

Supporting Information

Condensation Reactions of Chlorophosphanes with Chalcogenides

Sivathmeehan Yogendra, Saurabh S. Chitnis, Felix Hennersdorf, Michael Bodensteiner,
Roland Fischer, Neil Burford,* Jan J. Weigand*

Prof. Dr. Jan. J. Weigand,* SivathmeehanYogendra, Felix Hennersdorf,
TU Dresden, Department of Chemistry and Food Chemistry, Mommsenstraße 4, 01062
Dresden (Germany); [*] E-mail: jan.weigand@tu-dresden.de

Prof. Dr. Neil Burford,* Saurabh S. Chitnis
Department of Chemistry, University of Victoria, British Columbia, Canada V8W 3V6
[*] E-mail: nburford@uvic.ca

Michael Bodensteiner
University of Regensburg, 93053 Regensburg, Germany

Roland Fischer
Department of Inorganic Chemistry, TU Graz, Stremayrgasse 9, 8010 Graz, Austria

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1. Material and Methods

1.1. General Remarks

General Considerations: All manipulations were performed in a Glovebox MB Unilab or using Schlenk techniques under an atmosphere of purified Argon (Westfalen AG). Dry, oxygen-free solvents (CH_2Cl_2 , CH_3CN , $\text{C}_6\text{H}_5\text{F}$ (distilled from CaH_2), Et_2O , toluene (distilled from potassium/benzophenone), *n*-hexane, *n*-pentane (distilled from potassium) were employed. Deuterated benzene (C_6D_6) was purchased from Sigma-Aldrich and distilled from potassium. Anhydrous deuterated acetonitrile (CD_3CN), dichloromethane (CD_2Cl_2) and chloroform (CDCl_3) were purchased from Sigma-Aldrich. All distilled and deuterated solvents were stored either over molecular sieves (4 Å: CH_2Cl_2 , CH_3CN , $\text{C}_6\text{H}_5\text{F}$, C_6D_6 , CD_2Cl_2 ; 3 Å: CH_3CN , CD_3CN) or potassium mirror (Et_2O , *n*-hexane, *n*-pentane). All glassware was oven-dried at 160 °C prior to use. $(\text{Me})_2\text{PCl}$, $(\text{Ph})_2\text{PCl}$, $(i\text{Pr})_2\text{PCl}$, $(t\text{Bu})_2\text{PCl}$, $(\text{Mes})_2\text{PCl}$, $(\text{EtO})_2\text{PCl}$, $(\text{Me}_3\text{Si})_2\text{S}$, $(\text{Me}_3\text{Si})_2\text{Se}$, MeOTf , AgOTf , TMSCl , 15-crown-5, $\text{Fe}_2(\text{CO})_9$, were purchased from Aldrich, Strem or ABCR Chemicals and used as received. $\text{Na}_2\text{S}^{[1]}$, $\text{Na}_2\text{Se}^{[1]}$, $\text{Na}_2\text{Te}^{[1]}$, $(\text{C}_6\text{F}_5)_2\text{PCl}^{[2]}$, $(i\text{Pr}_2\text{N})_2\text{PCl}^{[3]}$, $(p\text{-Tol})_2\text{PCl}^{[4]}$ and $\text{Et}_2\text{PCl}^{[5]}$ were prepared according to procedure given in literature. NMR spectra were measured on a Bruker AVANCE III (^1H (400.13 MHz), ^{13}C (100.61 MHz), ^{31}P (161.98 MHz), ^{19}F (376.50 MHz) at 300 K. All ^{13}C NMR spectra were exclusively recorded with broad band proton decoupling. Reported numbers assigning atoms in the ^{13}C spectra were indirectly deduced from the cross-peaks in 2D correlation experiments (HMBC, HSQC). Chemical shifts were referenced to $\delta_{\text{TMS}} = 0.00$ ppm (^1H , ^{13}C) and $\delta_{\text{H}_3\text{PO}_4(85\%)} = 0.00$ ppm (^{31}P , externally). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. Assignments of individual resonances were done using 2D techniques (HMBC, HSQC, HH-COSY) where necessary. $^1J_{\text{PP}}$ coupling constants were set to negative values^[6] and all other signs of the coupling constants were obtained accordingly. $^1J_{\text{PSe}}$ coupling constants were set to negative values as well.^[7] The designation of the spin systems is performed by convention.^[8] The furthest downfield resonance is denoted by the latest letter in the alphabet and the furthest upfield by the earliest letter. Melting points were recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point M-560) in sealed capillaries under Argon atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd:YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given

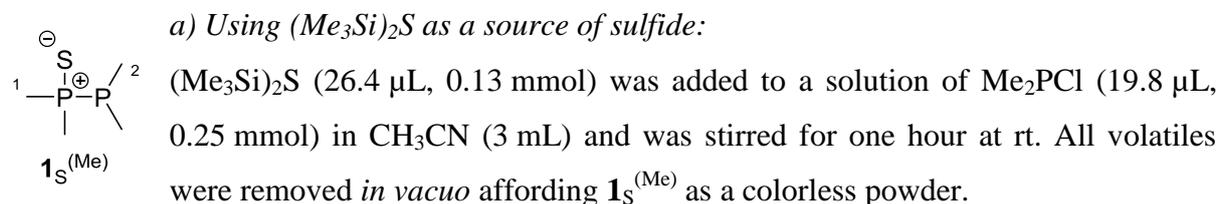
in parenthesis. An ATR unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong. Elemental analyses were performed on an EuroEA Elemental Analyzer from HEKAtech.

1.2. Xray structure refinements

Suitable single crystals were coated with Paratone-N oil, mounted using either a glass fibre or a nylon loop and frozen in the cold nitrogen stream. Crystals were measured on different diffractometers. Data of $\mathbf{2}_S^{(tBu)}$, $\mathbf{2}_{Se}^{(N(iPr)_2)}$ and $\mathbf{2}_S^{(C_6F_5)}$ were collected on an Agilent SuperNova system at 123 K using Cu K_α radiation ($\lambda = 1.54184 \text{ \AA}$) generated by a Nova micro-focus X-ray source. Reflections were collected with an Atlas S2 detector. Data reduction and absorption correction was performed with CrysAlisPro^[9] software. All other datasets were collected on a Bruker Kappa APEX II system at 100, 153 or 173 K (as indicated in **Tables 3.1 - 3.4**) using Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) generated by a fine-focus sealed tube. The data reduction and absorption correction was performed with the Bruker SMART^[10] and Bruker SADABS^[11], respectively. Using Olex2^[12], the structures were solved with SHELXS/T^[13] by direct methods and refined with SHELXL^[13] by least-square minimization against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions using the riding model. Images of the structures were produced with Diamond^[14] software.

2. Syntheses and Spectroscopic Data

2.1. Synthesis of Tetramethyldiphosphane monosulfide ($1_S^{(Me)}$)



Yield: 26.9 mg (70%).

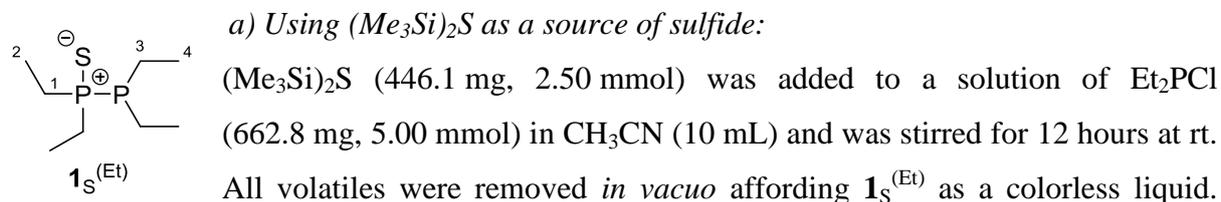
b) Using Na₂S as a source of sulfide:

Me₂PCl (96.5 mg, 1.00 mmol) was added to a suspension of Na₂S (40.1 mg, 0.50 mmol) in CH₃CN (4 mL) and was stirred for 12 h at rt. The suspension was filtered and the filtrate was concentrated *in vacuo*. The resulting colorless solid was washed with *n*-pentane (3 mL) and dried *in vacuo* affording $1_S^{(Me)}$ as a colorless powder.

Yield: 67.8 mg (88%).

Mp.: 65-66 °C; **¹H NMR (CD₂Cl₂, 300 K, in ppm):** δ = 1.71 (6H, dd, ³J_{HP} = 12.1 Hz, ²J_{HP} = 5.8 Hz, C2–H), 1.16 (6H, dd, ³J_{HP} = 17.6 Hz, ²J_{HP} = 4.0 Hz, C1–H); **¹³C{¹H} NMR (CD₂Cl₂, 300 K, in ppm):** δ = 20.6 (2C, dd, ¹J_{CP} = 46.8 Hz, ²J_{CP} = 15.7 Hz, C1), 7.8 (2C, dd, ¹J_{CP} = 18.0 Hz, ²J_{CP} = 2.8 Hz, C2); **³¹P{¹H} NMR (CD₂Cl₂, 300 K, in ppm):** AX spin system: δ(P_X) = 37.5 (d, ¹J_{PP} = -219.5 Hz), δ(P_A) = -56.5 (d, ¹J_{PP} = -219.5 Hz). Data is consistent with that presented in ref. [15].

2.2. Synthesis of Tetraethyldiphosphane monosulfide ($1_S^{(Et)}$)



Yield: 495 mg (94%).

b) Using Na₂S as a source of sulfide:

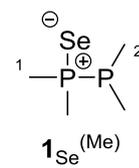
Et₂PCl (124.6 mg, 1.00 mmol) was added to a suspension of Na₂S (39.0 mg, 0.50 mmol) in CH₃CN (5 mL) and was stirred for 12 h at rt. The suspension was filtered and the filtrate was concentrated *in vacuo*. To the resulting pale yellow oil *n*-pentane (0.5 mL) was added and the

mixture was stored over night at $-30\text{ }^{\circ}\text{C}$ forming colorless crystals. The supernatant was decanted at $-30\text{ }^{\circ}\text{C}$. The crystals melt at rt, yielding a colorless oil after removal of all volatiles *in vacuo*.

Yield: 93.5 mg (89%).

Raman (32 mW, 600 scans, 300 K, in cm^{-1}): 2966(10), 2934(100), 2905(28), 2876(28), 2734(6), 1459(17), 1409(7), 1040(9), 981(6), 672(7), 633(12), 591(20), 460(24), 273(16), 166(6); **IR (300 K, ATR, $[\text{cm}^{-1}]$):** 2967(vw), 1200(s), 1144(vs), 1039(vw), 764(vw), 674(vw), 638(m), 626(vw); **^1H NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 2.03\text{--}1.84$ (4H, m, C1–H), $1.83\text{--}1.70$ (2H, m, $^3J_{\text{HH}} = 7.58$ Hz, C3–H), 1.65 (2H, nonet of d, $^3J_{\text{HH}} = 7.58$ Hz, $^2J_{\text{HP}} = 6.85$ Hz, $^3J_{\text{HP}} = 1.79$ Hz, C3–H) 1.22 (3H, t, $^3J_{\text{HH}} = 7.58$ Hz, C4–H), 1.19 (3H, t, $^3J_{\text{HH}} = 7.58$ Hz, C4–H), 1.18 (3H, t, $^3J_{\text{HH}} = 7.72$ Hz, C2–H), 1.15 (3H, t, $^3J_{\text{HH}} = 7.72$ Hz, C2–H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 25.1$ (2C, dd, $^1J_{\text{CP}} = 42.0$ Hz, $^2J_{\text{CP}} = 11.9$ Hz, C1), 15.9 (2C, dd, $^1J_{\text{CP}} = 15.8$ Hz, $^2J_{\text{CP}} = 2.6$ Hz, C3), 11.6 (2C, dd, $^2J_{\text{CP}} = 9.0$ Hz, $^3J_{\text{CP}} = 8.4$ Hz, C2), 7.3 (2C, t, $^2J_{\text{CP}} = 5.3$ Hz, C4); **$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** AX spin system: $\delta(\text{P}_X) = 54.9$ (d, $^1J_{\text{PP}} = -249.6$ Hz, $^1J_{\text{CP}} = 41.8$ Hz), $\delta(\text{P}_A) = -34.7$ (d, $^1J_{\text{PP}} = -249.6$ Hz).

2.3. Synthesis of Tetramethyldiphosphane monoselenide ($\mathbf{1}_{\text{Se}}^{(\text{Me})}$)

Using $(\text{Me}_3\text{Si})_2\text{S}$ as a source of sulfide:

 ($\text{Me}_3\text{Si})_2\text{Se}$ (125.0 μL , 0.50 mmol) was added to a solution of Me_2PCl (79.2 μL , 1.00 mmol) in CH_3CN (3 mL) and was stirred for one hour at rt. All volatiles were removed *in vacuo* affording $\mathbf{1}_{\text{Se}}^{(\text{Me})}$ as a colorless powder.

Yield: 74.9 mg (75%).

b) Using Na_2S as a source of sulfide:

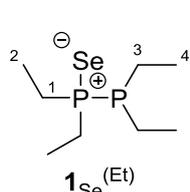
Me_2PCl (96.5 mg, 1.00 mmol) was added to a suspension of Na_2Se (62.5 mg, 0.50 mmol) in CH_3CN (4 mL) and was stirred for 12 h at rt. The suspension was filtered and the filtrate was concentrated *in vacuo*. The resulting colorless solid was washed with *n*-pentane (3 mL) and dried *in vacuo* affording $\mathbf{1}_{\text{Se}}^{(\text{Me})}$ as a colorless powder.

Yield: 89.5 mg (89%).

Mp.: $98\text{--}99\text{ }^{\circ}\text{C}$; **Raman (35 mW, 500 scans, 300 K, in cm^{-1}):** 2964(40), 2894(100), 1408(11), 751(4), 712(15), 670(11), 499(21), 385(94), 297(19), 271(13), 234(34), 198(7), 126(46), 78(12); **IR (CsI, nujol mull, in cm^{-1}):** 1412(w), 1280(m), 952(w), 930(w), 879(m),

747(w), 706(v), 668(vw), 500(m); ^1H NMR (CD_3CN , 300 K, in ppm): $\delta = 1.87$ (dd, $^3J_{\text{HP}} = 12.2$ Hz, $^2J_{\text{HP}} = 5.8$ Hz, 6H), 1.09 (dd, $^3J_{\text{HP}} = 18.2$ Hz, $^2J_{\text{HP}} = 4.1$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 300 K, in ppm): $\delta = 19.6$ (dd, $^1J_{\text{CP}} = 41.3$ Hz, $^2J_{\text{CP}} = 15.3$ Hz), 8.5 (dd, $^1J_{\text{CP}} = 18.3$ Hz, $^2J_{\text{CP}} = 3.1$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 300 K, in ppm): AX spin system: $\delta(\text{P}_\text{X}) = 21.6$ (d, $^1J_{\text{PP}} = -228.0$ Hz, $^1J_{\text{PSe}} = -694$ Hz), $\delta(\text{P}_\text{A}) = -56.6$ (d, $^1J_{\text{PP}} = -228.0$ Hz, $^2J_{\text{PSe}} = 21$ Hz); ^{77}Se NMR (CD_3CN , 300 K, in ppm): $\delta = -371.1$ (dd, $^1J_{\text{SeP}} = -694$ Hz, $^2J_{\text{SeP}} = 21$ Hz).

2.4. Synthesis of Tetraethyldiphosphane monoselenide ($\mathbf{1}_{\text{Se}}^{(\text{Et})}$)



a) Using $(\text{Me}_3\text{Si})_2\text{Se}$ as a source of selenide:

$(\text{Me}_3\text{Si})_2\text{Se}$ (291.3 mg, 1.29 mmol) was added to a solution of Et_2PCl (322.0 mg, 2.58 mmol) in CH_3CN (5 mL) and was stirred for 12 hours at rt. All volatiles were removed *in vacuo* affording $\mathbf{1}_{\text{Se}}^{(\text{Et})}$ as a light yellow liquid.

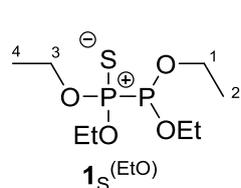
Yield: 295.1 mg (90%).

b) Using Na_2Se as a source of selenide:

Et_2PCl (124.6 mg, 1.00 mmol) was added to a suspension of Na_2Se (62.5 mg, 0.50 mmol) in CH_3CN (5 mL) and was stirred for 12 h at rt. The suspension was filtered and the filtrate was concentrated *in vacuo*, yielding a light yellow liquid.

Yield: 121.7 mg (95%).

Raman (32 mW, 600 scans, 300 K, in cm^{-1}): 2966(12), 2933(100), 2903(25), 2875(24), 2733(6), 1459(18), 1408(7), 1379(11), 1041(9), 980(8), 633(10), 433(16), 270(22), 82(29); **IR** (300 K, ATR, in cm^{-1}): 2967(vw), 1456(vw), 1202(s), 1147(vs), 759(vw), 638(m), 626(w); ^1H NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 2.18$ – 1.96 (4H, m, C1–H), 1.82– 1.69 (2H, m, $^3J_{\text{HH}} = 7.61$ Hz, C3–H), 1.65 (2H, nonet of d, $^3J_{\text{HH}} = 7.61$ Hz, $^2J_{\text{HP}} = 7.61$ Hz, $^3J_{\text{HP}} = 1.75$ Hz, C3–H), 1.25 (3H, t, $^3J_{\text{HH}} = 7.61$ Hz, C4–H), 1.22 (3H, t, $^3J_{\text{HH}} = 7.61$ Hz, C4–H), 1.20 (3H, t, $^3J_{\text{HH}} = 7.61$ Hz, C2–H), 1.18 (3H, t, $^3J_{\text{HH}} = 7.61$ Hz, C2–H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 24.0$ (2C, dd, $^1J_{\text{CP}} = 36.1$ Hz, $^2J_{\text{CP}} = 11.7$ Hz, C1), 16.6 (2C, dd, $^1J_{\text{CP}} = 17.2$ Hz, $^2J_{\text{CP}} = 2.4$ Hz, C3), 10.8 (2C, dd, $^2J_{\text{CP}} = 9.1$ Hz, $^3J_{\text{CP}} = 8.5$ Hz, C2), 7.6 (2C, t, $^2J_{\text{CP}} = 5.3$ Hz, C4); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): AX spin system: $\delta(\text{P}_\text{X}) = 44.2$ (d, $^1J_{\text{PP}} = -257.4$ Hz, $^1J_{\text{PC}} = 35.4$ Hz, $^1J_{\text{PSe}} = -691.0$ Hz), $\delta(\text{P}_\text{A}) = -35.2$ (d, $^1J_{\text{PP}} = -257.4$ Hz, $^1J_{\text{PC}} = 21.0$ Hz); ^{77}Se NMR (CD_2Cl_2 , 300 K, [ppm]): $\delta = -371.1$ (dd, $^1J_{\text{SeP}} = -691$ Hz, $^2J_{\text{SeP}} = 22$ Hz).

2.5 Synthesis of Tetraethoxydiphosphane monosulfide ($1_S^{(EtO)}$)


$(EtO)_2PCl$ (7.83 g, 50.00 mmol) was added to a suspension of Na_2S (1.95 g, 25.0 mmol) and 15-crown-5 (989.0 μL , 5.00 mmol) in CH_3CN (200 mL) and was stirred for 24 h at rt. The suspension was filtered and the filtrate was concentrated *in vacuo*, giving a colorless liquid. The crude product was contaminated by impurities (9%, determined by ^{31}P NMR spectroscopy). Separation by distillation failed.

Yield of crude product: 94% (contains 9% impurities)

1H NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 7.85\text{--}7.67$ (8H, m, C1-H/C3-H), 4.88 (12H, t, $^3J_{HH} = 7.1$ Hz, C2-H/C4-H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 300 K, in ppm): AX spin system: $\delta(P_X) = 159.0$ (d, $^1J_{PP} = -320.1$ Hz), $\delta(P_A) = 98.5$ (d, $^1J_{PP} = -320.1$ Hz). Data is consistent with that presented in ref.^[16].

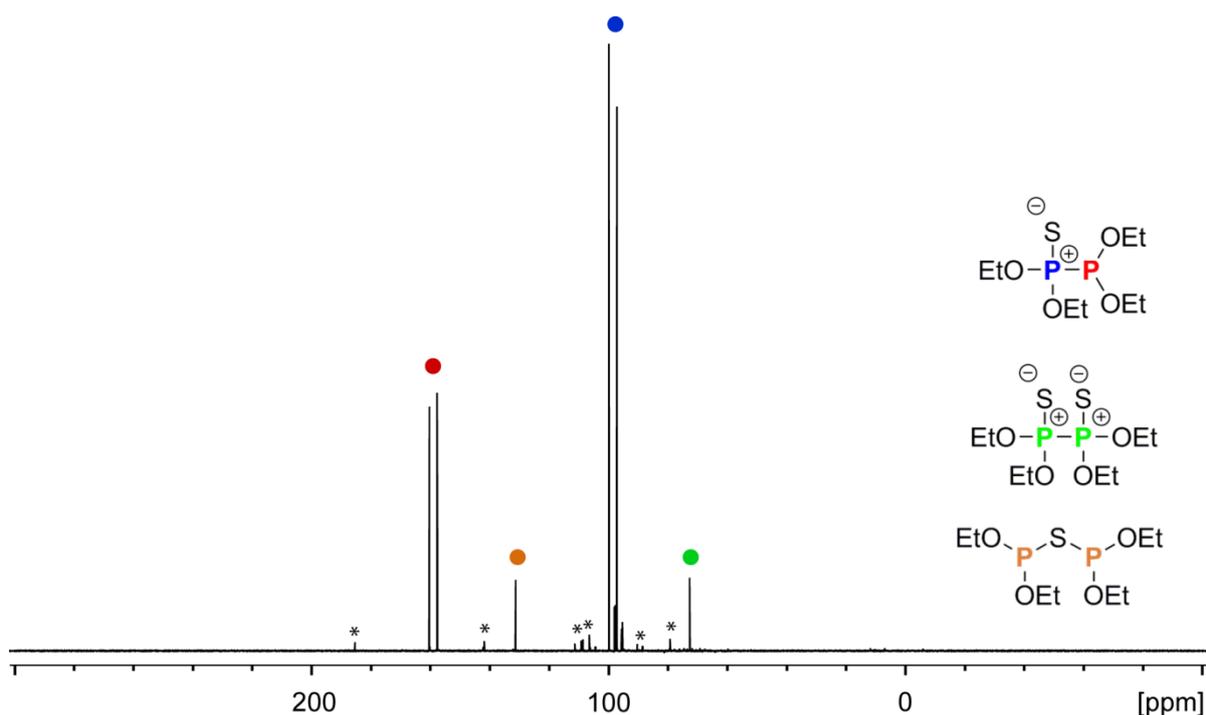


Figure S2.5.1. $^{31}P\{^1H\}$ NMR spectrum of the crude product of $1_S^{(EtO)}$ (CD_2Cl_2 , 300 K); unidentified side products are marked with asterisks (*).

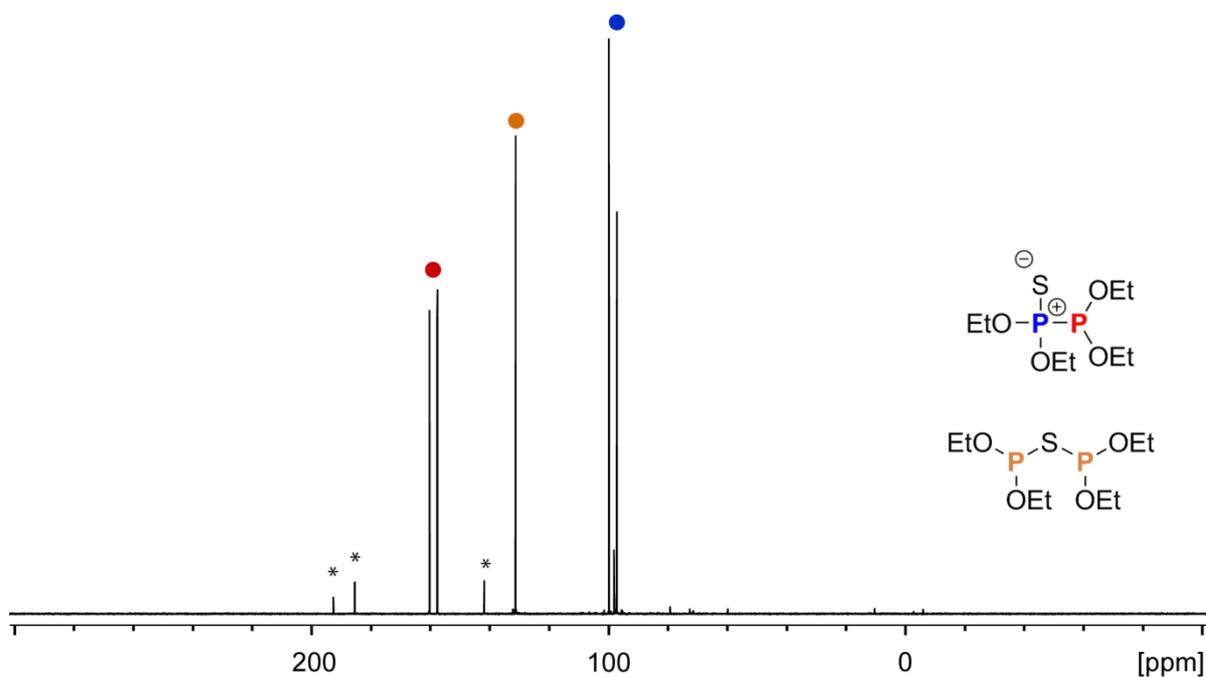


Figure S2.5.2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum $1_{\text{S}}^{(\text{EtO})}$ after distillation at 78°C , 10^{-2} mbar (CD_2Cl_2 , 300 K); unidentified side products are marked with asterisks (*).

2.6 Thermal induced isomerization of $1_{\text{S}}^{(\text{EtO})}$ to $2_{\text{S}}^{(\text{EtO})}$

$1_{\text{S}}^{(\text{EtO})}$ was heated at 100°C for 2 h, resulting in a partial isomerization of $1_{\text{S}}^{(\text{EtO})}$ to $2_{\text{S}}^{(\text{EtO})}$. NMR shifts are consistent with that presented in ref.^[16].

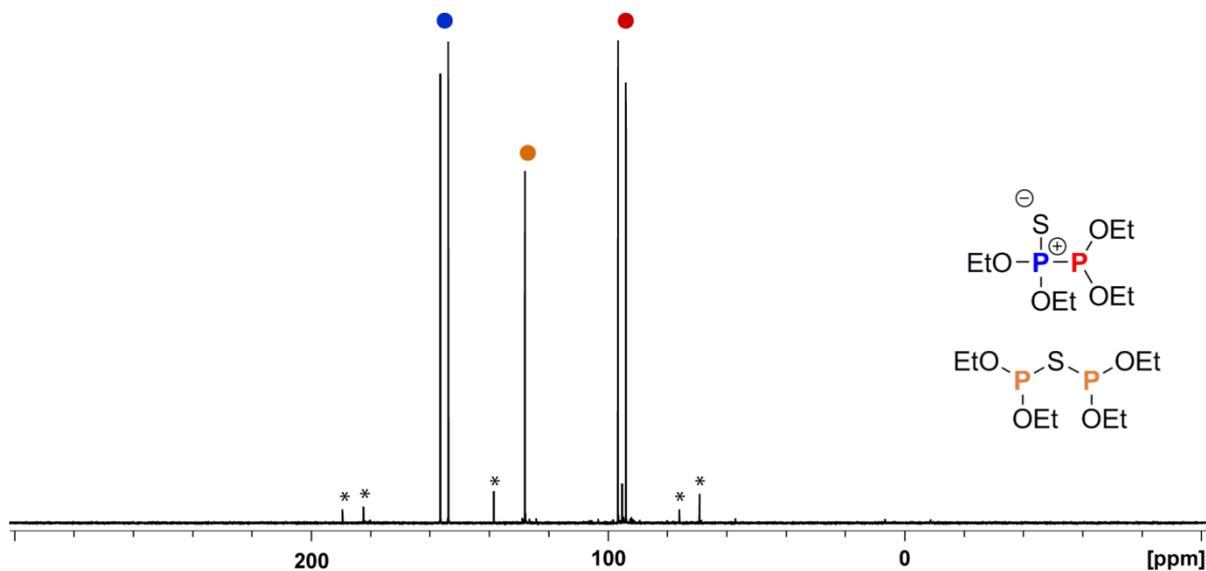


Figure S2.6.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $1_{\text{S}}^{(\text{EtO})}$, which was heated at 100°C for 2 h. (CD_2Cl_2 , 300 K); unidentified side products are marked with asterisks (*).

2.7 Reaction of (EtO)₂PCl with (Me₃Si)₂S

(Me₃Si)₂S (21.1 μL, 0.10 mmol) was added to a solution of (EtO)₂PCl (31.3 mg, 0.20 mmol) in CH₃CN (2 mL) and the clear solution was stirred for 24 hours at room temperature. The ³¹P{¹H} NMR spectrum of the reaction mixture shows the formation of **1_S^(EtO)** as the major product and many unidentified side products, which may form *via* *Arbuzov*-type reactions.

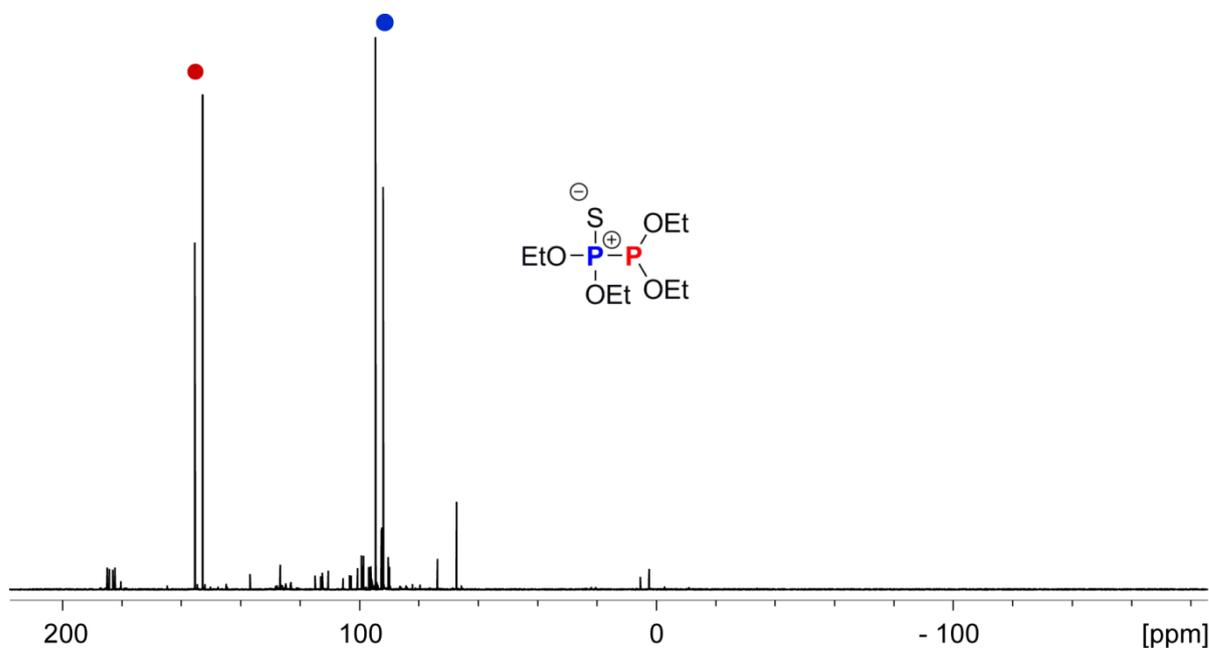


Figure S2.7.1. ³¹P{¹H} NMR spectrum of the reaction of (EtO)₂PCl with (Me₃Si)₂S, displaying many unidentified side products, which may form *via* *Arbuzov* -type reactions (CDCl₃, 300 K).

2.8 Synthesis of Tetraethoxydiphosphane monoselenide (**1_{Se}^(EtO)**)

(EtO)₂PCl (31.3 mg, 0.20 mmol) was added to a suspension of Na₂Se (13.0 mg, 0.10 mmol) in CH₃CN (4 mL) and was stirred for 12 h at rt. The suspension was filtered and the filtrate was concentrated *in vacuo*, giving a colorless liquid. The crude product was contaminated by impurities (**1_{Se}^(EtO)**: 26%, determined by ³¹P NMR spectroscopy). Isolation of the product was not attempted.

¹H NMR (CD₂Cl₂, 300 K, in ppm): δ = 7.94–7.59 (8H, m, C1–H), 4.98–4.79 (12H, m, C2–H); ³¹P{¹H} NMR (CD₂Cl₂, 300 K, in ppm): AX spin system: δ(P_X) = 158.0 (d, ¹J_{PP} = –342.6 Hz), δ(P_Y) = 102.8 (d, ¹J_{PP} = –342.6 Hz).

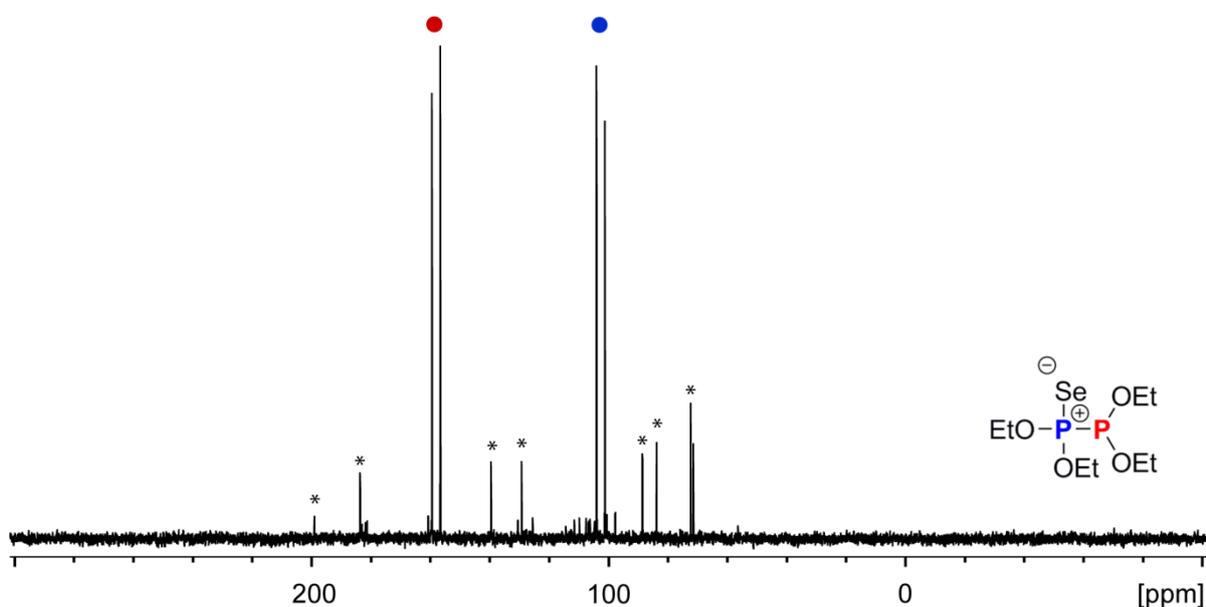
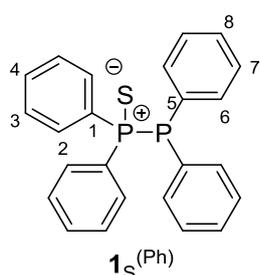


Figure S2.8.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture to yield $\mathbf{1}_{\text{Se}}^{(\text{EtO})}$ (CD_2Cl_2 , 300 K); unidentified side products are marked with asterisks(*).

2.9 Synthesis of Tetraphenyldiphosphane monosulfide ($\mathbf{1}_{\text{S}}^{(\text{Ph})}$)



a) Using $(\text{Me}_3\text{Si})_2\text{S}$ as a source of sulfide:

$(\text{Me}_3\text{Si})_2\text{S}$ (180.0 μL , 0.50 mmol) was added to a solution of Ph_2PCl (105.0 μL , 1.00 mmol) in CH_3CN (6 mL). After 10 minutes the clear solution turned to a colorless suspension, which was stirred for 4 hours at rt. All volatiles were removed *in vacuo*, resulting in a colorless powder, which was washed with *n*-pentane (3 x 2 mL) and dried *in vacuo*.

Yield: 188.0 mg (94%).

b) Using Na_2S as a source of sulfide:

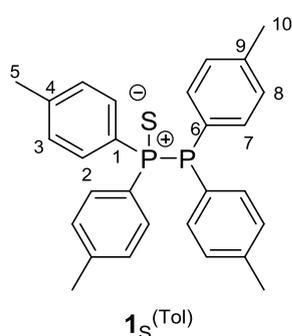
Me_3SiCl (63.6 μL , 0.50 mmol) was added to a suspension of Na_2S (195.1 mg, 2.50 mmol) in CH_3CN (20 mL). Ph_2PCl (898.0 μL , 5.00 mmol) was added and the resulting colorless suspension was stirred for 16 h at rt. The supernatant was decanted and to the residue CH_2Cl_2 (10 mL) was added to dissolve the formed product. The suspension was filtered over Celite and the filtrate was concentrated *in vacuo*. The resulting colorless solid was recrystallized from CH_2Cl_2 / *n*-pentane at $-30\text{ }^\circ\text{C}$ and dried *in vacuo*.

Yield: 840.0 mg (84%).

Mp.: $137\text{ }^\circ\text{C}$; ^1H NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 7.95$ (4H, dd, $^3J_{\text{HH}} = 10.1$ Hz, $^3J_{\text{HP}} = 6.2$ Hz, C2–H), 7.50 (4H, m, $^3J_{\text{HH}} = 6.3$ Hz, $^3J_{\text{HP}} = 6.3$ Hz, C6–H), 7.46 (2H, m,

C4–H/C8–H), 7.40 (4H, m, C3–H), 7.35 (2H, $^3J_{\text{HH}} = 5.9$ Hz, C4–H/C8–H), 7.25 (4H, m, C3–H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 135.0$ (4C, dd, $^2J_{\text{CP}} = 20.0$ Hz, $^3J_{\text{CP}} = 7.1$ Hz, C6), 133.3 (2C, dd, $^1J_{\text{CP}} = 68.8$ Hz, $^2J_{\text{CP}} = 14.0$ Hz, C1/C5), 132.2 (4C, dd, $^2J_{\text{CP}} = 9.2$ Hz, $^3J_{\text{CP}} = 2.5$ Hz, C4), 131.5 (2C, dd, $^4J_{\text{CP}} = 3.2$ Hz, C4/C8), 130.7 (2C, dd, $^1J_{\text{CP}} = 16.1$ Hz, $^2J_{\text{CP}} = 3.6$ Hz, C1/C5), 130.1 (2C, dd, $^4J_{\text{CP}} = 2.1$ Hz, C4/C8), 128.6 (4C, d, $^3J_{\text{CP}} = 11.6$ Hz, C3), 128.4 (4C, dd, $^3J_{\text{CP}} = 7.7$ Hz, C7); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): AX spin system: $\delta(\text{P}_\text{X}) = 44.7$ (d, $^1J_{\text{PP}} = -252.4$ Hz), $\delta(\text{P}_\text{A}) = -13.2$ (d, $^1J_{\text{PP}} = -252.4$ Hz). Data is consistent with that presented in ref.^[17].

2.10 Synthesis of Tetra(*p*-tolyl)diphosphane monosulfide ($1_{\text{S}}^{(\text{Tol})}$)



a) Using $(\text{Me}_3\text{Si})_2\text{S}$ as a source of sulfide:

$(\text{Me}_3\text{Si})_2\text{S}$ (187.4 mg, 1.00 mmol) was added to a solution of $(p\text{-Tol})_2\text{PCl}$ (497.4 mg, 2.00 mmol) in CH_3CN (6 mL). After 5 minutes the clear solution turned to a colorless suspension, which was stirred for 10 hours at rt. The supernatant was decanted and the residue was dried *in vacuo*. The resulting colorless powder was washed with *n*-pentane (2 x 4 mL) and dried *in vacuo*.

Yield: 403.0 mg (88%).

b) Using Na_2S as a source of sulfide:

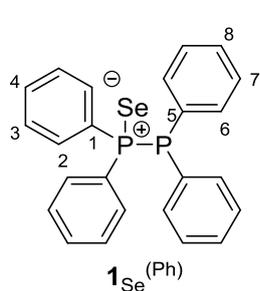
Me_3SiCl (101.5 μL , 0.80 mmol) was added to a suspension of Na_2S (156.1 mg, 2.00 mmol) in CH_3CN (25 mL). $(p\text{-Tol})_2\text{PCl}$ (994.8 mg, 4.00 mmol) was added and the resulting colorless suspension was stirred for 13 h at rt. The supernatant was decanted and to the residue CH_2Cl_2 (10 mL) was added to dissolve the formed product. The suspension was filtered over Celite and the filtrate was concentrated *in vacuo*. The resulting colorless solid was recrystallized in CH_2Cl_2 / *n*-pentane at -30 °C and dried *in vacuo*.

Yield: 365.5 mg (40%).

Mp.: 168–170 °C; **Raman (35 mW, 600 scans, 300 K, in cm^{-1}):** 3049(38), 3033(14), 2976(5), 2948(7), 2918(27), 2863(6), 1597(57), 1494(5), 1375(11), 1213(16), 1194(11), 1090(62), 796(18), 682(8), 639(9), 523(8), 464(16), 380(5), 345(5), 323(6), 295(7), 201(20), 179(15), 84(100); **IR (300 K, ATR, in cm^{-1}):** 3541(vw), 3403(vw), 3068(w), 3046(w), 3019(vw), 2947(vw), 2913(vw), 2860(vw), 2582(vw), 2163(vw), 2071(vw), 2035(vw), 2008(vw), 1977(w), 1903(vw), 1821(vw), 1654(vw), 1637(vw), 1596(m), 1559(vw),

1541(vw), 1493(s), 1444(w), 1395(m), 1376(vw), 1308(m), 1242(vw), 1212(vw), 1184(s), 1120(w), 1092(vs), 1033(w), 1020(m), 950(vw), 847(vw), 837(w), 803(vs), 709(s), 682(vs), 637(vs); **^1H NMR (CD_2Cl_2 , 300 K, in ppm):** δ = 7.81 (4H, dd, $^3J_{\text{HH}} = 12.3$ Hz, $^3J_{\text{HP}} = 4.5$ Hz, C2–H), 7.41 (4H, d, $^3J_{\text{HH}} = 8.1$ Hz, $^3J_{\text{HP}} = 1.2$ Hz, C7–H), 7.21 (4H, dd, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HP}} = 2.7$ Hz, C3–H), 7.08 (4H, d, $^3J_{\text{HH}} = 7.4$ Hz, C8–H), 2.36 (6H, s, C5–H), 2.32 (6H, s, C10–H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** δ = 142.4 (2C, dd, $^4J_{\text{CP}} = 3.1$ Hz, $^5J_{\text{CP}} = 1.1$ Hz, C4), 140.8 (2C, d, $^4J_{\text{CP}} = 2.8$ Hz, C9), 135.4 (4C, dd, $^2J_{\text{CP}} = 20.2$ Hz, $^3J_{\text{CP}} = 7.0$ Hz, C7), 132.5 (4C, dd, $^3J_{\text{CP}} = 9.4$ Hz, $^4J_{\text{CP}} = 2.9$ Hz, C2), 130.9 (2C, dd, $^1J_{\text{CP}} = 70.8$ Hz, $^3J_{\text{CP}} = 14.4$ Hz, C1), 129.6 (4C, d, $^3J_{\text{CP}} = 12.3$ Hz, C3), 129.6 (4C, dd, $^3J_{\text{CP}} = 7.8$ Hz, C8), 127.7 (2C, dd, $^1J_{\text{CP}} = 15.0$ Hz, $^2J_{\text{CP}} = 3.1$ Hz, C6), 21.7 (2C, d, $^5J_{\text{CP}} = 1.6$ Hz, C5), 21.7 (2C, m, C10); **$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** AX spin system: $\delta(\text{P}_\text{X}) = 42.9$ (d, $^1J_{\text{PP}} = -253.6$ Hz, $^1J_{\text{CP}} = 70.0$ Hz), $\delta(\text{P}_\text{A}) = -16.0$ (d, $^1J_{\text{PP}} = -253.6$ Hz); **elemental analysis:** calculated for $\text{C}_{28}\text{H}_{28}\text{P}_2\text{S}$: C 73.34, H: 6.16, N: -, S: 6.99, found: C: 73.18, H: 6.19, N: 0.1, S: 7.09.

2.11 Synthesis of Tetraphenyldiphosphane monoselenide ($\mathbf{1}_{\text{Se}}^{(\text{Ph})}$)



a) Using $(\text{Me}_3\text{Si})_2\text{Se}$ as a source of sulfide:

$(\text{Me}_3\text{Si})_2\text{Se}$ (125.0 μL , 0.50 mmol) was added to a solution of Ph_2PCl (180.0 μL , 1.00 mmol) in CH_3CN (4 mL). After 10 minutes the clear solution turned to a colorless suspension, which was stirred for 3 hours at rt. CH_2Cl_2 (3 mL) was added to dissolve the formed product. The volume of the solution was reduced slowly *in vacuo* yielding $\mathbf{1}_{\text{Se}}^{(\text{Ph})}$ as crystalline material, which was washed with CH_3CN (1 mL) and *n*-pentane (2 x 2 mL). All volatiles were removed *in vacuo*, resulting crystalline material. The product was contaminated with Ph_4P_2 (6%, determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy).

Crude yield: 203.0 mg (90%).

b) Using Na_2Se as a source of selenide:

Ph_2PCl (88.3 mg, 0.40 mmol) was added to a suspension of Na_2Se (25.0 mg, 0.20 mmol) in CH_3CN (4 mL) and was stirred for 12 h at rt. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture the formation of $\mathbf{1}_{\text{Se}}^{(\text{Ph})}$ (66 %), Ph_4P_2 (23%) and $\text{Ph}_2\text{P}(\text{S})\text{P}(\text{S})\text{Ph}_2$ (10%) was observed. The isolation of $\mathbf{1}_{\text{Se}}^{(\text{Ph})}$ was not attempted.

The characterization of $\mathbf{1}_{\text{Se}}^{(\text{Ph})}$ was conducted with the crude product from the reaction using method *a*), which was contaminated with Ph_4P_2 (6%).

Mp: 112-114 °C; **Raman (35 mW, 400 scans, 300 K, in cm^{-1}):** 3055(37), 1584(39), 1571(4), 1183(6), 1158(5), 1087(18), 1028(20), 999(45), 618(6), 564(6), 517(8), 446(8), 409(5), 326(14), 269(5), 257(12), 234(6), 207(24), 138(23), 89(100); **^1H NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 7.94$ (4H, dd, $^3J_{\text{HH}} = 8.13$ Hz, $^3J_{\text{HP}} = 12.77$ Hz, C2-H), 7.49 (4H, m, $^3J_{\text{HH}} = 8.0$ Hz, $^3J_{\text{HP}} = 8.0$ Hz, C6-H), 7.45–7.35 (16H, m, C3-H, C4-H, C8-H), 7.26 (4H, t, $^3J_{\text{HH}} = 7.00$ Hz, C7-H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 135.3$ (4C, dd, $^2J_{\text{CP}} = 20.0$ Hz, $^3J_{\text{CP}} = 7.1$ Hz, C6), 133.4 (4C, dd, $^2J_{\text{CP}} = 6.5$ Hz, $^3J_{\text{CP}} = 2.5$ Hz, C4), 132.5 (2C, d, $^1J_{\text{CP}} = 13.4$ Hz, C1/C5), 131.9 (2C, dd, $^4J_{\text{CP}} = 2.0$ Hz, $^5J_{\text{CP}} = 1.0$ Hz, C4/C8), 131.3 (2C, dd, $^1J_{\text{CP}} = 16.6$ Hz, $^2J_{\text{CP}} = 3.1$ Hz, C1/C5), 130.6 (2C, dd, $^4J_{\text{CP}} = 2.5$ Hz, $^5J_{\text{CP}} = 0.9$ Hz, C4/C8), 128.9 (4C, d, $^3J_{\text{CP}} = 11.7$ Hz, C3), 128.8 (4C, dd, $^3J_{\text{CP}} = 7.3$ Hz, $^4J_{\text{CP}} = 1.0$ Hz, C7); **$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** AX spin system: $\delta(\text{P}_\text{X}) = 34.0$ (d, $^1J_{\text{PP}} = -260.9$ Hz, $^1J_{\text{PSe}} = -750.2$ Hz), $\delta(\text{P}_\text{A}) = -12.5$ (d, $^1J_{\text{PP}} = -260.9$ Hz); **^{77}Se NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = -335.5$ (d, $^1J_{\text{SeP}} = -750$ Hz, $^2J_{\text{SeP}} = 29$ Hz).

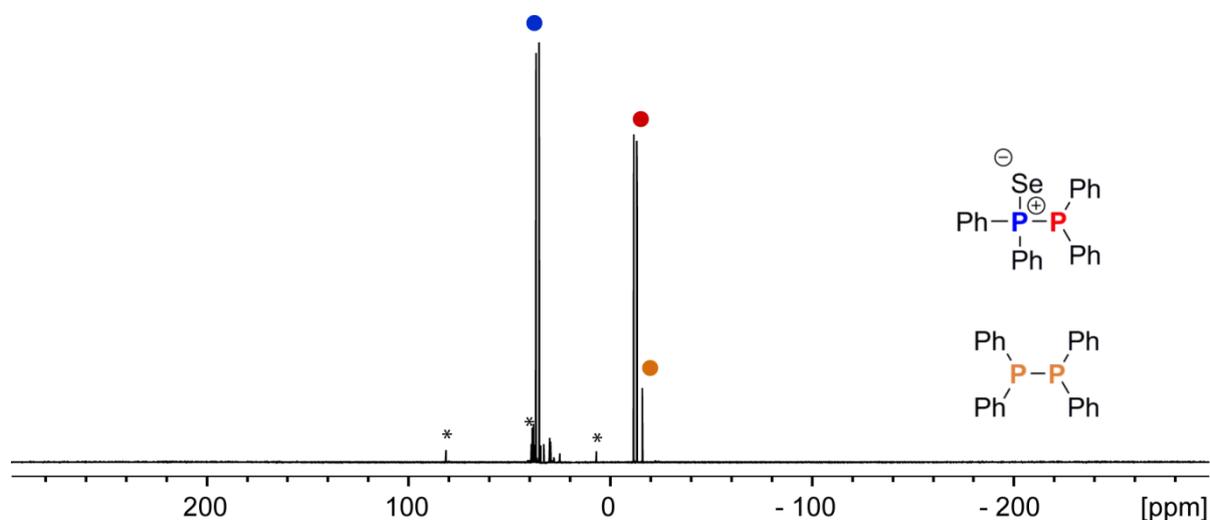
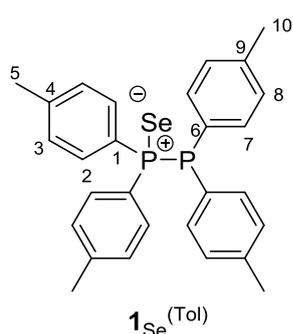


Figure S2.11.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude product of $\mathbf{1}_{\text{Se}}^{(\text{Ph})}$, using synthesis method *a*) (CD_2Cl_2 , 300 K); unidentified side products are marked with asterisks(*).

2.12 Synthesis of Tetra(*p*-tolyl)diphosphane monoselenide (**1_{Se}^(Tol)**)

(Me_3Si)₂Se (112.7 mg, 0.50 mmol) was added to a solution of (*p*-Tol)₂PCl (248.7 mg, 1.00 mmol) in CH_3CN (5 mL). After 5 minutes the clear solution turned to a colorless suspension., which was stirred for 12 hours at rt. The supernatant was decanted and the residue was dried *in vacuo*. The resulting colorless powder was washed with *n*-pentane (2 x 4 mL) and dried *in vacuo*. The product was contaminated with Tol₄P₂ (7%, determined by ³¹P{¹H} NMR

spectroscopy).

Crude yield: 196.5 mg (78%).

¹H NMR (CD₂Cl₂, 300 K, in ppm): δ = 7.78 (4H, dd, ³J_{HH} = 12.20 Hz, ³J_{HP} = 5.63 Hz, C2–H), 7.39 (4H, d, ³J_{HH} = 7.86 Hz, ³J_{HP} = 7.66 Hz, C7–H), 7.20 (4H, dd, ³J_{HH} = 8.42 Hz, ⁴J_{HP} = 2.46 Hz, C3–H), 7.08 (4H, d, ³J_{HH} = 7.71 Hz, C8–H), 2.37 (6H, s, C5–H), 2.36 (6H, s, C10–H); **¹³C{¹H} NMR (CD₂Cl₂, 300 K, in ppm):** δ = 142.5 (2C, dd, ⁴J_{CP} = 3.2 Hz, ⁵J_{CP} = 1.0 Hz, C4), 141.0 (2C, d, ⁴J_{CP} = 2.6 Hz, C9), 135.2 (4C, dd, ²J_{CP} = 20.5 Hz, ³J_{CP} = 7.0 Hz, C7), 133.3 (4C, dd, ³J_{CP} = 9.5 Hz, ⁴J_{CP} = 6.3 Hz, C2), 129.6 (4C, d, ³J_{CP} = 12.0 Hz, C3), 129.6 (4C, d, ³J_{CP} = 7.9 Hz, ⁴J_{CP} = 1.3 Hz, C8), 129.3 (2C, dd, ¹J_{CP} = 62.7 Hz, ²J_{CP} = 13.5 Hz C1), 127.9 (2C, dd, ¹J_{CP} = 15.5 Hz, ²J_{CP} = 3.1 Hz, C6), 21.7 (2C, m, C10), 21.7 (2C, ⁵J_{CP} = 1.5 Hz, C5); **³¹P{¹H} NMR (CD₂Cl₂, 300 K, in ppm):** AX spin system: $\delta(\text{P}_X)$ = 33.8 (d, ¹J_{PP} = –260.9 Hz, ¹J_{PSe} = –741.0 Hz, ¹J_{CP} = 62.7 Hz), $\delta(\text{P}_A)$ = –14.6 (d, ¹J_{PP} = –260.9 Hz). **⁷⁷Se NMR (CD₂Cl₂, 300 K, in ppm):** δ = –329.4 (d, ¹J_{SeP} = –741 Hz, ²J_{SeP} = 28 Hz).

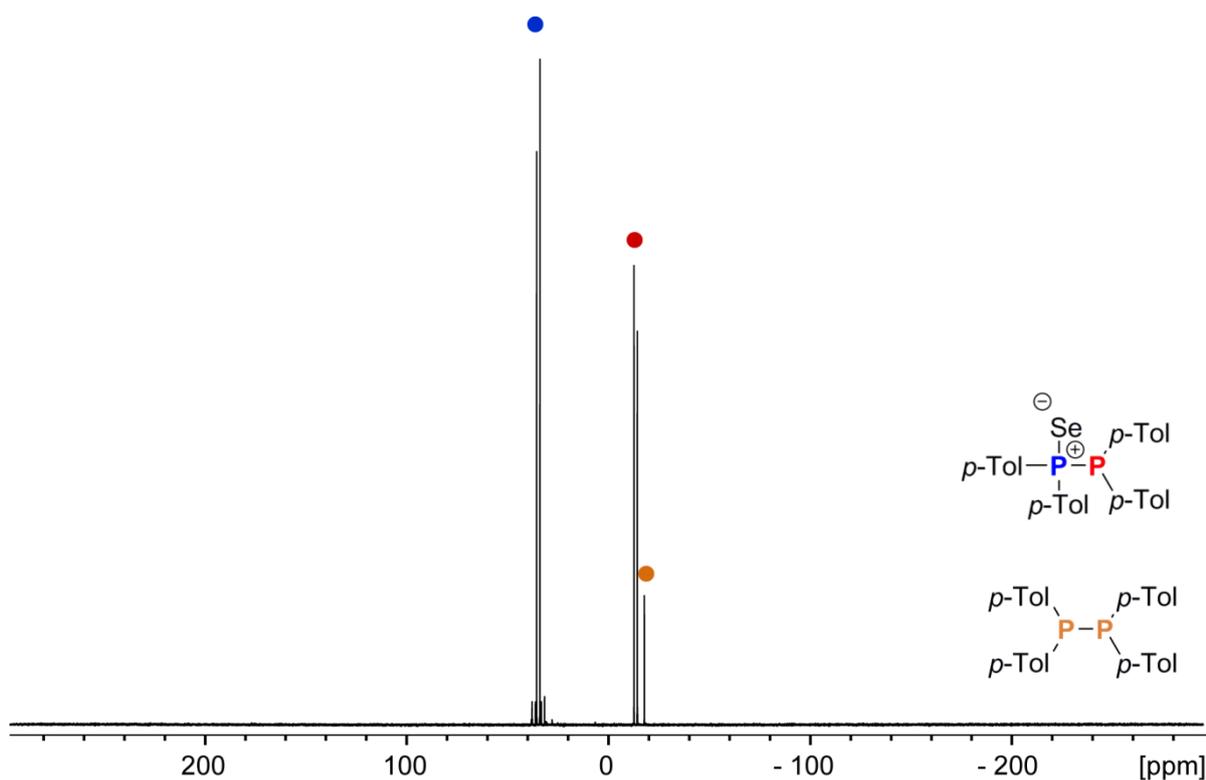


Figure S2.12.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the crude product of $1_{\text{Se}}^{(\text{Tol})}$, using synthesis method *a*) (CD_2Cl_2 , 300 K).

2.13 Reaction of $\text{Ph}_2\text{P}\text{Cl}$ and $(\text{Me}_3\text{Si})_2\text{Te}$ yielding tetraphenyldiphosphane Ph_4P_2

$(\text{Me}_3\text{Si})_2\text{Te}$ (27.40 mg, 0.10 mmol) was added to a solution of $\text{Ph}_2\text{P}\text{Cl}$ (44.13 mg, 0.20 mmol) in CH_3CN (2 mL), resulting in a black precipitate, which forms a metallic mirror on the glass wall. The ^{31}P NMR spectrum of the solution shows quantitative formation to Ph_4P_2 .

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 300 K, in ppm): $\delta = -15.5$ (s). Data is consistent with that presented in ref.^[18].

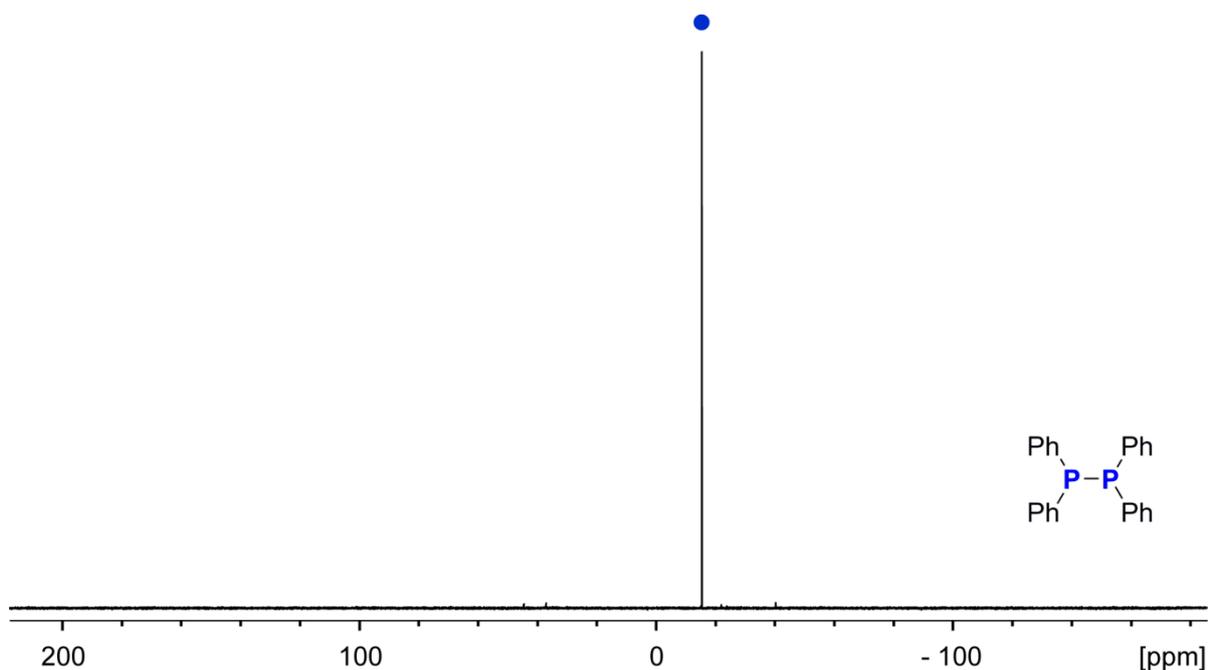
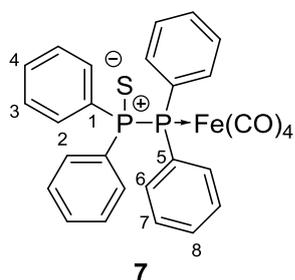


Figure S2.13.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of $\text{Ph}_2\text{P}\text{Cl}$ with $(\text{Me}_3\text{Si})_2\text{Te}$ yielding Ph_4P_2 (CD_2Cl_2 , 300 K).

2.14 Synthesis of Tetraphenyldiphosphane monosulfide iron tetracarbonyl (7)



$\mathbf{1}_S^{(\text{Ph})}$ (80.4 mg, 0.20 mmol) was added to a suspension of $\text{Fe}_2(\text{CO})_9$ (72.8 mg, 0.20 mmol) in THF (4 mL) and the resulting brown solution was stirred at rt for 12 h in the dark. All volatiles were removed *in vacuo* affording a brown oil. *N*-pentane (3 mL) was added and the reaction mixture was stirred for 10 minutes. The formed brown precipitation were recrystallized in CH_3CN at $-31\text{ }^\circ\text{C}$, yielding crystalline material, which was dried *in vacuo*. $^{31}\text{P}\{^1\text{H}\}$ NMR analysis of the crystalline material shows high purity of **7** (~95% by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy), accompanied by minor unidentified side products, which can not be separated by recrystallization.

Yield: 80.9 mg (71%).

Mp.: Decomp. $149\text{ }^\circ\text{C}$; **Raman (32 mW, 600 scans, 300 K, in cm^{-1}):** 3058(50), 2076(6), 2061(6), 2045(13), 1972(38), 1944(25), 1934(13), 1583(44), 1189(6), 1162(6), 1087(25), 1029(31), 1000(69), 644(6), 616(6), 541(6), 490(13), 435(25), 353(6), 319(6), 263(6), 224(6), 198(25), 136(6), 109(100), 93(19), 75(31); **IR (300K, ATR, in cm^{-1}):** 3055(vw), 2988(w), 2901(vw), 2045(m), 1973(w), 1931(vs), 1692(vw), 1582(vw), 1552(vw), 1535(vw), 1512(vw), 1479(w), 1435(m), 1314(w), 1250(vw), 1188(w), 1161(w), 1085(m), 1027(vw),

997(w), 861(vw), 743(s), 689(s), 644(w), 619(s); ^1H NMR (CDCl_3 , 300 K, in ppm): $\delta = 7.68$ (m, 8H), 7.50 (m, 4H), 7.37 (m, 8H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 300 K, in ppm): $\delta = 134.5$ (4C, dd, $^2J_{\text{CP}} = 9.8$ Hz, $^3J_{\text{CP}} = 2.5$ Hz, C6), 133.5 (4C, d, $^2J_{\text{CP}} = 9.7$ Hz, C2), 132.5 (2C, d, $^4J_{\text{CP}} = 3.1$ Hz, C4/C8), 131.6 (2C, m, C4/C8), 131.2 (2C, dd, $^1J_{\text{CP}} = 34.1$ Hz, $^2J_{\text{CP}} = 3.3$ Hz, C1/C5), 129.2 (2C, dd, $^1J_{\text{CP}} = 67.7$ Hz, $^2J_{\text{CP}} = 11.3$ Hz, C1/C5), 128.5 (4C, d, $^3J_{\text{CP}} = 12.5$ Hz, C7/C3), 128.3 (4C, d, $^3J_{\text{CP}} = 10.0$ Hz, C7/C3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): AM spin system: $\delta(\text{P}_\text{M}) = 79.1$ (d, $^1J_{\text{PP}} = -138.9$ Hz), $\delta(\text{P}_\text{A}) = 48.8$ (d, $^1J_{\text{PP}} = -138.9$ Hz); **elemental analysis**: calculated for $\text{C}_{28}\text{H}_{20}\text{FeO}_4\text{P}_2\text{S}$: C 58.97, H: 3.53, N: -, S: 5.62, found: C: 58.46, H: 3.52, N: 0.02 S: 5.10.

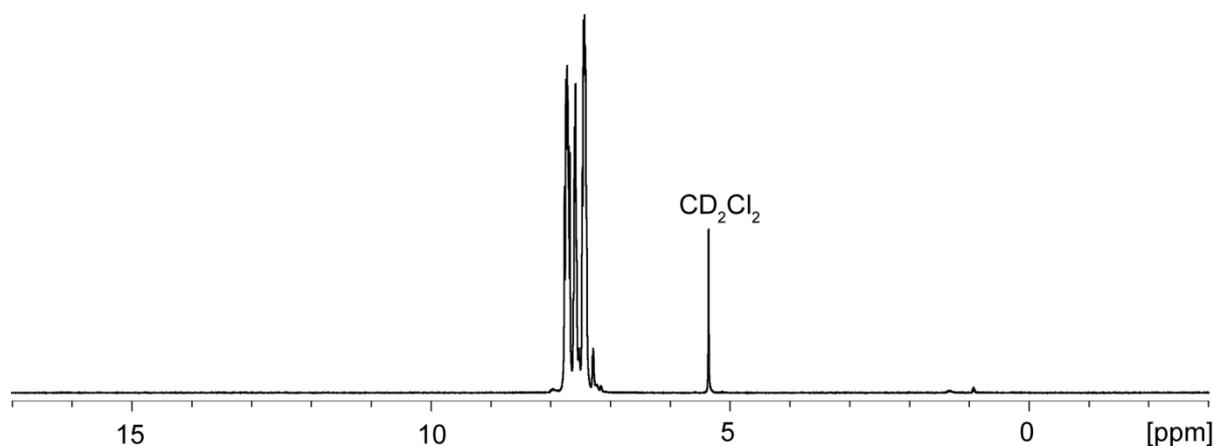


Figure S2.14.1. ^1H NMR spectrum of **7** (CD_2Cl_2 , 300 K).

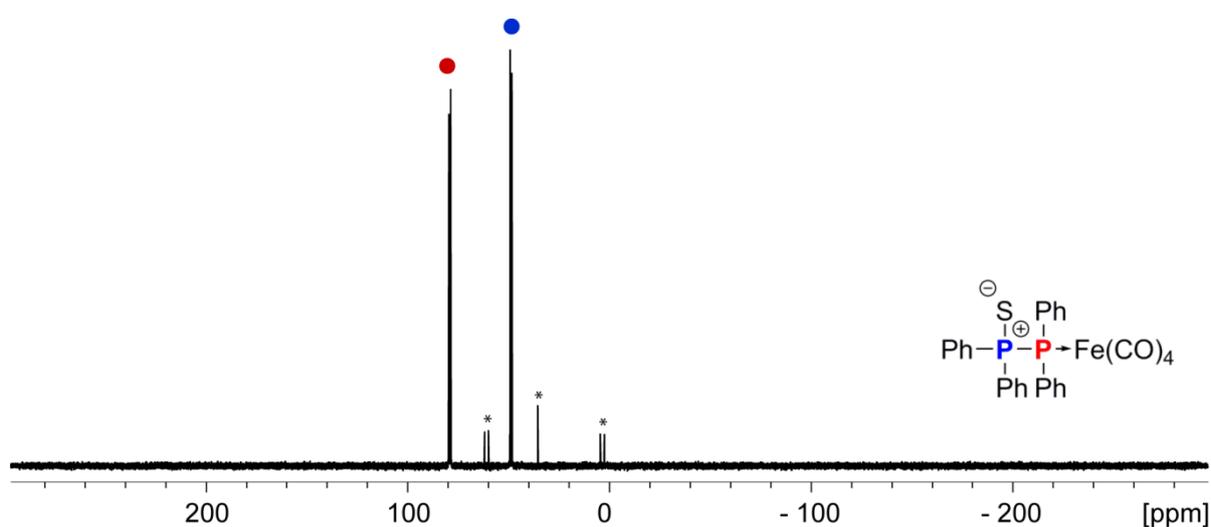


Figure S2.14.2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** (CD_2Cl_2 , 300 K); unidentified side products are marked with asterisks (*).

2.15 Reaction of $(i\text{Pr})_2\text{PCl}$ and $(\text{Me}_3\text{Si})_2\text{S}$

$(\text{Me}_3\text{Si})_2\text{S}$ (21.1 μL , 0.10 mmol) was added to a solution of $i\text{Pr}_2\text{PCl}$ (31.8 μL , 0.20 mmol) in CH_3CN (3 mL) and the clear solution was stirred for 12 hours at room temperature. The ^{31}P NMR spectrum of the reaction mixture shows the formation of approximately 85% to $(i\text{Pr})_2\text{P}(\text{S})\text{P}(i\text{Pr})_2$ ($1\text{S}^{(i\text{Pr})}$) and 15% to $(i\text{Pr}_2\text{P})_2\text{S}$ ($2\text{S}^{(i\text{Pr})}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 300 K, in ppm): $\delta = 69.3$ (s, $2\text{S}^{(i\text{Pr})}$, (Lit.: 67.0^[19])), 68.5 (d, $^1J_{\text{PP}} = -309.0$ Hz, $1\text{S}^{(i\text{Pr})}$ (Lit.: 69.0, $^1J_{\text{PP}} = -305.0$ Hz^[19])), -4.1 (d, $^1J_{\text{PP}} = -309.0$ Hz, $1\text{S}^{(i\text{Pr})}$ (Lit.: -6.3, $^1J_{\text{PP}} = -305.0$ Hz^[19])). Data is consistent with that presented in ref.^[19]. Separation of the products was not attempted.

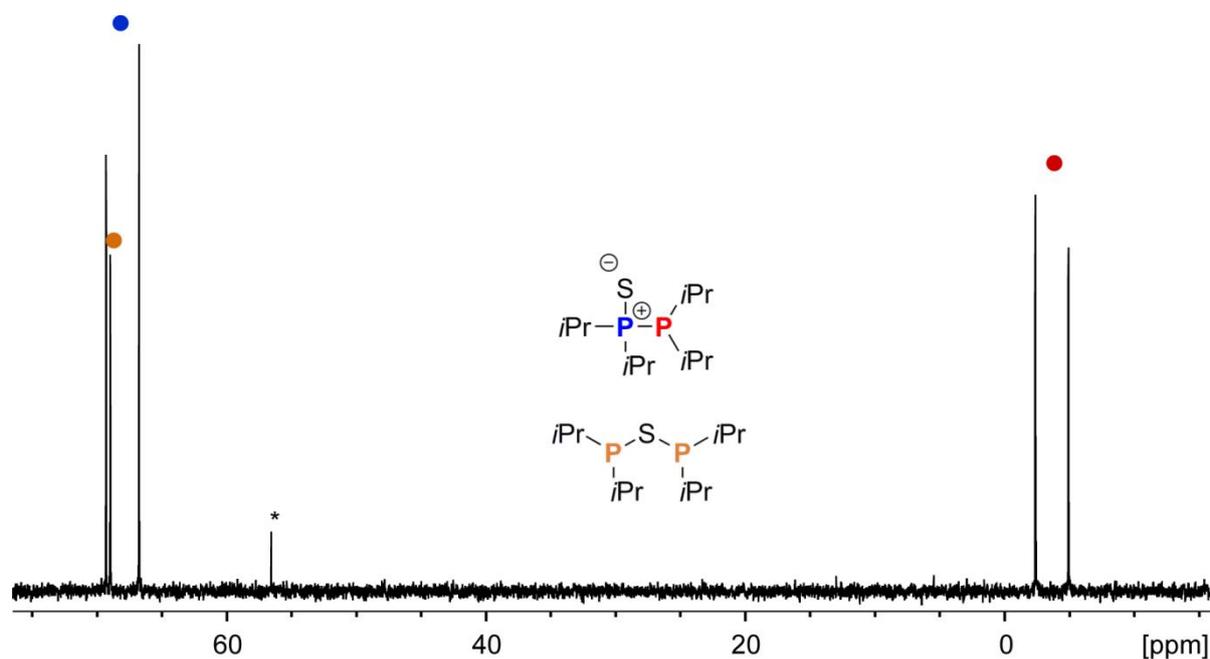
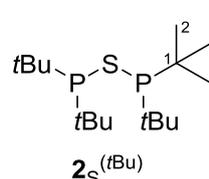


Figure S2.15.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of $i\text{Pr}_2\text{PCl}$ and $(\text{Me}_3\text{Si})_2\text{S}$ (CD_2Cl_2 , 300 K). Unidentified side product is marked with (*).

2.16 Synthesis of tetra-*tert*-butyldiphosphanylsulfane ($2\text{S}^{(t\text{Bu})}$)



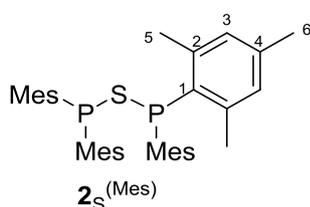
$(t\text{Bu})_2\text{PCl}$ (5.36 g, 29.65 mmol) was added to a suspension of Na_2S (1.22 g, 15.60 mmol) in CH_3CN (50 mL) and was stirred for 12 h at rt. CH_2Cl_2 (50 mL) was added to the suspension to dissolve the formed product. The suspension was filtered over Celite and the filtrate was concentrated *in vacuo*. The resulting colorless precipitation was recrystallized from CH_2Cl_2 / CH_3CN , resulting in colorless crystals, which were dried *in vacuo*.

Yield: 3.98 g (83%)

Mp.: 75-76 °C; **Raman (50 mW, 500 scans, 300 K, in cm^{-1}):** 2976(40), 2945(72), 2896(100), 2864(63), 2767(9), 2702(14), 1468(36), 1456(31), 1444(26), 1207(24), 1194(20),

1175(37), 1017(10), 938(25), 808(61), 593(23), 570(60), 526(20), 488(10), 294(18), 200(18), 135(52), 100(30); **IR (300K, ATR, in cm^{-1}):** 2975(w), 2942(m), 2891(w), 2858(m), 1478(vw), 1465(w), 1446(vw), 1387(w), 1361(vs), 1173(m), 1016(w), 934(w), 806(s), 690(vs); **$^1\text{H NMR}$ (CD_2Cl_2 , 300 K, in ppm):** $\delta = 1.30$ (36H, m, $^3J_{\text{HP}} = 5.72$ Hz, C2–H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 36.0$ (4C, t, $^1J_{\text{CP}} = 14.6$ Hz, C1), 29.7 (12C, t, $^2J_{\text{CP}} = 7.8$ Hz, C2); **$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 86.6$ (s); **elemental analysis:** calculated for $\text{C}_{16}\text{H}_{36}\text{P}_2\text{S}$: C 59.59, H: 11.25, N: -, S: 9.94, found: C: 59.22, H: 10.86, N:0.07, S: 9.72.

2.17 Synthesis of tetramesityldiphosphanylulfane ($2_{\text{S}}^{(\text{Mes})}$)



a) Using $(\text{Me}_3\text{Si})_2\text{S}$ as a source of sulfide:

$(\text{Me}_3\text{Si})_2\text{S}$ (105.0 μL , 0.50 mmol) was added to a solution of $(\text{Mes})_2\text{PCl}$ (305.0 mg, 1.00 mmol) in CH_3CN (5 mL). After 15 min the solution turned into a colorless suspension, which was stirred for 3 h at rt. The supernatant was decanted and the residue was washed with cold CH_3CN (2 x 3 mL, -30 $^\circ\text{C}$). All volatiles were removed *in vacuo*, resulting in a colorless solid.

Yield: 255.3 mg (89%).

b) Using Na_2S as a source of sulfide:

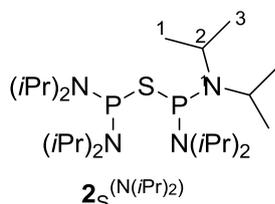
Mes_2PCl (304.8 mg, 1.00 mmol) was added to a suspension of Na_2S (39.02 mg, 0.50 mmol) in CH_3CN (3 mL) and was stirred for 5 h at rt. CH_2Cl_2 (2 mL) was added to the suspension to dissolve the formed product. The suspension was filtered over Celite and the filtrate was dried *in vacuo*. The resulting colorless precipitation washed with CH_3CN , and was dried *in vacuo*.

Yield: 245.4 mg, 86%;

Mp.: 138-139 $^\circ\text{C}$; **IR (300 K, ATR, in cm^{-1}):** 3018(vw), 2964(w), 2918(vw), 2853(vw), 1601(w), 1552(vw), 1465(w), 1435(vw), 1405(w), 1373(w), 1288(w), 1263(w), 1029(w), 886(vw), 848(vs), 738(s), 704(w), 615(w); **Raman (35 mW, 450 scans, 300 K, in cm^{-1}):** 3020(24), 2982(12), 2916(88), 2853(16), 2730(12), 1603(100), 1466(10), 1438(7), 1377(40), 1290(69), 1051(36), 1013(14), 706(9), 573(33), 555(14), 539(12), 493(17); **$^1\text{H NMR}$ (CD_2Cl_2 , 300 K, in ppm):** $\delta = 6.74$ (8H, s, C3–H), 2.29 (24H, s, C5–H), 2.21 (12H, s, C6–H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 141.8$ (8C, m, $^2J_{\text{CP}} = 8.6$ Hz, C2), 138.5 (4C, s, C4), 133.8 (4C, m, C1), 130.1 (8C, s, C3), 23.0 (8C, m, $^3J_{\text{CP}} = 7.3$ Hz, C5), 20.7 (4C, s, C6);

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 22.5$ (s); **elemental analysis**: calculated for $\text{C}_{36}\text{H}_{44}\text{P}_2\text{S}$: C 75.76, H: 7.77, N: -, S: 5.62, found: C: 75.93, H: 7.86, N: 0.02, S: 6.60.

2.18 Synthesis of tetrakis(di-*iso*-propylamino)diphosphanysulfane ($2_{\text{S}}^{(\text{N}(\text{iPr})_2)}$)

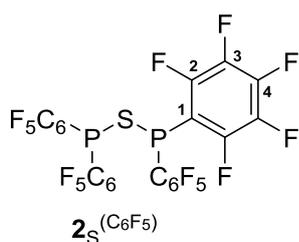


15-crown-5 (33.1 mg, 0.15 mmol) was added to a suspension of Na_2S (75.1 mg, 1.00 mmol) in CH_3CN (8 mL). $((\text{iPr})_2\text{N})_2\text{PCl}$ (533.6 mg, 2.00 mmol) was added to the colorless suspension, which was stirred for 24 hours at rt. The supernatant was decanted and to the residue CH_2Cl_2 (6 mL) was added to dissolve the formed product. The suspension was filtered over Celite and the filtrate was concentrated *in vacuo*. The resulting colorless solid was washed with CH_3CN (5 mL, -30°C) and dried *in vacuo*.

Yield: 382.5 mg (77%).

Mp.: 108-110 $^\circ\text{C}$; **Raman (40 mW, 400 scans, 300 K, in cm^{-1}):** 2968(42), 2931(100), 2867(7), 2702(10), 2283(4), 2244(4), 2185(6), 2158(4), 2117(7), 2077(4), 2062(6), 1984(6), 1457(28), 1392(6), 1352(10), 1316(7), 1115(13), 966(7), 930(10), 867(18), 620(27), 552(13), 499(4), 403(8), 282(11), 188(4), 128(6), 79(45); **IR (300K, ATR, in cm^{-1}):** 2964(s), 2928(w), 2868(vw), 2353(w), 1692(w), 1642(vw), 1552(vw), 1535(vw), 1454(w), 1387(w), 1359(m), 1308(vw), 1250(vw), 1180(m), 1156(w), 1113(s), 1066(w), 1018(m), 948(vs), 863(m), 844(w), 635(w), 618(w); **^1H NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 3.65$ (8H, sept., $^3J_{\text{HH}} = 6.48$ Hz, C2-H), 1.26 (24H, d, $^3J_{\text{HH}} = 6.62$ Hz, C1-H), 1.24 (24H, d, $^3J_{\text{HH}} = 6.74$ Hz, C3-H), **$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 47.6$ (8C, t, $^2J_{\text{CP}} = 6.2$ Hz, C2), 24.5 (8C, t, $^3J_{\text{CP}} = 2.8$ Hz, C3), 23.04 (8C, t, $^3J_{\text{CP}} = 6.2$ Hz, C1); **$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 89.1$ (s); Data is consistent with that presented in ref.^[20].

2.19 Synthesis of tetrakis(pentafluorophenyl)diphosphanysulfane ($1_{\text{S}}^{(\text{C}_6\text{F}_5)}$)

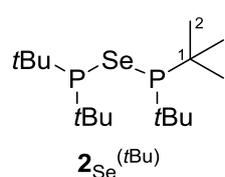


$(\text{Me}_3\text{Si})_2\text{S}$ (446.1 mg, 2.50 mmol) was added to a solution of $(\text{C}_6\text{F}_5)_2\text{PCl}$ (2.00 g, 5.00 mmol) in CH_3CN (10 mL) and was stirred for 12 h at rt. All volatiles were removed *in vacuo*. The resulting colorless solid was recrystallized in CH_2Cl_2 / *n*-pentane at -30°C and dried *in vacuo*.

Yield: 240.0 mg (67%)

Mp.: Decomp.: 119 °C; **Raman (32 mW, 600 scans, 300 K, in cm⁻¹):** 1642(75), 1393(24), 1385(9), 1291(9), 1142(4), 833(26), 713(5), 637(3), 587(60), 500(65), 466(3), 446(43), 428(6), 389(33), 362(3), 339(8), 321(3), 284(7), 236(6), 145(14), 100(9), 72(100); **IR (300 K, ATR, in cm⁻¹):** 1641(w), 1515(m), 1467(vs), 1382(w), 1290(m), 1266(vw), 1141(vw), 1085(s), 1016 (w), 973(vs), 842(w), 764(vw), 745(w), 727(w), 635(w); **¹⁹F NMR (CD₂Cl₂, 300 K, in ppm):** δ = -128.8 (8F, dd, ³J_{FP} = 18.8 Hz, ³J_{FF} = 19.8 Hz, ¹J_{FC} = 252.0 Hz, C2-F), -148.5 (4F, t, ³J_{FF} = 19.8 Hz, ¹J_{FC} = 261.0 Hz, C4-F), -160.4 (8F, t, ³J_{FF} = 19.8 Hz, ¹J_{FC} = 251.6 Hz, C3-F); **¹³C{¹H} NMR (CD₂Cl₂, 300 K, in ppm):** δ = 147.2 (8C, dm, ¹J_{CF} = 251.5 Hz, C2), 143.3 (4C, dm, ¹J_{CF} = 261.3 Hz, C4), 137.8 (8C, dm, ¹J_{CF} = 251.6 Hz, C3), 108.9 (4C, m, C1); **³¹P{¹H} NMR (CD₂Cl₂, 300 K, in ppm):** δ = -9.0 (nonett, ³J_{PF} = 18.8 Hz); **elemental analysis:** calculated for C₂₄F₂₀P₂S: C: 37.82, H: -, N: -, S: 4.21, found: C: 38.22, H: 0.39, N: 0.11, S: 4.54.

2.20 Synthesis of tetra-*tert*-butyldiphosphanyl selenane (**2_{Se}^(tBu)**)



a) Using (Me₃Si)₂Se as a source of sulfide:

(Me₃Si)₂Se (376.0 μL, 1.50 mmol) was added to a solution of (tBu)₂PCl (570.0 μL, 3.00 mmol) in CH₃CN (8 mL). The colorless solution was stirred under reflux for 12 h. The reaction mixture was stored at -30 °C

for 12 h, resulting in yellow needles, which were filtered and washed with CH₃CN (2 x 3 mL, -30 °C). Solvent was removed *in vacuo* resulting in a crystalline solid.

Yield: 408.8 mg (74%).

b) Using Na₂Se as a source of selenide:

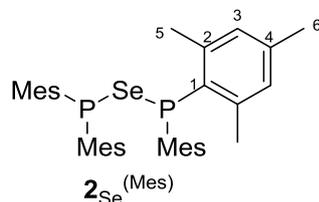
(tBu)₂PCl (180.7 mg, 1.00 mmol) was added to a suspension of Na₂Se (124.9 mg, 0.50 mmol) in CH₃CN (3 mL) and was stirred for 12 h at rt. CH₂Cl₂ (2 mL) was added to the suspension to dissolve the formed product. The suspension was filtered over Celite and the filtrate was concentrated *in vacuo*. The resulting yellow precipitation was recrystallized in CH₂Cl₂ and CH₃CN, resulting in yellow needles, which were dried *in vacuo*.

Yield: 126.0 mg (68%).

Mp.: 75-76 °C; **Raman (40 mW, 400 scans, 300 K, in cm⁻¹):** 2994(15), 2976(10), 2953(60), 2914(15), 2893(65), 2858(53), 2767(8), 2702(19), 1468(31), 1442(10), 1387(6), 1362(8), 1208(21), 1174(39), 1020(16), 936(42), 807(100), 590(18), 569(85), 472(24), 445(6), 367(11), 300(16), 245(19), 194(21); **IR (300 K, ATR, in cm⁻¹):** 2993(vw), 2974(w),

2939(m), 2890(w), 2857(w), 1471(w), 1462(w), 1443(vw), 1386(w), 1361(vs), 1204(vw), 1172(m), 1149(vs), 1015(w), 933(w), 806(s), 639(vw); $^1\text{H NMR}$ (CD_2Cl_2 , 300 K, in ppm): $\delta = 1.24$ (36H, m, C2–H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 35.4$ (4C, t, $^1J_{\text{CP}} = 16.1$ Hz, C1), 30.5 (12C, t, $^2J_{\text{CP}} = 7.2$ Hz, C2); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 94.7$ (s, $^1J_{\text{PSe}} = -211$ Hz); $^{77}\text{Se NMR}$ (CD_3CN , 300 K, in ppm): $\delta = -30.1$ (t, $^1J_{\text{SeP}} = -211$ Hz); **elemental analysis**: calculated for $\text{C}_{16}\text{H}_{36}\text{P}_2\text{Se}$: C 52.03, H: 9.82, N: -, S: -, found: C: 51.67, H: 9.60, N: -, S: 0.44.

2.21 Synthesis of tetramesityldiphosphanyl selenane ($2_{\text{Se}}^{(\text{Mes})}$)



a) Using $(\text{Me}_3\text{Si})_2\text{Se}$ as a source of sulfide:

$(\text{Me}_3\text{Si})_2\text{Se}$ (66.6 μL , 0.25 mmol) was added to a solution of $(\text{Mes})_2\text{PCl}$ (152.4 mg, 0.50 mmol) in CH_3CN (4 mL). After 2 min the solution turned into a colorless suspension, which was stirred for 2 h at rt. The supernatant was decanted and the residue was washed with cold CH_3CN (2 x 2 mL, -30 °C). All volatiles were removed *in vacuo*, resulting in a colorless solid.

Yield: 126.0 mg (81%).

Using Na_2Se as a source of selenide:

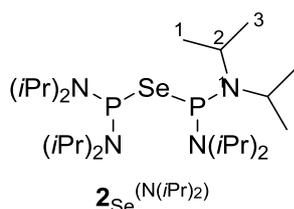
Mes_2PCl (914.4 mg, 3.00 mmol) was added to a suspension of Na_2Se (187.4 mg, 1.50 mmol) in CH_3CN (10 mL) and was stirred for 12 h at rt. CH_2Cl_2 (10 mL) was added to the suspension to dissolve the formed product. The suspension was filtered over Celite and the filtrate was dried *in vacuo*. The resulting colorless precipitation washed with CH_3CN , and was dried *in vacuo*.

Yield: 796.8 mg, (86%).

Mp.: Decomp. 129 °C; **IR** (300 K, ATR, in cm^{-1}): 3017(vw), 2956(w), 2917(w), 1601(m), 1553(w), 1465(w), 1440(m), 1400(w), 1377(w), 1289(w), 1243(vw), 1192(vw), 1027(w), 1012(w), 892(vw), 875(w), 843(vs), 712(w), 635(w), 614(w); **Raman** (40 mW, 400 scans, 300 K, in cm^{-1}): 3019(14), 2960(14), 2912(100), 2851(17), 2728(10), 1604(98), 1558(4), 1466(14), 1442(12), 1377(47), 1290(79), 1263(5), 1179(9), 1050(42), 1015(14), 956(5), 616(5), 602(4), 574(47), 553(14), 538(13), 431(29), 413(6), 389(17), 341(14); $^1\text{H NMR}$ (CD_2Cl_2 , 300 K, in ppm): $\delta = 6.76$ (8H, s, C3–H), 2.30 (24H, s, C5–H), 2.21 (12H, s, C6–H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 142.0$ (8C, t, $^2J_{\text{CP}} = 8.2$ Hz, C2), 138.6 (4C, s,

C4), 134.0 (4C, d, $^1J_{CP} = 16.4$ Hz, C1), 130.2 (8C, d, $^2J_{CP} = 2.8$ Hz, C3), 23.5 (8C, m, $^3J_{CP} = 7.4$ Hz, C5), 20.9 (4C, s, C6); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 15.7$ (s, $^1J_{PSe} = -192$ Hz); ^{77}Se NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = -246.1$ (t, $^1J_{SeP} = -192$ Hz); **elemental analysis**: calculated for $\text{C}_{36}\text{H}_{44}\text{P}_2\text{Se}$: C 70.01, H: 7.18, N: -, S: -, found: C: 69.69, H: 7.28, N: 0.00, S: 0.13.

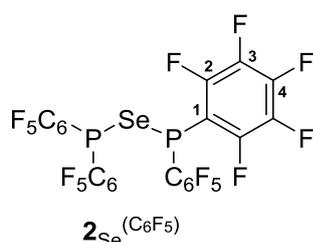
2.22 Synthesis of tetrakis(di-*iso*-propylamino)diphosphanylselane ($2_{\text{Se}}^{(\text{N}(\text{iPr})_2)}$)



15-crown-5 (31.0 μL , 0.16 mmol) was added to a suspension of Na_2Se (50.0 mg, 0.40 mmol) in CH_3CN (8 mL). $((\text{iPr})_2\text{N})_2\text{PCl}$ (213.4 mg, 0.8 mmol) was added to the colorless suspension, which was stirred for 24 hours at rt. The reaction mixture was cooled at -30 $^\circ\text{C}$ and the supernatant was decanted. To the residue CH_2Cl_2 (6 mL) was added to dissolve the formed product. The suspension was filtered over Celite and the filtrate was concentrated *in vacuo*. The resulting colorless solid was washed with cold CH_3CN (2 x 5 mL, -30 $^\circ\text{C}$) and dried *in vacuo*.

Yield: 180 mg (83%).

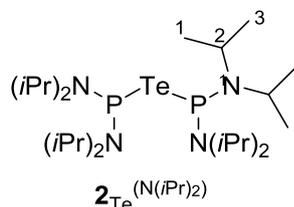
Mp.: 140-141 $^\circ\text{C}$; **Raman** (21 mW, 700 scans, 300 K, in cm^{-1}): 2964(69), 2923(100), 2867(39), 2701(10), 2186(6), 2138(6), 1454(39), 1391(82), 1351(14), 1316(10), 1115(20), 965(8), 931(18), 865(31), 621(37), 533(12), 377(16), 346(20), 276(24), 181(20), 128(18), 84(76); **IR** (300 K, ATR, in cm^{-1}): 3586(vs), 2960(w), 2924(w), 2866(m), 2703(vs), 2605(vs), 2351(s), 2326(s), 2164(vs), 2069(vs), 2048(vs), 2008(vs), 1977(vs), 1670(vs), 1636(vs), 1587(vs), 1542(vs), 1508(vs), 1453(m), 1360(w), 1306(s), 1194(w), 1177(w), 1158(vw), 1112(vw), 947(w), 845(w), 636(w), 618(m); **^1H NMR** (CD_2Cl_2 , 300 K, in ppm): $\delta = 3.60$ (8H, sept., $^3J_{\text{HH}} = 6.55$ Hz, C2-H), 1.23 (24H, d, $^3J_{\text{HH}} = 6.55$ Hz, C1-H), 1.20 (24H, d, $^3J_{\text{HH}} = 6.55$ Hz, C3-H), **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CD_2Cl_2 , 300 K, in ppm): $\delta = 49.3$ (8C, t, $^2J_{CP} = 5.7$ Hz, C2), 24.5 (8C, t, $^3J_{CP} = 2.6$ Hz, C3), 24.0 (8C, t, $^3J_{CP} = 6.4$ Hz, C1); **$^{31}\text{P}\{^1\text{H}\}$ NMR** (CD_2Cl_2 , 300 K, in ppm): $\delta = 96.8$ (s, $^1J_{PSe} = -264.4$ Hz). Data is consistent with that presented in ref.^[20].

2.23 Synthesis of tetrakis(pentafluorophenyl)diphosphanyselane ($1_{\text{Se}}^{(\text{C}_6\text{F}_5)}$)


$(\text{Me}_3\text{Si})_2\text{Se}$ (225.3 mg, 1.00 mmol) was added to a solution of $(\text{C}_6\text{F}_5)_2\text{PCl}$ (800.0 mg, 2.00 mmol) in CH_3CN (10 mL) and was stirred for 12 h at rt. All volatiles were removed *in vacuo*. The resulting colorless solid was recrystallized in CH_2Cl_2 / *n*-pentane at -30 °C and dried *in vacuo*.

Yield: 477.4 mg (59%).

Mp.: decomp.: 108 °C; **Raman (37 mW, 700 scans, 300 K, in cm^{-1}):** 1641(100), 1396(40), 1385(14), 1291(19), 1142(5), 846(12), 832(49), 585(70), 506(40), 446(44), 432(74), 419(5), 395(42), 384(9), 370(7), 359(22), 315(12), 284(7), 240(12), 221(16), 153(26), 97(30), 77(93); **IR (300 K, ATR, in cm^{-1}):** 2924(vw), 2432(vw), 2222(vw), 1979(vw), 1730(vw), 1641(m), 1589(vw), 1515(m), 1466(vs), 1384(m), 1291(s), 1144(w), 1084(vs), 1031(w), 1010(w), 971(vs), 845(m), 830(w), 764(w), 751(vw), 727(w), 634(w), 626(vw); **$^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = -127.9$ (8F, m, $^3J_{\text{FP}} = 17.9$ Hz, $^3J_{\text{FF}} = 21.3$ Hz, C2–F), -148.7 (4F, t, $^3J_{\text{FF}} = 21.3$ Hz, C4–F), -160.4 (8F, t, $^3J_{\text{FF}} = 21.3$ Hz, C3–F); **$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 147.2$ (8C, dm, $^1J_{\text{CF}} = 246.8$ Hz, C2), 143.2 (4C, dm, $^1J_{\text{CF}} = 258.4$ Hz, C4), 137.7 (8C, dm, $^1J_{\text{CF}} = 253.2$ Hz, C3), 108.4 (4C, m, C1); **$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = -25.1$ (nonett, $^3J_{\text{PF}} = 17.9$ Hz); **^{77}Se NMR (CD_2Cl_2 , 300 K, in ppm):** $\delta = 304.5$ (t of nonetts, $^1J_{\text{SeP}} = -185$ Hz, $^4J_{\text{SeF}} = 30$ Hz); **elemental analysis:** calculated for $\text{C}_{24}\text{F}_{20}\text{P}_2\text{Se}$: C: 35.63, H: –, N: –, found: C: 35.24, H: <0.10, N: <0.10.

2.24 Synthesis of tetrakis(di-*iso*-propylamino)diphosphanytellane ($2_{\text{Te}}^{(\text{N}(\text{iPr})_2)}$)


$((\text{iPr})_2\text{N})_2\text{PCl}$ (1.33 g, 5.00 mmol) was added to a suspension of Na_2Te (434.0 mg, 2.50 mmol) in CH_3CN (25 mL) and the orange suspension was stirred for 3 h at rt. CH_2Cl_2 (25 mL) was added to dissolve the product. The suspension was filtered over Celite and the volume of the filtrate was reduced *in vacuo*. The saturated solution

was layered with CH_3CN (12 mL) and stored at -30 °C, yielding orange crystals, which were dried *in vacuo*. $^{31}\text{P}\{^1\text{H}\}$ NMR analysis of the solid shows purity of 90%, accompanied by a side product, which might be the intermediate $[((\text{iPr})_2\text{N})\text{P}]\text{Te}^-$ ($^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 102.6$ (s, $^1J_{\text{PTe}(125)} = -485$ Hz), indicating incomplete reaction.

^1H NMR (CD_2Cl_2 , 300 K, in ppm): 3.54 (8H, sept., $^3J_{\text{HH}} = 6.37$ Hz, C2–H), 1.21 (24H, d, $^3J_{\text{HH}} = 6.37$ Hz, C1–H), 1.20 (24H, d, $^3J_{\text{HH}} = 6.37$ Hz, C3–H), $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 51.0$ (8C, t, $^2J_{\text{CP}} = 5.5$ Hz, C2), 24.5 (8C, t, $^3J_{\text{CP}} = 2.9$ Hz, C1/C3), 22.6 (8C, t, $^3J_{\text{CP}} = 6.4$ Hz, C1/C3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 92.5$ (s, $^1J_{\text{PTe}(125)} = -558$ Hz, $^1J_{\text{PTe}(129)} = -463$ Hz); Data is consistent with that presented in ref.^[20].

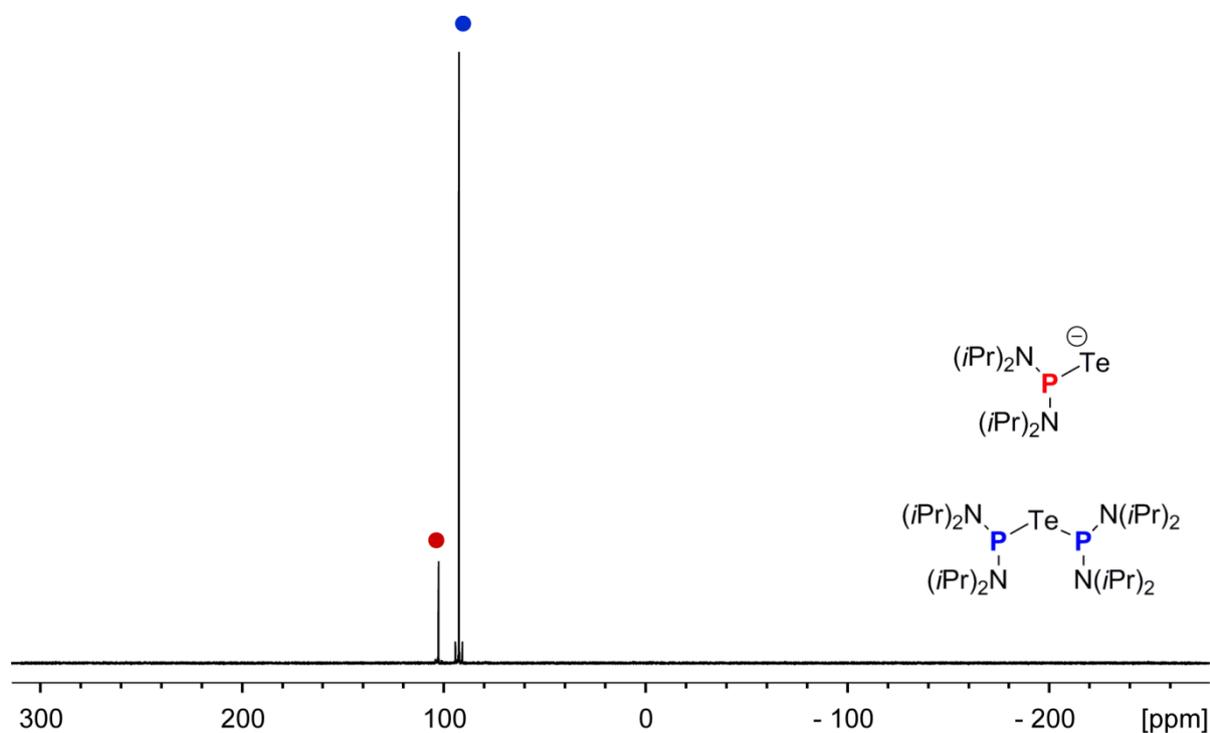
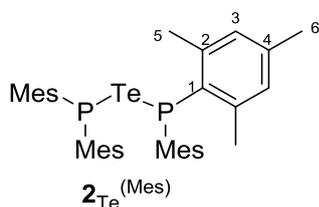


Figure S2.24.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture to yield $\mathbf{1}_{\text{Te}}^{(\text{N}(\text{iPr})_2)}$; contains ~10% of a side product, which might be the intermediate $[\text{Te}(\text{iPr})_2\text{P}]$ (CD_2Cl_2 , 300 K).

2.25 Synthesis of tetramesityldiphosphanyl tellane ($\mathbf{2}_{\text{Te}}^{(\text{Mes})}$)



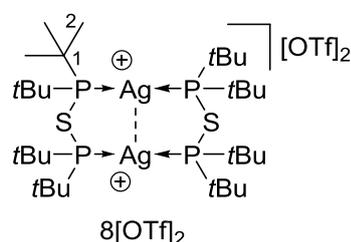
$(\text{Mes})_2\text{PCl}$ (914.4 mg, 3.00 mmol) was added to a suspension of Na_2Te (260.4 mg, 1.50 mmol) in a CH_3CN / toluene mixture (5 mL / 20 mL) and was stirred for 6 h at rt. The orange suspension was filtered over Celite and the filtrate was concentrated *in vacuo*. The resulting orange precipitation was

recrystallized in toluene / CH_3CN , resulting in orange crystals, which were dried *in vacuo*.

Yield: 179.6 mg, 54%; **mp.:** Decomp. 125 °C; **IR (300 K, ATR, in cm^{-1}):** 2958(vw), 2916(w), 2361(vw), 2089(vw), 1987(vw), 1954(vw), 1724(w), 1600(w), 1550(w), 1443(s), 1400(w), 1372(w), 1288(w), 1237(vw), 1026(m), 880(vw), 845(vs), 730(vw), 710(w), 616(w); **Raman (25 mW, 700 scans, 300 K, in cm^{-1}):** 2913(61), 1603(80), 1461(14),

1380(21), 1289(61), 1178(7), 1048(52), 617(8), 601(14), 574(20), 554(10), 412(25), 327(17), 171(20), 91(100); $^1\text{H NMR}$ (C_6D_6 , 300 K, in ppm): $\delta = 6.66$ (8H, s, C3–H), 2.49 (24H, s, C5–H), 2.06 (12H, s, C6–H); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 300 K, in ppm): $\delta = 142.2$ (8C, t, $^2J_{\text{CP}} = 8.2$ Hz, C2), 138.2 (4C, s, C4), 134.4 (4C, t, $^1J_{\text{CP}} = 18.6$ Hz, C1), 130.6 (8C, s, C3), 24.7 (8C, t, $^3J_{\text{CP}} = 7.4$ Hz, C5), 21.2 (4C, s, C6); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 300 K, in ppm): $\delta = -18.5$ (s, $^1J_{\text{PTe}(125)} = -413$ Hz, $^1J_{\text{PTe}(123)} = -344$ Hz); ^{125}Te NMR (C_6D_6 , 300 K, in ppm): $\delta = 527.1$ (t, $^1J_{\text{PTe}(125)} = -413$ Hz); **elemental analysis**: calculated for $\text{C}_{36}\text{H}_{44}\text{P}_2\text{Te}$: C 64.90, H: 6.66, N: -, S: - found: C: 64.71, H: 6.45, N: 0.10, S: 0.19.

2.26 Synthesis of the Ag-Complex $8[\text{OTf}]_2$



AgOTf (257.0 mg, 1.0 mmol) was added to a solution of $2_{\text{S}}^{\text{(tBu)}}$ in CH_2Cl_2 (4 mL) and the colorless solution was stirred for 2 h at rt. All volatiles were removed *in vacuo*, yielding a colorless solid, which was recrystallized in fluorobenzene / CH_2Cl_2 at -30 °C.

Yield: 981.4 mg, (82%).

Mp.: Decomp. 140 °C; **IR** (300K, ATR: in cm^{-1}): 2949(vw), 2867(vw), 1590(vw), 1474(w), 1394(w), 1369(w), 1283(m), 1237(w), 1219(w), 1169(vw), 1147(m), 1023(s), 938(vw), 804(w), 767(w), 754(vw), 689(vw), 634(vs); $^1\text{H NMR}$ (CD_2Cl_2 , 300 K, in ppm): $\delta = 1.57$ (36H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 121.4$ (2C, q, $^1J_{\text{CF}} = 322.8$ Hz, CF_3), 42.5 (8C, s, C1), 30.9 (24C, s, C2); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): $\delta = 123.2$ -119.8 (m); **Raman** (40 mW, 400 scans, 300 K, in cm^{-1}): 2905(17), 2905(49), 2867(14), 2781(11), 2721(11), 1471(31), 1443(14), 1396(9), 1372(9), 1211(9), 1174(23), 1026(86), 1001(11), 938(29), 805(86), 757(31), 599(11), 575(100), 518(9), 484(9), 384(9), 348(29); **elemental analysis**: calculated for $\text{C}_{37}\text{H}_{80}\text{Ag}_2\text{F}_6\text{O}_6\text{P}_4\text{S}_4 \cdot 0.5 \text{C}_6\text{H}_5\text{F}$: C 38.41, H: 6.65, N: -, S: 10.25, found: C: 38.44, H: 5.97, N: 0.04, S: 10.33.

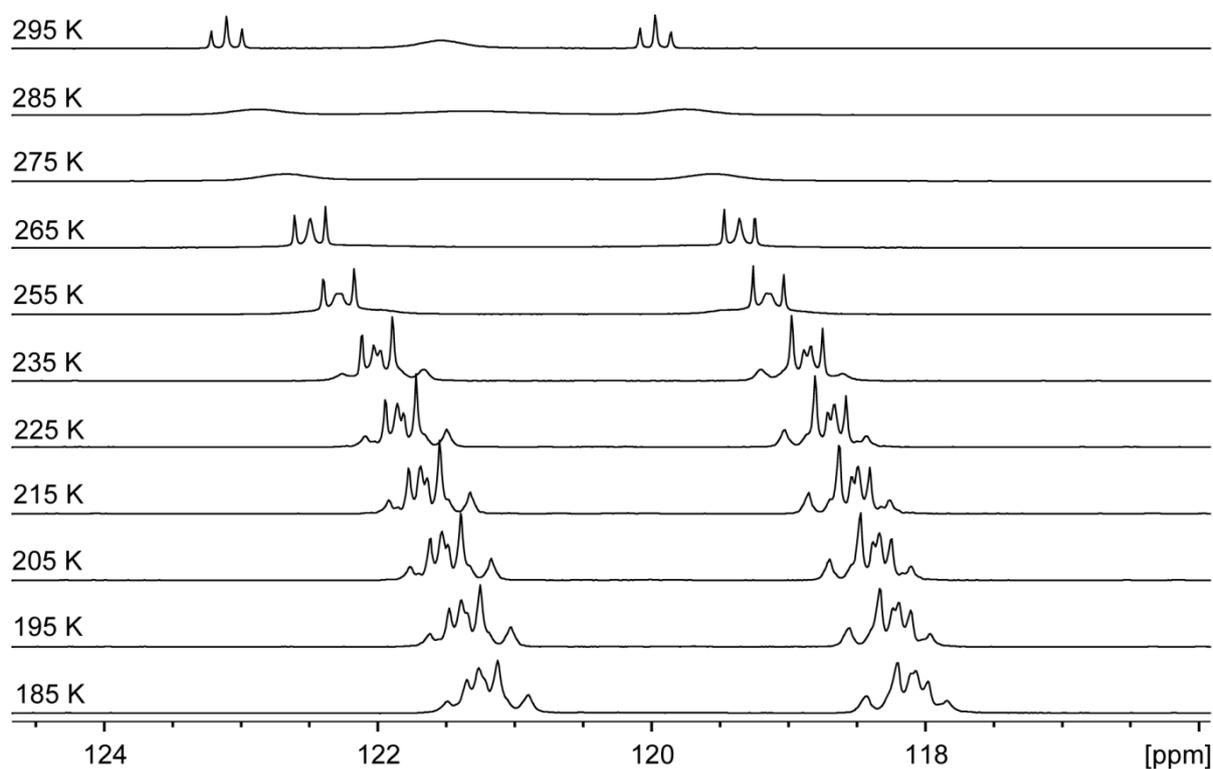
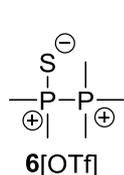


Figure S2.26.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **8**[OTf] $_2$ at different temperatures (CD_2Cl_2 , 185–295 K; 245 K is excluded).

2.27 Synthesis of **6**[OTf]



MeOTf (21.9 μL , 0.2 mmol) was added to a solution of **1** $_s^{(\text{Me})}$ (40.21 mg, 0.2 mmol) in CH_2Cl_2 (2 mL) and the clear solution was stirred for 30 minutes at room temperature. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture showed almost quantitative formation (~94%) of **5**[OTf].

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 300 K, in ppm): AM spin system: $\delta(\text{P}_M) = 38.2$ (d, $^1J_{\text{PP}} = -46.1$ Hz), $\delta(\text{P}_A) = 16.2$ (d, $^1J_{\text{PP}} = -46.1$ Hz). Data is consistent with that presented in ref.^[21]. Isolation of the product was not attempted.

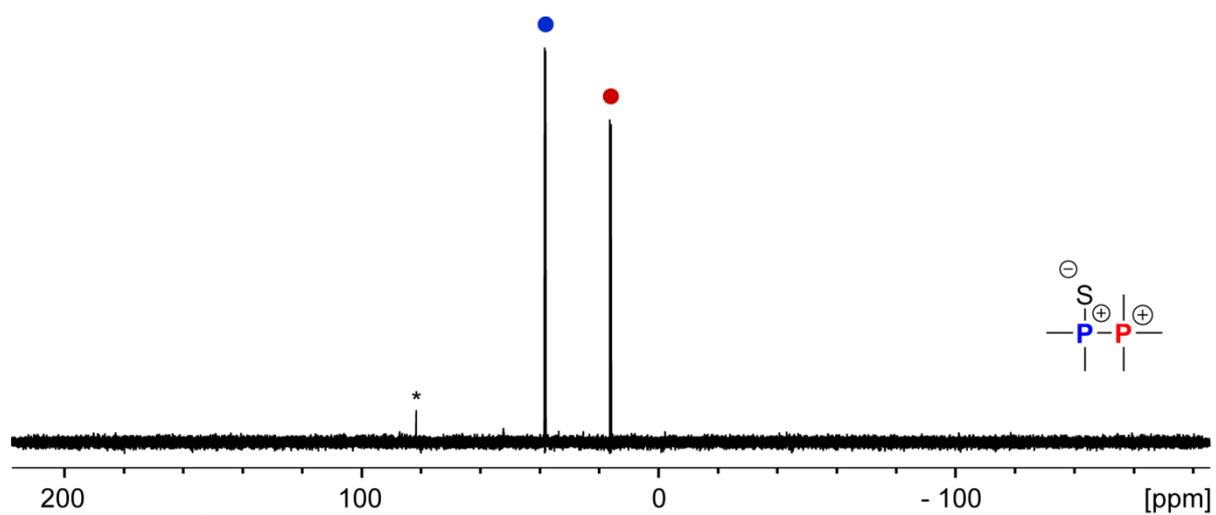


Figure S2.27.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction yielding **5[OTf]** (CD_2Cl_2 , 300 K); unidentified side product are marked with asterisks (*).

3 Crystallographic Details

Table 3.1 Crystallographic data and details of the structure refinements of compounds $\mathbf{1}_{\text{Se}}^{(\text{Me})}$, $\mathbf{1}_{\text{Se}}^{(\text{Ph})}$ and $\mathbf{2}_{\text{S}}^{(\text{tBu})}$.

	$\mathbf{1}_{\text{Se}}^{(\text{Me})}$	$\mathbf{1}_{\text{Se}}^{(\text{Ph})}$	$\mathbf{2}_{\text{S}}^{(\text{tBu})}$
formula	$\text{C}_4\text{H}_{12}\text{P}_2\text{Se}$	$\text{C}_{24}\text{H}_{20}\text{P}_2\text{Se}$	$\text{C}_{16}\text{H}_{36}\text{P}_2\text{S}$
M_r in g mol^{-1}	201.04	449.30	322.45
color, habit	colorless, block	yellow, plate	colorless, prism
crystal system	tetragonal	monoclinic	orthorhombic
space group	$P4_2/mbc$	$P2_1/c$	$P2_12_12_1$
a in \AA	12.5722(6)	9.2358(6)	8.8297(3)
b in \AA	12.5722(6)	13.6734(9)	14.8981(6)
c in \AA	10.7752(5)	16.3139(10)	15.2255(6)
α in $^\circ$	90	90	90
β in $^\circ$	90	91.974(2)	90
γ in $^\circ$	90	90	90
V in \AA^3	1703.1(1)	2059.0(2)	2002.84(13)
Z	8	4	4
T in K	153(2)	153(2)	123.01(10)
crystal size in mm^3	0.24 x 0.21 x 0.18	0.31 x 0.30 x 0.29	0.1 x 0.05 x 0.05
ρ_c in g cm^{-3}	1.568	1.449	1.069
$F(000)$	800	912	712.0
$\lambda_{\text{XK}\alpha}$ in \AA	0.71073	0.71073	1.54184
θ_{min} in $^\circ$	2.29	1.94	4.152
θ_{max} in $^\circ$	27.86	22.88	73.431
index range	$-16 \leq h \leq 16$ $-16 \leq k \leq 16$ $-14 \leq l \leq 14$	$-12 \leq h \leq 12$ $-17 \leq k \leq 17$ $-18 \leq l \leq 21$	$-10 \leq h \leq 7$ $-18 \leq k \leq 15$ $-18 \leq l \leq 17$
μ in mm^{-1}	4.689	1.985	2.834
absorption correction	multi-scan	multi-scan	multi-scan
reflections collected	15850	16724	9558
reflections unique	1077	4896	3710
R_{int}	0.0391	0.0265	0.0460
reflection obs. [$F > 2\sigma(F)$]	1046	4342	3422
residual density in e \AA^{-3}	1.06, -0.70	0.58, -0.24	1.185, -0.291
parameters	40	244	172
GOOF	1.083	1.083	1.071
R_1 [$I > 2\sigma(I)$]	0.0272	0.0291	0.0665
wR_2 (all data)	0.0783	0.0855	0.1787
CCDC	1059838	1059830	1059834

Table 3.2 Crystallographic data and details of the structure refinements of compounds $2_{\text{Se}}^{(\text{tBu})}$, $2_{\text{S}}^{(\text{Mes})}$ and $2_{\text{Se}}^{(\text{Mes})}$.

	$2_{\text{Se}}^{(\text{tBu})}$	$2_{\text{S}}^{(\text{Mes})}$	$2_{\text{Se}}^{(\text{Mes})}$
formula	$\text{C}_{16}\text{H}_{36}\text{P}_2\text{Se}$	$\text{C}_{77}\text{H}_{100}\text{P}_4\text{S}_2$	$\text{C}_{36}\text{H}_{44}\text{P}_2\text{Se}$
M_r in g mol^{-1}	369.35	1213.56	617.61
color, habit	colorless, plate	colorless, block	colorless, block
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1$	$P-1$	$P-1$
a in Å	8.8123(5)	11.7496(2)	10.8068(6)
b in Å	15.0897(8)	11.9819(2)	11.3444(7)
c in Å	15.0874(8)	13.2734(3)	13.3042(6)
α in $^\circ$	90	84.780(1)	81.832(2)
β in $^\circ$	91.709(2)	82.927(1)	80.203(2)
γ in $^\circ$	90	70.046(1)	83.225(2)
V in Å ³	2005.35(19)	1740.71(6)	1583.59(15)
Z	4	1	2
T in K	153(2)	153.15	100.01
crystal size in mm ³	0.33 x 0.31 x 0.29	0.30 x 0.22 x 0.20	0.37 x 0.28 x 0.14
ρ_c in g cm^{-3}	1.223	1.158	1.295
F(000)	784	654	648.0
$\lambda_{\text{XK}\alpha}$ in Å	0.71073	0.71073	0.71073
θ_{min} in $^\circ$	1.91	3.097	1.565
θ_{max} in $^\circ$	27.88	29.133	30.018
index range	-11 ≤ h ≤ 11 -19 ≤ k ≤ 19 -19 ≤ l ≤ 19	-16 ≤ h ≤ 16 -16 ≤ k ≤ 16 -18 ≤ l ≤ 18	-15 ≤ h ≤ 15 -15 ≤ k ≤ 15 -18 ≤ l ≤ 18
μ in mm^{-1}	2.022	0.210	1.310
absorption correction	multi-scan	multi-scan	multi-scan
reflections collected	25077	24051	63643
reflections unique	9535	9304	9191
R_{int}	0.0274	0.0201	0.0314
reflection obs. [F > 2σ(F)]	9051	7674	7920
residual density in e Å^{-3}	0.44, -0.34	1.405, -0.427	0.766, -0.456
parameters	367	439	364
GOOF	1.098	1.029	1.158
R_1 [I > 2σ(I)]	0.0264	0.0582	0.0282
wR_2 (all data)	0.0724	0.1686	0.0789
CCDC	1059831	1059835	1059836

Table 3.3 Crystallographic data and details of the structure refinements of compounds $\mathbf{2}_{\text{Te}}^{(\text{Mes})}$, $\mathbf{2}_{\text{Se}}^{(\text{N}(i\text{Pr})_2)}$ and $\mathbf{2}_{\text{S}}^{(\text{C}_6\text{F}_5)}$.

	$\mathbf{2}_{\text{Te}}^{(\text{Mes})}$	$\mathbf{2}_{\text{Se}}^{(\text{N}(i\text{Pr})_2)}$	$\mathbf{2}_{\text{S}}^{(\text{C}_6\text{F}_5)}$
formula	$\text{C}_{36}\text{H}_{44}\text{P}_2\text{Te}$	$\text{C}_{24}\text{H}_{56}\text{N}_4\text{P}_2\text{Se}$	$\text{C}_{38}\text{H}_{16}\text{F}_{20}\text{P}_2\text{S}$
M_r in g mol^{-1}	666.25	541.62	946.52
color, habit	orange, block	colorless, plate	colorless, prism
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2/n$
a in Å	20.1473(15)	23.7312(13)	11.5930(1)
b in Å	15.0130(13)	7.6556(4)	7.37622(9)
c in Å	22.7599(17)	17.9381(10)	21.8527(3)
α in °	90	90	90
β in °	111.289(3)	109.237(6)	102.186(1)
γ in °	90	90	90
V in Å ³	6414.4(9)	3077.0(3)	1826.57(4)
Z	8	4	2
T in K	153(2)	123	123.0(2)
crystal size in mm ³	0.2 x 0.14 x 0.09	0.13 x 0.07 x 0.02	0.28 x 0.05 x 0.03
ρ_c in g cm^{-3}	1.380	1.169	1.721
F(000)	2736.0	1168:0	940
$\lambda_{\text{XK}\alpha}$ in Å	0.71073	1.54184	1.54184
θ_{min} in °	2.17	3.946	4.012
θ_{max} in °	55.068	73.534	73.468
index range	-19 ≤ h ≤ 26 -19 ≤ k ≤ 16 -29 ≤ l ≤ 29	-28 ≤ h ≤ 29 -8 ≤ k ≤ 9 -22 ≤ l ≤ 21	-14 ≤ h ≤ 14 -9 ≤ k ≤ 7 -26 ≤ l ≤ 26
μ in mm^{-1}	1.050	2.749	2.860
absorption correction	multi-scan	analytical	analytical
reflections collected	59652	13404	12231
reflections unique	9535	3054	3597
R_{int}	0.0284	0.0340	0.0216
reflection obs. [$F > 2\sigma(F)$]	9051	2766	3263
residual density in e Å^{-3}	0.51, -0.36	0.394, -0.296	0.264, -0.265
parameters	727	141	276
GOOF	1.025	1.040	1.043
R_1 [$I > 2\sigma(I)$]	0.0285	0.0261	0.0276
wR_2 (all data)	0.0687	0.0655	0.0765
CCDC	1059832	1059837	1059833

Table 3.4 Crystallographic data and details of the structure refinements of compounds **2**_{Se}^(C₆F₅), **6** and **7**[OTf]₂.

	2 _{Se} ^(C₆F₅)	7	8 [OTf] ₂
formula	C ₃₈ H ₁₆ F ₂₀ P ₂ Se	C ₂₈ H ₂₀ FeO ₃ P ₂ S	C ₄₀ H ₇₇ Ag ₂ F ₇ O ₆ P ₄ S ₄
<i>M_r</i> in g mol ⁻¹	993.41	570.29	1254.87
color, habit	colorless, block	yellow, plate	colorless, block
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P2</i> / <i>n</i>	<i>P2</i> ₁ / <i>n</i>	<i>P2</i> ₁ / <i>n</i>
<i>a</i> in Å	11.6006(5)	10.5488(2)	21.2723(7)
<i>b</i> in Å	7.3766(3)	16.6943(3)	12.0446(4)
<i>c</i> in Å	22.0520(10)	14.8681(3)	23.0396(8)
<i>α</i> in °	90	90	90
<i>β</i> in °	101.6672(17)	96.7590(10)	115.8090(10)
<i>γ</i> in °	90	90	90
<i>V</i> in Å ³	1848.07(14)	2600.15(9)	5314.3(3)
<i>Z</i>	2	4	4
<i>T</i> in K	153(2)	153(2)	173.15
crystal size in mm ³	0.2 x 0.11 x 0.09	0.34 x 0.20 x 0.18	0.34 x 0.25 x 0.25
<i>ρ_c</i> in g cm ⁻³	1.785	1.457	1.568
F(000)	976.0	1168	2584
<i>λ_{XKα}</i> in Å	0.71073	0.71073	0.71073
<i>θ_{min}</i> in °	4.376	1.84	1.089
<i>θ_{max}</i> in °	58.398	27.88	29.177
index range	-15 ≤ <i>h</i> ≤ 13 -9 ≤ <i>k</i> ≤ 10 -30 ≤ <i>l</i> ≤ 30	-13 ≤ <i>h</i> ≤ 11 -21 ≤ <i>k</i> ≤ 21 -19 ≤ <i>l</i> ≤ 19	-25 ≤ <i>h</i> ≤ 29 -9 ≤ <i>k</i> ≤ 16 -31 ≤ <i>l</i> ≤ 29
<i>μ</i> in mm ⁻¹	1.234	0.816	1.080
absorption correction	multi-scan	multi-scan	multi-scan
reflections collected	13723	25897	43029
reflections unique	4941	6191	14352
<i>R_{int}</i>	0.0190	0.0426	0.0161
reflection obs. [<i>F</i> > 2σ(<i>F</i>)]	4193	5042	12529
residual density in e Å ⁻³	0.31, -0.25	0.51, -0.61	0.83, -1.23
parameters	277	325	623
GOOF	1.033	1.181	1.181
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0282	0.0358	0.0249
<i>wR</i> ₂ (all data)	0.0702	0.1310	0.0858
CCDC	1059840	1059829	1059839

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