Journal of Organometallic Chemistry, 117 (1976) 321—328
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NMR SPECTRA OF METAL CYCLOPENTADIENYLS

XIII. SYNTHESIS OF AND REARRANGEMENTS IN $C_5H_5GeX_3$

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(Received March 25th, 1976)

Summary

In this paper we present a detailed description of the synthesis of cyclopentadienylgermanium trichloride, cyclopentadienylgermanium trimethoxide and 1-cyclopentadienyl-2,8,9-trioxa-5-azagermatricyclo-3,3,3,0-undecane (cyclopentadienylgermatrane) $C_5H_5\overline{Ge(OCH_2CH_2)_3N}$, and the results of an NMR study of metallotropic rearrangement in these compounds.

Introduction

Cyclopentadienyl derivatives of Group IVB elements, $C_5H_5MR_3$ (M = Si, Ge, Sn), capable of fast 1,5-sigmatropic rearrangements involving migration of the MR_3 group are a good model for a study of the phenomenon of metallotropism [1,2]. Quantitative data on these processes are rather scarce; the rearrangement rates, especially those for germanium derivatives, have only been studied qualitatively [1,3]. The compounds described before our short communication [4] appeared were the hydrides $C_5H_5Ge(R)H_2$ (R = H, CH_3, C_2H_5) and $CH_3C_5H_4GeH_3$ [5,6], the methylated derivatives $C_5H_5Ge(CH_3)_3$ (I), [7a,b], $(C_5H_5)_2Ge(CH_3)_2$ [8] and $CH_3C_5H_4Ge(CH_3)_3$ [7,9], and the π-complex $(C_5H_5)_2Ge(Fe(CO)_2C_5H_5\text{-}h^5)_2$ [10]. The activation parameters were found [11] with sufficient accuracy for I only.

Results and discussion

The synthesis of cyclopentadienylgermanium trichloride (II) was carried out by two methods (eq. 1 and 2). These are promising routes for obtaining a

$$(C_6H_5)_3SnC_5H_5 + GeCl_4 \xrightarrow{120^\circ C} \underset{50\%}{C_5H_5GeCl_3} + (C_6H_5)_3SnCl \qquad (1)$$

$$GeCl_4 + C_5H_5Li \xrightarrow{-10\text{ to }15^\circ C} \underset{53\%}{C_5H_5GeCl_3} + LiCl \qquad (2)$$

greater number of compounds with functional groups attached to germanium. Cyclopentadienylgermanium trimethoxide (III) was prepared via the method outlined in [12] (eq. 3).

$$2\,C_5H_5GeCl_3 + 3\,(C_2H_5)_2Sn(OCH_3)_2 \rightarrow \underset{\text{(III)}}{2\,C_5H_5Ge(OCH_3)_3} + 3\,(C_2H_5)_2SnCl_2 \qquad (3)$$

Cyclopentadienylgermatrane (IV) was synthetised starting from tris(2-triethylstannoxyethyl)amine (V). The latter compound may be readily obtained from triethyltin methoxide and triethanolamine (eq. 4). The use of V allows one

$$3\,(C_2H_5)_3SnOCH_3 + N(CH_2CH_2OH)_3 \rightarrow N\,[CH_2CH_2OSn(C_2H_5)_3]_3 + CH_3OH \qquad (4)$$

to carry the reaction out in aprotic solvents and avoid hydrolysis of the labile R—M bonds. A model reaction, CH_3GeCl_3 with V in hexane, led to a 91% yield of methylgermatrane (eq. 5). In a similar way, IV was obtained in a yield of 98%

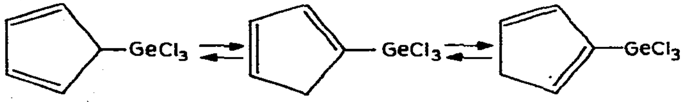
$$CH_3GeCl_3 + N[CH_2CH_2OSn(C_2H_5)_3]_3 \rightarrow CH_3\overleftarrow{Ge(OCH_2CH_2)_3N} + 3(C_2H_5)_3SnCl \qquad (5)$$

(eq. 6). Syntheses of other altranes via the method outlined will be published soon.

$$C_5H_5GeCl_3 + N[CH_2CH_2OSn(C_2H_5)_3]_3 \rightarrow C_5H_5\overleftarrow{Ge(OCH_2CH_2)_3N} + 3(C_2H_5)_3SnCl \qquad (6)$$

An ^1H NMR spectrum of $C_5H_5GeCl_3$ recorded at a 100 MHz operating frequency in CS_2 at —52°C is shown in Fig. 1, it shows that II is a mixture of isomers, IIa—IIc, resulting from a prototropic rearrangement. The 5-isomer IIa is the most stable thermodynamically, its protons give an AA′BB′X spectrum. The IIb protons give an $ABMX_2$ spectrum and the H(1) and H(5) signals of IIc can also be observed. The IIa/IIb/IIc ratio is 13.8 : 3.7 : 1 at room temperature. The assignment follows unambiguously from the multiplicity pattern and a

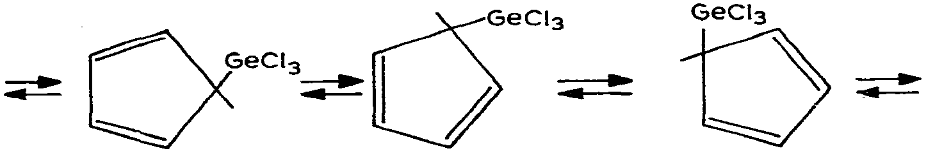
Fig. 1. 100 MHz PMR spectrum of II in CS_2 at —52°C.



(IIa) (IIb) (IIc)

comparison with the $C_5H_5SiCl_3$ spectra [3]. Complete analysis of the IIa spectrum was made by using the technique described [13] for $C_5H_5Si(CH_3)_3$ and I, an LCN-3 iteration program was employed in the final stage of the calculation. As with $C_5H_5SiR_3$, the AA′BB′X pattern does not depend on the relative signs of the $J(1,5)$ and $J(2,5)$ couplings. Therefore, the INDOR approach was used. The Overhouser effect for the terminal lowfield line of the X multiplet was observed while irradiating the terminal AA′BB′ lines. Consequently, $J(AX) < 0$ and $J(BX) > 0$ and, in accordance with the signs criterion [11], the H(2,3) signals lie at lower fields (in the AA′ part of the multiplet), Table 1.

The IIa AA′BB′X signals broaden gradually with temperature, and unsymmetrical broadening is readily observed in the olefine region. It is stronger for the H(1,4) signals. These facts suggest that a metallotropic rearrangement involving a $GeCl_3$ 1,2 shift occurs in the system. We could not, however, reach the fast exchange region in which the AA′BB′X spectrum would have collapsed to an A_5 spectrum, because the compound dimerises rapidly above 35° C. The rearrangement activation parameters were measured starting from the H(5) signal halfwidth (slow exchange region). The signal multiplicity was included by introducing the effective spin-lattice relaxation time. The values obtained are listed in Table 2.



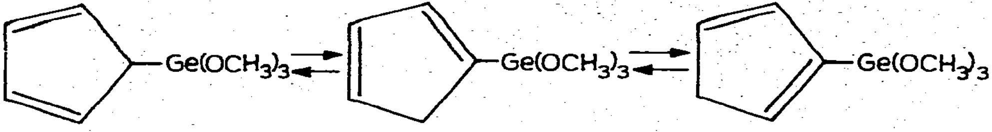
Similar to the silicon derivatives $C_5H_5Si(CH_3)_nCl_{3-n}$ [3], the free energy of activation increases on going from I to II. This is due to an increase in the electronegativity of the substituents attached to germanium, the increase that prevents the C—Ge bond from entering into σ—π-conjugation with the diene system of the ring. The entropy of activation is, within the accuracy achieved, not affected.

PMR Spectra of III were studied in CS_2 or $C_6H_5CH_3$-d_8 at −60 to +108°C. The spectrum recorded at room temperature contains two CH_3O signals at δ

TABLE 1

CHEMICAL SHIFTS AND SPIN—SPIN COUPLING CONSTANTS FOR II

Chemical shifts (ppm)			Spin—spin coupling constants (Hz)					
$\delta(1,4)$	$\delta(2,3)$	$\delta(5)$	$J(1,2) = J(3,4)$	$J(1,3) = J(2,4)$	$J(1,4)$	$J(2,3)$	$J(1,5) = J(4,5)$	$J(2,5) = J(3,5)$
6.443	6.847	4.111	5.02	1.19	2.24	2.24	1.32	−0.97



(IIIa) (IIIb) (IIIc)

3.43 and 3.53 ppm associated with the main isomers IIIa and IIIb, the isomer ratio being 2.64 : 1. There is a weak signal at δ 3.48 ppm assignable, probably, to IIIc. Also, the IIIb CH_2 signal may be readily assigned at δ 3.15 ppm, the IIIb olefine protons lying at δ 7.13 (H(2)) and δ 6.81 ppm (H(3), H(4)). The IIIa ring protons give a strongly broadened signal at about δ 6.50 ppm, indicative of a sufficiently fast metallotropic rearrangement. Cooling the sample down to —60° C allows one to observe the AA′BB′ part of the AA′BB′X spectrum of IIIa. The H(1,4) and H(2,3) chemical shifts are at δ 6.53 and 6.71 ppm respectively. The H(5) signal lies at about δ 3.5 ppm and is buried beneath the CH_3O signals. The spectrum displays a typical temperature dependence at —40 to +108° C. At —26 to —14° C, there is a characteristic broadening of the olefine signals with temperature, the broadening being stronger for the H(1,4) signal. At 108° C, the ring proton (H(1—5)) signals give, at δ 6 ppm, a singlet of half-width 2 Hz. Further increase of temperature makes the compound dimerise irreversibly. The IIIa stereochemical rigidity temperature lies at —28 to —22° C, corresponding to the $\Delta G^{\neq}_{300}$ of about 15 kcal/mol.

The activation parameters of the rearrangement occurring in IV may help to answer a fundamental question as to the nature of the role played by vacant 4*d* orbitals in the bonding which operates in the transition state. A 100 MHz PMR spectrum of IV recorded in $CDCl_3$ at room temperature contains two CH_2 triplets of the atrane sites (δ 2.62 and 3.58 ppm, ^3J 5.7 Hz) and two indistinct ring proton multiplets, δ 3.38 (H(5)) and 6.48 ppm (H(1—4)), of half-width 2.5 Hz, Fig. 2a. The chemical shifts of the two pairs of olefine protons are very close in the solvent used. At —5° C, there are observed external weak lines in the AA′BB′ part of the spectrum and a weak splitting of the H(5) signal, caused by spin—spin coupling with the olefine protons and proved by the double resonance experiment. The ring protons of the compound dissolved in C_5H_5N-d_5 or $C_6H_5CH_3$-d_8 display a typical AA′BB′X spectrum (Fig. 2c, Table 2). The increase in the difference between the olefine chemical shifts is due to the ASIS effect. The IV spectrum shape obtained at room temperature differs markedly from the shapes observed for other $C_5H_5GeR_3$ compounds usually leading to broadening-averaged

TABLE 2

PROTON CHEMICAL SHIFTS FOR IV IN DIFFERENT SOLVENTS

Solvents	Chemical shifts δ (ppm)				
	δ(—OCH_2—)	δ(—CH_2—N)	δ(1,4)	δ(2,3)	δ(5)
$CDCl_3$	3.66	2.70	6.60	6.60	3.52
C_5D_5N	3.70	2.60	7.06	6.80	3.96
$C_5D_5CD_3$	3.33	1.73	6.89	6.69	3.75

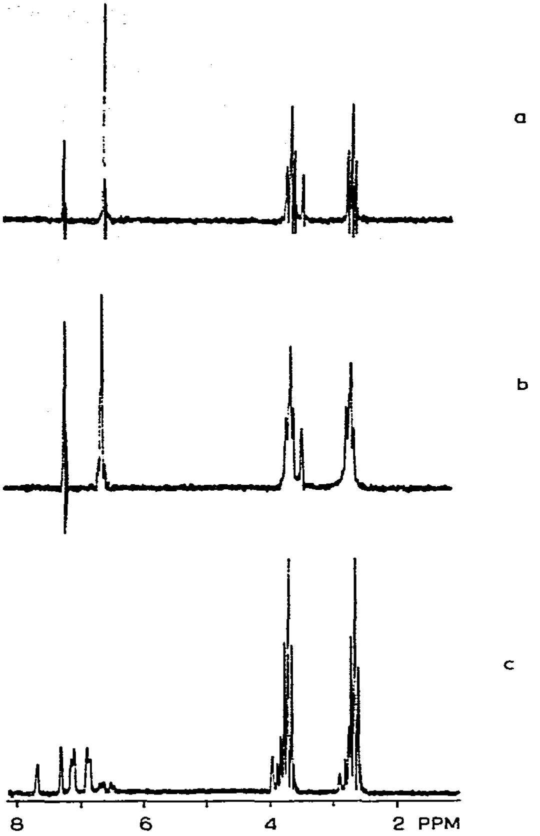


Fig. 2. 100 MHz PMR spectra of IV; (a) in $CDCl_3$ at 26°C; (b) in $CDCl_3$ at —5°C; (c) in C_5D_5N at 26°C.

signals responsible for all the ring protons. The broadening is due to a fast metallotropic rearrangement.

Heating IV in the solvents mentioned above broadens the signals, which is also indicative of the occurrence of metallotropic rearrangements, albeit at a much higher free energy of activation. The fast exchange region cannot be attained since IV dissolved in *in* C_5H_5N-d_5 or $C_6H_5CH_3$-d_8 decomposes when heated above 125°C. In the olefine region there is a distinct unsymmetrical broadening, with the lowfield signal being broadened more strongly; this is especially pronounced in the 270 MHz spectra (Fig. 3). Probably, the H(1,4) and H(2,3) sig-

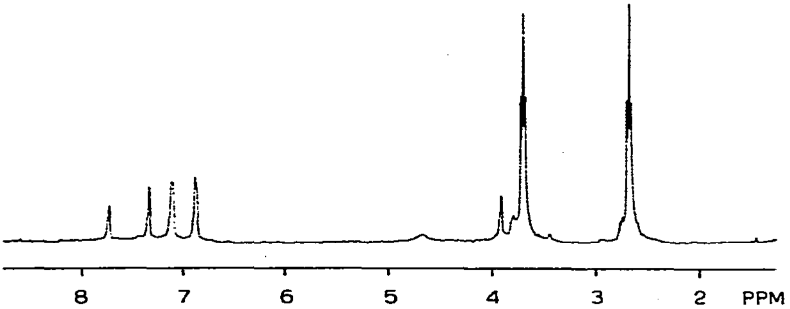


Fig. 3. 270 MHz PMR spectrum of IV in C_5D_5N at 26°C.

TABLE 3

ACTIVATION PARAMETERS FOR II, III AND IV

Substance	ΔE_a kcal/mol	$\Delta G^{\neq}_{300}$ kcal/mol	$\Delta S^{\neq}_{300}$ e.u.	$\Delta H^{\neq}_{300}$ kcal/mol
$C_5H_5GeCl_3$	11.9	16.1	—12.0	12.5
$C_5H_5Ge(OCH_2CH_2)_3N$	10.7	21.4	—35.2	11.3
$C_5H_5Ge(OCH_3)_3$		~15.0		

nals are in this case inverted and the H(1,4) signal lies at lower fields, as in the spectrum of $(C_5H_5)_2Ge[Fe(CO)_2C_5H_5\text{-}h^5]_2$ [10]. We obtained 270 MHz spectra of IV in $C_5H_5N\text{-}d_5$ at 20—70°C and found the parameters of activation in the way similar to that described for II, Table 3.

The data discussed above demonstrate that the energy of activation found for IV is, within the experimental error, identical with that found for I whereas the free energy, $\Delta G^{\neq}_{300}$, is significantly higher, owing to the high negative entropy value. This effect may be caused by spatial difficulties operating in the transition state and due to rigidity of the atrane system and to strong screening exerted by the oxygens upon the germanium. Consequently, the electronic properties of the group $\overline{Ge(OCH_2CH_2)_3N}$ are close to those of $Ge(CH_3)_3$, in accord with data obtained for the respective silicon derivatives [14]. The additional donor—acceptor, nitrogen—germanium bond does nothing but lower the energy of activation as compared with $C_5H_5Ge(OR)_3$. This substantiates our earlier conclusion [15] as to the prevailing role played by the σ—π C—Ge conjugation in governing the metallotropic rearrangement rates.

Experimental

All reactions were carried out in a dry nitrogen atmosphere.

Cyclopentadienlygermanium trichloride (II)

(a) Cyclopentadienyltriphenyltin (7.18 g, 17.32 mmol) and germanium tetrachloride (3.72 g, 17.33 mmol) were heated at 120°C for 1.5 h. The mixture was cooled down to room temperature, treated with 10 ml hexane, triphenyltin chloride was filtered off (yield 86%, m.p. 105°C, a mixture with the authentic compound melts without depression). The solvent was removed from the filtrate and the residue was distilled in vacuo at 180°C (bath temperature) to give cyclopentadienylgermanium trichloride, 2.1 g (50%), b.p. 60—62°C at 5 Torr. Found: C, 24.56; H, 2.09; Cl, 43.81; Ge, 29.90. $C_5H_5Cl_3Ge$ calcd.: C, 24.58; H, 2.09; Cl, 43.63; Ge, 29.74%.

(b) A suspension of cyclopentadienyllithium (6.75 g, 93.77 mmol) in 50 ml toluene was gradually added to a stirred solution of germanium tetrachloride (20.15 g, 93.90 mmol) in 15 ml toluene maintained at —10 to —15°C. The mixture was stirred at 0—20°C for 2 h and at 45°C for 30 min. The precipitate was filtered off, the solvent was removed and the residue was distilled in vacuo to give cyclopentadienylgermanium trichloride, 12.0 g (53.3%), b.p. 56—57°C at 3 Torr (bath temperature 180°C). Cyclopentadienylgermanium trichloride dimerises readily. It was distilled into an ampoule cooled by Dry Ice.

Cyclopentadienylgermanium trimethoxide (III)

Cyclopentadienylgermanium trichloride (5.2614 g, 21.5 mmol) was added to diethyltin dimethoxide (7.6703 g, 32.1 mmol) dissolved in 30 ml hexane. The addition rate was controlled so that the reaction temperature did not exceed 30°C. The mixture was refluxed for 20 min and cooled down to 0°C. The diethyltin dichloride precipitated was filtered off on a No. 4 glass filter and cooled with Dry Ice to give a compound, 10.44 g (93%), m.p. 84°C (crystallised from hexane). The filtrate was distilled in vacuo which gave cyclopentadienylgermanium trimethoxide, 3.61 (73.6), b.p. 52—53°C at 0.02 Torr. Found: C, 41.52; H, 6.00; Ge, 31.03. $C_8H_{14}GeO_3$ calcd.: C, 41.63; H, 6.07; Ge, 31.93%.

Methylgermatrane

A solution of methylgermanium trichloride (0.74 g, 3.769 mmol) in 20 ml hexane was added to a stirred solution of tris(2-triethylstannoxyethyl)amine (2.92 g, 3.826 mmol) in 20 ml hexane maintained at 0—10°C. The reaction was distinctly exothermic, a white precipitate was formed. The mixture was stirred at 0—10°C for 2 h and at room temperature for 30 min. The precipitate was filtered off, washed with cold hexane and dried at 0.02 Torr until its weight was constant, to give methylgermatrane, 0.81 g (91%), m.p. 158—159°C, lit. [16] m.p. 158—159°C.

Cyclopentadienylgermatrane (IV)

Cyclopentadienylgermanium trichloride (3.62 g, 14.8 mmol) dissolved in 30 ml hexane was added dropwise with stirring to tris(2-triethylstannoxyethyl)-amine (11.32 g, 14.8 mmol) dissolved in 30 ml hexane maintained at 0 to —10°C. The reaction was very exothermic and nothing but tar was obtained when the temperature exceeded 10°C. The mixture was stirred at 0 to —10°C for 1 h and at room temperature for another hour. The precipitate was filtered off, washed with cold hexane and dried at 0.02 Torr until its weight was constant. To purify it the compound was dissolved in chloroform, treated with several drops of hexane, the thin precipitate filtered off and the filtrate evacuated until the residue weight was constant. The yield of cyclopentadienylgermatrane was 98%, the decomposition point was 128—130°C (in a sealed capillary). Found: C, 46.90; H, 6.11; N, 5.01; Ge, 25.83. $C_{11}H_{17}GeNO_3$ calcd.: C, 46.54; H, 5.99; N, 4.93; Ge, 25.60%. Cyclopentadienylgermatrane is soluble in cold chloroform, dichloroethane, *o*-dichlorobenzene, benzonitrile, pyridine, tetrahydrofuran, warm methanol, ethanol, acetone, dioxan, carbon tetrachloride and aromatic hydrocarbons. It is insoluble, even when heated, in ethyl acetate, hexane, cyclohexane or light petroleum.

Tris(2-triethylstannoxyethyl)amine

A mixture of triethanolamine (22.83 g, 153.2 mmol) and triethyltin methoxide (108.83 g, 459.7 mmol) was heated in 200 ml benzene for 1.5 h. Volatile species were distilled off and the residue purified by molecular distillation. The yield of tris(2-triethylstannoxyethyl)amine was 93.2%, b.p. 210°C (bath temperature) at 0.001 Torr, n_D^{25} 1.5072. Found: C, 37.70; H, 7.49; N, 1.85; Sn, 46.55. $C_{24}H_{57}NO_3Sn_3$ calcd.: C, 37.74; H, 7.47; N, 1.83; Sn, 46.66%.

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