# DERIVATIVES OF DIVALENT GERMANIUM, TIN AND LEAD

IV. SYNTHESIS AND INFRARED SPECTRUM OF THE NOVEL ALU-MINIUM-TIN BONDED COMPLEX: BIS(METHYLCYCLOPENTA-DIENYL)TIN-ALUMINIUM TRICHLORIDE. A COMMENT ON THE STRUCTURE OF BIS(METHYLCYCLOPENTADIENYL)LEAD

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### SUMMARY

The novel aluminium-tin bonded complex, bis(methylcyclopentadienyl)tinaluminium trichloride has been synthesised from its two components. Its infrared spectrum has been recorded and normal modes assigned by comparison with bis-(methylcyclopentadienyl)tin. A structure for the complex is proposed in which the angular "sandwich" nature of the free ligand is preserved. From the infrared spectrum of the bis(methylcyclopentadienyl)lead, it is deduced that this compound is isostructural with the analogous tin compound.

#### INTRODUCTION

The structure and nature of the bonding in Group IV cyclopentadienyls has aroused much interest<sup>1-5</sup>. Initially it was suggested that the cyclopentadienyl rings in tin(IV) cyclopentadienyl compounds are  $\pi$ -bonded<sup>6.7</sup>. However infrared<sup>2</sup>, NMR<sup>2</sup> and structural<sup>8.9</sup> evidence has shown that these compounds possess a fluxional,  $\sigma$ bonded diene-type ring, around which the metal migrates via 1,2- or 1,3-metallotropic shifts. The cyclopentadienyls of tin in its lower oxidation state are also the subject of much investigation, since they account for the majority of known organotin(II) derivatives. Electron diffraction<sup>10</sup> has shown that dicyclopentadienyltin has an angular "sandwich" structure in the vapour phase, in which the rings are centrally  $\sigma$ - (pseudo  $\pi$ -) bonded. In an earlier report<sup>1</sup> we showed that the vibrational spectra of this compound are consistent with the preservation of the angular "sandwich" structure in both the solid and solution phases. This formulation, with a bond angle at tin of ca.  $120^{\circ 10}$ , indicates  $sp^2$  hybridisation for the tin valence electrons. The lone pair of electrons will therefore reside in an orbital possessing directional character\*.11. This has been confirmed by the formation of the donor-acceptor complex,  $(C_5H_5)_2$ -Sn · BF<sub>3</sub>, in which the tin atom acts as a Lewis base<sup>5</sup>. Bis(methylcyclopentadienyl)tin

\* Cf. SnCl<sub>3</sub>, in which the ClSnCl angles are ca. 90°, and the lone pair is located in the tin 5s orbital.

exhibits similar properties, and this paper reports the preparation and infrared spectrum of its adduct with aluminium trichloride. The infrared spectrum of bis-(methylcyclopentadienyl)lead<sup>12</sup> is also reported.

## EXPERIMENTAL

All manipulations were carried out under an atmosphere of dry argon. Bis-(methylcyclopentadienyl)tin was prepared as described previously<sup>13</sup>. Bis(methylcyclopentadienyl)lead was prepared similarly from lead acetate. Aluminium trichloride was sublimed immediately before use. Infrared measurements were carried out using a Perkin-Elmer 521 instrument calibrated with polystyrene and water vapour.

#### Bis(methylcyclopentadienyl)tin-aluminium trichloride adduct

Bis(methylcyclopentadienyl)tin (4.23 g, 15.3 mmol) in anhydrous benzene (5 ml) was added dropwise to a suspension of freshly sublimed aluminium trichloride (2.09 g, 15.7 mmol) in benzene (10 ml). After vigorous stirring for 20 min, all the aluminium trichloride had dissolved, and two liquid layers had formed. The lower layer was removed, and the solvent removed *in vacuo* to yield the adduct as a viscous, golden oil. (Found: C, 34.7; H, 3.5.  $C_{12}H_{14}AlCl_3Sn$  calcd.: C, 35.1; H, 3.4%.)

#### RESULTS AND DISCUSSION

Bis(methylcyclopentadienyl)tin (I) reacts readily with anhydrous aluminium trichloride in dry benzene to form a 1/1 adduct (II) as a viscous, golden oil [eqn. (1)].

$$(MeC_5H_4)_2Sn: +AlCl_3 \rightarrow (MeC_5H_4)_2Sn: \rightarrow AlCl_3$$
(1)  
(I) (II)

The similarity of the tin-119m Mössbauer parameters of the boron trifluoride adducts of dicyclopentadienyltin<sup>5</sup> and  $(I)^{14}$  and the ligands themselves has led us previously to suggest that the angular "sandwich" structure of the free ligands is preserved in the complexcs<sup>5</sup>. Although Mössbauer evidence is not available in the present case, the complex (II) readily reduces mercury(II) chloride to mercury, and so is postulated to have a similar structure (Fig. 1), in which the coordination numbers of the tin and aluminium are three and four respectively. As such it is, as far as we are aware, the first example of a coordinate tin—aluminium bond. Like the free ligand, the complex (II) is both moisture- and oxygen-sensitive.



344.

# TABLE 1

OBSERVED INFRARED BANDS OF  $(MeC_5H_4)_2Sn \cdot AlCl_3$ ,  $(MeC_5H_4)_2Sn \cdot AND (MeC_5H_4)_2Pb (cm^{-1})$ 

3975 vw         3920 w         39           3112 m         3100 w         31           3080 w         3080 w         30           2972 m         2965 w         25           2930 m         2925 m         25           2880 w(sh)         28         27           2755 vw         27         27           1825 vw(br)         17         1660 w(vbr)           1660 w(vbr)         1607 vw         16           1521 m         1526 vw         16           1507 m(sh)         1481 vs         1482 m         14           1456 vs         1458 w         14           1456 vs         1458 w         14           1456 vs         1458 w         14           1481 vs         1448 w(sh)         14           1483 m         1408 vw         14           1369 m         1378 w         13           1319 vw         12         12           1265 w         1260 vvw(br)         12           1238 w(sh)         1117 vvw         11           1209 vw         1062 w         100           1045 s         1042 m         100           1029 vw         1026 m	20 vvw 85 w 65 w 25 w 70 w 35 vvw	CH str. $A_1$ ; $v_1$ , $v_{5a}$ CH str. $B_1$ ; $v_{5b}$ , $v_{9b}$ CH str. $B_1$ , $B_2$ ; $m_4$ , $m_7$ CH str. $A_1$ ; $m_1$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	85 w 65 w 25 w 70 w 35 vvw	CH str. $A_1$ ; $v_1$ , $v_{5_1}$ CH str. $B_1$ ; $v_{5_5}$ , $v_{9_5}$ CH str. $B_1$ , $B_2$ ; $m_4$ , $m_7$ CH str. $A_1$ ; $m_1$
3112 m       3080 w         3050       2972 m       2965 w       29         2930 m       2925 m       25         2880 w(sh)       25       27         2755 vw       27       27         1825 vw(br)       17       1660 w(vbr)         1660 w(vbr)       1607 vw       16         1640 w(vbr)       1607 vw       16         1521 m       1526 vw       1481 vs         1507 m(sh)       1481 vs       1448 w(sh)       14         1481 vs       1458 w       14       1456 vs       1453 w         1448 vs(sh)       1448 w(sh)       14       1435 vs       1448 w(sh)       14         1383 m       1369 m       1378 w       13       13         1369 m       1378 w       13       13         1319 vw       1260 vvw(br)       12       12         1238 w(sh)       1117 vvw       11       111         1112 vw(sh)       1117 vvw       11       10         1005 m       1062 w       100       100         1003 m       1010 w(sh)       100       976 vvw       97         898 w       90       885 w       847 w(sh)       84	85 w 65 w 25 w 70 w 35 vvw	CH str. $B_1$ ; $v_{5b}$ , $v_{9b}$ CH str. $B_1$ , $B_2$ ; $m_4$ , $m_7$ CH str. $A_1$ ; $m_1$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	65 w 25 w 70 w 35 vvw	CH str. $B_1$ ; $v_{5b}$ , $v_{9b}$ CH str. $B_1$ , $B_2$ ; $m_4$ , $m_7$ CH str. $A_1$ ; $m_1$
3050 $2972  m$ $2965  w$ $2925  m$ $25280  w$ $25280  w$ $25280  w$ $25280  w$ $2755  w$ $2755  w$ $271825  w$ $171660  w$ $1607  w$ $1607  w$ $161788  w$ $14181  w$ $1481  w$ $1482  m$ $14488  w$ $141488  w$ $14181883  m$ $14181883  m$ $14181883  m$ $14181883  w$ $1414888888  w$ $14148888888888888888888888888888888888$	65 w 25 w 70 w 35 vvw	CH str. $B_1, B_2; m_4, m_7$ CH str. $A_1; m_1$
2972 m       2965 w       29         2930 m       2925 m       29         2880 w(sh)       26         2755 vw       27         1825 vw(br)       17         1825 vw(br)       16         1640 w(vbr)       16         1521 m       1526 vw         1507 m(sh)       16         1481 vs       1482 m         1485 vs       1488 w(sh)         1481 vs       1489 ww         1481 vs       1480 vw         1383 m       1369 m         1369 m       1378 w         1369 m       1378 w         1319 vw       13         1265 vw       1260 vvw(br)         1223 w(sh)       1117 vvw         1229 s       1229 s         1180 vw       1117 vvw         1112 vw(sh)       1117 vvw         1005 m       1062 w         0045 s       1042 m         0029 vw       1026 m         003 m       976 vvw         898 w       90 <td>65 w 25 w 70 w 35 vvw</td> <td>CH str. <math>B_1</math>, <math>B_2</math>; <math>m_4</math>, <math>m_7</math> CH str. <math>A_1</math>; <math>m_1</math></td>	65 w 25 w 70 w 35 vvw	CH str. $B_1$ , $B_2$ ; $m_4$ , $m_7$ CH str. $A_1$ ; $m_1$
2930 m       2925 m       25         2880 w(sh)       28         2880 w(sh)       28         2755 vw       27         1825 vw(br)       17         1825 vw(br)       16         1660 w(vbr)       16         1640 w(vbr)       16         1521 m       1526 vw         1507 m(sh)       14         1481 vs       1482 m       14         1456 vs       1458 w       14         1448 vs(sh)       1448 w(sh)       14         1438 m       1408 vw       14         1383 m       1369 m       1378 w       13         1369 m       1378 w       13       13         1369 w       1260 vvw(br)       12       12         1238 w(sh)       1229 s       12       12         1238 w(sh)       1117 vvw       11       106         1029 vw       1026 m       100       100         0045 s       1042 m       100         003 m       976 vvw       97       898 w       90         847 w(sh)       847 w(sh)       84       847 w(sh)       84         847 vvs(sh)       813 vs       81       81	25 w 70 w 35 vvw	CH str. $A_1$ ; m <sub>1</sub>
2880 w(sh)       28         2755 vw       27         1825 vw(br)       17         1660 w(vbr)       1607 vw         1640 w(vbr)       1607 vw         1521 m       1526 vw         1507 m(sh)       1482 m         1481 vs       1482 m         1481 vs       1448 w(sh)         1481 vs       1458 w         1483 m(sh)       1408 vw         1383 m       1306 m         1369 m       1378 w         1369 m       1378 w         1369 m       1378 w         1369 m       1378 w         1319 vw       1200 vvw(br)         1229 s       1229 s         1120 vw       1117 vvw         1112 vw(sh)       1117 vvw         1112 vw(sh)       1117 vvw         1120 vw       1002 w         0045 s       1042 m         0029 vw       1026 m         003 m       1010 w(sh)       100         978 w(sh)       976 vvw       97         898 w       90       885 w         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66	70 w 35 vvw	
2755 vw       27         1825 vw(br)       17         1660 w(vbr)       16         1640 w(vbr)       1607 vw         1521 m       1526 vw         1507 m(sh)       1482 m         1481 vs       1482 m         1456 vs       1458 w         1481 vs       1448 w(sh)         1481 vs       1448 w(sh)         1448 vs(sh)       1448 w(sh)         1448 m(sh)       1408 vw         1383 m       1369 m         1369 m       1378 w         1369 m       1378 w         1319 vw       12         1228 w(sh)       12         1229 s       1229 s         1112 vw(sh)       1117 vvw         1112 vw(sh)       1117 vvw         1065 m       1062 w         1005 m       1062 w         10029 vw       1026 m         1003 m       976 vvw         1003 m       976 vvw         887 w(sh)       813 vs         833 vvs(vbr)       767 vvs(br)         75       685 s         647 s       635	35 vvw	
1825 vw (br)       17         1660 w (vbr)       16         1640 w (vbr)       1607 vw         1521 m       1526 vw         1521 m       1526 vw         1481 vs       1482 m       14         1456 vs       1458 w       14         1455 vs       1458 w       14         1448 vs(sh)       1448 w(sh)       14         1481 vs       1448 w(sh)       14         1481 m(sh)       1408 vw       14         1383 m       1369 m       1378 w       13         1369 m       1378 w       13         1346 w       13       13       13         1205 vw       1260 vvw(br)       12       12         1238 w(sh)       112       12       13         129 s       1229 s       122       112         112 vw(sh)       1117 vvw       11       10         1025 m       1062 w       100       101         1029 vw       1026 m       100       101         1029 vw       1026 m       100       101         1003 m       976 vvw       97       898 w       80         103 vvs(vbr)       976 vvs       97	S	
1660 w (vbr)161640 w (vbr)1607 vw1521 m1526 vw1507 m (sh)1481 vs1481 vs1482 m1445 vs1448 w (sh)1448 vs (sh)1448 w (sh)1448 vs (sh)1448 w (sh)1448 n (sh)1408 vw1481 m (sh)1408 vw1369 m1378 w1369 m1378 w1369 m1378 w1319 vw131225 s1229 s1238 w (sh)1117 vvw111 12 vw (sh)1117 vvw112 vw (sh)1117 vvw1065 m1062 w1003 m1010 w (sh)1003 m976 vvw978 w (sh)976 vvw898 w90898 w847 w (sh)847 vvs (sh)813 vs803 vvs (vbr)767 vvs (br)75685 s647 s647	1	<b>Combination bands</b>
1660 w (vbr)       16         1640 w (vbr)       1607 vw       16         1521 m       1526 vw       1507 m(sh)         1507 m (sh)       1481 vs       1482 m       14         1456 vs       1458 w       14       14         1456 vs       1458 w       14       14         1448 vs (sh)       1448 w(sh)       14       14         1438 m (sh)       1408 vw       14         1383 m       1369 m       1378 w       13         1369 m       1378 w       13       13         1369 m       1378 w       13       13         1369 m       1378 w       13       13         1319 vw       12       13       13       13         1205 w       1260 vvw (br)       12       13         1319 vw       112       13       13       13         1229 s       1229 s       122       14       14         112 vw(sh)       1117 vvw       11       10         1065 m       1062 w       100       10         1029 vw       1026 m       107       107         1003 m       976 vvw       97       898 w       82      <	40 vw(vbr)	
1640 w(vbr) $1607 vw$ $16$ $1521 m$ $1526 vw$ $1507 m(sh)$ $1481 vs$ $1482 m$ $14$ $1485 vs$ $1448 w(sh)$ $14$ $1445 vs(sh)$ $1448 w(sh)$ $14$ $1448 vs(sh)$ $1448 w(sh)$ $14$ $1448 vs(sh)$ $1448 w(sh)$ $14$ $1448 w(sh)$ $1408 vw$ $14$ $1383 m$ $1408 vw$ $14$ $1383 m$ $1378 w$ $13$ $1369 m$ $1378 w$ $13$ $1369 m$ $1378 w$ $13$ $1369 m$ $1378 w$ $13$ $1346 w$ $13$ $13$ $1260 vvw(br)$ $12$ $13$ $129 vw$ $1260 vvw(br)$ $12$ $1238 w(sh)$ $1229 s$ $12$ $1212 vw(sh)$ $1117 vvw$ $111$ $1065 m$ $1062 w$ $100$ $1029 vw$ $1026 m$ $100$ $1003 m$ $976 vvw$ $97$ $898 w$ $86$ $847 w(sh)$ $84$ $847$	85 vw(vbr)	
1607 vw161521 m1526 vw1507 m(sh)1481 vs1481 vs1482 m1481 vs1456 vs1456 vs1458 w1448 w(sh)1448 w(sh)1448 m(sh)1408 vw1418 m(sh)1408 vw1369 m1378 w1369 m1378 w1369 m1378 w1359 w131369 m1260 vvw(br)120 vw121238 w(sh)1229 s1229 s1229 s1112 vw(sh)1117 vvw1112 vw(sh)1010 w(sh)105 m1062 w1003 m1010 w(sh)978 w(sh)976 vvw978 w(sh)813 vs847 vvs(sh)813 vs813 vs813 vs803 vvs(vbr)767 vvs(br)75685 s647 s647	J	-
1521 m       1526 vw         1507 m(sh)       1481 vs       1482 m       14         1481 vs       1458 w       14       14         1456 vs       1458 w       14         1448 vs(sh)       1448 w(sh)       14         1448 vs(sh)       1448 w(sh)       14         148 m(sh)       1408 vw       14         1383 m       1408 vw       14         1369 m       1378 w       13         1369 m       1378 w       13         1346 w       13       13         1346 w       13       13         1346 w       13       13         1346 w       13       13         1346 w       1260 vvw(br)       12         1238 w(sh)       1229 s       12         1238 w(sh)       1229 s       12         1205 m       1062 w       100         1045 s       1042 m       100         1045 s       1042 m       100         1003 m       1010 w(sh)       101         978 w(sh)       976 vvw       97         885 w       847 w(sh)       847 s         847 vvs(sh)       813 vs       81 <t< td=""><td>10 vw</td><td>CC str. <math>A_1; v_{12n}</math></td></t<>	10 vw	CC str. $A_1; v_{12n}$
1507 m(sh) $1481 vs$ $1482 m$ $14$ $1481 vs$ $1448 vs$ $14$ $1458 w$ $14$ $1448 vs$ $14$ $1448 vs$ $14$ $1448 w(sh)$ $14$ $1448 w(sh)$ $14$ $1418 m(sh)$ $1408 vw$ $14$ $1383 m$ $1408 vw$ $14$ $1383 m$ $1369 m$ $1378 w$ $13$ $1346 w$ $1378 w$ $13$ $1265 w$ $1260 vvw(br)$ $12$ $1238 w(sh)$ $1229 s$ $12$ $1229 s$ $1229 s$ $12$ $1120 vw$ $1117 vvw$ $111$ $1120 vw(sh)$ $1117 vvw$ $111$ $1065 m$ $1062 w$ $100$ $1045 s$ $1042 m$ $100$ $1029 vw$ $1026 m$ $100$ $978 w(sh)$ $976 vvw$ $97$ $898 w$ $90$ $885 w$ $847 vvs(sh)$ $813 vs$ $81$ $803 vvs(vbr)$ $767 vvs(br)$ $75$ $685 s$ $666$ $667$		CC str. $B_1; v_{12b}$
1481 vs       1482 m       14         1456 vs       1458 w       14         1456 vs       1458 w       14         1448 vs(sh)       1448 w(sh)       14         1418 m(sh)       1408 vw       14         1383 m       1408 vw       14         1383 m       1378 w       13         1369 m       1260 vvw(br)       12         1265 w       1260 vvw(br)       12         1238 w(sh)       117 vvw       11         1205 m       1062 w       100         1045 s       1042 m       104         1003 m       1010 w(sh)       101         1029 vw       1026 m       102         1030 m       976 vvw       97         885 w       847 w(sh)       84         847 vvs(sh)       <		
1456 vs       1458 w       14         1448 vs(sh)       1448 w(sh)       14         1448 m(sh)       1408 vw       14         1383 m       1408 vw       14         1383 m       1369 m       1378 w       13         1369 m       1378 w       13       13         1319 vw       13       13       13       13         1265 w       1260 vvw(br)       12       12         1238 w(sh)       1279 s       12       14         1229 s       1229 s       12       14       14         1180 vw       1117 vvw       11       14       14       14         1065 m       1062 w       100       101       101         1029 vw       1026 m       100       101       101         1003 m       976 vvw       97       898 w       847 w(sh)       84         847 vvs(sh) <td>85 mw</td> <td>HCH bend, <math>B_2</math>; m<sub>8</sub></td>	85 mw	HCH bend, $B_2$ ; m <sub>8</sub>
1448 vs(sh)       1448 w(sh)       14         1418 m(sh)       1408 vw       14         1383 m       1369 m       1378 w       13         1369 m       1378 w       13       13         1369 m       1378 w       13       13         1346 w       13       13       13       13         1350 xw       120       13       13       13         1205 xw       1209 s       121       14       14         112 vw(sh)       1117 vvw       11       14       14       14       14         112 vw(sh)       1117 vvw       11       14       14       14       14       14         1065 m       1062 w       100       100       100       100       100       100         1003 m       976 vvw       97       898 w       90       885 w<	50 w	HCH bend, $B_1$ ; m <sub>5</sub>
1418 m(sh)       1408 vw       14         1383 m       1369 m       1378 w       13         1369 m       1378 w       13         1346 w       13       13         1319 vw       12       13         1265 w       1260 vvw(br)       12         1238 w(sh)       129 s       12         129 s       1229 s       12         1180 vw       1117 vvw       11         11065 m       1062 w       100         1045 s       1042 m       104         1003 m       1010 w(sh)       101         1003 m       976 vvw       97         898 w       90       885 w         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66	50 w	CC str., $A_1$ ; $v_{8a}$
1383 m       1369 m       1378 w       13         1369 m       1378 w       13         1346 w       13         1319 vw       13         1265 w       1260 vvw(br)       12         1238 w(sh)       129 s       12         1229 s       1229 s       12         1180 vw       1117 vvw       11         1065 m       1062 w       100         1065 m       1062 w       100         1029 vw       1026 m       100         1003 m       1010 w(sh)       100         1003 m       976 vvw       97         898 w       90       885 w         847 vvs(sh)       813 vs       81         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66         647 s       647       647	)9 vw	CC str., $B_1$ ; $v_{8b}$
1369 m       1378 w       13         1346 w       13         1346 w       13         1319 vw       13         1265 w       1260 vvw(br)       12         1238 w(sh)       12         1238 w(sh)       1229 s       12         1209 s       1229 s       12         1100 vw       111       111         1065 m       1062 w       100         1065 m       1062 w       100         1005 m       1062 m       100         1005 m       1062 m       100         1003 m       1010 w(sh)       100         978 w(sh)       976 vvw       97         898 w       90       885 w         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66         647 s       647       647		
1346 w       13         1319 vw       13         1265 w       1260 vvw(br)       12         1238 w(sh)       12         1238 w(sh)       1229 s       12         1238 w(sh)       1229 s       12         1209 s       1229 s       12         112 vw(sh)       1117 vvw       11         1065 m       1062 w       100         1065 m       1062 w       100         1005 m       1026 m       100         1003 m       1010 w(sh)       100         978 w(sh)       976 vvw       97         898 w       90       885 w         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66         647 s       647       647	78 w	HCH bend, $A_1$ ; m <sub>2</sub>
13       13         1319 vw       1265 w         1265 w       1260 vvw(br)       12         1238 w(sh)       1229 s       12         1238 w(sh)       1229 s       12         1229 s       1229 s       12         118 ww       111       111         112 vw(sh)       1117 vvw       111         1065 m       1062 w       100         1045 s       1042 m       100         1029 vw       1026 m       100         1003 m       1010 w(sh)       100         978 w(sh)       976 vvw       97         898 w       90       885 w         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66         647 s       647 s       647	55 vw(sh)	
1319 vw       1260 vvw(br)       12         1255 w       1260 vvw(br)       12         1238 w(sh)       1229 s       12         1229 s       1229 s       12         1180 vw       11       11         112 vw(sh)       1117 vvw       11         1065 m       1062 w       100         1045 s       1042 m       100         10029 vw       1026 m       100         1003 m       1010 w(sh)       100         978 w(sh)       976 vvw       97         898 w       90       885 w         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66         647 s       647       647	35 vw (sh)	
1265 w       1260 vvw(br)       12         1238 w(sh)       1229 s       12         1229 s       1229 s       12         1180 vw       1117 vvw       11         1112 vw(sh)       1117 vvw       11         1065 m       1062 w       100         1045 s       1042 m       100         1003 m       1010 w(sh)       100         1003 m       976 vvw       97         898 w       90       885 w         847 w(sh)       84       843 vs         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66		
1238 w(sh)       1229 s       12         1229 s       1229 s       12         1180 vw       11       11         1112 vw(sh)       1117 vvw       11         1065 m       1062 w       100         1045 s       1042 m       100         1029 vw       1026 m       100         1003 m       1010 w(sh)       100         978 w(sh)       976 vvw       97         898 w       90       885 w         847 w(sh)       84         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66	55 mw	CH bend, $B_1$ ; $v_4$
1229 s       1229 s       12         1180 vw       11         1112 vw(sh)       1117 vvw       11         1065 m       1062 w       100         1045 s       1042 m       100         1029 vw       1026 m       100         1003 m       1010 w(sh)       100         978 w(sh)       976 vvw       97         898 w       90         885 w       847 w(sh)       84         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66		· · · · · ·
1180 vw       11         1112 vw(sh)       1117 vvw       11         1065 m       1062 w       10         1045 s       1042 m       10         1029 vw       1026 m       10         1003 m       1010 w(sh)       10         978 w(sh)       976 vvw       97         898 w       90       885 w         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66	30 w	CMe str., $A_1$ , $v_0$ ,
1112 vw(sh)       1117 vvw       11         1065 m       1062 w       10         1045 s       1042 m       10         1029 vw       1026 m       10         1003 m       1010 w(sh)       10         978 w(sh)       976 vvw       97         898 w       90         885 w       847 w(sh)       84         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66         647 s       645       645	30 vw(br)	· 1· 34
1065 m       1062 w       10         1045 s       1042 m       10         1029 vw       1026 m       10         1003 m       1010 w(sh)       10         978 w(sh)       976 vvw       97         898 w       90         885 w       847 w(sh)       84         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66         647 s       635       635	l8 mw	CH bend, A. : Vion
1045 s       1042 m       10         1029 vw       1026 m       10         1003 m       1010 w(sh)       10         978 w(sh)       976 vvw       97         898 w       90         885 w       847 w(sh)       84         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66	55 m	CH bend, $B_1$ ; $y_{ch}$
1029 vw     1026 m     10       1003 m     1010 w(sh)     10       978 w(sh)     976 vvw     97       898 w     90       885 w     847 w(sh)       847 vvs(sh)     813 vs       803 vvs(vbr)     767 vvs(br)       7685 s     685       647 s     647	4 ms	<sup>*</sup> Ring breathing, A <sub>1</sub> : v <sub>2</sub>
1003 m 1010 w(sh) 10. 978 w(sh) 976 vvw 97 898 w 90 885 w 847 vvs(sh) 813 vs 81 803 vvs(vbr) 767 vvs(br) 75 685 s 65 647 s 65	28 ms	CMe wag. $B_2$ : m <sub>o</sub>
1003 m       1010 w(sh)       10         978 w(sh)       976 vvw       97         898 w       90         885 w       847 w(sh)       84         847 vvs(sh)       813 vs       81         803 vvs(vbr)       767 vvs(br)       75         685 s       66       66		CMe wag, B. : m.
978 w(sh) 976 vvw 9 898 w 90 885 w 847 vvs(sh) 84 803 vvs(vbr) 767 vvs(br) 75 685 s 65 647 s 65	0 w(sh)	CH bend. A. : V.
898 w       90         885 w       847 w(sh)         847 vvs(sh)       813 vs         803 vvs(vbr)       767 vvs(br)         685 s       66         647 s       63	7 vvw	CH bend. $A_1$ : $v_2$ .
885 w           847 w(sh)         84           847 vvs(sh)         813 vs           803 vvs(vbr)         767 vvs(br)         75           685 s         66           647 s         63	I vw(sh)	
847 w(sh)         84           847 vvs(sh)         813 vs         81           803 vvs(vbr)         767 vvs(br)         75           685 s         66         66		UC bend, $B_1$ ; $v_{13b}$
847 vvs(sh)         813 vs         81           803 vvs(vbr)         767 vvs(br)         75           685 s         66         66	.8 mw	CC bend 4. * »
803 vvs(vbr) 767 vvs(br) 75 685 s 667 s 65	1 vs	CH hend $A_1$ , $v_{13a}$
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203 VS		

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# DERIVATIVES OF DIVALENT GERMANIUM, TIN AND LEAD. IV

The observed infrared spectrum of the complex, taken as a liquid film, is listed in Table 1, together with the previously measured spectrum of  $(I)^1$ . The assignment of the normal modes of the latter was accomplished by the application of the inequality rule of Whiffen and Steele<sup>15</sup> to the spectrum of the unsubstituted compound, dicyclopentadienyltin, together with Raman polarisation data<sup>1</sup>. In the present case, the complex fluoresced strongly in the laser beam, and a Raman spectrum could not be obtained. However, direct comparison with the spectrum of (I) using the principal of "local" symmetry greatly simplifies the assignment of the spectrum of (II).

Although the overall symmetry for the molecule will be  $C_2$ , using "local" symmetry, the rings, assumed to a first approximation to be equivalent, will belong to the  $C_{2c}$  point group if the methyl group be treated as a point mass. To a large extent, the assignment of the ring fundamentals follows directly from those of (I) and requires no further comment. The frequency numbers (v, m) noted in Table 1 refer to those used previously for the assignment of (I)<sup>1</sup>.

Assuming "local"  $C_{3\nu}$  symmetry for the AlCl<sub>3</sub> moiety, four normal modes  $(2A_1 + 2E)$  are expected from group theoretical considerations. Of these, two  $(A_1 + E)$  will refer to Al-Cl stretching and two to Al-Cl bending modes. The two stretching modes are readily identified as very strong, broad bands at 493 and 442 cm<sup>-1</sup>. The strong band at 327 cm<sup>-1</sup> is probably largely the  $A_1$  bending mode, although a ring CMe in-plane bending mode is expected to occur in a similar position. The  $E_1$  Al-Cl bending mode occurs below 250 cm<sup>-1</sup>, outside the range of this study, as do most of the skeletal modes involving the tin atom. However, the very strong band at 265 cm<sup>-1</sup> may be assigned to the antisymmetric tin-ring stretching mode. This mode occurs at 237 cm<sup>-1</sup> in (I), and its shift to high frequency is probably indicative of coupling between the tin-ring fundamentals and the Al-Cl stretching modes, which also differ significantly from those in complexes of aluminium trichloride with oxygen, sulphur<sup>16</sup> and nitrogen<sup>17</sup> donor ligands. In Table 2 are listed the skeletal modes of (II) together with the analogous vibrations in similar compounds.

No information concerning the position of the Al–Sn stretching vibration is available. However, it should occur close to the Si–Sn stretching vibration, which in (trimethylsilyl)trimethyltin is located at  $322 \text{ cm}^{-118}$ . In (II), the metal–metal stretching vibration is probably masked by the Al–Cl bending mode at  $327 \text{ cm}^{-1}$ .

In the region 620-700 cm<sup>-1</sup> there occur three bands of significantly intensity which can be assigned to neither ring modes nor skeletal modes of the Ring<sub>2</sub>Sn AlCl<sub>3</sub> framework. Parker and Stiddard<sup>19</sup> observed similar extra bands in the spectrum of



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 $[MeC_5H_4Fe(CO)_3]_2$ . Since they disappeared in solution, they were not assigned as fundamentals, and were rationalised as either (i) combination bands involving modes of the  $[Fe(CO)_2]_2$  moiety or Ring-Fe stretching vibrations, or (ii) bands resulting from interaction between the CH out-of-plane bending motions of the ring and the rest of the molecule. In view of the bulkiness of the AlCl<sub>3</sub> residue, the latter explanation is quite reasonable in the present case.

The infrared spectrum of the adduct (II) is, therefore, consistent with the structure formulated in Fig. 1, in which the "sandwich", centrally  $\sigma$ -bonded character of the methylcyclopentadienyl rings is retained. Investigations into the chemistry of this novel aluminium-tin bonded compound are continuing in this laboratory.

Also listed in Table 1 are the observed infrared bands of bis(methylcyclopentadienyl)lead<sup>12</sup> as a liquid film. The obvious similarity of the spectra of this compound and (I) leads us to conclude that the two compounds are isostructural in the liquid phase. Dicyclopentadienyllead on the other hand, although known to possess the angular "sandwich" structure in the vapour phase<sup>10</sup>, in the condensed phase (crystal) has a structure consisting of zig-zag chains in which the lead atoms alternate with cyclopentadienyl rings, equidistant from two lead atoms [r(Pb-C) 3.06 Å]. Each lead atom is further bonded to a third cyclopentadienyl ring at a closer distance [r(Pb-C) 2.76 Å]. In the solid therefore, the coordination number of each lead atom is raised to three<sup>20</sup>.

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