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Synthesis of novel polymetallated cyclopentadienes

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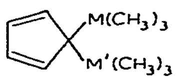
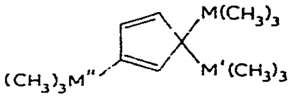
During a study of fluxional σ-cyclopentadienyl derivatives of the Group IVB elements[1–3] a number of polymetallated cyclopentadienes containing two, three, or four (equal or different) groups of the series $Si(CH_3)_3$, $Ge(CH_3)_3$, and $Sn(CH_3)_3$ (I to XI) have been synthesised.





	M	M'
I	Si	Si
II	Si	Ge
III	Ge	Ge
IV	Si	Sn
V	Sn	Sn
VI	Ge	Sn

	M	M'	M''
VII	Si	Sn	Si
VIII	Ge	Sn	Si
IX	Sn	Sn	Si
X	Sn	Sn	Sn
XI	$C_5H_2[Sn(CH_3)_3]_4$★		

Compounds I to IV (Table 1) were synthesised from $C_5H_5M(CH_3)_3$ (M = Si, Ge)★★ by metallating the starting compound with butyllithium and treating the mixture with $(CH_3)_3M'Cl$ (M' = Si, Ge, Sn).

Bis(trimethylsilyl)cyclopentadiene (I).

A solution of butyllithium (1.9 *N*, 6.35 ml, 12.0 mmole) in ligroin was added dropwise in an argon atmosphere to a stirred solution of freshly distilled trimethylsilylcyclopentadiene (1.6 g, 11.5 mmole) in 10 ml abs. ligroin. The mixture was stirred for an hour at room temperature, trimethylchlorosilane (2.6 g, 2.4 mmole) added in an argon

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★Because of the complicated low-temperature spectrum of compound XI the position of the organotin groups in this compound could not be determined.

★★Synthesised according to the method of Kraihanzel (for M = Si)[4] and of Mironov (for M = Ge)[5].

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sweep, and the resulting mixture heated for three hours at 40°. The ligroin solution was filtered, the solvent evaporated, and the residue distilled in vacuo to give bis(trimethylsilyl)cyclopentadiene, b.p. 45° at 3 mm, yield 1.45 g (60%).

Compounds II, III, and IV were obtained in a similar way. Their constants and analyses are shown in Table 1.

Compounds $C_5H_5Sn(CH_3)_3$★ and V were obtained by metallating cyclopentadiene with diethylaminotrimethylstannane using the modified procedure of Jones and Lappert[7].

TABLE 1

CONSTANTS AND ANALYSES OF THE COMPOUNDS I TO IV

Compound	Gross formula	Yield (%)	B.p. (°C/mm)	Analysis found (calcd.)			
				C	H	Si	Ge
I	$C_{11}H_{22}Si_2$	60	80/10	62.66 (62.78)	10.42 (10.54)	26.35 (26.69)	
II	$C_{11}H_{22}SiGe$	86	31/1	51.96 (51.82)	8.76 (8.70)		
III	$C_{11}H_{22}Ge_2$	67	42/1	44.52 (44.12)	7.39 (7.41)		48.19 (48.51)
IV	$C_{11}H_{22}SiSn$	22	42/1	43.69 (43.88)	7.38 (7.37)		

Trimethylstannylcyclopentadiene.

Freshly distilled cyclopentadiene (1.98 g, 30 mmole) and diethylaminotrimethylstannane (2.36 g, 10 mmole) were placed in a distillation assembly. The mixture was maintained in a dry argon atmosphere for 0.5 hour, the resulting diethylamine and excess of cyclopentadiene removed in vacuo, and the residue distilled in vacuo. The yield of $C_5H_5Sn(CH_3)_3$ was 2.1 g (92%), b.p. 38° at 3 mm.

Similar reaction of the aminostannane with the respective cyclopentadienes produced the compounds VI to XI. The experimental conditions, yields, boiling points, and analyses are summarised in Table 2.

The structures of compounds I–XI have been unambiguously verified by NMR and mass spectral measurements. Their fluxional behaviour has been studied through the use of temperature-dependent ^1H and ^{13}C NMR spectra. The data relative to these studies will be published shortly.

★NMR spectra and fluxional behaviour of $C_5H_5Sn(CH_3)_3$ have been previously reported[2,3,6].

TABLE 2

SYNTHESES AND CONSTANTS OF THE COMPOUNDS V TO XI

Compound	Gross formula	Initial cyclo-pentadiene	Molar ratio of initial cyclo-pentadiene to aminostannane	Reaction temperature (°C)	Reaction time (h)	Yield (%)	B.p. (°C/mm)	Analysis found (calcd.)		
								C	H	Sn
$C_5H_5Sn(CH_3)_3$	$C_8H_{14}Sn$	C_5H_6	3/1	room	0.5	92	38/3[a]	42.13 (41.98)	6.29 (6.16)	52.15 (51.86)
V	$C_{11}H_{22}Sn_2$	C_5H_6	1/2	40	2	90	80/3	33.55 (33.73)	5.42 (5.66)	60.83 (60.61)
VI	$C_{11}H_{22}GeSn$	$C_5H_5Ge(CH_3)_3$	1/1.2	40	2	84	82/3	38.08 (38.23)	6.42 (6.42)	
VII	$C_{14}H_{30}Si_2Sn$	I	1/1.2	40	2	64	102/4	45.20 (45.05)	7.85 (8.10)	
VIII	$C_{14}H_{30}SiGeSn$	II	1/1.2	40	2	77	68/1	40.45 (40.25)	6.81 (7.24)	
IX	$C_{14}H_{30}SiSn_2$	$C_5H_5Si(CH_3)_3$	1/2	40	2	80	84/3	36.44 (36.25)	6.49 (6.52)	
X	$C_{14}H_{30}Sn_3$	V	1/1.5	100	3	86	116/3	30.31 (30.33)	5.41 (5.45)	64.90 (64.22)
XI	$C_{17}H_{38}Sn_4$	X	1/2	150	4	60	122/1 m.p. 60–61	29.10 (28.47)	5.60 (5.34)	65.58 (66.19)

[a] Lit. 85/10 [8].

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