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Preliminary communication

A NEW APPROACH TO GROUP IVB METALLOCENES

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Summary

Reduction of bis(pentamethylcyclopentadienyl) dihalides of the Group IVB elements germanium and tin with alkali metal cyclooctatetraenides or naphthalenides gives the corresponding decamethylmetallocenes.

Up to now syntheses of Group IVB metallocenes have always started with divalent IVB compounds. The usual method involves reaction of the dihalides or dinitrates with alkali metal cyclopentadienides [1—9]; this can also be performed in two steps [9,10]. Some derivatives were prepared from the metallocenes themselves by modification [11—13] or substitution [14] of the cyclopentadienyl ligands. We now report a new approach to Group IVB metallocenes involving reduction of tetravalent halides bearing two pentamethylcyclopentadienyl ligands.

Treatment of bis(pentamethylcyclopentadienyl)tin dichloride (1) [4] or bis(pentamethylcyclopentadienyl)tin dibromide (2) [4] with dilithium cyclooctatetraenide, $Li_2C_8H_8$, in 1/1 molar ratio gives decamethylstannocene (3) [4] in good yield. $Li_2C_8H_8$, prepared from lithium and cyclooctatetraene in ether, is added to a solution of 1 or 2 in THF at —80°C. Evaporation of the solvent and extraction of the residue with petroleum ether gives a bright yellow solution, from which the metallocene 3 crystallizes after concentration. Analytical data are given in Table 1. Using lithium naphthalenide $LiC_{10}H_8$ as reducing agent, complete conversion of 1 and 2 was confirmed by NMR spectroscopy. However, the separation from naphthalene proved to the difficult, and an analytical pure product was obtained only in low yield (Table 1).

$$\underset{\substack{(1,\ X = Cl;\\ 2,\ X = Br)}}{(C_5Me_5)_2SnX_2} \xrightarrow[2\ LiC_{10}H_8]{Li_2C_8H_8} \underset{(3)}{(C_5Me_5)_2Sn}$$

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$$\underset{(4)}{(C_5Me_5)_2GeCl_2} \xrightarrow{K_2C_8H_8} \underset{(5)}{(C_5Me_5)_2Ge}$$

For preparation of decamethylgermanocene (5) [5] via reduction of bis(pentamethylcyclopentadienyl)germanium dichloride (4) [15], a slight excess of potassium cyclooctatetraenide is used. The reaction is carried out at −80°C in THF in the way described for reduction of the tin compounds. Analytical data are again given in Table 1.

The reduction of di(cyclopentadienyl)substituted tetravalent halides provides a satisfactory alternative synthetic approach to germanocenes and stannocenes, and points a possible path to the (as yet unknown) analogous silicon compounds.

TABLE 1

EXPERIMENTAL DETAILS AND ANALYTICAL DATA

Educt (g (mmol))	Agent	Metallocene			
		(Found (calcd.) (%)) [a]			
		C	H	Yield (g) (% Th.)	NMR [b] (δ in ppm; *J* in Hz)
1 5.51 (12.0)	$Li_2C_8H_8$	61.86 (61.72)	7.74 (7.77)	3.14 (67)	^{1}H (C_6H_6) 2.07 *J*(SnH) 3.6 ^{119}Sn (C_6D_6) −2121
2 6.80 (12.4)	$Li_2C_8H_8$	61.52 (61.72)	7.64 (7.77)	3.36 (70)	^{1}H (C_6H_6) 2.08 *J*(SnH) 3.7 ^{119}Sn ($CDCl_3$) −2142
1 2.81 (6.1)	$LiC_{10}H_8$	—	—	*c*	^{1}H (CH_2Cl_2) 2.03 *J*(SnH) 3.6
2 11.5 (21.4)	$LiC_{10}H_8$	61.38 (61.72)	7.57 (7.77)	0.30 (4)	^{1}H (CH_2Cl_2) 2.03 *J*(SnH) 3.7
4 5.48 (13.2)	$K_2C_8H_8$	69.95 (70.02)	8.84 (8.82)	2.45 (54)	^{1}H (C_6H_6) 2.04 ^{13}C ($CDCl_3$) CCH_3 9.82 CCH_3 118.12

[a] Elemental analyses by Mikroanalytisches Labor Beller, Göttingen. [b] ^{1}H NMR: Varian EM 360L (60 MHz) ^{119}Sn NMR: Bruker AM 300 (111.92 MHz), ^{13}C NMR: Bruker AM 300 (75.473 MHz). [c] No naphthalene-free product was obtained.

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