

Novel 1,2-Dicarba-*closo*-dodecaborane(12) Derivatives of Selenium

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Lithiation of 1,2-dicarba-*closo*-dodecaborane(12) (**1**) followed by insertion of selenium into both C–Li bonds leads to the 1,2-diselenolato-1,2-dicarba-*closo*-dodecaborane(12) dianion (**3**), which is converted by oxidative coupling into the cyclic eight-membered bis(diselane) **4** with annellated carborane moieties. Oxidative addition of **4** to ethenebis(triphenylphosphane)platinum(0) gives the bis(triphenylphosphane)platinum(II) complex **7**, which contains a chelating 1,2-diselenol-

ato-1,2-dicarba-*closo*-dodecaborane(12) ligand, by symmetric cleavage of the eight-membered ring in **4** and displacement of ethene. The molecular structures of **4** and **7** were determined by X-ray analysis. The solution-state structures of the new compounds are supported by multinuclear NMR data (¹H, ¹¹B, ¹³C, ²⁹Si, ³¹P, ⁷⁷Se, ¹⁹⁵Pt).

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Introduction

An important aspect of the rich chemistry of 1,2-dicarba-*closo*-dodecaborane(12) (**1**) (“*ortho*-carborane”) is the variation of substituents at the carbon atoms in the 1,2-positions.^[1,2] Most conveniently, this chemistry starts with metallation at the carbon atom(s), for example to form the dilithiated carborane 1,2-Li₂-1,2-C₂B₁₀H₁₀ (**2**), followed by further transformations.^[1,2] We and others became interested in the 1,2-dichalcogenolato-1,2-dicarba-*closo*-dodecaborane(12) anions [1,2-(1,2-C₂B₁₀H₁₀)E₂]²⁻ (E = S, Se, Te) as chelating ligands,^[3–10] and this chemistry has been further developed into various areas.^[11–15] Tellurium derivatives are rarely studied since clean access to the anion [1,2-(1,2-C₂B₁₀H₁₀)Te₂]²⁻ appears to be difficult.^[16,17] However, the corresponding anions with sulfur or selenium are more readily accessible, and the anion containing selenium [1,2-(1,2-C₂B₁₀H₁₀)Se₂]²⁻ (**3**) is particularly attractive considering the useful NMR properties of ⁷⁷Se^[18] (*I* = 1/2; natural abundance 7.58%; about three times more sensitive in NMR experiments than ¹³C). In the present work, we report on observations of oxidative coupling of **3**, or derivatives of **3**, and cleavage of the resulting Se–Se bonds by oxidative addition to [Pt(PPh₃)₂(CH₂=CH₂)].

Results and Discussion

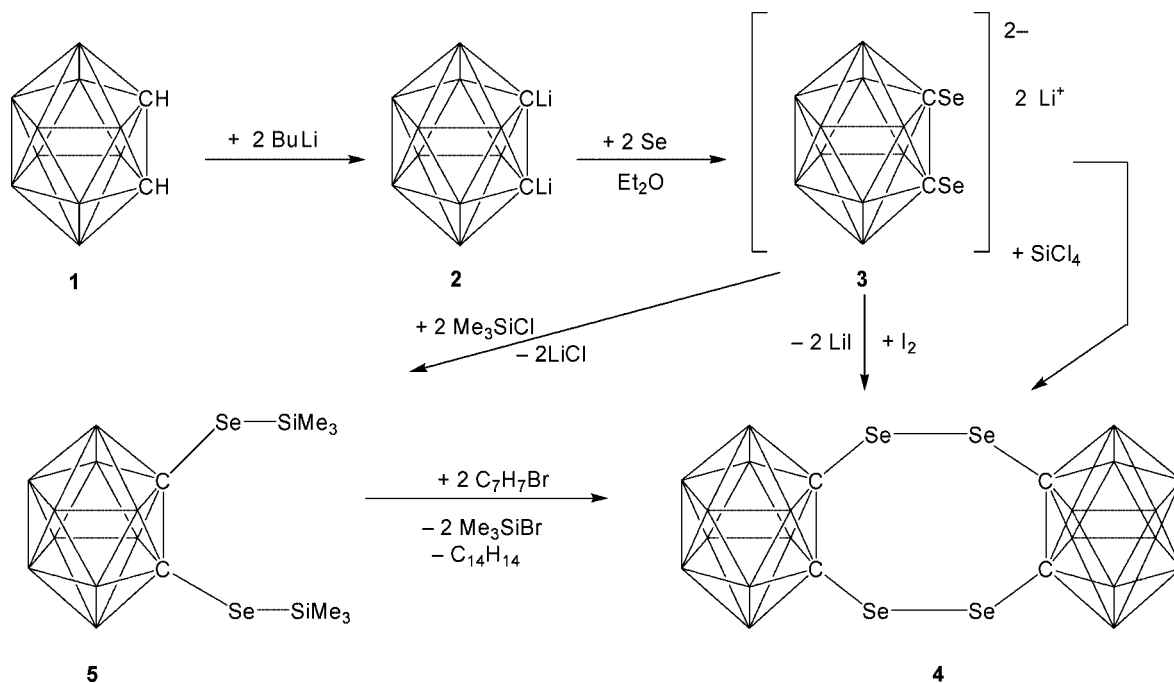
Formation of the anion [1,2-(1,2-C₂B₁₀H₁₀)Se₂]²⁻ (**3**) and its conversion into the cyclic bis(diselane) **4** are shown in

Scheme 1. The reaction of **3** with an excess of Me₃SiCl gave the disilylated derivative **5** in high yield along with a small amount of 1-Me₃SiSe-1,2-C₂B₁₀H₁₁ (**6**) and unreacted carborane **1**, thus indicating the preferred conversion of **1** into **2**, followed by double insertion of selenium into the C–Li bonds to give **3**. In context with the chemistry of heterosubstituted tropylium derivatives we have attempted to prepare a 1,2-bis(tropyliumseleno)-1,2-dicarba-*closo*-dodecaborane(12) by cleavage of the Se–Si bonds. Surprisingly, the reaction of **5** with two equivalents of tropylium bromide, C₇H₇Br, gave **4** as the final product of a complex redox reaction together with the expected Me₃SiBr and various organic compounds. The oxidative coupling of **3** with iodine led directly to **4**, as expected. Attempts to prepare a spirosilane from the reaction of **3** with SiCl₄ again gave **4** together with unidentified materials. The bis(diselane) **4** could be isolated as yellow crystals from benzene or toluene solutions and its molecular structure was determined by X-ray analysis (*vide infra*).

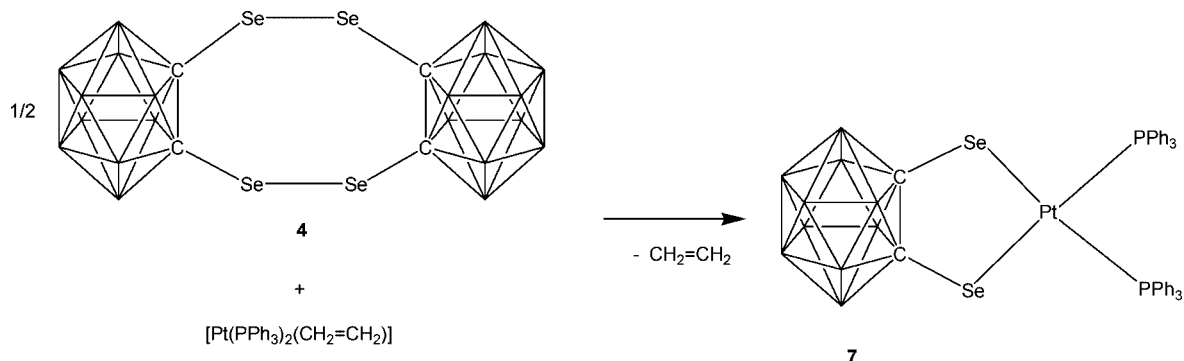
Diselanes are known as reagents for oxidative addition reactions.^[19] Thus, the reaction of [Pt(PPh₃)₂(CH₂=CH₂)] with **4** was studied (Scheme 2). Monitoring of the reaction by ³¹P NMR spectroscopy showed that the eight-membered ring in **4** was cleaved symmetrically to give the platinum(II) complex **7** in essentially quantitative yield. Orange crystals of **7** were isolated and studied by X-ray analysis (*vide infra*). Complexes of type **7** or their palladium analogues are potential catalysts of the *cis*-addition of the Se–Se bond to the C≡C bond in alkynes.^[19c,19d]

Addition of an excess of methyl iodide to a solution of **7** in dichloromethane led to cleavage of the Pt–Se bonds to give a mixture containing in the beginning *cis*-[PtI₂(PPh₃)₂], and the anionic complexes [PtI₃(PPh₃)]⁻ and

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Scheme 1. Oxidative coupling: three routes to the bis(diselane) 4.



Scheme 2. Oxidative addition of the bis(diselane) 4 to give the platinum(II) complex 7.

$[\text{PtI}_4]^{2-}$ with $[\text{P}(\text{Me})\text{Ph}_3]^+$ as the counterion. The complex *cis*- $[\text{PtI}_2(\text{PPh}_3)_2]$ slowly rearranges into the more stable *trans*-isomer.

NMR Spectroscopic Studies in Solution

The proposed structures of the new compounds are fully supported by the solution-state NMR spectroscopic data (see Table 1 and Experimental Section). The ^{13}C (carborane) NMR signals are frequently not reported in the literature since they tend to be weak and broad.^[1a,20] However, careful setting of the experimental conditions enables the measurement of these signals readily, and further information is provided by observation of ^{77}Se satellite signals, as shown in the case of **5** (Figure 1). The $^1J_{^{77}\text{Se},^{13}\text{C}}$ and $^2J_{^{77}\text{Se},^{13}\text{C}}$ coupling constants measured here are the first examples for this type of carbon atom. The magnitude of $^1J_{^{77}\text{Se},^{13}\text{C}}$ in **5** (158.9 Hz) is markedly increased when compared with

phenylselenium derivatives^[18a,21,22] (e.g. in Ph_2Se : $^1J_{^{77}\text{Se},^{13}\text{C}} = 103.1 \text{ Hz}$ ^[21]).

^{29}Si NMR spectra helped us to monitor the reaction of **5** with tropylium bromide (Scheme 1), and they also established the formation of the monosubstituted species **6** as a side product (Figure 2). The presence of the ^{77}Se satellite signals corresponding to $^1J_{^{77}\text{Se},^{29}\text{Si}}$ indicates the presence of an Si–Se bond; the magnitude of $^1J_{^{77}\text{Se},^{29}\text{Si}}$ is similar in **5** and **6** and also to data reported for other silylselanes.^[23,24]

The formation of complex **7** is best monitored by ^{31}P NMR spectroscopy. The ^{31}P NMR signal of **7** is accompanied by ^{195}Pt and ^{77}Se satellites. The magnitude of the coupling constant $^1J_{^{195}\text{Pt},^{31}\text{P}}$ is in the usual range for this type of complex.^[25] The situation is somewhat more complex for the $^2J_{^{77}\text{Se},^{31}\text{P}}$ data. In the literature, the *cis* and *trans* coupling pathway for comparable complexes has not been clearly distinguished.^[19a,26a,26b] In the case of a platinum(II) diselenolene complex containing the ligand tri(1-cyclohepta-2,4,6-trienyl)phosphane, this discrimination was

Table 1. ^{13}C , ^{29}Si , ^{31}P , ^{77}Se and ^{195}Pt NMR spectroscopic data^[a] of the 1,2-dicarba-*closo*-dodecaborane(12) derivatives 4–7.

	[(B ₁₀ H ₁₀)C ₂] ₂ Se ₄ (4)	(B ₁₀ H ₁₀)C ₂ (SeSiMe ₃) ₂ (5)	(B ₁₀ H ₁₀)CHCSeSiMe ₃ (6)	(B ₁₀ H ₁₀ C ₂)Se ₂ Pt(PPh ₃) ₂ (7) ^[b]
$\delta_{77\text{Se}}$	733.8 (s)	308.6 (s)	338.7 (s)	573.0 (t) 313.7 ($^1J_{195\text{Pt},77\text{Se}}$) ca. 51 ($^2J_{77\text{Se},31\text{P}}$) ^[c]
$\delta_{13\text{C}}$				
C ¹ , C ²	69.1 (s)	69.5 (s)	70.1 (s, C–Se) 66.4 (s, C–H)	71.8 (t) 16 ($^3J_{31\text{P},13\text{C}}$) ^[c]
SiMe ₃	–	158.9 ($^1J_{77\text{Se},13\text{C}}$) 2.0 (s) 53.4 ($^1J_{29\text{Si},13\text{C}}$)	1.3 (s) 53.5 ($^1J_{29\text{Si},13\text{C}}$)	–
$\delta_{29\text{Si}}$	–	20.9 (s) 112.6 ($^1J_{77\text{Se},29\text{Si}}$) 53.4 ($^1J_{29\text{Si},13\text{C}}$)	21.0 (s) 109.9 ($^1J_{77\text{Se},29\text{Si}}$) 53.5 ($^1J_{29\text{Si},13\text{C}}$)	–
$\delta_{31\text{P}}$	–	–	–	15.7 (s) 2972.5 ($^1J_{195\text{Pt},31\text{P}}$) ca. 51 ($^2J_{77\text{Se},31\text{P}}$) ^[d]
$\delta_{195\text{Pt}}$	–	–	–	–89.1 (t) 2972.5 ($^1J_{195\text{Pt},31\text{P}}$) 313.7 ($^1J_{195\text{Pt},77\text{Se}}$)

[a] NMR measurements in CD₂Cl₂ at 23 °C, coupling constants J are given in Hz. [b] $\delta_{13\text{C}}$ (phenyl) ($^nJ_{31\text{P},13\text{C}}$): 138.1 (45) C^{*ipso*}, 134.9 (11) C^{*ortho*}, 128.3 (11) C^{*meta*}, 131.5 C^{*para*}. [c] The signal appears as a multiplet, typical of an AA'X spin system, for which $\Sigma(^3J_{31\text{P},\text{Pt},\text{Se},13\text{C}}^{cis} + ^3J_{31\text{P},\text{Pt},\text{Se},13\text{C}}^{trans}) = 16$ Hz can be determined from the spectrum. Simulation suggests that $^3J_{31\text{P},\text{Pt},\text{Se},13\text{C}}$ values are around 20 and 4 Hz, with opposite signs, and that $^2J_{31\text{P},31\text{P}} = 15$ Hz. [d] Coupling appears to be similar for *cis* and *trans* coupling pathway.

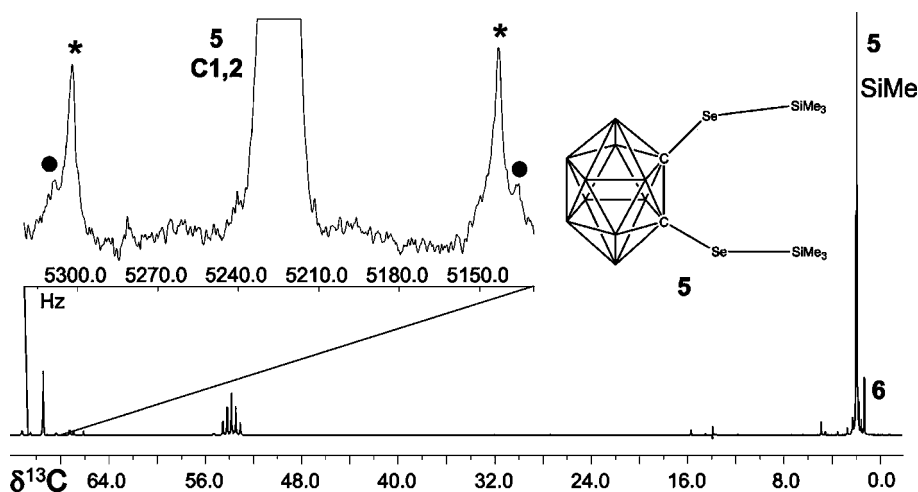


Figure 1. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75.4 MHz) of a mixture of [1,2-(Me₃SiSe)₂-1,2-C₂B₁₀H₁₀] (5) together with a small amount of [1-Me₃SiSe-1,2-C₂B₁₀H₁₀] (6; in CD₂Cl₂ at 23 °C). The ^{77}Se satellites marked by asterisks due to $^1J_{77\text{Se},13\text{C}} = 158.9$ Hz are clearly visible in the expanded spectral region. The weak outer lines (marked by full circles) arise from the isotopomer containing one ^{13}C and two ^{77}Se nuclei and correspond to the transitions of an AA'X spin system, separated by $\Sigma(^1J_{77\text{Se},13\text{C}} + ^2J_{77\text{Se},13\text{C}}) = 172.8$ Hz, from which the magnitude of $^2J_{77\text{Se},13\text{C}}$ (13.9 Hz) can be deduced. Both the one- and two-bond coupling constants possess the same sign (<0). Simulation suggests that $^3J_{77\text{Se},77\text{Se}}$ is between 20 and 40 Hz.

straightforward and a positive sign of $^2J_{77\text{Se},31\text{P}}^{cis,trans}$ was determined [$^2J_{77\text{Se},31\text{P}}^{cis} = 35.1$ Hz and $^2J_{77\text{Se},31\text{P}}^{trans} = 88.7$ Hz].^[26c] The observation of only one pair of satellites with approximately correct intensities in the case of 7 (Figure 3) indicates that the magnitude of these two-bond coupling constants is similar. Simulation of the spectrum as an AA'X spin system for the ^{77}Se and two ^{31}P nuclei suggests that $^2J_{31\text{P},31\text{P}}^{cis}$ is of the order of 15–20 Hz (vide infra) and of either sign, and that the values for $^2J_{77\text{Se},31\text{P}}^{cis,trans}$ can range between about 45 and 60 Hz, but are more likely to be close to 50 Hz for both coupling constants. The simula-

tion suggests that their signs should be alike. The ^{13}C (carborane) signals of 7 reveal a pattern corresponding to an AA'X spin system, and reasonable agreement between simulated and experimental spectra is observed if the signs of $^3J_{31\text{P},\text{Pt},\text{Se},13\text{C}}$ are opposite and $^2J_{31\text{P},31\text{P}} \approx 15$ Hz.

The evidence from the ^{31}P NMR spectra is supported by the ^{77}Se NMR spectrum (Figure 4), which reveals an apparently simple triplet accompanied by ^{195}Pt satellites ($^1J_{195\text{Pt},77\text{Se}} = 313.7$ Hz). The value of this coupling is similar to that reported for a platinum(II) diselenolene complex^[26c] ($^1J_{195\text{Pt},77\text{Se}} = -327.6$ Hz), where the ^{31}P nucleus is *trans* with

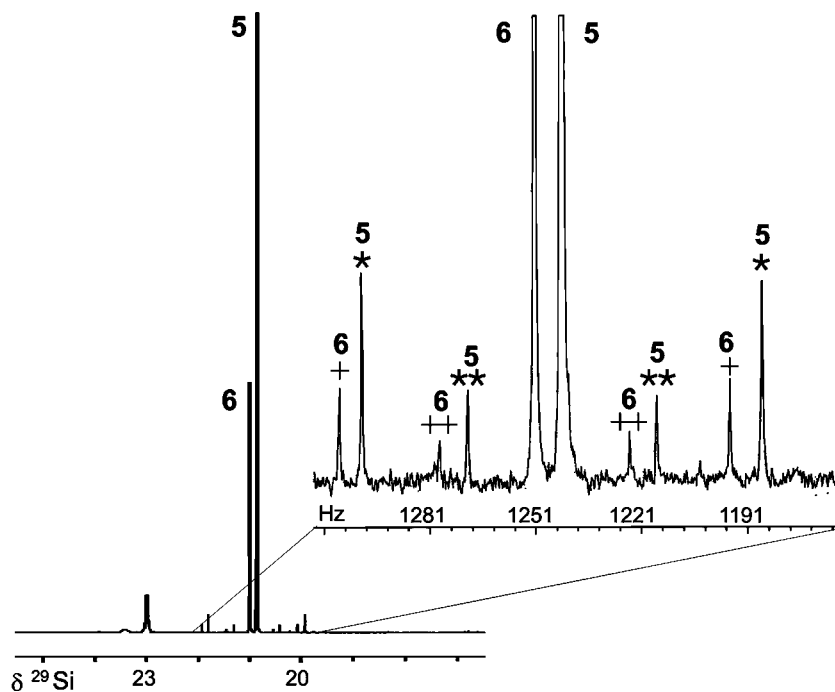


Figure 2. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (59.6 MHz; INEPT, refocused^[32]) of an unpurified reaction mixture containing mainly [1,2-(Me₃SiSe)₂-1,2-C₂B₁₀H₁₀] (5) together with [1-Me₃SiSe-1,2-C₂B₁₀H₁₁] (6; in CD₂Cl₂ at 25 °C). The ^{77}Se and ^{13}C satellites are marked for the coupling constants (* and +) $^1J_{^{77}\text{Se},^{29}\text{Si}} = 112.6$ Hz (5) and 109.9 Hz (6); (** and ++) $^1J_{^{29}\text{Si},^{13}\text{C}} = 53.4$ (5) and 53.5 Hz (6).

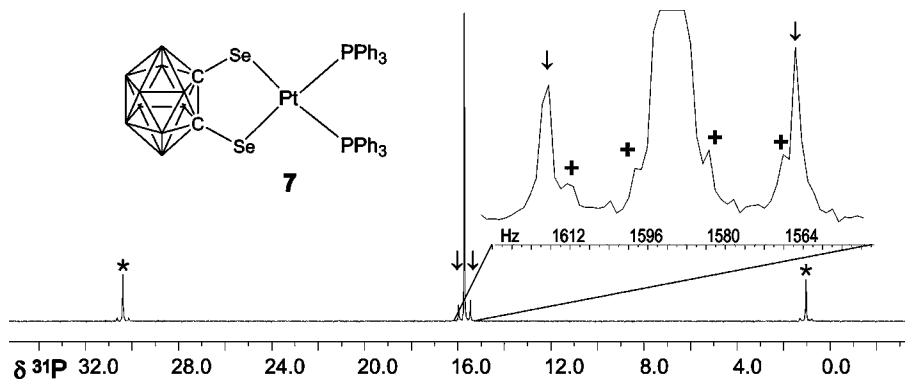


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121.4 MHz) of the complex [Pt(PPh₃)₂(1,2-Se₂-1,2-C₂B₁₀H₁₀)] (7; in CD₂Cl₂ at 25 °C). The ^{31}P NMR signal is accompanied by ^{195}Pt (asterisks) and ^{77}Se satellites (arrows) due to $^1J_{^{195}\text{Pt},^{31}\text{P}} (2972.5$ Hz) and $^2J_{^{77}\text{Se},^{31}\text{P}}$ (ca. 51 Hz). The signals marked by (+) are some of the ^{13}C satellites.

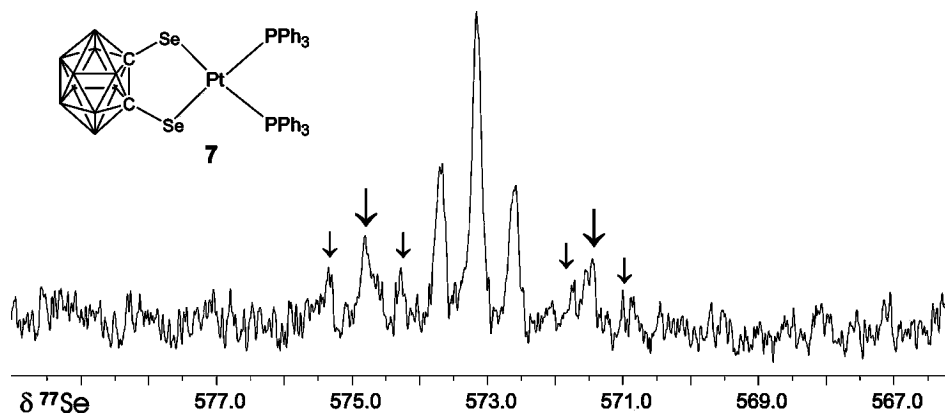


Figure 4. $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum (57.2 MHz; FT with LB = 2.5 Hz) of the complex [Pt(PPh₃)₂(1,2-Se₂-1,2-C₂B₁₀H₁₀)] (7; in CD₂Cl₂ at 25 °C) showing the splitting due to $^1J_{^{195}\text{Pt},^{77}\text{Se}} (313.7$ Hz, arrows) and $^2J_{^{77}\text{Se},^{31}\text{P}}$ (ca. 51 Hz).

respect to selenium. The ^{195}Pt NMR spectrum shows a triplet accompanied by ^{77}Se satellites with the same splitting as in the ^{31}P and ^{77}Se NMR spectra, respectively.

X-ray Structural Studies of the Bis(diselane) **4** and the Platinum(II) Complex **7**

The molecular structures of the bis(diselane) **4** and of the platinum(II) complex **7** are shown in Figures 5 and 6, respectively. Selected structural data are listed in Table 2, together with some data for the tellurium analogue of **4**.^[17]

The geometry of the carborane moiety^[1] in molecules **4** and **7** is scarcely affected by the various substituents at carbon. The C–C bond lengths appear to be slightly elongated when compared with the *ortho*-carborane itself, although it is difficult to relate these data owing to different experimental conditions. The Se–Se bond lengths are found in the

usual range for diselanes (2.28–2.39 Å).^[27] A comparison between the crystal systems of **4** and its tellurium analogue^[17] is meaningless since the former crystallises with benzene.

The cycle Pt–Se–C–C–Se is close to planar within the experimental error. The Pt–Se bond lengths in **7** [2.4372(6) and 2.4371(6) Å] tend to be slightly shorter than in *cis*-[Pt(PPh₃)₂(SePh)₂]^[26a] [2.4885(3) and 2.4506(3) Å]. The Pt–Se distance for the selenium *trans* to phosphorus in the platinum(II) diselenolene complex is also fairly short [2.4310(8) Å], and the one for selenium *trans* to the $\eta^2\text{-C}=\text{C}$ bond is even shorter [2.3698(9) Å]. However, the data reported here for **7** compare well with other Pt–Se bond lengths given in the literature.^[28] The Pt–P bond lengths in Pt^{II} complexes (2.22–2.32 Å) depend on the polarizing ability of the other ligands, mainly on the *trans* ligand.^[29] Thus, the Pt–P distances found here are typical of selenium in a

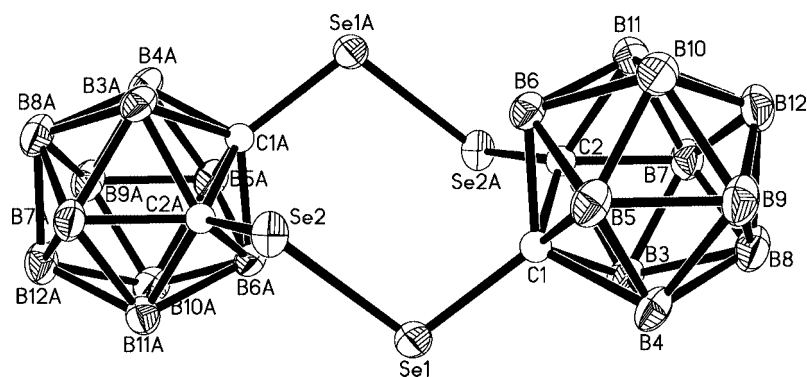


Figure 5. ORTEP plot (50% probability) of the molecular structure of the bis(diselane) **4**; hydrogen atoms have been omitted for clarity. See Table 2 for selected structural parameters.

Table 2. Selected bond lengths [Å] and angles [°] for [(B₁₀H₁₀)C₂]₂Se₄ (**4**), [(B₁₀H₁₀)C₂]₂Te₄ for comparison^[17] and [(B₁₀H₁₀)C₂Se₂]Pt(PPh₃)₂·CH₂Cl₂ (**7**).

	[(B ₁₀ H ₁₀)C ₂] ₂ Te ₄	[(B ₁₀ H ₁₀)C ₂] ₂ Se ₄ ·C ₆ H ₆ (4)	[(B ₁₀ H ₁₀)C ₂ Se ₂]Pt(PPh ₃) ₂ ·CH ₂ Cl ₂ (7)
C–C	1.70(3)	1.691(6), 1.689(6)	1.625(8)
C–E	2.15(3), 2.17(2)	1.944(4), 1.940(4)	1.938(5), 1.939(6)
C–C–E	123.9(15), 123.2(17)	1.935(4) 121.5(3), 120.9(3) 123.5(3), 123.3(3)	119.2(4)
E–C–C–E	4.204, –4.205	0.41, –1.23	2.23
E···E	4.048, 4.900, 4.885	3.822, 3.703 4.408, 4.412	3.49
E–E	2.676(3)	2.302(7)	–
C–E–E	104.0(7), 102.7(8)	103.85(13), 103.81(13) 104.12(13), 104.78(13)	–
C–E–E–C	112.8	113.7, –112.5	–
E–E···E	89.9, 90.2	88.4, 91.5	–
Pt(PPh ₃) ₂ in 7			
Se–Pt	2.4372(6), 2.4371(6)	Se–Pt–Se	91.45(2)
P–Pt	2.2958(15), 2.2770(15)	P–Pt–P	96.22(5)
Pt–Se–C	103.94(17), 103.73(17)	C–C–Se–Pt	10.9, –14.1
Se–Pt–P	86.47(4), 86.58(4), 173.22(4), 173.18(4)	C–Se–Pt–P	56.7, 89.3, –157.2, 171.2
		SePtSe/PPtP	8.7

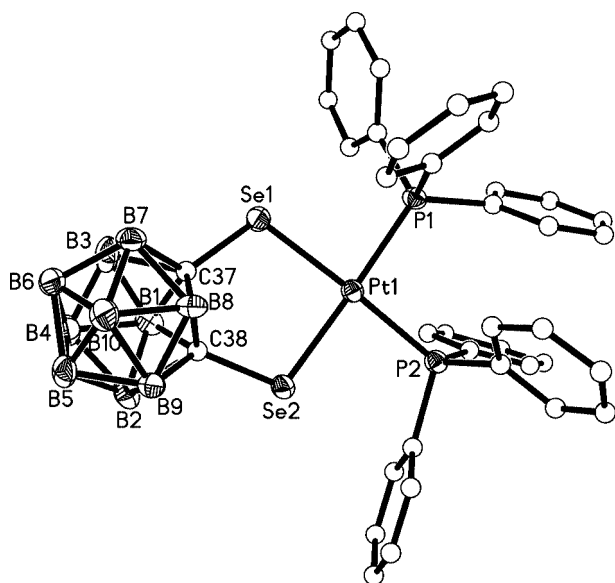


Figure 6. ORTEP plot (50% probability) of the molecular structure of the platinum(II) complex **7**; hydrogen atoms have been omitted for clarity. See Table 2 for selected structural parameters.

trans position, as evident, for example, by comparison with the data for *cis*-[Pt(PPh₃)₂(SePh)₂]^[26a] [2.2900(6) and 2.2937(6) Å].

Experimental Section

General: All syntheses and the handling of the samples were carried out in the absence of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The complex [Pt-(PPh₃)₂(C₂H₄)],^[30] 1,2-dicarba-*closo*-dodecaborane-1,2-diselenolate^[16] and tropylium bromide^[31] were prepared according to established procedures; the *ortho*-carborane 1,2-C₂B₁₀H₁₂ (Katchem), BuLi (1.6 M in hexane), iodomethane and selenium (Aldrich) were commercially available. NMR measurements: Bruker ARX 250, Varian Inova 300 and Varian Inova 400 NMR spectrometers; chemical shifts are given relative to SiMe₄ [CD₂Cl₂: δ_{1H} = 5.33; δ_{13C} = 53.8; δ_{29Si} = 0 ppm for \mathcal{E} (²⁹Si) = 19.867184 MHz], external Et₂O·BF₃ [δ_{11B} = 0 ppm for \mathcal{E} (¹¹B) = 32.083971 MHz], external 85% aqueous H₃PO₄ [δ_{31P} = 0 ppm for \mathcal{E} (³¹P) = 40.480747 MHz], external Me₂Se [δ_{77Se} = 0 for \mathcal{E} (⁷⁷Se) = 19.071523 MHz]. \mathcal{E} (¹⁹⁵Pt) = 21.4 MHz for δ_{195Pt} = 0 ppm. Except for the ²⁹Si NMR spectra (refocused INEPT^[32]) all other NMR spectra were recorded by single pulse methods. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

1,2-Bis(trimethylsilylseleno)-1,2-dicarba-*closo*-dodecaborane(12) [1,2-(Me₃SiSe)₂-1,2-C₂B₁₀H₁₀] (5): Butyllithium (2.94 mL of a 1.6 M solution in hexane 4.7 mmol) was added to a solution of *ortho*-carborane **1** (0.34 g, 2.35 mmol) in diethyl ether (100 mL) at room temperature. A white suspension was obtained and stirred for 2 h. Addition of selenium (0.37 g; 4.7 mmol) gave, after 24 h, a yellow solution containing **3**, which was cooled to -78 °C and added to a cold (-78 °C) solution of chlorotrimethylsilane (1.2 mL, 9.40 mmol) in diethyl ether (50 mL). A white precipitate was formed; the mixture was stirred overnight, concentrated, insoluble materials were filtered off and washed with 30 mL of pentane. Volatile materials were then removed in vacuum, and compound **5** was obtained as the main product in a mixture. The NMR analysis

showed the presence of the monoselenosilylated derivative **6** along with unreacted carborane as minor products.

5: ¹H NMR (300 MHz, CD₂Cl₂): δ = 0.59 ppm (s, 18 H, SiMe₃). ¹¹B{¹H} NMR (96.2 MHz, CD₂Cl₂): δ = -4 (2 B), -8 ppm (8 B).

6: ¹H NMR (300 MHz, CD₂Cl₂): δ = 0.11 (s, 9 H, SiMe₃), 2.25 ppm (s, 1 H, CH). ¹¹B{¹H} NMR (96.2 MHz, CD₂Cl₂): δ = -2 (s, 2 B), -8 (s, 2 B), -9 (s, 2 B), -14 ppm (s, 4 B).

3,4,7,8-Bis(1,2-dicarba-*closo*-dodecaborano[1,2])-1,2,5,6-tetraselenacyclooctane, [1,2-(1,2-C₂B₁₀H₁₀)-Se-Se]₂ (4). **Method A:** In an NMR tube, tropylium bromide (0.15 g, 0.88 mmol) was added to a solution of compound **5** (0.1 g, 0.224 mmol) in deuterated toluene (1.0 mL). A yellow solution was observed and analysed by NMR spectroscopy. The NMR analysis showed the mixture consisted of [(B₁₀H₁₀C₂)₂Se₄ (**4**) and organic compounds, e.g. (C₇H₇)₂ and bromotrimethylsilane. After one month, the formation of yellow crystals was observed on the walls of the NMR tube; the crystals (yield: 12%; 0.012 g; 0.02 mmol; m.p. 170 °C decomp.) were isolated and analysed by NMR and X-ray diffraction.

Method B: Addition of an ethereal solution of iodine (0.22 g, 0.9 mmol) to a solution of **3** (starting from 0.9 mmol of *ortho*-carborane) in diethyl ether (100 mL) gave the instantaneous formation of an orange-red suspension, which was stirred overnight at room temperature. The precipitate was filtered off, washed three times with pentane and diethyl ether, dried under high vacuum, and identified as **4** (yield: 150 mg, 30%).

Method C: A solution of **3** (0.89 mmol) in Et₂O (100 mL) was added to a solution of SiCl₄ (0.075 g, 0.44 mmol) in pentane (100 mL) at -78 °C. After 24 h of stirring at room temperature, the mixture was concentrated, and insoluble materials were separated. After removal of the solvents under vacuum, a yellow solid was obtained and analysed by NMR spectroscopy. It contained mainly **4** (yield 0.19 g, 72%) along with a small amount of unidentified compounds.

4: ¹H{¹¹B} NMR (250 MHz, CD₂Cl₂): δ = 1.56 (br., 1 H), 2.25 (br., 1 H), 2.44 (br., 2 H), 2.53 (br., 2 H), 2.72 (br., 3 H), 3.27 ppm (br., 1 H). ¹¹B{¹H} NMR (80.2 MHz, CD₂Cl₂): δ = -1.0 (2 B), -7.0 (4 B), -8.0 (2 B), -11.0 ppm (2 B).

1,2-Diselenolato-1,2-dicarba-*closo*-dodecaboranebis(triphenylphosphane)platinum [Pt(PPh₃)₂(1,2-Se₂-1,2-C₂B₁₀H₁₀)] (7): A solution of bis(*ortho*-carboran-1,2-diyl)tetraselenide (**4**; 0.0125 g, 0.017 mmol) in CD₂Cl₂ (0.5 mL) was added to a solution of ethenebis(triphenylphosphane)platinum(0) (0.02 g, 0.033 mmol) in CD₂Cl₂ (0.5 mL) at room temperature. A yellow-orange solution was obtained. After one day the formation of orange crystals was observed, which were isolated in essentially quantitative yield (m.p. 344 °C, decomp.) and characterised as complex **7** by NMR and X-ray diffraction. ¹H NMR (300 MHz, CD₂Cl₂): δ = 1.0–3.5 (br., m, 10 H, B₁₀H₁₀), 7.35 ppm (m, 30 H, PPh₃). ¹¹B{¹H} NMR (96.2 MHz, CD₂Cl₂): δ = -1.0 (2 B), -7.0 (2 B), -8.0 (4 B), -12.0 ppm (2 B).

Reaction of [Pt(PPh₃)₂(1,2-Se₂-1,2-C₂B₁₀H₁₀)] (7) with Methyl Iodide: An excess of methyl iodide (0.46 g, 3.2 mmol) was added to a solution of complex **7** (0.005 g, 0.005 mmol) in CD₂Cl₂ (0.5 mL). A yellow solution was obtained, and the reaction mixture was analysed by ³¹P NMR spectroscopy. The spectrum of the equilibrated mixture showed the formation of *cis*-[Pt₂(PPh₃)₂] (δ_{31P} = 12.5 ppm, ¹J_{195Pt,31P} = 3454 Hz; decreasing signal), *trans*-[Pt₂(PPh₃)₂] (δ_{31P} = 13.0 ppm, ¹J_{195Pt,31P} = 2486 Hz; increasing signal), [MePh₃P]⁺ (δ_{31P} = 22.5 ppm; the cation was also evident from the ¹³C{¹H} NMR spectrum) and [PtI₃(PPh₃)]⁻ {δ_{31P} = 12.0 ppm, ¹J_{195Pt,31P} = 3633 Hz}; one weak signal at δ_{31P} = 12.3 ppm (¹J_{195Pt,31P} = 3472 Hz) could

not be assigned. The assigned data are similar to those reported previously.^[25b,25c]

Crystal Structure Determinations of the Bis(diselane) 4 and the Platinum Complex 7: Details pertinent to the crystal structure determinations are listed in Table 3. The X-ray crystal structural analyses were carried out for single crystals using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit. Crystals of appropriate size were selected in perfluorinated oil at room temperature, and the data collections were carried out at 193(2) K (for 4) and 191(2) K (for 7). Structure solution and refinement were accomplished using SIR97,^[33] SHELXL-97,^[34] and WinGX.^[35]

Table 3. Details of the X-ray crystal structure analyses of 4 and 7.

	4·C ₆ H ₆	7·CH ₂ Cl ₂
Crystal system	triclinic	triclinic
Space group	P1̄	P1̄
a [Å]	7.3750(7)	11.1600(10)
b [Å]	10.5270(10)	15.1370(14)
c [Å]	11.0290(11)	15.5910(15)
α [°]	100.050(7)	62.034(7)
β [°]	103.862(7)	83.856(7)
γ [°]	96.740(7)	69.006(7)
V [Å ³]	807.13(14)	2165.8(3)
Z	2	2
Crystal size [mm]	0.9 × 0.32 × 0.24	0.38 × 0.28 × 0.23
ρ _{calcd.} [g cm ⁻³]	1.614	1.691
μ _{calcd.} [mm ⁻¹] (Mo-K _α)	0.71069	0.71069
T [K]	193(2)	191(2)
θ range [°]	1.95–25.72	1.96–25.11
Reflections collected	3034	7127
Independent reflections	3034	7127
F(000)	380	1068
R ₁	0.0338	0.0355
wR ₂ (all data)	0.1190	0.0956
No. of parameters	190	505

CCDC-613551 (for 4) and -613552 (for 7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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