Journal of Organometallic Chemistry, 365 (1989) 37–46
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09603

π-Bonding to tetravalent main-group IV elements; an experimental effort *

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(Received July 29th, 1988)

Abstract

$Ph_5C_5GeCl_3$ (**1**) and $Ph_5C_5SnCl_3$ (**2**) have been synthesized by oxidative addition of Ph_5C_5Cl to $GeCl_2$ or $SnCl_2$, respectively, and were characterized by ^{13}C NMR and mass spectroscopy. Both compounds are fluxional in solution. The crystal structure of $\mathbf{1} \cdot 0.5Et_2O$ has been determined. $\mathbf{1} \cdot 0.5Et_2O$ crystallizes in the space group $C2/c$ with a 21.988(4), b 15.484(4), c 19.913(3) Å, β 111.411(14)°, V 6312(4) Å^3, and $Z = 8$. Solution of the structure led to final values of $R = 0.0303$ ($R_w = 0.0395$) for 4989 observed reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$. The germanium is σ-bonded to the pentaphenylcyclopentadienyl ligand.

Introduction

π-Complexes and π-bonding have been of major interest in organo-transition metal chemistry. On the other hand, main-group organometallic chemistry has been mainly concerned with σ-bonded organoelement derivatives, e.g. silicones, lead alkyls, aluminum and tin organyls, because of the industrial use of these compounds [1,2].

The interest in π-complexes of main group elements, especially of group III and IV, has grown steadily during the last decade, and such complexes now form a well established class of compounds [3]. However, examples of π-complexes of the heaviest main group III element (Tl), all group IV and V elements (Si, Ge, Sn, Pb, and As, Sb, Bi, respectively) are limited to the formal low-valent +1 (Tl), as well as +2 (Si-Pb) or +3 (As-Bi) oxidation state, i.e. to electronic s^2-species with a free electron pair.

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* In memoriam Professor Dr. Jerold J. Zuckerman.

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0022-328X/89/$03.50

So far, only boron, aluminum, gallium and indium are known to exhibit π-bonding in their high-valent, +3, oxidation state [3], examples being: $[(\eta^5\text{-Me}_5C_5)B^{III}R,\text{Hal}]^+[B,AlHal_4]^-$ [4,5], $[(\eta^3\text{-Me}_5C_5)Al^{III}(CH_3)(\mu\text{-Cl})]_2$ [6], $[(CH_3)_2Ga^{III}(\mu\text{-}C{\equiv}CPh)]_2$ [7], $(R_2Ga^{III}(\mu\text{-}C_5H_5)]_\infty$ [8], $[(CH_3)_2In^{III}(\mu\text{-}C{\equiv}CCH_3)]_\infty$ [9], and $[(CH_3)_2In^{III}(\mu\text{-}C_5H_5)_3]_\infty$ [10].

No π-complexes of Tl^{III}, Ge^{IV}, Sn^{IV}, Pb^{IV}, As^V, Sb^V, or Bi^V have yet been conclusively identified [3]. Known compounds of these elements with π ligands, e.g. cyclopentadienyl, prove to be η^1-bonded and highly fluxional [11]. Compounds like $(C_5H_5)ER_3$ (E = Si, Ge, Sn, Pb) and also many B^{III}, Al^{III}, Ga^{III}, In^{III}, As^{III}, Sb^{III}, and Bi^{III} compounds of the type $C_5H_5ER_2$ give fast 1,2-element shifts (metallotropic rearrangement) with estimated activation energies lower than 5 kcal/mol [11*].

However, some theoretical studies show that η^1-, η^2- and η^5-structures may be very close in energy [12]. Reference 11 discusses and describes the effects of substituents at the E center and at the cyclopentadienyl ring on the migration rate and activation energy.

In our project, we attempted the synthesis of a π-bonded E^{IV} (E = Si, Ge, Sn, Pb) species. The pentaphenylcyclopentadienyl ligand, Ph_5C_5, was considered a good candidate to achieve our aim, since its steric constraints [13] together with the electron withdrawal by the phenyl groups [14] should have substantial effects on the η^1-ground state. These effects might lead to η^5-coordination for the Ph_5C_5 ligand.

Results and discussion

The synthesis of pentaphenylcyclopentadienylelement(IV) trichloride (E = Ge (**1**), Sn (**2**)) was carried out by oxidative addition of the pentaphenylcyclopentadienyl chloride [15] to germanium dichloride(dioxane) or tin dichloride in tetrahydrofuran (thf) at room temperature (eq. 1).

$$Ph_5C_5Cl + ECl_2 \xrightarrow{\text{thf}} Ph_5C_5ECl_3 \qquad (1)$$

(E = Ge (**1**), Sn (**2**))

This reaction proceeds in reasonable yield (52% for **1** or 45% for **2**). Recrystallization from diethyl ether gives **1** as yellow platelets and **2** as red needles ($Me_5C_5SnCl_3$ also shows an intense red color [16]). Both compounds are air stable and freely soluble in thf, $CHCl_3$, and CH_2Cl_2, less so in diethyl ether. Insertion reactions of divalent germanium and tin species into carbon–halogen bonds have been well documented [17,18].

Nuclear magnetic resonance

Owing to the nature of the ligand involved, proton NMR studies are not very helpful. Thus, carbon-13 NMR is the primary source of information concerning the mode of Cp–Ge/Sn interaction in solution. While Ph_5C_5Cl shows 17 different carbon signals, in agreement with the different number of carbon atoms seen in this compound, only 4 carbon signals are observed for **1** and **2** at ambient temperature

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* Reference numbers with asterisks indicate notes in the list of references.

(ca. 40 °C). These signals correspond to four different types of phenyl carbon atoms. No peak can be found for the cyclopentadienyl carbons in either complex. This observation may result from either one of two causes: (i) the relaxation time is very slow and saturation with loss of the signal is reached after a short time or (ii) due to a ligand exchange the signal is broadened and lost in the base line. The recording of just one signal for the *ortho*- or *meta*-phenyl carbons is also unexpected, since the *o/m* phenyl carbons on the side of the ECl_3 moiety should be different from the ones on the reverse side of the cyclopentadienyl ring plane. Thus free rotation of the phenyl groups around the Ph–C_5 bond must be assumed. An intermolecular exchange of the Ph_5C_5 ligands, however, seems unlikely because the observation of Sn-quaternary and *ortho*-phenyl carbon coupling [19]. At low temperature (−75 °C) no additional peaks were detected in the ^{13}C-spectrum for **2**. However, the spectrum of the germanium analogue approaches the expected richness at −75 °C with 11 peaks clearly resolvable. Rigidity of **1** upon cooling is in good agreement with the higher activation energy measured for the 1,2-metallotropic rearrangement of germanium versus tin [11*].

X-ray structure of 1

Atomic coordinates for **1** · $0.5Et_2O$ are listed in Table 2. Figure 1 shows an ORTEP plot of a molecule of **1** with the employed numbering scheme. Bond distances and angles are summarized in Tables 3 and 4. The X-ray structure analysis

Table 1

Crystal and Data Collection Parameters for **1**·$0.5et_2O$

Formula	$C_{37}H_{30}Cl_3GeO_{0.5}$
MW, amu	661.5
a, Å	21.988(4)
b, Å	15.484(4)
c, Å	19.913(3)
β, °	111.411(14)
V, Å³	6312(4)
Space group	*C*2/*c*, no. 15
Z	8
μ, cm^{-1}	12.39
d_o, g/cm³	1.38
d_c, g/cm³	1.39
Total data collected	14479
	h: −28 → 28
	k: 0 → 20
	l: −25 → 25
Unique data	7246
$R_{ave(I)}$	0.034
observed data, $F_o^2 \geq 3\sigma(F_o^2)$	4989
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.0303
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.0395
$w = 1/[\sigma(F_o)]^2 = 4F_o^2/[\sigma(F_o^2)]^2$	
$\sigma(F_o^2) = \sqrt{[\sigma(I)]^2 + [pF_o^2]^2}$, $p = 0.034$	
goodness of fit	1.233
no. of parameters	376

Table 2

Non-hydrogen positional parameters for **1**·0.5et$_2$O [a,b]

Atom	x	y	z	B(eq) (Å^2)
Ge	0.21709(1)	0.12418(2)	0.12275(1)	1.653(4)
Cl1	0.26909(3)	0.14828(4)	0.05334(3)	2.36(1)
Cl2	0.12657(3)	0.06882(4)	0.05516(3)	2.24(1)
Cl3	0.26952(3)	0.02385(4)	0.19419(3)	2.81(1)
O1	0.500	−0.0453(3)	0.250	6.4(1) [c]
C1	0.2085(1)	0.2252(2)	0.1791(1)	1.50(4)
C2	0.2782(1)	0.2508(2)	0.2251(1)	1.58(4)
C3	0.2893(1)	0.2303(1)	0.2947(1)	1.48(4)
C4	0.2299(1)	0.1910(2)	0.3000(1)	1.48(4)
C5	0.1824(1)	0.1877(1)	0.2236(1)	1.49(4)
C6	0.4595(2)	−0.0937(4)	0.1918(2)	7.0(1)
C7	0.4243(3)	−0.0382(5)	0.1309(3)	10.4(2)
C11	0.1678(1)	0.2984(2)	0.1335(1)	1.57(4)
C12	0.1533(1)	0.3666(2)	0.1710(1)	2.15(5)
C13	0.1174(1)	0.4367(2)	0.1347(1)	2.65(6)
C14	0.0962(1)	0.4402(2)	0.0603(2)	2.66(6)
C15	0.1107(1)	0.3739(2)	0.0228(1)	2.34(5)
C16	0.1462(1)	0.3029(2)	0.0590(1)	1.92(5)
C21	0.3260(1)	0.2845(2)	0.1951(1)	1.72(5)
C22	0.3831(1)	0.2372(2)	0.2064(1)	2.42(5)
C23	0.4269(1)	0.2644(2)	0.1746(1)	2.97(6)
C24	0.4142(1)	0.3376(2)	0.1325(1)	2.85(6)
C25	0.3585(1)	0.3859(2)	0.1222(1)	2.59(5)
C26	0.3145(1)	0.3590(2)	0.1531(1)	2.04(5)
C31	0.3508(1)	0.2481(2)	0.3560(1)	1.56(4)
C32	0.3745(1)	0.3324(2)	0.3699(1)	1.93(5)
C33	0.4334(1)	0.3493(2)	0.4255(1)	2.43(5)
C34	0.4692(1)	0.2833(2)	0.4681(1)	2.49(6)
C35	0.4460(1)	0.2001(2)	0.4549(1)	3.05(6)
C36	0.3869(1)	0.1827(2)	0.3995(1)	2.52(6)
C41	0.2225(1)	0.1651(2)	0.3681(1)	1.67(4)
C42	0.2525(1)	0.0918(2)	0.4055(1)	2.71(6)
C43	0.2458(2)	0.0696(2)	0.4702(2)	3.56(7)
C44	0.2089(1)	0.1197(2)	0.4972(1)	3.41(6)
C45	0.1784(1)	0.1928(2)	0.4606(1)	3.10(6)
C46	0.1848(1)	0.2153(2)	0.3960(1)	2.34(5)
C51	0.1172(1)	0.1460(2)	0.2121(1)	1.62(4)
C52	0.1136(1)	0.0588(2)	0.2291(1)	2.21(5)
C53	0.0548(1)	0.0157(2)	0.2044(1)	2.70(6)
C54	−0.0014(1)	0.0579(2)	0.1633(1)	3.16(6)
C55	0.0005(1)	0.1446(2)	0.1477(1)	3.05(6)
C56	0.0598(1)	0.1886(2)	0.1721(1)	2.33(5)

[a] Estimated standard deviations of the last significant figure are given in parentheses in this and all subsequent tables. [b] The isotropic equivalent thermal parameter B(eq) is defined as: $(4/3)[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$, where a, b and c are real cell parameter and $\beta(i,j)$ are anisotropic β. [c] 01 occupies a special position on the twofold axis (Wyckoff position e).

shows a somewhat distorted tetrahedral enviroment around Ge and C1 with angles around Ge from 105.07(2)° to 114.61(6)° and angles around C1 from 104.1(1)° to 114.8(2)°. The Ge–C1 distance (1.975(2) Å) agrees well with the sum of the covalent

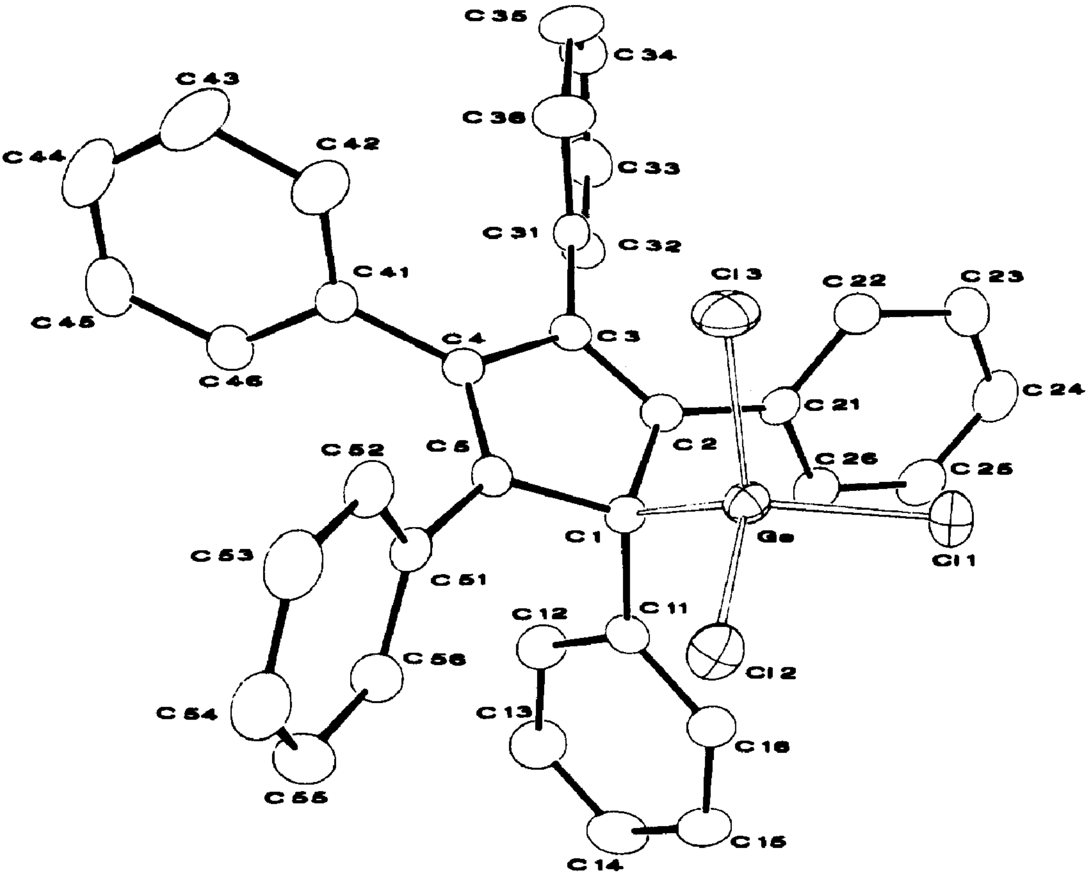

Fig. 1. ORTEP plot of one molecule **1**. The 1/2 ether molecule per asymmetric unit was omitted for clarity.

Table 3

Bond distances [Å] in **1**·0.5et$_2$O

Atom 1 Atom 2	Distance	Atom 1 Atom 2	Distance	Atom 1 Atom 2	Distance
Ge–Cl1	2.1240(6)	C6–C7	1.456(6)	C33–C34	1.376(3)
Ge–Cl2	2.1335(6)	C11–C12	1.397(3)	C34–C35	1.376(4)
Ge–Cl3	2.1374(6)	C11–C16	1.383(3)	C35–C36	1.389(3)
Ge–C1	1.975(2)	C12–C13	1.381(3)	C41–C42	1.387(3)
O1–C6	1.395(5)	C13–C14	1.382(4)	C41–C46	1.391(3)
O1–C6	1.395(5)	C14–C15	1.374(4)	C42–C43	1.392(4)
C1–C2	1.522(3)	C15–C16	1.387(3)	C43–C44	1.368(4)
C1–C5	1.517(3)	C21–C22	1.399(3)	C44–C45	1.380(4)
C1–C11	1.522(3)	C21–C26	1.393(3)	C45–C46	1.390(3)
C2–C3	1.354(3)	C22–C23	1.397(3)	C51–C52	1.401(3)
C2–C21	1.481(3)	C23–C24	1.376(4)	C51–C56	1.389(3)
C3–C4	1.480(3)	C24–C25	1.385(4)	C52–C53	1.377(3)
C3–C31	1.480(3)	C25–C26	1.387(3)	C53–C54	1.374(4)
C4–C5	1.353(3)	C31–C32	1.396(3)	C54–C55	1.381(4)
C4–C41	1.478(3)	C31–C36	1.379(3)	C55–C56	1.391(3)
C5–C51	1.485(3)	C32–C33	1.388(3)		

Table 4

Bond angles [°] in **1**·0.5Et_2O

Atom 1–2–3	Angle	Atom 1–2–3	Angle	Atom 1–2–3	Angle
Cl1–Ge–Cl2	105.07(2)	C1–C5–C4	109.0(2)	C32–C31–C36	118.3(2)
Cl1–Ge–Cl3	105.85(3)	C1–C5–C51	122.5(2)	C31–C32–C33	120.4(2)
Cl1–Ge–C1	114.61(6)	C4–C5–C51	128.1(2)	C32–C33–C34	120.6(2)
Cl2–Ge–Cl3	106.27(3)	O1–C6–C7	111.0(5)	C33–C34–C35	119.3(2)
Cl2–Ge–C1	114.61(6)	C1–C11–C12	116.3(2)	C34–C35–C36	120.5(2)
Cl3–Ge–C1	109.74(6)	C1–C11b1C16	125.2(2)	C31–C36–C35	120.9(2)
C6–O1–C6	115.0(5)′^{a}	C12–C11–C16	118.5(2)	C4–C41–C42	121.7(2)
Ge–C1–C2	105.3(1)	C11–C12–C13	120.9(2)	C4–C41–C46	119.7(2)
Ge–C1–C5	104.1(1)	C12–C13–C14	119.8(2)	C42–C41–C46	118.6(2)
Ge–C1–C11	114.0(1)	C13–C14–C15	119.9(2)	C41–C42–C43	120.6(2)
C2–C1–C5	103.3(2)	C14–C15–C16	120.5(2)	C42–C43–C44	120.2(3)
C2–C1–C11	114.1(2)	C11–C16–C15	120.4(2)	C43–C44–C45	120.0(2)
C5–C1–C11	114.8(2)	C2–C21–C22	118.6(2)	C44–C45–C46	120.1(2)
C1–C2–C3	108.7(2)	C2–C21–C26	122.2(2)	C41–C46–C45	120.4(2)
C1–C2–C21	123.8(2)	C22–C21–C26	119.1(2)	C5–C51–C52	118.9(2)
C3–C2–C21	127.2(2)	C21–C22–C23	119.7(2)	C5–C51–C56	122.6(2)
C2–C3–C4	109.6(2)	C22–C23–C24	120.3(2)	C52–C51–C56	118.4(2)
C2–C3–C31	124.7(2)	C23–C24–C25	120.4(2)	C51–C52–C53	120.6(2)
C4–C3–C31	125.6(2)	C24–C25–C26	119.6(2)	C52–C53–C54	120.4(2)
C3–C4–C5	109.4(2)	C21–C26–C25	120.8(2)	C53–C54–C5	120.1(2)
C3–C4–C41	124.9(2)	C3–C31–C32	120.0(2)	C54–C55–C56	119.9(2)
C5–C4–C41	125.5(2)	C3–C31–C36	121.7(2)	C51–C56–C55	120.5(2)

[a] Primed atoms represent transformed coordinates of the type $1-x$, y, $1/2-z$.

radii (1.99 Å). The cyclopentadienyl ring is planar and σ-bonded. The least-squares planes of the phenyl rings are tilted by 57.3(1)° to 85.76(8)° against the cyclopentadienyl plane, with the C1-bonded phenyl ring being almost perpendicular. The different C–C distances within the Cp-ring show the localized double bonds (C2–C3, C4–C5). The $GeCl_3$ moiety is bonded in an allylic position, as could be expected from NMR-investigations of $C_5H_5ER_3$ compounds [11*].

While **1** failed to exhibit the hoped for π-bonding in the solid state, the situtation might still be different in **2**, where the intense red color already indicates a different electronic situation.

Experimental section

All manipulations were carried out in a nitrogen atmosphere using standard Schlenk and vacuum techniques and dried solvents.

Pentaphenylcyclopentadienyl chloride

The synthesis was carried out according to lit. 15 by passing gaseous hydrogen chloride through a refluxing solution of pentaphenylcyclopentadienol in glacial acetic acid for 1 h. The product was obtained as a yellow precipitate after the solution was allowed to cool to room temperature. After washing with dilute acetic acid and water, Ph_5C_5Cl was dried in vacuo at elevated temperature to remove residual acetic acid and water (mp. 165–166 °C, lit. [15] 157 °C). ^{13}C-NMR [20]

($CDCl_3$, conc. 105 mg/ml): δ (ppm) 81.83 (C_5–*C*Cl), 126.35 (*para*-Ph–C), 127.12, 127.20, and 128.42 (*ortho, meta-, para*-Ph–CCl–C), 127.47, 127.76 (*meta*-Ph–C), 129.97, 130.13 (*ortho*-Ph–C), 133.82, 134.57 (quaternary-Ph–C), 136.36 (quaternary-Ph–CCl–C), 142.58, 147.97 (quaternary-C_5–C).

Pentaphenylcyclopentadienylgermanium trichloride, 1

An orange-yellow solution of Ph_5C_5Cl (2.08 g, 4.32 mmol) in 25 ml of tetrahydrofuran is added dropwise to a colorless solution of $GeCl_2$(dioxane) (1.00 g, 4.32 mmol) in 10 ml of thf at room temperature. Soon, a clear red solution is obtained. After complete addition of the Ph_5C_5Cl solution stirring is continued for one more hour. The solution is then concentrated to about 15–20 ml and carefully overlayered with 40 ml of hexane. Only a small amount of minute orange crystals (which were discarded) forms upon diffusion of hexane into thf. After two days, the clear and red solution was decanted. Decolorization ocurred to give a yellow solution (suggesting that the red color might have been due to traces of the stable pentaphenylcyclopentadienyl radical [16]). However, the decanting served as initiation for the spontaneous growth of a large amount of yellow, needle shaped crystals. Cooling and carefully concentrating in vacuo increases the yield. Recrystallization from diethyl ether gives bright yellow platelets (the crystals contain half a molecule of $(C_2H_5)_2O$ per $Ph_5C_5GeCl_3$) (yield 1.55 g, 52%; mp. softening at 140 °C).

^1H NMR [21*] ($CDCl_3$, saturated solution): δ (ppm) 7.14 (narrow multiplet, Ph–H); (thf-d_8, saturated): δ (ppm) 7.12 (s, Ph–H).

^{13}C NMR [20*] ($CDCl_3$, saturated solution, T 40 °C): δ (ppm) 127.57 (*para*-Ph–C), 127.91 (*meta*-Ph–C), 130.08 (*ortho*-Ph–C), 134.05 (C_5–C); (thf-d_8, saturated): δ (ppm) 128.44 (*para*-Ph–C), 128.70 (*meta*-Ph–C), 130.99 (*ortho*-Ph–C), 133.05 (C_5–C); (dmso-d_6, saturated, T 85 °C): δ (ppm) 126.84 (*para*-Ph–C), 127.32 (*meta*-Ph–C), 129.57 (*ortho*-Ph–C), 134.23 (C_5–C); (CD_2Cl_2, conc. 12 mg/ml, T −75 °C): δ (ppm) 65.82 (C_5–*C*–$GeCl_3$), 127.11 (*para*-Ph–C), 127.36 (*meta*-Ph–C), 128.53 (*ortho*-Ph–$CGeCl_3$–C), 129.39, 129.85 (splitted), 130.32 (*ortho*-Ph–C), 133.28, 134.16 (quaternary-Ph–C), 140.42, 149.40 (quaternary-C_5–C); the quaternary-Ph–$CGeCl_3$-carbon signal was not clearly visible, due to the spectrum quality.

MS [22*] (70 eV, 150 °C): $m/e = 624$ (2.4%) $[Ph_5C_5\,^{74}Ge^{35}Cl_3]^+ = M^+$ (isotopic pattern clearly visible), 446 (15) $[Ph_5C_5H]^+$, or $[Ph_5C_5]^+$ with one ^{13}C, 445 (32) $[Ph_5C]^+$, 367 (15) $[Ph_5C_5 - PhH]^+$, 289 (11) $[Ph_5C_5 - 2\ PhH]^+$, 265 (7) $[Ph_5C_5 - 2\ PhH - C_2]^+$, 167 (9) $C_{13}H_{11}]^+$, 74 (62) $[(C_2H_5)_2O]^+$, 59 (100) $[C_2H_5OCH_2]^+$, 45 (73) $[C_2H_5O]^+$. Analysis Found: C, 68.64; H, 4.63; Ge, 9.48%. $C_{35}H_{25}GeCl_3(C_4H_{10}O)_{0.5}$ (661.59); calc.: C, 67.17; H, 4.57; Ge, 10.97%.

Due to the solvent in the crystal lattice, correct elemental analyses are difficult to obtain. Prolonged drying of crystals of **1** · $0.5Et_2O$ leads to the solvent-free, noncrystalline material, while a short drying period gives crystals of **1** which still contain diethyl ether on the surface.

Pentaphenylcyclopentadienyltin trichloride, 2

An orange-yellow solution of Ph_5C_5Cl (3.04 g, 6.33 mmol) in 25 ml of thf is added dropwise to a colorless solution of $SnCl_2$ (1.20 g, 6.3 mmol) in 10 ml thf at room temperature. After a few drops a red color develops and in the end a clear wine-red solution is obtained. Stirring is continued for one more hour. The solution was concentrated to 15–20 ml and overlayered with hexane. After 2 days a small amount of minute, orange crystals is obtained. Decanting and ice cooling of the red thf/hexane mixture produces some more of the small orange and some larger white crystals ($SnCl_2$). The wine-red thf/hexane mixture is decanted again and the solvent removed completely in vacuo. The solid red residue is recrystallized from diethyl ether through ice cooling to give red needle shaped crystals (containing the ether as a coordinated solvent) (yield 2.00 g, 45%; mp. 175–180 °C, dec.).

^1H NMR [21*] ($CDCl_3$, conc. 130 mg/ml): δ (ppm) 7.00–7.25 (broad multiplet, Ph–H).

^{13}C NMR [20*] ($CDCl_3$, conc. 130 mg/ml, T 40 °C): δ (ppm) 127.76 (*para*-Ph–C), 128.15 (*meta*-Ph–C), 130.37 (*ortho*-Ph–C, $^3J(^{117,119}Sn,^{13}C)$ 34.5 Hz), 133.34 (quaternary-Ph–C, $^2J(^{117,119}Sn,^{13}C)$ 23.2 Hz). (CD_2Cl_2, conc. 67 mg/ml, T −75 °C): δ (ppm) 127.58, 127.82, 129.75, 132.35; assignments, see above; at −75 °C the intensity of the tertiary-Ph-carbons is lowered relative to quaternary-Ph–C and compared to the 40 °-spectra.

MS [22*] (70 eV, 180 °C): m/e (%) = 670 (1%) $[Ph_5C_5^{120}Sn^{35}Cl]^+ = M^+$ (isotopic pattern clearly visible), 480 (27) $[Ph_5C_5{}^{35}Cl]^+$, 446 (100) $[Ph_5C_5H]^+$ or $[Ph_5C_5]^+$ with one ^{13}C, 445 (80) $[Ph_5C_5]^+$, 367 (42) $[Ph_5C_5 - PhH]^+$, 289 (32) $[Ph_5C_5 - 2\ PhH]^+$, 267/265 (14/17) $[Ph_5C_5 - 2\ Ph - C]^+$, 225 (16) $[^{120}Sn^{35}Cl_3]^+$, 190 (4) $[^{120}Sn^{35}Cl_2]^+$, 167 (18) $[C_{13}H_{11}]^+$, 120 (3) $[^{120}Sn]^+$. Analysis Found: C, 62.78; H, 3.90; Sn, 16.79. $C_{35}H_{25}SnCl_3(C_4H_{10}O)_{1/2}$ (707.69); calc.: C, 62.79; H, 4.27; Sn, 16.77%.

Reaction of Ph_5C_5Cl/Br with $PbCl_2/Br_2$

Using similar reaction condition as for **1** or **2** (stirring for five days) failed to give an oxidative addition reaction. The insoluble lead(II) halides did not dissolve upon addition of pentaphenylcyclopentadienyl chloride or bromide and both starting materials were recovered unchanged.

X-Ray structure analysis

A pale yellow crystal of **1** · $0.5Et_2O$ with the dimensions 0.43 × 0.28 × 0.18 mm was mounted on an automatic CAD-4 single crystal diffractometer. The crystal system was found to be monoclinic. Final cell parameters were obtained by least-squares refinement of the angular settings of 24 reflections well separated throughout reciprocal space (2θ-range 27.3 to 31.5 °). Applying θ–2θ scan techniques and Mo-K_α radiation all intensity data $\pm h$, k, $\pm l$ were collected at −100 °C in 2θ-range $2° \leq 2\theta \leq 55°$. The intensities of three standard reflections, [(8, −2, −13), (−3, −5, −10), (−9,3,12)] were remeasured every 2 h of X-ray exposure time. Three orientation check reflections were remeasured after each 200 intensity measurements. A new orientation matrix was calculated from an array of 24 reflections if any of the orientation standards was offset from its predicted position by more than 0.1°. Reorientation was necessary ten times during data collection. Azimuthal scans were recorded at the end of the data collection for 5 reflections near χ 90 °. Final crystal and data collection details are summerized in Table 1 [23*].

The raw intensity data were converted into structure factor amplitudes (and their e.s.d.'s) by correcting for scan speed, background, Lorentz and polarization effects [24]. Inspection of the list of intensity standards revealed that no correction for decay was necessary (maximum loss of 0.8% over the 184.3 h of X-ray exposure time). The azimuthal scan data showed a variation of ±13.9% for the average curve. An emperical absorption correction was applied (maximum and minimum correction factors: 0.9998, 0.9284).

The systematic extinctions (hkl, $h+k=2n+1$, $h0l$, $l=2n+1$) made the space groups Cc and $C2/c$ possible choices. The latter one was shown by the structure solution and refinement to be the correct choice. Systematically absent reflections were removed from the dataset and redundant data were averaged leaving 7246 unique data.

A three-dimensional Patterson map revealed the position of the germanium atom. Subsequent Fourier analyses and least-squares refinements showed the positions of all non-hydrogen atoms (structure solution and refinement was carried out with the SDP programm package [24]; atomic scattering factors are from ref. 25, scattering factors for all non-hydrogen atoms were corrected for both the real and imaginary contribution of anonmalous dispersion [26]). A difference Fourier map calculated after refinement of all non-hydrogen atoms revealed all hydrogen positions. All hydrogen atoms were added to the structure model at calculated positions (d(C–H) 0.95 Å) with fixed isotropic temperature factors 1.3 times the magnitude of the B(eq) of the parent atom.

The maximum shift/e.s.d. in the final cycle of refinement was 0.03. A difference Fourier map calculated from the final structure factors showed a maximum of 0.533 e/Å^3 located in the vicinity of the Ge atom.

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