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Diselenastanna-, -sila- and -carbacycles with an annelated dicarba-*closo*-dodecaborane(12) unit

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The reactions of the 1,2-diselenolato-1,2-dicarba-*closo*-dodecaborane(12) dianion 1 with diorganoelement(IV) dichlorides (Ph_2CCl_2, Me_2SiCl_2, Ph_2SiCl_2, Me_2SnCl_2, Ph_2SnCl_2) gave novel five-member heterocycles along with other products. The molecular structures of the five-member rings containing CPh_2 (2) and $SnPh_2$ (9) moieties between the selenium atoms were determined by X-ray analyses. In the case of the chlorosilanes, the analogous five-member ring containing the $SiPh_2$ unit (4) could be identified in mixtures. The expected reaction was accompanied by rearrangement leading to formation of another five-member ring 6 containing the Ph_2Si–Se–Se moiety. Oxidative addition of the five-member heterocycles containing tin (7, 9) to ethene-bis(triphenylphosphane)platinum(0) gave at low temperature the bis(triphenylphosphane)platinum(II) complexes 12 and 13, where the $Pt(PPh_3)_2$ fragment had been inserted into one of the Sn–Se bonds. Extensive decomposition of these complexes was observed above −20 °C. The proposed solution-state structures of the new compounds are supported by multinuclear magnetic resonance data (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{31}P, ^{77}Se, ^{119}Sn and ^{195}Pt NMR). Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: carborane; selenium; silicon; tin; platinum; NMR; X-ray

INTRODUCTION

After more than four decades of extensive studies of 1,2-dicarba-*closo*-dodecaborane(12) (‘*ortho*-carborane’) and its isomers, the chemistry of carborane-derived metal complexes[1–5] and the variation of substituents at the carbon atoms in the 1,2-positions[6–16] has been most rewarding and is still a highly attractive area of research. The chemistry usually starts with metalation at the carbon atom(s), e.g. to the dilithiated carborane $1,2\text{-}Li_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, by which useful precursors for further transformations become available. There is considerable interest in 1,2-dichalcogenolato-1,2-dicarba-*closo*-dodecaborane(12) anions $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})E_2]^{2-}$ (E = S, Se, Te) as chelating ligands in transition metal compounds,[17–35] including novel cluster-type complexes.[36–48] In contrast to E = Te,[49–50] these dianions are readily accessible for E = S and Se by insertion of the chalcogen into the C–Li bonds. The dianion $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})Se_2]^{2-}$, **1**, is particularly attractive considering the useful NMR properties of ^{77}Se (spin I = 1/2; natural abundance 7.58%; about three times more sensitive than ^{13}C).[51–53] In the present work we focus for the first time on applications of this dianion **1** on main group chemistry with emphasis on five-member heterocycles, where a Group 14 element such as carbon, silicon or tin is placed between the selenium atoms.

RESULTS AND DISCUSSION

The dianion $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})Se_2]^{2-}$ **1** reacts with diorganoelement dichlorides as shown in Scheme 1. It should be noted that the complete and defined dilithiation of the *ortho*-carborane is not possible owing to an equilibrium with the mono-lithiated species and the unreacted *ortho*-carborane.[11,12] Reasonable yields (>70%) could be obtained in the reaction of **1** with Ph_2SnCl_2, where pure samples of **9** were isolated and recrystallized for X-ray analysis. The reaction of **1** with Me_2SnCl_2 towards **7** and **8** was similarly straightforward;

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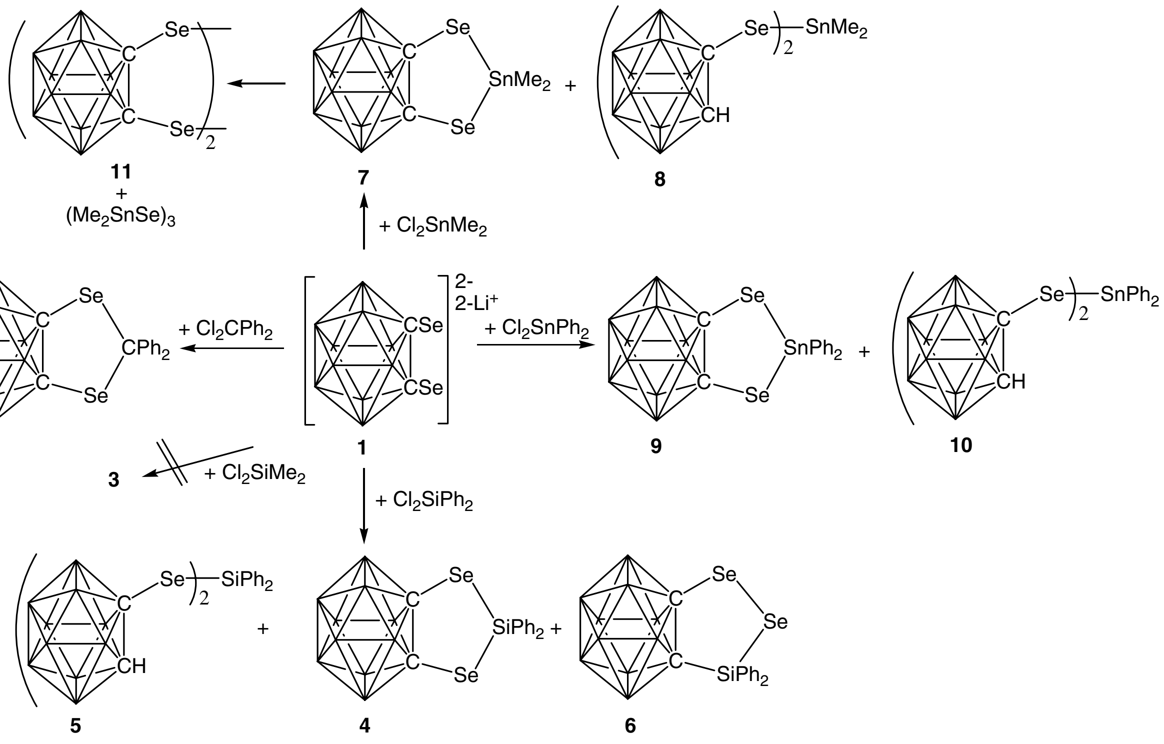


Scheme 1. Reactions of the dianion **1** with various diorganoelement dichlorides.

however, the product **7** turned out to be fairly unstable. Decomposition products were the known bis(diselane) **11**[53] and dimethyltin selenide $(Me_2SnSe)_3$. In spite of the low yield of pure **2**, crystalline material suitable for X-ray analysis could be isolated. The attempts to prepare the silaheterocycle **3** with the $SiMe_2$ unit were not successful, and unidentified polymers were obtained. Using Ph_2SiCl_2 instead gave better results. In the mixtures, it proved possible to identify the expected five-member ring **4** along with traces of a non-cyclic product **5** arising from the mono-substitution of the *ortho*-carborane. In addition, the presence of another defined product **6** was noted by ^{13}C, ^{29}Si and ^{77}Se NMR spectroscopy, and the data appear to be consistent with a five-member ring containing the Se–Se–$SiPh_2$ unit, a rearrangement product of **4**. Redox reactions between **1** and silicon chlorides appear to be common, since in a previous study[54] it was found that the reaction of two equivalents of **1** with $SiCl_4$ gave mainly the bis(diselane) **11** instead of a spirosilane.

The five-member rings **4, 7** and **9** are characterized by deshielded ^{29}Si and ^{119}Sn nuclei, when compared with non-cyclic derivatives such as **5, 8** and **10**, respectively (Table 1). This deshielding effect is known for both ^{29}Si[55,56] and ^{119}Sn nuclei,[57–61] when they are part of a five-member ring, and is further enhanced by its proximity to sulfur, for which several examples are known.[60,62,63] Most likely, selenium produces a similar effect in this respect. The nuclear shielding of ^{77}Se is affected by the adjacent carborane moiety, which exerts a strongly deshielding effect,[54] >300 ppm when compared with a primary alkyl group,[51–53] and it is also influenced by its proximity to silicon, to another selenium or to tin. Usually the tin atom in Se–Sn bonds leads to increased ^{77}Se nuclear shielding when compared with the effect of silicon in Se–Si bonds.[51–53] This is evident when comparing the $\delta^{77}Se$ data of **4** and **9**. The presence of methyl or phenyl groups on tin in **7–10** does not have a large influence on the $\delta^{77}Se$ values. The ^{13}C(carborane) signals are found in the usual range between $\delta^{13}C$ 60 and 80. In some cases, the signal-to-noise ratio was sufficient for the observation of ^{77}Se or $^{117/119}Sn$ satellites corresponding to $^{1}J(^{77}Se, ^{13}C)$ and $^{2}J(^{119}Sn, ^{13}C)$ respectively (Fig. 1).

The proposed structure of the five-member ring **6** containing the $Ph_2SiSeSe$ unit is based in the first place on the ^{77}Se NMR signals (Fig. 2), both accompanied by ^{77}Se satellites owing to $^{1}J(^{77}Se, ^{77}Se) = 300$ Hz. The ^{77}Se NMR signal at low frequency is also accompanied by ^{29}Si satellites corresponding to $^{1}J(^{77}Se, ^{29}Si) = 132$ Hz, typical of silylselanes.[64–69] In ^{29}Si and ^{13}C NMR spectra, the typical signals expected for the compound **6** are observed in addition to those of **4**. In repeated attempts to prepare **4**, we obtained mixtures consisting mainly of **4** and **6** in variable amounts, frequently slightly more of **6** than of **4**.

Many organotin compounds are known as useful reagents for oxidative addition reactions.[70–74] Thus, the reactivity of **7** and **9** towards $[Pt(PPh_3)_2(CH_2{=}CH_2)]$ was studied (Scheme 2). The reaction had to be monitored by ^{31}P NMR

Table 1. ^{13}C, ^{29}Si, ^{77}Se and ^{119}Sn NMR data[a] of the caborane derivatives **2, 4, 6–10**

	$\delta^{77}Se$ $[^1J(^{77}Se, ^{29}Si)]$ $[^1J(^{119}Sn, ^{77}Se)]$	$\delta^{13}C$ $[^1J(^{77}Se, ^{13}C)]$ $\delta^{29}Si$ $[^1J(^{77}Se, ^{29}Si)]$ $\delta^{119}Sn$ $[^1J(^{119}Sn, ^{77}Se)]$	$\delta^{13}C$(carborane) $[^1J(^{77}Se, ^{13}C)]$ $[^2J(^{119}Sn, ^{13}C)]$	$\delta^{13}C$(Me), $\delta^{13}C(Ph)[J(^{119/117}Sn, ^{13}C)]$
$[(B_{10}H_{10})(CSe)_2]CPh_2$ **2**	859	86.5 (82)	74.9 (157)	143.3(i), 133.0(*o*), 126.4(*m*). 128.8(*p*)
$[(B_{10}H_{10})(CSe)_2]SiPh_2$ **4**	334 (131)	37.6 (131)	71.8 (154)	129.7(i), 136.5(*o*), 129.3(*m*), 132.8(*p*)
$[(B_{10}H_{10})CSeSeSi(Ph)_2C]$ **6**	558 (C–Se) $^1J(^{77}Se, ^{77}Se) = 300$ Hz 148 (Si–Se) (132)	17.7 (132)	78.5 (CSi) 63.7 (CSe) (152)	127.3(i), 136.7(*o*), 129.0(*m*), 132.5(*p*)
$[(B_{10}H_{10})(CSe)_2]SnMe_2$ **7**	309 [1054]	213.2 [1054]	73.1 (163)/{27}	4.9 {353}
$[(B_{10}H_{10}CH)CSe]_2SnMe_2$ **8**	399 —	90.4	73.0 (CSe) 66.6 (CH)	4.6 {354}
$[(B_{10}H_{10})(CSe)_2]SnPh_2$ **9**	281 [1169]	101 [1169]	72.3 (163)/{26}	136.9 {566}(*i*), 136.3 {35}(*o*), 130.1 {54}(m), 131.8 {15}(p)
$[(B_{10}H_{10}CH)Cse]_2SnPh_2$ **10**	355 [968]	−78 —	71.7 (CSe) (174)/{33} 66.2 (CH)	137.1 {544}(i), 136.9 {35}(*o*), 129.0 {56}(m), 129.7(p)

[a] NMR measurements in CD_2Cl_2 at 23 °C, except for the ^{119}Sn chemical shifts of 7 and **8** (−20 °C); coupling constants *J* are given in Hz (±1).

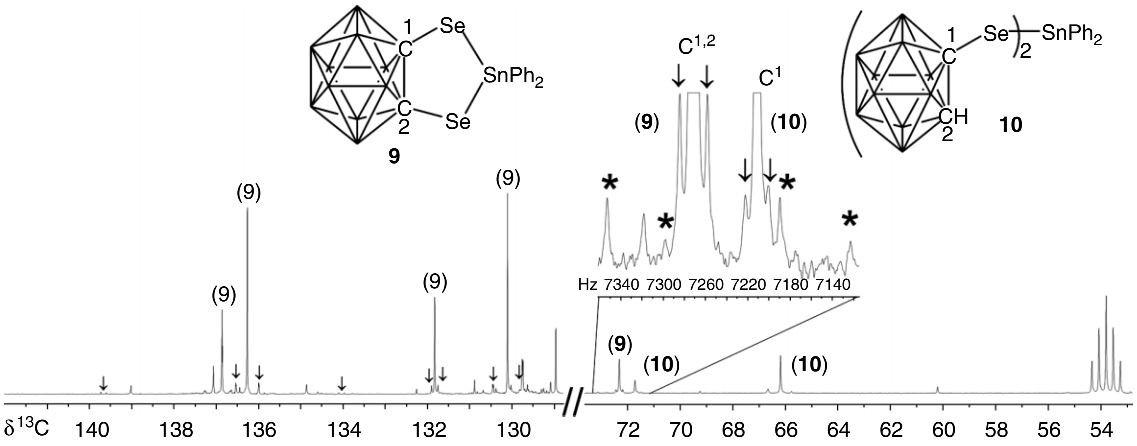


Figure 1. 75.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the mixture of the carboranes **9** and **10**. The region of the ^{13}C(carborane) signals is expanded and most $^{117/119}Sn$ (arrows) and ^{77}Se satellites (asterisks) are clearly visible. Other $^{117/119}Sn$ satellites in the aromatic region for **9** are marked by arrows.

spectroscopy (Fig. 3) at low temperature in order to pick the correct conditions for measuring meaningful ^{119}Sn and ^{195}Pt NMR spectra. At low temperature (ca. −78 to −40 °C) ethene is slowly displaced from the platinum(0) complex, and the $Pt(PPh_3)_2$ fragment inserts into one of the Sn–Se bonds leading to the platinum(II) complexes **12** and **13** (see Table 2 for relevant NMR data). Above −20 °C extensive decomposition of **12** and **13** becomes evident from the appearance of numerous new ^{31}P NMR signals, of which those for $Ph_3P{=}Se$ and the

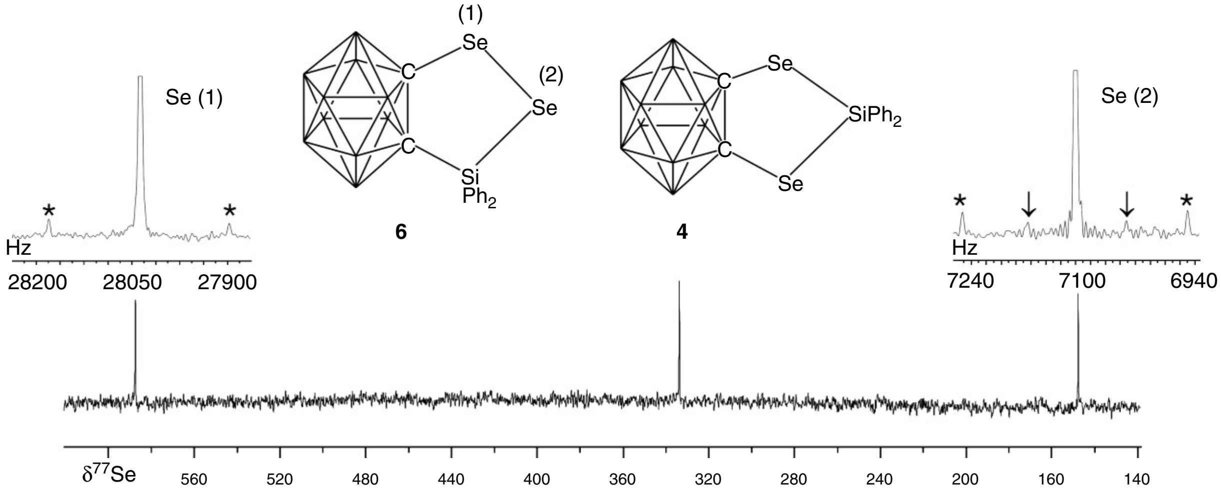
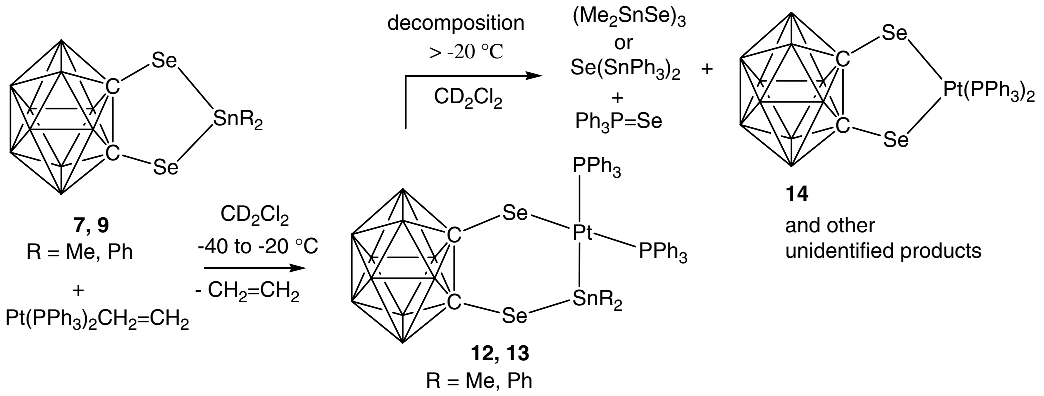


Figure 2. 47.7 MHz ^{77}Se{^{1}H} NMR spectrum of the reaction mixture containing the diphenylsilicon compounds **4** and **6**. The ^{77}Se NMR signals for **6** at high and low frequencies are accompanied by ^{77}Se satellites (asterisks) corresponding to $^{1}J(^{77}\text{Se}, ^{77}\text{Se}) = 300$ Hz. The signal at the lowest frequency shows also ^{29}Si satellites (arrows) typical of $^{1}J(^{77}\text{Se}, ^{29}\text{Si}) = 132$ Hz.



Scheme 2. Oxidative addition of the cyclic tin compounds **7** and **9** to Pt(PPh$_3$)$_2$CH$_2$=CH$_2$ to give first the platinum(II) complexes **12** and **13**, which decompose rapidly above −20 °C.

known complex **14**[54] could be assigned unambiguously. In the ^{119}Sn NMR spectrum of the reaction mixture containing **12** or **13**, measured at room temperature, only one signal is visible, which on the basis of the ^{119}Sn NMR data belongs to (Me$_2$SnSe)$_3$ and Se(SnPh$_3$)$_2$, resepctively.[60,75]

The formation of **12** and **13** is clearly indicated by ^{31}P, ^{119}Sn and ^{195}Pt NMR spectroscopy (Table 2). The *cis*-positions of the phosphane ligands follow from the small $^{2}J(^{31}\text{P}, ^{31}\text{P})$ values (18 Hz). The positions of the phosphane ligands relative to tin is indicated by the large and small values $^{2}J(^{119}\text{Sn}, ^{31}\text{P})_{trans}$ and $^{2}J(^{119}\text{Sn}, ^{31}\text{P})_{cis}$,[74] respectively, which can be measured both from $^{117/119}$Sn satellites in the ^{31}P NMR (Fig. 3) and from splitting in the ^{119}Sn NMR spectrum (Fig. 4). Finally, the ^{195}Pt NMR spectrum shows doublet of doublets with the splittings due to $^{1}J(^{195}\text{Pt}, ^{31}\text{P})$,[76] as in the ^{31}P NMR spectra. Since the NMR data of **14** are known,[54] this stable complex could be readily identified as a major decomposition product. It should be noted that in the case of neither **12** nor **13** could the presence of conceivable decomposition products containing tin, such as oligomeric stannylenes (SnR$_2$)$_n$, be detected in the ^{119}Sn NMR spectra measured at ambient temperature.

X-Ray structural studies of the carborane derivatives 2 and 9

The molecular structures of the compounds **2** and **9** are shown in the Figs 5 and 6, respectively. Intermolecular contacts are negligible for both molecules **2** and **9**. Expectedly, the carborane moieties are similar in these carborane derivatives. However, there is a significant difference in the C–C(carborane) distances. Since the differences in the bond angles at the selenium atoms are small for **2** and **9**, the shorter distance in **2** can be traced to the wider bond

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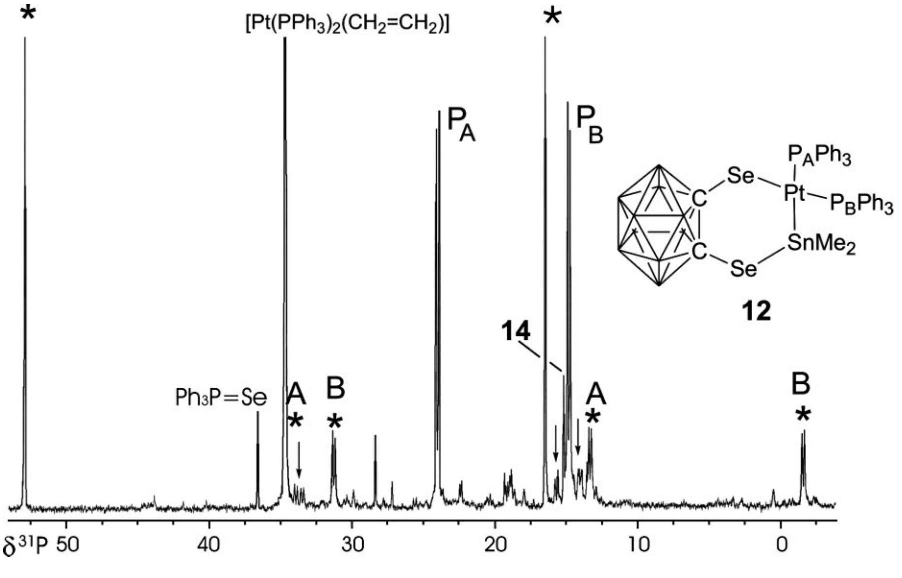
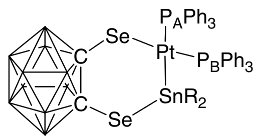


Figure 3. 101.3 MHz $^{31}P\{^1H\}$ NMR spectrum of the reaction solution (Scheme 2) in CD_2Cl_2 (recorded at −20 °C, immediately after mixing the starting materials and warming from −78 to −20 °C). There is still much $[Pt(PPh_3)_2(CH_2{=}CH_2)]$ left, and the Pt(II) complex **12** starts to be formed as the result of oxidative addition. However, there are already weak signals for decomposition products. ^{195}Pt and $^{117/119}Sn$ satellites are marked by asterisks and arrows, respectively. The assignment of the latter is confirmed by the ^{119}Sn NMR spectrum (see Fig. 4).

Table 2. ^{31}P, ^{119}Sn and ^{195}Pt NMR data[a] of the platinum(II) complexes **12** and **13**

	12 R = Me		**13** R = Ph	
	PA	PB	PA	PB
$\delta^{31}P$	23.8 (d)	14.6 (d)	24.5 (d)	15.1 (d)
$^2J(^{31}P, ^{31}P)$	19	19	18.0	18.0
$^1J(^{195}Pt, ^{31}P)$	2158	3319	2381	3330
$^2J(^{119}Sn, ^{31}P)$	2003	174	1809	151
$^2J(^{77}Se, ^{31}P)$	64	42	n.m.	n.m.
$^3J(^{77}Se, ^{31}P)$	10	11	n.m.	n.m.
$\delta^{119}Sn$	58 (dd)		81 (dd)	
$^2J(^{119}Sn, ^{31}P_B)$	174		151	
$^2J(^{119}Sn, ^{31}P_A)$	2003		1809	
$^1J(^{195}Pt, ^{119}Sn)$	10121		n.m.	
$\delta^{195}Pt$	−574(dd)		−619(dd)	
$^1J(^{195}Pt, ^{31}P)_{B/A}$	3319/2158		3330/2381	

[a] NMR measurements in CD_2Cl_2 at −20 °C; coupling constants *J* are given in Hz (±1); n.m. not measured.

angle Se1–C3–Se2 [105.59(9)°] compared with Se1–Sn1–Se2 [94.88(3)°] in **9**. The C–C(carborane) distances are known to vary over a fairly large range from about 1.60 to 1.80 Å,[1–49] although these changes have not been studied in a systematic way so far.

The C–Se bond lengths are in the expected range,[77] with the Se–C(carborane) distances being shorter in **2** and **9**, when compared with C3–Se1 and C3–Se2 bonds in **2**. The Sn–Se bond lengths are also found in the usual range.[78–82] There are very small deviations from a plane for the carborane carbon and the selenium atoms (mean deviations 0.0019 Å in **2** and 0.0022 Å in **9**). Both five-member rings deviate from a planar geometry, and therefore, the phenyl groups linked either to carbon in **2** or to tin in **9** are different. The planes Se1C1C2Se2 and C3C4C10 in **2** and Se1C13C14Se2 and Sn1C1C7 form angles of 91 and 92°, respectively.

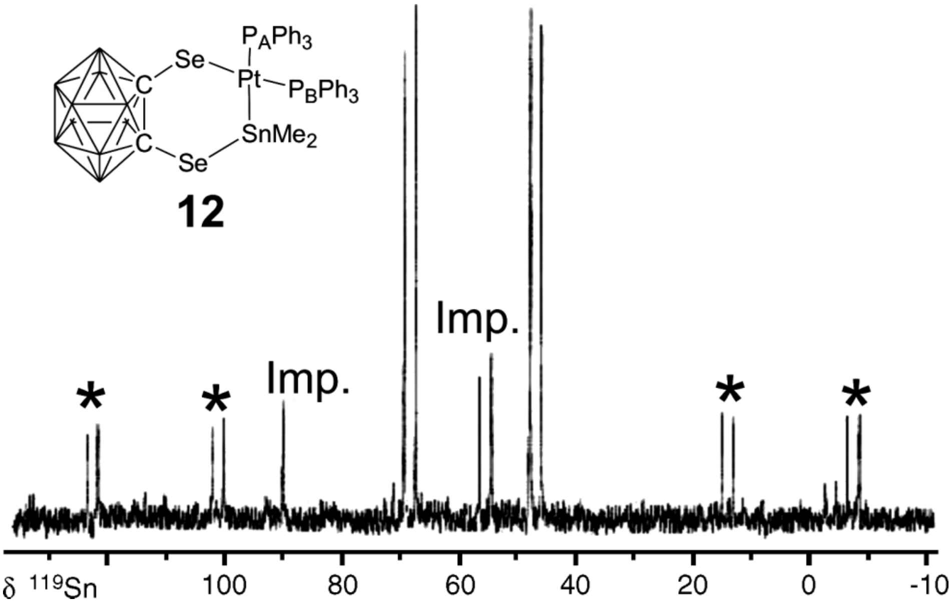


Figure 4. 93.3 MHz $^{119}Sn\{^1H\}$ NMR spectrum of the reaction mixture (Scheme 2) in CD_2Cl_2 at −20 °C containing the platinum(II) complex **12**. The parent ^{119}Sn NMR signals appear as doublet of doublets [$^2J(^{119}Sn, ^{31}P_A)_{trans} = 2003$ Hz and $^2J(^{119}Sn, ^{31}P_B)_{cis} = 174$ Hz], as expected from the satellites in the ^{31}P NMR spectrum (Fig. 3). These signals are accompanied by ^{195}Pt satellites (asterisks) corresponding to $^1J(^{195}Pt, ^{119}Sn) = 10\,121$ Hz, typical of a Pt–Sn bond.

EXPERIMENTAL

General

All syntheses and the handling of the samples required precautions to exclude traces of air and moisture, and therefore, carefully dried solvents and oven-dried glassware were used throughout. The complex $[Pt(PPh_3)_2(C_2H_4)]$[83] and 1,2-dicarba-*closo*-dodecaborane-1,2-diselenolate[49,54] were prepared according to established procedures; the *ortho*-carborane 1,2-$C_2B_{10}H_{12}$ (Katchem), BuLi [1.6 M in hexane], selenium (Aldrich) and all diorganoelement dichlorides were commercially available. NMR measurements (at 23 °C in CD_2Cl_2, if not noted otherwise): Bruker ARX 250, DRX 500, Varian Inova 300 and 400 spectrometers; chemical shifts are given relative to $SiMe_4$ (CD_2Cl_2: $\delta^1H = 5.33$; $\delta^{13}C = 53.8$; $\delta^{29}Si = 0$), external $Et_2O–BF_3$ [$\delta^{11}B = 0$ for $\Xi(^{11}B) = 32.083971$ MHz], external 85% aqueous H_3PO_4 [$\delta^{31}P = 0$ for $\Xi(^{31}P) = 40.480747$ MHz], external Me_2Se [$\delta^{77}Se = 0$ for $\Xi(^{77}Se) = 19.071523$ MHz]; external $SnMe_4$ [$\delta^{119}Sn = 0$ for $\Xi(^{119}Sn) = 37.290665$ MHz]; $\Xi(^{195}Pt) = 21.4$ MHz for $\delta^{195}Pt = 0$,]. ^{29}Si and some ^{119}Sn NMR spectra were recorded using the refocused INEPT pulse sequence.[84–86] Melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

2,2-Diphenyl-4,5-[1,2-dicarba-closo-dodecaborano(12)]-1,3-diselenacyclopentane, ***2***

To a yellow solution of 1,2-dicarba-*closo*-dodecaborane-1,2-diselenolate (*1*) (1.1 mmol in 100 ml of diethyl ether) at −78 °C was added α,α-dichlorodiphenylmethane (0.26 g; 0.21 ml; 1.1 mmol). The mixture was warmed to room temperature and concentrated; insoluble materials were filtered off and washed with 30 ml of pentane. Then, the volatile materials were removed in a vacuum. The NMR analysis of the crude product showed mainly the presence of compound **2** (>80%) along with several undefined side-products.

2: m.p. (isolated crystals) 149–151 °C. ^1H NMR (300 MHz; CD_2Cl_2): $\delta = 1.5–3.5$ (m, broad, 10H, $B_{10}H_{10}$), 7.10–7.80 (m, 10H, Ph); $^{11}B\{^1H\}$ NMR (96.2 MHz; CD_2Cl_2): $\delta = -2, -3, -4, -6, -7, -9, -11, -13, -14, -15$ (overlapping signals for the crude product **2**).

The compounds **3**–**10** were prepared in the same way as **2**.

Reactions of 1 with Me_2SiCl_2 and Ph_2SiCl_2

2,2-Dimethyl-4,5-[1,2-dicarba-closo-dodecaborano(12)]-1,3-diselena-2-silacyclopentane, ***3***

Equimolar amounts of 1,2-dicarba-*closo*-dodecaborane-1,2-diselenolate (**1**) (1.04 mmol in 100 ml of diethylether), dimethyldichlorosilane (0.12 g, 1.04 mmol) in pentane (30 ml) were used. When the mixture was warmed to room temperature, the yellow color of the solution changed immediately, first to orange-red and then to red. During the evaporation of the solvents, the formation of a black solid was observed at the bottom of the flask. The NMR analysis of the soluble materials in this mixture indicated only unidentified decomposition products.

2,2-Diphenyl-4,5-[1,2-dicarba-closo-dodecaborano(12)]-1,3-diselena-2-silacyclopentane, ***4***

Equimolar amounts of 1,2-dicarba-*closo*-dodecaborane-1,2-diselenolate (**1**) (0.76 mmol in 100 ml of diethylether)

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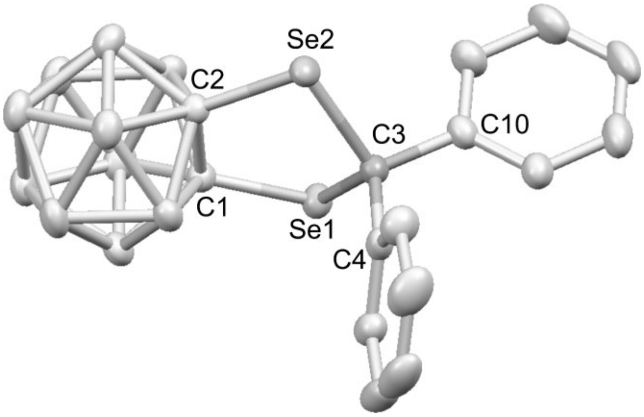

Figure 5. Molecular structure of **2** (hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2 1.627(3), C3−C4 1.523(3), C3−C10 1.533(3), C1−Se1 1.930(2), C2−Se2 1.9190(19), C3−Se1 1.998(2), C3−Se2 2.010(2), C4 C3 C10 112.67(17), C4 C3 Se1 113.66(14), C10 C3 Se1 107.07(13), C4 C3 Se2 111.28(14), C10 C3 Se2 106.02(13), Se1 C3 Se2 105.59(9), C1 Se1 C3 96.20(8), C2 Se2 C3 96.76(8).

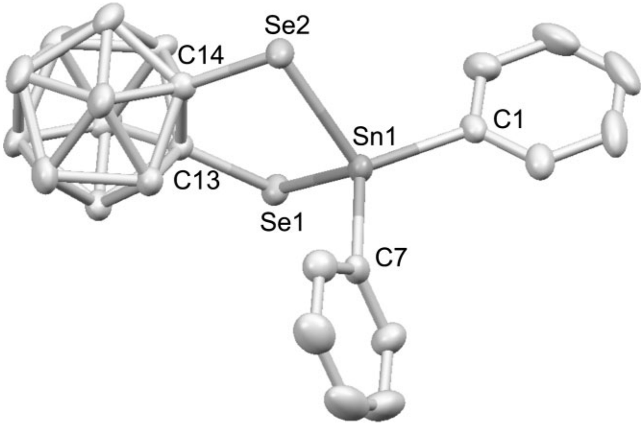

Figure 6. Molecular structure of **9** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): C13−C14 1.678(5), C1−Sn1 2.110(4), C7−Sn1 2.128(4), C13−Se1 1.931(4), C14−Se2 1.938(4), Se1−Sn1 2.5377(9), Se2−Sn1 2.5390(11), C1 Sn1 C7 115.61(16), C1 Sn1 Se1 111.10(11), C7 Sn1 Se1 110.49(11), C1 Sn1 Se2 109.15(11), C7 Sn1 Se2 113.75(11), Se1 Sn1 Se2 94.88(3), C13 Se1 Sn1 95.03(11), C14 Se2 Sn1 95.24(12).

and dichlorodiphenylsilane (0.19 g; 0.16 ml; 0.76 mmol) in pentane (30 ml) were used. The analysis of the reaction mixture by NMR spectroscopy showed the formation of the expected five-member ring $[(B_{10}H_{10})(CSe)_2]SiPh_2$ **4** along with traces of a non-cyclic product $[(B_{10}H_{10}CH)CSe]_2SiPh_2$ **5** and a five-member ring $[(B_{10}H_{10})(C{-}Se{-}Se{-}SiPh_2{-}C)]$ **6**. In repeated reactions, compound **6** was present in comparable amounts to **4**. Various attempts failed to separate the heterocycles **4** and **6** by fractional crystallization.

NMR data for the mixture of **4**–**6**: ^{1}H NMR (300 MHz; CD_2Cl_2): $\delta = 1.5{-}3.5$ (m, broad, 10H, $B_{10}H_{10}$), 7.10–7.80 (m, 10H, Ph); $^{11}B\{^1H\}$ NMR (96.2 MHz; CD_2Cl_2): $\delta = -2, -3, -4, -6, -7, -9, -11, -13, -14, -15$ (overlapping signals).

Reactions of 1 with Me_2SnCl_2 and Ph_2SnCl_2

2,2-Dimethyl-4,5-[1,2-dicarba-closo-dodecaborano(12)]-1,3-diselena-2-stannacyclopentane, 7

1,2-Dicarba-*closo*-dodecaborane-1,2-diselenolate (**1**) (1.23 mmol in 100 ml of ether) and dimethyltin dichloride (0.27 g; 1.23 mmol) were combined at −78 °C. The mixture was stirred at −78 °C during 4 h, warmed to −30 °C and concentrated; insoluble materials were filtered off and washed with 30 ml of precooled pentane. Then, the volatile materials were removed in a vacuum. The NMR analysis showed the presence of compound **7** as the major product and a small amount of the non-cyclic compound **8**. The heterocycle **7** decomposes above −10 °C in CH_2Cl_2 solution into the bis(diselane) **11**, $[(B_{10}H_{10})(CSe)_2]_2$ and dimethyltin selenide $(Me_2SnSe)_3$.

7: ^{1}H NMR (300 MHz; CD_2Cl_2): $\delta = 1.4{-}3.4$ (m, broad, 10H, $B_{10}H_{10}$); 1.24 (s, 6H, $SnMe_2$, $^2J(^{119}Sn, ^1H) = 60$ Hz); $^{11}B\{^1H\}$ NMR (96.2 MHz; CD_2Cl_2): $\delta = -4, -6, -7, -8$ for the mixture of **7** and **8** (overlapping signals).

8: ^{1}H NMR (300 MHz; CD_2Cl_2): $\delta = 1.4{-}3.4$ (m, broad, 10H, $B_{10}H_{10}$); 0.97 (s, 6H, $SnMe_2$, $^2J(^{119}Sn, ^1H) = 59$ Hz).

2,2-Diphenyl-4,5-[1,2-dicarba-closo-dodecaborano(12)]-1,3-diselena-2-stannacyclopentane, 9

1,2-Dicarba-*closo*-dodecaborane-1,2-diselenolate (**1**) (0.9 mmol in 100 ml of ether) and diphenyltin dichloride (0.3 g; 0.9 mmol) were combined at −78 °C, and the mixture was slowly warmed to room temperature. The NMR analysis showed the presence of **9** as main product and a small amount of **10** (see also Fig. 1). The formation of colorless crystals of **9** was observed in CH_2Cl_2 at room temperature after one month. Yield (0.36 g; 71%).

9: m.p. 228–230 °C. ^{1}H NMR (300 MHz; CD_2Cl_2): $\delta = 1.0{-}4.0$ (m, broad, 10H, $B_{10}H_{10}$); 7.25–7.53 (m, 10H, Ph_2); $^{11}B\{^1H\}$ NMR (96.2 MHz; CD_2Cl_2): $\delta = -5$ (1B), −6 (1B), −8 (6B), −12 (2B) (overlapping signals). **10**: ^{1}H NMR (300 MHz; CD_2Cl_2): $\delta = 1.0{-}4.0$ (m, broad, 10H, $B_{10}H_{10}$); 7.21–7.74 (m, 10H, Ph_2).

Reactions of the 1,3,2-diselenastannacycles 7 and 9 with $[Pt(PPh_3)_2(CH_2{=}CH_2)]$

6,6-Dimethyl-1,1-bis(triphenylphosphane)-[1,2-dicarba-closo-dodecaborano(12)]-1-platina-2,5-diselena-6-stannacyclohexane, 12

To a solution of ethene-bis(triphenylphosphane)platinum(0) (0.14 g, 0.19 mmol) in CD_2Cl_2 (0.5 ml) at −78 °C was added a solution of **7** (0.086 g, 0.19 mmol) in CD_2Cl_2 (0.5 ml). An orange-red reaction solution was obtained and studied immediately by ^{31}P NMR spectroscopy. At −80 °C, the

^{31}P NMR spectrum already showed the presence of complex **12** [$\delta^{31}P = 23.8$(d) and 14.6(d), Table 2] in addition to the starting material [$Pt(PPh_3)_2(CH_2{=}CH_2)$] [$\delta^{31}P = 34.9$(s), $^1J(^{195}Pt, ^{31}P) = 3720$ Hz]. At $-20\,°C$, the ^{31}P NMR spectra indicated an increase in the concentration of complex **12**, accompanied by signals for $Ph_3P{=}Se$ [$\delta^{31}P = 36.6$, $^1J(^{77}Se, ^{31}P) = 722$ Hz], [$(B_{10}H_{10})(CSe)_2]Pt(PPh_3)_2$] **14** [$\delta^{31}P = 15.7$(s), $^1J(^{195}Pt, ^{31}P) = 2972.5$ Hz], and strong signals of the starting ethene–platinum(0) complex. At room temperature, both the reaction and the decomposition were complete, and the presence of complex **14** as the main product was evident from the ^{31}P NMR spectrum, and some ^{31}P NMR signals for undefined compounds in low concentration ($\delta^{31}P$ 24.0(s) [$^1J(^{195}Pt, ^{31}P) = 2819$ Hz], 20.9(s), 19.7(s) [$^1J(^{195}Pt, ^{31}P) = 3259$ Hz], 19.5(s) [$^1J(^{195}Pt, ^{31}P) = 3247$ Hz], 19.0 [$^1J(^{195}Pt, ^{31}P) = 3210$ Hz] and 13.4(s) were detected. The ^{119}Sn NMR spectrum at room temperature showed the presence of $(Me_2SnSe)_3$ [$\delta^{119}Sn = 46.6$, $^1J(^{119}Sn, ^{77}Se) = 1193$ Hz, $^1J(^{119}Sn, ^{119}Sn) = 262$ Hz] as another decomposition product.

12: ^1H NMR (300 MHz; CD_2Cl_2): $\delta = 1.4$–3.4 (m, broad, 10H, $B_{10}H_{10}$), 0.90 (s, 6H, $SnMe_2$, $^2J(^{119}Sn, ^1H) = 59$ Hz), 7.11–7.44 (m, 30H, PPh_3).

Complex **13** was prepared in the same way as **12**.

The ^{31}P NMR spectrum of the reaction mixture, recorded at $-20\,°C$, showed the presence of complex **13** (Table 2), the starting material [$Pt(PPh_3)_2(CH_2{=}CH_2)$], $Ph_3P{=}Se$ and [$(B_{10}H_{10})(CSe)_2]Pt(PPh_3)_2$] **14**. At room temperature, the ^{31}P NMR spectrum showed the presence of complex **14** as main product, $Ph_3P{=}Se$ and some undefined compounds in low concentration [$\delta^{31}P$ 24.0(s, broad) [$^1J(^{195}Pt, ^{31}P) = 2818$ Hz], 19.9(s) and 17.9(s)]. In the ^{119}Sn NMR spectrum of the reaction solution, only one ^{119}Sn NMR signal was observed and assigned to $Se(SnPh_3)_2$ [$\delta^{119}Sn = -79$, $^1J(^{119}Sn, ^{78}Se) = 1204$ Hz and $^2J(^{119}Sn, ^{117}Sn) = 227$ Hz[74]].

13: ^1H NMR (300 MHz; CD_2Cl_2): $\delta = 1.3$–3.6 (m, broad, 10H, $B_{10}H_{10}$), 7.15–7.40 (m, 30H, PPh_3).

Crystal structure determinations of the carborane derivatives 2 and 9

Details pertinent to the crystal structure determinations are given in Table 3. Crystals of appropriate size were selected, taken up in perfluorinated oil at room temperature, and the data collections were carried out at 193(2) K using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit.

Supplementary material

Structure solution and refinement were accomplished using SIR97,[87] SHELXL-97[88] and WinGX.[89] The data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications CCDC 621822 (**2**) and 621821 (**9**). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 3. Details of X-ray crystal structure analyses of **2** and **9**

Compound	**2**	**9**
	$C_{15}H_{20}B_{10}Se_2$	$C_{14}H_{20}B_{10}Se_2Sn$
	466.33	573.01
crystal system	Monoclinic	Triclinic
space group	$P2_1/c$	$P-1$
a, Å	8.8880(5)	9.1720(7)
b, Å	16.1870(9)	10.696(1)
c, Å	13.8360(8)	12.023(1)
α, deg		84.045(6)
β, deg	93.966(5)	69.450(6)
γ, deg		75.532(6)
V, Å^3	1985.82(19)	1069.3(3)
Z	4	2
Crystal size, mm	0.28 × 0.55 × 0.64	0.15 × 0.18 × 0.27
D_{calcd}, g cm^{-3}	1.560	1.780
μ, mm^{-1} (Mo Kα)	3.721	4.596
θ range, deg	1.9–25.7	1.8–25.7
No. of reflections unique	3754	4022
No. of reflections obs. [$I > 2\sigma(I)$]	3370	3338
No. of parameters	325	239
wR^2 (all data)	0.059	0.073

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