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# 1,3,2-Diselena- and 1,3,2-Ditelluraphospholanes with an Annelated 1,2-Dicarba-*closo*-dodecaborane(12) Unit

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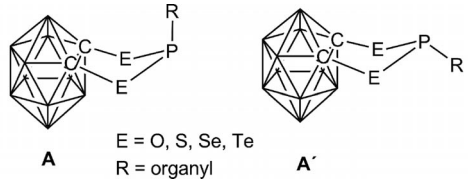
The exchange reactions of phosphorus dihalides $RPX_2$ [R = *i*Pr, cyclohexyl (Cy), *t*Bu, (3,5-$Me_2$-$C_6H_3$)$CH_2$, Ph; X = Cl, Br], $EtOPCl_2$, $Et_2NPCl_2$, $Cl_2PCH_2PCl_2$, and $Cl_2PCH_2CH_2PCl_2$ with 2,2-dimethyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-diselena-2-silacyclopentane provide a straightforward route to 1,3,2-diselenaphospholanes. Some tellurium analogues were prepared from the dilithium salt [1,2-$(LiTe)_2$-1,2-$C_2B_{10}H_{10}$] and were more difficult to characterize. For the selenium compounds, some of the P-organosubstituted five-membered rings dimerize to give ten-membered rings, most readily with the more bulky alkyl groups such as *t*Bu. This was not observed for the tellurium compounds. The conformations of the five-membered rings were studied by NMR spectroscopy and DFT methods. Striking structural differences were clear for the 2-phenyl-1,3,2-diselenaphospholane derivative in solution and in the solid state. All reactions were monitored by multinuclear magnetic resonance spectroscopy ($^1H$, $^{11}B$, $^{13}C$, $^{31}P$, $^{77}Se$, and $^{125}Te$ NMR), and solution-state structures could be proposed. Remarkably large secondary isotope effects as isotope-induced chemical shifts $^2\Delta^{12/13}C(^{31}P)$ exerted by the carborane carbon atoms were observed; this is apparently a special property of the five-membered ring. The gas-phase structures were optimized by DFT methods [B3LYP/6-311+G(d,p) level of theory], and the NMR parameters were calculated. Two 1,3,2-diselenaphospholanes and one dimer were characterized by X-ray analysis.

## Introduction

1,3,2-Dichalcogenophospholanes are well known for oxygen and sulfur,[1,2] less well studied for selenium,[3] and virtually unknown for tellurium. We are interested in the annelation of these five-membered rings with the 1,2-dicarba-*closo*-dodecaborane(12) unit (see **A** and **A′**) to study the kinetic and steric or electronic effects.




The kinetic stabilization provided by the bulky carborane unit may be potentially useful for E = Se and Te. By contrast, destabilization may be expected for E = O in particular because of repulsive interactions (short C–O and P–O distances) between the rigid three-dimensional carborane unit and both of the lone pairs of electrons and the respective substituent at the phosphorus atom. This repulsion has been shown to cause facile dimerization for E = O,[4] which is known for many 1,3,2-dioxaphospholanes in general,[1,5] as well as for E = S;[6] dimerization is unusual for 1,3,2-dithiaphospholanes.[1,7] Although the synthesis, structures, and first aspects of the reactivity of some derivatives **A** or **A′** with E = Se have been reported,[8–11] the nature of their solution-state structures in comparison to their solid-state structures has not been addressed in detail, and potential dimerization has not been studied. In this work, we report mainly our results for the derivatives of **A** or **A′** with E = Se and our first attempts to prepare 1,3,2-ditelluraphospholanes. Solution-state multinuclear magnetic resonance spectroscopic methods ($^1H$, $^{11}B$, $^{13}C$, $^{31}P$, $^{77}Se$, and $^{125}Te$ NMR) were used as the major analytical tool. In particular, the $^{31}P$,[12] $^{77}Se$,[13] and $^{125}Te$ NMR parameters[14] accompanied by DFT calculations should be helpful. Example solid-state structures were studied by X-ray structural analysis (for E = Se).

The synthetic approach is outlined in Scheme 1 and starts from the parent carborane **1** and involves dilithiation to form **2** and insertion of Se or Te into the C–Li bonds. Although this protocol is fairly straightforward in the case of **3** (E = Se)[15] and for E = S,[16] problems are encountered for **4** (E = Te).[17] Reactions with phosphorus halides afford more pure products in better yield when the silane **5** is used

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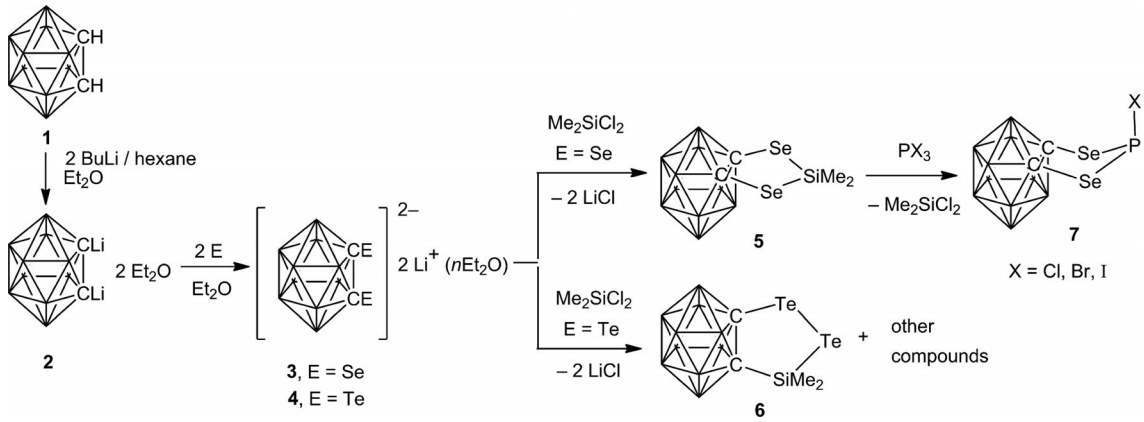



Scheme 1. Synthesis of starting materials **4** and **5**, mainly used in this work for reactions with organophosphorus dihalides and diethylamino- and ethoxyphosphorus dichloride.

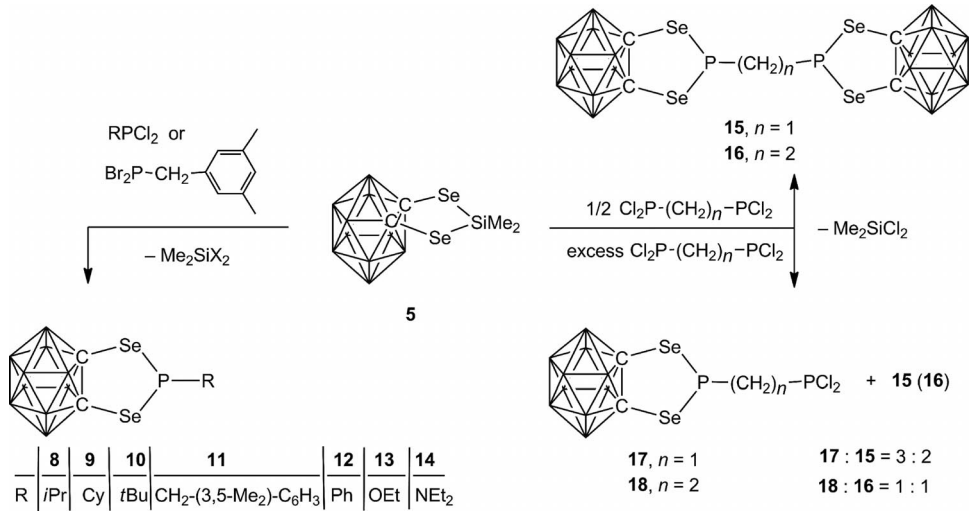
instead of **3**, as has been shown for phosphorus trihalides to give **7**.[10] The analogous route for E = Te is not feasible, as all attempts so far to obtain the tellurium analogue of **5** gave mainly the ditellane **6**.[17a] Thus, the major starting materials in this study are the carborane derivatives **4** and **5**, together with various phosphorus dihalides.

## Results and Discussion

### 1,3,2-Diselenaphospholanes

In principle, all reactions of the silane **5** with phosphorus dihalides in toluene (Scheme 2) proceed smoothly and quantitatively to afford the desired 1,3,2-diselenaphospholanes **8**–**18**. However, for **8**–**10**, the formation of other products can be observed, depending on the reaction time and the solvent. The air- and moisture-sensitive products **8**–**18** were readily identified by their diagnostic NMR spectroscopic data (Table 1), which were confirmed by DFT calculations (see below). For **11** and **15**, suitable crystalline material could be isolated for X-ray structural analysis (see below).

A representative example of the NMR spectroscopic characterization is shown for **11** in Figure 1. The spectra demonstrate the purity of the compound, its stability in solution, and the complementary nature of the NMR parameters measured. Moreover, some of the spectra reveal rather new aspects, for example, in Figure 1 (C) the isotope-induced chemical shifts $^{n}\Delta^{12/13}C(^{31}P)$ ($n$ = 1, 2). These effects are readily measured in favorable cases. We were not surprised to find that the effect for $n$ = 1 covers a substantial range.[18] More exciting was the observation of the effect for $n$ = 2, exerted by the carborane $^{12/13}C$ nuclei across the selenium atoms, as it had the same negative sign and often even exceeded the effect for $n$ = 1 (Supporting Information, Table S1]. The assignment of the $^{13}C$ satellites in Figure 1 (C) is unambiguous because their relative intensities were confirmed by the $^{13}C$ NMR spectroscopic data. Usually such effects for $n$ = 2 are much smaller than for $n$ = 1 and are often negligible and difficult to detect. We assume that this effect for $n$ = 2, as observed here, is related to properties of the five-membered ring, as it was not observed for ten-membered rings (see below).




Scheme 2. Reactions of the silane **5** in [$D_8$]toluene or $CD_2Cl_2$ with various phosphorus dihalides to form 1,3,2-diselenaphospholanes.

Table 1. $^{13}C$, $^{31}P$, and $^{77}Se$ NMR spectroscopic data[a] of the *ortho*-carborane derivatives ($Se_2PR$ monomer).

| R | Solvent | $\delta^{13}C(C_{carb})$ [ppm] | $^2J_{^{31}P,^{13}C_{carb}}$ [Hz] | Other $\delta^{13}C$ [ppm] | $\delta^{31}P$ [ppm] | $\delta^{77}Se$ [ppm] | $^1J_{^{77}Se,^{31}P}$ [Hz] | Type |
|---|---|---|---|---|---|---|---|---|
| *i*Pr (**8**) | [D$_8$]toluene | 80.5 [171.2] {–7.3} | 13.7 | 18.3 (27.6), 30.2 (47.9) | 110.4 ⟨240.9⟩ 47.6 ($^1J$), 27.6 ($^2J$), 13.7 ($^2J$) | 629.6 ⟨241.5⟩ | 241 | **A** |
| | $CD_2Cl_2$ | 80.6 | 12.6 | 18.8 (27.3), 30.4 (47.5) | 110.8 ⟨242.9⟩ | 628.6 ⟨242.7⟩ | 243 | **A** |
| | [D$_8$]THF | – | – | – | 116.9 ⟨248.2⟩ | 632.6 ⟨247.8⟩ | 248 | **A** |
| Cy (**9**) | [D$_8$]toluene | 80.5 [171.6] {–7.6} | 13.7 | 25.6 (2.0), 26.2 (13.4), 29.1 (22.4), 39.9 (49.9) [31.8] | 105.1 ⟨237.2⟩ | 613.1 ⟨236.4⟩ | 237 | **A** |
| | [D$_8$]THF | 81.5 | 12.9 | 26.6 (2.0), 27.2 (13.2), 30.0 (22.5), 41.1 (50.7) | 110.9 ⟨244.4⟩ | 617.6 ⟨244.2⟩ | 244 | **A** |
| *t*Bu (**10**) | [D$_8$]toluene | 75.0 [157.7] {–7.6} | 2.6 | 28.4 (18.5), 35.0 (48.3) | 161.3 ⟨152.6⟩ | 531.1 ⟨153.0⟩ | 153 | **A′** |
| | [D$_8$]THF | 74.7 | 5.7 | 28.8 (18.4), 36.0 (49.8) | 161.8 ⟨158.2⟩ | 542.2 ⟨158.9⟩ | 158 | **A′** |
| (3,5-$Me_2$-$C_6H_3$)$CH_2$ (**11**) | $CD_2Cl_2$ | 80.8 [170.8] {–8.4} | 13.3 | 21.4 (0.4), 41.0 (53.8), 127.7 (6.8) $C_o$, 129.7 (4.4) $C_p$, 134.5 (9.9) [1.2] $C_i$, 139.2 (3.4) $C_m$ | 98.8 ⟨232.0⟩ 53.8 ($^1J$) | 639.4 ⟨232.5⟩ | 232 | **A** |
| | [D$_8$]THF | 80.8 | 11.5 | 20.8, 40.8 (55.6), 127.7 (6.7) $C_o$, 129.3 (4.3) $C_p$, 135.1 (10.5)$C_i$, 138.7 (3.2) $C_m$ | 107.4 ⟨233.1⟩ | 642.5 ⟨233.5⟩ | 233 | **A** |
| Ph (**12**)[8] | [D$_8$]toluene | 80.6 [169.0] {–8.0} | 15.4 | 128.9 (3.5) $C_m$, 130.1 (1.7) $C_p$, 130.2 (19.8) $C_o$, 134.7 (60.0)$C_i$ | 96.5 ⟨268.5⟩ | 644.5 ⟨268.2⟩ | 268 | **A** |
| | $CD_2Cl_2$ | 80.5 [169.1] {–7.7} | 14.9 | 129.4 (3.7) $C_m$, 130.5 (1.8) $C_p$, 130.6 (19.7) [2.2] $C_o$, 134.7 (59.3)$C_i$ | 96.2 ⟨269.1⟩ | 643.2 ⟨269.0⟩ | | **A** |
| | [D$_8$]THF | – | – | – | 99.5 ⟨270.6⟩ | – | – | **A** |
| OEt (**13**) | [D$_8$]toluene | 82.8 [172.8] {–8.0} | 15.2 | 15.8 (6.0), 67.2 (7.7) | 209.8 ⟨279.2⟩ | 777.3 ⟨278.6⟩ | 279 | **A** |
| $NEt_2$ (**14**) | [D$_8$]toluene | 77.1 [171.3] {–9.5} | 4.9 | 13.8 (4.4), 45.4 (18.4) | 168.0 ⟨208.9⟩ | 631.7 ⟨209.9⟩ | 209 | **A′** |
| $(C_2B_{10}Se_2P)_2CH_2$ (**15**) | [D$_8$]toluene | 80.5 | 13.0 | 31.3 (71.6) | 95.3 ⟨–227.0⟩ "90.0" ⟨+20.0⟩ | 623.2 [b] | 227.0 | **A** |
| | $CD_2Cl_2$ | 80.9 | 12.8 | 33.8 (70.6) | 92.3 ⟨–235.0⟩ "121.0" ⟨+17.0⟩ | 629.2 [b] | 235.0 | **A** |
| | [D$_8$]THF | 81.2 | 9.6 | 36.2 (74.7) | 107.4 ⟨–235.0⟩ "119.0" ⟨+14.0⟩ | 633.1 [b] | 235.0 | **A** |
| $(C_2B_{10}Se_2PCH_2)_2$ (**16**) | [D$_8$]toluene | 80.7 [170.0] {–7.6} | 13.5 | 29.5 (–58.0, +15.5) | 101.1 ⟨–240.0⟩ "16.5" ⟨+4.0⟩ | 632.8 ⟨240.0⟩ | 240 | **A** |
| | $CD_2Cl_2$ | 80.8 | 13.0 | 30.2 (–58.0, +15.0) | 100.3 ⟨–242.5⟩ "20.5" ⟨+3.0⟩ | 634.0 ⟨242.5⟩ | 242.5 | **A** |
| | [D$_8$]THF | 81.4 | 10.9 | 31.3 (–59.0, +16.5) | 112.5 ⟨–244.0⟩ "10.0" | 638.2 ⟨244.0⟩ | 244 | **A** |
| $CH_2PCl_2$ (**17**) | [D$_8$]toluene | 80.9 [169.1] | 15.0 | 44.8 (79.5, 60.7) | 87.8 "40.2" ⟨227.7⟩, 181.4 "40.2" | 666.2 ⟨227.7, 8.1⟩ | 227.7 | **A** |
| | [D$_8$]THF | – | – | – | 91.5 "44.8", 182.2 "44.8" | – | – | **A** |
| $CH_2CH_2PCl_2$ (**18**) | [D$_8$]toluene | 80.7 | 13.9 | 26.5 (57.2) (10.2), 38.3 (50.6) (17.4) | 101.4 "6.4" ⟨237.7⟩, 187.7 "6.4" | 637.7 ⟨237.1⟩ | 237.1 | **A** |

[a] Coupling constants $^nJ_{^{31}P,^{13}C}$ are given in parentheses (± 0.5 Hz); $^nJ_{^{77}Se,^{13}C}$ are given in square brackets [± 0.5 Hz]; $^nJ_{^{77}Se,^{31}P}$ are given in angle brackets ⟨± 0.5 Hz⟩; $^nJ_{^{31}P,^{31}P}$ are given in quotation marks "± 0.5 Hz"; $^1\Delta^{10/11}B[^{13}C(carb)]$[19] are given in braces {± 0.5 Hz}; isotope-induced chemical shifts $^1\Delta$ are given in ppb, and the negative sign denotes a shift of the NMR signal of the heavy isotopomer to a lower frequency. [b] $|^1J_{^{77}Se,^{31}P} + {}^3J_{^{77}Se,^{31}P}| = 218.0$ (in $CD_2Cl_2$), 207.0 (in [D$_8$]toluene), and 221.0 Hz (in [D$_8$]THF).

The isotope-induced chemical shifts $^n\Delta^{12/13}C(^{31}P)$ ($n$ = 1, 2) are also essential for the simulation of the complex $^{13}C$ NMR spectra (for example, that of **16** is shown in Figure 2). As has been noted for other 1,2-diphosphinylethane derivatives,[20] the interpretation of $^{13}C$ NMR spectra requires the assumption of an ABX spin system, instead of an AA′X system, in which A and B are $^{31}P$ nuclei that become chemically different because of $^n\Delta^{12/13}C(^{31}P)$ ($n$ = 1, 2). Again, we note that the $^{13}C$ NMR signals for the carborane $^{13}C$ nuclei (Figure 2) can only be simulated by taking into account a

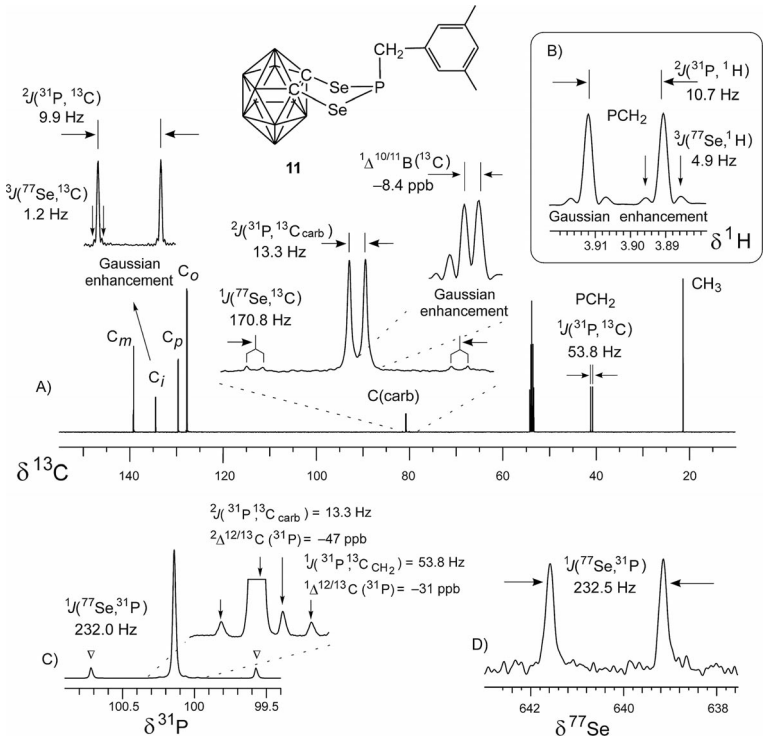



Figure 1. NMR spectra of **11** in $CD_2Cl_2$ at 23 °C. (A) 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of **11**. The typical pattern[19] for the isotope-induced chemical shift $^1\Delta^{10/11}B(^{13}C_{carb})$ is observed. (B) 500.13 MHz $^1H(PCH_2)$ NMR spectrum of **11**. (C) 202.5 MHz $^{31}P\{^1H\}$ NMR spectrum (refocused INEPT) of **11**. The $^{77}Se$ satellites for $^1J_{^{77}Se,^{31}P}$ are marked by ∇. The $^{13}C$ satellites for $^nJ_{^{31}P,^{13}C}$ ($n$ = 1, 2) are marked by arrows; the isotope-induced chemical shifts $^n\Delta^{12/13}C(^{31}P)$ ($n$ = 1, 2; ± 1 ppb) are given. (D) 95.4 MHz $^{77}Se$ NMR spectrum of **11**.

rather large value $|^2\Delta^{12/13}C(^{31}P)|$ = 70 ppb. The magnitude of the $^nJ_{^{31}P,^{31}P}$ coupling constants in **15** and **16** depend markedly on the solvent (Table 1), which indicates that they have different preferred conformations because of distinct solute–solvent interactions.

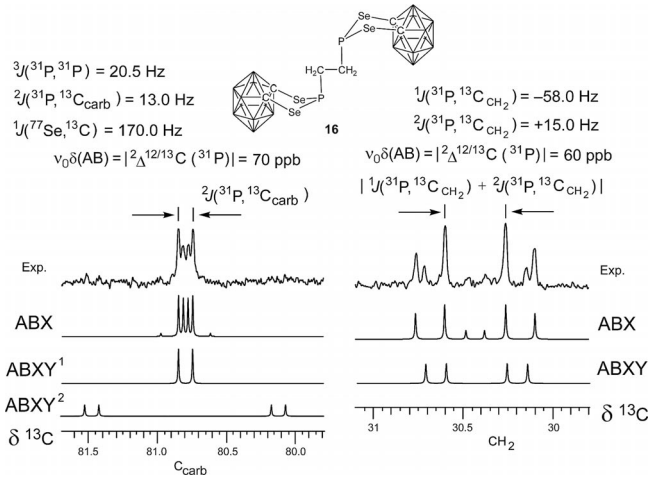



Figure 2. Experimental ($CD_2Cl_2$ at 23 °C) and simulated $^{13}C$ NMR spectra of **16** [A, B = $^{31}P$, X = $^{13}C$, Y = $^{77}Se$; $^1J_{^{77}Se,^{31}P}$ = –242.5 Hz, $^4J_{^{77}Se,^{31}P}$ = +3.0 Hz, $^2J_{^{77}Se,^{13}C_{CH2}}$ = 0 Hz].

For complex $^{31}P$ and $^{77}Se$ NMR spectra (e.g., those of **16** and **15**), AA′X and minor intensity AA′XX′ spin systems can be assumed (Figure 3), as the isotope effects exerted by the different selenium isotopes can be regarded as negligible.

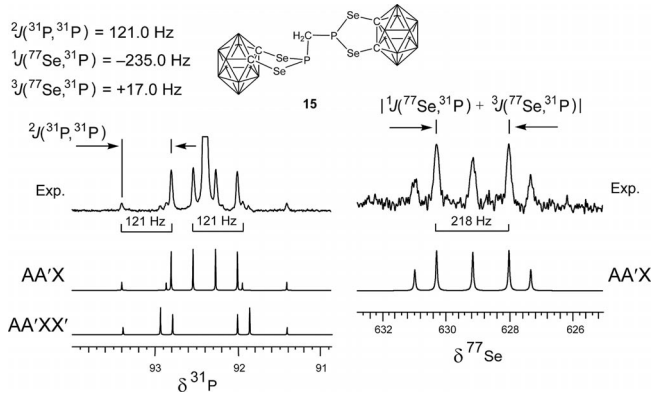
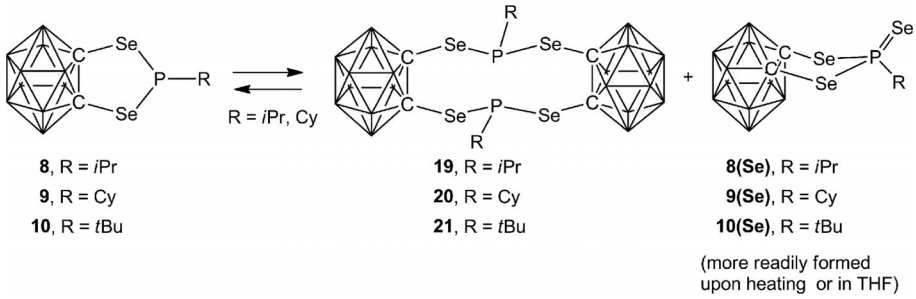



Figure 3. Experimental ($CD_2Cl_2$, at 23 °C) and simulated $^{31}P$ and $^{77}Se$ NMR spectra of **15**, revealing the coupling constants as shown (A = $^{31}P$, X = $^{77}Se$). Some additional weak intensities arise from species containing two $^{77}Se$ nuclei (AA′XX′ spin system; the $AA'X_2$ spin system was not considered, because of the low natural abundance of $^{77}Se$).

## Dimerization of 1,3,2-Diselenaphospholanes

Annelation with a carborane unit increases the ring strain in 1,3,2-diselenaphospholanes, in particular, if the substituent R at the phosphorus atom is bulky. The rigid




Scheme 3. Dimerization of 2-alkyl-1,3,2-diselenaphospholanes.

carborane cage cannot avoid contacts with R in the axial position (see **A**); this forces bulky R groups such as *t*Bu into an equatorial position (see **A′**). As this unfavorable situation represents a bad compromise, dimerization appears to be the way out, at least for R = alkyl (Scheme 3).

For R = *i*Pr (**8**), the dimer **19** forms only in ca. 10–15% in concentrated reaction solutions of **5** with *i*PrPCl$_2$ in toluene at room temp. In tetrahydrofuran (THF), the equilibrium shifts almost completely towards the monomer, accompanied by formation of a minor amount of the selenide **8**(Se). For R = cyclohexyl (Cy, **9**), reversible dimerization occurs in toluene solution to form **20** in only ca. 15–20% at room temp. and ca. 30–40% at –30 °C, at which temperature a white powder forms because of the low solubility of **20**. The dimer **20** dissociates in THF at 50 °C after 1 h, again accompanied by the formation of a small amount of the selenide **9**(Se) (see Experimental Section). The NMR spectroscopic data of the dimers and selenides are listed in Tables 2 and 3, respectively.

The dimerization process for **9** is demonstrated by the $^{31}$P NMR spectra measured under different conditions (Figure 4). We note a pronounced effect of the solvent THF on $\delta^{31}$P of the monomer **9** (see Figure 4, A and C); in contrast, a small effect on $\delta^{31}$P of the dimer **20** was observed. The low solubility of the dimer **20** enables its separation from **9** and **9**(Se) (Figure 4, B]. The addition of THF causes immediate dissociation of **20** into **9** (Figure 4, C), which is almost complete after 30 min at 50 °C (Figure 4, D). This behavior together with the strong solvent dependence of $\delta^{31}$P for the monomer **9** indicates a bonding interaction between THF and the 1,3,2-diselenaphospholane.

The situation is different for R = *t*Bu (**10** and **21**); dimerization of **10** towards **21** was irreversible under the experimental conditions (Scheme 4). In contrast to its effect on **8** and **9**, the addition of THF as a solvent increases the speed of dimerization of **10**, which already occurs in [D$_8$]toluene or $CD_2Cl_2$ at room temp. Although the dimers **19** and **20** dissociate to some extent into the monomers in toluene solution at 100 °C, this is not the case for **21**.

Monitoring of the dimerization of **10** by $^{31}$P NMR spectroscopy (Figure 5) showed first the sharp $^{31}$P NMR signal of **10** and broad unresolved $^{31}$P NMR signals in the region assigned to the dimer, which probably arise from stereoisomers and/or oligomers (Figure 5, A). The addition of THF (Figure 5, B) reduced the amount of the monomer and converted the broad signals into two sharp signals. Compound **21′** possesses almost identical NMR parameters as those of **21** and could be a trimer. After 2 d in THF at room temp.

Table 2. $^{13}$C, $^{31}$P, and $^{77}$Se NMR spectroscopic data[a] of the *ortho*-carborane derivatives ($Se_2PR$ dimer).

| R | Solvent | Dimer (exp.) | | | | | Dimer (calcd.) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta^{13}C(C_{carb})$ [ppm] | $^2J_{^{31}P,^{13}C_{carb}}$ [Hz] | Other $\delta^{13}$C [ppm] | $\delta^{31}$P [ppm] | $\delta^{77}$Se [ppm] | $\delta^{13}C(C_{carb})$ [ppm] | $\delta^{77}$Se [ppm] | $\delta^{31}$P [ppm] |
| *i*Pr (**19**) | $CD_2Cl_2$ | 76.5 [166.0] {–9.6} | 27.5 | 20.6 (15.5), 34.4 (32.6) [10.6] | 115.3 ⟨232.6⟩ | 524.1 ⟨233.0⟩ | 100.4 | 626.5 | 197.7 |
| Cy (**20**) | $CD_2Cl_2$ | 76.8 [165.9] {–12.4} | 27.8 | 25.9 (1.4), 27.3 (11.1), 30.9 (13.7), 43.8 (34.2) | 108.0 ⟨233.4⟩ | 524.1 ⟨232.9⟩ | – | – | – |
| | [D$_8$]toluene | 76.6 [165.8] {–9.9} | 27.5 | 25.6, 26.9 (10.9), 30.5 (13.6), 43.3 (34.2) | 106.7 ⟨231.2⟩ | 521.8 ⟨232.5⟩ | – | – | – |
| *t*Bu (**21**), (dimer) | $CD_2Cl_2$ | 77.0 {–11.0} | 28.1 | 28.1 (16.4), 39.4 (39.2) | 129.3 ⟨243.7⟩ | 522.6 ⟨241.6⟩ | 100.6 | 596.5 | 219.9 |
| | [D$_8$]THF | 78.0 [168.0] {–10.4} | 28.5 | 28.3 (16.4) [2.5], 39.9 (34.4) [7.2] | 129.7 ⟨240.9⟩ | 523.1 ⟨241.2⟩ | – | – | – |
| *t*Bu (**21′**), (trimer) | $CD_2Cl_2$ | 76.2 | 30.0 | 28.2 (16.2) | 129.8 | 501.3 ⟨228.4⟩ | – | – | – |
| H | – | – | – | – | – | – | 102.1[b] | 617.0 | 67.8 |

[a] Coupling constants $^nJ_{^{31}P,^{13}C}$ are given in parentheses (± 0.5 Hz); $^nJ_{^{77}Se,^{13}C}$ are given in square brackets [± 0.5 Hz]; $^nJ_{^{77}Se,^{31}P}$ are given in angle brackets ⟨± 0.5 Hz⟩; $^1\Delta^{10/11}B(^{13}C_{carb})$[19] are given in braces {± 0.5 Hz}; isotope-induced chemical shifts $^1\Delta$ are given in ppb, and the negative sign denotes a shift of the NMR signal of the heavy isotopomer to a lower frequency. [b] $^2J_{^{31}P,^{13}C_{carb}}$ = +23.5 Hz; $^1J_{^{77}Se,^{13}C}$ = –197.7 Hz; $^1J_{^{77}Se,^{31}P}$ = –176.9 Hz.

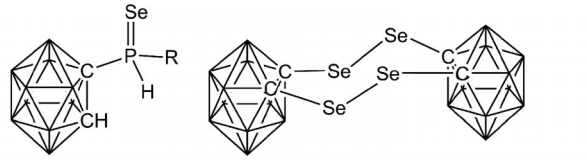
Table 3. $^{13}C$, $^{31}P$, and $^{77}Se$ NMR spectroscopic data[a] of the *ortho*-carborane derivatives (P=Se, P=S).

| | Solvent | $\delta^{13}C(C_{carb})$ [ppm] | $^2J_{^{31}P,^{13}C_{carb}}$ [Hz] | Other $\delta^{13}C$ [ppm] | $\delta^{31}P$ [ppm] | $\delta^{77}Se$ [ppm] |
|---|---|---|---|---|---|---|
| *i*Pr–P($Se_2$)=Se [**8**(Se)] [11] | $CD_2Cl_2$ | 75.7 [163.0] {–8.7} | 7.3 | 18.5 (1.8), 48.2 (26.6) | 92.8 ⟨363.7⟩ ⟨802.5⟩ | 716.9 ⟨364⟩ (P–Se), 60.9 ⟨802⟩ (P=Se) |
| Cy–P($Se_2$)=Se [**9**(Se)] | [$D_8$]toluene | 75.4 {–8.8} | 7.2 | 25.1 (2.8), 25.8 (17.8), 28.6 (4.4), 57.4 (25.0) | 83.8 ⟨358.1⟩ ⟨808.0⟩ | 726.9 ⟨359.0⟩ (P–Se), 139.8 ⟨809.6⟩ (P=Se) |
| *t*Bu–P($Se_2$)=Se [**10**(Se)] | [$D_8$]toluene | 74.1 [161.6] {–8.2} | 6.3 | 26.7 (3.0), 50.2 (22.2) [4.2] | 106.7 ⟨346.9⟩ ⟨807.8⟩ | 736.0 ⟨347.8⟩ (P–Se), 290.5 ⟨807.8⟩ (P=Se) |
| (3,5-Me-$C_6H_3$)$CH_2$P($Se_2$)=Se [**11**(Se)] | $CD_2Cl_2$ | 75.9 {–8.2} | 7.1 | 21.4 (0.7), 57.5 (23.5) [4.9], 128.8 (7.7) $C_o$, 130.8 (6.7) $C_p$, 130.9 (10.8)$C_i$, 138.9 (5.6) $C_m$ | 64.6 ⟨363.3⟩ ⟨802.9⟩ | 738.3 ⟨363.4⟩ (P–Se), 183.9 ⟨803.5⟩ (P=Se) |
| Ph–P($Se_2$)=Se [**12**(Se)][8,11] | $CD_2Cl_2$ | 75.5 [161] {–8.0} | 6.0 | 129.4 (16) $C_m$, 132.8 (13) $C_o$, 134.0 (4) $C_p$, 135.2 (57)$C_i$ | 49.6 ⟨350.7⟩ ⟨815.6⟩ | 802.1 ⟨350.2⟩ ≪34≫ (P–Se), 251.4 ⟨815.4⟩ ≪34≫ (P=Se) |
| | [$D_8$]toluene | – | – | – | 46.9 ⟨348.9⟩ ⟨827.2⟩ | 805.1 ⟨350.2⟩ (P–Se), 261.3 ⟨825.1⟩ (P=Se) |
| EtO–P($Se_2$)=Se [**13**(Se)][11] | $CD_2Cl_2$ | – | – | – | 67.8 ⟨448.8⟩ ⟨869.2⟩ | 797.2 ⟨449⟩ (P–Se), 104.4 ⟨869⟩ (P=Se) |
| $Et_2N$–P($Se_2$)=Se [**14**(Se)] | [$D_8$]toluene | – | – | – | 52.4 ⟨359.7⟩ ⟨855.3⟩ | 767.2 ⟨360.5⟩ (P–Se), 304.7 ⟨857.0⟩ (P=Se) |
| (3,5-Me-$C_6H_3$)$CH_2$P($Se_2$)=S [**11**(S)] | $CD_2Cl_2$ | 73.8 [160.6] {–9.0} | 6.2 | 21.4, 57.5 (33.6), 128.6 (7.7) $C_o$, 130.7 (11.1)$C_i$, 130.8 (6.4) $C_p$, 139.1 (5.3) $C_m$ | 91.3 ⟨361.5⟩ (33.5) | 740.2 ⟨362.1⟩ |
| (3,5-Me-$C_6H_3$)$CH_2$P($Se_4$)=Se (**25**) | $CD_2Cl_2$ | 80.3 {–10.5} | 2.9 | 21.36 (0.8), 46.9 (18.8), 129.1 (7.7) $C_o$, 129.7 (9.5)$C_i$, 130.8 (6.7) $C_p$, 138.9 (5.1) $C_m$ | 24.8 ⟨28.2⟩ ⟨439.0⟩ ⟨730.5⟩ | 698.2 ⟨27.5⟩ (C–Se), 558.0 ⟨439.4⟩ (P–Se), –51.9 ⟨726.9⟩ (P=Se) |
| C–PH(*i*Pr)=Se (**22**) | $CD_2Cl_2$ | 62.7 (CH), 63.7 (PC) | 21.8 | 19.4 (2.2), 28.2 (43.1) | 47.1 ⟩477.5⟨ ⟨798.5⟩ | 467.5 ⟨797.8⟩ |
| C–PH(Cy)=Se (**23**) | [$D_8$]toluene | 62.7 (CH), 63.5 (PC) | 20.3 | 37.2 (42.4) (PC) | 40.3 ⟩478.0⟨ ⟨805.0⟩ | 140.1 ⟨805.0⟩ |

[a] Coupling constants $^nJ_{^{31}P,^{13}C}$ are given in parentheses (± 0.5 Hz); $^nJ_{^{77}Se,^{13}C}$ are given in square brackets [± 0.5 Hz]; $^nJ_{^{77}Se,^{31}P}$ are given in angle brackets ⟨± 0.5 Hz⟩; $^nJ_{^{31}P,^1H}$ are given in angle brackets ⟩± 0.5 Hz⟨; $^2J_{^{77}Se,^{77}Se}$ are given in quotation marks "± 0.5 Hz"; $^1\Delta^{10/11}B(^{13}C_{carb})$[19] are given in braces {± 0.5 Hz}; isotope-induced chemical shifts $^1\Delta$ are given in ppb, and the negative sign denotes a shift of the NMR signal of the heavy isotopomer to a lower frequency.

(Figure 5, C), the monomer was almost consumed, the signal for **21′** had disappeared, and that for the selenide **10**(Se) was still present and slightly more intense than at the beginning. We isolated crystalline samples of **21** that were suitable for X-ray analysis (see below), and after redissolving this material, the identity with **21** in the reaction solution was evident. In particular, the $^{77}Se$ NMR parameters (Figure 5, D and F) proved helpful. With excess *t*$BuPCl_2$ for the synthesis of **10**, the formation of the expected monomer **10** was observed, together with a small amount of acyclic derivatives $B_{10}H_{10}C_2$[SeP(*t*Bu)Cl]$_2$ ($\delta^{31}P$ = 187.2 and 187.9 ppm in [$D_8$]toluene).

Although the dimers **19**–**21** survived in toluene at 100 °C, slow decomposition became evident, for example, by the formation of small amounts of **22**, **23**, and **24**[21] as side products, which were also present when solutions of the dimers were kept in THF for prolonged periods of time.

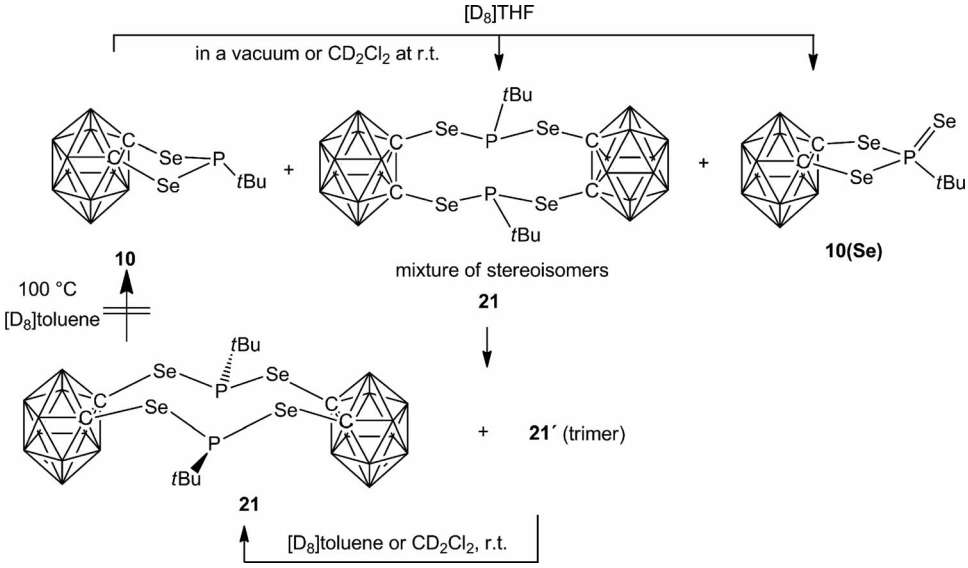



**22**, R = *i*Pr
**23**, R = Cy

**24**

Since the monomers **8**–**10** can be converted partly (**8**, **9**; R = *i*Pr, Cy) or completely (**10**; R = *t*Bu) into the dimers after some time at room temp. or by heating, this was also investigated with **11** [R = $CH_2$(3,5-$Me_2C_6H_3$)], **12** (R = Ph),[8] **13** (R = OEt), and **14** (R = $NEt_2$; Scheme 5). Although dimers did not form, the respective selenides **11**(Se), **12**(Se),[11] **13**(Se),[11] and **14**(Se) could be identified (NMR spectroscopic data in Table 3), in addition to numerous un-




Scheme 4. Irreversible dimerization of **10** via a mixture of stereoisomers towards pure **21**.

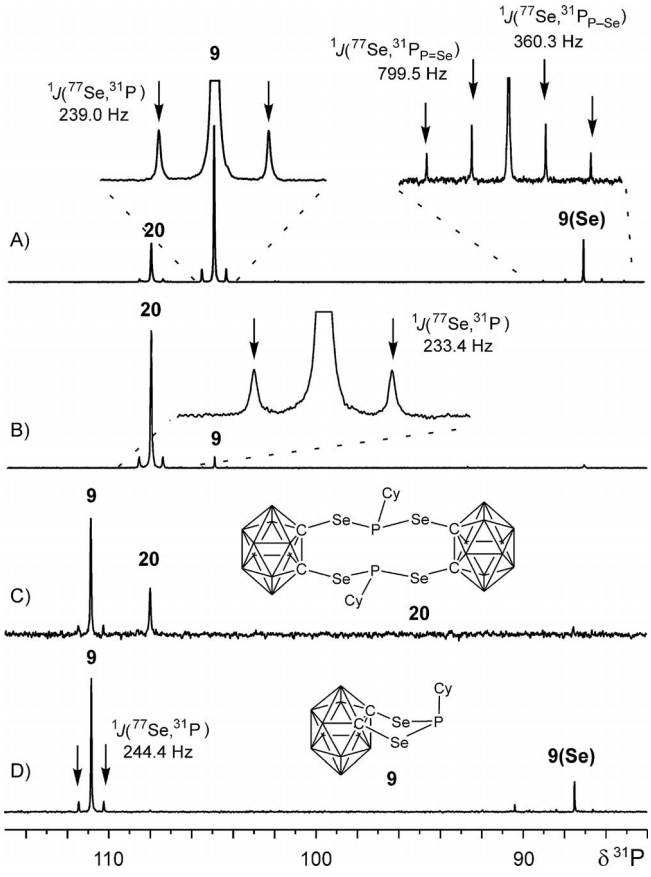



Figure 4. 202.5 MHz $^{31}P\{^1H\}$ NMR spectra of the reaction solutions obtained from the reaction of **5** with $CyPCl_2$. (A) $[D_8]$Toluene at 25 °C after 1 d at room temp.; the mixture contains **9** and **20** together with **9**(Se). (B) Compound **20** after 1 d in $CD_2Cl_2$ at 25 °C. (C) Compound **20** after 1 h in $[D_8]$THF at room temp. (D) The same solution as that in (C) after 30 min at 50 °C.

identified decomposition products. The absence of dimers for R = Ph and $CH_2$-(3,5-$Me_2$)$C_6H_3$ is remarkable, as the analogous oxygen and sulfur derivatives **A** (E = O, S), in which apparently the ring strain is greater, dimerize readily.[4,6] By heating **11** in $[D_8]$toluene solution at 100 °C for 20 h, the selenide **11**(Se) was observed in a mixture with **25**, as a result of further insertion of selenium. Similar to previous findings (for R = *i*Pr, Ph),[11] compound **25** could be prepared independently as a single isomer by oxidation of **11** with excess selenium. Oxidation with sulfur led only to the sulfide **11**(S) (Table 3, Supporting Information: Scheme S1 and Figure S1).

### 1,3,2-Ditelluraphospholanes

The reactions of the dilithium compound **4** with three organophosphorus dichlorides $RPCl_2$ (R = *i*Pr, *t*Bu, Ph) and $Et_2NPCl_2$ were performed (Scheme 6). Although the desired 1,3,2-ditelluraphospholanes **26a**–**26d** were the major products, their formation was accompanied by many side products, some of which could be identified. For instance, the bis(ditellane) **31**[17] was always present in the reaction mixtures, as shown by its $^{125}Te$ NMR signal (Figure 6). Except for the formation of **31**, the reaction of **4** with bis(dichlorophosphanyl)methane (Scheme 7) afforded the desired product **32** without significant amounts of side products. The NMR spectra (experimental and simulated; Figure S2) support the proposed structure, which corresponds to that determined for the selenium analogue **15**. Compounds **26** and **32** appear to be air- and moisture-sensitive and also decompose in solution or in the solid state in daylight. When crystalline materials were collected for X-ray analysis, decomposition upon irradiation was observed at low temperature. The proposed structures of **26a**–**26d** follow conclusively from the consistent NMR spectroscopic data

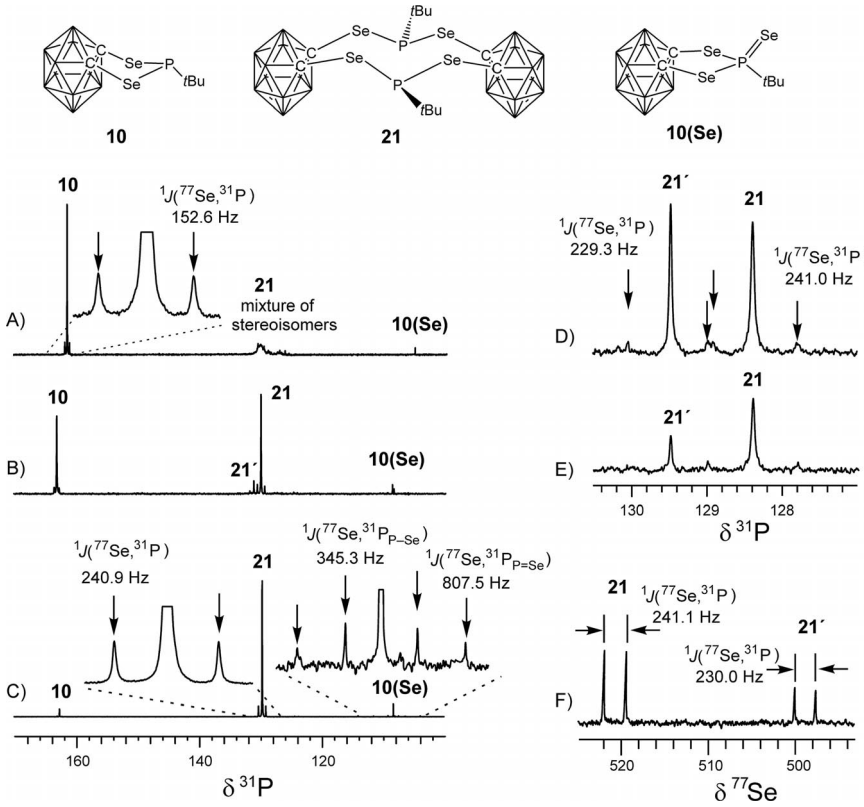
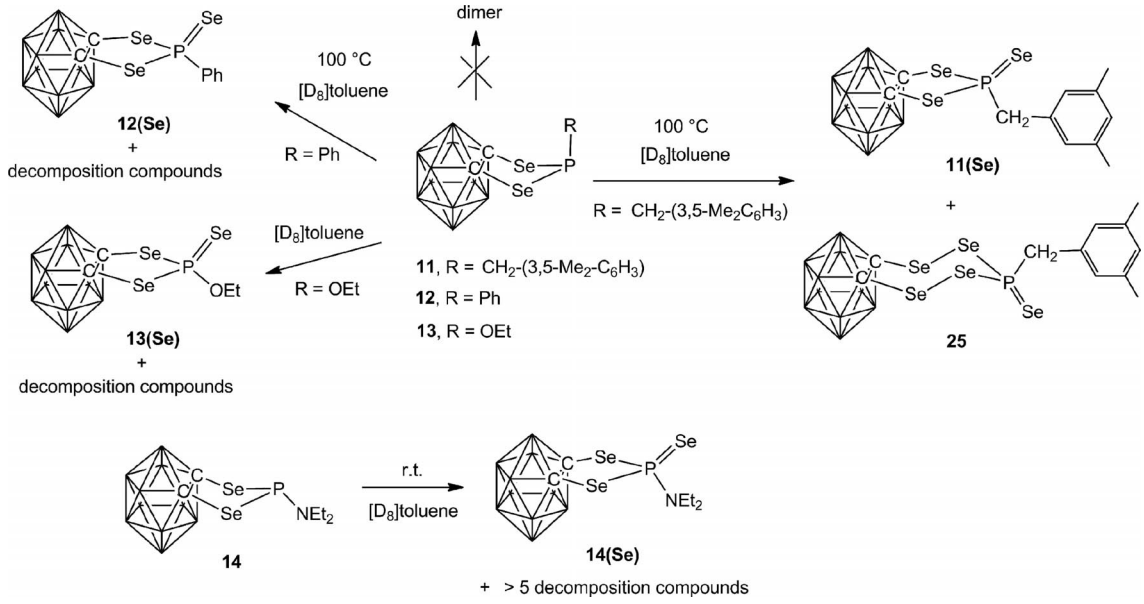
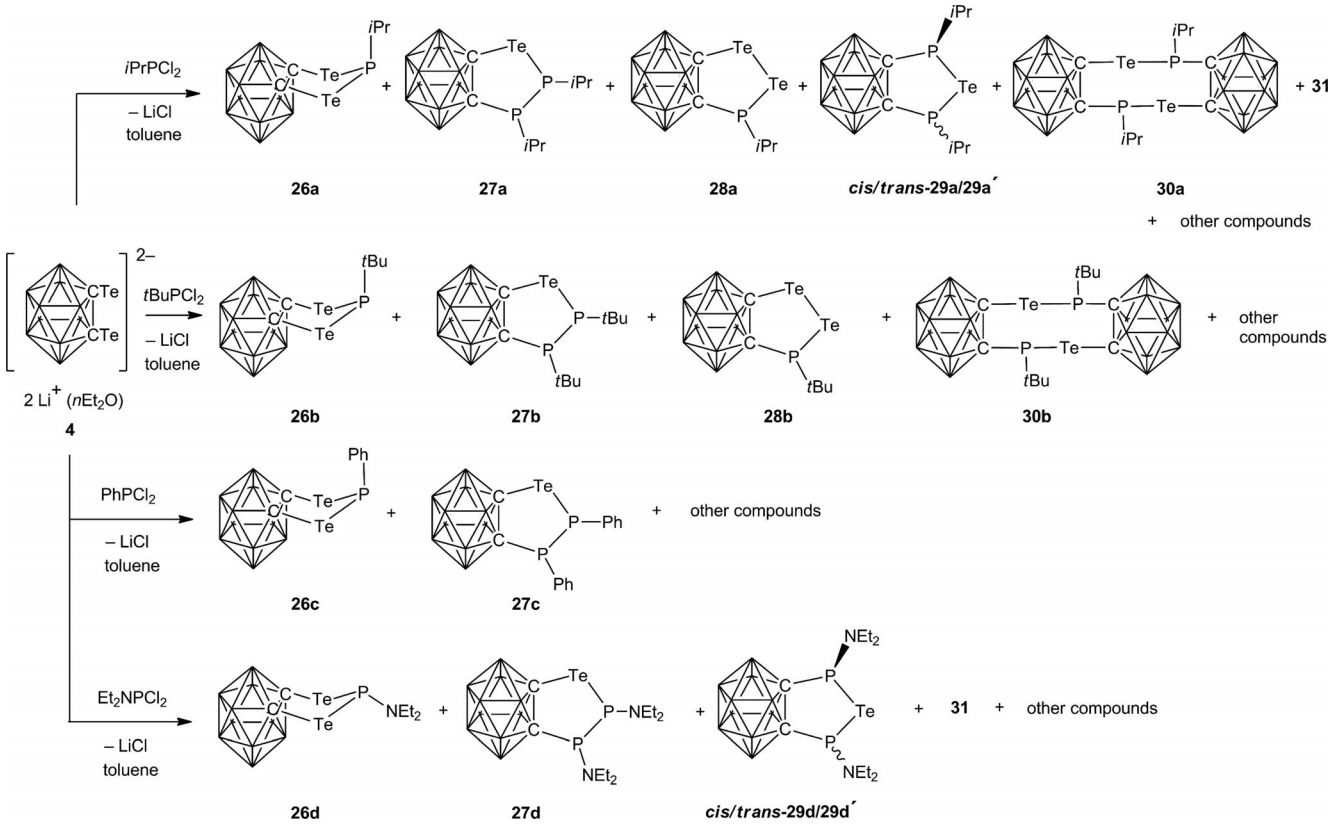



Figure 5. NMR spectra of the reaction solution obtained from the reaction of **5** with $t$BuPCl$_2$. (A) 202.5 MHz $^{31}P\{^1H\}$ NMR spectrum (in [D$_8$]toluene, 25 °C) of the mixture of **10** and stereoisomers including **21** (after 2 h at room temp. in [D$_8$]toluene). (B) 202.5 MHz $^{31}P\{^1H\}$ NMR spectrum ([D$_8$]THF, 25 °C); note the solvent dependence of $\delta^{31}$P of **10**) of the mixture of **10** and **21/21′** (possibly a trimer) after 2 h at room temp. in [D$_8$]THF. (C) 202.5 MHz $^{31}P\{^1H\}$ NMR spectrum ([D$_8$]THF) of the dimer **21** together with **10** (5%) and **10**(Se) (5%) after 2 d at room temp. in [D$_8$]THF. (D) $^{31}P\{^1H\}$ NMR spectrum ([D$_8$]toluene, 25 °C) of the separated fraction of the less soluble solid (**21/21′**) from the reaction of **5** with $t$BuPCl$_2$ in [D$_8$]toluene. (E) The same solution as that in (D) after 20 h at room temp. (F) 95.4 MHz $^{77}$Se NMR spectrum of the same mixture as that in (E).

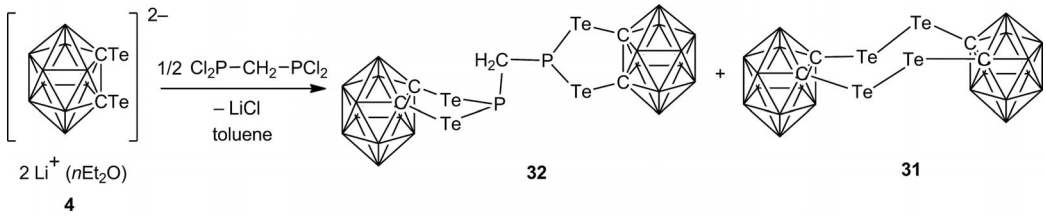



Scheme 5. Conversion (and partial decomposition) of the monomers **11**, **12**, **13**, and **14** into the respective selenides by heating or over time at room temp.




Scheme 6. Attempted syntheses of 1,3,2-ditelluraphospholanes **26a**–**26d**.




Scheme 7. Reaction of **4** with bis(dichlorophospino)methane.

(Table 4; Figures 6 and 7), and dimerization was not observed, even for R = *t*Bu (**26b**). By contrast with the selenium analogues, for which the NMR spectroscopic data strongly suggest a different preferred conformation for R = *t*Bu (**10**), the three 1,3,2-ditelluraphospholanes **26a**–**26c** seem to possess similar structures in solution (see below), that is, the usual envelope structure with the phosphorus atom in the flap and the phosphorus substituent in the axial position. According to calculated structures, the $NEt_2$ derivative **26d** adopts a conformation with the $NEt_2$ group in an equatorial position, as in the analogous selenium compound **14**. The NMR spectra shown in Figure 7 give an idea of the purity that can be achieved under favorable conditions. The cyclic structures of the side products shown in Scheme 6 are proposed mainly on the basis of $^{31}P$ and $^{125}Te$ NMR spectroscopic data, and the various $^{125}Te$–$^{31}P$ and $^{31}P$–$^{31}P$ coupling constants were the most useful parameters (see Figure 6).

## Molecular Orbital Calculations – Molecular Geometries, NMR Parameters

The gas-phase geometries of most 1,3,2-diselenaphospholanes and their respective dimers were optimized at the B3LYP/6-311+G(d,p) level of theory.[23] The structures of the 1,3,2-ditelluraphospholanes **26** were also optimized at the B3LYP/6-311+G(d,p) level by using pseudopotentials for Te.[24] For the monomeric selenium compounds, both structures corresponding to **A** and **A′** were optimized, if possible, and the NMR parameters [chemical shifts and coupling constants, Table S2] were calculated at the same level of theory. For the dimers, only chemical shifts were calculated, except for dimer with R = H (not available experimentally; Table 2).

The comparison of the relevant calculated[25,26] and experimental NMR spectroscopic data for the 1,3,2-diselenaphospholanes indicates that structure **A** is preferred over

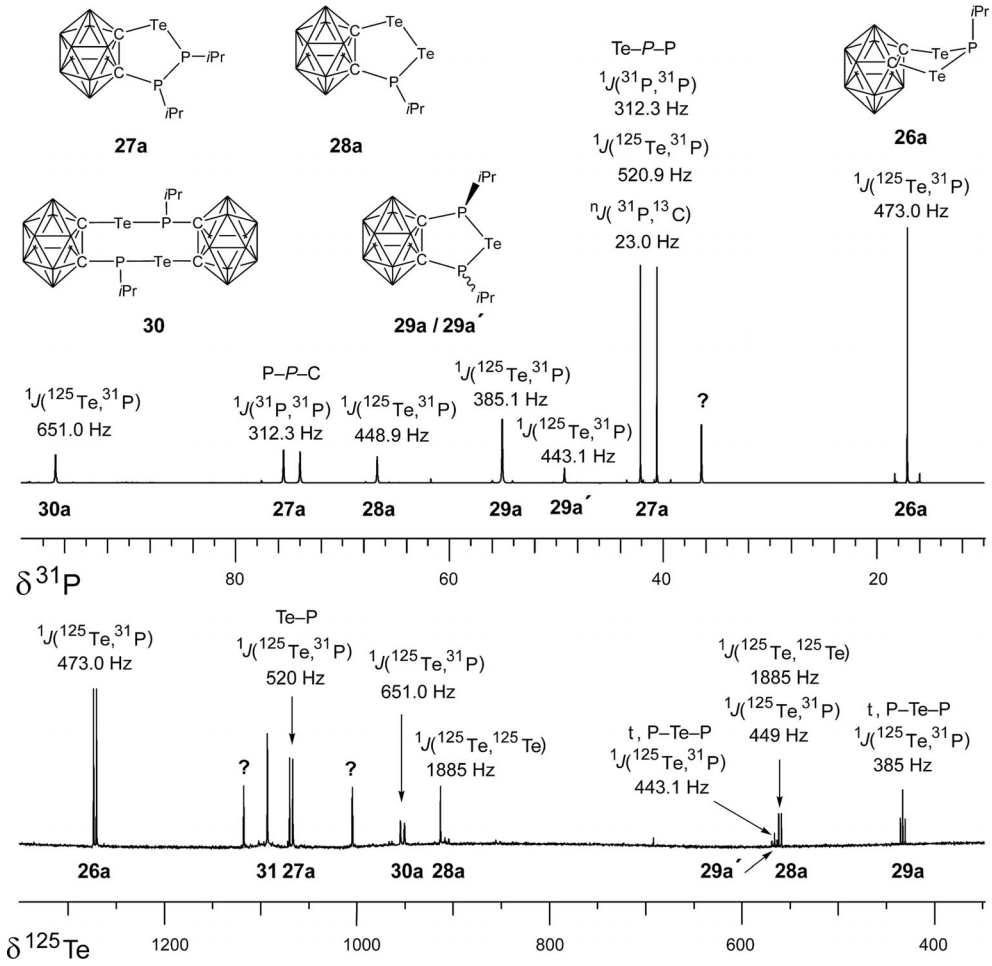



Figure 6. NMR spectra of the solution obtained from the reaction of **4** with *i*PrPCl$_2$ in [D$_8$]toluene at 23 °C. Upper trace: 202.5 MHz $^{31}P\{^1H\}$ NMR spectrum (refocused INEPT)[22] showing the mixture of **26a**, **27a**, **28a**, **29a/29a′**, and **30a**. Lower trace: 157.9 MHz $^{125}Te$ NMR spectrum of the same mixture. Question marks indicate unidentified products.

**A′** except for the heterocycles with P–*t*Bu (**10**) and P–NEt$_2$ (**14**) units. The *t*Bu group is forced into an equatorial position (**A′**) mainly for steric reasons. In the P–NEt$_2$ unit, an orthogonal arrangement of the assumed orientations of the lone pairs of electrons of the phosphorus and nitrogen atoms can be conveniently accommodated solely with the NEt$_2$ group in the equatorial position (**A′**), as in the axial position one ethyl group would be too close to the carborane skeleton. This is mirrored by the $^2J_{^{31}P,^{13}C_{carb}}$ coupling constants, which are close to zero for **A′** and much larger and positive for **A**. The $^{31}P$ nuclei in **A** are better shielded than those in **A′**, and the opposite is true for the carborane $^{13}C$ nuclei. The $^2J_{^{31}P,^{13}C_{carb}}$ coupling constants measured for the dimers **19**–**21** are larger than those for the monomers with type **A** structures,[6] in agreement with the calculated value for the hypothetical dimer with R = H ($^2J_{^{31}P,^{13}C_{carb}}$ = +24.5 Hz; Table 2).

It should be noted that the important features of the experimentally determined solid-state molecular structures do not necessarily agree with the situation in solution. Thus, in the case of **12**, the X-ray structural analysis revealed a structure of type **A′**,[8] whereas the NMR parameters, in light of the present results, clearly suggest dominant contributions of the structure of type **A**. Therefore, ring inversion in solution is a likely process, and the solution-state NMR spectroscopic data represent the average from different conformations. For **11** and **15**, the NMR parameters (exp. and calcd.) agree well with those of type **A** structures, both in the solid state and in solution. The calculated differences in energies for structures **A** and **A′** show that **12** (R = Ph) with gas-phase structure **A** is slightly more stable than **A′** (–1.1 kcal/mol) and **8** (R = *i*Pr) with structure **A** is more stable than **A′** (–3.8 kcal/mol), in contrast to **10** (R = *t*Bu), for which **A′** is more stable than **A** (–1.9 kcal/mol).

The optimization of the gas-phase geometries for the 1,3,2-ditelluraphospholanes **26a**–**26c** leads to energy minima only for structures of type **A**. Apparently, longer Te–C and Te–P bond lengths significantly reduce the repulsive interactions in the five-membered rings when compared with the selenium homologues. Again, the values for the $^2J_{^{31}P,^{13}C_{carb}}$ coupling constants are indicative of the type **A** structure, as the experimental data are well reproduced by

Table 4. $^{13}C$, $^{31}P$, and $^{125}Te$ NMR spectroscopic data[a] of the *ortho*-carborane derivatives **26**–**30** and **32**.

| R | Solvent | $\delta^{13}C(C_{carb})$ [ppm] | $^{n}J_{^{31}P,^{13}C_{carb}}$ [Hz] | Other $\delta^{13}C$ [ppm] | $\delta^{31}P$ [ppm] | $\delta^{125}Te$ [ppm] | Type |
|---|---|---|---|---|---|---|---|
| *i*Pr (**26a**) | [D$_8$]toluene | 58.2 [445.2] {–8.2} | 16.3 ($^2J$), calcd. +15.3 | 20.2 (25.9), 28.1 (46.0) | 17.2 ⟨473.0⟩ ⟩391.9⟨ (46.0) ($^1J$) (25.8) ($^2J$) | 1271.5[b] ⟨473.2⟩ | **A** |
| | $CD_2Cl_2$ | 58.1 [446] {–8.0} | 15.5 ($^2J$) | 20.6 (25.8), 28.4 (45.8) | 16.2 ⟨474.9⟩ | 1264.9 ⟨475.9⟩ | **A** |
| *t*Bu (**26b**) | [D$_8$]toluene | 56.5 [460] {–7.2} | 14.4 ($^2J$), calcd. +14.4 | 28.9 (20.7), 35.0 (57.7) | 39.7 ⟨426.1⟩ ⟩353.5⟨ (57.5) ($^1J$) (21.0) ($^2J$) | 1230.4 [c] ⟨426.1⟩ | **A** |
| Ph (**26c**) | [D$_8$]toluene | 59.3{–8.4} | 17.6 ($^2J$), calcd. +18.9 | 129.0 (3.4) $C_m$, 129.4 (1.6) $C_p$, 132.3 (18.3) $C_o$, n.o. $C_i$ | 5.0 ⟨530.6⟩ | 1317.6 ⟨533.2⟩ | **A** |
| $Et_2N$ (**26d**) | [D$_8$]toluene | – | calcd. +0.3 | – | 89.7 ⟨438.9⟩ | 1416.2 ⟨438.4⟩ | **A′** |
| $(C_2B_{10}Se_2P)_2CH_2$ (**32**) | [D$_8$]toluene | 58.8 | 14.7 | 25.8 (68.8) | 4.9 ⟨–421.0⟩ "122.0" ⟨+31.0⟩ ⟩–349.0⟨ ⟩+25.0⟨ | 1268.8 [d] | **A** |
| *i*Pr (**27a**) | [D$_8$]toluene | 100.0 (C–P), 57.0 (C–Te, pseudo-t) | 106.3 ($^1J$), 8.9 ($^2J$) | 20.6 (24.8) (9.4), 21.3 (21.2) (9.4), 22.3 (22.7) (6.1), 23.1 (29.1) (4.1), 26.4 (30.7) (9.8), 28.7 (20.4) (8.6) | 41.4 (d) "312.3" ⟨520.9⟩ ⟩431.4⟨ (23.0), 74.8 (d) "312.3" | 1068.4 ⟨520⟩, 1093.1 | |
| *t*Bu (**27b**) | [D$_8$]toluene | – | – | – | 49.1 (d) "287.6" ⟨415.9⟩, 95.4 (d) "287.6" | 969.1 ⟨415.0⟩ | |
| Ph (**27c**) | [D$_8$]toluene | 99.1 (C–P), 56.9 (C–Te, pseudo-t) [409] | 104.0 ($^1J$), 8.5 ($^2J$) | | 49.1 (d) "304.5" ⟨587.7⟩, 61.0 (d) "304.5" | 1083.3 ⟨588⟩ | |
| $Et_2N$ (**27d**) | [D$_8$]toluene | – | – | – | 111.0 (d) "196.9" ⟨253.8⟩, 113.0 (d) "196.9" | 752.3 ⟨260⟩ | |
| *i*Pr (**28a**) | [D$_8$]toluene | 91.6 (C–P), 39.3 (C–Te) [267] | 100.8 ($^1J$) | – | 66.8 ⟨448.9⟩ | 560.5 ⟨449⟩ ≪1885≫, 913.3 ≪1885≫ | |
| *t*Bu (**28b**) | [D$_8$]toluene | 88.7 (C–P) {–7.5}, 39.6 (C–Te) | 123.6 ($^1J$) | 28.9 (17.9), 38.1 (44.2) | 96.2 ⟨371.5⟩ | 447.4 ⟨371.8⟩ ≪1870≫, 923.0 ≪1870≫ | |
| *i*Pr (**29a**) | [D$_8$]toluene | 95.6 (C–P) | 108.7 ($^1J$) | – | 55.1 ⟨385.1⟩ | 433.1 (t) ⟨385⟩ | |
| *i*Pr (**29a′**) | [D$_8$]toluene | 97.0 (C–P) | 110.5 ($^1J$) | – | 49.2 ⟨443.1⟩ | 566.3 (t) ⟨443⟩ | |
| $Et_2N$ (**29d**) | [D$_8$]toluene | – | – | – | 92.2 ⟨490.4⟩ | 147.7 (t) ⟨488⟩ | |
| $Et_2N$ (**29d′**) | [D$_8$]toluene | – | – | – | 105.6 ⟨501.8⟩ | 262.0 (t) ⟨500⟩ | |
| *i*Pr (**30a**) | [D$_8$]toluene | – | – | – | 96.7 ⟨651.0⟩ | 952.8 ⟨651.0⟩ | |
| *t*Bu (**30b**) | [D$_8$]toluene | 75.9 (C–P, d) {–10.0}, 43.1 (C–Te, dd) {–10.0} | 93.9 ($^1J$), 37.5, 48.2 ($^2J$) | 29.1 (br), 38.1 (39.8) | 107.2 ⟨641.1⟩ ⟩536.1⟨ | 1079.9 ⟨640⟩ | |

[a] Coupling constants $^{n}J_{^{31}P,^{13}C}$ are given in parentheses (± 0.5 Hz); $^{n}J_{^{125}Te,^{13}C}$ are given in square brackets [± 0.5 Hz]; $^{n}J_{^{125}Te,^{31}P}$ are given in angle brackets ⟨± 0.5 Hz⟩; $^{n}J_{^{123}Te,^{31}P}$ are given in angle brackets ⟩± 0.5 Hz⟨; $^{n}J_{^{31}P,^{31}P}$ are given in quotation marks "± 0.5 Hz"; $^{1}J_{^{125}Te,^{125}Te}$ are given in double angle brackets ≪± 0.5 Hz≫; $^{1}\Delta^{10/11}B(^{13}C_{carb})$[19] are given in braces {± 0.5 Hz}; isotope-induced chemical shifts $^{1}\Delta$ are given in ppb, and the negative sign denotes a shift of the NMR signal of the heavy isotopomer to a lower frequency; n.o. = not observed. [b] $\delta^{123}Te$ = 1271.7 ppm ($^{1}J_{^{123}Te,^{31}P}$ = 391 Hz). [c] $\delta^{123}Te$ = 1229.3 ppm ($^{1}J_{^{123}Te,^{31}P}$ = 353.9 Hz). [d] $|^{1}J_{^{125}Te,^{31}P} + {}^{3}J_{^{125}Te,^{31}P}|$ = 390 Hz; $\delta^{123}Te$ = 1267.8 ppm.

the calculated data (Tables 4 and S2) for the type **A** geometry. For the $NEt_2$ derivative **26d**, the optimization of the gas-phase geometry converged to structure **A′**.

The experimental observations for the dimerization of the 1,3,2-diselenaphospholanes are reflected by the calculated relative energies. A dimer for R = H was not observed,[10] in agreement with calculations, which show that the dimer is energetically slightly less favored than two monomers (+0.3 kcal/mol). The dimer with R = *i*Pr (**19**) was experimentally observed and found to be slightly favored with respect to the monomers by –0.5 kcal/mol. By contrast, the dimer for R = *t*Bu (**21**) is much more favored by –7.8 kcal/mol.

## X-ray Structural Analyses of the *ortho*-Carborane Derivatives 11, 15, and 21

The molecular structures of **11**, **15** and **21** are shown in Figures 8–10. The carborane units possess typical structural

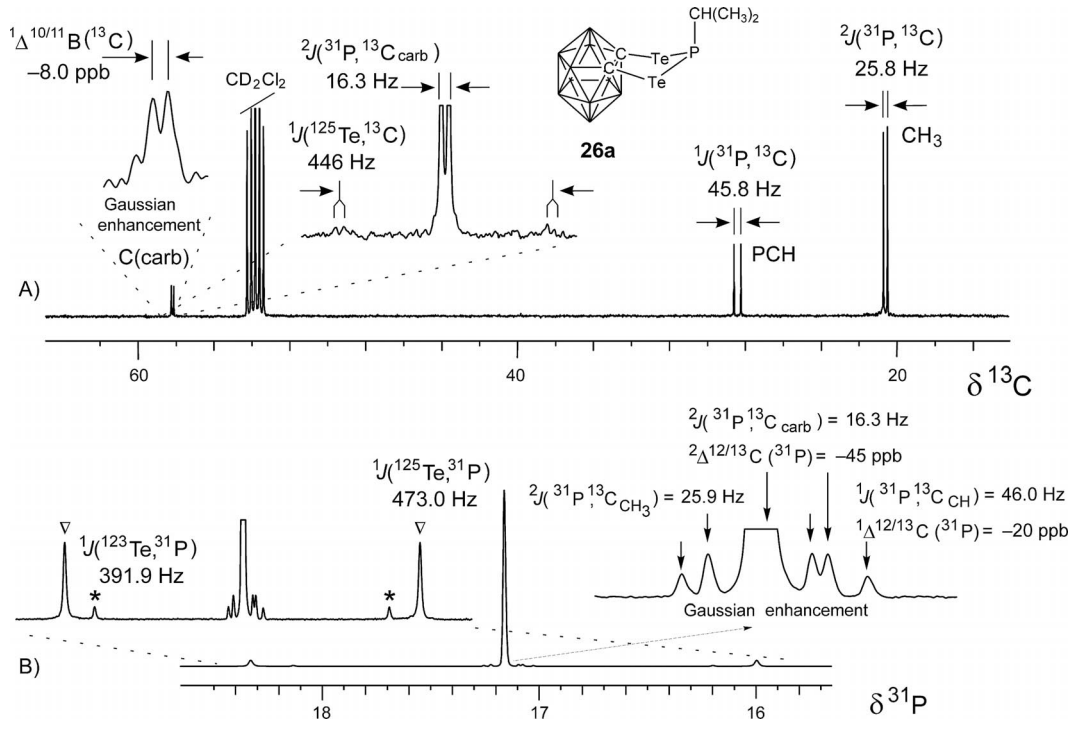



Figure 7. (A) 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of **26a** in $CD_2Cl_2$ at 23 °C; the typical pattern[19] for the isotope-induced chemical shift $^1\Delta^{10/11}B(^{13}C_{carb})$ is observed. (B) 202.5 MHz $^{31}P\{^1H\}$ NMR spectrum (refocused INEPT)[22] of **26a** in [$D_8$]toluene at 23 °C. The $^{125}Te$ satellites for $^1J_{^{125}Te,^{31}P}$ are marked by ∇; the $^{123}Te$ satellites for $^1J_{^{123}Te,^{31}P}$ are marked by asterisks. The $^{13}C$ satellites for $^nJ_{^{31}P,^{13}C}$ are marked by arrows; the isotope-induced chemical shifts $^n\Delta^{12/13}C(^{31}P)$ are given (± 1 ppb). Note the absence of such an effect ($n$ = 2) for the $^{13}CH_3$ groups in contrast to the carborane $^{13}C$ nuclei.

parameters[27,28] that differ in the C–C bond lengths (shorter in **11** and **15**, ca. 10 pm longer in **21**). The structure of **11** corresponds to that of the iodide **7**,[10] and the folding of the C–C–Se–P–Se rings along the Se···Se axis is also similar (154.7° for **11** and 158.4° for **7**). The main structural properties of both halves of **15** are similar to those of **11** (the angles between the Se–C–C–Se/Se–P–Se planes are 151.9 and 154.7°, Table 5). Expectedly, the structure of the dimer **21** is closely related to that of the sulfur analogue.[6] For all three compounds studied here, the four atoms C–C–Se–Se are in a plane (close to the experimental error). In the dimer **21**, the four selenium atoms form a plane (mean deviation 1.4 pm). All distances and angles are found in the expected ranges (Table 5).

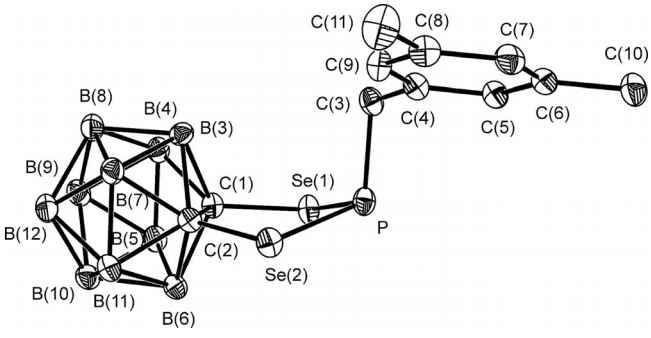



Figure 8. ORTEP plot (40% probability; hydrogen atoms omitted for clarity) of the molecular structure of **11** (for selected distances and angles, see Table 5).

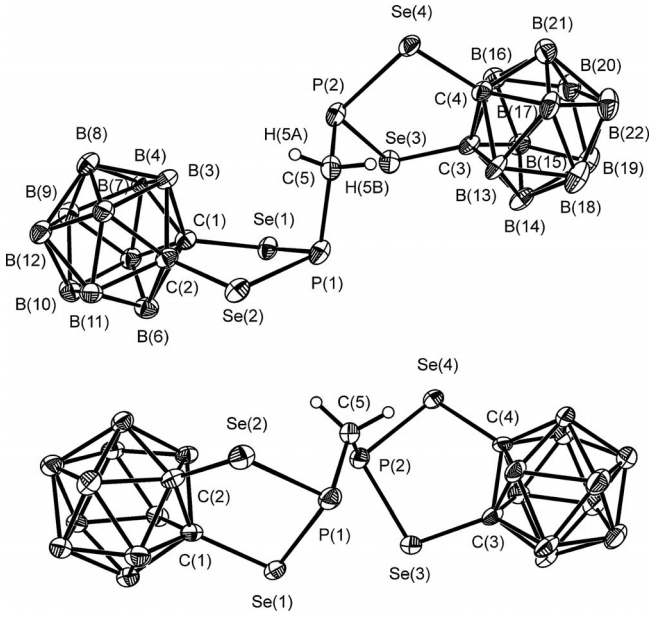



Figure 9. Two views of ORTEP plots (40% probability; hydrogen atoms omitted for clarity) of the molecular structure of **15** (for selected distances and angles, see Table 5).

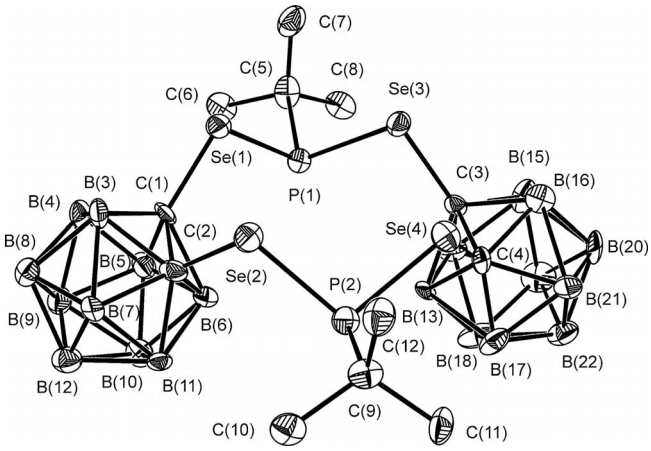



Figure 10. ORTEP plot (50% probability; hydrogen atoms and $CD_2Cl_2$ omitted for clarity) of the molecular structure of dimer **21** (for selected distances and angles, see Table 5).

## Conclusions

The most convenient access to 1,3,2-diselenaphospholanes with an annelated 1,2-dicarba-*closo*-dodecaborane(12) unit is provided by cleavage of Si–Se bonds by phosphorus halides, whereas the corresponding tellurium derivatives have to be prepared from reactions of the 1,2-ditellurolato-1,2-dicarba-*closo*-dodecaborane(12) dianion $[1,2\text{-}(1,2\text{-}C_2B_{10}H_{10})Te_2]^{2-}$ with phosphorus halides. The selenium compounds are fairly stable and invite further transformations that make use of the P–Se bonds, whereas the light-sensitive tellurium compounds are obtained in complex mixtures. Depending on the organo group at the phosphorus atom, dimerization of the 1,3,2-diselenaphospholanes occurs and leads to ten-membered rings. This was not observed for the analogous tellurium compounds. Most phosphorus substituents in the 1,3,2-diselenaphospholanes prefer the axial position in spite of the repulsive interactions with the rigid carborane framework. However, the bulky *t*Bu group and the $NEt_2$ group are forced into the equatorial position, for steric (*t*Bu) and electronic ($NEt_2$) reasons, as indicated by NMR spectroscopic data and confirmed by DFT calculations. Other noteworthy NMR parameters are the isotope-induced chemical shifts exerted by the carborane carbon atoms $^n\Delta^{12/13}C(^{31}P)$, which are large in the five-membered rings and large and unprecedented for $n = 2$.

## Experimental Section

All syntheses and sample handling were performed with necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. $CD_2Cl_2$ was distilled from $CaH_2$ in an atmosphere of argon. All other solvents were distilled from Na metal in an atmosphere of argon. The starting silane **5**[15] and $[(1,2\text{-}C_2B_{10}H_{10})Te_2Li_2](Et_2O)$ (**4**)[17a] were prepared according to the published procedures. Other starting materials were purchased from KatChem (*ortho*-carborane **1**), MCAT GmbH (3,5-dimethylbenzylphosphorus dibromide), Aldrich [butyllithium (1.6 M in hexane), *i*PrPCl$_2$ (97%), *t*BuPCl$_2$ (97%), PhPCl$_2$ (97%), EtOPCl$_2$ (98%), $Et_2NPCl_2$ (97%), CyPCl$_2$ (95%), 1,1-bis(dichlorophosphanyl)methane (95%), 1,2-bis(dichlorophosphanyl)ethane, selenium (powder, 100 mesh, 99.99% trace metals basis), sulfur (powder, 99.98% trace metals basis), tellurium (powder, 200 mesh, 99.8% metals basis)]. Most syntheses were performed on small scales sufficient for NMR studies. Owing to the small scale of the reactions, the sensitivity of the compounds to hydrolysis, and the multiple reaction pathways, it proved difficult to obtain materials suitable for elemental analysis. Furthermore, small carbon content and high boron content caused problems in reproducibility. NMR measurements were performed with a Bruker DRX 500 spectrometer. $^1H$, $^{11}B$, $^{13}C$, $^{31}P$, $^{77}Se$, $^{125}Te$, and $^{123}Te$ chemical shifts are given relative to $Me_4Si$ [$\delta^1H$ = 5.33 ($CHDCl_2$), 2.08 ($\pm$0.01) ppm ($C_6D_5CD_2H$); $\delta^{13}C$ = 53.8 ($CD_2Cl_2$), 20.4 ($C_6D_5CD_3$), 25.4 ($\pm$0.1) ppm ($C_4D_8O$)], external $BF_3{\cdot}OEt_2$ [$\delta^{11}B = 0 \pm 0.3$ ppm for $\Xi(^{11}B)$ = 32.083971 MHz], neat $Me_2Se$ [$\delta^{77}Se = 0 \pm 0.1$ ppm for $\Xi(^{77}Se)$ = 19.071523 MHz], external aqueous $H_3PO_4$ [85%; $\delta^{31}P = 0$ ppm for $\Xi(^{31}P)$ = 40.480747 MHz], and neat $Me_2Te$ [$\delta^{125}Te = 0$ ppm for $\Xi(^{125}Te)$ = 31.549802 MHz; $\delta^{123}Te = 0$ ppm for $\Xi(^{123}Te)$ = 26.169773 MHz]. The assignments of $^1H$ and $^{11}B$ NMR signals are based on $^1H\{^{11}B\}$ selective heteronuclear decoupling experiments. Mass spectra (EI, 70 eV) were recorded with a Finnigan MAT 8500 instrument with a direct inlet (data for $^{12}C$, $^1H$, $^{11}B$, $^{31}P$, $^{80}Se$, $^{130}Te$). Melting points were determined with a Büchi 510 melting point apparatus.

All quantum chemical calculations were performed with the Gaussian 09 program package.[29] The optimized geometries at the B3LYP/6-311+G(d.p) level of theory[23] were found to be minima by the absence of imaginary frequencies. The NMR parameters were calculated[25,26] at the same level of theory. The calculated $\delta^{13}C$, $\delta^{31}P$, $\delta^{11}B$, and $\delta^{77}Se$ values were converted by $\delta^{13}C$ (calcd.) = $\sigma(^{13}C, TMS) - \sigma(^{13}C)$ ppm with $\sigma(^{13}C, TMS)$ = +181 [$\delta^{13}C$ (TMS) = 0 ppm], $\delta^{31}P$(calcd.) = $\sigma[^{31}P, P(OMe)_3] - \sigma(^{31}P)$ + 138 ppm with $\sigma[^{31}P, P(OMe)_3]$ = 159.8 ppm {$\delta^{31}P$ = 138 ppm and $\delta^{31}P$[aqueous $H_3PO_4$ (85%)] = 0 ppm}, $\delta^{11}B$ (calcd.) = $\sigma(^{11}B) - \sigma(^{11}B, B_2H_6)$ ppm with $\sigma(^{11}B, B_2H_6)$ = +84.1 [$\delta^{11}B$ ($B_2H_6$) = 18 ppm and $\delta^{11}B$ ($BF_3{\cdot}OEt_2$) = 0 ppm], and $\delta^{77}Se$ (calcd.) = $\sigma(^{77}Se) - \sigma(^{77}Se, SeMe_2)$ ppm with $\sigma(^{77}Se, SeMe_2)$ = +1621.7 ppm.

**2-(1-Methylethyl)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholane (8):** A solution of **5** (74 mg, 0.205 mmol) in [$D_8$]-toluene (0.6 mL) was cooled to –20 °C, and *i*PrPCl$_2$ (0.025 mL, 0.203 mmol) was added through a microsyringe. The progress of the reaction was monitored by $^{31}P$ and $^{29}Si$ NMR spectroscopy. After 1 h at room temp., the mixture contained **8** together with $Me_2SiCl_2$. The volatile materials were removed under vacuum (3 h, $8 \times 10^{-3}$ Torr) to give **8** as a white solid; m.p. 100–110 °C (dec.). $^1H\{^{11}B\}$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 0.68 (dd, $^3J_{^{31}P,^1H}$ = 21.4 Hz, $^3J_{^1H,^1H}$ = 7.1 Hz, 6 H, $CH_3$), 2.47 [doublet of septets (dsept), $^2J_{^{31}P,^1H}$ = 3.4 Hz, $^3J_{^1H,^1H}$ = 7.1 Hz, 1 H, PCH], 2.60 [br. s, 2 H, HB for $\delta(^{11}B)$ = –10.5 ppm], 2.66 [br. s, 1 H, HB for $\delta(^{11}B)$ = –7.8 ppm], 2.73 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.4 ppm], 2.79 [br. s, 3 H, HB for $\delta(^{11}B)$ = –6.0 ppm], 2.82 [br. s, 1 H, HB for $\delta(^{11}B)$ = –3.3 ppm], 3.13 [br. s, 1 H, HB for $\delta(^{11}B)$ = 0.1 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –10.5 (2 B), –8.4 (2 B), –7.8 (1 B), –6.0 (3 B), –3.3 (1 B), 0.1 (1 B) ppm. $^{11}B$ NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –10.5 (d, $^1J_{^{11}B,^1H}$ = 172 Hz, 2 B), –8.4 (d, $^1J_{^{11}B,^1H}$ = 164 Hz, 2 B), –7.8 (d, 1 B), –6.0 (d, $^1J_{^{11}B,^1H}$ = 151 Hz, 3 B), –3.3 (d, $^1J_{^{11}B,^1H}$ = 156 Hz, 1 B), 0.1 (d, $^1J_{^{11}B,^1H}$ = 181 Hz, 1 B) ppm. $^1H$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 1.18 (dd, $^3J_{^{31}P,^1H}$ = 21.6 Hz, $^3J_{^1H,^1H}$ = 7.2 Hz, 6 H, $CH_3$), 2.97 (dsept, $^2J_{^{31}P,^1H}$ = 3.3 Hz, $^3J_{^1H,^1H}$ = 7.2 Hz, 1 H, PCH) ppm. EI-MS (70 eV): *m*/*z* (%) = 374 (10) $[M]^+$, 358 (5) $[M - CH_4]^+$, 331 (15) $[M - C_3H_7]^+$, 236 (4), 43 (100).

Table 5. Selected bond lengths [pm] and angles [°] of the *ortho*-carborane derivatives **11**, **11**(calcd.), **15**, **15**(calcd.), **21**, **21**(calcd.), and **21**($S_2$).[6]

| | **11** | **11** (calcd.) | **15** | **15** (calcd.) | **21** | **21** (calcd.) | | **21**($S_2$)[6] |
|---|---|---|---|---|---|---|---|---|
| C(1)–Se(1) | 194.1(3) | 197.0 | 194.8(4) | 197.3 | 191.4(11) | 195.8 | C(1)–S(1) | 178.3(7) |
| C(2)–Se(2) | 194.4(3) | 197.4 | 194.1(4) | 197.1 | 198.5(15) | 195.8 | C(2)–S(2) | 178.5(8) |
| C(3)–Se(3) | – | – | 195.3(4) | 197.3 | 193.3(13) | 195.8 | C(3)–S(3) | 177.9(9) |
| C(4)–Se(4) | – | – | 193.9(4) | 197.2 | 192.5(13) | 195.8 | C(4)–S(4) | 178.3(9) |
| C(1)–C(2) | 164.0(3) | 163.7 | 163.3(5) | 163.9 | 173(2) | 177.2 | C(1)–C(2) | 175.6(10) |
| C(3)–C(4) | – | – | 164.1(5) | 163.7 | 175(2) | 177.2 | C(3)–C(4) | 181.3(11) |
| Se(1)–P | 226.77(8) | 231.6 | 226.65(13) | 230.4 | 227.1(3) | 232.7 | S(1)–P(1) | 213.5(3) |
| Se(2)–P | 226.37(10) | 231.3 | 227.06(13) | 230.6 | 226.9(4) | 232.7 | S(2)–P(2) | 214.1(3) |
| Se(3)–P | – | – | 227.20(13) | 230.9 | 227.0(4) | 232.7 | S(3)–P(1) | 213.5(3) |
| Se(4)–P | – | – | 227.27(13) | 231.1 | 227.9(4) | 232.7 | S(4)–P(2) | 214.4(3) |
| P(1)–C | 186.4(3) | 189.0 | 186.6(4) | 189.3 | 187.6(16) | 192.2 | P(1)–C | 186.6(8) |
| P(2)–C | – | – | 185.3(4) | 188.1 | 189.2(16) | 192.2 | P(2)–C | 188.6(9) |
| P(1)–Se(1)–C(1) | 101.17(7) | 100.6 | 100.11(12) | 99.6 | 99.7(4) | 101.6 | P(1)–S(1)–C(1) | 103.1(3) |
| P–Se(2)–C(2) | 100.60(8) | 100.5 | 100.04(12) | 99.6 | 100.1(4) | 101.6 | P(1)–S(3)–C(3) | 102.8(3) |
| P–Se(3)–C(3) | – | – | 100.08(13) | 100.3 | 100.3(4) | 101.6 | P(2)–S(2)–C(2) | 101.4(3) |
| P(2)–Se(4)–C(4) | – | – | 100.67(12) | 100.2 | 100.8(4) | 101.6 | P(2)–S(4)–C(4) | 103.2(3) |
| Se(1)–C(1)–C(2) | 116.49(17) | 117.9 | 116.9(3) | 117.7 | 119.0(9) | 118.8 | S(1)–C(1)–C(2) | 116.7(5) |
| Se(2)–C(2)–C(1) | 117.62(18) | 117.9 | 117.5(3) | 117.5 | 116.1(8) | 118.8 | S(2)–C(2)–C(1) | 117.9(5) |
| Se(3)–C(3)–C(4) | – | – | 117.0(3) | 117.8 | 117.9(8) | 118.8 | S(3)–C(3)–C(4) | 114.0(6) |
| Se(4)–C(4)–C(3) | – | – | 117.6(3) | 118.0 | 118.4(8) | 118.8 | S(4)–C(4)–C(3) | 119.3(6) |
| Se(1)–P(1)–Se | 97.51(3) | 97.5 | 97.41(5) | 97.1 | 98.94(15) | 99.5 | S(1)–P(1)–S(3) | 98.39(12) |
| Se–P(2)–Se(4) | | | 97.96(5) | 98.0 | 99.36(15) | 99.5 | S(2)–P(2)–S(4) | 98.48(11) |
| P(1)–C(5)–P(2) | | | 116.0(2) | 107.8 | | | | |
| Se(1)–P(1)–C | 104.86(9) | 104.5 | 104.01(13) | 104.9 | 98.9(5) | 101.0 | S(1)–P(1)–C | 99.4(3) |
| Se(2)–P–C | 105.39(10) | 105.3 | 106.30(14) | 104.7 | 100.0(5) | 101.1 | S(2)–P–C | 99.7(4) |
| Se(3)–P–C | – | – | 100.86(14) | 103.8 | 100.2(5) | 101.0 | S(3)–P–C | 98.8(3) |
| Se(4)–P–C | – | – | 106.46(14) | 104.2 | 99.6(5) | 101.0 | S(4)–P–C | 99.2(3) |
| Se(1)–C(1)–C(2)–Se(2) Δ [pm][a] | 0.19 | | 0.3 | – | 1.1 | – | plane S(1)–C(1)–C(2)–S(2) Δ [pm][a] | 0.02 |
| Se(3)–C(3)–C(4)–Se(4) Δ [pm][a] | – | – | 1.7 | – | 1.1 | – | plane S(3)–C(3)–C(4)–S(4) Δ [pm][a] | 0.08 |
| Distance of P(1) from the plane Se(1)–C(1)–C(2)–Se(2) [pm] | 63.8 | – | 70.5 | – | – | – | | |
| Distance of P(2) from the plane Se(3)–C(3)–C(4)–Se(4), [pm] | – | – | 63.7 | – | – | – | | |
| Se(1)–Se(2)–Se(3)–Se(4) Δ [pm][a] | – | – | – | – | 1.4 | – | plane S(1)–S(2)–S(3)–S(4) Δ [pm][a] | 0.9 |
| Distance of P(1) from the plane Se(1)–Se(2)–Se(3)–Se(4) [pm] | – | – | – | – | 129.5 | – | distance of P(1) from the plane S(1)–S(2)–S(3)–S(4) | 120.5 |
| Distance of P(2) from the plane Se(1)–Se(2)–Se(3)–Se(4) [pm] | – | – | – | – | 130.8 | – | distance of P(2) from the plane S(1)–S(2)–S(3)–S(4) | 121.4 |
| Plane Se(1)–C(1)–C(2)–Se(2)/ plane Se(1)–P(1)–Se(2) [°] | 154.7 | – | 151.9 | – | – | – | | |
| Plane Se(3)–C(3)–C(4)–Se(4)/ plane Se(3)–P(2)–Se(4) [°] | – | – | 154.7 | – | – | – | | |

[a] Mean deviation from plane.

**2,7-Bis(1-methylethyl)-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano-(12)]-2,7-diphospha-1,3,6,8-tetraselenacyclodecane (19):** *i*PrPCl$_2$ (0.080 mL, 0.65 mmol) was added through a microsyringe to a solution of **5** (233.6 mg, 0.65 mmol) in [D$_8$]toluene (0.6 mL) at room temp. The progress of the reaction was monitored by $^{31}$P and $^{29}$Si NMR spectroscopy. After 1 h at room temp., the mixture contained **8** (ca. 85%) and **19** (15%) together with **8**(Se)[11] and $Me_2SiCl_2$. The volatile materials were removed under vacuum (1 h, $8 \times 10^{-3}$ Torr), and the residue was dissolved in [D$_8$]toluene. This solution was kept for 2 d at room temp., and the formation of a white powder of **19** was observed. The precipitate was separated by centrifugation, washed with [D$_8$]toluene, and dried under vacuum to give **19** as a light yellow solid; m.p. 145–155 °C (dec.). The dimer **19** was dissolved in $CD_2Cl_2$; after 2 d at –30 °C, the solution contained **8** (20%) and **19** (80%). The dimer **19** was dissolved in [D$_8$]-THF, after 2 d at room temp., the solution contained **8** (70%), **8**(Se) (15%), and **22** (15%) as determined by $^{31}$P NMR spectroscopy.

**19:** $^1$H{$^{11}$B} NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 1.34 (dd, $^3J_{^{31}P,^1H}$ = 16.4 Hz, $^3J_{^1H,^1H}$ = 7.0 Hz, 12 H, $CH_3$), 2.14 [br. s, 2 H, HB for $\delta(^{11}B)$ = –9.3 ppm], 2.21 [br. s, 2 H, HB for $\delta(^{11}B)$ = –9.3 ppm], 2.25 [br. s, 2 H, HB for $\delta(^{11}B)$ = –7.4 ppm], 2.44 (dsept, $^2J_{^{31}P,^1H}$ = 12.1 Hz, $^3J_{^1H,^1H}$ = 7.0 Hz, 2 H, PCH), 2.45 [br. s, 4 H, HB for $\delta(^{11}B)$ = –2.3 ppm], 2.57 [br. s, 4 H, HB for $\delta(^{11}B)$ = –9.3 ppm], 2.68 [br. s, 4 H, HB for $\delta(^{11}B)$ = –6.3 ppm], 2.99 [br. s, 2 H, HB for $\delta(^{11}B)$ = –9.3 ppm] ppm. $^{11}$B{$^1$H} NMR (160.5 MHz,

[$D_8$]toluene, 25 °C): $\delta$ = –9.3 (10 B), 7.4 (2 B), –6.3 (4 B), –2.3 (4 B) ppm. EI-MS (70 eV): *m/z* (%) = 705 (2) $[M - C_3H_7]^+$, 374 (20) $[M/2]^+$, 358 (5) $[M/2 - CH_4]^+$, 331 (20) $[M/2 - C_3H_7]^+$, 43 (100).

**22:** $^1$H NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 4.43 (s, 1 H, $C_{carb}$H), 6.57 (d, $^1J_{^{31}P,^1H}$ = 477.3 Hz, 1 H, PH) ppm. $^1H\{^{31}P\}$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 4.43 (s, 1 H, $C_{carb}$H), 6.57 (s, 1 H, PH).

**2-Cyclohexyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholane (9):** $CyPCl_2$ (0.032 mL, 0.21 mmol) was added through a microsyringe to a solution of **5** (75.5 mg, 0.211 mmol) in $CD_2Cl_2$ (0.6 mL) at room temp. The progress of the reaction was monitored by $^{31}$P and $^{29}$Si NMR spectroscopy. After 1 h at room temp., the mixture contained **9** together with $Me_2SiCl_2$. The volatile materials were removed under vacuum (3 h, $8 \times 10^{-3}$ Torr) to give **9** as a white solid. $^1H\{^{11}B\}$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 1.07 [dm, $^3J_{^{31}P,^1H}$ = 8.3 Hz, 2 H, C(2)H$^a$], 1.22 [m, 1 H, C(4)H$^a$], 1.37 [m, 2 H, C(3)H$^a$], 1.71 [m, 1 H, C(4)H$^b$], 1.87 [m, 2 H, C(3)H$^b$], 1.94 [m, 2 H, C(2)H$^b$], 2.28 [br. s, 2 H, HB for $\delta(^{11}B)$ = –6.5 ppm], 2.38 [br. s, 1 H, HB for $\delta(^{11}B)$ = –6.5 ppm], 2.40 [br. s, 1 H, HB for $\delta(^{11}B)$ = –3.8 ppm], 2.43 [br. s, 2 H, HB for $\delta(^{11}B)$ = –10.7 ppm], 2.57 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.6 ppm], 2.73 [dtt, $^2J_{^{31}P,^1H}$ = 3.5 Hz, $^3J_{^1H,^1H_{trans}}$ = 12.2 Hz, $^3J_{^1H,^1H_{cis}}$ = 3.6 Hz, 1 H, PC(1)H], 2.78 [br. s, 1 H, HB for $\delta(^{11}B)$ = –8.0 ppm], 3.01 [br. s, 1 H, HB for $\delta(^{11}B)$ = 0.2 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.7 (2 B), –8.6 (2 B), –8.0 (1 B), –6.5 (3 B), –3.8 (1 B), 0.2 (1 B) ppm. $^{11}$B NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.7 (d, $^1J_{^{11}B,^1H}$ = 165 Hz, 2 B), –8.6 (d, $^1J_{^{11}B,^1H}$ = 168 Hz, 2 B), –8.0 (d, 1 B), –6.5 (d, $^1J_{^{11}B,^1H}$ = 153 Hz, 3 B), –3.8 (d, $^1J_{^{11}B,^1H}$ = 148 Hz, 1 B), 0.2 (d, $^1J_{^{11}B,^1H}$ = 176 Hz, 1 B) ppm. $^1H\{^{11}B\}$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 0.59 [dm, $^3J_{^{31}P,^1H}$ = 8.2 Hz, 2 H, C(2)H$^a$], 0.86 [m, 1 H, C(4)H$^a$], 0.92 [m, 2 H, C(3)H$^a$], 1.37 [m, 1 H, C(4)H$^b$], 1.47 [m, 2 H, C(3)H$^b$], 1.56 [m, 2 H, C(2)H$^b$], 2.44 [dtt, $^2J_{^{31}P,^1H}$ = 2.9 Hz, $^3J_{^1H,^1H_{trans}}$ = 12.3, $^3J_{^1H,^1H_{cis}}$ = 3.8 Hz, 1 H, PC(1)H], 2.59 [br. s, 2 H, HB for $\delta(^{11}B)$ = –10.5 ppm], 2.73 [br. s, 5 H, HB for $\delta(^{11}B)$ = –6.0, –8.4 ppm], 2.77 [br. s, 2 H, HB for $\delta(^{11}B)$ = –3.3, –7.8 ppm], 3.14 [br. s, 1 H, HB for $\delta(^{11}B)$ = 0.2 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –10.5 (2 B), –8.4 (2 B), –7.8 (1 B), –6.0 (3 B), –3.3 (1 B), 0.2 (1 B) ppm. $^{11}$B NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –10.5 (d, $^1J_{^{11}B,^1H}$ = 166 Hz, 2 B), –8.4 (d, $^1J_{^{11}B,^1H}$ = 164 Hz, 2 B), –7.8 (d, 1 B), –6.0 (d, $^1J_{^{11}B,^1H}$ = 150 Hz, 3 B), –3.3 (d, $^1J_{^{11}B,^1H}$ = 147 Hz, 1 B), 0.2 (d, $^1J_{^{11}B,^1H}$ = 180 Hz, 1 B) ppm. EI-MS (70 eV): *m/z* (%) = 415 (12) $[M]^+$, 332 (5) $[M - C_6H_{11}]^+$, 83 (100).

**2,7-Di(cyclohexyl)-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraselenacyclodecane (20):** A solution of **5** (100.9 mg, 0.28 mmol) in [$D_8$]toluene (0.6 mL) was cooled to –30 °C, and $CyPCl_2$ (0.043 mL, 0.28 mmol) was added through a microsyringe. The progress of the reaction was monitored by $^{31}$P and $^{29}$Si NMR spectroscopy. After 30 min at room temp., the mixture contained **9** together with $Me_2SiCl_2$. After 24 h at room temp., the mixture contained **9** (ca. 85%), **20** (10%), and **9**(Se) (5%) together with $Me_2SiCl_2$. The volatile materials were removed under vacuum (1 h, $8 \times 10^{-3}$ Torr), and the residue was dissolved in [$D_8$]-toluene. This solution in [$D_8$]toluene was kept for 1 week at –30 °C, and the formation of **20** as a fairly insoluble white powder was observed. The precipitate was separated by centrifugation, washed with [$D_8$]toluene, and dried under vacuum to give **20** as a light yellowish solid; m.p. 165–175 °C (dec.). The dimer **20** was dissolved in [$D_8$]THF; after 1 h at room temp., the solution contained **9** (75%), **20** (20%), and **9**(Se) (5%), and after 30 min at 50 °C, the mixture contained **9** (80%), **9**(Se) (15%), and **23** (5%; Figure 4). The residual solution in [$D_8$]toluene was left at room temperature for two months, after which transparent yellow crystals of **9**(Se) [m.p. 140–150 °C (dec.)] could be collected. The principle structure of **9**(Se) was confirmed by X-ray analysis, although severe disorder in the region of the selenium atoms prevented an exact determination of a meaningful data set. The solution in [$D_8$]toluene contained **9**, **9**(Se), **23**, bis(diselane) **24**,[21] and several unidentified products (from $^{31}$P and $^{77}$Se NMR spectroscopy).

**20:** $^1H\{^{11}B\}$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 1.22 [m, 2 H, C(4)H$^a$ from PCy], 1.35 [m, 8 H, C(2)H$^a$ and C(3)H$^a$ from PCy], 1.71 [m, 2 H, C(4)H$^b$ from PCy], 1.87 [m, 4 H, C(3)H$^b$ from PCy], 2.13 [m, 6 H, C(2)H$^b$ and PC(1)H from Cy], 2.21 [br. s, 2 H, HB for $\delta(^{11}B)$ = –9.0 ppm], 2.25 [br. s, 2 H, HB for $\delta(^{11}B)$ = –7.3 ppm], 2.47 [br. s, 4 H, HB for $\delta(^{11}B)$ = –2.4 ppm], 2.56 [br. s, 6 H, HB for $\delta(^{11}B)$ = –9.0 ppm], 2.70 [br. s, 4 H, HB for $\delta(^{11}B)$ = –6.5, –7.3 ppm], 2.99 [br. s, 2 H, HB for $\delta(^{11}B)$ = –9.0 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –9.0 (10 B), –7.3 (4 B), –6.6 (2 B), –2.4 (4 B) ppm.

**9(Se):** $^1H\{^{11}B\}$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 0.82 [m, 1 H, C(4)H$^a$], 0.90 [m, 2 H, C(3)H$^a$], 1.31 [m, 3 H, C(2)H$^a$ and C(4)H$^b$], 1.49 [m, 2 H, C(3)H$^b$], 1.64 [m, 2 H, C(2)H$^b$], 2.60 [m, $^3J_{^1H,^1H_{trans}}$ = 11.9 Hz, 1 H, PC(1)H], 2.61 [br. s, 4 H, HB for $\delta(^{11}B)$ = –9.0 ppm], 2.75 [br. s, 3 H, HB for $\delta(^{11}B)$ = –6.4, –4.2 ppm], 2.88 [br. s, 1 H, HB for $\delta(^{11}B)$ = –5.3 ppm], 3.00 [br. s, 1 H, HB for $\delta(^{11}B)$ = –0.6 ppm], 3.50 [br. s, 1 H, HB for $\delta(^{11}B)$ = –4.2 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –9.0 (4 B), –6.4 (1 B), –5.3 (1 B), –4.2 (3 B), –0.6 (1 B) ppm. $^{11}$B NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –9.0 (d, $^1J_{^{11}B,^1H}$ = 180 Hz, 4 B), –6.4 (d, $^1J_{^{11}B,^1H}$ = 155 Hz, 1 B), –5.3 (d, 1 B), –4.2 (d, $^1J_{^{11}B,^1H}$ = 157 Hz, 3 B), –0.6 (d, $^1J_{^{11}B,^1H}$ = 142 Hz, 1 B) ppm. EI-MS (70 eV): *m/z* (%) = 493 (5) $[M]^+$, 414 (4) $[M - Se]^+$, 379 (2), 331 (12) $[M - Se - C_6H_{11}]^+$, 83 (100) $[C_6H_{11}]$.

**23:** $^1$H NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 4.23 (s, 1 H, $C_{carb}$H), 5.79 (d, $^1J_{^{31}P,^1H}$ = 476.5 Hz, 1 H, PH) ppm. $^1H\{^{31}P\}$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 4.23 (s, 1 H, $C_{carb}$H), 5.79 (s, 1 H, PH).

**2-(1,1-Dimethylethyl)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholane (10):** A solution of **5** (92 mg, 0.257 mmol) in [$D_8$]toluene (0.4 mL) was cooled to –30 °C, and a solution of *t*BuPCl$_2$ (40.8 mg, 0.257 mmol) in [$D_8$]toluene (0.2 mL) was added. The progress of the reaction was monitored by $^{31}$P and $^{29}$Si NMR spectroscopy. After 2 h at room temp., the mixture contained **10** (ca. 80%) and a stereoisomeric mixture of oligomers (20%) together with $Me_2SiCl_2$. The volatile materials were removed under vacuum (2 h, $8 \times 10^{-3}$ Torr) to give a white solid. One part of the remaining solid was dissolved in [$D_8$]THF. After 2 h at room temp., the mixture contained **10** (ca. 65%), **21** (30%), and **21′** (possibly a trimer, 5%). After 1 d at room temp., the mixture contained **10** (5%), **21** (90%), and **10**(Se) (5%; Figure 5, A–C). A second part of the remaining solid was dissolved in [$D_8$]toluene, and the precipitate was separated by centrifugation and redissolved in [$D_8$]toluene; the mixture contained **21** (70%) and **21′** (possibly a trimer, 30%) as determined by $^{31}$P NMR spectroscopy. After 20 h at room temp., the mixture contained **21** (90%), **21′** (10%), and bis(diselane) **24** (from $^{31}$P and $^{77}$Se NMR spectroscopy; Figure 5, D–F).

**10:** $^1$H NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 0.81 (d, $^3J_{^{31}P,^1H}$ = 13.2 Hz, 9 H, $CH_3$) ppm.

**21:** $^1$H NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 0.98 (d, $^3J_{^{31}P,^1H}$ = 15.2 Hz, 18 H, $CH_3$) ppm.

**21′:** $^1$H NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 1.07 (d, $^3J_{^{31}P,^1H}$ = 15.2 Hz, 27 H, $CH_3$) ppm.

The solution containing **10** (50%), **21** (45%), and **10**(Se) (5%) in [$D_8$]toluene was added to an excess of dry degassed elemental selenium. The progress of the reaction was monitored by $^{31}P$ NMR spectroscopy. After 24 h at 60 °C, the solution contained **21** (5%), **10**(Se) (90%), and several unidentified side products.

**10(Se):** $^1H\{^{11}B\}$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 0.92 (d, $^3J_{^{31}P,^1H}$ = 24.3 Hz, 9 H, $CH_3$), 2.19 [br. s, 1 H, HB for $\delta(^{11}B)$ = –11.7 ppm], 2.51 [br. s, 2 H, HB for $\delta(^{11}B)$ = –9.5 ppm], 2.74 [br. s, 5 H, HB for $\delta(^{11}B)$ = –8.1, –5.7, –4.6 ppm], 2.84 [br. s, 1 H, HB for $\delta(^{11}B)$ = –5.7 ppm], 3.73 [br. s, 1 H, HB for $\delta(^{11}B)$ = –7.5 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –11.7 (1 B), –9.5 (2 B), –8.1 (2 B), –7.5 (1 B), –5.7 (2 B), –4.6 (2 B) ppm.

**2,7-Bis(1,1-dimethylethyl)-4,5,9,10-bis[1,2-dicarba-*closo*-dodecaborano(12)]-2,7-diphospha-1,3,6,8-tetraselenaacyclodecane (21):** Degassed **5** (40 mg, 0.111 mmol) was added to *t*BuPCl$_2$ (17.7 mg, 0.111 mmol). The mixture was cooled to –30 °C, and [$D_8$]toluene (1 mL) was added. After 1 d at room temp., the volatile materials were removed in vacuo. The resulting mixture thus obtained contained **10** (ca. 50%) and a stereoisomeric mixture of **21** (ca. 50% by $^{31}P$ NMR spectroscopy). The remaining white solid was washed with [$D_8$]toluene, the insoluble materials were dissolved in $CD_2Cl_2$ and centrifuged, and the liquid phase was collected. Transparent crystals of **21** for X-ray analysis were grown from $CD_2Cl_2$ solution after 1 week at –30 °C; m.p. 215–225 °C (dec.). $^1H\{^{11}B\}$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 1.37 (d, $^3J_{^{31}P,^1H}$ = 15.5 Hz, 18 H, $CH_3$), 2.17 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.8 ppm], 2.21 [br. s, 2 H, HB for $\delta(^{11}B)$ = –9.6 ppm], 2.27 [br. s, 2 H, HB for $\delta(^{11}B)$ = –7.2 ppm], 2.47 [br. s, 4 H, HB for $\delta(^{11}B)$ = –2.5 ppm], 2.61 [br. s, 4 H, HB for $\delta(^{11}B)$ = –9.6 ppm], 2.71 [br. s, 4 H, HB for $\delta(^{11}B)$ = –6.3 ppm], 2.95 [br. s, 2 H, HB for $\delta(^{11}B)$ = –9.6 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –9.6 (8 B), –8.8 (2 B), –7.2 (2 B), –6.3 (4 B), –2.5 (4 B) ppm. EI-MS (70 eV): *m*/*z* (%) = 776 (1) $[M]^+$, 719 (2) $[M - C_4H_9]^+$, 389 (6) $[M/2]^+$, 232 (4) $[M/2 - C_4H_9]^+$, 57 (100) $[C_4H_9]^+$.

**2-[3,5-Dimethylphenylmethyl]-4,5-[1,2-dicarba-*closo*-dodecaborano-(12)]-1,3,2-diselenaphospholane (11):** A solution of **5** (1144 mg, 0.319 mmol) in $CD_2Cl_2$ (0.6 mL) was added through a microsyringe to (3,5-$Me_2$–$C_6H_3$)$CH_2PBr_2$ (99 mg, 0.319 mmol) at room temp. The progress of the reaction was monitored by $^{31}P$ and $^{29}Si$ NMR spectroscopy. After 1 h at room temp., the mixture contained **11** together with $Me_2SiBr_2$. The volatile materials were removed under vacuum (3 h, $8 \times 10^{-3}$ Torr). The residue was washed with [$D_8$]toluene and dried in a vacuum to give **11** as a white solid. Transparent crystals of **11** for X-ray analysis were grown from $CD_2Cl_2$ solution after 1 week at room temp.; m.p. 140–150 °C (dec.). The monomer **11** was dissolved in [$D_8$]THF, and after 2 d at room temp., the solution contained **11** (85%), **11**(Se) (5%), and several unidentified products (from $^{31}P$ NMR spectroscopy). $^1H\{^{11}B\}$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 2.30 (s, 6 H, $CH_3$), 2.45 [br. s, 1 H, HB for $\delta(^{11}B)$ = –3.8 ppm], 2.49 [br. s, 5 H, HB for $\delta(^{11}B)$ = –6.1, –6.5, –10.4 ppm], 2.67 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.6 ppm], 3.05 [br. s, 1 H, HB for $\delta(^{11}B)$ = –0.2 ppm], 3.15 [br. s, 1 H, HB for $\delta(^{11}B)$ = –7.6 ppm], 3.85 [d, $^2J_{^{31}P,^1H}$ = 10.7 Hz, $^3J_{^{77}Se,^1H}$ = 4.9 Hz, 2 H, $PCH_2$), 6.83 (s, 2H, Ph), 6.93 (s, 1 H, Ph) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.4 (2 B), –8.6 (2 B), –7.6 (1 B), –6.5 (2 B), –6.1 (1 B), –3.8 (1 B), –0.2 (1 B) ppm. $^{11}B$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.4 (d, $^1J_{^{11}B,^1H}$ = 160 Hz, 2 B), –8.6 (d, $^1J_{^{11}B,^1H}$ = 171 Hz, 2 B), –7.6 (d, 1 B), –6.5 (d, $^1J_{^{11}B,^1H}$ = 148 Hz, 2 B), –6.1 (d, $^1J_{^{11}B,^1H}$ = 153 Hz, 1 B), –3.8 (d, $^1J_{^{11}B,^1H}$ = 152 Hz, 1 B), –0.2 (d, $^1J_{^{11}B,^1H}$ = 180 Hz, 1 B) ppm. EI-MS (70 eV): *m*/*z* (%) = 451 (20) $[M]^+$, 332 (10) $[M - C_9H_{11}]^+$, 119 (100) $[C_9H_{11}]^+$.

**2-[3,5-Dimethylphenylmethyl]-2-selenide-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholane [11(Se)] and 3-[3,5-Dimethylphenylmethyl]-3-selenide-6,7-[1,2-dicarba-*closo*-dodecaborano(12)]-1,2,4,5-tetraselena-3-phosphacycloheptane (25):** A solution of **11** (0.30 mmol) in $CD_2Cl_2$ (1.0 mL) was added to an excess of dry degassed elemental selenium (80 mg, 1.01 mmol). After 48 h at 50 °C, the mixture contained **11**(Se) (ca. 25%) and **25** (ca. 75%; from $^{31}P$ and $^{77}Se$ NMR spectroscopy). The excess selenium was separated by centrifugation, and the volatile materials were removed under vacuum (1 h, $8 \times 10^{-3}$ Torr). The residue was washed with [$D_8$]toluene and dried under vacuum to give **25** as a yellow-green solid.

**11(Se):** $^1H$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 2.33 (m, 6 H, $CH_3$), 4.61 (d, $^2J_{^{31}P,^1H}$ = 9.5 Hz, 2 H, $PCH_2$), 7.02 (dm, $^4J_{^1H,^1H}$ = 4.3 Hz, 2 H, Ph), 7.05 (dm, $^4J_{^1H,^1H}$ = 4.3 Hz, 1 H, Ph) ppm.

**25:** $^1H\{^{11}B\}$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 2.02 [br. s, 1 H, HB for $\delta(^{11}B)$ = –10.9 ppm], 2.27 [br. s, 1 H, HB for $\delta(^{11}B)$ = –8.2 ppm], 2.34 (m, 6 H, $CH_3$), 2.43 [br. s, 1 H, HB for $\delta(^{11}B)$ = –10.9 ppm], 2.59 [br. s, 4 H, HB for $\delta(^{11}B)$ = –8.2, –1.3 ppm], 2.79 [br. s, 2 H, HB for $\delta(^{11}B)$ = –7.1 ppm], 3.20 [br. s, 1 H, HB for $\delta(^{11}B)$ = –10.9 ppm], 4.59 (d, $^2J_{^{31}P,^1H}$ = 9.5 Hz, 2 H, $PCH_2$), 6.96 (d, $^4J_{^1H,^1H}$ = 3.8 Hz, 2 H, Ph), 7.03 (dm, $^4J_{^1H,^1H}$ = 3.8 Hz, 1 H, Ph) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.9 (3 B), –8.2 (3 B), –7.1 (2 B), –1.3 (2 B) ppm. $^{11}B$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.9 (d, $^1J_{^{11}B,^1H}$ = 158 Hz, 3 B), –8.2 (d, $^1J_{^{11}B,^1H}$ = 168 Hz, 3 B), –7.1 (d, 2 B), –1.3 (d, $^1J_{^{11}B,^1H}$ = 139 Hz, 2 B) ppm.

**2-[3,5-Dimethylphenylmethyl]-2-thio-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholane [11(S)]:** A solution of **11** (0.15 mmol) in $CD_2Cl_2$ (0.6 mL) was added to an excess of dry and degassed elemental sulfur (ca. 8 mg). The progress of the reaction was monitored by $^{31}P$ NMR spectroscopy. The mixture was stirred for 10 d at room temp. and then centrifuged from the unreacted sulfur. The reaction solution contained **11**(S) (ca. 90%) together with bis(diselane) **24**[21] and several unidentified side products (from $^{13}C$, $^{31}P$, and $^{77}Se$ NMR spectroscopy).

**11(S):** $^1H$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 2.32 (m, 6 H, $CH_3$), 2.41 [br. s, 1 H, HB for $\delta(^{11}B)$ = –6.8 ppm], 2.45 [br. s, 1 H, HB for $\delta(^{11}B)$ = –5.8 ppm], 2.56 [br. s, 5 H, HB for $\delta(^{11}B)$ = –0.8, –9.0 ppm], 2.70 [br. s, 1 H, HB for $\delta(^{11}B)$ = –6.8 ppm], 2.96 [br. s, 1 H, HB for $\delta(^{11}B)$ = –4.2 ppm], 3.33 [br. s, 1 H, HB for $\delta(^{11}B)$ = –4.2 ppm], 4.33 (d, $^2J_{^{31}P,^1H}$ = 10.2 Hz, 2 H, $PCH_2$), 7.00 (dm, $^4J_{^1H,^1H}$ = 4.2 Hz, 2 H, Ph), 7.03 (dm, $^4J_{^1H,^1H}$ = 4.2 Hz, 1 H, Ph) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –9.0 (4 B), –6.8 (2 B), –5.8 (1 B), –4.2 (2 B), –0.8 (1 B) ppm.

**2-Phenyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholane (12):** A solution of **5** (53 mg, 0.148 mmol) in [$D_8$]toluene (0.6 mL) was cooled to –30 °C, and $PhPCl_2$ (0.020 mL, 0.148 mmol) was added through a microsyringe. The progress of the reaction was monitored by $^{31}P$ and $^{29}Si$ NMR spectroscopy. After 1 h at room temp., the mixture contained **12** together with $Me_2SiCl_2$. The volatile materials were removed under vacuum (1 h, $8 \times 10^{-3}$ Torr) to give **12** (purity ca. 95%) as a white oil. The monomer **12** can be stored for prolonged periods of time in [$D_8$]toluene or $CD_2Cl_2$ at –30 °C. After 12 h at 50 °C in [$D_8$]toluene, the solution contained **12** (ca. 50%), **12**(Se)[8,11] (ca. 10%), and several unidentified products (from $^{31}P$ NMR spectroscopy).

**12:** $^1H\{^{11}B\}$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 2.50 [br. s, 1 H, HB for $\delta(^{11}B)$ = –6.7 ppm], 2.58 [br. s, 3 H, HB for $\delta(^{11}B)$ = –9.9, –11.0 ppm], 2.61 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.3 ppm], 2.72 [br. s, 2 H, HB for $\delta(^{11}B)$ = –5.8 ppm], 2.80 [br. s, 1 H, HB for

$\delta(^{11}B)$ = –3.3 ppm], 3.16 [br. s, 1 H, HB for $\delta(^{11}B)$ = 0.0 ppm], 6.90 (m, 3 H, Ph), 7.22 (m, 2 H, Ph) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): $\delta$ = –11.0 (2 B), –9.9 (1 B), –8.3 (2 B), –6.7 (1 B), –5.8 (2 B), –3.3 (1 B), 0.0 (1 B) ppm. $^{11}B$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): $\delta$ = –11.0 (d, $^1J_{^{11}B,^1H}$ = 166 Hz, 2 B), –9.9 (d, 1 B), –8.3 (d, $^1J_{^{11}B,^1H}$ = 167 Hz, 2 B), –6.7 (d, $^1J_{^{11}B,^1H}$ = 148 Hz, 1 B), –5.8 (d, $^1J_{^{11}B,^1H}$ = 151 Hz, 2 B), –3.3 (d, $^1J_{^{11}B,^1H}$ = 151 Hz, 1 B), 0.0 (d, $^1J_{^{11}B,^1H}$ = 180 Hz, 1 B) ppm.

**2-Ethoxy-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholane (13):** A solution of **5** (51.9 mg, 0.145 mmol) in [D$_8$]-toluene (0.6 mL) was cooled to –30 °C, and $EtOPCl_2$ (0.016 mL, 0.14 mmol) was added through a microsyringe. The progress of the reaction was monitored by $^{31}P$ and $^{29}Si$ NMR spectroscopy. After 2 h at room temp., the mixture contained **13** together with $Me_2SiCl_2$. The volatile materials were removed under vacuum (1 h, $8 \times 10^{-3}$ Torr) to give **13** (ca. 90%) together with **13**(Se) (ca. 10%).[11] The monomer **13** decomposes slowly in [D$_8$]toluene or in $CD_2Cl_2$ under Ar at –30 °C to form **13**(Se) and several unidentified products (from $^{31}P$ NMR).

**13:** $^1H$ NMR (500.13 MHz, [D$_8$]toluene, 25 °C): $\delta$ = 0.80 (t, $^3J_{^1H,^1H}$ = 7.0 Hz, 3 H, $CH_3$), 3.21 (dq, $^3J_{^{31}P,^1H}$ = 9.8 Hz, $^3J_{^1H,^1H}$ = 7.0 Hz, 2 H, $POCH_2$) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): $\delta$ = –10.0 (2 B), –8.4 (2 B), –6.3 (3 B), –5.6 (1 B), –4.1 (1 B), –1.2 (1 B) ppm. $^{11}B$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): $\delta$ = –10.0 (d, $^1J_{^{11}B,^1H}$ = 167 Hz, 2 B), –8.4 (d, $^1J_{^{11}B,^1H}$ = 170 Hz, 2 B), –6.3 (d, $^1J_{^{11}B,^1H}$ = 145 Hz, 3 B), –5.6 (d, 1 B), –4.1 (d, $^1J_{^{11}B,^1H}$ = 148 Hz, 1 B), –1.2 (d, $^1J_{^{11}B,^1H}$ = 180 Hz, 1 B) ppm. $^1H$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 1.37 (t, 3 H, $CH_3$, $^3J_{^1H,^1H}$ = 7.0 Hz), 3.98 (dq, $^3J_{^{31}P,^1H}$ = 9.9 Hz, $^3J_{^1H,^1H}$ = 7.0 Hz, 2 H, $POCH_2$) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.3 (2 B), –8.6 (2 B), –6.8 (3 B), –6.1 (1 B), –4.5 (1 B), –1.2 (1 B) ppm. $^{11}B$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.3 (d, $^1J_{^{11}B,^1H}$ = 166 Hz, 2 B), –8.6 (d, $^1J_{^{11}B,^1H}$ = 172 Hz, 2 B), –6.3 (d, $^1J_{^{11}B,^1H}$ = 150 Hz, 3 B), –6.1 (d, 1 B), –4.5 (d, $^1J_{^{11}B,^1H}$ = 154 Hz, 1 B), –1.2 (d, $^1J_{^{11}B,^1H}$ = 189 Hz, 1 B) ppm.

**13(Se):** $^1H$ NMR (500.13 MHz, [D$_8$]toluene, 25 °C): $\delta$ = 0.87 (t, $^3J_{^1H,^1H}$ = 7.1 Hz, 3 H, $CH_3$), 3.71 (dq, $^3J_{^{31}P,^1H}$ = 12.2 Hz, $^3J_{^1H,^1H}$ = 7.1 Hz, 2 H, $POCH_2$) ppm. $^1H$ NMR (500.1 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 1.45 (t, $^3J_{^1H,^1H}$ = 7.1 Hz, 3 H, $CH_3$), 4.32 (dq, $^3J_{^{31}P,^1H}$ = 11.8 Hz, $^3J_{^1H,^1H}$ = 7.1 Hz, 2 H, $POCH_2$) ppm.

**2-Diethylamino-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholane (14):** A solution of **5** (78.6 mg, 0.22 mmol) in [D$_8$]-toluene (0.6 mL) was cooled to –30 °C, and $Et_2NPCl_2$ (0.032 mL, 0.22 mmol) was added through a microsyringe. The progress of the reaction was monitored by $^{31}P$ and $^{29}Si$ NMR spectroscopy. After 2 h at –10 °C, the mixture contained **14** together with $Me_2SiCl_2$. The volatile materials were removed under vacuum (1 h, $8 \times 10^{-3}$ Torr) to give **14** (90%) together with several unidentified products. The monomer **14** decomposes in [D$_8$]toluene under Ar at –30 °C to form **14**(Se), bis(diselane) **24**, and several unidentified products (from $^{31}P$ and $^{77}Se$ NMR spectroscopy).

**14:** $^1H$ NMR (500.13 MHz, [D$_8$]toluene, 25 °C): $\delta$ = 0.62 (t, $^3J_{^1H,^1H}$ = 7.1 Hz, 6 H, $CH_3$), 2.78 (dq, $^3J_{^{31}P,^1H}$ = 11.7 Hz, $^3J_{^1H,^1H}$ = 7.1 Hz, 4 H, $PNCH_2$) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): $\delta$ = –9.7 (2 B), –8.2 (2 B), –6.9 (1 B), –4.8 (4 B), –2.2 (1 B) ppm. $^{11}B$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): $\delta$ = –9.7 (d, $^1J_{^{11}B,^1H}$ = 170 Hz, 2 B), –8.2 (d, $^1J_{^{11}B,^1H}$ = 170 Hz, 2 B), –6.9 (d, $^1J_{^{11}B,^1H}$ = 163 Hz, 1 B), –4.8 (d, $^1J_{^{11}B,^1H}$ = 151 Hz, 4 B), –2.2 (d, $^1J_{^{11}B,^1H}$ = 180 Hz, 1 B) ppm.

**2-{4,5-[1,2-Dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholan-2-yl}methyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholane (15):** A solution of **5** (99.7 mg, 0.28 mmol) in [D$_8$]toluene (0.6 mL) was cooled to 0 °C, and $Cl_2PCH_2PCl_2$ (0.019 mL, 0.14 mmol) was added through a microsyringe. The progress of the reaction was monitored by $^{31}P$ and $^{29}Si$ NMR spectroscopy. After 2 h at room temp., the mixture contained **15** together with $Me_2SiCl_2$. A white powder of **15** formed and had rather low solubility in [D$_8$]toluene. The precipitate was separated by centrifugation, washed with [D$_8$]toluene, and dried under vacuum to give **15** as a light yellowish solid. Compound **15** can be stored for prolonged periods of time in [D$_8$]toluene at room temp., survives in toluene solution at 100 °C, and decomposes slowly in [D$_8$]THF under Ar at –30 °C into several unidentified products. Transparent crystals of **15** for X-ray analysis were grown from a hot saturated [D$_8$]toluene solution after 1 d at room temp.; m.p. 220–235 °C (dec.).

**15:** $^1H\{^{11}B\}$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 2.49 [br. s, 4 H, HB for $\delta(^{11}B)$ = –6.0 ppm], 2.58 [br. s, 8 H, HB for $\delta(^{11}B)$ = –3.5, –6.0, –10.5 ppm], 2.73 [br. s, 4 H, HB for $\delta(^{11}B)$ = –8.5 ppm], 3.03 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.5 ppm], 3.14 [br. s, 2 H, HB for $\delta(^{11}B)$ = –0.3 ppm], 3.92 (t, $^2J_{^{31}P,^1H}$ = 13.9 Hz, $^3J_{^{77}Se,^1H}$ = 4.5 Hz, 2 H, $CH_2$) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.5 (4 B), –8.5 (6 B), –6.0 (6 B), –3.5 (2 B), –0.3 (2 B) ppm. $^{11}B$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.5 (d, $^1J_{^{11}B,^1H}$ = 156 Hz, 4 B), –8.5 (d, $^1J_{^{11}B,^1H}$ = 156 Hz, 6 B), –6.0 (d, $^1J_{^{11}B,^1H}$ = 151 Hz, 6 B), –3.5 (d, $^1J_{^{11}B,^1H}$ = 158 Hz, 2 B), –0.3 (d, $^1J_{^{11}B,^1H}$ = 157 Hz, 2 B) ppm. EI-MS (70 eV): *m/z* (%) = 677 (45) $[M]^+$.

**2-Dichlorophosphinomethyl-4,5-[1,2-dicarba-*closo*-dodecaborano-(12)]-1,3,2-diselenaphospholane (17):** A solution of **5** (59.9 mg, 0.167 mmol) in [D$_8$]toluene (0.6 mL) was cooled to –30 °C, and $Cl_2PCH_2PCl_2$ (0.023 mL, 0.169 mmol) was added through a microsyringe. The progress of the reaction was monitored by $^{31}P$ and $^{29}Si$ NMR spectroscopy. After 1 h at room temp., the mixture contained **17** (60%) and **15** (40%) together with $Me_2SiCl_2$ and $Cl_2PCH_2PCl_2$. The formation of a white powder of **15** was observed. The precipitate of **15** was separated by centrifugation; the reaction solution contained **17** (80%) and **15** (20%) together with $Me_2SiCl_2$ and $Cl_2PCH_2PCl_2$ (from $^{31}P$ and $^1H$ NMR spectroscopy).

**17:** $^1H\{^{11}B\}$ NMR (500.13 MHz, [D$_8$]toluene, 25 °C): $\delta$ = 2.51 [br. s, 1 H, HB for $\delta(^{11}B)$ = –10.6 ppm], 2.54 (dd, $^2J_{^{31}P_{PCl_2},^1H}$ = 20.0 Hz, $^2J_{^{31}P_{PSe},^1H}$ = 9.3 Hz, 2 H, $CH_2$), 2.58 [br. s, 1 H, HB for $\delta(^{11}B)$ = –8.0 ppm], 2.68 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.5 ppm], 2.77 [br. s, 5 H, HB for $\delta(^{11}B)$ = –5.8, –3.3 ppm], 2.98 [br. s, 1 H, HB for $\delta(^{11}B)$ = –0.6 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): $\delta$ = –10.6 (1 B), –8.5 (2 B), –8.0 (1 B), –5.8 (4 B), –3.3 (1 B), –0.6 (1 B) ppm. $^{11}B$ NMR (160.5 MHz, [D$_8$]toluene, 25 °C): $\delta$ = –10.6 (d, $^1J_{^{11}B,^1H}$ = 168 Hz, 1 B), –8.5 (d, $^1J_{^{11}B,^1H}$ = 158 Hz, 2 B), –8.0 (1 B), –5.8 (d, $^1J_{^{11}B,^1H}$ = 150 Hz, 4 B), –3.3 (d, $^1J_{^{11}B,^1H}$ = 152 Hz, 1 B), –0.6 (d, $^1J_{^{11}B,^1H}$ = 175 Hz, 1 B) ppm.

**15:** $^1H$ NMR (500.13 MHz, [D$_8$]toluene, 25 °C): $\delta$ = 2.87 (t, $^2J_{^{31}P,^1H}$ = 15.3 Hz, 2 H, $CH_2$) ppm.

**2-(2-{4,5-[1,2-Dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholan-2-yl}ethyl)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-diselenaphospholane (16):** A solution of **5** (117 mg, 0.33 mmol) in [D$_8$]toluene (0.6 mL) was cooled to –30 °C, and $Cl_2PCH_2CH_2PCl_2$ (0.025 mL, 0.165 mmol) was added through a microsyringe. The progress of the reaction was monitored by $^{31}P$ and $^{29}Si$ NMR spectroscopy. After 1 h at room temp., the mixture contained **16** together with $Me_2SiCl_2$. A white powder of **16** formed and had rather low solubility in [D$_8$]toluene. The precipitate was separated by centrifugation, washed with [D$_8$]toluene, and dried under vacuum to give **16** as a white solid; m.p. 185–195 °C (dec.). Compound **16** can be stored for prolonged periods of time in

[$D_8$]toluene at room temp. and decomposes slowly in toluene at 100 °C.

**16:** $^1H\{^{11}B\}$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 1.78 (pseudo-t, $|^2J_{^{31}P,^1H} + {}^3J_{^{31}P,^1H}|$ = 22.1 Hz, 4 H, $CH_2$), 2.56 [br. s, 4 H, HB for $\delta(^{11}B)$ = –10.4 ppm], 2.71 [br. s, 4 H, HB for $\delta(^{11}B)$ = –6.0 ppm], 2.76 [br. s, 10 H, HB for $\delta(^{11}B)$ = –3.1, –6.0, –8.5 ppm], 3.07 [br. s, 2 H, HB for $\delta(^{11}B)$ = –0.5 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –10.4 (4 B), –8.5 (6 B), –6.0 (6 B), –3.2 (2 B), –0.5 (2 B) ppm. $^1H\{^{11}B\}$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 2.35 [br. s, 4 H, HB for $\delta(^{11}B)$ = –6.4 ppm], 2.49 [br. s, 8 H, HB for $\delta(^{11}B)$ = –3.4, –6.4, –10.6 ppm], 2.64 [br. s, 4 H, HB for $\delta(^{11}B)$ = –8.6 ppm], 2.68 (pseudo-t, $|^2J_{^{31}P,^1H} + {}^3J_{^{31}P,^1H}|$ = 22.2 Hz, 4 H, $CH_2$), 2.91 [br. s, 2 H, HB for $\delta(^{11}B)$ = –8.6 ppm], 3.05 [br. s, 2 H, HB for $\delta(^{11}B)$ = 0.1 ppm] ppm. $^1H$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 2.68 (pseudo-t, 4 H, $CH_2$, $|^2J_{^{31}P,^1H} + {}^3J_{^{31}P,^1H}|$ = 22.2 Hz, $^3J_{^{77}Se,^1H}$ = 2.1 Hz, 4 H, $CH_2$) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.6 (4 B), –8.6 (6 B), –6.4 (6 B), –3.4 (2 B), 0.1 (2 B) ppm. $^{11}B$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –10.6 (d, $^1J_{^{11}B,^1H}$ = 166 Hz, 4 B), –8.6 (d, $^1J_{^{11}B,^1H}$ = 165 Hz, 6 B), –6.4 (d, $^1J_{^{11}B,^1H}$ = 155 Hz, 6 B), –3.4 (d, $^1J_{^{11}B,^1H}$ = 150 Hz, 2 B), –0.1 (d, $^1J_{^{11}B,^1H}$ = 170 Hz, 2 B) ppm. $^1H\{^{11}B\}$ NMR (500.13 MHz, [$D_8$]THF, 25 °C): $\delta$ = 2.26 [br. s, 4 H, HB for $\delta(^{11}B)$ = –6.7 ppm], 2.41 [br. s, 8 H, HB for $\delta(^{11}B)$ = –4.0, –6.7, –10.3 ppm], 2.64 [br. s, 4 H, HB for $\delta(^{11}B)$ = –8.5 ppm], 2.72 (pseudo-t, $|^2J_{^{31}P,^1H} + {}^3J_{^{31}P,^1H}|$ = 20.0 Hz, 4 H, $CH_2$), 2.96 [br. s, 2 H, HB for $\delta(^{11}B)$ = –6.7 ppm], 3.00 [br. s, 2 H, HB for $\delta(^{11}B)$ = –0.2 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [$D_8$]THF, 25 °C): $\delta$ = –10.3 (4 B), –8.5 (4 B), –6.7 (8 B), –4.0 (2 B), –0.2 (2 B) ppm. EI-MS (70 eV): *m/z* (%) = 691 (30) $[M]^+$.

**2-(2-Dichlorophosphinoethyl)-4,5-[1,2-dicarba-*closo*-dodecaborano-(12)]-1,3,2-diselenaphospholane (18):** A solution of **5** (67 mg, 0.187 mmol) in [$D_8$]toluene (0.6 mL) was cooled to 0 °C, and $Cl_2PCH_2CH_2PCl_2$ (0.028 mL, 0.186 mmol) was added through a microsyringe. The progress of the reaction was monitored by $^{31}P$ and $^{29}Si$ NMR spectroscopy. After 1 h at room temp., the mixture contained **18** (ca. 50%) and **16** (ca. 50%) together with $Me_2SiCl_2$ and $Cl_2PCH_2CH_2PCl_2$. The formation of a white powder of **16** was observed. The precipitate was separated by centrifugation; the solution contained **18** (60%) and **16** (40%) together with $Me_2SiCl_2$ and $Cl_2PCH_2PCl_2$ (from $^{31}P$ and $^1H$ NMR spectroscopy).

**18:** $^1H$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 1.49 (m, 2 H, $PCH_2$), 2.15 (m, 2 H, $PCH_2$).

**Reactions of 4 with $RPCl_2$:** All preparative work as well as handling of the samples was performed in the dark to shield the samples as much as possible from light. Thus, the reaction flasks and NMR sample tubes were wrapped in aluminum foil. All tellurium-containing compounds studied here decompose under Ar as solids, in solution at room temp., and in the presence of light, accompanied by the formation of black elemental tellurium.

**2-(1-Methylethyl)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-ditelluraphospholane (26a):** Freshly prepared **4** (844 mg, 1.74 mmol) was cooled to –40 °C and suspended in toluene (50 mL); the suspension was cooled to –40 °C, and *i*PrPCl$_2$ (0.214 mL, 1.74 mmol) was injected slowly through a syringe. The reaction mixture was stirred for 1.5 h at –40 °C and 30 min at 10 °C, the insoluble materials were separated by centrifugation, and the clear liquid was collected. The volatile materials were removed under vacuum to give a yellow-brown solid (597 mg). The resulting mixture thus obtained contained **26a** (ca. 50%), **27a** (15%), **28a** (15%), **29a** (8–9%), **29a′** (1–2%), **30a** (10%), together with bis(ditellane) **31**[17] and several unidentified products (from $^{31}P$ and $^{125}Te$ NMR spectroscopy; Figure 6). The remaining insoluble materials were washed with toluene (20 mL) and centrifuged. The remaining solid was dissolved in $CD_2Cl_2$ (2 mL) and centrifuged; the liquid phase was separated and dried under vacuum to give an orange-brown solid of **26a**. Compound **26a** was only sparingly soluble in toluene.

**26a:** $^1H\{^{11}B\}$ NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 1.38 (dd, $^3J_{^{31}P,^1H}$ = 21.2, $^3J_{^1H,^1H}$ = 7.0 Hz, 6 H, $CH_3$), 2.32 [br. s, 1 H, HB for $\delta(^{11}B)$ = –2.4 ppm], 2.37 [br. s, 3 H, HB for $\delta(^{11}B)$ = –4.4, –9.3 ppm], 2.62 [br. s, 2 H, HB for $\delta(^{11}B)$ = –3.9 ppm], 2.71 [br. s, 2 H, HB for $\delta(^{11}B)$ = –7.1 ppm], 3.03 [br. s, 1 H, HB for $\delta(^{11}B)$ = –7.1 ppm], 3.19 (dsept, $^2J_{^{31}P,^1H}$ = 3.8 Hz, $^3J_{^1H,^1H}$ = 7.0 Hz, 1 H, PCH), 3.54 [br. s, 1 H, HB for $\delta(^{11}B)$ = 0.5 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –9.3 (2 B), –7.1 (3 B), –4.4 (1 B), –3.9 (2 B), –2.4 (1 B), 0.5 (1 B) ppm. $^{11}B$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = –9.3 (d, $^1J_{^{11}B,^1H}$ = 158 Hz, 2 B), –7.1 (d, $^1J_{^{11}B,^1H}$ = 160 Hz, 3 B), –4.4 (d, $^1J_{^{11}B,^1H}$ = 153 Hz, 1 B), –3.9 (d, $^1J_{^{11}B,^1H}$ = 149 Hz, 2 B), –2.4 (d, $^1J_{^{11}B,^1H}$ = 150 Hz, 1 B), 0.5 (d, $^1J_{^{11}B,^1H}$ = 176 Hz, 1 B) ppm. $^1H$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 0.87 (dd, $^3J_{^{31}P,^1H}$ = 21.0 Hz, $^3J_{^1H,^1H}$ = 7.1 Hz, 6 H, $CH_3$), 2.69 (dsept, $^2J_{^{31}P,^1H}$ = 3.5 Hz, $^3J_{^1H,^1H}$ = 7.1 Hz, 1 H, PCH) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –9.2 (2 B), –7.0 (3 B), –4.1 (1 B), –3.4 (2 B), –1.9 (1 B), 0.5 (1 B) ppm. $^{11}B$ NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –9.2 (d, $^1J_{^{11}B,^1H}$ = 170 Hz, 2 B), –7.0 (d, $^1J_{^{11}B,^1H}$ = 164 Hz, 3 B), –4.1 (d, $^1J_{^{11}B,^1H}$ = 150 Hz, 1 B), –3.4 (d, $^1J_{^{11}B,^1H}$ = 150 Hz, 2 B), –1.9 (d, $^1J_{^{11}B,^1H}$ = 155 Hz, 1 B), 0.5 (d, $^1J_{^{11}B,^1H}$ = 185 Hz, 1 B) ppm.

**2-(1,1-Dimethylethyl)-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-ditelluraphospholane (26b):** Freshly prepared **4** (895 mg, 1.84 mmol) was cooled to –40 °C and suspended in toluene (50 mL). The suspension was cooled to –40 °C, and a solution of *t*BuPCl$_2$ (293 mg, 1.84 mmol) in toluene (0.3 mL) was added. The reaction mixture was stirred for 1.5 h at –40 °C and 1 h at room temp., the insoluble materials were separated by centrifugation, and the clear liquid was collected. The volatile materials were removed under vacuum to give a brown solid (769 mg). The resulting mixture thus obtained contained **26b** (ca. 45%), **27b** (5%), **28b** (40%), **30b** (10%), and several unidentified products (from $^{31}P$ and $^{125}Te$ NMR spectroscopy). This mixture in [$D_8$]toluene was kept for 1 week at –30 °C, and the formation of an orange solid of **30b** was observed. The precipitates were separated by centrifugation, washed with [$D_8$]toluene, and dried in a vacuum to give **30b** as a yellow-orange solid. The remaining insoluble materials from the initial reaction were washed with toluene (2 × 10 mL) and centrifuged. The remaining powder was dried under vacuum to give an orange-brown solid of **28b**.

**26b:** $^1H$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 0.95 (d, 9 H, $CH_3$, $^3J_{^{31}P,^1H}$ = 16.2 Hz) ppm.

**28b:** $^1H\{^{11}B\}$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 1.01 (d, 9 H, $CH_3$, $^3J_{^{31}P,^1H}$ = 14.6 Hz), 2.49, 2.60 [br. s, br. s, 1 H, 1 H, HB for $\delta(^{11}B)$ = –8.5 ppm], 2.66 [br. s, 1 H, HB for $\delta(^{11}B)$ = –9.1 ppm], 2.77 [br. s, 1 H, HB for $\delta(^{11}B)$ = 0.1 ppm], 2.83 [br. s, 2 H, HB for $\delta(^{11}B)$ = –4.6, –5.0 ppm], 2.89 [br. s, 1 H, HB for $\delta(^{11}B)$ = –6.6 ppm], 3.09 [br. s, 1 H, HB for $\delta(^{11}B)$ = –1.5 ppm], 3.31 [br. s, 1 H, HB for $\delta(^{11}B)$ = –7.3 ppm], 3.71 [br. s, 1 H, HB for $\delta(^{11}B)$ = –2.1 ppm] ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, [$D_8$]toluene, 25 °C): $\delta$ = –9.1 (1 B), –8.5 (2 B), –7.3 (1 B), –6.6 (1 B), –5.0 (1 B), –4.6 (1 B), –2.1 (1 B), –1.5 (1 B), 0.1 (1 B) ppm.

**30b:** $^1H$ NMR (500.13 MHz, [$D_8$]toluene, 25 °C): $\delta$ = 1.06 (d, $^3J_{^{31}P,^1H}$ = 15.8 Hz, 18 H, $CH_3$) ppm.

**2-Phenyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3-ditellura-2-phospholane (26c):** Freshly prepared **4** (2104 mg, 4.34 mmol) was cooled to –20 °C and suspended in toluene (60 mL). The suspen-

Table 6. Crystallographic data of the *ortho*-carborane derivative **11**, **15**, and **21**.

| | **11** | **15** | **21**[b] |
|---|---|---|---|
| Formula | $C_{11}H_{21}B_{10}PSe_2$ | $C_5H_{22}B_{20}P_2Se_4$ | $C_{12}H_{40}B_{20}P_2Se_4 \cdot 1.4CD_2Cl_2$ |
| Crystal | colorless prism | colorless prism | colorless prism |
| Dimensions [mm] | 0.25 × 0.22 × 0.16 | 0.19 × 0.14 × 0.12 | 0.22 × 0.18 × 0.15 |
| Temperature [K] | 133(2) | 133(2) | 133(2) |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $C2/c$ |
| $a$ [pm] | 1051.2(2) | 1459.0(3) | 2024.3(4) |
| $b$ [pm] | 1132.4(2) | 848.96(17) | 1154.0(2) |
| $c$ [pm] | 1604.3(3) | 1943.7(4) | 3203.6(6) |
| $\beta$ [°] | 99.29(3) | 92.53(3) | 92.74(3) |
| $Z$ | 4 | 4 | 8 |
| Absorption coefficient $\mu$ [mm$^{-1}$] | 3.998 | 6.231 | 4.224 |
| Diffractometer | STOE IPDS II; Mo-$K_\alpha$, $\lambda$ = 71.073 pm, graphite monochromator | | |
| Measuring range ($\theta$) [°] | 2.17–25.62 | 1.71–25.64 | 2.01–25.70 |
| Reflections collected | 24731 | 16272 | 8403 |
| Independent reflections [$I \geq 2\sigma(I)$] | 3224 | 4057 | 2146 |
| Absorption correction | none[a] | numerical | none[a] |
| Max./min. transmission | – | 0.7541/0.4000 | – |
| Refined parameters | 217 | 280 | 386 |
| $wR_2/R_1$ [$I \geq 2\sigma(I)$] | 0.081/0.032 | 0.116/0.044 | 0.149/0.066 |
| Max./min. residual electron density [10$^{-6}$ e pm$^{-3}$] | 1.228/–0.613 | 1.079/–1.452 | 0.750/–0.459 |

[a] Absorption corrections did not improve the parameter set. [b] The D atoms of the disordered $CD_2Cl_2$ molecule could not be found in the difference Fourier syntheses.

sion was cooled to –40 °C, and $PhPCl_2$ (775 mg, 0.588 mL, 4.34 mmol) in toluene (0.3 mL) was injected slowly through a syringe. The reaction mixture was stirred for 1.5 h at –30 °C and 1 h at 10 °C, the insoluble materials were washed with toluene (2 × 10 mL) and separated by centrifugation, and the clear liquid was collected. The volatile materials were removed under vacuum to give a brown oil (110 mg). The resulting mixture thus obtained contained **26c** (ca. 80%), **27c** (20%), and several unidentified products (from $^{31}$P and $^{125}$Te NMR spectroscopy). The remaining insoluble materials from the initial reaction were washed with hexane (2 × 10 mL), dissolved in toluene (10 mL), and centrifuged. The liquid phase was separated and dried under vacuum to give a green-brown solid (760 mg). The resulting mixture thus obtained contained **27c** (ca. 20%) and several unidentified products (from $^{31}$P and $^{125}$Te NMR spectroscopy).

**2-Diethylamino-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-ditelluraphospholane (26d):** Freshly prepared **4** (747 mg, 1.54 mmol) was cooled to –40 °C and suspended in toluene (50 mL). The suspension was cooled to –40 °C, and $Et_2NPCl_2$ (0.223 mL, 1.54 mmol) was injected slowly through a syringe. The reaction mixture was stirred for 1 h at –40 °C and 30 min at 0 °C, the insoluble materials were separated by centrifugation, and the clear liquid was collected. The volatile materials were removed under vacuum to give a yellow-brown oil (690 mg). The resulting mixture thus obtained contained **26d** (ca. 35%), **27d** (20%), **29d** (20%), **29d′** (25%), together with bis(ditellane) **31**[17] and several unidentified products (from $^{31}$P and $^{125}$Te NMR spectroscopy). The product **26d** decomposes in [D$_8$]toluene under Ar at room temp. or at –30 °C to form **31** and black elemental tellurium powder.

**2-{4,5-[1,2-Dicarba-*closo*-dodecaborano(12)]-1,3,2-ditelluraphospholan-2-yl}methyl-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-1,3,2-ditelluraphospholane (32):** Freshly prepared **4** (430 mg, 0.89 mmol) was cooled to –40 °C and suspended in toluene (30 mL). The suspension was cooled to –40 °C, and $Cl_2PCH_2PCl_2$ (0.060 mL, 0.445 mmol) was injected slowly through a syringe. The reaction mixture was stirred for 1 h at –40 °C and 30 min at 0 °C, the insoluble materials were separated by centrifugation, and the clear liquid was collected. The remaining insoluble materials were washed with toluene (2 × 20 mL) and centrifuged. The centrifuged solutions were combined, and the volatile materials were removed in vacuo to give an orange solid (286 mg). The resulting mixture contained **32** (ca. 70%) and bis(ditellane) **31**[17] (ca. 30% from $^{13}$C and $^{125}$Te NMR spectroscopy). The product **32** decomposes in $CD_2Cl_2$ under Ar.

**32:** $^1$H{$^{11}$B} NMR (500.13 MHz, [D$_8$]toluene, 25 °C): $\delta$ = 2.45 [br. s, 4 H, HB for $\delta(^{11}B)$ = –9.1 ppm], 2.74 [br. s, 2 H, HB for $\delta(^{11}B)$ = –2.1 ppm], 2.84 [br. s, 6 H, HB for $\delta(^{11}B)$ = –3.9, –6.9 ppm], 2.97 [br. s, 2 H, HB for $\delta(^{11}B)$ = –6.9 ppm], 3.15 [br. s, 4 H, HB for $\delta(^{11}B)$ = –3.1 ppm], 3.61 [br. s, 2 H, HB for $\delta(^{11}B)$ = –0.1 ppm], 3.70 (t, $^2J_{^{31}P,^1H}$ = 13.9 Hz, 2 H, $CH_2$) ppm. $^{11}$B{$^1$H} NMR (160.5 MHz, [D$_8$]toluene, 25 °C): $\delta$ = –9.1 (4 B), –6.9 (6 B), –3.9 (2 B), –3.1 (4 B), –2.1 (2 B), –0.1 (2 B) ppm. $^1$H NMR (500.13 MHz, $CD_2Cl_2$, 25 °C): $\delta$ = 4.57 (t, $^2J_{^{31}P,^1H}$ = 11.9 Hz, 2 H, $CH_2$) ppm. EI-MS (70 eV): *m/z* (%) = 872 (5) [M]$^+$.

**Crystal Structure Determination of 11, 15, 21:** Structure solutions and refinements were performed with the program package SHELXTL-PLUS V.5.1.[30] Details pertinent to the crystal structure determination are listed in Table 6. Crystals of appropriate size were sealed under argon in Lindemann capillaries, and the data collections were performed at 133 K.[31]

**Supporting Information** (see footnote on the first page of this article): $^nJ_{^{31}P,^{13}C}$ ($n$ = 1,2) data together with isotope-induced chemical shifts $^n\Delta^{12/13}C(^{31}P)$ ($n$ = 1,2), depiction of the oxidation of **11** with sulfur and selenium, $^{31}$P and $^{77}$Se NMR spectra, $^{31}$P and $^{125}$Te NMR spectra of **32** (calcd. and exp.), and calculated NMR spectroscopic data of some 1,3,2-diselenaphospholanes prepared in this work and their selenides.

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