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Novel 1,3-Dichalcogeno-2-phospholanes with an Annelated 1,2-Dicarba-closo-dodecaborane(12) Unit. Synthesis, Structures and Reactivity

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Abstract

The most efficient strategies for the synthesis of novel 1,3-dichalcogeno-2-phospholanes (chalcogen E = O, S, Se, Te) are introduced, starting from 1,2-dicarba-closo-dodecaborane(12) ("ortho-carborane"), its 1,2-di-lithiated derivative, and various phosphorus halides. The annelation of the phospholane ring with the rigid three-dimensional carborane framework causes markedly different properties when compared with other phospholanes. Most noteworthy are the structural alternatives concerning the orientation of the lone pair of electrons at phosphorus, the instability of P-halides in particular for E = O, and the pronounced tendency for dimerization in the case of P-organo derivatives, which increases from E = Te < Se < S << O. The latter is a consequence of spatial proximity between P-R or electron density at phosphorus and the carborane skeleton. Direct structural evidence is provided for monomers and dimers by single crystal X-ray structural analysis. The solution-state structures follow from consistent sets of multinuclear magnetic resonance data (\(^1\)H, \(^{11}\)B, \(^{13}\)C, \(^{31}\)P, \(^{77}\)Se, \(^{125}\)Te NMR). This is complemented by calculations leading to optimized gas-phase geometries at the B3LYP/6-311+G(d,p) level of theory. Most NMR parameters (chemical shifts δ and indirect nuclear spin-spin coupling constants \(^aJ\)) are calculated at the same level of theory. These studies indicate that there are cases, for which important features of the solid-state structures may not be retained in solution. Examples are given for E = Se, showing that reactions with Lewis acids such as borane reagents (BH\(_3\)-D with D = THF, Me\(_2\)S) or Cp*MC\(_2\) (M = Rh, Ir) follow the same pattern, i. e. adduct formation, insertion and exchange.

Keywords: Carboranes, Phosphorus, Diols, Sulfur, Selenium, Tellurium, Dimerization, Heterocycles, Lewis acids, NMR spectroscopy, DFT calculations, X-Ray analysis

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Introduction

1,3-Dichalcogeno-2-phospholanes have been known for some time, in particular the 1,3-dioxo- (Arbuzov, 1948; Lucas, 1950; Burg, 1961; Fontal, 1966) and less so the 1,3-dithia derivatives (Arbuzov, 1952; Weber, 1964; Peake, 1972; Albrand, 1973), by contrast to rare examples for 1,3-diselena- (Ogawa, 1995) and non-existent 1,3-ditellura compounds. These cyclic phosphines differ in many respects from their six-membered or non-cyclic counterparts. The carbon backbone frequently consists of the CH$_2$-CH$_2$-moiety (A) or is a benzo group (B). The typical structures, of which many have been determined by X-ray analysis, are presented in Fig. 1. Usually one finds an envelope structure with the phosphorus atom in the flap and the substituent at phosphorus in the axial position, leaving the equatorial space for the lone pair of electrons. In the solid state, the CH$_2$ units may be arranged as in A or twisted against each other (A'), to escape the maximum of steric repulsion exerted by the substituent at phosphorus. The latter alternative is unnecessary in the case of the benzo derivatives (B). A rigid three-dimensional unit instead of the CH$_2$-CH$_2$- or the benzo group could change the principal structure (see D as compared with C) and by this the properties of such compounds. Therefore, we have set out to synthesize an and investigate 1,3-dichalcogeno-2-phospholanes with an annelated 1,2-dicarba-closo-dodecaborane(12) unit (C and/or D). Of particular interest is the behaviour of these phospholanes towards different Lewis acids, considering the presence of E and phosphorus as potential basic sites. In this respect we have focused on E = Se.

Figure 1. Principal Structures of 1,3-Dichalcogeno-2-phospholanes (E = O, S, Se, Te)

The chemistry of 1,2-dicarba-closo-dodecaborane(12) 1 (so called "orthocarborane") in general is well developed (Grimes, 2011; Bregadze, 1992). One important step for derivatization involves di-lithiation (2), and for our purposes insertion of sulfur (Smith, 1966; Herberhold, 1999; Popescu, 2012), selenium (Herberhold, 1999; Jin, 2004) or tellurium (Herberhold, 1999; Wrackmeyer, 2013, 398-408) into the C–Li bonds (3). The oxygen derivatives 4 (Ohta, 2007) and 5 have to be prepared by a different route, and the silanes 6 (Wrackmeyer, 2010; Wrackmeyer, 2014, Dalton Trans.) turned out to be particularly useful for further transformations. Scheme 1 shows the starting materials which can be used in reactions with phosphorus halides to obtain the desired novel 1,3-dichalcogeno-2-phospholanes.

NMR spectroscopy ($^1$H, $^{13}$C, $^{11}$B, $^{29}$Si, $^{31}$P, $^{77}$Se and $^{125}$Te NMR) is the major analytical tool for the assessment of solution-state structures. These
measurements are accompanied by quantum-chemical analyses aiming for optimization [B3LYP/6-311+G(d,p) level of theory (Becke, 1993; Lee, 1988, Stevens, 1994, McLean, 1980; Krishnan, 1980)] of gas-phase structures and calculation of NMR parameters [chemical shifts $\delta_X$ ($X = ^{11}\text{B}$, $^{13}\text{C}$, $^{31}\text{P}$, $^{77}\text{Se}$) (Wollinski, 1990) and indirect nuclear spin-spin coupling constants $^2J(A,X)$ (Helgaker, 2008; Contreras, 2003)].

**Scheme 1. The Most Useful Starting Materials for Reactions with Phosphorus Halides**

![Scheme 1](image)

**Results & Discussion**

*1,3-Dioxa-2-phospholanes with an Annelated 1,2-Dicarba-closododecaborane(12) Unit*

Scheme 2 shows that the phosphorus halides 7 are formed as expected. However, after short time in the reaction solutions or in the course of work-up procedures disproportionation reactions towards phosphite derivatives 8 take place (Wrackmeyer, 2014, 233-246). Apparently, the phosphorus halides 7 are less stable than comparable halides of the type A or B ($E = O$; Fig. 1), some of which are commercially available. So far neither the parent phosphine compound with a P-H unit nor the fluoride has been obtained. According to calculated gas-phase structures, solely the unavailable parent phosphine adopts the structure C, and all others prefer structure D ($E = O$; Fig. 1) (Wrackmeyer, 2014, 233-246).

**Scheme 2. Synthesis and Major Way of Decomposition of 2-Halogeno-1,3-dioxa-2-phospholanes**

![Scheme 2](image)
All monomeric P-organo derivatives 9a–d and even the P-ethoxy- (9e) and P-diethylamino derivative (9f) tend to dimerize within hours or days (Wrackmeyer, 2014, 233-246). Again this is in contrast to A or B (E = O; Fig. 1) which dimerize very slowly or not at all (Dutasta, 1980; Pudovik, 1983). Figure 2 shows the molecular structure of the dimer 10c, as determined by X-ray analysis. In the ten-membered ring the four oxygen atoms are in one plane (mean deviation 1.9 pm), and both phosphorus atoms are shifted out of this plane (88.8 pm, 88.5 pm).

Scheme 3. Synthesis and Dimerization of 2-R-1,3-dioxa-2-phospholanes

\[
\begin{align*}
5 & \quad \text{RPX}_3 \quad \text{[D$_8$]toluene} \\
& \quad \text{– LiX}
\end{align*}
\]

Figure 2. ORTEP Plot (50% Probability; Hydrogen Atoms are Omitted for Clarity) of the Molecular Structure of Dimer 10c. Selected Bond Lengths (pm) and Angles (°): C(1)–C(2) 171.7(5), C(3)–C(4) 169.7(5), C(1)–O(1) 136.9(5), P(1)–O(1) 167.0(2), P(1)–C(5) 190.9(4); O(1)–P(1)–O(2) 95.24(12), C(2)–C(1)–O(1) 116.4(3).

$^{31}$P NMR spectra show significant deshielding of the $^{31}$P nuclei in the five-membered rings relative to those in the dimers. This mirrors partly the ring strain together with repulsive effects in the small rings. The structural assignments for the solution-state of monomers and dimers are strongly...
supported by a linear correlation between calculated [given for the shortcomings of the theoretical approach (van Wüllen, 2000)] and experimental $\delta^{31}\text{P}$ values.

The annelated carborane skeleton destabilizes monomeric 1,3-dioxa-2-phospholanes. Any gain in kinetical stabilization is more than counterbalanced by steric repulsion between the carborane skeleton and the lone pair of electrons at phosphorus in axial position. According to calculations, solely the hydrogen atom is tolerated in axial position, and all other substituents are forced into the equatorial position to avoid close contacts with the rigid carborane skeleton.

1,3-Dithia- and 1,3-Diselena-2-phospholanes with an Annelated 1,2-Dicarba-closo-dodecaborane(12) Unit

The best synthetic strategy starts from the silanes 6 (Scheme 4) (Wrackmeyer, 2012; Wrackmeyer, 2014, 1929-1948), although the di-lithium salts 3 (E = S, Se) can also be used (Wrackmeyer, 2007; Wrackmeyer, 2014, Dalton Trans.). However, the reactions of the silanes 6 with phosphorus halides afford the products in higher purity and much better yield.

**Scheme 4. General Synthesis of 1,3-Dithia- and 1,3-Diselena-2-phospholanes**

The phosphorus halides 11 are more stable than their oxygen analogues 7, since the disproportionation products analogous to 8 play a minor role for X = Cl and even less so for X = Br, I. Therefore, the halides can be used to generate the parent compound 13 (R = H) as well as the fluoride 14 (X = F, for E = S) (Scheme 5), at least in reaction solutions in order to measure the most relevant NMR data (Wrackmeyer, 2012; Wrackmeyer, 2014, Dalton Trans.).

**Scheme 5. Synthesis of the Parent Compounds 13 and the Fluoride 14 for NMR Spectroscopy**
Figure 3 shows the results of some NMR spectroscopic measurements for 13 (E = S) as an instructive example (Wrackmeyer, 2014, Dalton Trans.). The NMR data for the corresponding 13 (E = Se) contain even more information, since the 77Se NMR parameters are also accessible (Wrackmeyer, 2012). Of particular interest is the spin-spin coupling between $^1$H(B-3) and $^1$H(P) (Fig. 2(A)), which can be regarded as a "through-space" coupling. This is not resolved in the case of 13 (E = Se), most likely because of a slightly longer H-H distance. We note reasonably good agreement between calculated and experimental NMR parameters (shown for example in Fig. 2(G, H) for $\delta^{11}$B values). Calculated data were based on the optimized geometry corresponding to C (Fig. 1).

**Figure 3.** Compound 13 (E = S) (in [D₈]toluene, at 23 °C), showing Long Range or through-space $^1$H-$^1$H and $^{31}$P-$^1$H Spin-Spin Coupling, and Assignment of $^{11}$B and $^1$H(BH) NMR Signals. (A) 500.13 MHz $^1$H NMR Spectrum. (B) 500.13 MHz $^1$H($^{31}$P) NMR Spectrum. (C) 202.5 MHz $^{31}$P NMR Spectrum. The Isotope-induced Chemical Shift $^1$J$^{32/34}$S($^{31}$P) (Bjorholm, 1989) is observed. (D) 202.5 MHz $^{31}$P($^1$H) NMR Spectrum with $^1$H Broad-band Decoupling. (E) 202.5 MHz $^{31}$P($^1$H) NMR Spectrum with Selective Decoupling of $^1$H at 2.55 ppm. (F) 500.13 MHz $^1$H($^{11}$B) NMR Spectrum of 13 with Side Product (Marked by Asterisks), Assigned by Selective $^1$H($^{11}$B) Experiments. (G) 160.5 MHz $^{11}$B($^1$H) NMR Spectrum of 13. (H) Stick Diagram of calc'd. $^{11}$B NMR Signals of 13.
The P-organo derivatives 12a–d stay as monomers in solution for a sufficient length of time to measure all important NMR parameters. Any tendency for dimerization is more pronounced for E = S than for E = Se. Thus, for R = Ph, 12d (E = S) dimerizes, whereas 12d (E = Se) does not. By contrast, for R = 1Bu both 12b (E = S, Se) dimerize readily. Also in contrast to 10c (E = O), 12c (E = S, Se) do not dimerize. Similarly, dimers are not formed in the cases of the P–OEt- and P–NEt2 derivatives 12e, f.

In the cases of 12b with R = 1Bu and 12f with R = NEt2, calculations predict minima in energy for structure D (E = S, Se; Fig. 1), and the calcd. NMR parameters are in agreement with the experimental data (Wrackmeyer, 2014, Dalton Trans.; Wrackmeyer, 2014, 1929-1948). The delicate balance between the structures C and D (Fig. 1) becomes obvious by comparing the solid-state structure of 12d (E = Se) (Wrackmeyer, 2007), corresponding to D, with that in solution (Wrackmeyer, 2014, 1929-1948), corresponding to C, inferred by NMR spectroscopic data and quantum-chemical analysis (Fig. 4).

**Figure 4.** The Solid-State Structure of 12d Leads to calcd. NMR Parameters at Drastic Variance with Experimental Data. The Latter are Almost Exactly Reproduced by Calculations Based on the Optimized Structure Shown.
Figure 5. Compound 12c (E = Se) (in CD$_2$Cl$_2$, at 23 °C). (A) 125.8 MHz $^{13}$C($^1$H) NMR Spectrum. (B) 500.13 MHz $^1$H(PCH$_2$) NMR Spectrum. (C) 202.5 MHz $^{31}$P($^1$H) NMR Spectrum. The $^{77}$Se Satellites for $^1$J($^{77}$Se,$^{31}$P) are Marked by V. The $^{13}$C Satellites for $^n$J($^{31}$P,$^{13}$C) (n = 1, 2) are Marked by Arrows; Isotope-Induced Chemical Shifts $^n$$\Delta$$^{12/13}$C($^{31}$P) (n = 1, 2; ± 1 ppb) are given; Note that the Effect for n = 2 is Larger than for n = 1. (D) 95.4 MHz $^{77}$Se NMR Spectrum.

Of course, as it is frequently true, we also find that major structural features of the solid state are retained in solution, as shown for both 12c (E = Se) and 15, for which relevant experimental NMR parameters (Fig. 5) are reproduced by calculations (Fig. 6) (Wrackmeyer, 2014, 1929-1948).

The $^{13}$C NMR spectrum of 12c (E = Se) [Fig. 5(A)] shows the doublet for the $^{13}$C$_{carb}$ nuclei, and the signals are further split by isotope-induced chemical shifts $^1$$\Delta$$^{10/11}$B($^{13}$C) (Wrackmeyer, 2009). An interesting observation concerns exceptionally large isotope-induced chemical shifts $^2$$\Delta$$^{12/13}$C$_{carb}$($^{31}$P) = −47 ppb (Fig. 5(C)). This appears to be a property of the five-membered ring. Isotope-induced chemical shifts $^1$$\Delta$$^{12/13}$C($^{31}$P) are known to cover a substantial range (Tattershall, 1990; Heckmann, 1999), whereas effects $^2$$\Delta$$^{12/13}$C($^{31}$P) are usually regarded as extremely small or negligible. We have observed the large effects $^2$$\Delta$$^{12/13}$C$_{carb}$($^{31}$P) for all 1,3-dichalcogeno-2-phospholanes studied here for E = S, Se, Te (Wrackmeyer, 2014, 1929-1948).
There are notable differences between the sulfur and selenium compounds studied here. Thus, the P–Se bonds are more reactive than the P–S bonds, as shown by oxidative additions (Wrackmeyer, 2007). Even the apparently simple addition of selenium to prepare phosphorus selenides (e.g. 16a) turned out to be accompanied by insertion of selenium into the P–Se bonds (17a) (Scheme 6). With the iPr group (E = Se; 12a) a single isomer is formed, whereas two isomers 17d are observed for R = Ph, starting from 12d (Wrackmeyer, 2013, 140-147). Again, a single isomer 17c is formed starting from 12c (Wrackmeyer, 2014, 1929-1948). The solid-state structure of 17a could be characterized by X-ray structural analysis (Fig. 7), and its formation was conveniently monitored by $^{31}$P and $^{77}$Se NMR spectroscopy (Fig. 8) (Wrackmeyer, 2013, 140-147).

**Scheme 6. Reaction of 12a with Selenium via the Expected 16a towards 17a**
Figure 7. ORTEP Plot (50% Probability; Hydrogen Atoms are Omitted for Clarity) of the Molecular Structure of 17a. Selected Bond Lengths (pm) and Angles(°):
C(1)–C(2) 171.1(1), C(1)–Se(1) 194.6(1), Se(1)–Se(3) 231.1(2), Se(3)–P 225.1(3), P–Se(5) 207.4(4), P–C(3) 184.4(1); Se(3)–P–Se(4) 111.4(1).

Figure 8. NMR Spectra of the Reaction Solution Obtained from the Reaction of 12a with Se (Scheme 6). Upper Trace: 202.5 MHz $^{31}$P{1H} NMR Spectrum after 24 h at 55 °C in CD$_2$Cl$_2$, the Mixture of 16a and 17a. $^{77}$Se Satellites are Marked by Arrows. Lower Trace: 95.4 MHz $^{77}$Se NMR Spectrum of the Same Mixture.

1,3-Ditellura-2-phospholanes with an Annelated 1,2-Dicarba-closo-dodecaborane(12) Unit

Since the silane with E = Te analogous to 6 is not accessible so far (Wrackmeyer, 2013, 398-408), the di-lithium salt 3 (E = Te) is used in reactions with phosphorus halides (Scheme 7). Problems are encountered because the nature of 3 depends in an unpredictable way on experimental conditions (Herberhold, 2006; Wrackmeyer, 2013, 398-408). Therefore, the
desired products 18 are formed, readily shown by $^{31}$P and $^{125}$Te NMR spectroscopy, accompanied by numerous side-products which are difficult to separate (Wrackmeyer, 2014, 1929-1948). NMR data indicate that, except of 18e, all others adopt the structure of type C (Fig. 1), even 18b, for which the sulfur and selenium analogues (12b) prefer D (Fig. 1). The 1,3-ditetulla-2-phospholanes 18 do not dimerize. In constrast to their analogues with E = O, S, Se, compounds 18 are light-sensitive in solution as well as in the solid state.

Scheme 7. Synthesis of 1,3-Ditetulla-2-phospholanes

Reactions of 1,3-Diselena-2-phospholanes with Lewis Acids

Expectedly, the first strong interaction of borane reagents with 1,3-diselena-2-phospholanes (Scheme 8) involves adduct formation (19). The compounds 12a,d were selected for these studies, because they stay mainly as monomers in solution and their solution-state structures are comparable, both with R in axial position. The adducts 19 rearrange into ring insertion products 20, depending on conditions, and finally exchange takes place (21, 22) accompanied by decomposition. Monitoring of the reactions using $^{1}$H, $^{11}$B, $^{13}$C, $^{31}$P and $^{77}$Se NMR spectroscopy enabled to assign the proposed structures for 19 to 22 on the basis of consistent NMR parameters (chemical shifts and coupling constants), confirmed by quantum-chemical calculations. Moreover, these calculations also showed that the relative energies of the isomers decrease markedly in going from 19 to 20 and finally to 21 (R = 'Pr) (Wrackmeyer, 2014, DOI:10.1002/ejic.201402486).

Scheme 8. Reaction of Borane Reagents with 1,3-Diselena-2-phospholanes

Similar to boranes, Lewis acids containing transition metal centers are expected to prefer the phosphorus atom as a Lewis base. Thus [Cp*MCl$_2$]$_2$ (M = Rh, Ir; Cp* = pentamethylcyclopentadienyl) will be split into the monomer...
and give the phosphine adduct 23 (Scheme 9). The next step can be insertion into the ring, giving various isomers (24 – 26), and finally, as for borane, exchange leads to 27. The relative energies of conceivable isomers were calculated, and only geometries with a minimum in energy are shown in Scheme 9. The energies decrease significantly from the adduct 23, to the ring insertion products 24 to 26 to the exchange product 27 [calculated for R = iPr at the B3LYP/6-311+G(d,p), Rh, Ir (LANL2DZ) level of theory]. In all cases, relevant NMR spectroscopic data, in particular 31P NMR data, helped with structural assignments, and crystal structures were determined for major products such as 24 (M = Ir, R = iPr; Fig. 9) and 27 (M = Rh, R = iPr; Fig. 10) (Wrackmeyer, 2014, DOI:10.1002/ejic.201402486).

**Scheme 9. Some Products from the Reactions of Cp*MCl2 (M = Rh, Ir) with 1,3-Diselena-2-phospholanes**

There are no comparable structures to 24 in the literature. The shape of the six-membered folded ring (Fig. 9) is however typical (Wrackmeyer, 2010; Wrackmeyer, 2013, Eur. J. Inorg. Chem.), and the structural parameters correspond closely to expectations.

**Figure 9. The Molecular Structure of the Ring Insertion Product 24 (M = Ir, R = iPr; Major Isomer); ORTEP Plot (50% Probability; Hydrogen Atoms are Omitted for Clarity). Selected Bond Lengths (pm) and Angles (°):**

Ir–P 226.0(2), Ir–Se(1) 248.41(10), Ir–Cl(2) 239.6(2), P–Cl(1) 206.7(3), P–Se(2) 226.1(2), Se(1)–Ir–P 92.96(6), Se(2)–P–Ir 120.56(10), C(1)–Se(1)–Ir 110.2(3), C(2)–Se(2)–P 103.9(3).
In the case of 27 (M = Rh, R = Pr; Fig. 10), comparable complexes, namely \((\text{B}_{10}\text{H}_{10}\text{C}_{2}\text{Se}_2)\text{M(Cp'^*})\text{–PMe}_3 (\text{M} = \text{Rh}, \text{Ir})\), have been structurally characterized previously, prepared via different routes (Herberhold, 1999, *Eur. J. Inorg. Chem.*, Herberhold 1999, *J. Organomet. Chem.*). The structural parameters found for 27 (M = Rh, R = Pr) are in good agreement with reported data. (Wrackmeyer, 2014, DOI:10.1002/ejic.201402486).

**Figure 10. Molecular Structure of 27 (M = Rh, R = Pr). Selected Bond Lengths (pm) and Angles (°):**

C(1)–C(2) 167.9, C(1)–Se(1) 199.5, C(2)–Se(2) 190.2, Se(1)–Rh 248.0, Se(2)–Rh 246.2, Rh–P 221.5; Se(1)–Rh–Se(2) 90.8, Se(1)–Rh–P 92.0, Se(2)–Rh–P 87.8, Rh–Se(1)–C(1) 102.5, Rh–Se(2)–C(2) 101.7, Se(1)–C(1)–C(2) 118.7, Se(2)–C(2)–C(1) 123.5, Se(1)–Rh–Cp'(Z) 122.5, Se(2)–Rh–Cp'(Z) 124.2, P–Rh–Cp'(Z) 128.6, plane Se(1)–C(1)–C(2)–Se(2)/plane Se(1)–Rh–Se(2) 152.4°.

**Conclusions**

In principle, 1,3-dichalcogeno-2-phospholanes with an annelated 1,2-dicarba-closo-dodecaborane(12) unit are accessible taking advantage of the availability of starting materials shown in Scheme 1 and their reactions with phosphorus halides. The annelated rigid three-dimensional carborane skeleton causes repulsive interactions either with the substituent at phosphorus or with the electron density of the lone pair of electrons at phosphorus, depending on the respective structure (C or D; Fig. 1). This destabilizes the five-membered rings, in particular if E–P and E–C_carb distances are short, as for E = O, and for many P-organo derivatives, even for E = S and E = Se, dimerization is the way out. All dimers studied so far possess analogous structures, in which the four chalcogen atoms are in one plane leaving room for the complexation or even encapsulating of various cations. It was shown that multinuclear magnetic resonance methods (\(^1\)H, \(^{11}\)B, \(^{13}\)C, \(^{31}\)P, \(^{77}\)Se and \(^{125}\)Te NMR spectroscopy) together with quantum-chemical analyses were suitable to unravel the solution-state structures which sometimes were found to be at variance with those in the solid state. Apparently, the derivatives with E = Se react with greatly different
Lewis acids first by adduct formation, expectedly, followed by insertion of the Lewis acid into the five-membered ring, and finally by exchange forcing the phosphorus out of the ring.

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