadienyl [3], indenyl [4–7], fluorenyl [8] and higher benzannulated rings [9,10].

In (trimethylsilyl)cyclopentadiene both degenerate 1,2-silatropic and non-degenerate 1,2-prototropic shift occur at ambient temperature, but the latter is 10^6 slower than the former one [11]. The molecule exists mainly (up to 90%) as an allylic isomer and the remaining two vinylic isomers were proved by trapping with strong dienophiles [11,12]. A step-wise replacement of methyl groups bonded to silicon atom by more electronegative chlorine atoms led to a decrease in allylic/vinylic isomer ratio, and an increase in free energy value (e.g., 15.2 kcal/mol for $SiMe_3$ and 16.3 kcal/mol for $SiCl_3$) [13]. In silyl substituted pentamethylcyclopentadienes, however, the trend for free energy of activation was found to be quite opposite (e.g., 15.3 kcal/mol for $SiMe_3$ and 13.1 kcal/mol for $SiCl_3$) [14]. NMR

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doi:10.1016/j.jorganchem.2004.09.081

investigations of chiral silylcyclopentadienes at different temperatures proved that 1,2-silyl migration proceeds with retention of configuration on silicon atom [15,16]. Compounds with general formula $C_5(SiMe_3)_nH_{6-n}$ show fluxional behavior for $n = 1$–3, but the compound for $n = 4$ possesses only 2,3,5,5-isomer in the normal range of temperatures [2].

Although chemistry of cyclopentadienes and methylcyclopentadienes bearing organosilyl groups was widely investigated, only a few examples of cyclopentadienes with other non-migrating group(s) beside silyl group(s) were published. A non-degenerate exchange process between 1,2-$(SiMe_3)_2$-4-(*t*-Bu)C_5H_3 and 2-(*t*-Bu)-5,5-$(SiMe_3)_2C_5H_3$ isomers was described in *t*-butyl-bis(trimethylsilyl)cyclopentadiene [17]. A fluxional behavior of a compound resulting from introduction of one trimethylsilyl group on 1,4-bis(*t*-butyl)cyclopentadiene was assigned by Jutzi and coworkers to a degenerate 1,2-silyl shift [18] and by Royo and coworkers to a non-degenerate 1,3-shift [19].

Here, we report the synthesis of five new ((alkyl)trimethylcyclopentadienyl)silanes with sterically demanding alkyls, their dynamic NMR study showing thermal dependence of the silyl migration rate, and an evidence for isomer structures involved in the fluxional process.

2. Results and discussion

2.1. Synthesis of silyl substituted alkyltrimethylcyclopentadienes

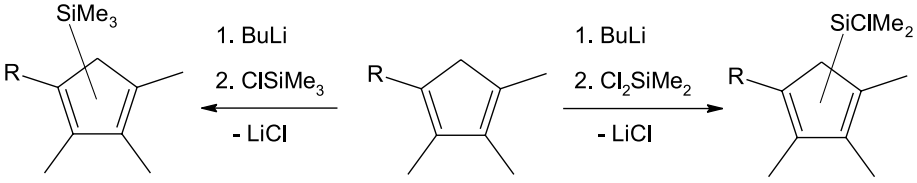
1-Alkyl-2,3,4-trimethylcyclopentadienes (mixture of isomers, where alkyl = *i*-Pr (**1**), *s*-Bu (**2**), cyclohexyl (**3**), *t*-Bu (**4**)) were prepared by the reaction of appropriate alkyl Grignard (or lithium) reagent with a mixture of 2,3,4-trimethylcyclopent-2-en-1-one and 3,4,5-trimethylcyclopent-2-en-1-one [20], followed by hydrolysis, and an iodine catalyzed dehydration. The cyclopentadienes were obtained in rather low yields (36–47%), presumably due to a steric hindrance of secondary or tertiary alkyl group. According to ^{1}H NMR spectra all the prepared cyclopentadienes contained predominantly isomers with two protons in allylic position (up to 91% in **1**, 85% in **2**, 90% in **3**, and 66% in **4**).

Trimethylsilyl or chlorodimethylsilyl substituted cyclopentadienes **5**–**9** were obtained by the reaction of 1-alkyl-2,3,4-trimethylcyclopentadienyl lithium salts with an excess of chlorotrimethylsilane or dichlorodimethylsilane, respectively, in THF (Scheme 1).

2.2. Temperature-dependent NMR spectroscopic studies of 5–9

The ^{1}H NMR spectra of compounds **5**–**9** were measured in the temperature range 200–360 K. The shape of ^{1}H NMR spectra of compounds **5**–**8** in toluene-d_8 strongly depended on the temperature, whereas the changes in the spectrum of **9** were rather marginal. The temperature-dependent spectra can be explained by assuming a non-degenerate [1,5] sigmatropic rearrangement due to trimethylsilyl 1,2-shift (Scheme 2).

Cooling to temperatures below 240 K slowed down this process on the NMR time scale and gave rise to sets of signals representing "frozen" isomers **a** and **b** for compounds **6** and **8**, or isomers **a**, **b** and **c** for compounds **5** and **7**. The isomers **b** predominate (60–72%) in all cases, presumably due to the absence of steric repulsion between the bulky secondary alkyl group and the silyl group. Abundances of isomer **c** in compounds **5** and **7** are only 6% and 4%, respectively. The signals of allylic and vinylic protons broadened with increasing temperature, and showed coalescence at about 330 K for **6** and **8**, at 340 K for **7**, and at 360 K for **5** (Fig. 1). The further increase in temperature above 350 K resulted in merging the signals to a single resonance at 4.94 ppm for **6**, 4.80 ppm for **7**, and 4.93 ppm for **8**. The proportion between isomers **a**, **b** (and **c** in compounds **5** and **7**) is unaffected by increase in the temperature, and it indicates the absence of other

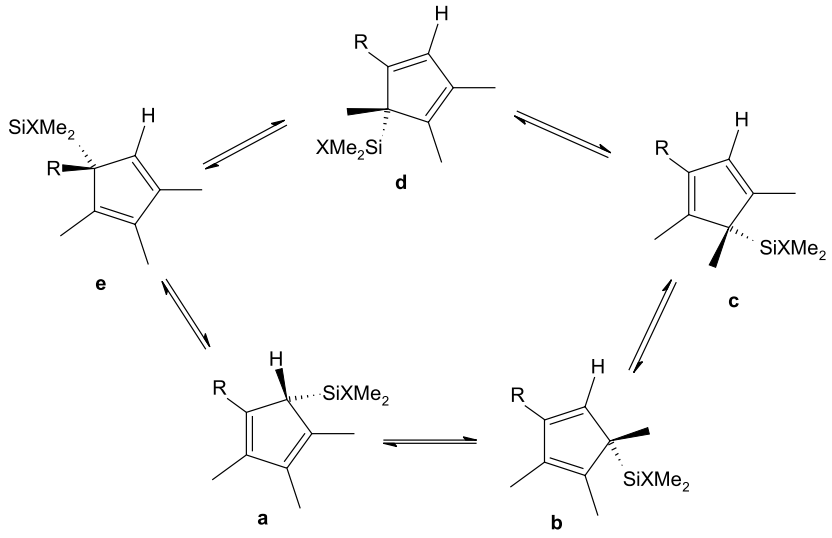


R=*i*-Pr **5**
R=*t*-Bu **9**

R=*i*-Pr **1**
R=*s*-Bu **2**
R=cyclohexyl **3**
R=*t*-Bu **4**

R=*i*-Pr **6**
R=*s*-Bu **7**
R=cyclohexyl **8**

Scheme 1. Preparation of silanes **5**–**9**.



R=*i*-Pr	X=Me	**5**
R=*i*-Pr	X=Cl	**6**
R=*s*-Bu	X=Cl	**7**
R=cyclohexyl	X=Cl	**8**
R=*t*-Bu	X=Me	**9**

Scheme 2. Non-degenerate silyl group rearrangement in silyl substituted (alkyl)trimethylcyclopentadienes.

fluxional processes. The migration of trimethylsilyl group in compound **9** was evidenced by the shift of vinylic proton signal from 5.86 ppm at 280 K to an averaged signal positioned at 5.82 ppm at 370 K. This estimates the content of isomer **b** to be higher than 99%. This circumstance precludes the evaluation of relevant activation parameters for **9**.

The careful band-shape analysis of recorded spectra (for details see Section 3) provided the rate constants for **b** → **a** and **b** → **c** processes. The simulation of experimental spectra excluded **a** → **c** (due to 1,3-silyl shift) process in the range of studied temperatures. In compounds **5** (Fig. 2) and **7**, the silyl migration **b** → **a** was found significantly faster than **b** → **c** (evaluated rate constants k_{ba} are about 20 times higher than k_{bc}). Activation parameters (free energy of activation $\Delta G^{\ddagger}_{300}$, free enthalpy $\Delta H^{\ddagger}$, and entropy $\Delta S^{\ddagger}$) for **b** → **a** and for **b** → **c** (in compounds **5** and **7**) generated from Eyring plots are summarised in Table 1. The obtained $\Delta G^{\ddagger}_{300}$ values show only marginal influence of bulky alkyl groups on free energy of rearrangement **b** → **a** in compounds **5**–**8**, or **b** → **c** in compounds **5** and **7**. Significantly higher $\Delta G^{\ddagger}_{300}$ values for **b** → **c** process compared to $\Delta G^{\ddagger}_{300}$ values for **b** → **a** in compounds **5** and **7** can be attributed to steric repulsion between silyl and methyl groups during the transition state formation. A slightly higher $\Delta G^{\ddagger}_{300}$ for **b** → **a** in **5** compared to **6** is in rough agreement with previously reported lowering of $\Delta G^{\ddagger}_{300}$ in a series of $C_5Me_5SiMe_nCl_{3-n}$ (for $n = 0$–3) compounds upon replacing of electron-donating methyl groups by electron-attracting chlorine atoms (e.g., 14.8 kcal/mol for $C_5Me_5SiMe_3$, and 13.8 kcal/mol for $C_5Me_5SiMe_2Cl$) [14].

2.3. Diels–Alder reaction of 5 with dienofiles

In order to confirm the isomers assumed from low temperature ^1H and ^{13}C $\{^1H\}$ NMR measurements, compound **5** was reacted with strong dienophiles: tetracyanoethylene (TCNE), and dimethylacetylenedicarboxylate (DMAD) (Scheme 3). The reaction with less reactive DMAD [21,22] independently of the reaction temperature (25 and 140 °C) gave only one product. A typical proton bridgehead signal of relative intensity 1 at 3.67 ppm, together with only one downfield shifted methyl signal at 1.64 ppm (due to the methyl group attached to the double bond) is compatible with structure **10**. The orientation of 7-positioned trimethylsilyl group in *exo* position towards the dimethylethenediylcarboxylate bridge was deduced from NOESY experiment showing a strong through-space interaction of $SiMe_3$ protons with the methyl group placed on the double bound.

On the other hand, the reaction of **5** with TCNE at 25 °C afforded product **11** arising from isomer **5a**. The proton NMR spectrum of **11** showed the bridging proton signal at 1.51 ppm, and two signals at 1.31 and 1.45 ppm of methyl groups placed on double bond, showing a mutual homoallylic interaction ($^5J_{HH}$ = 1.0 Hz). The structure of **11** was also confirmed by X-ray diffraction analysis (vide infra).

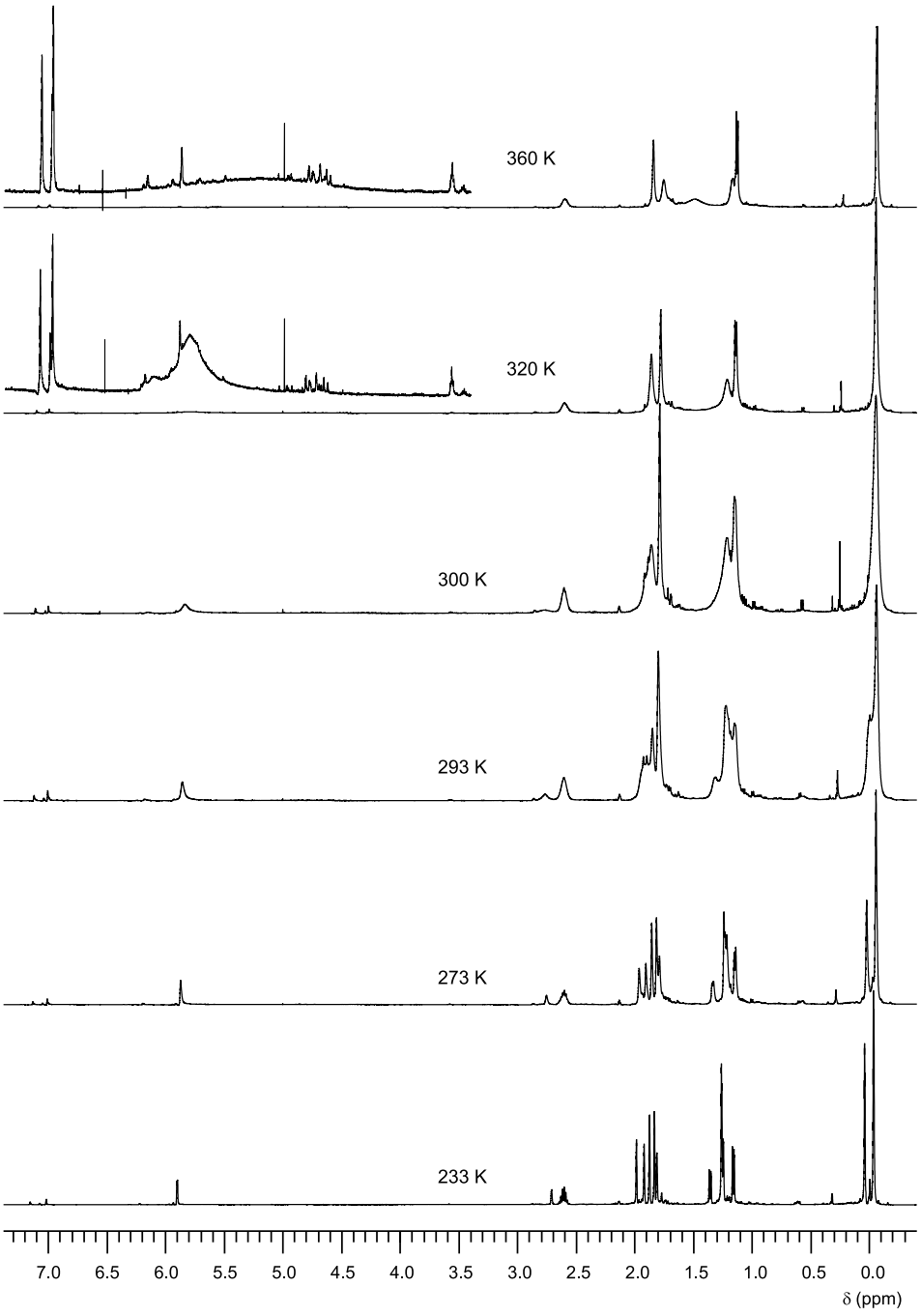


Fig. 1. Dynamic ^{1}H NMR spectra of **5** in the temperature range 233–360 K.

These results can be accounted for by different steric crowding in **5a** and **5b** isomers with respect to entering dienophiles. Whereas a mutual steric congestion of *iso*-propyl and methylcarboxylate groups disfavours the approach of DMAD to isomer **5a**, the reaction of DMAD with **5b** is possible. For TCNE, the reaction with "more hindered" isomer **5a** took place only to give **11** as a kinetically preferred product. Our attempts to obtain an expected thermodynamic product at 140 °C gave a number of unidentifiable products, and heating of crystalline **11** resulted in its decomposition above 122 °C. The easy dissociation of **11** was corroborated by its EI-MS spectra showing the ionised products of retro Diels–Alder reaction only.

2.4. Crystal structure of *11*

The structure of Diels–Alder adduct **11** was corroborated by X-ray diffraction analysis (Fig. 3). The selected bond lengths and angles are given in Table 2. The most

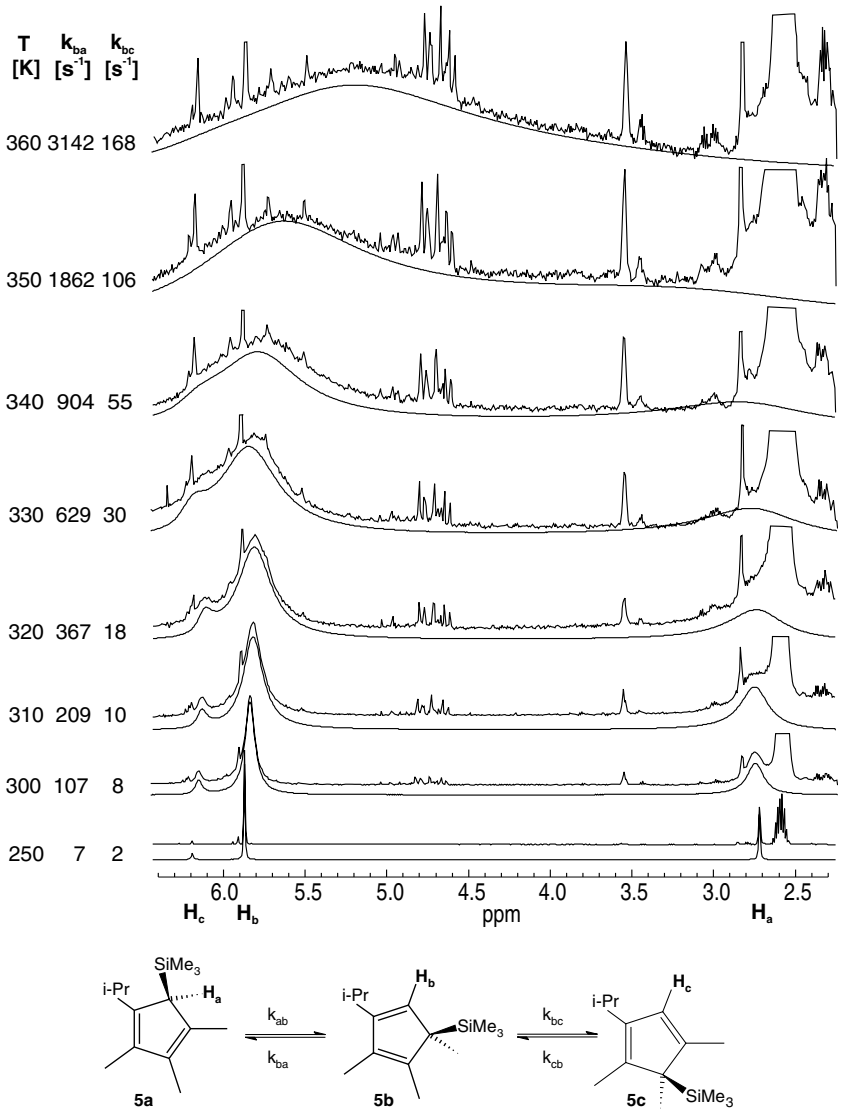
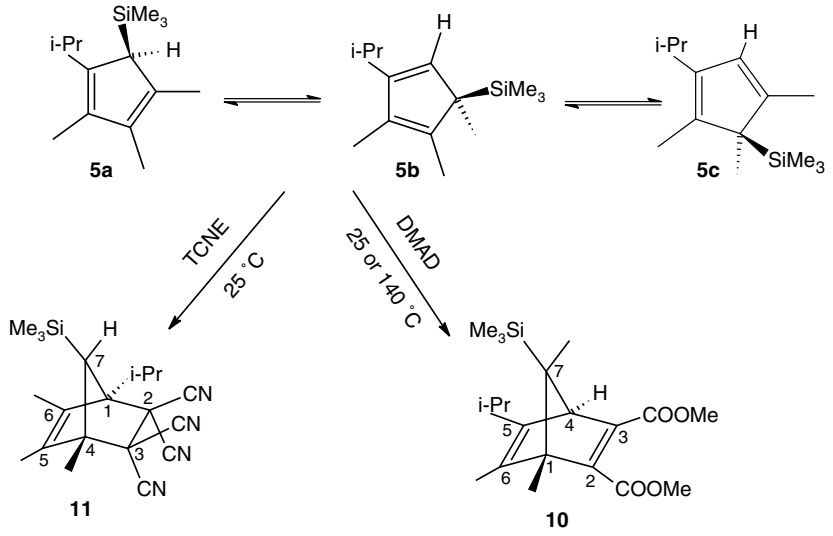


Fig. 2. Expanded region of experimental (upper) and simulated (lower) ^{1}H NMR spectra for **5** in toluene-d_8 in the temperature range 250–360 K. The simulated signals are denoted H_{a-c}, and their assignment is depicted in the attached scheme.

Table 1
Activation parameters obtained from an Eyring plot for **b** → **a** and **b** → **c** rearrangements in compounds **5**–**8**

Compound	**b** → **a**			**b** → **c**		
	$\Delta G^{\ddagger}_{300}$ (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/K/mol)	$\Delta G^{\ddagger}_{300}$ (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/K/mol)
5	14.8 ± 0.1	11.2 ± 0.1	−12.1 ± 0.4	16.6 ± 0.2	12.0 ± 0.1	−15.3 ± 0.6
6	14.5 ± 0.3	6.2 ± 0.3	−27.5 ± 1.1	Not observed		
7	14.2 ± 0.2	10.3 ± 0.1	−13.0 ± 0.6	15.9 ± 0.3	11.4 ± 0.1	−14.9 ± 0.9
8	14.1 ± 0.2	9.9 ± 0.1	−13.9 ± 0.7	Not observed		

important factor indicating the stability of **11** towards the retro-Diels–Alder reaction is the length of new C–C bonds. Whereas the C3–C4 value (1.608(2) Å) lies in the range typical for new formed bonds in other Diels–Alder adducts of TCNE with, e.g., chlorocyclopentadiene (1.604 and 1.607 Å) [23], chloropentamethylcyclopentadiene (1.602 and 1.603 Å) [23], 6,6-dimethylfulvene (1.601 and 1.607 Å) [24], isodicyclopentadiene (1.591 and 1.600 Å) [25], and (trimethylsilyl)indene (1.582(2) and 1.593(8) Å) [7], the C1–C2 length of 1.628(2) Å is significantly longer, apparently due to a steric hindrance of neighbouring *iso*-propyl group. These structural data are in agreement with a facile decomposition of **11** to starting materials as it was



Scheme 3. Reaction of **5** with TCNE and DMAD.

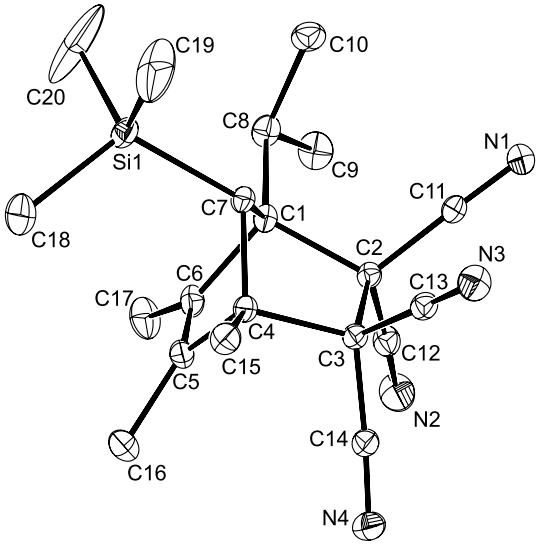


Fig. 3. Molecular structure of **11** (30% probability thermal motion ellipsoids) showing the atom numbering scheme. The hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **11**

Si–C7	1.935(2)	C–N[a]	1.141(2)–1.146(2)
C1–C2	1.628(2)	C1–C6	1.539(2)
C1–C7	1.553(2)	C2–C3	1.600(2)
C3–C4	1.608(2)	C4–C7	1.551(2)
C4–C5	1.525(2)	C5–C6	1.337(2)
Si–C7–C(1)	120.44(10)	Si–C7–C4	113.77(10)
C–C–N[b]	176.33(17)–178.65(16)		

[a] Range of C–N bond lengths in four carbonitrile groups.
[b] Range of angles in four carbonitrile groups.

observed by EI-MS. The steric hindrance of *iso*-propyl group is also responsible for declination of trimethylsilyl group from the *iso*-propyl-substituted side of the molecule, as evidenced by remarkably larger Si–C7–C1 angle (120.44(10)°) compared to Si–C7–C4 (113.77(10)°).

3. Experimental

3.1. General procedures

All reactions with moisture- and air-sensitive compounds were carried out under an atmosphere of argon. Solvents were dried by potassium benzophenone (tetrahydrofuran, diethylether), $LiAlH_4$ (xylene), and CaH_2 (dichloromethane), and freshly distilled prior to use. A mixture of trimethylcyclopentenones was prepared according to the literature procedure [26]. Cyclohexylbromide, *iso*-propylchloride, *sec*-butylchloride, dichlorodimethylsilane, chlorotrimethylsilane, tetracyanoethylene (TCNE), and dimethylacetylenedicarb oxylate (DMAD) were obtained from Aldrich and used as received. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) were measured on a Bruker DRX500 spectrometer in benzene-d_6 solution at 300 K, or in toluene-d_8 for temperature-dependent experiments in the temperature range 200–360 K. EI-MS spectra were measured on a KRATOS Concept 32S instrument (Centre de Spectroscopie Moléculaire de l'Université de Bourgogne) at 70 eV, or on a VG-7070E mass spectrometer at 70 eV. GC–MS analyses were carried out on a Hewlett–Packard gas chromatograph (5890 series II; capillary column SPB-1 (Supelco)) interfaced to a mass spectrometric detector (5791 A). Infrared spectra were recorded on a Nicolet Avatar FT-IR spectrometer in the range 400–4000 cm^{-1}. Melting points were measured on a Koffler block and were uncorrected.

3.2. Preparation of 1-iso-propyl-2,3,4-trimethyl-cyclopenta-1,3-diene (**1**)

A solution of *iso*-propylchloride (23.5 g, 300 mmol) in diethyl ether (80 ml) was added drop-wise to a mixture of magnesium turnings (9.4 g, 400 mmol) with a small amount (ca. 0.1 g) of iodine in diethyl ether (50 ml) at a rate maintaining a mild reflux. After the reaction ceased the mixture was refluxed for additional 30 min. After cooling, a mixture of trimethylcyclopentenones (24.8 g, 200 mmol) in 50 ml of diethyl ether was slowly added and the reaction mixture was refluxed for 2 h. Resulting grey-green mixture was poured onto crushed ice (ca. 50 g) and the product was extracted with diethyl ether (4×100 ml). Volume of combined organic phases was reduced to ca. 100 ml and a few crystals of iodine were added to induce dehydration of the obtained alcohol. The mixture was left standing overnight, while a water layer separated. The resulting brown mixture was washed subsequently with saturated aqueous sodium thiosulphate solution (2×40 ml), water (20 ml) and dried over sodium sulphate. The solvent was removed on a rotary evaporator and the crude product was distilled at reduced pressure (11 mmHg). The product distilled at 72–74 °C as a colorless liquid. Yield: 10.7 g (36%).

^{1}H NMR (C_6D_6): 1.03 (d, $^3J_{HH} = 6.9$ Hz, 6H, CHMe_2); 1.71, 1.74, 1.84 ($3 \times$ s, 3×3H, C_5Me_3); 2.59 (br s, 2H, Me_3(*i*-Pr)C_5H_2); 2.82 (septuplet, $^3J_{HH} = 6.9$ Hz, 1H, C*H*Me$_2$). ^{13}C {^{1}H} (C_6D_6): 11.23, 11.26, 13.58 (C_5Me_3); 23.60 (CHMe_2); 27.59 (*C*HMe$_2$); 42.28 (*C*H$_2$, Me_3(*i*-Pr)C_5H_2); 131.61, 134.67, 136.06, 142.66 (C_q, Me_3(*i*-Pr)C_5H_2). GC–MS, *m*/*z* (relative abundance): 151 (8), 150 ($M^{+\cdot}$; 41), 136 (17), 135 ([M – Me]$^+$; 100), 120 (13), 119 (28), 108 (7), 107 (16), 105 (14), 93 (19), 91 (26), 79 (9), 77 (11), 65 (6), 41 (7), 39 (7). IR (neat, cm^{-1}): 2959 (vs), 2924 (s), 2869 (s), 1656 (vw), 1625 (vw), 1444 (m), 1382 (m), 1360 (w), 1309 (w), 1235 (w), 1171 (w), 1123 (w), 1088 (w), 1050 (w), 853 (w), 693 (w).

3.3. Preparation of 1-sec-butyl-2,3,4-trimethyl-cyclopenta-1,3-diene (**2**)

The above-described procedure was used. A Grignard reagent prepared from *sec*-butylchloride (22.2 g, 240 mmol) was reacted with a mixture of trimethylcyclopentenones (19.8 g, 160 mmol) to give a magnesium alcoholate which afforded after hydrolysis, iodine-catalyzed dehydration and distillation at 71–74 °C/7 mmHg compound **2** as a colorless liquid. Yield: 10.0 g (38%).

^{1}H NMR (C_6D_6): 0.79 (t, $^3J_{HH} = 7.5$ Hz, 3H, CH_2Me); 1.02 (d, $^3J_{HH} = 7.0$ Hz, 3H, CH*Me*); 1.28–1.45 (m, 2H, CH_2Me); 1.71, 1.74, 1.84 ($3 \times$ s, 3×3H, C_5Me_3); 2.50–2.55 (m, 1H, C*H*Me); 2.56–2.60 (m, 2H, Me_3(*s*-Bu)C_5H_2). ^{13}C {^{1}H} (C_6D_6): 11.39, 11.55, 13.69 (C_5Me_3); 12.96 (CH_2Me); 21.83 (CH*Me*); 31.44 (*C*$_2$Me); 34.99 (*C*HMe); 42.39 (*C*H$_2$, Me_3(*s*-Bu)C_5H_2); 131.94, 136.06, 136.14, 141.39 (C_q, Me_3(*s*-Bu)C_5H_2). GC–MS, *m*/*z* (relative abundance): 165 (6), 164 ($M^{+\cdot}$; 32), 149 ([M – Me]$^+$; 14), 136 (22), 135 ([M – Et]$^+$; 100), 121 (12), 120 (16), 119 (34), 107 (20), 105 (28), 93 (24), 91 (39), 79 (16), 77 (21), 65 (12), 41 (24). IR (neat, cm^{-1}): 2960 (vs), 2917 (vs), 2872 (vs), 1655 (vw), 1453 (s), 1377 (s), 1332 (vw), 1311 (w), 1286 (vw), 1228 (vw), 1168 (m), 1123 (w), 1089 (w), 1057 (vw), 988 (w), 952 (vw), 859 (vw), 693 (vw), 513 (w).

3.4. Preparation of 1-cyclohexyl-2,3,4-trimethyl-cyclopenta-1,3-diene (**3**)

The above-described procedure was used. A Grignard reagent prepared from cyclohexylbromide (21.5 g, 130 mmol) was reacted with a mixture of trimethylcyclopentenones (14.9 g, 120 mmol) to give a magnesium alcoholate which afforded after hydrolysis, iodine-catalyzed dehydration, and distillation at 75–78 °C/2 mmHg compound **3** as a slightly yellow liquid. Yield: 10.4 g (46%).

^{1}H NMR (C_6D_6): 1.15–1.32 (m, 6H, β-CH_2 and γ-CH_2, cyclohexyl); 1.62–1.79 (partially overlapped by a stronger signal of methyl protons, m, 4H, α-CH_2, cyclohexyl); 1.73, 1.77, 1.85 ($3 \times$ s, 3×3H, C_5Me_3); 2.50 (tt, $^3J_{HH} = 11.4$ Hz, $^4J_{HH} = 3.3$ Hz, 1H, C*H*, cyclohexyl); 2.62 (br s, 2H, Me_3(cyclohexyl)C_5H_2). ^{13}C {^{1}H} (C_6D_6): 10.87, 10.91, 13.34 (C_5Me_3); 23.58, 26.97, 33.91 (*C*H$_2$, cyclohexyl); 37.85 (*C*H, cyclohexyl); 43.13 (*C*H$_2$, Me_3(cyclohexyl)C_5H_2); 131.55, 134.58, 135.84, 141.91 (C_q, Me_3(cyclohexyl)C_5H_2). GC–MS, *m*/*z* (relative abundance): 190 ($M^{+\cdot}$; 26), 175 ([M – Me]$^+$; 10), 147 (29), 134 (13), 133 (13), 121 (9), 119 (26), 109 (9), 108 (37), 107 (14), 105 (16), 93 (26), 91 (32), 79 (12), 77 (15), 65 (9), 55 (22), 53 (11), 41 (100), 39 (32). IR (neat, cm^{-1}): 2923 (vs), 2852 (vs), 1653 (vw), 1448 (s), 1380 (s), 1333 (w), 1299 (vw), 1262 (w), 1243 (vw), 1162 (m), 1122 (w), 1085 (m), 1043 (w), 1026 (w), 990 (w), 949 (w), 889 (m), 850 (w), 781 (vw), 692 (vw), 510 (m).

3.5. Preparation of 1-tert-butyl-2,3,4-trimethyl-cyclopenta-1,3-diene (**4**)

A slightly modified procedure was used. A pentane solution of *t*-BuLi (55 ml, 1.7 M, 93 mmol) was reacted with a mixture of trimethylcyclopentenones (10.5 g, 85 mmol) in pentane (100 ml) to give after hydrolysis, iodine-catalyzed dehydration and distillation at 80–82 °C/5 mmHg compound **4** as a colorless liquid. Yield: 6.5 g (47%).

^{1}H NMR (C_6D_6): 1.19 (s, 9H, CMe_3); 1.68, 1.82, 1.88 ($3 \times$ s, 3×3H, C_5Me_3); 2.59 (br s, 2H, Me_3(*t*-Bu)C_5H_2). ^{13}C {^{1}H} (C_6D_6): 11.05, 13.14, 13.26 (C_5Me_3); 30.75

(CMe_3); 32.93 (CMe_3); 45.51 (CH_2, $Me_3(t\text{-Bu})C_5H_2$); 130.78, 134.34, 136.71, 143.82 (C_q, $Me_3(t\text{-Bu})C_5H_2$). GC–MS, *m*/*z* (relative abundance): 165 (6), 164 ($M^{+\cdot}$; 37), 150 (13), 149 ($[M - Me]^+$; 100), 134 (22), 133 (21), 119 (15), 108 (57), 93 (54), 91 (37), 79 (13), 77 (17), 57 (22), 41 (17). IR (neat, cm^{-1}): 2962 (vs), 2909 (vs), 2868 (vs), 1653 (m), 1624 (w), 1447 (s), 1382 (s), 1326 (w), 1294 (vw), 1253 (m), 1213 (w), 1188 (m), 1124 (w), 1081 (w), 1044 (w), 1014 (w), 856 (w), 793 (w), 748 (vw), 696 (vw), 510 (w).

3.6. Preparation of **5**

To a stirred solution of **1** (6.2 g, 41 mmol) in THF (350 ml) was slowly dropped butyllithium solution in hexane (21 ml, 2.5 M, 52 mmol). A voluminous white precipitate formed after several minutes. After stirring for additional 5 h, chlorotrimethylsilane (7.0 ml, 57 mmol) was added in one portion, and the mixture was then stirred overnight. Volatiles were removed at a reduced pressure, and the residue was fractionally distilled in vacuum. The core fraction distilled at 60–61 °C (0.5 mmHg) as a slightly yellow liquid (a mixture of isomers). Yield: 3.3 g (37%).

GC–MS, *m*/*z* (relative abundance): 223 (10), 222 ($M^{+\cdot}$; 46), 208 (6), 207 ($[M - Me]^+$; 31), 149 (12), 148 (42), 147 (6), 134 (10), 133 (46), 119 (16), 105 (8), 91 (9), 75 (5), 74 (8), 73 ($[SiMe_3]^+$; 100), 59 (6), 45 (11). IR (neat, cm^{-1}): 2958 (vs), 2927 (s), 2867 (s), 1658 (vw), 1614 (vw), 1547 (vw), 1513 (vw), 1453 (m), 1404 (w), 1381 (w), 1361 (w), 1260 (m), 1248 (vs), 1147 (w), 1119 (w), 1069 (w), 1027 (w), 983 (w), 837 (vs), 798 (m), 751 (m), 684 (m), 624 (m).

3.6.1. Isomer **5a**: (2-iso-propyl-3,4,5-trimethylcyclopenta-2,4-dien-1-yl)trimethylsilane

^{1}H NMR (toluene-d_8, 233 K): 0.04 (s, 9H, SiMe_3); 1.25, 1.36 (2 × d, 2 × $^3J_{HH}$ = 7.0 Hz, 2 × 3H, CHMe_2); 1.81, 1.92, 1.98 (3 × s, 3 × 3H, C_5Me_3); 2.55–2.65 (m, 1H, C*H*Me_2); 2.71 (br s, 1H, Me_3(*i*-Pr)($SiMe_3$)C_5H). ^{13}C {^{1}H} (toluene-d_8 233 K): −1.04 (SiMe_3); 11.62, 13.28, 15.25 (C_5Me_3); 22.20, 23.35 (CHMe_2); 29.76 (*C*HMe_2); 55.49 (*C*H, Me_3(*i*-Pr)($SiMe_3$)C_5H); 132.24, 133.52, 136.96, 143.54 (C_q, Me_3(*i*-Pr)($SiMe_3$)C_5H).

3.6.2. Isomer **5b**: (4-iso-propyl-1,2,3-trimethylcyclopenta-2,4-dien-1-yl)trimethylsilane

^{1}H NMR (toluene-d_8, 233 K): −0.04 (s, 9H, SiMe_3); 1.16, 1.25 (2 × d, 2 × $^3J_{HH}$ = 7.0 Hz, 2 × 3H, CHMe_2); 1.26 (s, 3H, C($SiMe_3$)*Me*); 1.83, 1.87 (2 × s, 2 × 3H, 2 × =C*Me*); 2.55–2.65 (m, 1H, C*H*Me_2); 5.90 (s, 1H, =C*H*). ^{13}C {^{1}H} (toluene-d_8 233 K): −2.66 (SiMe_3); 11.30, 12.40, 14.48 (C_5Me_3); 22.57, 24.02 (CHMe_2); 27.62 (*C*HMe_2); 51.23 (C_{ipso}); 127.94 (=*C*H); 137.57, 142.54, 151.93 (C_q, Me_3(*i*-Pr)($SiMe_3$)C_5H).

3.7. Preparation of **6**

A hexane solution of *n*-butyllithium (17.5 ml, 1.6 M, 28 mmol) was slowly dropped at 0 °C to a solution of **1** (4.17 g, 28 mmol) in diethyl ether (80 ml). The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting white precipitate was filtered, washed three times with 20 ml of diethyl ether and suspended in THF (60 ml). The THF suspension was transferred to an excess of dichlorodimethylsilane (6.1 g, 56 mmol) in the same solvent previously cooled to −78 °C. The reaction mixture was allowed to warm to room temperature and then stirred for additional 14 h. Volatiles were removed in vacuum, and an oily residue was dissolved in pentane (30 ml), and filtered to remove LiCl. The pentane was evaporated in vacuum to leave compound **6** (a mixture of isomers) as a slightly yellow liquid. Yield: 5.57 g (82%).

EI-MS, *m*/*z* (relative abundance): 244 (29), 243 (16), 242 ($M^{+\cdot}$; 80), 229 (42), 228 (21), 227 ($[M - Me]^+$; 100), 207 ($[M - Cl]^+$;13), 149 ($[M - SiMe_2Cl]^+$; 48), 135 (15), 134 (18), 133 (80), 119 (27), 105 (14), 95 (31), 93 ($[SiMe_2Cl]^+$; 94), 91 (20), 79 (7), 77 (8). IR (neat, cm^{-1}): 2961 (vs), 2927 (s), 2869 (s), 1615 (vw), 1544 (vw), 1456 (m), 1403 (w), 1383 (m), 1362 (w), 1316 (vw), 1252 (vs), 1200 (vw), 1171 (vw), 1147 (w), 1122 (w), 1072 (w), 1030 (w), 988 (w), 959 (vw), 922 (vw), 843 (vs), 811 (vs), 787 (vs), 726 (vw), 687 (w), 665 (m), 584 (vw), 544 (w), 499 (m), 471 (s), 423 (vw).

3.7.1. Isomer **6a**: chloro(2-iso-propyl-3,4,5-trimethylcyclopenta-2,4-dien-1-yl)dimethylsilane

^{1}H NMR (toluene-d_8, 233 K): 0.20, 0.21 (2 × s, 2 × 3H, SiMe_2Cl); 1.20, 1.32 (2 × d, 2 × $^3J_{HH}$ = 7.0 Hz, 2 × 3H, CHMe_2); 1.71, 1.88, 1.93 (3 × s, 3 × 3H, C_5Me_3); 2.77 (septuplet, $^3J_{HH}$ = 7.0 Hz, 1H, C*H*Me_2); 2.93 (br s, 1H, Me_3(*i*-Pr)($SiMe_2Cl$)C_5H).

3.7.2. Isomer **6b**: chloro(4-iso-propyl-1,2,3-trimethylcyclopenta-2,4-dien-1-yl)dimethylsilane

^{1}H NMR (toluene-d_8, 233 K): 0.03, 0.24 (2 × s, 2 × 3H, SiMe_2Cl); 1.05, 1.16 (2 × d, 2 × $^3J_{HH}$ = 7.0 Hz, 2 × 3H, CHMe_2); 1.37 (s, 3H, C($SiMe_2Cl$)*Me*); 1.78, 1.91 (2 × s, 2 × 3H, 2 × =C*Me*); 2.50 (septuplet, $^3J_{HH}$ = 7.0 Hz, 1H, C*H*Me_2); 5.81 (s, 1H, =C*H*).

3.8. Preparation of **7**

The above procedure for obtaining **6** was used. The lithium salt prepared from **2** (5.57 g, 34 mmol) and *n*-butyllithium hexane solution (21.3 ml, 1.6 M, 34 mmol) was reacted with an excess of dichlorodimethylsilane affording **7** as a yellow liquid (a mixture of isomers). Yield: 5.70 g (66%).

EI-MS, *m*/*z* (relative abundance): 258 (11), 257 (6), 256 ($M^{+\cdot}$; 30), 229 (16), 228 (8), 227 ($[M - Et]^+$; 44),

163 ([M − $SiMe_2Cl$]$^+$; 9), 135 (17), 134 (19), 133 (26), 119 (30), 105 (14), 95 (60), 94 (14), 93 ([$SiMe_2Cl$]$^+$; 100), 91 (16), 79 (11), 78 (13), 77 (11), 67 (14), 65 (40), 63 (25). IR (neat, cm^{-1}): 2962 (vs), 2928 (s), 2872 (s), 1615 (vw), 1542 (vw), 1455 (m), 1377 (m), 1252 (vs), 1196 (vw), 1145 (w), 1118 (w), 1074 (w), 1025 (w), 989 (m), 961 (w), 843 (vs), 812 (vs), 787 (vs), 666 (m), 544 (w), 499 (m), 474 (s).

*3.8.1. Isomer **7a**: (2-(sec-butyl)-3,4,5-trimethylcyclopenta-2,4-dien-1-yl)chlorodimethylsilane*

^{1}H NMR (toluene-d_8, 233 K): 0.14, 0.19 (2 × s, 2 × 3H, SiMe_2Cl); 0.78 (t, $^3J_{HH}$ = 6.5 Hz, 3H, CH_2Me); 0.99 (d, $^3J_{HH}$ = 6.0 Hz, 3H, CHMe); 1.20–1.55 (m, 2H, CH_2Me); 1.67, 1.83, 1.90 (3 × s, 3 × 3H, C_5Me_3); 2.38–2.48 (m, 1H, CHMe); 2.80 (s, 1H, Me_3(*s*-Bu)($SiMe_2Cl$)C_5H).

*3.8.2. Isomer **7b**: (4-(sec-butyl)-1,2,3-trimethylcyclopenta-2,4-dien-1-yl)chlorodimethylsilane*

^{1}H NMR (toluene-d_8, 233 K): −0.01, 0.21 (2 × s, 2 × 3H, SiMe_2Cl); 0.88 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_2Me); 1.08 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CHMe); 1.20–1.55 (m, 2H, CH_2Me); 1.31 (s, 3H, C($SiMe_2Cl$)Me); 1.73, 1.85 (2 × s, 2 × 3H, 2 × =CMe); 2.21–2.30 (m, 1H, CHMe); 5.80 (s, 1H, =CH).

*3.9. Preparation of **8***

The above-described procedure was used. The lithium salt prepared from **3** (3.30 g, 17.4 mmol) and *n*-butyllithium hexane solution (10.9 ml, 1.6 M, 17.4 mmol) was reacted with excess dichlorodimethylsilane to give **8** (a mixture of isomers) as a yellow liquid. Yield: 3.40 g (69%).

EI-MS, *m*/*z* (relative abundance): 284 (18), 283 (14), 282 ($M^{+\cdot}$; 55), 239 (7), 200 (13), 189 ([M − $SiMe_2Cl$]$^+$; 26), 147 (6), 145 (9), 133 (21), 119 (10), 105 (14), 95 (39), 94 (10), 93 ([$SiMe_2Cl$]$^+$; 98), 91 (19), 65 (22), 55 (18), 43 (100), 42 (71), 41 (91), 40 (14), 39 (60). IR (neat, cm^{-1}): 2919 (vs), 2850 (vs), 1614 (w), 1541 (vw), 1448 (s), 1403 (m), 1385 (m), 1344 (w), 1251 (vs), 1223 (w), 1190 (vw), 1179 (vw), 1147 (m), 1124 (m), 1078 (m), 1027 (m), 993 (s), 959 (w), 929 (w), 889 (s), 846 (vs), 810 (vs), 787 (vs), 754 (m), 671 (s), 638 (w), 535 (m), 502 (s), 470 (s), 432 (w).

*3.9.1. Isomer **8a**: chloro(2-cyclohexyl-3,4,5-trimethylcyclopenta-2,4-dien-1-yl)dimethylsilane*

^{1}H NMR (toluene-d_8, 233 K): 0.15, 0.18 (2 × s, 2 × 3H, SiMe_2Cl); 0.98–1.20 (m, 6H, β-CH_2 and γ-CH_2, cyclohexyl); 1.66–1.78 (m, α-CH_2, cyclohexyl); 1.67, 1.81, 1.88 (3 × s, 3 × 3H, C_5Me_3); 2.25–2.35 (m, 1H, CH, cyclohexyl); 2.87 (s, 1H, Me_3(cyclohexyl)($SiMe_2Cl$)C_5H).

*3.9.2. Isomer **8b**: chloro(4-cyclohexyl-1,2,3-trimethylcyclopenta-2,4-dien-1-yl)dimethylsilane*

^{1}H NMR (toluene-d_8, 233 K): −0.01, 0.21 (2 × s, 2 × 3H, SiMe_2Cl); 1.10–1.31 (m, 6H, β-CH_2 and γ-CH_2, cyclohexyl); 1.33 (s, 3H, C($SiMe_2Cl$)Me); 1.66–1.78 (m, α-CH_2, cyclohexyl); 1.75, 1.86 (2 × s, 2 × 3H, 2 × =CMe); 2.08–2.18 (m, 1H, CH, cyclohexyl); 5.74 (s, 1H, =CH).

*3.10. Preparation of **9***

The above procedure for obtaining **6** was used. The lithium salt prepared from **4** (2.30 g, 14 mmol) and *n*-butyllithium hexane solution (8.8 ml, 1.6 M, 14 mmol) was reacted with an excess of chlorotrimethylsilane yielding **9** as a yellow liquid. Yield: 2.40 g (73%).

EI-MS, *m*/*z* (relative abundance): 237 (11), 236 ($M^{+\cdot}$; 44), 222 (11), 221 ([M − Me]$^+$; 50), 180 (10), 163 ([M − $SiMe_3$]$^+$; 11), 162 ([M − $SiMe_3H$]$^+$; 35), 148 (21), 147 (97), 133 (17), 119 (8), 105 (13), 91 (15), 77 (8), 75 (20), 74 (33), 73 ([$SiMe_3$]$^+$; 100), 59 (14), 45 (32), 43 (17), 41 (21). IR (neat, cm^{-1}): 2954 (vs), 2926 (s), 2902 (s), 2867 (s), 1602 (vw), 1477 (w), 1456 (w), 1382 (w), 1360 (m), 1283 (vw), 1259 (m), 1247 (vs), 1213 (w), 1200 (w), 1155 (w), 1111 (vw), 1070 (w), 1038 (vw), 1009 (w), 839 (vs), 801 (m), 751 (m), 687 (m), 622 (w), 550 (vw), 416 (w).

*3.10.1. Isomer **9b**: (4-tert-butyl-1,2,3-trimethylcyclopenta-2,4-dien-1-yl)trimethylsilane*

^{1}H NMR (C_6D_6): 0.09 (s, 9H, SiMe_3); 1.22 (s, 3H, C($SiMe_3$)Me); 1.28 (s, 9H, CMe_3); 1.76, 2.00 (2 × s, 2 × 3H, 2 × =CMe); 5.90 (s, 1H, =CH). ^{13}C {^{1}H} (C_6D_6): −2.65 (SiMe_3); 12.16, 13.93 (2 × =CMe); 14.18 (C($SiMe_3$)Me); 30.44 (CMe_3); 32.99 (CMe$_3$); 45.84 (C($SiMe_3$)Me); 129.76 (br, =CH); 133.33, 144.01, 153.47 (C_q).

*3.11. Preparation of 5-iso-propyl-1,6,7-trimethyl-7-trimethylsilyl-bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester (**10**)*

At 140 °C: To a xylene solution (20 ml) of preequilibrated (by reflux for 20 min) silanes **5** (636.0 mg, 2.86 mmol) DMAD (407.0 mg, 2.86 mmol) was added by syringe. The reaction mixture was refluxed with stirring for additional 2 h, and the main part of the solvent was evaporated at a reduced pressure. An orange oily residue was diluted by minimum amount of hexane (5 ml), and the solution was cooled to −78 °C. A brownish precipitate was separated, washed by cold hexane (3 × 2 ml), and dried in vacuum. Yield: 810.0 mg (78%).

At 25 °C: The mixture of isomers **5** (320.0 mg, 1.44 mmol) was diluted by dichloromethane (15 ml), and DMAD (205.0 mg, 1.44 mmol) was added. The reaction mixture was stirred in the dark for 30 h. A ^{1}H NMR

spectroscopy of resulting yellow solution revealed the same product as in the above-described case.

M.p. 77–79 °C. ^{1}H NMR (C_6D_6): −0.07 (s, 9H, Si*Me*$_3$); 0.83, 1.05 (2 × d, 2 × $^3J_{HH}$ = 7.0 Hz, 2 × 3H, CH*Me*$_2$); 1.11 (s, 3H, C(7)*Me*); 1.20 (s, 3H, C(1)*Me*); 1.64 (s, 3H, C(6)*Me*); 2.57 (septuplet, 1H, $^3J_{HH}$ = 7.0 Hz, C*H*Me$_2$); 3.39, 3.49 (2 × s, 2 × 3H, COO*Me*); 3.67 (s, 1H, C(4)*H*). ^{13}C {^{1}H} (C_6D_6): 0.10 (Si*Me*$_3$); 10.97 (C(1)*Me*); 11.78 (C(6)*Me*); 16.69 (C(7)*Me*); 20.58, 20.85 (CH*Me*$_2$); 27.64 (*C*HMe$_2$); 51.25, 51.34 (2 × COO*Me*); 58.76 (*C*(4)H); 69.81, 78.67 (C_q(1) and C_q(7)); 145.94 (C_q(6)); 148.34 (C_q(5)); 152.77, 158.62 (C_q(2) and C_q(3)); 164.98, 167.56 (2 × *C*OOMe). EI-MS, *m*/*z* (relative abundance): 365 (3), 364 ($M^{+\cdot}$; 10), 349 ([M − Me]$^+$; 13), 333 ([M − OMe]$^+$; 5), 317 (6), 305 ([M − COOMe]$^+$; 9), 291 ([M − SiMe$_3$]$^+$; 16), 290 (12), 289 (6), 275 (10), 260 (11), 259 (23), 258 (9), 245 (12), 233 (10), 232 (17), 231 (34), 229 (12), 222 ([Me$_3$(*i*-Pr)SiMe$_3$C$_5$H]$^+$; 25), 217 (29), 215 (12), 207 (12), 201 (24), 199 (12), 178 (14), 173 (14), 171 (14), 157 (11), 149 (8), 148 (30), 134 (10), 133 (14), 119 (9), 91 (11), 89 (18), 75 (11), 74 (16), 73 ([SiMe$_3$]$^+$; 100), 59 ([COOMe]$^+$; 25), 45 (27), 41 (10). IR (KBr, cm^{-1}): 2953 (s), 2933 (m), 2901 (m), 2872 (m), 1727 (s), 1708 (vs), 1624 (s), 1468 (m), 1456 (m), 1429 (s), 1404 (vw), 1383 (m), 1373 (w), 1311 (s), 1277 (vs), 1249 (vs), 1209 (s), 1170 (w), 1142 (m), 1106 (m), 1071 (w), 1042 (s), 991 (w), 969 (vw), 934 (w), 905 (vw), 866 (s), 833 (s), 803 (w), 793 (vw), 777 (w), 763 (w), 752 (m), 684 (w), 631 (vw), 604 (vw), 560 (vw).

3.12. Preparation of 1-iso-propyl-4,5,6-trimethyl-7-trimethylsilyl-bicyclo[2.2.1]hept-5-ene-2, 2,3,3-tetracarbonitrile (*11*)

The mixture of isomers **5** (473.5 mg, 2.13 mmol) was diluted by dichloromethane (40 ml), and TCNE (273.0 mg, 2.13 mmol) was added. The reaction mixture was stirred for 30 h at 25 °C, concentrated to ca. 5 ml, and layered by hexane (30 ml). Light brown crystals separated after several hours. Analytically pure slightly yellowish crystals of **11** were obtained by double recrystallization from diethyl ether (611.5 mg, 82%).

M.p. 122 °C (dec.). ^{1}H NMR (C_6D_6): −0.40 (s, 9H, Si*Me*$_3$); 1.03, 1.21 (2 × d, 2 × $^3J_{HH}$ = 7.5 Hz, 2 × 3H, CH*Me*$_2$); 1.22 (s, 3H, C(4)*Me*); 1.31, 1.45 (2 × q, $^5J_{HH}$ = 1.0 Hz, 2 × 3H, C(5)*Me* and C(6)*Me*); 1.51 (s, 1H, C(7)*H*); 1.84 (septuplet, $^3J_{HH}$ = 7.5 Hz, 1H, C*H*Me$_2$). ^{13}C {^{1}H} (C_6D_6): 0.64 (Si*Me*$_3$); 11.29, 12.86 (C(5)*Me* and C(6)*Me*); 15.23 (C(4)*Me*); 20.16, 20.57 (CH*Me*$_2$); 29.46 (*C*HMe$_2$); 49.07, 66.03 (C_q(1) and C_q(4)); 51.18, 52.08 (C_q(2) and C_q(3)); 55.98 (*C*(7)H); 111.71, 112.89, 113.14, 113.83 (4 × *C*N); 141.76, 143.08 ((C_q(5) and C_q(6)). EI-MS, *m*/*z* (relative abundance): 350 ($M^{+\cdot}$; not observed), 223 (7), 222 ([Me$_3$(*i*-Pr)SiMe$_3$C$_5$H]$^+$; 30), 208 (6), 207 (24), 149 (11), 148 (48), 147 (5), 134 (9), 133 (44), 128 ([(CN)$_2$C=C(CN)$_2$]$^+$; 21), 119 (12), 105 (8), 103 (6), 91 (11), 77 (7), 76 (24), 75 (12), 74 (25), 73 ([SiMe$_3$]$^+$; 100), 59 (16), 45 (30), 41 (12). IR (KBr, cm^{-1}): 3000 (m), 2981 (s), 2950 (s), 2926 (m), 2900 (m), 2856 (m), 2245 (vw), 1651 (vw), 1471 (m), 1455 (m), 1395 (m), 1385 (m), 1344 (vw), 1300 (vw), 1256 (vs), 1228 (m), 1181 (w), 1130 (vw), 1101 (vw), 1078 (w), 1059 (w), 1041 (w), 1000 (vw), 943 (vw), 918 (w), 860 (vs), 844 (vs), 789 (vw), 768 (m), 753 (m), 688 (w), 669 (vw), 655 (vw), 622 (vw), 439 (vw).

3.13. Evaluation of activation parameters from variable temperature NMR spectra

^{1}H NMR spectra were acquired under conditions of slow and moderate exchange. The resultant band-shape of allylic and vinylic protons was then iteratively simulated and fitted by WINDNMR-Pro program [27] as two spin (for **6** and **8**), or three spin (for **5** and **7**) system.

Activation parameters were obtained from modified Eyring equation: $\ln(k/T) = -\Delta H^{\ddagger}/RT + (23.76 + \Delta S^{\ddagger}/R)$ using least-squares fit to linear plot $\ln(k/T)$ versus $1/T$ [28].

3.14. X-ray crystallography

The slightly yellowish crystals of **11** were grown from diethyl ether solution. All diffraction data were collected

Table 3
Crystallographic data, data collection and structure refinement data for compound **11**

Chemical formula	$C_{20}H_{26}N_4Si$
Molecular weight	350.54
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
T (K)	150(2)
a (Å)	8.9573(2)
b (Å)	18.0626(4)
c (Å)	12.6512(3)
α (°)	90.000
β (°)	94.2644(14)
γ (°)	90.000
Z	4
Crystal size (mm^3)	0.40 × 0.30 × 0.20
D_{calc} (g cm^{-3})	1.141
μ (Mo Kα) (mm^{-1})	0.124
F(000)	752
θ range (°)	3.21–29.13
hkl range	−12/12, −24/24, −17/17
Unique diffractions	5481
Observed diffractions	4577
Parameters	234
R, wR^a[$I > \sigma I$)]	0.0536, 0.1401
R, wR^a (all data)	0.0655, 0.1478
S^b	1.057
$\Delta\rho_{max,\ min}$ (e Å^{-3})	0.521, −0.546

[a] $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$.
[b] $S = [\sum(w(F_o^2 - F_c^2)^2) / (N_{diffrs} - N_{params})]^{1/2}$.

on a Nonius KappaCCD diffractometer at 150 K. The structures were solved by direct methods (SIR-97 [29]) and refined by weighted full-matrix least-squares on F^2 (SHELXL-97 [30]). All non-hydrogen atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms were included in calculated position. Relevant crystallographic data are collected in Table 3.

4. Supplementary material

Crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (**11**: 241844). Copies of the data can be obtained free of charge upon application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgement

J.P. thanks French Government (Grant for doctorate No. 20006842) for financial support.

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