

Regioselective *versus* complete chalcogen transfer reactions of the bis(bidentate) phosphine *cis,trans,cis*-1,2,3,4-tetrakis-(diphenylphosphino)cyclobutane: full characterization of new, hemilabile ligands and their complexes with palladium(II) and platinum(II)

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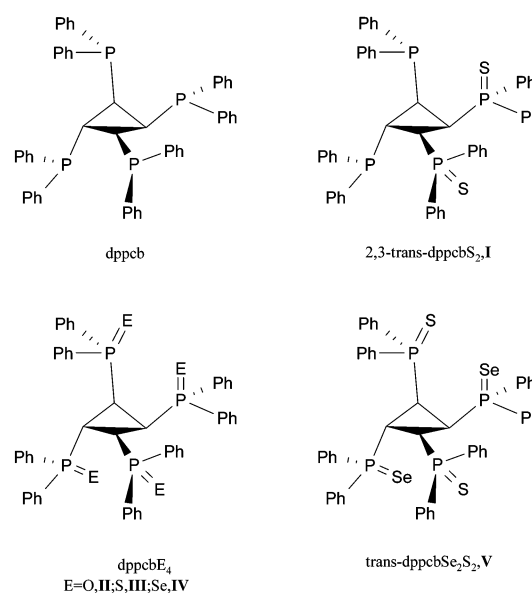
The bis(bidentate) phosphine *cis,trans,cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane (dppcb) has been regioselectively oxidized by sulfur to the novel, hemilabile disulfide *cis,trans,cis*-2,3-bis(diphenylphosphinothioyl)-1,4-bis(diphenylphosphino)cyclobutane (2,3-*trans*-dppcbS₂, **I**). Also the tetrachalcogenides *cis,trans,cis*-1,2,3,4-tetrakis(diphenylphosphinothioyl)cyclobutane (dppcbO₄, **II**), *cis,trans,cis*-1,2,3,4-tetrakis(diphenylphosphinothioyl)cyclobutane (dppcbS₄, **III**), and *cis,trans,cis*-1,2,3,4-tetrakis(diphenylphosphinoselenoyl)cyclobutane (dppcbSe₄, **IV**) have been obtained. Regioselective selenization of the previously prepared disulfide *cis,trans,cis*-1,3-bis(diphenylphosphinothioyl)-2,4-bis(diphenylphosphino)cyclobutane (1,3-*trans*-dppcbS₂) leads to the unique, mixed chalcogenide *cis,trans,cis*-1,3-bis(diphenylphosphinoselenoyl)-2,4-bis(diphenylphosphinothioyl)cyclobutane (*trans*-dppcbSe₂S₂, **V**). All of the new ligands **I–V** have been fully characterized by X-ray structure analyses showing folded cyclobutane rings. The coordination chemistry of the previously prepared hemilabile diselenide *cis,trans,cis*-1,3-bis(diphenylphosphinoselenoyl)-2,4-bis(diphenylphosphino)cyclobutane (1,3-*trans*-dppcbSe₂), 1,3-*trans*-dppcbS₂, **I**, **III**, and **IV** with PdCl₂ or PtCl₂ has been studied. The novel complexes [Pd₂Cl₄(1,3-*trans*-dppcbSe₂-P,P',Se,Se')] (**1**), [Pt₂Cl₄(1,3-*trans*-dppcbS₂-P,P',S,S')] (**2**), [PtCl₂(2,3-*trans*-dppcbS₂-P,P')] (**3**), [Pt₂Cl₄(dppcbS₄-S,S',S',S'')] (**4**), [PtCl₂(2,3-*trans*-dppcbSe₂-P,P')] (**5**), and [Pt₂Cl₄(2,3-*trans*-dppcbSe₂-P,P',Se,Se')] (**6**) have been obtained. **6** has been fully characterized by an X-ray structure analysis.

Introduction

Though new classes of unsymmetrical bidentate hemilabile ligands were recently developed and used in organometallic chemistry, which associate the phosphorus atom with donor atoms such as oxygen, nitrogen or sulfur,¹ particularly few reports exist on selenium. Especially in the case of selenium the chemistry of hypercoordination continues to be an active research field.² Furthermore, selenium would be better suited than sulfur as a protecting group for P^{III} when this is required.³ Due to the different donor/acceptor properties of the two Lewis basic centres of a bidentate hemilabile ligand, its reactions are highly selective and no isomers of the resulting complexes are observed.⁴ Valuable hemilabile ligands have proven usefulness in homogeneous catalysis, analytical chemistry, cancer and AIDS research, chemistry of materials, *etc.*⁵ Particularly tertiary phosphine chalcogenides have been used in extraction, catalysis and biochemical studies and it appears a greater effort is needed in investigating further applications of these ligands.⁶

In this work a comparative study of O, S, and Se transfer reactions of the bis(bidentate) phosphine *cis,trans,cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane (dppcb) and the resulting complexes is given. Examples of the coordination chemistry of dppcb itself and its applicability to homogeneous catalysis and photochemical devices have been given recently.⁷ Furthermore, the heterodifunctional, hemilabile ligands *cis,trans,cis*-1,3-bis(diphenylphosphinothioyl)-2,4-bis(diphenylphosphino)cyclobutane (1,3-*trans*-dppcbS₂) and *cis,trans,cis*-1,3-bis(diphenylphosphinoselenoyl)-2,4-bis(diphenylphosphino)cyclobutane (1,3-*trans*-dppcbSe₂), obtained via the first regioselective sulfurization or selenization of a bis(bidentate) phosphine, have also been presented only recently.⁸ Following these initial reports of S and Se transfer reactions of dppcb, our

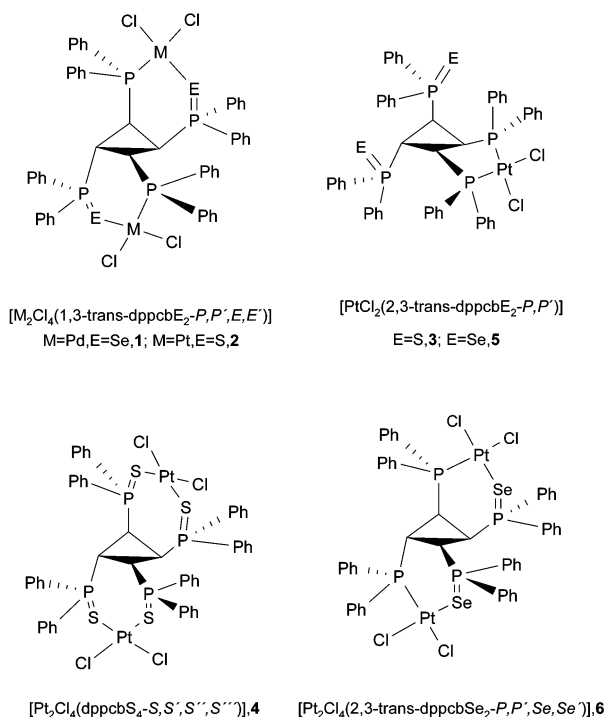
group has prepared the five new ligands *cis,trans,cis*-2,3-bis(diphenylphosphinothioyl)-1,4-bis(diphenylphosphino)cyclobutane (2,3-*trans*-dppcbS₂, **I**),⁹ *cis,trans,cis*-1,2,3,4-tetrakis(diphenylphosphinothioyl)cyclobutane (dppcbO₄, **II**), *cis,trans,cis*-1,2,3,4-tetrakis(diphenylphosphinothioyl)cyclobutane (dppcbS₄, **III**), *cis,trans,cis*-1,2,3,4-tetrakis(diphenylphosphinoselenoyl)cyclobutane (dppcbSe₄, **IV**), and *cis,trans,cis*-1,3-bis(diphenylphosphinoselenoyl)-2,4-bis(diphenylphosphinothioyl)cyclobutane (*trans*-dppcbSe₂S₂, **V**) (Scheme 1). The



Scheme 1

pure isolation of **I** from a reaction mixture of seven possible compounds⁸ and the production of regioselectively pure **V** are unique, where for example the reaction of bis(2,2-bis(diphenylphosphino)ethyl)phenylphosphine with elemental sulfur simultaneously gives nine from a possible total of 19 different phosphine sulfides and only the pentasulfide has been isolated.¹⁰ The new ligands **II–IV** are comparable to $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$ (E = O, S or Se), which have found important uses as selective metal extractants, NMR shift reagents and in catalysis.¹¹

Since there seems to be general belief that the ring closure driving force for six-membered rings is weak and the formation of seven-membered rings must compete with other reaction pathways, in particular with the possibility of obtaining polynuclear species,¹ a study of the coordination properties of the ligands presented herein is interesting. This allows the comparison of oxygen and sulfur *versus* selenium as the donor set in a series of bis(bidentate) chelates, where similar studies for $\text{Ph}_2\text{P}(\text{E})\text{NHP}(\text{E})\text{Ph}_2$ (E = O, S or Se) have been presented.¹² The use of comparable ligands as promoters in oxidation, water–gas shift reaction, and as catalysts in the polymerization of olefins and hydrogenation reactions, promise further applications of their complexes.⁶ Herein, we present the new complexes $[\text{Pd}_2\text{Cl}_4(1,3\text{-trans-dppcbSe}_2\text{-P,P',Se,Se}')]$ (**1**), $[\text{Pt}_2\text{Cl}_4(1,3\text{-trans-dppcbS}_2\text{-P,P',S,S}')]$ (**2**), $[\text{PtCl}_2(2,3\text{-trans-dppcbS}_2\text{-P,P}')]$ (**3**), $[\text{Pt}_2\text{Cl}_4(\text{dppcbS}_4\text{-S,S',S'',S'''})]$ (**4**), $[\text{PtCl}_2(2,3\text{-trans-dppcbSe}_2\text{-P,P}')]$ (**5**), and $[\text{Pt}_2\text{Cl}_4(2,3\text{-trans-dppcbSe}_2\text{-P,P',Se,Se}')]$ (**6**) (Scheme 2). During the formation of **5** or **6** the new, hemilabile ligand *cis,trans,cis*-2,3-bis(diphenylphosphinoselenoyl)-1,4-bis(diphenylphosphino)cyclobutane (2,3-*trans*-dppcbSe₂) is produced. In the case of sulfur, the transfer of sulfur atoms from tertiary phosphine sulfides to more basic phosphine molecules is well documented, and finds numerous synthetic applications.¹³ However, migration or elimination reactions of selenium leading to pure compounds like **5** or **6** are rare.¹⁴



Experimental

Reagents and general procedures

Dppcb, 1,3-*trans*-dppcbS₂, and 1,3-*trans*-dppcbSe₂ were prepared as described earlier.^{7,8} PdCl₂, PtCl₂, and elemental

sulfur and selenium of purissimum grade quality were purchased from Aldrich. Dry solvents of purissimum grade quality and 30% H₂O₂ were obtained from Fluka. A Schlenk apparatus and oxygen-free, dry Ar were used in the syntheses of all ligands and complexes. Solvents were degassed by several freeze–pump–thaw cycles prior to use.

Instrumentation

Fourier-mode ¹⁹⁵Pt{¹H}, ⁷⁷Se{¹H}, ³¹P{¹H}, ¹³C{¹H} and ¹H NMR spectra were obtained using a Bruker DPX-300 spectrometer (internal deuterium lock). Positive chemical shifts are downfield from the standards: 1.0 M Na₂PtCl₆ for the ¹⁹⁵Pt{¹H}, (CH₃)₂Se for the ⁷⁷Se{¹H}, 85% H₃PO₄ for the ³¹P{¹H}, and TMS for the ¹³C{¹H} and ¹H resonances.

Syntheses

2,3-*trans*-dppcbS₂ (I). Dppcb (0.50 g, 0.63 mmol) was dissolved in toluene (150 mL) and sulfur (0.040 g, 1.26 mmol) was added with vigorous stirring. The reaction mixture was stirred at ambient temperature for 30 h and a clear solution was obtained. The solution was cooled down to 5 °C and after 3 days colourless crystals were filtered off. These crystals correspond to 1,3-*trans*-dppcbS₂.^{8b} The volume of the filtrate was reduced to 70 mL. The yellow–greenish solution was cooled down to 5 °C and after 10 days colourless crystals were filtered off and dried *in vacuo*. The crystals were recrystallized from dichloromethane–n-hexane at ambient temperature. (Yield: 0.089 g, 16%.) Mp 248–252 °C. (Found: C, 72.73; H, 5.31; S, 7.60; C₅₂H₄₄P₄S₂ requires C, 72.89; H, 5.18; S, 7.48%.) ³¹P{¹H} NMR (CH₂Cl₂): δ 39.9 (dd, P(S)Ph₂), –20.2 (dd, PPh₂), ³J(P,P) = 12 Hz, ⁴J(P,P) = 6 Hz. Positive ion FAB-MS: *m/z* (*m/z*_{calcd}) 857.2 (856.9) [M]⁺, 825.2 (824.8) [M – S]⁺, 779.1 (778.8) [M – H – Ph]⁺, 671.0 (670.7) [M – H – PPh₂]⁺, 639.0 (638.7) [M – H – P(S)Ph₂]⁺. Single crystals suitable for an X-ray structure analysis with the composition 2,3-*trans*-dppcbS₂ were obtained from a CH₂Cl₂ solution of 2,3-*trans*-dppcbS₂ *via* gas-phase diffusion of CH₂Cl₂ into n-hexane under reduced pressure and at ambient temperature.

dppcbO₄ (II). Dppcb (0.10 g, 0.126 mmol) was dissolved in DMF (4 mL) and 30 mL of 30% H₂O₂ was added drop by drop with vigorous stirring at ambient temperature. A white voluminous precipitate formed. It was filtered off, washed with DMF and water, and dried *in vacuo*. A white powder was recrystallized from a 1 : 2 DMF–water mixture. (Yield: 0.090 g, 83%.) Mp 264–267 °C. (Found: C, 72.78; H, 5.23; O, 7.25; C₅₂H₄₄O₄P₄ requires C, 72.90; H, 5.18; O, 7.47%.) ³¹P{¹H} NMR (CH₂Cl₂): δ 25.9 (s). Positive ion FAB-MS: *m/z* (*m/z*_{calcd}) 858.0 (857.8) [M + H]⁺, 780.2 (779.7) [M – Ph]⁺, 655.2 (655.6) [M – P(O)Ph₂]⁺. Single crystals suitable for an X-ray structure analysis with the composition dppcbO₄·toluene were obtained from a toluene solution of dppcbO₄ at ambient temperature.

dppcbS₄ (III). Powdered sulfur (0.022 g, 0.686 mmol) was dissolved in toluene (20 mL) at 50 °C and dppcb (0.100 g, 0.126 mmol) was added with vigorous stirring. The solution was stirred at 50 °C for 48 h. Then the solution was cooled down to 5 °C and after several days colourless crystals formed. They were filtered off, washed with toluene in order to remove excess sulfur and dried *in vacuo*. The volume of the filtrate was reduced to 10 mL and the crystallization procedure was repeated. (Overall yield: 0.085 g, 70%.) Mp 318–320 °C. (Found: C, 68.75; H, 5.11; S, 13.35; C₅₂H₄₄P₄S₄·0.5toluene requires C, 68.93; H, 5.01; S, 13.26%.) ³¹P{¹H} NMR (toluene): δ 43.2 (s, P_{axial}), 32.6 (s, P_{equatorial}). Positive ion FAB-MS: *m/z* (*m/z*_{calcd}) 921.3 (921.0) [M]⁺, 764.8 (764.8) [M – 2H – 2Ph]⁺, 703.2 (702.8) [M – H – P(S)Ph₂]⁺. Single crystals suitable for an X-ray structure analysis with the composition dppcbS₄·

0.5toluene were obtained from a toluene solution of dppcbS₄ at ambient temperature.

dppcbSe₄ (IV). Dppcb (0.100 g, 0.126 mmol) was dissolved in toluene (20 mL) and powdered selenium (0.060 g, 0.760 mmol) was added with vigorous stirring. The reaction mixture was stirred at 45 °C for 3 days. The slurry was filtered in order to remove excess selenium and the volume of the filtrate was reduced to 10 mL. The yellow–greenish solution was cooled down to 5 °C and after several days colourless crystals formed. They were filtered off, washed with toluene and dried *in vacuo*. The volume of the filtrate was reduced to 8 mL and the crystallization procedure was repeated. (Overall yield: 0.101 g, 69%.) Mp 295.7 °C (DSC under nitrogen). (Found: C, 57.63; H, 4.31; C₅₂H₄₄P₄Se₄·0.5toluene requires C, 57.73; H, 4.19%.) ⁷⁷Se{¹H} NMR (CH₂Cl₂): δ -373.5 (d, Se_{axial}, ¹J(Se,P) = -759 Hz), -400.7 (d, Se_{equatorial}, ¹J(Se,P) = -777 Hz). ³¹P{¹H} NMR (CH₂Cl₂): δ 38.2 (s, P_{axial}), 28.9 (s, P_{equatorial}). Positive ion FAB-MS: *m/z* (*m/z*_{calcd}) 1110.9 (1110.7) [M + 2H]⁺, 1032.2 (1031.7) [M + 2H - Se]⁺, 766.8 (766.6) [M + H - Se - P(Se)Ph₂]⁺. Single crystals suitable for an X-ray structure analysis with the composition dppcbSe₄·0.5toluene were obtained from a toluene solution of dppcbSe₄ at 55 °C.

trans-dppcbSe₂S₂ (V). Powdered selenium (0.039 g, 0.500 mmol) was suspended in toluene (20 mL) and 1,3-*trans*-dppcbS₂ (0.121 g, 0.141 mmol) dissolved in toluene (20 mL) was added with vigorous stirring. The reaction mixture was stirred at 65 °C for 5 days. The slurry was filtered in order to remove excess selenium and the volume of the filtrate was reduced to 10 mL. Then colourless crystals were obtained according to the procedure described in the case of IV. (Overall yield: 0.096 g, 64%.) Mp 310–314 °C. (Found: C, 62.70; H, 4.71; S, 6.15; C₅₂H₄₄P₄Se₂S₂·0.5toluene requires C, 62.83; H, 4.56; S, 6.04%.) ⁷⁷Se{¹H} NMR (CH₂Cl₂): δ -401.0 (d, Se_{axial}, ¹J(Se,P) = -740 Hz), -424.7 (d, Se_{equatorial}, ¹J(Se,P) = -790 Hz). ³¹P{¹H} NMR (CH₂Cl₂, 193 K): δ 40.9 (dd, P(S)_{axial}), 38.2 (dd, P(Se)_{axial}), 32.6 (d, P(S)_{equatorial}), 28.7 (d, P(Se)_{equatorial}), ³J(P(Se)_{axial}-P(S)_{axial}) = 28 Hz, ³J(P(Se)_{axial}-P(S)_{equatorial}) = ³J(P(S)_{axial}-P(Se)_{equatorial}) = 9 Hz. Positive ion FAB-MS: *m/z* (*m/z*_{calcd}) 1016.0 (1015.9) [M + H]⁺, 984.1 (983.8) [M + H - S]⁺, 952.1 (951.8) [M + H - 2S]⁺. Single crystals suitable for an X-ray structure analysis with the composition *trans*-dppcbSe₂S₂·0.5toluene were obtained from a toluene solution of *trans*-dppcbSe₂S₂ at ambient temperature.

[Pd₂Cl₄(1,3-*trans*-dppcbSe₂-P,P',Se,Se')] (1). 1,3-*trans*-dppcbSe₂ (0.143 g, 0.150 mmol) was dissolved in CH₂Cl₂ (30 mL) and PdCl₂ (0.053 g, 0.300 mmol) was added with vigorous stirring. The reaction mixture was stirred at 40 °C for 5 days with prevention of light. The slurry was filtered, and the solvent of the filtrate was completely removed. The brown residue was washed with toluene and dried *in vacuo*. A brown powder was recrystallized from CH₂Cl₂. (Yield: 0.088 g, 45%.) Mp > 190 °C dec. (Found: C, 47.96; H, 3.31; C₅₂H₄₄Cl₄P₄Pd₂Se₂ requires C, 47.85; H, 3.40%.) ³¹P{¹H} NMR (CH₂Cl₂): δ 58.1 (s), 33.4 (s, ¹J(Se,P) = -583 Hz). Positive ion FAB-MS: *m/z* (*m/z*_{calcd}) 1232.2 (1232.4) [M - 2HCl]⁺, 1127.1 (1127.0) [M - HCl - Cl - Pd]⁺, 1093.1 (1092.6) [M - 3Cl - Pd]⁺, 871.0 (870.8) [M - HCl - 3Cl - 2Pd - Se]⁺.

[Pt₂Cl₄(1,3-*trans*-dppcbS₂-P,P',S,S')] (2). 1,3-*trans*-dppcbS₂ (0.080 g, 0.093 mmol) was dissolved in CH₂Cl₂ (15 mL) and PtCl₂ (0.0495 g, 0.186 mmol) was added with vigorous stirring. The reaction mixture was stirred at 40 °C for 10 days. The slurry was filtered, and the solvent of the filtrate was completely removed producing a brown residue. A brown powder was recrystallized from CH₂Cl₂. (Yield: 0.081 g, 63%.) Mp > 320 °C. (Found: C, 45.10; H, 3.03; S, 4.75; C₅₂H₄₄Cl₄P₄Pt₂S₂ requires C,

44.97; H, 3.19; S, 4.62%.) ¹⁹⁵Pt{¹H} NMR (CH₂Cl₂): δ -3942.6 (dd, ¹J(Pt,P) = 3789 Hz, ²J(Pt,P) = 116 Hz). ³¹P{¹H} NMR (CH₂Cl₂, 310 K): δ 29.3 (dd, P(S)Ph₂), -4.7 (dd, PPh₂), ³J(P,P)*cis* = 31 Hz, ³J(P,P)*trans* = 7 Hz. Positive ion FAB-MS: *m/z* (*m/z*_{calcd}) 1387.6 (1387.9) [M - H]⁺, 1352.6 (1352.4) [M - HCl]⁺, 1316.1 (1316.0) [M - 2HCl]⁺, 1281.8 (1281.5) [M - HCl - 2Cl]⁺.

[PtCl₂(2,3-*trans*-dppcbS₂-P,P')] (3). 2,3-*trans*-dppcbS₂ (I, 0.064 g, 0.075 mmol) was dissolved in CH₂Cl₂ (25 mL) and PtCl₂ (0.020 g, 0.075 mmol) was added with vigorous stirring. Then compound 3 was prepared in an analogous manner to 2. (Yield: 0.040 g, 47%.) Mp > 320 °C. (Found: C, 55.80; H, 4.12; S, 5.83; C₅₂H₄₄Cl₂P₄PtS₂ requires C, 55.62; H, 3.95; S, 5.71%.) ¹⁹⁵Pt{¹H} NMR (CH₂Cl₂): δ -4470.3 (t, ¹J(Pt,P) = 3666 Hz). ³¹P{¹H} NMR (CH₂Cl₂): δ 40.1 (s, P(S)Ph₂), 32.4 (s, PPh₂). Positive ion FAB-MS: *m/z* (*m/z*_{calcd}) 1121.6 (1121.9) [M - H]⁺, 1086.7 (1086.5) [M - HCl]⁺.

[Pt₂Cl₄(dppcbS₄-S,S',S'',S''')] (4). DppcbS₄ (III, 0.068 g, 0.074 mmol) was dissolved in CH₂Cl₂ (10 mL) and PtCl₂ (0.0394 g, 0.148 mmol) was added with vigorous stirring. The reaction mixture was stirred at 40 °C for 10 days. Then the solvent was completely removed, and the residue was washed with toluene and dried *in vacuo*. DMF (10 mL) was added to the greyish brown powder and the slurry was stirred at ambient temperature for 20 h. The slurry was filtered, and the solvent of the filtrate was completely removed producing a brown powder. It was recrystallized from DMF/Et₂O. (Yield: 0.059 g, 55%.) Mp > 320 °C. (Found: C, 43.12; H, 3.25; S, 9.01; C₅₂H₄₄Cl₄P₄Pt₂S₄ requires C, 42.98; H, 3.05; S, 8.83%.) ³¹P{¹H} NMR (CH₂Cl₂): δ 33.9 (s, ²J(Pt,P) = 115 Hz). Positive ion ESI-MS: *m/z* (*m/z*_{calcd}) 1454.3 (1454.0) [M + H]⁺, 1416.2 (1416.6) [M - HCl]⁺, 1187.2 (1187.0) [M - PtCl₂]⁺, 1018.2 (1018.5) [M - 2P(S)Ph₂]⁺.

[PtCl₂(2,3-*trans*-dppcbSe₂-P,P')] (5). 1,3-*trans*-dppcbSe₂ (0.114 g, 0.120 mmol) was dissolved in CH₂Cl₂ (30 mL) and PtCl₂ (0.032 g, 0.120 mmol) was added with vigorous stirring. The reaction mixture was stirred at ambient temperature for 4 days. Then compound 5 was prepared in an analogous manner to 1. (Yield: 0.044 g, 30%.) Mp 294–296 °C. (Found: C, 51.15; H, 3.73; C₅₂H₄₄Cl₂P₄PtSe₂ requires C, 51.33; H, 3.65%.) ¹⁹⁵Pt{¹H} NMR (CH₂Cl₂): δ -4473.9 (t, ¹J(Pt,P) = 3664 Hz). ³¹P{¹H} NMR (CH₂Cl₂): δ 33.2 (s, P(Se)Ph₂), ¹J(Se,P) = -764 Hz), 32.5 (s, PPh₂). Positive ion FAB-MS: *m/z* (*m/z*_{calcd}) 1217.1 (1216.7) [M]⁺, 1181.1 (1181.3) [M - Cl]⁺, 1103.2 (1103.3) [M + H - Cl - Se]⁺, 1022.0 (1022.3) [M - HCl - 2Se]⁺.

[Pt₂Cl₄(2,3-*trans*-dppcbSe₂-P,P',Se,Se')] (6). DppcbSe₄ (IV, 0.150 g, 0.135 mmol) was dissolved in CH₂Cl₂ (20 mL) and PtCl₂ (0.0718 g, 0.270 mmol) dissolved in CHCl₃ (20 mL) was added with vigorous stirring. The solution was stirred at 50 °C for 6 days. Then the solvent was completely removed, and the dark brown residue was washed with toluene and dried *in vacuo*. A dark brown powder was recrystallized from CH₂Cl₂. (Yield: 0.072 g, 36%.) Mp > 320 °C dec. (Found: C, 41.97; H, 3.10; C₅₂H₄₄Cl₄P₄Pt₂Se₂ requires C, 42.12; H, 2.99%.) ³¹P{¹H} NMR (CH₂Cl₂): δ 12.5 (d, P(Se)Ph₂), ¹J(Se,P) = -604 Hz, ²J(Pt,P) = 121 Hz), 6.9 (d, PPh₂), ¹J(Pt,P) = 3780 Hz), ³J(P,P)*cis* = 26 Hz. Positive ion ESI-MS: *m/z* (*m/z*_{calcd}) 1483.9 (1483.7) [M + H]⁺, 1445.9 (1446.2) [M - HCl]⁺, 1404.8 (1404.7) [M + H - Se]⁺. Solutions of the dark brown residue in DMF contain a small amount of [Pt₂Cl₄(dppcb)], which is not soluble in CH₂Cl₂. Single crystals suitable for an X-ray structure analysis with the composition [Pt₂Cl₄(2,3-*trans*-dppcbSe₂-P,P',Se,Se')]·0.5[Pt₂Cl₄(dppcb)]·5.5DMF were obtained by gas-phase diffusion of Et₂O into a solution of the dark brown residue in DMF at 4 °C.

Table 1 Crystallographic data for 2,3-*trans*-dppcbS₂ (**I**), dppcbO₄ (**II**), and dppcbS₄ (**III**)

Compound	I	II	III
Formula	C ₅₂ H ₄₄ P ₄ S ₂	C ₅₂ H ₄₄ O ₄ P ₄ ·C ₇ H ₈	C ₅₂ H ₄₄ P ₄ S ₄ ·0.5C ₇ H ₈
Fw	856.92	948.94	967.11
Crystal system, space group	Triclinic, <i>P1</i>	Orthorhombic, <i>Pna</i> 2 ₁	Tetragonal, <i>I4</i> ₁ / <i>a</i>
<i>a</i> /Å	12.6057(2)	31.5748(3)	38.638(3)
<i>b</i> /Å	13.0547(2)	13.0352(1)	
<i>c</i> /Å	15.4843(2)	24.7531(3)	13.102(4)
<i>a</i> °	98.1899(9)		
<i>β</i> °	107.8746(8)		
<i>γ</i> °	109.6632(9)		
<i>U</i> /Å ³	2196.22(6)	10188.0(2)	19560(7)
<i>Z</i>	2	8	16
<i>T</i> /K	218(2)	223(2)	183(2)
Measured reflections	17807	43171	12402
Independent reflections	5546	14543	8402
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 3σ(<i>I</i>)]	0.0413, 0.1111	0.0396, 0.0999	0.0436, 0.0993

Table 2 Crystallographic data for dppcbSe₄ (**IV**), *trans*-dppcbSe₂S₂ (**V**), and [Pt₂Cl₄(2,3-*trans*-dppcbSe₂-*P,P',Se,Se'*)] (**6**)

Compound	IV	V	6
Formula	C ₅₂ H ₄₄ P ₄ Se ₄ ·0.5C ₇ H ₈	C ₅₂ H ₄₄ P ₄ S ₂ Se ₂ ·0.5C ₇ H ₈	C ₅₂ H ₄₄ Cl ₄ P ₄ Pt ₂ Se ₂ ·0.5C ₅₂ H ₄₄ Cl ₄ P ₄ Pt ₂ ·5.5C ₃ H ₇ NO
Fw	1154.71	1060.91	2547.12
Crystal system, space group	Tetragonal, <i>I4</i> ₁ / <i>a</i>	Tetragonal, <i>I4</i> ₁ / <i>a</i>	Triclinic, <i>P1</i>
<i>a</i> /Å	38.730(3)	38.688(1)	14.9398(5)
<i>b</i> /Å			18.8634(6)
<i>c</i> /Å	13.281(2)	13.1777(3)	19.2668(6)
<i>a</i> °			68.799(2)
<i>β</i> °			80.929(2)
<i>γ</i> °			87.253(2)
<i>U</i> /Å ³	19921(4)	19724(1)	4998.6(3)
<i>Z</i>	16	16	2
<i>T</i> /K	183(2)	213(2)	223(2)
Measured reflections	10844	17829	20732
Independent reflections	6281	6042	10537
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 3σ(<i>I</i>) IV , 6 ; <i>I</i> > 2σ(<i>I</i>) V]	0.0474, 0.0600	0.0425, 0.0879	0.0355, 0.0780

X-Ray crystallography

Details of the crystals and data collections are summarized in Tables 1 and 2. In the cases of **I**, **II**, **V**, and **6**, the data collections were performed on a Nonius Kappa CCD diffractometer using combined ϕ - ω -scans. Cell refinement, data reduction, and the empirical absorption correction were done by Denzo and Scalepack programs.¹⁵ In the cases of **III** and **IV**, all data were collected on a Siemens P4 diffractometer using ω -scans. Cell refinement and data reduction were done by the software of the Siemens P4 diffractometer,¹⁶ and the empirical absorption corrections were based on ψ -scans of nine reflections, respectively ($\chi = 78$ to 102° , 360° scans in 10° steps in ψ).¹⁷

All structure determination calculations were carried out using SHELXTL NT 5.10 including SHELXS-97¹⁸ and SHELXL-97.¹⁹ Final refinements on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms in the cases **I–V** and **6**. Except for **IV**, the protons attached to the cyclobutane rings were located and isotropically refined with fixed *U*. All other hydrogen atoms were included using a riding model with isotropic *U* values depending on the *U*_{eq} of the adjacent carbon atoms. The toluene solvent molecules of **III–V** are disordered. In the case of **6**, one DMF solvent molecule is also disordered. In compound **V** additional disorder occurs with respect to the selenium and sulfur positions, where the occupancy factors have been refined. Tables 3 and 5 contain selected bond distances and bond angles of **I–V** and **6**, respectively.

CCDC reference numbers 211317–211322.

See <http://www.rsc.org/suppdata/dt/b3/b305775e/> for crystallographic data in CIF or other electronic format.

¹³C{¹H} and ¹H NMR and IR spectroscopies

Within the classes of compounds **I–V** and **1–6**, the ¹³C{¹H} and ¹H NMR spectra in CH₂Cl₂-d₂ are rather insensitive to structural variations. The ¹³C{¹H} NMR resonances of the phenyl rings occur in the range 128–136 as multiplets. The cyclobutane rings show broad ¹³C{¹H} NMR signals centred at 39. In the ¹H NMR spectra the phenyl rings show multiplets in the range 6.5–8.0. Broad peaks centred at 4.3 are attributed to the cyclobutane hydrogen atoms, where the integrated relative intensities are correct. For all compounds **I–V** and **1–6**, the $\nu(\text{P}=\text{E}; \text{E} = \text{O}, \text{S}, \text{Se})$ vibrations in the IR spectra (KBr) are obscured by lattice vibrations of dppcb.

Results and discussion

Dppcb is the first case of a bis(bidentate) phosphine containing four phosphorus atoms, where a regioselective sulfurization or selenization leading to pure products is possible.⁸ For comparable polyphosphorus ligands like bis(2,2-bis(diphenylphosphino)ethyl)phenylphosphine, different phosphine chalcogenides are only present in slightly unequal proportions, indicating a small degree of steric control over the chalcogen transfer reactions.¹⁰ Nevertheless also for this phosphine, two sulfurization rules acting in concert reduce the number of actual reaction products from a possible 19 to just nine. In the case of the oxidation of dppcb by S or Se as many as seven different species could be present in the reaction system: dppcb, its monochalcogenide, three isomers of the dichalcogenides, the trichalcogenide, and the tetrachalcogenide. Also the reaction between 1,1,2-tris(diphenylphosphino)ethane and an atomic equivalent of elemental selenium in refluxing benzene yields a

Table 3 Selected bond lengths (Å) and angles (°) for 2,3-*trans*-dppcbS₂ (**I**), dppcbO₄ (**II**), dppcbS₄ (**III**), dppcbSe₄ (**IV**), and *trans*-dppcbSe₂S₂ (**V**)

Compound I			
P(2)–S(1)	1.9546(15)	P(4)–C(4)	1.877(3)
P(3)–S(2)	1.9575(15)	C(1)–C(2)	1.571(4)
P(1)–C(1)	1.894(3)	C(1)–C(4)	1.564(4)
P(2)–C(2)	1.845(3)	C(2)–C(3)	1.540(4)
P(3)–C(3)	1.830(3)	C(3)–C(4)	1.561(4)
C(4)–C(1)–C(2)	87.92(19)	C(2)–C(3)–C(4)	89.16(19)
C(3)–C(2)–C(1)	88.38(19)	C(3)–C(4)–C(1)	87.88(19)
Compound II			
P(1)–O(1)	1.485(3)	P(3)–C(3)	1.819(3)
P(2)–O(2)	1.482(3)	P(4)–C(4)	1.812(3)
P(3)–O(3)	1.480(3)	C(1)–C(2)	1.561(5)
P(4)–O(4)	1.481(3)	C(1)–C(4)	1.587(5)
P(1)–C(1)	1.831(4)	C(2)–C(3)	1.561(5)
P(2)–C(2)	1.848(3)	C(3)–C(4)	1.558(5)
C(2)–C(1)–C(4)	86.5(2)	C(4)–C(3)–C(2)	87.5(2)
C(1)–C(2)–C(3)	87.4(2)	C(3)–C(4)–C(1)	86.7(2)
Compound III			
P(1)–S(1)	1.9514(14)	P(3)–C(3)	1.822(4)
P(2)–S(2)	1.9426(14)	P(4)–C(4)	1.845(4)
P(3)–S(3)	1.9425(16)	C(1)–C(2)	1.575(5)
P(4)–S(4)	1.9544(14)	C(1)–C(4)	1.584(5)
P(1)–C(1)	1.856(4)	C(2)–C(3)	1.548(5)
P(2)–C(2)	1.834(4)	C(3)–C(4)	1.580(5)
C(2)–C(1)–C(4)	86.7(3)	C(2)–C(3)–C(4)	87.8(3)
C(3)–C(2)–C(1)	88.3(3)	C(3)–C(4)–C(1)	86.9(3)
Compound IV			
P(1)–Se(1)	2.120(3)	P(3)–C(3)	1.854(8)
P(2)–Se(2)	2.096(3)	P(4)–C(4)	1.826(9)
P(3)–Se(3)	2.096(3)	C(1)–C(2)	1.564(11)
P(4)–Se(4)	2.128(3)	C(1)–C(4)	1.603(11)
P(1)–C(1)	1.875(9)	C(2)–C(3)	1.522(10)
P(2)–C(2)	1.847(9)	C(3)–C(4)	1.570(11)
C(2)–C(1)–C(4)	86.1(6)	C(2)–C(3)–C(4)	88.8(6)
C(3)–C(2)–C(1)	88.7(6)	C(3)–C(4)–C(1)	85.6(6)
Compound V			
P(1)–S(1)	1.977(17)	P(3)–C(3)	1.830(4)
P(2)–Se(2)	2.073(3)	P(4)–C(4)	1.856(4)
P(3)–S(3)	1.983(9)	C(1)–C(2)	1.563(5)
P(4)–Se(4)	2.132(4)	C(1)–C(4)	1.573(5)
P(1)–C(1)	1.850(4)	C(2)–C(3)	1.547(5)
P(2)–C(2)	1.836(4)	C(3)–C(4)	1.570(5)
C(2)–C(1)–C(4)	86.9(3)	C(2)–C(3)–C(4)	87.6(3)
C(3)–C(2)–C(1)	88.1(3)	C(3)–C(4)–C(1)	86.9(3)

mixture of products together with some unreacted material, producing ten different phosphorus environments in the mixture.²⁰ Like dppcb, this phosphine shows considerable steric crowding, and consequently certain conformations are likely to be strongly favoured. However, in the case of bis(diphenylphosphino)methane (dppm) the monochalcogenides (dppmE; E = S, Se) are easily obtained, which is in contrast to 1,2-bis(diphenylphosphino)ethane (dppe).^{13,21} This difference is because the more electron deficient P^V atom affects the activity of the P^{III} atom in dppmE, but not in the monochalcogenides of dppe where the phosphorus atoms are separated by two carbon atoms like in dppcb. Furthermore, since both sides of dppcb are equal, no preference for the monochalcogenides of dppcb is possible, and they have not been obtained in pure form. The production of 1,3-*trans*-dppcbE₂ (E = S, Se) is favoured by steric hindrance, and a subtle choice of solvents makes it possible to synthesize both ligands in pure form.⁸ However, the steric control over the formation of 1,3-*trans*-

dppcbS₂ is not complete, and the by-product 2,3-*trans*-dppcbS₂ (**I**) is presented as clean substance in this work. *Trans*-dppcbSe₂S₂ (**V**) is only obtainable starting from 1,3-*trans*-dppcbS₂, since the rate of chalcogen atom transfer between phosphines is seen to increase in the order S ≪ Se < Te.¹³ Comparable to this, the importance of the rate of chalcogen transfer is also illustrated by the preparation of the mixed dichalcogenide derivative diphenylphosphinoselenoyldiphenylphosphinothiomethane (dppmSeS).³ It is only possible to produce dppmSeS from dppmS and elemental selenium. Due to the more efficient steric control over the regioselective formation of 1,3-*trans*-dppcbSe₂ than over 1,3-*trans*-dppcbS₂, the ligand 2,3-*trans*-dppcbSe₂ was not obtained in pure form. However, using PtCl₂ as template this ligand can be prepared from 1,3-*trans*-dppcbSe₂ as well as from dppcbSe₄ (**IV**). *Via* regioselective selenium migration or extrusion the unique complexes [PtCl₂(2,3-*trans*-dppcbSe₂-P,P')] (**5**) and [Pt₂Cl₄(2,3-*trans*-dppcbSe₂-P,P',Se,Se')] (**6**) are produced.

Crystal structures of 2,3-*trans*-dppcbS₂ (**I**), dppcbO₄ (**II**), dppcbS₄ (**III**), dppcbSe₄ (**IV**), and *trans*-dppcbSe₂S₂ (**V**)

A view of **I** is shown in Fig. 1 and Table 3 contains selected bond lengths and angles. The crystal structure of **I** consists of a pair of MMMP- and MPPP-enantiomers per unit cell. The chirality of **I** is induced by the axes of the folded cyclobutane ring,^{7f,8b} where in the case of the MMMP-enantiomer the sign of the torsion angles along P(1)–C(1)–C(2)–P(2), P(2)–C(2)–C(3)–P(3), and P(3)–C(3)–C(4)–P(4) is negative, thus three times minus (MMM) and the sign of the torsion angle along P(4)–C(4)–C(1)–P(1) is positive, thus plus (P) (see Fig. 1). The dihedral angle between the planes through C(1), C(2), C(3) and C(1), C(3), C(4), respectively, is 152.6°. This folding of the cyclobutane ring is nearly identical with the corresponding value of 151.8° in [Pd₂Cl₄(1,3-*trans*-dppcbS₂-P,P',S,S')] (**7**) and consistent with the usual range from 145 to 160°. The C–C bond lengths of the cyclobutane ring in **I** (see Table 3) are also comparable with the typical range of 1.545–1.607 Å.^{7c,d,f,8} Interestingly, the significantly different cyclobutane C–C bond lengths of **I** indicate that the phenyl rings of all four phosphorus moieties are involved in steric interactions. This is a consequence of the “*anti*” conformation of the P(S)Ph₂ groups, thus giving rise to the possibility of the observed regioselective oxidation of dppcb due to steric hindrance. The solid state structure of **I** shows the isomer with two equatorial P(S)Ph₂ and two axial PPh₂ groups, respectively (see Fig. 1). The P–S distances of 1.9546(15) and 1.9575(15) Å are within the usual range of 1.89–1.97 Å for non-coordinating P=S groups,^{8b,22} being shorter than the sum of the covalent radii of the P and S

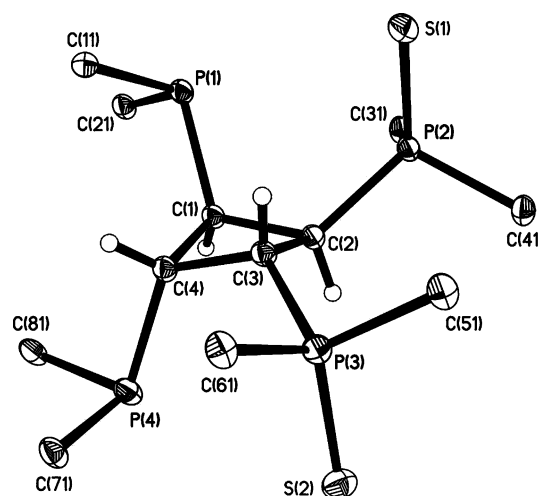


Fig. 1 Molecular structure of the MMMP-enantiomer of 2,3-*trans*-dppcbS₂ (**I**). For clarity only the first atoms of the phenyl rings are shown.

atoms (2.12 Å)²³ and corresponding to a double-bond.⁶ Since only 1,3-*trans*-dppcbS₂ and **I** are formed of a total of three possible disulfides of dppcb, the sulfurization of dppcb shows that through steric substituent effects, the geometry of tetra-tertiary phosphines can be tailored such that access to a reactive centre is only possible from certain directions leading to regioselectivity.²⁴

A view of **II** is presented in Fig. 2 and Table 3 contains selected bond lengths and angles. Two independent MMMP- and MPPP-enantiomers are present in the crystals of **II**. The folding angles of the cyclobutane rings are 142.2 and 143.3°, respectively. This means that this cyclobutane folding is even more pronounced in **II** than in the “free” ligand dppcb showing 145.6°.^{7f} Nevertheless, the C–C bond lengths of the cyclobutane rings in **II** (see Table 3) remain within the usual range given above. Typically, all axial P–C_{cyclobutane} bond lengths are longer in **II** than the corresponding equatorial ones.^{7f,8b} The P=O distances ranging from 1.478(3) to 1.496(3) Å in **II** are comparable to the corresponding parameters of 1.465(5) and 1.478(4) Å for P-unidentate Ph₂PNHP(O)Ph₂ in *trans*-[Pt(CH₃)Cl{Ph₂PNHP(O)Ph₂-P}₂],²¹ but shorter than in *trans*-[Hg{Ph₂PNP(O)Ph₂-P,O}₂] showing 1.5035(15) Å.²⁵ Nevertheless, these P=O bond lengths are consistent with typical double-bonds, since the sum of the covalent radii of the P and O atoms is 1.85 Å.²⁶ Tertiary phosphine oxide ligands play an important role in transition metal chemistry due to the fact that the steric and electronic properties of the ligands can be tuned by modifying the substituents bonded to the phosphorus atom.²⁷ In the case of **II** its conformation changes, when water molecules are incorporated in the lattice.²⁸ This fine tuning of the conformation of **II** leads to perfect chelating orientations of the two *cis*-diphenylphosphinoyl groups attached to each side of the cyclobutane rings *via* hydrogen bonding to the water molecules, which is not present in the actual conformation of **II** presented in this work (see Fig. 2).

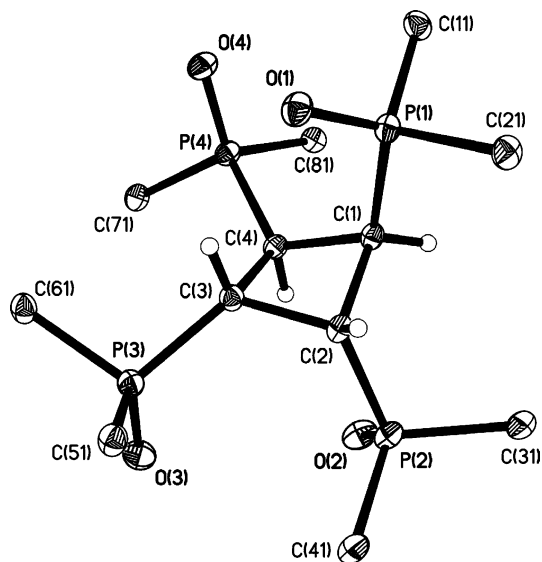


Fig. 2 Molecular structure of the MPPP-enantiomer of dppcbO₄ (**II**). For clarity only the first atoms of the phenyl rings are shown.

The crystal structures of **III–V** are isomorphous, thus allowing a comparison of the electronic influences of sulfur *versus* selenium.^{7f,29} As an example a view of **III** is shown in Fig. 3. Table 3 contains selected bond lengths and angles for **III–V**. Pairs of MMMP- and MPPP-enantiomers are present in the lattices. In the lattice of **V** disorder occurs with respect to the sulfur and selenium positions due to site sharing of two flipped configurations. Selenium produces a slightly larger folding of the cyclobutane rings than sulfur, where the corresponding folding angles for **III–V** are 145.7, 145.2 and 145.5°, respectively. These values are nearly identical with the folding angle of

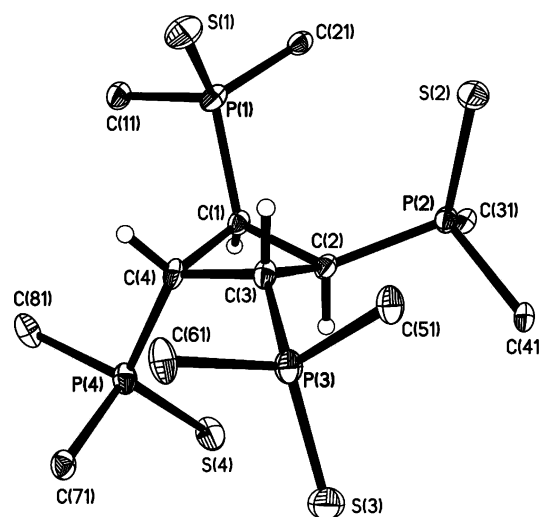


Fig. 3 Molecular structure of the MMMP-enantiomer of dppcbS₄ (**III**). For clarity only the first atoms of the phenyl rings are shown.

dppcb of 145.6°.^{7f} Within statistical significance all C–C bond lengths of the cyclobutane rings in **III–V** (see Table 3) are again typical. Also all axial P–C_{cyclobutane} bond lengths are longer in **III** and **V** than the equatorial ones.^{7f,8b} However, the equatorial P–C_{cyclobutane} bond lengths of **IV** are elongated (see Table 3) as a consequence of attractive interactions between the equatorial selenium atoms and hydrogen atoms attached to adjacent phenyl groups (Se(2) ··· H = 3.081 Å, Se(3) ··· H = 2.895 Å). Nevertheless, the equatorial P=E distances (E = S or Se) in **III** and **IV** are significantly smaller than the axial ones. Since no short intermolecular contact approaches are present in the lattice of **III** and steric differences are negligible within isomorphous crystal structures, this must be attributed to an electronic effect, being more pronounced in the case of selenium than for sulfur. Of course, this effect is obscured by the disorder in **V**. Unsymmetrical ligands like **V** or [Ph₂P(O)N–P(E)Ph₂][–] (E = S or Se), bearing a mismatch in donor atoms, have been remarkably poorly studied.¹¹ The dissimilar donor properties of asymmetrical ligands could play a role in catalysis and in the synthesis of heterobimetallic compounds. Comparable to the P=S bonds in **I** and **III**, also the P=Se bond distances in **IV** are shorter than the sum of covalent radii of P and Se atoms (2.27 Å).²³ Furthermore, the lattices of **II–V** contain incorporated toluene solvent molecules. In the case of the diselenide of dppe (dppeSe₂), its marked selective inclusion behaviour is of interest with respect to the separation of solvent mixtures.³⁰ When a mixture of two isotopic liquid guests is equilibrated with a host like dppeSe₂ capable of forming a clathrate phase with them the mole ratio of the guests in the clathrate phase differs from that in the coexisting liquid.³¹ It seems possible that other sulfur or selenium derivatives of ditertiary phosphines of these types like the bis(bidentate) ligands **III–V** might also show significant inclusion behaviour.

Investigation of **I–V** in the solution state

There is a formal analogy between the addition of sulfur or other chalcogens to phosphorus(III) and its coordination to a metal atom, both in terms of the change in phosphorus hybridization which occurs and in the ³¹P NMR parameters.¹⁰ This leads to a pronounced down-field shift of the P=E (E = O, S, Se) ³¹P resonances compared with the related phosphines. In the case of **I** the ³¹P{¹H} NMR signals for the P(S)Ph₂ and PPh₂ groups occur at 39.9 and –20.2, respectively, indicating that the folding of the cyclobutane ring is fast on the NMR time-scale at ambient temperature. The ³J(P,P) value of 12 Hz is typical, since it is conformationally dependent and the variations in ³J(P,P) where at least one phosphorus atom is trivalent arise

Table 4 Activation energy (ΔG^\ddagger), activation entropy (ΔS^\ddagger) and coalescence temperature (T_c) for the folding of the cyclobutane ring

Compound	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	T_c/K
Dppcb ^a	37.4	57.9	200
2,3- <i>Trans</i> -dppcbS ₂ (I)	40.0	348.2	220
DppcbO ₄ (II)	51.1	99.9	273
DppcbS ₄ (III)	61.2	179.1	333
DppcbSe ₄ (IV)	63.5	132.6	343
<i>Trans</i> -dppcbSe ₂ S ₂ (V)	62.2	132.6	338
[Pt ₂ Cl ₄ (1,3- <i>trans</i> -dppcbS ₂ - <i>P,P',S,S'</i>)] (2)	41.8	65.2	223
[Pd ₂ Cl ₄ (1,3- <i>trans</i> -dppcbS ₂ - <i>P,P',S,S'</i>)] (7)	38.0	614.0	203

^a Data from ref. 7f.**Table 5** Selected bond lengths (Å) and angles (°) for [Pt₂Cl₄(2,3-*trans*-dppcbSe₂-*P,P',Se,Se'*)] (6)

Pt(1)–Se(1)	2.4063(12)	Pt(2)–Se(2)	2.3975(14)
Pt(1)–P(1)	2.237(3)	Pt(2)–P(4)	2.237(3)
Pt(1)–Cl(1)	2.359(3)	Pt(2)–Cl(3)	2.319(3)
Pt(1)–Cl(2)	2.320(3)	Pt(2)–Cl(4)	2.359(3)
P(2)–Se(1)	2.162(3)	P(3)–Se(2)	2.153(3)
P(1)–C(1)	1.886(10)	P(3)–C(3)	1.820(10)
P(2)–C(2)	1.813(9)	P(4)–C(4)	1.908(10)
C(1)–C(2)	1.570(12)	C(2)–C(3)	1.552(13)
C(1)–C(4)	1.557(12)	C(3)–C(4)	1.541(13)
P(1)–Pt(1)–Se(1)	103.93(7)	P(4)–Pt(2)–Se(2)	103.67(8)
Cl(1)–Pt(1)–Se(1)	79.93(8)	Cl(3)–Pt(2)–Se(2)	169.46(8)
Cl(2)–Pt(1)–Se(1)	167.78(8)	Cl(4)–Pt(2)–Se(2)	80.92(9)
P(1)–Pt(1)–Cl(1)	174.66(10)	P(4)–Pt(2)–Cl(3)	86.87(10)
P(1)–Pt(1)–Cl(2)	87.80(10)	P(4)–Pt(2)–Cl(4)	175.38(11)
Cl(1)–Pt(1)–Cl(2)	88.60(11)	Cl(3)–Pt(2)–Cl(4)	88.55(11)
P(2)–Se(1)–Pt(1)	102.74(8)	P(3)–Se(2)–Pt(2)	103.68(9)
C(4)–C(1)–C(2)	88.3(7)	C(4)–C(3)–C(2)	89.5(7)
C(3)–C(2)–C(1)	88.1(7)	C(3)–C(4)–C(1)	89.0(7)

mainly from lone-pair orientation effects determined by steric interactions between adjacent diphenylphosphino groups.^{10,20,32} Also ⁴J(P,P) of 6 Hz is reasonable, because it is expected that long-range couplings are observed in certain rigid systems like **I** where particular geometrical relationships prevail.^{32e} In the case of **I** the folding of the cyclobutane ring leads to an exchange between equatorial and axial positions of the P(S)Ph₂ and PPh₂ groups, respectively. On cooling, the ³¹P{¹H} NMR signals for both groups broaden and at 193 K the signal for the PPh₂ groups is split into two peaks at –21.6 and –27.5. Integration shows that the peak at –27.5 corresponds to 82.8% and this main fraction is attributed to equatorial P(S)Ph₂ groups consistent with the solid state structure of **I** (see Fig. 1). Obviously, the bulkier P(E)Ph₂ groups (E = O, S, Se) compared with PPh₂ prefer equatorial positions, since the same conformation is observed for **6** and [Co₂X₄(2,3-*trans*-dppcbO₂-*P,P',O,O'*)] (X[–] = Cl[–], Br[–]), where 2,3-*trans*-dppcbO₂ is *cis*-, *trans*-, *cis*-, 2,3-bis(diphenylphosphino)-1,4-bis(diphenylphosphino)cyclobutane.³³ Using the variable-temperature ³¹P{¹H} NMR parameters obtained for **I** in CH₂Cl₂ and the DNMR3 program,³⁴ the ΔG^\ddagger and ΔS^\ddagger values of 40.0 kJ mol^{–1} and 348.2 J mol^{–1} K^{–1}, respectively, for the folding of the cyclobutane ring have been obtained. Compared with the corresponding data for dppcb (see Table 4), the folding of the cyclobutane ring has slowed down due to the presence of two further sulfur atoms in **I**. ΔS^\ddagger is dramatically increased as a consequence of the two different conformations of **I**.

In the series **II–IV** only the ³¹P{¹H} NMR spectrum of **II** remains a single resonance at 25.9 at ambient temperature comparable to dppcb.^{7f} In both cases **III** and **IV** two distinct signals corresponding to axial and equatorial phosphorus atoms occur at 43.2 and 32.6 and at 38.2 and 28.9, respectively. The low-field peaks of **III** and **IV** are attributed to the axial P(E)Ph₂ groups (E = S, Se).^{7f} Interestingly, oxidation by sulfur

produces the largest down-field shift with respect to dppcb at –19.0, followed by selenium and oxygen. A typical example for the temperature-dependent ³¹P{¹H} NMR spectra in this series of ligands is given in Fig. 4 for the case of **IV**. For **II** the decoalescence of the single peak occurs below 273 K resulting in resonances at 27.2 for the axial P(O)Ph₂ groups and at 19.5 for the equatorial ones at 253 K. The kinetic parameters for **II–IV** are summarized in Table 4. The ΔG^\ddagger values clearly show that heavier elements (Se > S > O) slow down the folding of the cyclobutane rings. Nevertheless, around room temperature all the phosphorus atoms of dppcb and **II–V** readily invert between axial and equatorial positions, thus adopting the conformation of the cyclobutane ring to the stereochemical requirements of a complexed metal. By contrast, the high pyramidal inversion barrier of trivalent phosphorus implies that a macrocyclic polyphosphine exists at room temperature as a complex mixture of diastereomers.³⁵ This is an advantage of dppcb and its derivatives, since in a macrocycle all the lone pairs may point away from each other, so that no chelation is possible in that conformation.³⁵

The ⁷⁷Se chemical shifts of phosphine selenides occur at the extreme high-shielding end of the selenium chemical shift range.^{32e} This has been attributed to major contributions from the polar structure R₃P⁺–Se[–], where the ⁷⁷Se{¹H} NMR resonances of **IV** and **V** occurring from –373.5 to –424.7 are located within the typical range.^{6,8a,32e,36} It has been suggested that when the two P(Se)Ph₂ groups are close, the polar form R₃P⁺–Se[–] is somewhat disfavoured.^{32e} Since **IV** and **V** show identical conformations in the solid state and an analogous variable-temperature solution behaviour, the mean values for the chemical shifts of –387.1 in **IV** and –412.9 in **V** confirm this effect. The smaller van der Waals radius of sulfur *versus* selenium favours R₃P⁺–Se[–] in **V**. It is well established that the sign of ¹J(Se,P) is negative in the type of compound **IV** or **V**, where their magnitudes are located within the typical range.^{2,6,20,32a,e,37} Interestingly, in **IV** and **V** ¹J(Se,P) is larger for the equatorial P(Se)Ph₂ groups than for the axial ones. The ³J(P(Se),P(S)) values in **V** are typical for ³J(P^V,P^V) couplings.^{32e} ΔG^\ddagger for the folding of the cyclobutane ring in **V** nicely fits in the corresponding values for **III** and **IV** (see Table 4), clearly indicating that ΔG^\ddagger depends on the atomic mass of the chalcogen in this class of compounds.

Investigation of [Pd₂Cl₄(1,3-*trans*-dppcbSe₂-*P,P',Se,Se'*)] (1), [Pt₂Cl₄(1,3-*trans*-dppcbS₂-*P,P',S,S'*)] (2), [PtCl₂(2,3-*trans*-dppcbS₂-*P,P'*)] (3), [Pt₂Cl₄(dppcbS₄-*S,S',S',S''*)] (4), [PtCl₂(2,3-*trans*-dppcbSe₂-*P,P'*)] (5), and [Pt₂Cl₄(2,3-*trans*-dppcbSe₂-*P,P',Se,Se'*)] (6) in the solution state

Since especially with respect to their catalytic application, particularly few reports exist on bis-phosphine monosulfide complexes,³⁸ an investigation of the related compounds **1–6** is interesting. Compared with P[∧]O chelating ligands, hemilabile P[∧]P(E) (E = S, Se) ligands act as much stronger chelates to transition metals. In the case of [PtPh₂(CO)(η¹-P[∧]S)] bidentate phosphorus–sulfur ligands (P[∧]S) are bound to the metal centre in a monodentate fashion, but these initially formed species undergo a slow ring closure process with extrusion of carbon

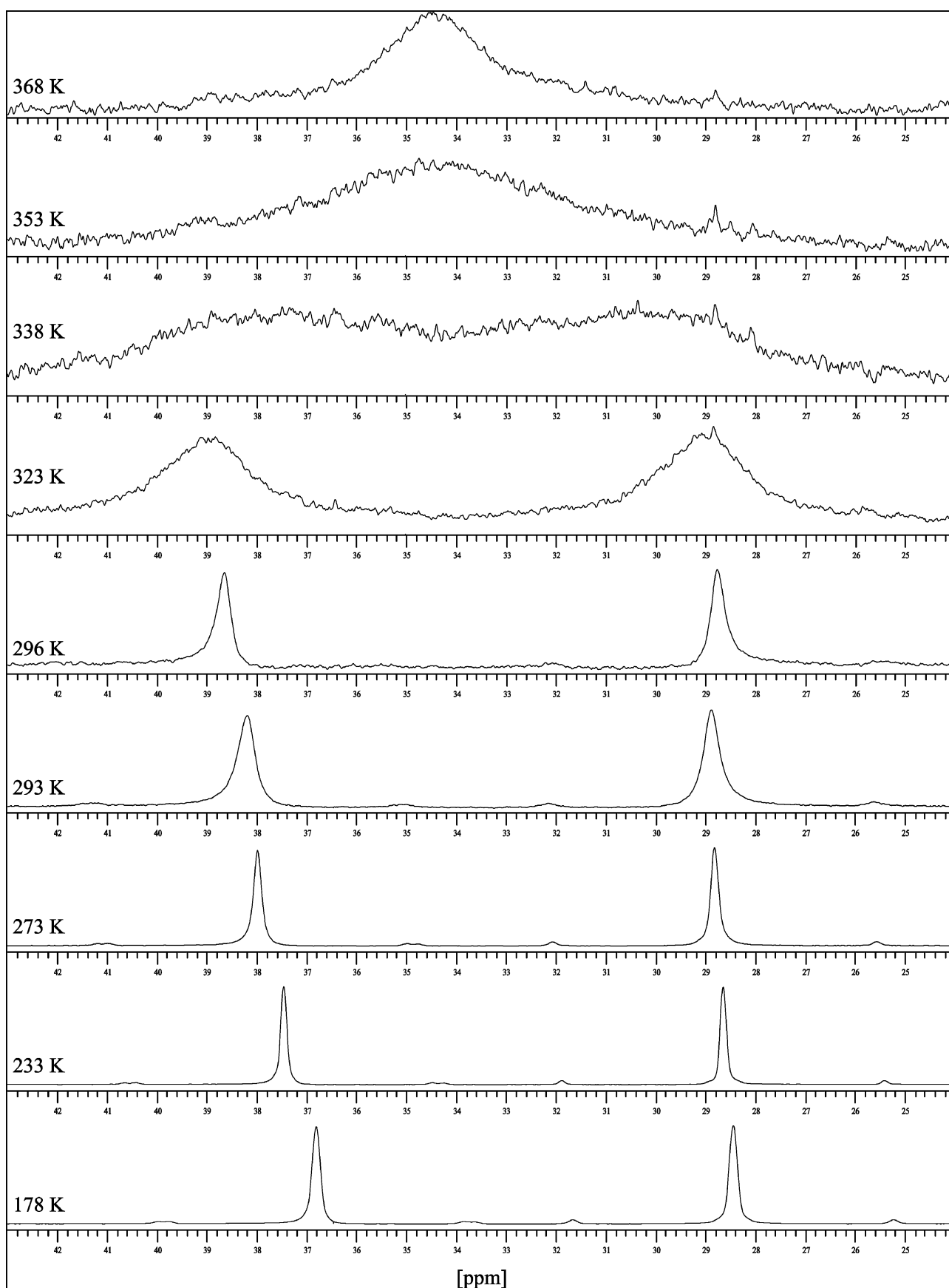


Fig. 4 Temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for dppcbSe_4 (**IV**) in toluene (296–368 K) and in CH_2Cl_2 (178–293 K).

monoxide and formation of the chelate $[\text{PtPh}_2(\text{P}^{\wedge}\text{S})]$ products.¹ For the ligands 1,3-*trans*- dppcbE_2 (E = S, Se) also the formation of $\eta^2\text{-P}^{\wedge}\text{P}(\text{E})$ (E = S, Se) chelate complexes leading to **1**, **2**, and **7**^{8b} has been achieved (see Scheme 2). However, for the ligands 2,3-*trans*- dppcbE_2 (E = S, Se) both monometallic (**3**, **5**) as well as bimetallic coordinations (**6**) are possible. This complexation

behaviour is comparable to the ligand $o\text{-Ph}_2\text{PNHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2$, where monodentate *P*-bound or $\kappa^2\text{-P,S}$ -bound compounds result.³⁹ The selenium donor groups of 1,3-*trans*- dppcbSe_2 and **IV** can be readily de-coordinated and migration or elimination of selenium followed by subsequent re-coordination leads to **5** or **6**. This de-coordination effect is also typical for hemilabile

P^{AN} ligands.⁴ In contrast to **5** and **6**, the selenium migration during the reaction of bis(diphenylphosphinoselenoyl)methane (dppmSe₂) with [PtCl{PhP(CH₂CH₂PPh₂)₂}]Cl produces no pure complex.³⁶ Obviously, the ability of the selenium-based ligand 2,3-*trans*-dppcbSe₂ to fulfil the requirements imposed by the central atoms is due to its great flexibility and notable chelating ability as well as the employment of soft donor atoms.¹²

The structure type of **1** and **2** (see Scheme 2) has been confirmed by the X-ray structure analysis of the analogous compound **7**.^{8b} ¹J(Se,P) of -755 Hz for the "free" ligand 1,3-*trans*-dppcbSe₂^{8a} is reduced to -583 Hz in **1**, clearly indicating coordinated P(Se)Ph₂ groups.^{2,6,11,36,37,40} Compared with δ(Pt) of -4577 for [Pt₂Cl₄(dppcb)] (**8**),^{7f} the corresponding parameter of -3942.6 for **2** is shifted to lower field, but remains located within the usual range for analogous complexes containing hemilabile ligands.^{4,11,14a,21,29,37a,b} ¹J(Pt,P) of 3630 Hz is smaller in **8** than the same coupling of 3789 Hz in **2**, being a consequence of the enlargement of the chelate ring size, since this is also observed in **6** and comparable compounds.³⁹ Also ²J(Pt,P) of 116 Hz in **2** is typical.^{11,14a,21,29,37a,b,39} ³J(P,P)*cis* of 31 Hz is similar to the corresponding parameter in 1,3-*trans*-dppcbE₂ (E = S, Se), **6**, and **7**,⁸ ³J(P,P)*trans* of 7 Hz in **2** being smaller for this structure type. Due to the good solubility of **2** in CH₂Cl₂, a series of temperature-dependent ³¹P{¹H} NMR spectra is possible. At 193 K the resonances for the axial and equatorial P(S)Ph₂ and PPh₂ groups, respectively, are clearly resolved. The resulting kinetic parameters³⁴ are summarized in Table 4, where for purposes of comparison also the corresponding data for **7** have been determined. As a consequence of the smaller square-planar stabilization energy for Pd^{II} than for Pt^{II},^{7d} ΔG[‡] for the folding of the cyclobutane ring is smaller in **7** than in **2**. This flexibility of the Pd-P bonds if reflected in the large positive ΔS[‡] for **7**, allowing easy access to different conformations of the six-membered rings.^{8b}

The complexes **3**, **5**, and **6** contain the ligands **I** and 2,3-*trans*-dppcbSe₂ (see Schemes 1 and 2). The *P,P'*-coordination of these ligands leads to the monometallic species **3** and **5**, whereas the *P,P',Se,Se'*-coordination of 2,3-*trans*-dppcbSe₂ produces the bimetallic compound **6**. This is an intriguing example of the versatile coordination behaviour of these hemilabile ligands. The structure type of **3** and **5** has been confirmed by the X-ray structure analysis of the analogous complex [PtCl₂(2,3-*trans*-dppcbO₂-*P,P'*)]⁴¹ and the X-ray structure of **6** is given below. Compared with δ(Pt) of -3942.6 for **2**, the corresponding parameters of -4470.3 for **3** and -4473.9 for **5** are shifted to higher fields and are nearly identical with δ(Pt) of -4577 for **8**,^{7f} clearly indicating the five-membered ring *P,P'*-coordination for **3** and **5**. This is confirmed by the reduction of ¹J(Pt,P) of 3789 Hz in **2** to 3666 Hz in **3** and 3664 Hz in **5**, where the latter two couplings are again in line with ¹J(Pt,P) of 3630 Hz in **8**.^{7f} Furthermore, ¹J(Se,P) of -764 Hz in **5** is comparable to the magnitudes of the same parameter in **IV** and **V** and typical for non-coordinating P(Se)Ph₂ groups,^{2,6,20,32a,e,37} thus also confirming its structure type shown in Scheme 2. By contrast, ¹J(Se,P) of -604 Hz in **6** is reduced similar to **1** as a consequence of coordination.^{2,6,11,36,37,40} As in **2**, the so formed six-membered rings of **6** produce an enlargement of ¹J(Pt,P) of 3780 Hz.³⁹ Also ²J(Pt,P) of 121 Hz in **6** is comparable to the same parameter of 116 Hz in **2** and 115 Hz in **4** and located within the usual range.^{11,14a,21,29,37a,b,39} In the case of **4** (see Scheme 2) the occurrence of two seven-membered rings joined by cyclobutane is confirmed by the X-ray structure analyses of [Co₂X₄(dppcbO₄-*O,O',O'',O'''*)] (X⁻ = Cl⁻, Br⁻, I⁻).⁴² **4** is a rare example of seven-membered chelate ring formation among metal-phosphine sulfides or selenides, where the seven-membered metallacyclic rings are interestingly stable and flexible similar to complexes of the disulfide of dppe.⁴³ However, since the relative donor- versus acceptor-strength follows the order P(O)Ph₂ < P(S)Ph₂ ≤ P(Se)Ph₂, the lack of acceptor

properties especially in the latter case leads to the instability of seven-membered ring systems.⁴⁴

Crystal structure of **6**

Though ligand **IV** contains only selenium donor atoms, it is hemilabile because upon coordination the resulting seven-membered rings are unstable and in the case of **6** de-coordination followed by regioselective extrusion of selenium and re-coordination occurs.^{4,14a} In order to characterize **6** definitely an X-ray structure analysis was performed. Views of **6** are shown in Fig. 5 and 6 and Table 5 contains selected bond lengths and angles. The crystals containing **6** are a unique example of a co-crystallization of two different complexes, namely **6** and **8**. As a consequence the unit cell consists of two discrete [Pt₂Cl₄(2,3-*trans*-dppcbSe₂-*P,P',Se,Se'*)] molecules, one discrete [Pt₂Cl₄(dppcb)] molecule, and eleven DMF solvent molecules. [Pt₂Cl₄(dppcb)] and one disordered DMF solvent molecule are located on centres of symmetry. As in the cases **I-V** the folding of the cyclobutane ring in **6** (see Fig. 6) induces chirality and a pair of MMMP- and MPPP-enantiomers is present in the unit cell. This folding is reduced to 155.9° in **6** compared with the range of 142.2–152.6° in **I-V** and 151.8° in **7**. Nevertheless, the C-C bond lengths of the cyclobutane ring in **6** (see Table 5)

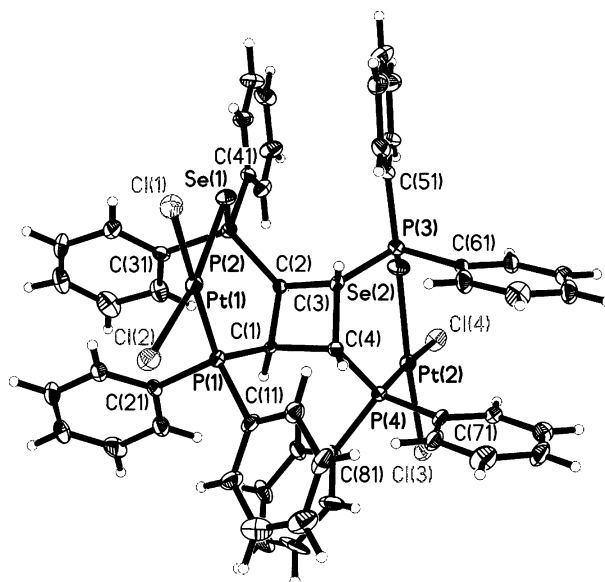


Fig. 5 Molecular structure of the MMMP-enantiomer of [Pt₂Cl₄(2,3-*trans*-dppcbSe₂-*P,P',Se,Se'*)] (**6**).

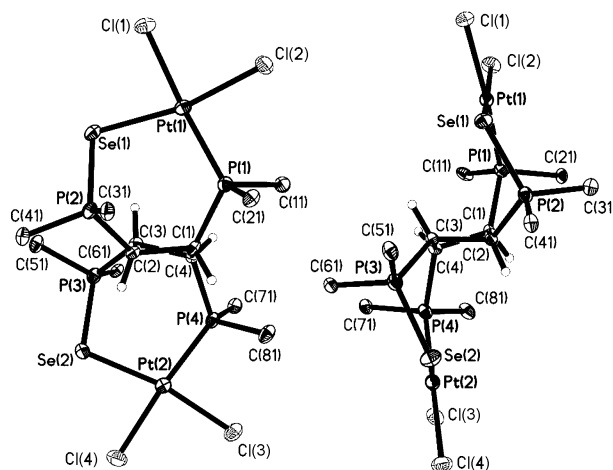


Fig. 6 Views of the MMMP-enantiomer of [Pt₂Cl₄(2,3-*trans*-dppcbSe₂-*P,P',Se,Se'*)] (**6**) with the least-squares plane through the cyclobutane ring perpendicular to the projection plane. For clarity only the first atoms of the phenyl rings are shown.

remain located within the typical range of 1.545–1.607 Å.^{7c,d,f,8} Since 2,3-*trans*-dppcbSe₂ is analogous to **I**, the X-ray structures of **I** and **6** reveal, how the conformation of this type of ligand changes upon coordination neglecting packing differences. In **I** the torsion angle along P(1)–C(1)–C(2)–P(2) of 22.9(3)° (see Fig. 1) is significantly different from the corresponding parameter along P(3)–C(3)–C(4)–P(4) of 35.6(3)°. However, in **6** (see Fig. 5) the same parameters are identical within statistical significance leading to a mean value of 23.0(8)°. The same effect is observed for the *cis* phosphorus ⋯ phosphorus distances in **I** and **6**. In **I** P(1) ⋯ P(2) of 3.430(2) Å is significantly shorter than P(3) ⋯ P(4) of 3.647(2) Å, whereas in **6** the analogous parameters are again identical within statistical significance showing a mean value of 3.511(3) Å. Thus, the conformation of the 2,3-*trans*-dichalcogenides of dppcb is easily adjusted to fulfil the requirements of a hemilabile bis(bidentate) ligand. In the case of the tetrasulfide of bis[(diphenylphosphino)ethyl]-phenylphosphino]methane two pairs of sulfur atoms point in opposite directions and such an arrangement would preclude chelation to a metal.⁴⁵ The six-membered Pt–Se–P–C–C–P ring conformations in **6** can be most readily described as pseudo-boats (see Fig. 5 and 6) with P(2) or P(3) at the prow (0.976 and 0.926 Å above the plane, respectively) and P(1) or P(4) at the stern (0.327 and 0.274 Å above the plane, respectively) of the “boats”.¹¹ These conformations are comparable to the pseudo-boat structure of the six-membered Pd–O–P–N–P–S ring in [Pd{Ph₂P(O)NP(S)Ph₂-O,S}(tmeda)]PF₆, where tmeda is *N,N,N',N'*-tetramethylethylenediamine.¹¹ The two coordination planes of **6** include an angle of 11.2°. Interestingly, the atoms Pt(2), Cl(3), Cl(4), P(4), and Se(2) are completely coplanar within statistical significance (see Fig. 6). The same near-perfect square-planar geometry at the metal centre is evident in *trans*-[Pt{Ph₂PNHC₆H₄P(S)Ph₂-P,S₂}[ClO₄]₂, presumably because of the lack of strain imposed at the platinum centre by the seven-membered rings.³⁹ However, the largest deviation of 0.083 Å from the least-squares plane through Pt(1), Cl(1), Cl(2), P(1), and Se(1) in **6** is similar to the largest deviation of 0.068 Å from the least-squares coordination plane in co-crystallized **8**. Thus, since packing differences are negligible within the same crystal, the degree of co-planarity of the coordination planes for five- and six-membered rings depends on the specific steric requirements of the chelating ligands, being different for the two chelating moieties of 2,3-*trans*-dppcbSe₂. In **6** this leads to a significantly longer Pt(1)–Se(1) bond length of 2.4063(12) Å than Pt(2)–Se(2) of 2.3975(14) Å. Upon coordination the P=Se bond lengths in **6** are significantly elongated compared with the corresponding parameters for the “free” ligand **IV** (see Tables 3 and 5), where this effect is typical for phosphine chalcogenides.^{2,6,8b,11,21,22,37a,b,39,46} The P(E)Ph₂ (E = Se, S) groups show a weaker *trans* influence than the PPh₂ groups in **6** and **7**.^{8b} As a consequence the M–Cl (M = Pt, Pd) bond lengths of **6** and **7** are significantly shorter *trans* to P(E)Ph₂ (E = Se, S) than *trans* to PPh₂ (see Table 5 and ref. 8b).

Summary

We have reported the preparation and full characterization in the solid as well as in solution state of five new ligands, 2,3-*trans*-dppcbS₂ (**I**), dppcbO₄ (**II**), dppcbS₄ (**III**), dppcbSe₄ (**IV**), and *trans*-dppcbSe₂S₂ (**V**), derived from a bis(bidentate) phosphine *via* regioselective or complete chalcogen transfer reactions. Furthermore, palladium(II) and platinum(II) complexes of **I**, **III**, and the previously prepared 1,3-*trans*-dppcbE₂ (E = S, Se) have been presented. They correspond to [Pd₂Cl₄(1,3-*trans*-dppcbSe₂-P,P',Se,Se')] (**1**), [Pt₂Cl₄(1,3-*trans*-dppcbS₂-P,P',S,S')] (**2**), [PtCl₂(2,3-*trans*-dppcbS₂-P,P')] (**3**), [Pt₂Cl₄(dppcbS₄-S,S',S'',S''')] (**4**), [PtCl₂(2,3-*trans*-dppcbSe₂-P,P')] (**5**), and [Pt₂Cl₄(2,3-*trans*-dppcbSe₂-P,P',Se,Se')] (**6**). The compounds containing hemilabile selenium-based ligands

(**1**, **5**, **6**) are unique,⁸ where **5** and **6** show the novel ligand 2,3-*trans*-dppcbSe₂, and **6** has also been characterized definitely. Typically, dppcb has been converted to all respective chalcogenides with retention of stereochemical configuration.⁴⁷ It has often been observed that the non-phosphorus donor E (E = S, Se) of the ligands in complexes like **1**, **2**, and **6** is weakly coordinated in solution to the metal centre, generating potential catalytically active systems, by providing, under mild conditions, a vacant site for the coordination and activation of organic substrates.¹ A further application of this class of ligands is that they are able to form complexes with unusual structures.^{25,46b} Among the methods for the synthesis of transition-metal clusters containing bridging chalcogenido ligands, that involving tertiary phosphine chalcogenide R₃PE (E = S, Se or Te) has been proved to be one of the most effective.⁴⁸ Also the considerable difference between BINAP and BINAP(O) complexes bears important implications for catalysis.⁴⁹ As in the cases **1–6**, for an increase in the potential catalytic activity of mono- and bimetallic systems it is important to constrain the chelating groups in mutually *cis* positions.⁴⁵ The chirality of **1–6** is also a desirable feature.⁵⁰ Our future studies will focus on the catalytic applications of these systems.

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