Novel main group chemistry of the 1,2-diselenido-1,2-dicarba-*closo*-dodecaborane(12) dianion

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Dedicated to Rosalinda Contreras

Abstract

Recent results are summarized on some new aspects of the main group chemistry of the 1,2-diselenido-1,2-dicarba-*closo*-dodecaborane(12) dianion **3**, $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})Se_2]^{2-}$. The reactions of **3** with organoelement-Group 14 dichlorides (Ph_2CCl_2, Me_2SiCl_2, Ph_2SiCl_2, Me_2SnCl_2, Ph_2SnCl_2) and phenylphosphorus dichloride ($PhPCl_2$) afforded novel five-member heterocycles along with other products. In the case of Ph_2SiCl_2, the expected product **6** was accompanied by another five-member ring **8** containing the Ph_2Si-Se-Se moiety. The phospholane **13** could be oxidised to the sulfide **14** and the selenide **15**, and partial hydrolysis gave the selenophosphonic acid **16** along with the bis(diselane) **18** and decomposition. The dianion **3** was converted by oxidative coupling into the bis(diselane) **18**, an eight-member ring with annellated carborane moieties. Symmetric cleavage of this ring in **18** took place by oxidative addition of **18** to bis(triphenylphosphane)ethene-platinum(0) to give the $(Ph_3P)_2Pt(II)$ complex **20** with the chelating 1,2-diselenido-1,2-dicarba-*closo*-dodecaborane(12) ligand. Oxidative addition of the five-member heterocycles containing Se-Sn-Se fragments (**9**, **11**) to bis(triphenylphosphane)ethene-platinum(0) proceeded at low temperature by insertion of the $(PPh_3)_2Pt$ fragment into one of the Sn-Se bonds (**21**, **22**). The reaction of **11** with bis(triphenylphosphane)ethene-platinum(0) took place by oxidative addition of the P-Se bond, followed by rearrangement (**25**). The molecular structures of the five-member rings with annellated carborane units **4** (CPh_2), **11** ($SnPh_2$), **13** (PPh), **14** (PhP=S), **20** ($Pt(PPh_3)_2$, and of the bis(diselane) **18** were determined by X-ray analyses.The proposed solution-state structures of the new compounds followed from consistent sets of multinuclear magnetic resonance data (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{31}P, ^{77}Se, ^{119}Sn and ^{195}Pt NMR).

Keywords: Carborane, selenium, silicon, tin, phosphorus, platinum, oxidative addition, oxidative coupling, NMR, X-ray

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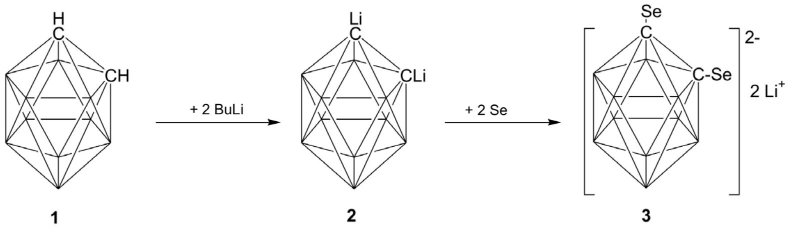
Introduction

1,2-Dicarba-*closo*-dodecaborane(12) **1**, "*ortho*-carborane", has attracted extensive chemical research for more than four decades because of its unique stability, its unusual electronic structure, the ease to modify its substituents as well as the principal cage structure.[1-4] A major impact of the rich chemistry of **1** can be traced to metalation at the carbon atom(s).[2-6] Thus, the dilithiated carborane 1,2-Li_2 -1,2-$C_2B_{10}H_{10}$ **2** can be prepared in solution (in equilibrium with small amounts of **1** and the monolithiated species), and is a highly convenient precursor for further transformations. In the present context, the insertion of chalcogen atoms into the C-Li bonds (Scheme 1) to form the 1,2-dichalcogenido-1,2-dicarba-*closo*-dodecaborane(12) dianions $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})E_2]^{2-}$ (E = S, Se, Te) has been widely used to take advantage of these chelating ligands in transition metal chemistry.[7-13] In contrast, the main group chemistry of the dianions has received much less attention. Although the tellurium derivatives are rarely studied, since the clean access to the anion $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})Te_2]^{2-}$ appears to be difficult,[14] the dianions with sulfur or selenium are readily accessible. The dianion $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})Se_2]^{2-}$ **3** is particularly attractive from the NMR point of view[15] (^{77}Se NMR: spin I = ½; natural abundance 7.58 %; about three times more sensitive to NMR experiments than ^{13}C). We have explored for the first time the reactivity of the dianion **3** in more detail for main group chemistry, with emphasis on the synthesis of five-member heterocycles containing a Group 14 element (carbon, silicon, tin) or phosphorus between the selenium atoms. Furthermore, we were interested in oxidative coupling of the dianion **3** as well as in the reactivity of some of the new heterocycles with respect to oxidative addition. Here, we present a summary of our recent results in this field.[16]



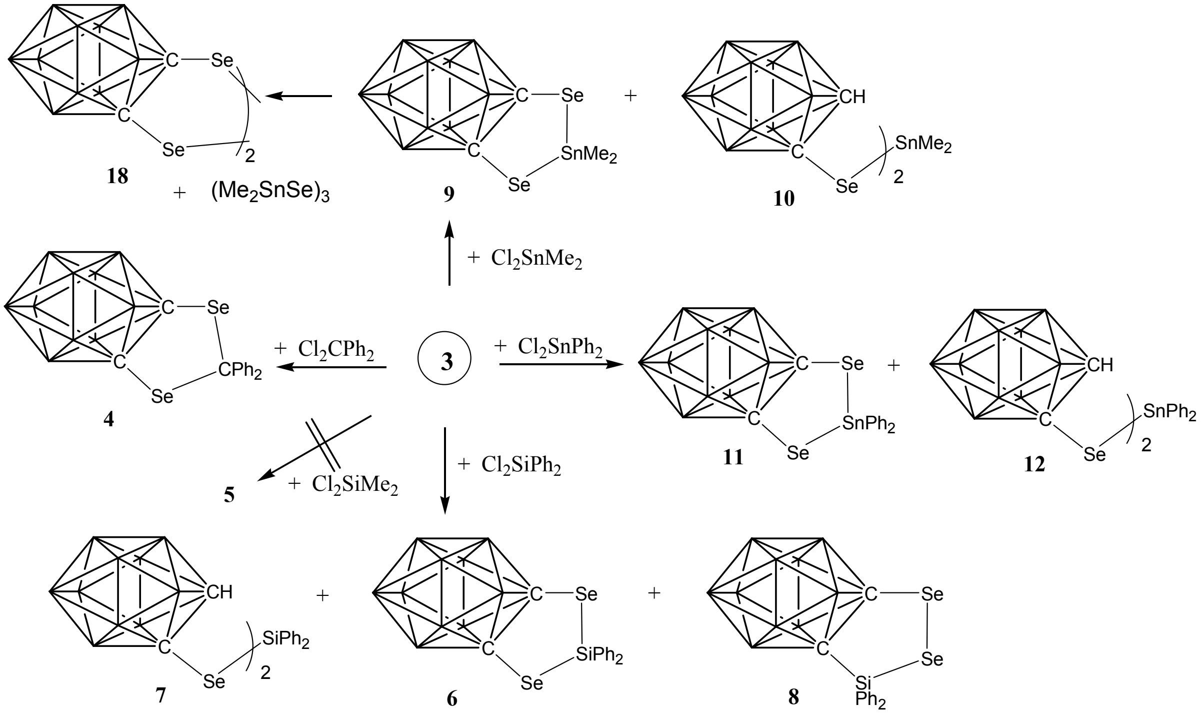
Scheme 1

Results and Discussion

Reactions of the 1,2-diselenido-1,2-dicarba-closo-dodecaborane(12) dianion 3 with element chlorides

The reactions of the dianion $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})Se_2]^{2-}$ **3** with diorganoelement dichlorides are shown in Scheme 2 (C, Si, Sn) and Scheme 3 (P). The complete dilithiation of the *ortho*-carborane **1** is not possible.[4a-b] However, **1** and side products arising from the monolithiated carborane can be separated by purification of the final products, and in some cases, useful NMR spectroscopic data could be obtained for the side products.

The five-member ring **4** containing the CPh_2 unit was identified in the reaction mixture, and crystalline material suitable for X-ray structural analysis (*vide infra*) could be isolated.[16b] In the case of the chlorosilanes, repeated attempts failed to prepare the silaheterocycle **5** with the $SiMe_2$ unit. In contrast, the reaction of **3** with Ph_2SiCl_2 gave the expected five-member ring **6** along with traces of a non-cyclic product **7**, from the monosubstituted *ortho*-carborane, and another five-member ring **8**.[16b] The latter results either from rearrangement of **4** or from changes in the nature of the dianion **3** during its reaction with the silicon chloride, taking into account the somewhat unpredictable behavior of the analogous ditellurido dianion.[14] The proposed structure of **8** follows from the ^{77}Se NMR spectrum (Fig. 1). The NMR parameters (δ^{77}Se and $^1J(^{77}\text{Se},^{77}\text{Se})$, and $^1J(^{77}\text{Se},^{29}\text{Si})$[16b]] were confirmed by calculations[17a] based on the optimized [B3LYP/6-311+G(d,p) level of theory][17b-f] gas phase structures of the parent compounds corresponding to **6** and **8**. Unexpected reactions between **3** and silicon chlorides appear to be common (see Scheme 4 for the reaction of two equivalents of **3** with $SiCl_4$).[16a]



Scheme 2

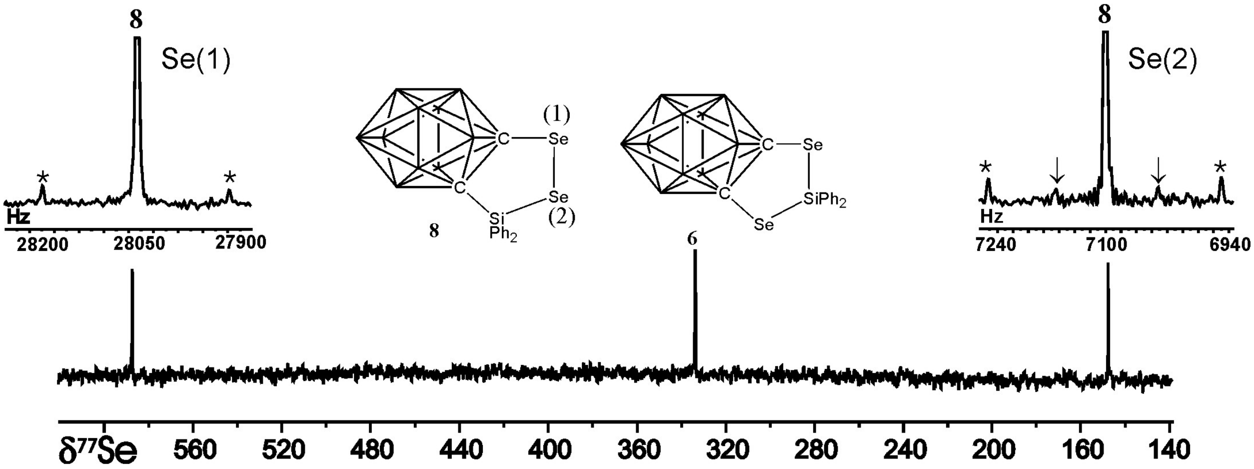


Figure 1. 47.7 MHz ^{77}Se{^{1}H} NMR spectrum of the mixture containing **6** and **8** (in CD_2Cl_2 at 23 ºC). The ^{77}Se NMR signals for **8** at high and low frequencies are accompanied by ^{77}Se satellites (asterisks) corresponding to $^{1}J(^{77}Se,^{77}Se)$ = 300 Hz. The signal at lowest frequency shows also ^{29}Si satellites (arrows) typical of $^{1}J(^{77}Se,^{29}Si)$ = 132 Hz.

In the cases of the diorganotin chlorides, the expected products could be isolated in reasonable yields (> 70%). Thus, the reaction of **3** with Ph_2SnCl_2 afforded pure samples of **11**, after recrystallization, suitable for X-ray structural analysis (*vide infra*). The ^{13}C NMR spectrum of the reaction mixture shows the presence of both **11** and **12** (Fig. 2). Frequently, the ^{13}C(carborane) NMR signals are not reported in the literature, since there intensity is rather weak and the signals are broadened by partially relaxed ^{13}C-^{11}B spin-spin coupling.[3] However, the δ^{13}C values are diagnostic and coupling constants such as $^{1}J(^{77}Se,^{13}C)$ or $^{2}J(^{117/119}Sn,^{13}C)$ are extremely useful in structural assignments. Similarly to Ph_2SnCl_2, the reaction of **3** with Me_2SnCl_2 gave **9** along with a small amount of **10**, although **9** turned out to be fairly instable.[16b] Decomposition products were the known bis(diselane) **18**[16a] and dimethyltin selenide $(Me_2SnSe)_3$.

Depending on the orientation of the phenyl group, the phospholane **13** (Scheme 3) can in principle be formed as a mixture of isomers. However, only a single isomer **13** was observed in the reaction solutions and could be isolated as a crystalline solid (X-ray analysis; *vide infra*). The calculation of the gas phase structures [B3LYP/6-311+G(d,p) level of theory][17b-f] of the parent isomers of **13** gave the lower energy for the structure analogous to **13**.[16c] As usual for phosphanes, the configuration of **13** was retained upon oxidation with elemental sulfur (X-ray analysis; *vide infra*) or selenium.[16c] The formation of the selenide **15** required prolonged times of heating in inert solvents, much longer than for the sulfide **14**, and was accompanied by extensive decomposition. The bis(diselane) **18** was identified as the major decomposition product along with Ph_3PSe and various unidentified phosphorus compounds in low concentration.[16c] Attempts failed to prepare a phosphonium salt from the reaction of **13** with an excess of methyl iodide. Instead, the selenophosphonic acid **16** was formed, because of partial hydrolysis of **13** owing to traces of water present in the commercial methyl iodide. ^{31}P NMR spectra showed again the formation of the bis(diselane) **18** along with other unknown side products in low concentration.[16c] In one further attempt to prepare a larger amount of **13**, a few crystals of another less soluble phosphorus compound **17** could be isolated, and its molecular structure was determined by X-ray analysis.[16e] The analogous sulfur compound has been described previously.[6b]

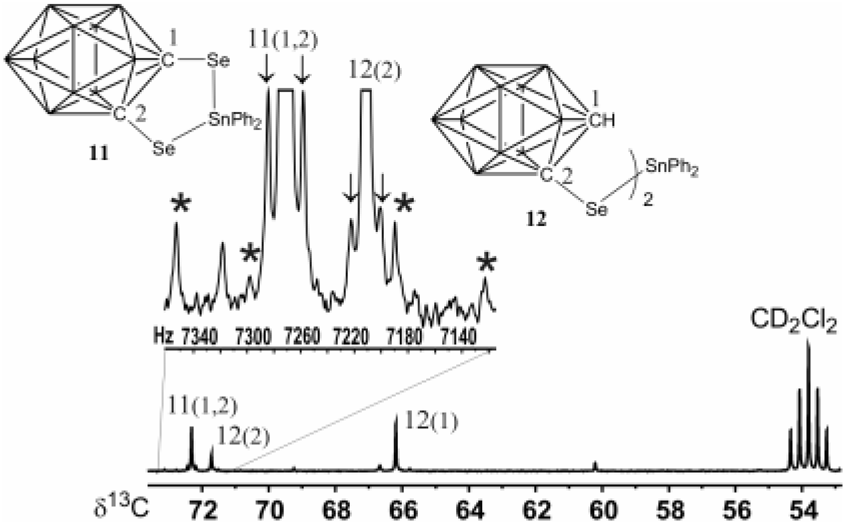
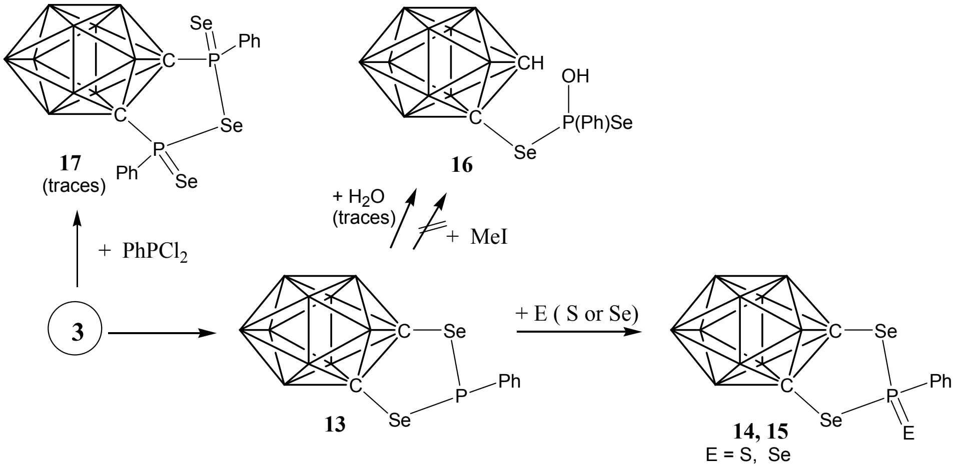


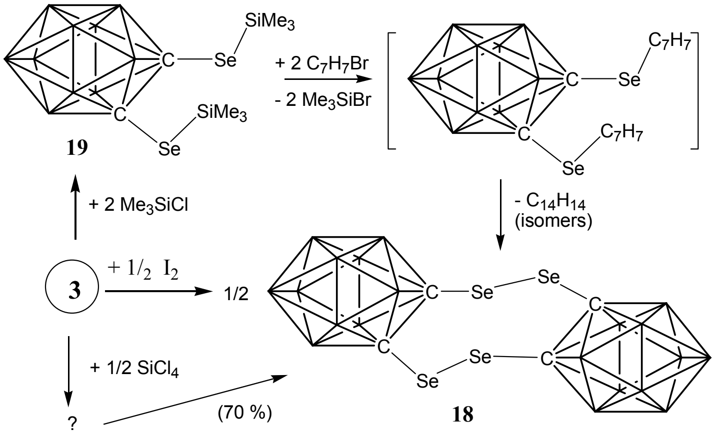
Figure 2. 75.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the mixture of the diphenyltin compounds **11** and **12** (in CD_2Cl_2 at 23 ºC). The region of the ^{13}C(carborane) signals is shown, and $^{117/119}Sn$ (arrows) and ^{77}Se satellites (asterisks) are clearly visible.



Scheme 3

Oxidative coupling of the 1,2-diselenido-1,2-dicarba-closo-dodecaborane(12) dianion 3

Oxidative coupling of the dianion **3** by its reaction with iodine afforded the bis(diselane) **18** in high yield (Scheme 4). Interestingly, **18** was found also as the major product of other reactions which originally were intended to serve quite different purposes.

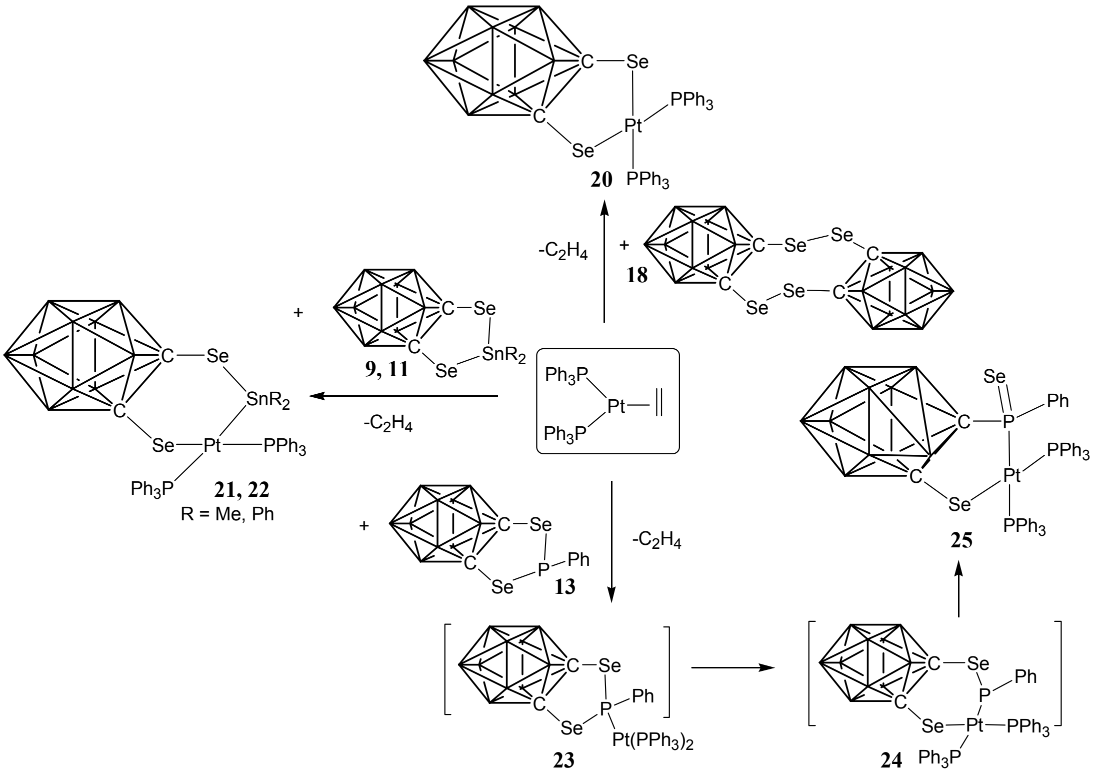


Scheme 4

The reaction of **3** with two equivalents of Me_3SiCl gave the silane derivative **19** in high yield, together with a small amount of the monosubstituted carborane, proving the maximum conversion of **2** into **3**. Our current interest in tropylium derivatives [18-20] prompted us to study the reaction of **19** with tropylium bromide, C_7H_7Br. Surprisingly, the reaction went towards the bis(diselane) **18**, and the tropylium derivative could not be observed. In the case of other trimethylsilylselanes Me_3Si-SeR, this type of reaction gave tropylium selenides C_7H_7-Se-R, most of which are fairly stable until room temperature before they decompose.[20] Another attempt was made to extend the silane chemistry of **3**, aiming at the synthesis of a spirosilane by treatment of $SiCl_4$ with two equivalents of **3**. Instead of the desired silane, again the bis(diselane) **18** could be obtained and could be isolated in reasonably high yield.[16a]

Oxidative addition of the new cyclic selanes to bis(triphenylphosphane)ethene-platinum(0)

The Se-Se in diselanes[21] and Sn-element bonds in many organotin compounds[22-25] invite for application in oxidative addition reactions. On the other hand, the phospholane **13** can react with a Pt(0) complex either as a donor via the lone pair of electrons at phosphorus or by oxidative addition of one of the P-Se bonds. Therefore, we have studied the reactivity of **18**, **9**, **11** and **13** towards bis(triphenylphosphane)ethene-platinum(0) (Scheme 5).



Scheme 5

In a clean reaction, oxidative addition of the bis(diselane) **18** to [Pt(PPh$_3$)$_2$CH$_2$=CH$_2$] afforded the complex **20** with the chelating 1,2-diselenido-1,2-dicarba-*closo*-dodecaborane(12) ligand and displacement of ethene.[16a] Complex **20** deserves interest as a potential catalyst for the *cis*-addition of the Se-Se bond to the C≡C bond in alkynes.[21c-d] It is fairly stable and well characterized by all spectroscopic data in solution and X-ray structural analysis in the solid state.[16a] Cleavage of the Pt-Se bonds in **20** was observed, when it was reacted with an excess of methyl iodide, giving in the beginning *cis*-[Pt(PPh$_3$)$_2$I$_2$], and the anionic complexes [Pt(PPh$_3$)I$_3$]$^-$ and [PtI$_4$]$^{2-}$ with [P(Me)Ph$_3$)]$^+$ as the counterion. The complex *cis*-[Pt(PPh$_3$)$_2$I$_2$] slowly rearranged into its more stable *trans*-isomer.[16a]

Oxidative addition of the 1,3,2-diselenastannacycles **9** and **11** to [Pt(PPh$_3$)$_2$CH$_2$=CH$_2$] gave at low temperature the bis(triphenylphosphane)platinum(II) complexes **21** and **22**, respectively, where in each case the (PPh$_3$)$_2$Pt fragment was inserted into one of the Sn-Se bonds. The complexes **21** and **22** decompose at temperatures above – 20 °C. The proposed structure is supported by the NMR data (see Fig. 3 for the ^{31}P NMR spectrum). The complex **20** was found as the major decomposition product, accompanied by (Me$_2$SnSe)$_3$ in the case of **21**, and Ph$_3$PSe and Se(SnPh$_3$)$_2$ in the case of **22**, and numerous other compounds which could not be identified unambiguously.[16b]

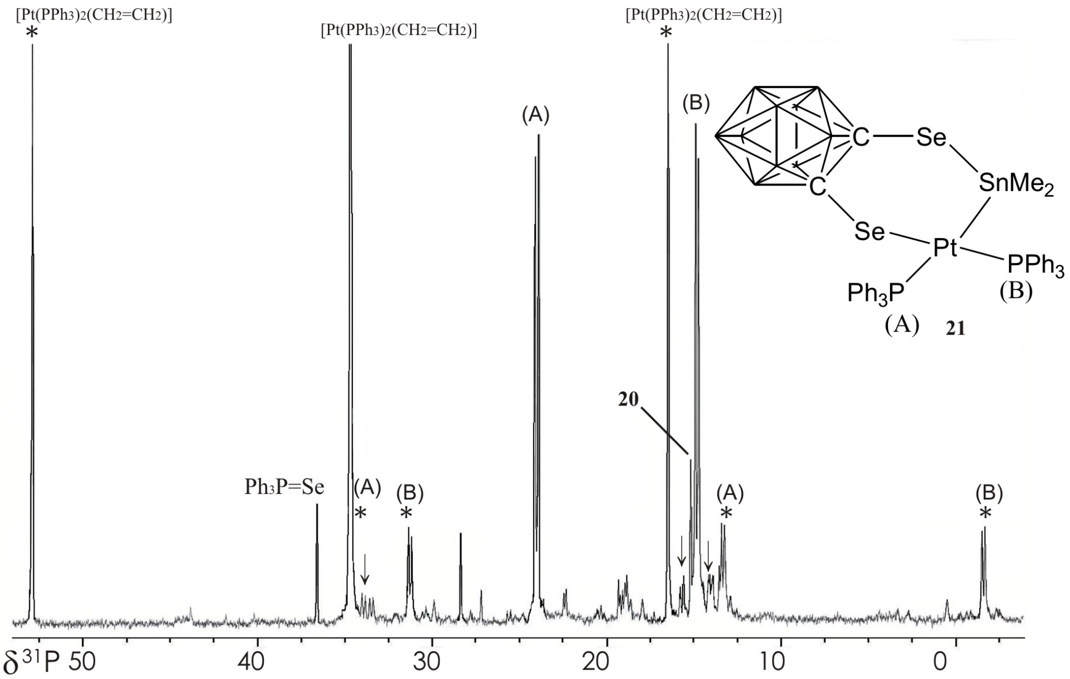


Figure 3. 101.3 MHz $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution in CD_2Cl_2 (recorded at -20 °C, immediately after mixing the starting materials and warming from -78 to -20 °C). There is still much left of [Pt(PPh_3)$_2$$CH_2$=$CH_2$], and the Pt(II) complex **21** starts to be formed as the result of oxidative addition. However, there are already weak signals belonging to decomposition products (e.g. **20** and Ph_3P=Se). ^{195}Pt and $^{117/119}$Sn satellites are marked by asterisks and arrows, respectively. The assignment of the $^{2}J(^{119}Sn,^{31}P)$ data is confirmed by the ^{119}Sn NMR spectrum, and the data are typical for a *trans*- and *cis*-coupling pathway.

The reaction of the phospholane **13** with [Pt(PPh_3)$_2$$CH_2$=$CH_2$] displaces ethene. The conceivable first reaction products **23** or **24** were not detected by ^{31}P NMR spectroscopy at -40 °C. However, oxidative addition of one P-Se bond must have occurred, followed immediately by an Arbusov-type rearrangement [25] into the platinum(II) complex **25**. In **25**, the new chelating ligand is linked to platinum via Pt-Se and Pt-P(Se) bonds, a rare example of a metallophosphane selenide.[16c] As for **21** and **22**, the complex **25** turned out to be fairly instable at temperatures above – 20 °C, and the identification of **25** had to rely entirely on NMR data (Figs. 4, 5). Prominent decomposition products were the complex **20**,[16a] Ph_3PSe, and other unknown species. So far, selenophosphanes comparable with **13** have not been used for oxidative addition reactions of a P(III)-Se bond to Pt(0) or Pd(0) centers. A single report describes the reaction of [M(PEt_3)$_3$] (M = Pd, Pt) with P(O)(OPh)$_2$SePh, where a P(V)-Se bond is added to the metal.[24] Attempts to prepare a Pd(II) complex from the reaction of **13** with [Pd(PPh_3)$_4$] were not successful. A large number of broad ^{31}P NMR signals in the range for coordinated PPh_3 and **13** was observed, indicating an exchange between **13** and PPh_3 at palladium without addition of a P-Se bond.[16c]

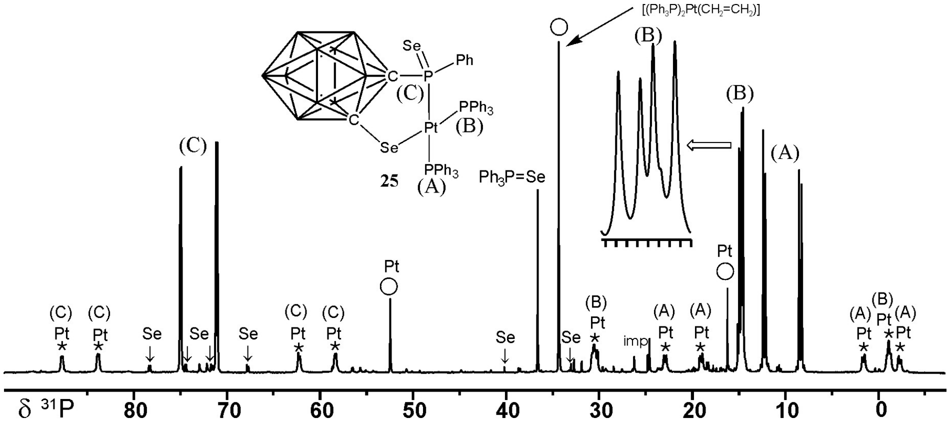


Figure 4. $^{31}P\{^{1}H\}$ NMR spectrum (121.4 MHz) of the complex **25** (in CD_2Cl_2 at -40 ºC). The $^{31}P^{(A.B.C)}$ NMR signals, split into doublets of doublets owing to $^{2}J(^{31}P,^{31}P)$, are accompanied by ^{195}Pt (asterisks, Pt) and ^{77}Se satellites (arrows, Se) due to $^{1}J(^{195}Pt,^{31}P)$ (see also Figure 5) and $^{1}J(^{77}Se,^{31}P)$. Starting material (marked with a cycle) is still present, and decomposition has already started (signal for Ph_3PSe).

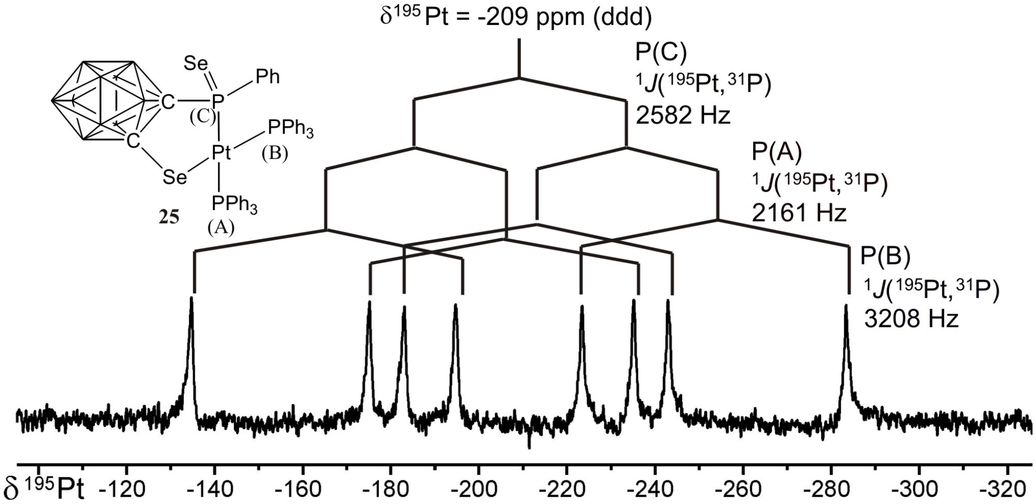
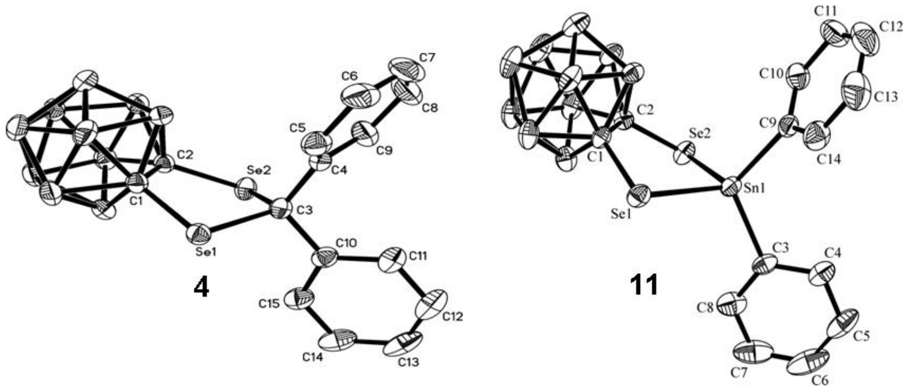


Figure 5. 53.5 MHz $^{195}Pt\{^{1}H\}$ NMR spectrum of the platinum complex **25**. The splitting into doublets of doublets of doublets corresponds exactly to the ^{195}Pt-^{31}P spin-spin coupling observed in the ^{31}P NMR spectrum (see Figure 4).

Solid-state structures

The molecular structures of the compounds **4**,[16b], **11**,[16b] **13**,[16c] **14**,[16c] **18**,[16a] and **20** [16a] are shown in Figs. 6 - 8. Expectedly, the geometry of the carborane moiety[3-4] in this new group of molecules (**4**, **11**, **13**, **14**, **18** and **20**) is hardly disturbed by the various substituents at carbon.



4 **11**

Figure 6. Molecular structures of the compounds **4** and **11**. Selected bond lengths [pm] and angles [°]: **4**: C1-C2 162.7(4), Se1-C1 193.0(2), Se2-C2 191.9(1), Se1-C3 199.8(2), Se2-C3 201.0(2); Se1-C3-Se2 105.59(9), C4-C3-C10 112.67(17). **11**: C13-C14 167.8(5), Se1-C13 193.1(4), Se2-C14 193.8(4), Sn1-Se1 253.77(9), Sn1-Se2 253.9(1); Se1-Sn-Se2 94.88(3), C1-Sn-C7 115.61(16).

Although the C-C(carborane) bond lengths are in the known range [1.60-1.80 Å],[2,3] this distance can change to some extend depending even on remote substituents. This is evident for **4** (d_{CC} = 162.7(3) pm) and **11** (d_{CC} = 167.8(5) pm), where the shorter distance in **4** can be traced to the wider bond angle Se1-C3-Se2 [105.59(9)°] compared with Se1-Sn1-Se2 [94.88(3)°] in **11**. The C-Se bond lengths are in the expected range.[26] In **4**, the Se-C(carborane) bond lengths (193.0(2), 191.9(1) pm) are markedly shorter in comparison with Se1-C3 and Se2-C3 bonds (199.8(2), 201.0(2) pm). The Sn-Se bond lengths (230 – 231 pm) are also found in the usual range.[27] In the compounds **4**, **11**, **13** and **14**, the five member rings deviate from a planar geometry, the folding being most pronounced in the case of the phosphorus compounds, in particular for **13** (angle CSeSeC/SePSe = 133.5°). There are hardly any data available to compare the P-Se bond lengths in **13**.[28] However, one finds the expected slight shortening upon oxidising the phosphorus (**14**). The P=S bond length in **14** is slightly longer than in many other phosphorus sulfides,[29] including the 2,5-dithia-1-phenyl-1-thio-1-phospha-2,5-dithia-cyclopentane.[30]

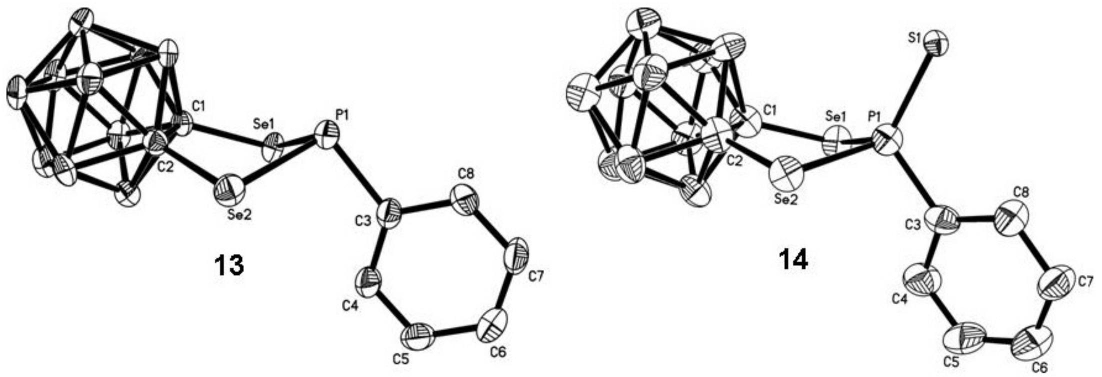


Figure 7. Molecular structures of the phosphorus compounds **13** and **14**. Selected bond lengths [pm] and angles [°]: **13**: C1-C2 164.7(6), C1-Se1 193.0(4), C2-Se2 193.1(4), Se1-P1 231.06(15), Se2-P1 230.61(16), P1-C3 184.3(6); Se1-P-Se2 95.15(5). **14**:C1-C2 162.3(12), Se1-C1 194.4(9), Se2-C2 193.3(9), P1-Se1 228.6(2), P1-Se2 228.1(2), P1-S1 203.3(3), P1-C3 180.6(9); Se1-P1-Se2 99.45(12).

The structure of the bis(diselane) **18** (crystallized with a molecule of benzene [16a] or toluene [16d]) is similar to that of the analogous bis(ditellane).[14b] The corresponding sulphur compound $[(B_{10}H_{10})C_2]_2S_4$ had been described[31] but not structurally characterized. The four selenium atoms in **18** lie almost exactly in a rectangular plane (mean deviation 6 pm). All bond lengths and angles fall into the expected ranges. This also true for the platinum complex **20**, e.g. by comparison with data for *cis*-$[Pt(PPh_3)_2(SePh)_2]$.[32] In **20**, the cycle Pt-Se-C-C-Se is close to planar within the experimental error. The positions of the four atoms around the platinum deviate slightly from a planar geometry (angle SePtSe/PPtP = 8.7°), which is most likely the result of steric interactions between the PPh_3 ligands, considering the wide bond angle PPtP = 96.22(5)°.

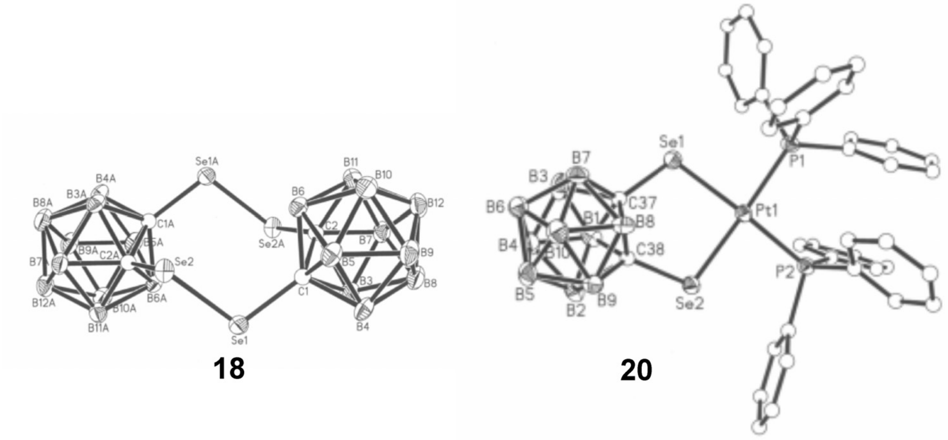


Figure 8. Molecular structures of the bis(diselane) **18** and the platinum complex **20**. Selected bond lengths [pm] and angles [°]: **18**: C1-C2 1.691(6), C1-Se1 1.944(4), C2-Se2 1.940(4), Se-Se 3.822(2); 3.703(2); C-Se-Se 103.85(13), 103.81(13), 104.12(13), 104.78(13). **20**: C37-C38 162.5(8), C37-Se1 193.8(5), C38-Se2 193.9(6), Pt1-Se1 243.72(6), Pt1-Se2 243.71(6), Pt1-P1 229.58(17), Pt1-P2 227.70(15); Se1-Pt1-Se2 91.45(2), P1-Pt-P2 96.22(5).

Experimental Section

General Procedures. 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 $[(Ph_3P)_2PtC_2H_4]$[33], 1,2-dicarba-*closo*-dodecaborane-1,2-diselenolate[14a,16a] and tropylium bromide[34] were prepared according to established procedures; the *ortho*-carborane 1,2-$C_2B_{10}H_{12}$ (Katchem), BuLi [1.6 M in hexane], iodine, iodomethane, sulphur and selenium (Aldrich), chlorotrimethylsilane, silicon tetrachloride 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 $\delta^{195}Pt = 0$]. Except ^{29}Si and some ^{119}Sn NMR spectra (refocused INEPT)[35] all other NMR spectra were recorded by single pulse methods. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus. All calculations were carried out using the Gaussian program package.[17a] The optimized structures were identified as minima on the potential energy surface by the absence of imaginary frequencies in the corresponding calculations.

General procedure. 2,2-Diphenyl-4,5-[1,2-dicarba-closo-dodecaborano(12)]-1,3-diselena cyclopentane (4)

To a yellow solution of 1,2-dicarba-*closo*-dodecaborane-1,2-diselenolate **3** (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 (room temperature) and concentrated, insoluble materials were filtered off and washed with 30 mL of pentane. Then volatile materials were removed in a vacuum. The NMR analysis of the raw product showed mainly the presence of compound **4** (>80 %) along with several undefined compounds. M. p. (isolated crystals) 149-151 ºC. ^1H NMR (300 MHz; CD_2Cl_2): δ = 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): δ = -2, -3, -4, -6, -7, -9, -11, -13, -14, -15, signals for the mixture of **4** and undefined compounds.

The compounds **5**, **6**, **9**, **11** and **13** were prepared in the same way as **4**. With the exception of the reaction temperature for **11** [from – 78 to - 30 °C] (For more details, see reference 16). The preparation of the compounds **14**-**22** and **25** is described in the references 16a-c.

Reaction of 13 with methyl iodide

To a solution of **13** (0.13 g, 0.32 mmol) in CD_2Cl_2 (1 mL) at room temperature was added methyl iodide (0.07 g, 0.48 mmol) (without previous purification). The mixture was stirred overnight at room temperature and analysed by NMR spectroscopy. The ^{31}P, ^{77}Se, ^{13}C and ^1H

NMR spectra showed the presence of selenophosphonic acid **16** as the main product (see Scheme 1, the bis(diselane) **18**[16a] and other unidentified compounds in low yield [δ^{31}P = 28.8 $^1J(^{77}\text{Se},^{31}\text{P})$ = 816 Hz; 76.1; 73.7 and 72.2 ppm]. ^{1}H NMR (400 MHz; CD_2Cl_2): δ [$^4J(^{31}\text{P},^1\text{H})$] = 7.45-8.05 (m, 5H, Ph), 2.29 [4] (d, 1H, CH), 1.30-3.30 (m (broad), 10H, $B_{10}H_{10}$). ^{11}B{^{1}H} NMR (96.2 MHz; CD_2Cl_2): δ = -3 (2B), -7 (1B), -8 (1B), -10 (1B), -12 (2B), -13 (3B).

Supplementary material

The supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications CCDC-621822 (for **4**)[16b], -621821 (for **11**)[16b], -628971 (for **13**)[16c], -628972 (for **14**)[16c], 613551 (for **18**)[16a,d] and -613552 (for **20**)[16a]. These data can be obtained free of charge at http://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).

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