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Synthesis, structure and fluxional behavior of di-t-butylcyclopentadienyl compounds of Group IV elements

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Abstract

The syntheses of di-t-butylcyclopentadienyltrimethylsilane, di-t-butylcyclopentadienyltrimethylstannane, di-t-butylcyclopentadienylmethyldichlorogermane, and di-t-butylcyclopentadienyltrichlorosilane are described. The influence of the Group IVB fragment on the structure and the dynamic behavior (sigmatropic rearrangements) is discussed on the basis of ^{1}H and ^{13}C NMR spectra.

Introduction

The fluxional behavior of σ-cyclopentadienyl derivatives of the Main-Group elements caused by sigmatropic rearrangements of hydrogen atoms or Main-Group fragments has attracted much interest [1–7]. Several review articles have considered the mechanism by which an atom migrates around a cyclopentadienyl ring [8–13].

The fluxional behavior of cyclopentadienyl compounds of Main-Group elements is influenced by three factors: (1) The nature of the Main-Group element itself, (2) the type of substituents on the Main-Group element, and (3) the type of substituents on the cyclopentadienyl ring. These factors influence the rates of the sigmatropic rearrangements and the proportion of allylic and vinylic isomers. The first two factors have been investigated in detail for compounds with elements of Main-Groups III, IV, and V; e.g. for $C_5H_5SiMe_3$ [14], $C_5H_5SiCl_3$ [15], $C_5H_5GeCl_3$, and $C_5H_5Ge(OMe)_3$ [16], $C_5H_5PF_2$ and $(C_5H_5)_2PF$ [17], $C_5H_5AlMe_2$ [18], $C_5H_5GaMe_2$ [19], and $C_5H_5Pb(C_6H_5)_3$ [20].

The third factor which affects the migration rate and the isomer ratio is related to the presence of substituents on the cyclopentadienyl ring. Two different situations must be considered: In the first, all five hydrogens on the cyclopentadienyl ring are substituted by other atoms or groups of atoms; examples of this class are penta-

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methylcyclopentadienyl compounds of the Main-Groups III, IV, and V, which have been investigated in detail [21–23]. In the second, only some of the hydrogen atoms on the cyclopentadienyl ring are substituted by other groups. In the case of Main-Group IV compounds of this type, several research groups have investigated methylcyclopentadienyl derivatives [24–27]. Kläui and Werner have studied the fluxional behavior of (triphenylmethyl)cyclopentadienyltrimethylsilane and -stannane [28]. Only few examples of methylcyclopentadienyl compounds of Main-Group V elements have been reported [17,29,30]. The fluxional behavior of poly-metallated cyclopentadienes (compounds of the type $C_5H_4El_2$, $C_5H_3El_3$, and $C_5H_2El_4$ with El = Main-Group fragment) has also been discussed in detail [31–37].

On the other hand, compounds of the type $C_5H_3R_2El$, where R is a non-migrating group, seem not to have been reported previously. This prompted us to synthesize di-t-butylcyclopentadienyl compounds of Group IV and to study their fluxional behavior.

Results and discussion

Di-t-butylcyclopentadienyltrimethylsilane (I), di-t-butylcyclopentadienyltrimethylstannane (II), di-t-butylcyclopentadienylmethyldichlorogermane (III), and di-t-butylcyclopentadienyltrichlorosilane (IV) were obtained in very good yields as distillable, air sensitive liquids by reaction of di-t-butylcyclopentadienyllithium $Li(Me_3C)_2C_5H_3$ with the corresponding chlorosilanes, -stannanes, and -germanes as shown:

$$(^tC_4H_9)_2C_5H_3Li + ElCl \xrightarrow[-LiCl]{} (^tC_4H_9)_2C_5H_3El$$

Compound	I	II	III	IV
El	$SiMe_3$	$SnMe_3$	$GeMeCl_2$	$SiCl_3$

The identities of the compounds I–IV were confirmed by their ^1H, ^{13}C, ^{119}Sn NMR and their MS data.

In cyclopentadienyl compounds of the type $C_5H_3R_2El$ (R non-migrating), two sigmatropic processes can be expected (Fig. 1): firstly, a non-degenerate 1,2-hydrogen shift corresponding to a 1,5-sigmatropic rearrangement, producing isomers with the element fragment in an allylic (**A**) or vinylic (**B–E**) position of the cyclopentadiene ring; second, a non-degenerate 1,2-element shift producing isomers with the element fragment in an allylic position (**A'–H**). The dynamic behavior in compounds I–IV, considering both 1,2-H and 1,2-El shifts, was investigated by variable temperature ^1H NMR studies. The ^1H NMR spectra were recorded at 300 MHz in $C_6H_5CH_3$-d_8 as solvent.

The ^1H NMR spectra of di-t-butylcyclopentadienyltrimethylsilane (I) were determined over the range -70 to $+105\,^\circ C$ (see Fig. 2). Chemical shifts at the various temperatures are listed in Table 1.

The spectrum at room temperature ($+20\,^\circ C$) shows only the signals for a trimethylsilyl group (0.04 ppm), two t-butyl groups (1.21 ppm), and one vinylic proton (6.46 ppm). The signals for the other remaining vinylic and the allylic proton cannot be observed, but they finally appear as an averaged broad signal at 4.55 ppm at higher temperatures ($105\,^\circ C$). On going from room temperature to lower temper-

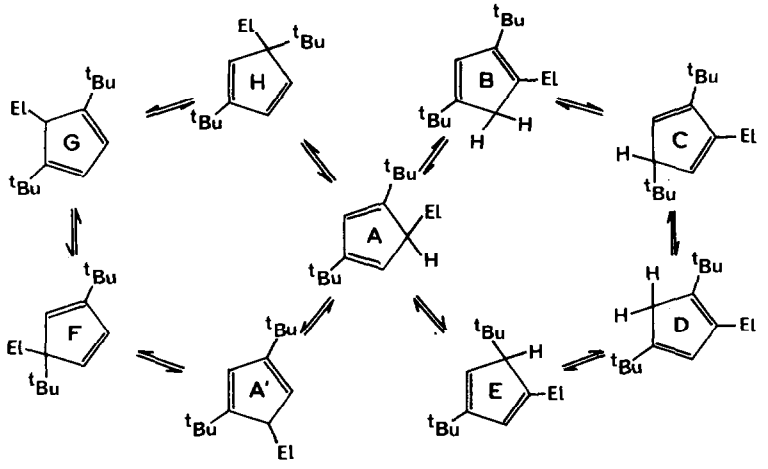


Fig. 1. Sigmatropic processes in $(Me_3C)_2C_5H_3El$ compounds.

atures a further change in the NMR spectrum takes place: at $-30\,^{\circ}C$, the signal for the two t-butyl groups broadens, while signals appear for a vinylic hydrogen atom at 5.93 ppm and an allylic hydrogen atom at 3.16 ppm. At $-50\,^{\circ}C$, two distinct signals for t-butyl groups appear, and those for the vinylic and allylic hydrogen atoms sharpen.

The temperature-dependent ^1H NMR spectra of I can be explained by assuming a degenerate 1,2-shift (1,5-sigmatropic rearrangement) of a trimethylsilyl group involving the isomers IA and IA′, as indicated in Fig. 3.

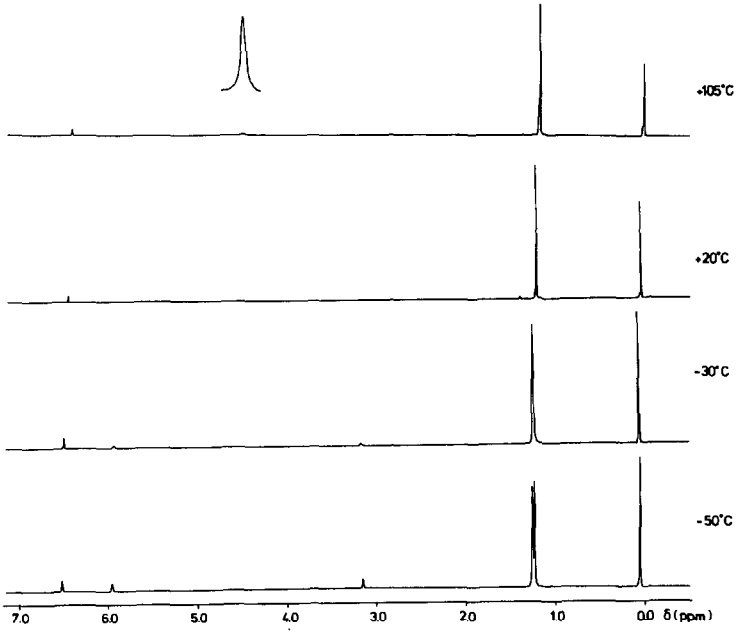


Fig. 2. ^1H NMR spectra of I in $C_6H_5CH_3$-d_8 at various temperatures

Table 1

Proton chemical shifts for I in $C_6H_5CH_3$-d_8 at various temperatures

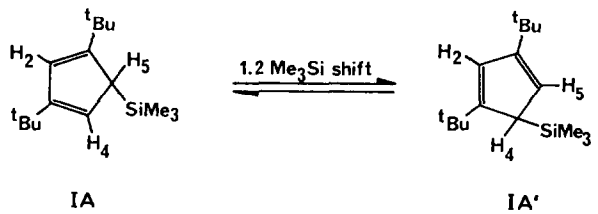
T (°C)	H^2	H^4	H^5	Me_3Si	Me_3C
+105	6.41	4.55 br		0.01	1.18
+80	6.42	4.55 br		0.01	1.18
+60	6.43	–	–	0.03	1.19
+40	6.45	–	–	0.03	1.20
+30	6.46	–	–	0.04	1.21
−30	6.50	5.93	3.16	0.05	1.23 br
−50	6.52	5.95	3.16	0.05	1.24, 1.26
−70	6.54	5.97	3.15	0.06	1.25, 1.28

At lower temperatures, this dynamic process is slow on the NMR time scale, so that the static structures are observed. Thus, different chemical shifts for the two vinylic protons (H^2 and H^4), for the allylic proton (H^5), and for the two non-equivalent t-butyl groups are expected. A rise in temperature finally leads to an averaged signal for the two t-butyl groups and for the hydrogen atoms H^4 and H^5, corresponding to faster degenerate Me_3Si shifts. The chemical shifts for the H^2 hydrogen and for the trimethylsilyl group remain unchanged. Thus, the DNMR spectra of I exclude other rearrangement processes.

The ^1H NMR spectrum of di-t-butylcyclopentadienyltrimethylstannane (II) is not affected by temperature over the range −70 to +80 °C except for small changes in the chemical shift values. In the spectrum measured at 30 °C (in $CDCl_3$), singlets are observed for the trimethylstannyl group (0.05 ppm) and the two t-butyl groups (1.20 ppm). The cyclopentadienyl ring protons give rise to a doublet at 4.86 and a triplet at 6.40 ppm (J 1 Hz) in the ratio 2/1. Furthermore, coupling of the tin isotopes $^{117,119}Sn$ to the protons of the $SnMe_3$ group and to the ring protons represented by the doublet is observed.

The temperature-independence of the ^1H NMR spectrum of compound II is consistent with a high fluxionality caused by degenerate 1,2 shifts of the trimethylstannyl group in the isomers IIA and IIA′ (see Fig. 1 and compare with Fig. 3). The estimated low activation energy for the dynamic process (E_a ~ 5 kcal/mol) is characteristic of cyclopentadienyltin compounds [8]. It is noteworthy that coupling of the tin isotopes is observed only to adjacent hydrogens, i.e. to the $SnMe_3$ group and the tin hydrogens H^4 and H^5.

The ^1H NMR spectrum of di-t-butylcyclopentadienylmethyldichlorogermane (III) was recorded over the range −70 to 70 °C. All the chemical shifts are listed in



IA IA′

Fig. 3. Degenerate 1,2 Me_3Si shift in compound I.

Table 2

Proton chemical shifts for III in $C_6H_5CH_3$-d_8 at various temperatures

T (°C)	H^2	H^4	H^5	$GeCH_3$	Me_3C
+70	6.44	4.91 br		0.58	1.12
+30	6.43	4.92 br		0.54	1.12
−30	6.40	–	–	0.45	1.10
−60	6.37	6.00 br	3.75 br	0.41	1.10 br
−70	6.37	6.02	3.77	0.41	1.03, 1.14

br = broad signal

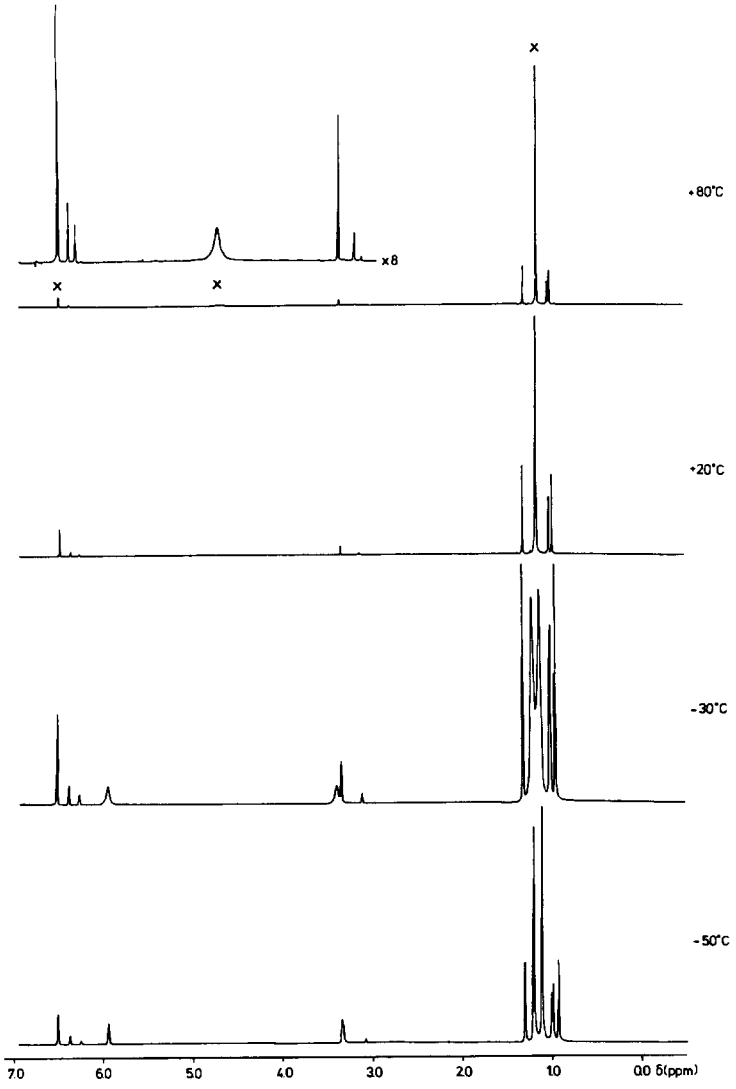


Fig. 4. ^1H NMR spectra of IV at various temperatures.

Table 2. The observation of the chemical shifts for the t-butyl groups and the two protons $H^{4,5}$ in the temperature dependent spectra indicates that this compound is similar to compound I in terms of its fluxional behavior. Both t-butyl groups give one common singlet over the range +70 to −30 °C, but this signal broadens gradually upon cooling the sample. Finally, at −70 °C, two signals appear for the two t-butyl groups. The two protons $H^{4,5}$ give rise to a broad peak in the range from +70 to +30 °C, when the temperature is lowered gradually from +30 to −70 °C the broad peak for $H^{4,5}$ completely disappears at −30 °C, and then gradually reappears at −60 °C in the form of two rather broad peaks at 6.00 and 3.75 ppm. At −70 °C, two sharp signals at 6.02 and 3.77 ppm are observed for H^4 and H^5. It can be concluded from the NMR data that compound III mainly exists in form of the isomer IIIA, which is interconvertible with the identical isomer IIIA′ by degenerate 1,2 shifts of the methyldichlorogermyl group.

The ^1H NMR spectra of di-t-butylcyclopentadienyltrichlorosilane (IV) were recorded in the range −70 to +105 °C; the spectra measured at −50, −30, +20, and +80 °C are depicted in Fig. 4.

According to the NMR spectra there are several isomers, the one with the highest abundance (about 68%, marked with × in Fig. 4) corresponding to those found for the compounds I, II, and III. The dynamic behavior of IV is consistent with a degenerate 1,2 trichlorosilyl shift which transforms isomer IVA into IVA′ (see Fig. 1 and compare with Fig. 3). The spectrum at −50 °C corresponds to the static structure IVA (or IVA′) and shows separate signals for the protons H^2 (6.51 ppm), H^4 (5.94 ppm), H^5 (3.35 ppm) and for the two t-butyl groups (1.20 and 1.12 ppm). The spectrum at −30 °C shows broadening of the signals for $H^{2,4}$, and separate signals for the two t-butyl groups are observed owing to faster shifts of the silyl group (IVA ⇌ IVA′). At higher temperatures, averaged signals arise for the t-butyl groups at 1.15 ppm (at 20 °C) and for $H^{2,4}$ at 4.71 ppm (at 80 °C).

From these studies it is not possible to identify the structures and dynamic processes for the other isomers detected in the DNMR spectra. Temperature-dependent signals are observed in the t-butyl region. Triplet-type structures in the region for vinylic and allylic hydrogens indicate the presence of isomers of type **B** or **D** and of the symmetrical isomer 1,4-di-t-butyl-5-trichlorosilyl-cyclopentadiene [2,4].

Conclusion

Di-t-butylcyclopentadienyl compounds of Group IV elements can be synthesized by the reaction of di-t-butylcyclopentadienyllithium with the corresponding element halide. These thermally stable species mainly exist in the form of the isomer with the Group IV element in the (allylic) 1-position and the two t-butyl groups in the 2- and 4-positions. Their dynamic behavior is characterized by degenerate 1,2-sigmatropic element shifts. As expected [8] the activation parameters depend on the nature of the Main-Group fragment.

Experimental

1,3-Di-t-butylcyclopentadiene was prepared as previously described [38,39]. All reactions were performed under dried, oxygen-free nitrogen using Schlenk-type flasks. Solvents and reagents were dried and purified by standard methods.

NMR spectra were recorded on a Bruker AM 300 spectrometer: ^{1}H (300 MHz), $^{13}C\{^{1}H\}$ (75 MHz), $^{29}Si\{^{1}H\}$ (59.6 MHz), $^{119}Sn\{^{1}H\}$ (111.9 MHz); the spectra were recorded in $CDCl_3$ and in $C_6H_5CH_3$-d_8 for variable temperature with benzene as an internal reference; shifts (δ) are reported in ppm. Mass spectra were obtained with a Varian 311 A spectrometer instrument (70 eV, 300 μA emission); only important characteristic ions are listed. Elemental analyses were performed by "Mikroanalytisches Laboratorium Beller" (Göttingen) and the Analytical Laboratory of the Universität Bielefeld.

Di-t-butylcyclopentadienyltrimethylsilane (I)

A 1.57 *M* solution of n-BuLi in hexane (40 mmol) was added dropwise to a mixture of 1,3-di-t-butylcyclopentadiene (7.12 g, 40 mmol) in 80 ml of THF at ice temperature. The mixture was allowed to warm to room temperature and stirred for 3 h, then cooled again in an ice bath, and 6.52 g (60 mmol) of $(CH_3)_3SiCl$ was added. The mixture was stirred at room temperature overnight, then the solvent was removed in vacuo and 40 ml of petroleum ether were added. The precipitated LiCl was filtered off, the solvent was removed, and the residue was distilled in vacuo to give di-t-butylcyclopentadienyltrimethylsilane, 9.0 g (90%); b.p. 50–52°C at 0.01 torr. ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H, Me_3Si), 1.19 (s, 18H, Me_3C), 4.55 (br, 2H, $H^{4,5}$), 6.42 (s, 1H, H^{2}) ppm. ^{13}C NMR ($CDCl_3$): δ −0.08 (Me_3Si), 31.13 (CMe_3), 32.79 (CMe_3), 124.73 (C^{1} and C^{3}), and 153.6 (C^{2}) ppm. ^{29}Si NMR ($CDCl_3$) δ 0.94 ppm. Anal. Found: C, 76.40; H, 11.97. $C_{16}H_{30}Si$ calc: C, 76.72; H, 12.07%. MS: *M/e* 250 (M^+, 7), 235 ($M^+ - CH_3$, 10), 73 ($SiMe_3^+$, 100), 57 (Me_3C^+, 7).

Di-t-butylcyclopentadienyltrimethylstannane (II)

A solution of 4.0 g (20 mmol) Me_3SnCl was treated with an equimolar amount of di-t-butylcyclopentadienyllithium in 50 ml THF. The mixture was stirred at room temperature overnight. After removal of the solvent and addition of 40 ml of petroleum ether, the precipitated LiCl was filtered off. From the residue, di-t-butylcyclopentadienyltrimethylstannane was isolated by distillation in vacuo, 5.6 g (82%), b.p. 58–60°C at 0.05 torr. ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9H, Me_3Sn, $J(^{117,119}SnH)$ 54.8 Hz), 1.20 (s, 18H, Me_3C), 4.86 (d, 2H, $H^{4,5}$, J 1.2, $J(^{117,119}SnH)$ 43.0 Hz), 6.40 (t, 1H, H^{2}, J 1.2 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ −6.6 (Me_3Sn), 31.4 (CMe_3), 32.6 (CMe_3) 84.0 (C^{4} and C^{5}), 121.0 (C^{1} and C^{3}), 154.3 (C^{2}) ppm. ^{119}Sn NMR ($CDCl_3$) δ 20.23 ppm. Anal. Found: C, 56.23; H, 8.73. $C_{16}H_{30}Sn$ calc: C, 56.34; H, 8.87%. MS: *m/e* 342 (M^+, 8), 327 ($M^+ - CH_3$, 18), 297 ($M^+ - 3CH_3$, 11), 165 ($SnMe_3^+$, 100), 57 (Me_3C^+, 46).

Di-t-butylcyclopentadienylmethyldichlorogermane (III)

In a similar procedure, a solution of 8.73 g CH_3GeCl_3 (45 mmol) in 50 ml THF was treated with an equimolar solution of di-t-butylcyclopentadienyllithium in THF to give di-t-butylcyclopentadienylmethyldichlorogermane, 11.2 g (84%), b.p. 77–80°C at 0.01 torr. ^{1}H NMR ($CDCl_3$) δ 0.75 (s, 3H, $GeCH_3$), 1.21 (s, 18H, Me_3C), 4.98 (br, 2H, $H^{4,5}$), 6.53 (s, 1H, H^{2}) ppm. Anal. Found: C, 50.78; H, 7.39, $C_{14}H_{24}GeCl_2$ calc: C, 50.07; H, 7.20%. MS: *M/e* 338 (M^+, 2), 336 (M^+, 4), 321 (M^+ − Me, 10), 57 (Me_3C^+, 100).

Di-t-butylcyclopentadienyltrichlorosilane (IV)

Similarly, a solution of 10.0 g $SiCl_4$ (60 mmol) in 50 ml THF was treated with an equimolar solution of di-t-butylcyclopentadienyllithium in THF to give di-t-butylcyclopentadienyltrichlorosilane, 11.5 g (84%), b.p. 72–74°C at 0.05 torr. ^{1}H NMR (toluene-d_8) for undistilled product before isomerization δ 1.16 (s, 18H, Me_3C), 4.73 (br, 2H, $H^{4,5}$), 6.51 (s, 1H, H^2). ^{29}Si NMR ($CDCl_3$) δ 2.73 and −7.16 ppm. Anal. Found: C, 50.25; H, 7.09. $C_{13}H_{21}SiCl_3$ calc: C, 50.09; H, 6.79%. MS: *M/e* 312 (M^+, 2), 297 (M^+ − Me, 3), 341 (M^+ − 2Cl, 2), 121 (M^+ − CMe_3–$SiCl_3$, 7), 57 (Me_3C^+, 100).

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