# Complexes of elements of groups 9 and 10 with new chiral chelating bisphosphine monosulfide and monoselenide ligands

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The chiral bisphosphine prepared from the reaction of (*S*)-α-methylbenzyl amine with two equivalents of chlorodiphenylphosphine can be oxidised by direct reaction with one equivalent of either of the elemental chalcogens sulfur or selenium to prepare new chiral monoxidised bisphosphines. These chiral ligands can be used to prepare complexes with group nine [Rh(I), Ir(I)] and group ten [Pd(II) and Pt(II)] metals. These complexes were characterised by spectroscopic and, in four cases, crystallographic techniques.

In recent years there has been an increasing interest in chelating ligands that comprise mixed donor sets. These ligands can bring a range of properties to the complexes that they comprise, such as hemilability or electronic asymmetry. This latter property is of particular interest if the complexes have applications as reagents or in homogeneous catalysis. Some of the most well studied chelating ligands are bisphosphines, so it is perhaps not surprising that heterobidentate ligands prepared from these, particularly bisphosphine monoxides (BPMO's), are now being actively studied.[1–5]

The role of chiral bisphosphines in making complexes that are useful for selective homogeneous catalysis is well developed and so it seems reasonable that monoxidised chiral bisphosphines could be of interest, as they bring to the complexes that they form the added feature of electronic asymmetry. The publication of a route to chiral BPMO's from commercial chiral bisphosphines[6] has resulted in a number of publications detailing the successful use of complexes of such ligands in catalytic reactions.[7]

A further family of chiral monoxidised bisphosphines is available from the oxidation of chiral bisphosphines by chalcogens other than oxygen. There is a wealth of literature on the preparation of phosphine sulfides and selenides by direct reaction of the corresponding phosphine with the elemental chalcogen.[8] Such ligands are potentially very interesting, since the donor properties of phosphine sulfides and selenides are quite different from the parent phosphines and indeed, from phosphine oxides. A bisphosphine monosulfide or monoselenide might well prove to induce a more pronounced electronic asymmetry and in its complexes may be able to exhibit different coordination behaviour. Further, it is possible to imagine a family of chiral monoxidised bisphosphines that comprise chelate rings that are entirely inorganic, in contrast to the BPMO's previously reported. The ligands reported here chelate to form carbon free M–E–P–N–P rings and are related to achiral ligands that form similar rings, such as imidotetraaryldichalcogenodiphosphinates, which have enjoyed a great deal of success and are capable of coordinating to a wide range of metals.[9]

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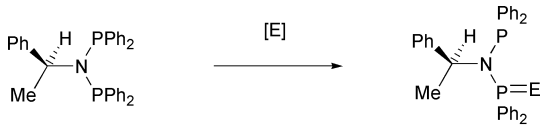


**L1** E = S, **L2**; E = Se, **L3**

**Fig. 1** The formation of L2 and L3.

We report here the new chiral bisphosphine monosulfide L2 and monoselenide L3, Fig. 1, along with some complexes with group nine and ten metals.

## Experimental

### General

All reactions were performed under nitrogen unless otherwise stated. All reagents were commercial and used as received except $[(cod)MCl]_2$ (M = Rh, Ir), which were prepared according to reported procedures,[10] and $Et_3N$ and $Ph_2PCl$, which were distilled prior to use.

Infrared spectra were recorded as KBr pellets in the range 4000–200 $cm^{-1}$ on a Perkin–Elmer System 2000 FT-IR spectrometer. The $^1H$ NMR spectra (250 MHz) were recorded on a Bruker AC250 FT spectrometer with chemical shifts ($\delta$) in ppm to high frequency of $SiMe_4$ and coupling constants ($J$) in Hz. The $^{31}P\{^1H\}$ NMR spectra (36.2 MHz) were recorded on a JEOL FX90Q spectrometer with chemical shifts ($\delta$) in ppm to high frequency of 85% $H_3PO_4$ and coupling constants ($J$) in Hz. All spectra were recorded in $CDCl_3$ unless otherwise stated. Elemental analyses (Perkin–Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

### Synthesis of ligands

**(*S*)-$(Ph_2P)_2$NC(H)(Me)Ph (L1).** (i) A solution of (*S*)-phenylethylamine (1.08 $cm^3$, 8.42 mmol) and $Et_3N$ (2.25 $cm^3$, 16 mmol) in diethyl ether (10 $cm^3$) was added dropwise to a stirred solution

of $ClPPh_2$ (3.0 $cm^3$, 16.71 mmol) in diethyl ether (15 $cm^3$) under nitrogen. During the addition, the reaction formed a white precipitate. After 1.5 h the reaction mixture was filtered. The liquid fraction was evaporated to dryness, giving a yellow oil. Treatment with MeOH (3 $cm^3$) overnight at 0 °C led to the formation of a white solid, which was collected by filtration and washed successively with hexane ($3 \times 5$ $cm^3$) and diethyl ether ($2 \times 3$ $cm^3$). Yield 2.7 g, 65%.

(ii) An alternative preparation followed the same route until the addition to $ClPPh_2$ was complete. After 10 h of stirring, the solvent was removed to give a white solid that was washed with 50 $cm^3$ of distilled degassed water. The white solid product was collected by filtration and was washed successively with hexane ($3 \times 5$ $cm^3$) and diethyl ether ($3 \times 3$ ml) and the solid was dried under vacuum. Yield: 3.52 g, 85%.

**(*S*)-$(Ph_2P)N\{Ph_2P(S)\}C(H)(Me)Ph$ ($L_2$).** A solution of L1 (375 mg, 0.77 mmol) in THF (10 $cm^3$) and elemental sulfur (24.5 mg, 0.77 mmol) was stirred 2.5 h at room temperature and then filtered through a Celite plug. The volume was reduced to *ca.* 1 $cm^3$ under reduced pressure and the product was precipitated as a white solid by addition of MeOH (2 $cm^3$) and collected by filtration. Yield: 250 mg, 61%. $^{31}P\{^1H\}$ NMR: 71.95 [d, $^2J_{PP} = 13.2$, P(V)], 52.42 [d, $^2J_{PP} = 13.2$, P(III)]. $^1H$ NMR: 7.76–6.91 (m, 25H, arom.), 5.11 (m, 1H, CH), 1.75 (d, $^3J = 7$, 3H, $CH_3$). IR: 1436, 1090, 944, 848, 673, 774, 742, 691, 673, 515 $cm^{-1}$. Anal. found (calcd. for $C_{32}H_{29}NP_2S$): C = 73.50 (73.60); H = 5.45 (5.55); N = 2.50 (2.70)%.

**(*S*)-$(Ph_2P)N\{Ph_2P(Se)\}C(H)(Me)Ph$ (L3).** A solution of L1 (1 g, 2.04 mmol) in THF (10 $cm^3$) and grey selenium (160 mg, 2.04 mmol) were stirred together for 17 h at room temperature. The volume was then reduced to *ca.* 1 $cm^3$ under reduced pressure and the product was precipitated as a white solid by addition of MeOH (2 $cm^3$) and collected by filtration. Yield: 890 mg, 76.6%. $^{31}P\{^1H\}$ NMR: 70.43 [d, $^2J_{PP} = 8.8$, $^1J_{PSe} = 757$, P(V)], 53.08 [d, $^2J_{PP} = 8.8$, P(III)]. $^1H$ NMR: 7.72–6.71 (m, 25H, arom), 5.22 (m, 1H, CH), 1.77 (d, $^3J_{HH} = 7$, 3H, $CH_3$). IR: 1436, 1089, 945, 845, 774, 742, 690, 554 $cm^{-1}$. Anal. found (calcd. for $C_{32}H_{29}NP_2Se$): C = 67.60 (67.90); H = 5.15 (5.10); N = 2.40 (2.50)%.

## Synthesis of complexes

**[{$\kappa^2$-(*S*)-$\{(Ph_2P)_2NC(H)(Me)Ph$-*P*,*P*}$RhCl]_2$ [L1RhCl]$_2$.** A solution of $[(cod)RhCl]_2$ (56 mg, 0.114 mmol) and L1 (114 mg, 0.23 mmol) in $CH_2Cl_2$ (8 $cm^3$) was stirred for 4 h. The solvent was reduced to *ca.* 2 $cm^3$ and the product was precipitated as an orange solid by the addition of diethyl ether (10 $cm^3$). The solid was collected by filtration and dried *in vacuo*. Yield: 70 mg, 49%. $^{31}P\{^1H\}$ NMR: 72.74 ($^1J_{RhP} = 123.2$ Hz.). $^1H$ NMR: 8.10–6.48 (m, 50H, arom), 4.27 (m, 2H, CH), 0.97 (d, $^3J_{HH} = 6.8$, 6H, $CH_3$). IR: 1435, 1097, 967, 864, 745, 693, 593, 528, 505, 431 $cm^{-1}$. Anal. found (calcd. for $C_{64}H_{58}N_2P_4Cl_2Rh_2$): C = 61.20 (61.40); H = 4.60 (4.65); N 2.05 (2.25)%.

**[{$\kappa^2$-(*S*)-$\{(Ph_2P)_2NC(H)(Me)Ph$-*P*,*P*}$IrCl]_2$ [L1IrCl]$_2$.** A solution of $[(cod)IrCl]_2$ (115 mg, 0.17 mmol) and L1 (170 mg, 0.34 mmol) in $CH_2Cl_2$ (10 $cm^3$) was stirred overnight. The solvent was reduced to *ca.* 2 $cm^3$ by evaporation under reduced pressure and the product was precipitated by addition of diethyl ether (10 $cm^3$). The brown solid was collected by filtration and dried *in vacuo*. Yield: 100 mg, 41%. $^{31}P\{^1H\}$ NMR: 3.48. $^1H$ NMR: 8.05–6.51 (m, 50H, arom), 4.24 (m, 2H, CH), 0.98 (d, $^3J_{HH} = 6.8$, 6H, $CH_3$). IR: 1435, 1098, 970, 857, 746, 693, 569, 534, 515, 439, 217 $cm^{-1}$. Anal. found (calcd for $C_{64}H_{58}N_2P_4Cl_2Ir_2$): C = 53.70 (53.60); H = 4.00 (4.10); N = 2.15 (1.95)%.

**[{$\kappa^2$-(*S*)-$\{(Ph_2P)(Ph_2P\{S\})NC(H)(Me)Ph$-*P*,*S*}$RhCl]_2$ [L2RhCl]$_2$.** A solution of $[(cod)RhCl]_2$ (35 mg, 0.0713 mmol) and L2 (75 mg, 0.144 mmol) in $CH_2Cl_2$ (10 $cm^3$) was stirred for 5 h. The solvent was reduced to *ca.* 1 $cm^3$ by evaporation under reduced pressure and the product was precipitated by addition of diethyl ether (10 $cm^3$). The dark red solid was collected by filtration and dried *in vacuo*. Yield: 79 mg, 83%. $^{31}P\{^1H\}$ NMR: 104.6 [dd, $^1J_{PP} = 66.0$, $^1J_{PRh} = 158.4$, P(III)]; 70.9 [d, $^1J_{PP} = 66.0$, P(V)]. $^1H$ NMR: 8.11–6.24 (m, 50H, arom.), 4.92 (m, 2H, CH), 0.83 (d, $^3J_{HH} = 7.2$, 6H, $CH_3$). IR: 1436, 1099, 943, 864, 746, 693 $cm^{-1}$. Anal. found (calcd. for $C_{64}H_{58}N_2P_4Cl_2Rh_2S_2$): C = 58.20 (58.30); H = 4.35 (4.45); N = 2.10 (2.10)%.

**[{$\kappa^2$-(*S*)-$\{(Ph_2P)(Ph_2P\{S\})NC(H)(Me)Ph$-*P*,*S*}$IrCl]_2$ [L2IrCl]$_2$ (Isomer 1).** A solution of $[(cod)IrCl]_2$ (65 mg, 0.0968 mmol) and L2 (100 mg, 0.192 mmol ) in $CH_2Cl_2$ (10 $cm^3$) was stirred for *ca.* 2 h. The solvent was removed by evaporation under reduced pressure and the residue dissolved in $CH_2Cl_2$ (2 $cm^3$). Addition of diethyl ether (10 $cm^3$) formed an orange precipitate that was collected by filtration and dried *in vacuo*. Yield: 60 mg, 40%. $^{31}P\{^1H\}$ NMR: 95.11 [d, $^1J_{PP} = 65.9$, P(III)], 72.92 [$^1J_{PP} = 65.9$, P(V)]. $^1H$ NMR: 8.44–6.46 (m, 50H, arom.), 4.75 (m, 2H, CH), 0.84 (d, $^3J_{HH} = 7.2$, 6H, $CH_3$). IR: 1436, 1097, 939, 770, 747, 692, 618, 595, 571, 542, 521, 496, 459, 398, 376 $cm^{-1}$. Anal. found (calcd. for $C_{64}H_{58}N_2P_4Cl_2S_2Ir_2$): C = 51.30 (51.25); H = 4.00 (3.90); N = 1.80 (1.90)%.

**[{$\kappa^2$-(*S*)-$\{(Ph_2P)(Ph_2P\{S\})NC(H)(Me)Ph$-*P*,*S*}$IrCl]_2$ [L2IrCl]$_2$ (Isomer 2).** A solution of $[(cod)IrCl]_2$ (67 mg, 0.10 mmol) and L2 (105 mg, 0.20 mmol) in $CH_2Cl_2$ (10 $cm^3$) was stirred for *ca.* 6 h. The solvent was removed under reduced pressure and the residue was dissolved in $CDCl_3$ (1 $cm^3$). Addition of diethyl ether (10 $cm^3$) led to the formation of an orange precipitate that was collected by suction filtration and dried *in vacuo*. Yield: 100 mg, 67%. $^{31}P\{^1H\}$ NMR: 82.01 [d, $^2J_{PP} = 57.2$, P(III)], 77.04 [$^2J_{PP} = 57.2$, P(V)]. $^1H$ NMR: 8.54–6.28 (m, 50H, arom), 4.75 (m, 2H, CH), 1.78 (d, $^3J_{HH} = 8.0$, 6H, $CH_3$). IR: 1436, 1104, 1027, 998, 817, 744, 696, 618, 570, 544, 513, 398 $cm^{-1}$. Anal. found (calcd. for $C_{64}H_{58}N_2P_4Cl_2S_2Ir_2$): C = 51.30 (51.25); H = 3.95 (3.90); N = 2.00 (1.90)%.

**{$\kappa^2$-(*S*)-$\{(Ph_2P)(Ph_2P\{S\})NC(H)(Me)Ph$-*P*,*S*}$PdCl_2$ (L2PdCl$_2$).** A solution of $(cod)PdCl_2$ (22 mg, 0.077 mmol) and L2 (40 mg, 0.077 mmol) in $CH_2Cl_2$ (10 $cm^3$) was stirred for 2 h. The solvent was removed by evaporation under reduced pressure and the residue dissolved in the minimum quantity of $CDCl_3$ to give an orange solution, from which crystals of the product were obtained by slow evaporation. Yield: 49 mg, 91%. $^{31}P\{^1H\}$ NMR: 98.02 [d, $^2J_{PP} = 48.4$, P(III)] 75.9 [d, $^2J_{PP} = 48.4$, P(V)]. $^1H$ NMR: 8.32–6.34 (m, 50H, arom), 4.88 (m, 2H, CH), 1.1 (d, $^3J_{HH} = 7.2$, 6H, $CH_3$). IR: 1437, 1104, 997, 936, 918, 878, 773, 751, 727, 691, 645, 588, 524, 493, 478, 401, 364, 318, 226 $cm^{-1}$. Anal. found (calcd. for $C_{32}H_{29}NP_2SCl_2Pd$): C = 55.00 (55.10); H = 4.20 (4.15); N = 1.80 (2.00)%.

**{$\kappa^2$-(*S*)-$\{(Ph_2P)(Ph_2P\{S\})NC(H)(Me)Ph$-*P*,*S*}$PtCl_2$ (L2PtCl$_2$).** A solution of $(cod)PtCl_2$ (29 mg, 0.075 mmol) and L2 (40 mg, 0.077 mmol) in $CH_2Cl_2$ (10 $cm^3$) was stirred for 2 h. The solvent was removed by evaporation under reduced pressure and the residue dissolved in the minimum quantity of $CDCl_3$ to give a red solution from which red crystals of the product were obtained after 15 min. Yield: 58 mg, 96%. $^{31}P\{^1H\}$ NMR: 70.24 [d, $^1J_{PP} = 47.6$, $^1J_{PPt} = 3976$, P(III)], 72.69 [$^1J_{PP} = 47.6$, $^2J_{PPt} = 104$, P(V)]. $^1H$ NMR: 8.25–6.12 (m, 25H, arom), 4.95 (m, 1H, CH), 1.10 (d, $^3J_{HH} = 7.2$, 3H, $CH_3$). IR: 1437, 1104, 937, 876, 751, 726, 691, 524, 494, 480, 402, 365, 330

$cm^{-1}$. Anal. found (calcd. for $C_{32}H_{29}NP_2SCl_2Pt$): C = 48.95 (48.80); H = 2.95 (3.05); N = 1.65 (1.80)%.

**[{κ²-(*S*)-{(Ph₂P)(Ph₂P{Se})NC(H)(Me)Ph-*P*,*Se*}RhCl]₂ [L3-RhCl]₂.** A solution of $[(cod)RhCl]_2$ (45 mg, 0.092 mmol) and L3 (104 mg, 0.183 mmol) in $CH_2Cl_2$ (10 $cm^3$) was stirred for 4 h. The solvent was reduced to *ca.* 2 $cm^3$ by evaporation under reduced pressure and the product was precipitated by addition of diethyl ether (10 $cm^3$). The brown solid was collected by filtration and dried *in vacuo*. Yield: 122 mg, 94%. Isomer 1: $^{31}P\{^1H\}$ NMR: 108.69 [d, $^2J_{PP} = 74.8$, $^1J_{PRh} = 158.4$, P(III)], 59.04 [$^2J_{PP} = 74.8$, $^1J_{PSe} = 553$, P(V)]. $^1H$ NMR: 8.24–6.46 (m, 50H, arom.), 4.81 (m, 2H, CH), 1.09 (d, $^3J_{HH} = 7.6$, 6H, $CH_3$). IR: 1435, 1126, 1096, 863, 744, 695, 545, 505 $cm^{-1}$. Isomer 2: 93.40 [d, $^2J_{PP} = 70.4$, $^1J_{PRh} = 145.7$, P(III)], 50.31 [$^2J_{PP} = 70.4$, $^1J_{Pse} = 556$, P(V)]. $^1H$ NMR: 8.22–6.45 (m, 50H, arom.), 4.51 (m, 2H, CH), 1.78(d, $^3J_{HH} = 6.8$, 6H, $CH_3$). IR: 1435, 1128, 1097, 856, 743, 693, 539, 506 $cm^{-1}$. Anal. found (calcd.) for $C_{64}H_{58}N_2P_4Cl_2Se_2Rh_2$: C 54.70 (54.40); H = 4.20 (4.25); N = 2.0 (1.95)%.

**[{κ²-(*S*)-{(Ph₂P)(Ph₂P{Se})NC(H)(Me)Ph-*P*,*Se*}IrCl]₂ [L3-IrCl]₂.** A solution of $[(cod)IrCl]_2$ (51 mg, 0.076 mmol) and L3 (86 mg, 0.152 mmol) in $CH_2Cl_2$ (10 $cm^3$) was stirred overnight. The solution was initially orange, and the colour changed to red by the end of the reaction. The solvent was reduced to *ca.* 1 $cm^3$ by evaporation under reduced pressure and the product was precipitated by addition of diethyl ether (10 $cm^3$). The brown solid was collected by filtration and dried *in vacuo*. Yield: 162 mg, 67%. Isomer 1: $^{31}P\{^1H\}$ NMR: 88.21 [d, $^2J_{PP} = 70.4$, P(III)], 51.83 [$^2J_{PP} = 73.1$, $^1J_{PSe} = 551$, P(V)]. $^1H$ NMR: 8.10–6.40 (m, 50H, arom.), 4.81 (m, 2H, CH), 1.09 (d, $^3J_{HH} = 7.6$, 6H, $CH_3$). Isomer 2: $^{31}P\{^1H\}$ NMR: 85.72 [d, $^2J_{PP} = 68.0$, P(III)], 58.60 [$^2J_{PP} = 68.0$, $^1J_{PSe} = 550$, P(V)]. $^1H$ NMR: 8.12–6.41 (m, 50H, arom.), 4.51 (m, 2H, CH), 1.84 (d, $^3J_{HH} = 6.9$, 6H, $CH_3$). IR: 1435, 1128, 1097, 856, 743, 693, 539, 506 $cm^{-1}$. Anal. found (calcd.) for $C_{64}H_{58}N_2P_4Cl_2Se_2Ir_2$: C = 48.40 (48.50); H = 3.70 (3.65); N = 1.75 (1.80)%.

**{κ²-(*S*)-{(Ph₂P)(Ph₂P{Se})NC(H)(Me)Ph-*P*,*Se*}PdCl₂ (L3-PdCl₂).** A solution of $(NCPh)_2PdCl_2$ (68 mg, 0.177 mmol) and L3 (100 mg, 0.176 mmol) in $CH_2Cl_2$ (10 $cm^3$) was stirred for 2 h. The solvent was reduced to *ca.* 1 $cm^3$ by evaporation under reduced pressure and the product was precipitated by addition of diethyl ether (10 $cm^3$). The orange solid was collected by filtration and dried *in vacuo*. Yield: 97 mg, 73%. $^{31}P\{^1H\}$ NMR: 103.36 [d, $^2J_{PP} = 57.2$, P(III)], 62.73 [$^2J_{PP} = 57.2$, $^1J_{PSe} = 546$, P(V)]. $^1H$ NMR: 8.31–6.55 (m, 25H, arom), 4.81 ($^3J_{HH} = 7.2$, 1H, CH), 1.11 (d, $^3J_{HH} = 7.2$, 3H, $CH_3$). IR: 1436, 1102, 928, 875, 743, 689, 549, 519, 492, 369, 325, 293 $cm^{-1}$. Anal. found (calcd.) for $C_{32}H_{29}NP_2Cl_2SePd$: C = 51.40 (51.85); H = 3.65 (3.95); N = 1.70 (1.90)%.

**{κ²-(*S*)-{(Ph₂P)(Ph₂P{Se})NC(H)(Me)Ph-*P*,*Se*}PtCl₂ (L3-PtCl₂).** A solution of $(cod)PtCl_2$ (68 mg, 0.18 mmol) and L3 (100 mg, 0.176 mmol) in $CH_2Cl_2$ (10 $cm^3$) was stirred for 2 h. The solvent was reduced to *ca.* 1 $cm^3$ by evaporation under reduced pressure and the product was precipitated by addition of diethyl ether (15 $cm^3$). The pale yellow solid was collected by filtration and dried *in vacuo*. Yield: 102 mg, 69%. $^{31}P\{^1H\}$ NMR: 73.25 [d, $^2J_{PP} = 52.8$, $^1J_{PPt} = 3897$, P(III)], 57.8 [$^2J_{PP} = 52.8$, $^1J_{Pse} = 512$, $^2J_{PPt} = 109.9$, P(V)]. $^1H$ NMR: 8.52–5.59 (m, 25H, arom), 4.22 (m, 1H, CH), 1.06 (d, $^3J_{HH} = 6.8$, 3H, $CH_3$). IR: 1436, 1102, 932, 870, 743, 688, 554, 525, 492, 373, 320, 291 $cm^{-1}$. Anal. found (calcd.) for $C_{32}H_{29}NP_2Cl_2SePt$: C = 46.30 (46.20); H = 3.10 (3.50); N = 1.60 (1.70)%.

## X-Ray crystallography

Structural analyses were performed on crystals of $L2PdCl_2$ $L2PtCl_2$, $L3PdCl_2$ and $L3PtCl_2$ at −90 ± 1 °C using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystal data, a summary of the data collection and the structural refinement parameters for these are given in Table 1 and selected bond lengths and angles are collected in Table 2. Structures were solved by direct methods for the L2 compounds and Patterson heavy atom methods for the L3 compounds and all were expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. One might expect that all would be isostructural; however, $L2PtCl_2$ and $L2PdCl_2$ crystallise with two molecules of $CHCl_3$ and have space group $P2_1$ instead of $P2_12_12_1$. Absolute configurations were determined by reference to the configuration of the ligands as well as observing lower $R_w$ for the enantiomer.

CCDC reference numbers: 175774–175777 (see http://www.rsc.org/suppdata/nj/b1/b111422k/ for crystallographic data in CIF or other electronic format.

**Table 1** Crystallographic data for the X-ray diffraction studies of $L2PdCl_2$, $L2PtCl_2$, $L3PdCl_2$ and $L3PtCl_2$

| | $L2PdCl_2$ | $L2PtCl_2$ | $L3PdCl_2$ | $L3PtCl_2$ |
|---|---|---|---|---|
| Formula | $C_{34}H_{31}Cl_8NP_2PdS$ | $C_{34}H_{31}Cl_8NP_2PtS$ | $C_{32}H_{29}Cl_2NP_2PdSe$ | $C_{32}H_{29}Cl_2NP_2PtSe$ |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic | Orthorhombic |
| Space group | $P2_1$ (no. 4) | $P2_1$ (no. 4) | $P2_12_12_1$ (no. 19) | $P2_12_12_1$ (no. 19) |
| $a$/Å | 10.2033(5) | 10.2048(3) | 11.8372(7) | 11.8948(4) |
| $b$/Å | 16.3289(8) | 16.3146(9) | 15.8445(9) | 15.3216(5) |
| $c$/Å | 11.7551(5) | 11.7788(5) | 16.8452(7) | 16.8763(6) |
| $\alpha$/° | 90 | 90 | 90 | 90 |
| $\beta$/° | 96.269(3) | 96.615(3) | 90 | 90 |
| $\gamma$/° | 90 | 90 | 90 | 90 |
| $U$/Å$^3$ | 1946.8(1) | 1947.96(13) | 3159.4(3) | 3075.7(2) |
| $\mu$/$cm^{-1}$ | 11.88 | 50.81 | 20.33 | 60.28 |
| $T$/°C | −90 | −90 | −90 | −90 |
| Refl. measured | 14 270 | 12 258 | 13 999 | 17 433 |
| Unique refl. | 7818 | 7551 | 7200 | 8171 |
| $R_{int}$ | 0.044 | 0.057 | 0.054 | 0.070 |
| Data used [$I>3\sigma(I)$] | 3179 | 3685 | 2368 | 2641 |
| Final $R$ | 0.036 | 0.045 | 0.038 | 0.037 |
| Final $R_w$ | 0.041 | 0.051 | 0.041 | 0.039 |

**Table 2** Selected bond lengths (Å) and angles (°) for $L2PdCl_2$, $L2PtCl_2$, $L3PdCl_2$ and $L3PtCl_2$

| | $L2PdCl_2$ (E = S) | $L2PtCl_2$ (E = S) | $L3PdCl_2$ (E = Se) | $L3PtCl_2$ (E = Se) |
|---|---|---|---|---|
| M–Cl(1) *trans* to E | 2.310(2) | 2.324(3) | 2.321(3) | 2.313(3) |
| M–Cl(2) *trans* to P | 2.369(2) | 2.346(3) | 2.366(2) | 2.312(3) |
| M–E | 2.274(2) | 2.260(3) | 2.377(1) | 2.369(1) |
| M–P(1) | 2.214(2) | 2.212(3) | 2.218(3) | 2.152(3) |
| E–P(2) | 2.011(3) | 2.016(4) | 2.164(2) | 2.129(3) |
| Cl(1)–M–Cl(2) | 92.73(7) | 90.7(1) | 93.30(9) | 89.46(12) |
| P(1)–M–Cl(1) | 87.73(7) | 88.6(1) | 87.33(9) | 90.1(1) |
| P(1)–M–E | 91.21(7) | 92.1(1) | 92.94(8) | 92.44(9) |
| Cl(2)–M–E | 88.67(7) | 88.7(1) | 86.15(7) | 87.76(8) |
| P(2)–E–M | 101.8(1) | 101.2(2) | 97.55(7) | 98.54(10) |
| P(1)–N–P(2) | 116.0(3) | 115.1(6) | 116.4(4) | 116.5(6) |

## Results and discussion

### Ligand synthesis

By a refinement of the method reported by Krishnamurthy *et al.*[11] we have prepared the chiral chelating bisphosphine (*S*)-*N,N*-bis(diphenylphosphino)methylbenzylamine (L1) and used this to prepare two new chiral bisphosphine monochalcogenides by direct reaction with one equivalent of either elemental sulfur (L2) or selenium (L3).

The $^{31}P\{^1H\}$ NMR spectrum of L1 is a singlet at $\delta = 53.20$, whereas L2 exhibits two doublets, at 71.95 [P(v)] and 54.42 [P(III)], with a $^2J(^{31}P\text{-}^{31}P)$ coupling of 13.2 Hz. The spectrum of L3 is similar, with doublets at 70.43 [P(v)] and 53.08 [P(III)], with a $^2J(^{31}P\text{-}^{31}P)$ coupling of 8.8 Hz. Additionally, the lower field resonance shows selenium satellites with $^1J(^{31}P\text{-}^{77}Se)$ of 756.6 Hz, a value typical for phosphine selenides.[12]

There is a well-developed field of coordination chemistry based upon bisphosphines doubly oxidised by sulfur or selenium, but very few reports of the monoxidised versions have appeared. In the case of an achiral analogue of L3 prepared from aniline, the value for $^2J(^{31}P\text{-}^{31}P)$ is *ca.* 110 Hz and $^1J(^{31}P\text{-}^{77}Se)$ is 766 Hz.[12] In a related system, Smith *et al.* have reported *N,N*-bis(diphenylphosphino)-2-methoxyaniline, an analogue of L1 that has a coupling between the two phosphorus nuclei of 103 Hz.[13] We attribute the variation between the values of the phosphorus-to-phosphorus coupling to the difference in the basicity of the nitrogens. In these two previously reported cases, where the amine is aromatic, there is a marked difference in basicity at the nitrogen with respect to that of the ligands L2 and L3 reported here, wherein the amine is essentially alkyl. This in turn will have an effect on the nature of the (P–N) bonds and thus the extent to which the phosphorus centres will couple.

The new ligands L2 and L3 present a mixed [P,E] donor set that can chelate to a metal centre to form a five-membered inorganic ring. Perhaps the main feature that they offer is electronic asymmetry, and with specific reference to this property, we have prepared a number of complexes of transition metals using these ligands to explore their characteristics.

### Complexes of L1–3 with Rh(I) and Ir(I)

Two equivalents of the bisphosphine L1 react with $[(cod)M(I)Cl]_2$ (M = Rh or Ir) to give the neutral chloro-bridged dimers $[(\kappa^2\text{-L1-}P,P)M(I)Cl]_2$ $[L1RhCl]_2$ and $[L1IrCl]_2$ in preference to the monoanionic bridge-cleaved products $[(\kappa^2\text{-L1-}P,P)(cod)M(I)]Cl$. This is established by the NMR spectra, which indicate the presence of complexed L1 and the absence of cod, and the IR spectra, which show the presence of the chloro bridge. The chemical shift in the $^{31}P\{^1H\}$NMR spectra show characteristic downfield shifts, and the coupling $^1J(^{31}P\text{-}^{103}Rh)$ of 123.2 Hz in $[L1RhCl]_2$ is typical for phosphines coordinated to rhodium(I) centres.

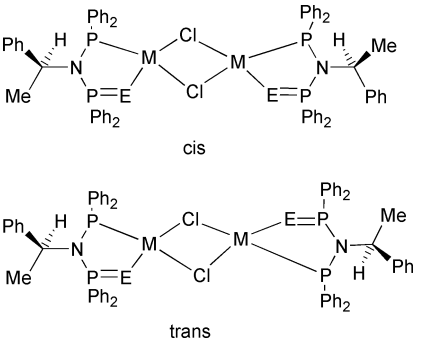


**Fig. 2** The geometric isomers of complexes $[\kappa^2\text{-(L)-}MCl]_2$.

Prepared in the same way, complexes of L2 are also of the form $[(\kappa^2\text{-L2-}P,S)M(I)Cl]_2$. As L2 has two different donor groups, in this case there is the possibility of geometric isomers, Fig. 2. The reaction of two equivalents of L2 with $[(cod)Rh(I)Cl]_2$ for a period of five hours leads to a red solution, and the red solid product isolated from the reaction at this time shows both a $^{31}P\{^1H\}$ and a $^1H$ NMR spectrum indicative of a single isomer product. The analogous reaction with L3, however, leads after the same time interval to a solution that has $^{31}P\{^1H\}$ and $^1H$ NMR spectra indicative of a more complex situation, with two isomers present in approximately equal concentrations. On standing such a solution for a further three days, the concentrations of these two components are changed, such that the resonances to higher field are of greater intensity with respect to those at lower field in a ratio of 4 : 1. This slow interconversion indicates that, although both isomers are formed initially, there is a thermodynamically preferred isomer, and that over time, the less favoured kinetic product isomerises to the more stable geometry. The rate at which the equilibrium is reached is somewhat dependent upon the solvent, such that solutions kept in $CDCl_3$ show a slightly reduced rate of equilibration with respect to those kept in $CH_2Cl_2$.

This kind of isomerism is also seen for the corresponding iridium complexes. In the case of L2, after five hours reaction the $^{31}P\{^1H\}$NMR spectrum shows a single set of resonances indicative of a single isomer product. After a period of five days in chloroform solution at room temperature, a second set of resonances is present at intermediate field suggesting the formation of the second isomer. For the complex with L3, the rate of isomerisation is somewhat slower.

To further probe the isomerisation processes, we added aliquots of THF or excess ligand to the solutions of the samples. Addition of THF to a $CH_2Cl_2$ solution of $[L3RhCl]_2$ increases the rate of interconversion. For $[L2IrCl]_2$ and $[L3IrCl]_2$ similar results are seen, where addition of THF accelerates the rate of interconversion. The addition of a catalytic quantity of excess ligand in both cases gives a much

greater increase in the rate of isomerisation. These findings together indicate that the interconversion is catalysed by the addition of a ligand species, which may suggest that the mechanism involves an intermediate in which an incoming ligand forms initially a five-coordinate metal centre. This can then either undergo a pseudorotation to exchange the ligand positions or cleavage of one halide bridge followed by rotation about the remaining M–X–M axis before re-establishment of the M–X–M bridge to reform the dimer, a process that could lead to exchange of the P and E positions.

We were interested in assigning geometries to the two isomers and so examined the spectroscopic data to this end. In the case of the cis isomers, the two P(III) termini of the ligands are both trans to a single chloro group in the halide bridge, and so it seems reasonable to assume that the extent to which electron density is back-donated to the σ* orbital of these phosphorus is reduced with respect to the trans isomers, in which each phosphorus has a different trans halide. From this, it can be inferred that the cis isomers will show a greater coupling between the phosphorus centres, as the degree of back-donation is reduced with respect to the trans isomers and so the P(III)–N bond length will be shorter in the cis isomer. Furthermore, the cis isomer might also be expected to show a more low-field value for $\delta$ as the electron density about the nucleus is, by the same arguments, reduced. In the case of $[L3RhCl]_2$, the less stable isomer shows a greater coupling than the more stable one and resonates at a lower field. In the case of both $[L2IrCl]_2$ and $[L3IrCl]_2$ the less stable isomer again shows a greater coupling, although the chemical shift data is less conclusive. In this case, the chemical shifts for the more stable isomer occur at a field between the P(V) and P(III) resonances of the less stable isomer.

Considering the IR data, and in particular the bands associated with the halide bridge, for the cis isomer a greater degree of asymmetry is expected in the M–X system. In the case of the complex $[L2IrCl]_2$ it was possible to isolate samples of the two isomers independently. Comparing the spectra from these two isomers, there are more $\nu$(M–X) absorptions seen for the initially produced isomer than in the final isomer. The inference from this data is consistent with that from the $^{31}P\{^1H\}$NMR data, and so we tentatively assign the initially formed isomer to the cis geometry and the preferred isomer to trans.

### Complexes of L2 and 3 with Pd(II) and Pt(II)

Reaction of L2 or L3 with (cod)M(II)$Cl_2$ (M = Pd or Pt) forms complexes of general formula ($\kappa^2$-L-*P,E*)M(II)$Cl_2$. The chemical shift in the $^{31}P\{^1H\}$ NMR spectra and the values of the couplings $^2J(^{31}P\text{-}^{31}P)$, $^1J(^{31}P\text{-}^{77}Se)$, $^1J(^{31}P\text{-}^{31}Pt)$ and $^2J(^{31}P\text{-}^{31}Pt)$ all fall within the range of typical values. The structures of ($\kappa^2$-L2-*P,S*)Pd(II)$Cl_2$, ($\kappa^2$-L3-*P,Se*)Pd(II)$Cl_2$, ($\kappa^2$-L2-*P,S*)Pt(II)$Cl_2$ and ($\kappa^2$-L3-*P,Se*)Pt(II)$Cl_2$ were all determined by single crystal X-ray diffraction measurements and are presented in Figs. 3 and 4. The metrical parameters are presented in Table 1 and the values of selected bond lengths and angles are given in Table 2.

The overall structure of the complexes is square planar in each case with cis disposition of the chloro ligands and in each case the chelate ring is almost flat. The structures of the palladium and platinum complexes of the same ligand are isomorphous. The conformations of the ligands in all four complexes are very similar, even though the phosphine sulfide complexes and phosphine selenide complexes crystallise in different space groups and one lattice accommodates a solvent. Comparison of the structures of the two pairs of complexes allows for discussion of the effect of varying the chalogen. The distances M–Cl can be used to evaluate and compare the trans influence of the phosphine sulfide with respect to the phosphine selenide. For the monosulfide complex of palladium, the Pd–Cl trans to the chalcogen is 0.059 Å shorter than the Pd–Cl trans to the P(III) terminus of L2. For the corresponding platinum complex, a similar though smaller variation is seen, with the Pt–Cl trans to the chalcogen 0.022 Å shorter than the Pt–Cl trans to the P(III). For the complexes of L3, the effect is similar but smaller, with 0.045 Å between the two Pd–Cl distances and no measurable difference between the two Pt–Cl distances. The implication of this latter observation is that the overall trans influence of the phosphine selenide is in this case not greatly different from the phosphine itself. For the palladium complex of L3, however, there is a difference between the two Pd–Cl distances and this may indicate that the extent to which there is a hard-soft match between the metal and the chalcogen on the P(V) terminus of the ligand controls the degree to which the trans influence is expressed.

The distance M–E is significantly longer in the cases where E is Se than those where E is S, and for the platinum complexes, there is a corresponding compression of the M–P distance in the selenium-containing ring compared to the sulfur-containing ring. This allows an internal compensation for the change in size and softness of the chalcogen whilst maintaining the overall geometry of the ring. There is also a corresponding compression of the angle Pt–E–P from 101.2 to 98.5° between the sulfide and the selenide as part of the same reorganisation of the ring.

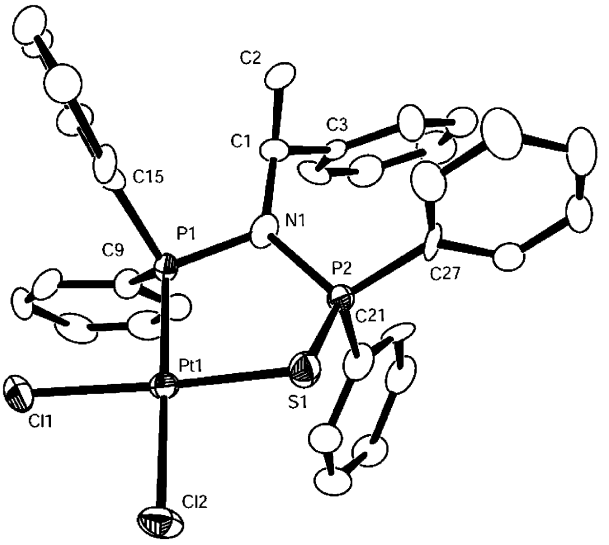


**Fig. 3** The molecular structure of ($\kappa^2$-L2)$PtCl_2$, an ORTEP drawing with 50% probability ellipsoids.

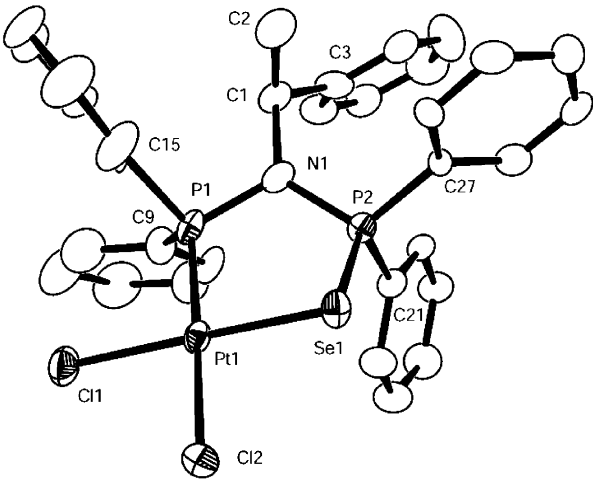


**Fig. 4** The molecular structure of ($\kappa^2$-L3)$PtCl_2$, an ORTEP drawing with 50% probability ellipsoids.

## Conclusion

By direct reaction of a simple chiral bisphosphine with elemental sulfur or selenium, we have prepared the first chiral bisphosphine monosulfide and -selenide. These ligands coordinate metals from group nine or ten to form chelated complexes. The ease of preparation of such ligands would suggest that there is a wealth of coordination chemistry available using such new heterobidentate chiral ligands prepared from chiral bisphosphines and elemental sulfur or selenium.

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