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Diphosphine mono-sulfides: readily available chiral monophosphines

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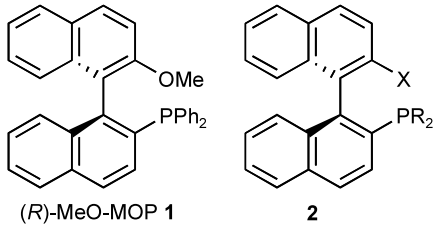
Abstract—Enantiomerically pure (*R*)-BINAP, (*R*)-Tol-BINAP, (*R*,*R*)-Me-DUPHOS and (*R*,*R*)-DIOP were converted into the corresponding mono-sulfides by treatment with elemental sulfur in benzene.

1. Introduction

Enantiomerically pure diphosphines occupy a pre-eminent position as the ligands of choice for a number of transition metal catalysed processes.[1] Central in these reactions are rhodium and ruthenium-catalysed homogeneous hydrogenations of C=X bonds.[2] The success of diphosphines in hydrogenation chemistry, together with the potential commercial importance of this process, has resulted in a considerable body of work detailing efforts to design diphosphines capable of generating more selective and efficient catalysts. Several members of this ligand class are now commercially available at reasonable cost. In comparison the number of reports concerned with the development of chiral monophosphines, traditionally viewed as generating poorly enantioselective hydrogenation catalysts, is more limited.[3] However it is recognised that there are several catalytic processes, such as asymmetric Grignard cross-coupling reactions, where a monodentate or hemilabile ligand is needed to generate an active catalyst.[4] This, together with the discovery that enantiomerically pure phosphorus based monodentate ligands can deliver highly enantioselective hydrogenation catalysts, has resulted in a recent upturn in interest in chiral monophosphine development.[5]

Of the reported monophosphines MeO-MOP **1** has arguably received most attention.[6] It is the ligand of choice for the asymmetric hydrosilylation of C=C bonds[7a,b] and has also been shown to generate highly enantioselective catalysts for palladium catalysed allylic substitution[7c] and rhodium catalysed boronic acid-aldehyde additions.[7d]



(*R*)-MeO-MOP **1** **2**

The use of MeO-MOP is limited by its high cost and non-trivial preparation.[8] Several other successful monophosphines also suffer from difficult preparative syntheses.[9] Herein we detail a new route to a range of chiral monophosphines; crucially the preparation of these new ligands is achieved in a one-step modification of commercial chiral diphosphines and allows rapid access to MeO-MOP analogues such as **2**.

2. Results and discussion

In our desire to access rapidly a range of chiral monophosphine ligands we elected to focus on the derivatisation of commercially available chiral diphosphines. To convert diphosphines into effective monophosphines we needed to either block or remove one of the phosphine groups and reasoned that conversion to either the mono-phosphine oxide, mono-phosphine borane or mono-phosphine sulfide would serve this purpose. When selecting which of these approaches to employ we considered ease of preparation and stability of the expected products. We were also mindful that

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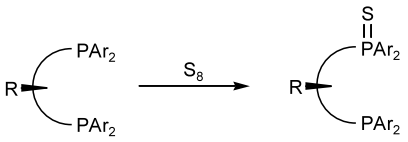


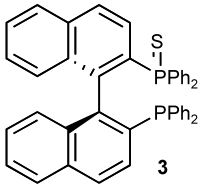
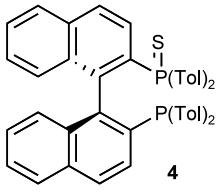
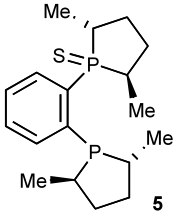
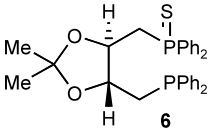
Scheme 1. Preparation of mono-phosphine sulfides.

in any synthesis we developed we could expect to form reasonable amounts of the doubly derivatised products, and as such, a simple method to recycle this valuable material would be beneficial. Phosphine sulfides can be readily prepared by treatment of the corresponding phosphine with elemental sulfur.[10] For the reverse transformation, reduction of the phosphine sulfide with lithium aluminium hydride is known to provide the phosphine.[11] Given these considerations we chose to focus on the synthesis of a range of mono-phosphine sulfides (Scheme 1).[12]

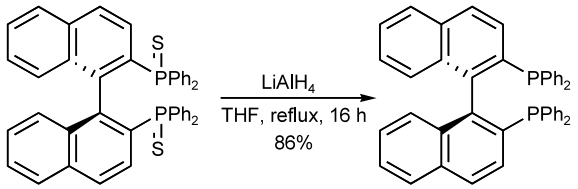
Treatment of (*R*)-BINAP with one equivalent of elemental sulfur in refluxing benzene provided a 37:27:20 mix of the mono-sulfide:disulfide:diphosphine in 84% overall yield. (Table 1, entry 1). The individual components could be readily separated by flash chromatography on silica gel and fully characterised. When subjected to identical conditions (*R*)-Tol-BINAP generated a similar mixture of products (entry 2). Under the given reaction conditions (*R*,*R*)-Me-DUPHOS produced a much higher yield of the mono-sulfide (70%) with only small amounts of the starting diphosphine being isolated (entry 3). We suggest that this high selectivity for mono-sulfide formation is attributed to adverse steric interactions present in the disulfide as a consequence of increased rigidity of the ligand backbone.[13] (*R*,*R*)-DIOP provided lower overall yields of the three components. This is ascribed to contamination with non-isolable phosphine oxide impurities (entry 4). Given that in all cases examined the individual reaction products could be separated we elected not to optimise individual reactions.

In the preparation of all four mono-sulfides we isolated significant quantities of the corresponding disulfides. Given the valuable nature of these compounds we desired a method of re-converting these to the starting diphosphines. Hydride reduction of P=S bonds to deliver the free phosphine is an established conversion,[11] and in our hands treatment of BINAP disulfide with lithium aluminium hydride in refluxing THF provided BINAP in 86% yield (Scheme 2).

Table 1. Preparation of diphosphine mono-sulfides[a]

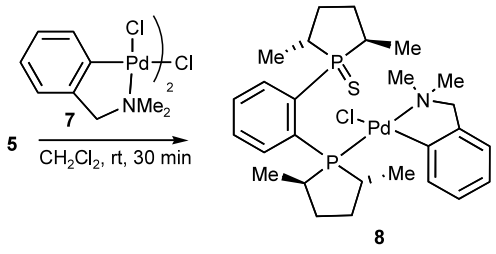
entry	diphosphine	monophosphine (%)		disulfide (%)	diphosphine (%)
1	(*R*)-BINAP	 **3**	37	27	20
2	(*R*)-Tol-BINAP	 **4**	40	27	20
3	(*R*,*R*)-Me-DUPHOS	 **5**	70	18	3
4	(*R*,*R*)-DIOP	 **6**	24	27	26

[a]Conditions: diphosphine (1.0 equiv.), S_8 (1.2 equiv.), PhH, reflux, 2.5 h.



Scheme 2. Reduction of BINAP disulfide.

A brief investigation of the metal binding properties of this new family of monophosphines was undertaken. (*R*,*R*)-Me-DUPHOS monosulfide **5** was treated with $[Pd(dmba)(\mu\text{-}Cl)]_2$ **7** to generate complex **8** (Scheme 3).[14] Crystallisation of **8** from methylene chloride/hexane yielded crystals suitable for diffraction studies; the ensuing structure is shown in Fig. 1.[15] Inspection of Fig. 1 shows that only the free phosphine is coordinating to the palladium centre (Pd–P1, 2.2518(4) Å). In the solid-state the monophosphine ligand is disordered, showing two conformations of the phosphacyclopentane rings. This leads to two different Pd–S distances, 3.552(7) and 3.019(3) Å, to be resolved. However, given that both of these are longer than the combined covalent radii of Pd+S (2.33 Å), no significant Pd–S interaction is apparent.



Scheme 3. Formation of Pd complex **8**.

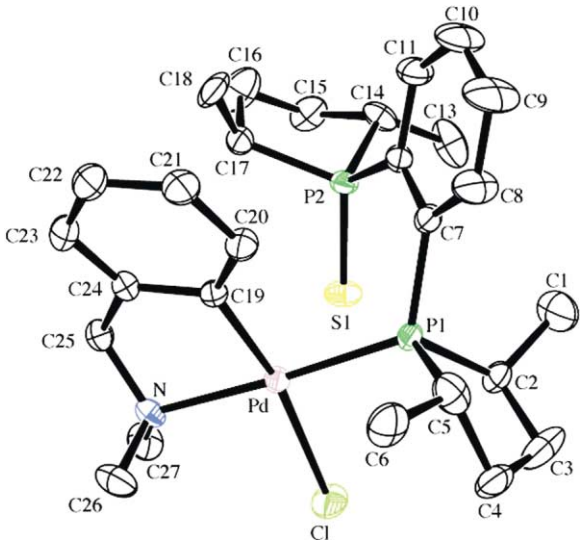


Figure 1. ORTEP[16] drawing of the major disordered component of **8**, ellipsoids are depicted at 50% probability. Selected bond lengths (Å): Pd–S(1) 3.552(7), Pd–S(1A) 3.019(3), Pd–P1 2.2518(4).

3. Conclusion

We have demonstrated that a range of commercially available chiral diphosphines can be readily converted to the corresponding diphosphine mono-sulfides. The mono-sulfides are stable, readily purified compounds, which in certain cases can be obtained in high yield. Preliminary investigations indicate that the mono-sulfides bind palladium complexes as mono-phosphines. We are currently investigating the use of these new ligands in a range of transition metal catalysed processes and the results of these studies will be reported in due course.

4. Experimental

4.1. General

All reactions were performed under an inert atmosphere of argon, in oven or flame dried glassware. Flash chromatography was carried out using Merck Kieselgel 60H silica and Fisher Matrex Silica 60 silica. TLC was performed using Merck Kieselgel G/UV_{254} coated glass, aluminium and plastic plates. Melting points were measured on a Buchi 535 melting point apparatus and are uncorrected. IR spectra measurements were carried out as thin or liquid films on NaCl discs recorded on a Perkin–Elmer FTIR 1600 spectrometer. Mass Spectra were carried out on a Finnigan MAT 8340 instrument at the University of Bath and by the EPSRC mass spectrometry service, Swansea. ^{1}H NMR spectra were recorded in $CDCl_3$, unless otherwise stated, on a JEOL GX 400 or Bruker AM 300 instruments at 400 and 300 MHz, respectively. Chemical shifts are reported in ppm using tetramethyl silane or residual $CHCl_3$ as an internal reference. Coupling constants are measured in hertz. ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise stated, on the same instruments at 100 and 75.5 MHz, respectively. $CDCl_3$ resonance used as an internal reference. Optical rotations were performed on an Optical Activity LTD: AA-10 automatic polarimeter.

4.2. (*R*)-[2′-(Diphenyl-phosphinothioyl)-[1,1′]binaphthalenyl-2-yl]-diphenyl-phosphane and (*R*)-2,2′-bis-(diphenyl-phosphinothioyl)-[1,1′]binaphthalenyl (Table 1, entry 1)

Sulfur (12.4 mg, 0.385 mmol) was added to a stirring solution of (*R*)-BINAP (200 mg, 0.321 mmol) in degassed benzene (6 mL). The resulting solution was heated to reflux for 2.5 h before being allowed to cool to rt. The solvent was removed in vacuo and the resulting residue was purified via flash chromatography (gradient elution, 10:1–5:1, petrol:EtOAc) to yield in order of elution; (*R*)-BINAP (40 mg, 20%). And *mono sulfide* **3** (78 mg, 37%) as a colourless solid; mp discolours above 225°C, decomposition begins at 243–244°C, melts at 250–251°C; R_f (5:1, petrol:EtOAc) 0.45; ν_{max} (film) 3052, 1584, 1551, 1502, 1479; δ_H (300 MHz) 7.86–7.72 (2H, m) 7.66–7.41 (6H, m), 7.35–7.30 (2H, m), 7.24–7.12 (6H, m), 7.09–6.96 (6H, m), 6.86 (4H, app. t, $J=7.6$), 6.74 (2H, app. t, $J=7.9$), 6.38 (2H, app.

t, $J=7.9$), 6.23 (2H, d, $J=8.5$); δ_C (75.5 MHz) 142.67, 142.46, 138.41, 138.22, 136.29, 136.07, 134.91, 134.61, 133.48, 138.25, 132.96, 132.27, 132.13, 132.03, 131.91, 130.54, 130.51, 130.19, 130.15, 129.53, 128.62, 128.36, 128.08, 128.01, 127.94, 127.88, 127.78, 127.72, 127.67, 127.65, 127.49, 127.37, 127.29, 127.13, 127.04, 127.01, 126.19, 125.97, 125.70; δ_P (121.5 MHz) 45.24 (P=S), −14.44 (P); m/z (FAB+) 655.2 (20%, (M+H)), 469.2 ((M+)−PPh_2), 437.2 (100%, (M+)−S=PPh_2), 217.1 (S=PPh_2+); Found (FAB+) 655.1800; $C_{44}H_{33}P_2S$ (M+H), requires 655.1778; $[\alpha]_D^{20}=+35$ ($CHCl_3$, c 0.5). And *bis sulfide* (60 mg, 27%) as a colourless solid; mp >315°C, discolours slightly over 303°C; R_f (5:1, petrol:EtOAc) 0.25; ν_{max} (film) 3053, 1586, 1548, 1501, 1479; δ_H (300 MHz) 7.82–7.65 (12H, m), 7.53–7.45 (4H, m), 7.32–7.24 (12H, m), 6.74 (2H, app. d, $J=8.4$), 6.66 (2H, app. t, J=7.1); δ_C (75.5 MHz) 140.50, 140.43, 140.32, 136.14, 134.99, 133.91, 133.88, 133.39, 133.23, 132.80, 132.67, 132.14, 132.12, 132.00, 131.01, 130.83, 130.79, 130.55, 130.51, 129.34, 129.19, 129.03, 128.02, 127.92, 127.69, 127.69, 127.56, 127.39, 127.19, 125.60; δ_P (121.5 MHz) 43.70 (2×(S=P)); m/z (FAB+) 687.1 (50%, (M+H)), 655.2 ((M+H)−S), 469.2 (100%, (M+)−S=PPh_2), 437.2 ((M+)−S=PPh_2, −S), 217.1 (S=PPh_2+); Found (FAB+) 687.1479; $C_{44}H_{33}P_2S_2$ (M+H), requires 687.1499; $[\alpha]_D^{20}=+72$ ($CHCl_3$, c 0.5).

4.3. (*R*)-[2′-(Di-*p*-tolyl-phosphinothioyl)-[1,1′]binaphthalenyl-2-yl]-di-*p*-tolyl-phosphane and (*R*)-2,2′-bis-(di-*p*-tolyl-phosphinothioyl)-[1,1′]binaphthalenyl (Table 1, entry 2)

Sulfur (4.7 mg, 0.162 mmol) was added to a solution of (*R*)-Tol-BINAP (100 mg, 0.147 mmol) in degassed benzene (3 mL). The reaction mixture was heated to reflux for 2.5 h before being cooled and the solvent removed in vacuo. The solid residue was purified via flash chromatography (gradient elution, petrol to 7:1, petrol:EtOAc) to yield in order of elution, (*R*)-Tol-BINAP as a colourless solid (20 mg, 20%). And *mono-sulfide* **4** (42 mg, 40%) as a colourless solid, mp >300°C; R_f (10:1, petrol:EtOAc) 0.29; ν_{max} (film) 3049, 1598, 1551, 1496, 1448; δ_H (300 MHz) 7.89–7.69 (2H, m), 7.62 (1H, d, $J=8.1$), 7.48–7.30 (5H, m), 7.24–7.18 (3H, m), 7.10 (1H, t, $J=6.9$), 7.02–7.00 (3H, m), 6.89–6.75 (6H, m), 6.65–6.57 (5H, m), 6.36 (1H, t, $J=7.5$), 6.18 (1H, d, $J=8.5$), 2.23 (3H, s), 2.13 (3H, s), 2.10 (3H, s), 2.07 (3H, s); δ_C (75.5 MHz) 141.85, 140.3, 134.8, 134.5, 133.5, 133.2, 132.1, 128.8, 128.1, 128.02, 127.95, 127.90, 127.84, 127.80, 127.04, 126.98, 126.04, 125.89, 21.2, 21.1; δ_P (121.5 MHz) 45.2 (S=$P(Tol)_2$), −15.4 ($P(Tol)_2$; m/z (FAB+) 711.3 (25%, (M+H)), 465.3 (100%, (M+)−$P(Tol)_2$); Found (FAB+) 711.2431; $C_{48}H_{41}P_2S$ (M+H), requires 711.2404; $[\alpha]_D^{20}=-4$ ($CHCl_3$, c 0.5). And *bis-sulfide* (30 mg, 27%) as a colourless solid; mp >300°C; R_f (10:1, petrol:EtOAc) 0.14; ν_{max} (film) 3050, 1599, 1550, 1497, 1449; δ_H (300 MHz) 7.74–7.69 (4H, m), 7.62–7.48 (10H, m), 7.34–7.29 (2H, m), 7.03–6.97 (8H, m), 6.80–6.70 (4H, m), 2.34 (6H, s), 2.30 (6H, s); δ_C (75.5 MHz) 140.90, 140.87, 140.67, 140.63, 139.93, 139.87, 139.83, 139.76, 133.72, 132.69, 132.54, 132.38, 132.22, 132.08, 131.22, 129.50, 129.34, 129.18, 128.97, 128.58, 128.45, 128.41, 128.28, 128.05, 127.72, 127.61, 127.45, 127.22, 127.49, 125.64, 21.33, 21.31;δ_P (121.5 MHz) 43.9 (2×(S=P)); m/z (FAB+) 743.1 (50%, (M+)), 497.1 (100%, (M+)−P(S)Tol_2), 465.2 ((M+)−P(S)Tol_2, −S); Found (FAB+) 743.2152; $C_{48}H_{41}P_2S_2$ (M+H), requires 743.2406; $[\alpha]_D^{20}=-18$ ($CHCl_3$, c 0.5).

4.4. (*R*,*R*)-1-[2-(2,5-Dimethyl-phospholan-1-yl)-phenyl]-2,5-dimethyl-phospholane 1-sulfide and (*R*,*R*)-1,2-bis-(2,5-dimethyl-phospholane 1-sulfide)benzene (Table 1, entry 3)

Sulfur (31.4 mg, 0.979 mmol) was added to a stirring solution of (*R*,*R*)-Me-DUPHOS (250 mg, 0.816 mmol) in degassed benzene (12 mL). The resulting solution was heated to reflux for 2.5 h before being allowed to cool to rt. The solvent was removed in vacuo and the resulting residue was purified via flash chromatography (gradient elution, 10:1–5:1, petrol:EtOAc) to yield in order of elution, to yield in order of elution, (*R*,*R*)-Me-DUPHOS (8 mg, 3%). And *mono-sulfide* **5** (194 mg, 70%) as a colourless solid; mp 142–143°C; R_f (5:1, petrol:EtOAc) 0.45; ν_{max} (film) 3049, 2949, 2924, 2862, 1448; δ_H (300 MHz) 7.69–7.66 (1H, m), 7.41–7.39 (2H, m), 7.32–7.31 (1H, m), 3.04–2.98 (1H, m), 2.76–2.47 (4H, m), 2.13–1.89 (4H, m), 1.55–1.33 (6H, m), 1.25–1.14 (3H, m), 0.98–0.82 (6H, m); δ_C (75.5 MHz) 142.50, 142.35, 142.05, 140.80, 140.34, 139.87, 139.41, 135.61, 135.58, 135.47, 135.43, 130.16, 130.02, 129.98, 129.89, 128.61, 128.49, 41.88, 41.32, 36.83, 36.81, 36.34, 36.27, 36.17, 36.02, 34.90, 34.74, 31.84, 31.14, 30.48, 30.46, 30.39, 30.22, 20.55, 19.58, 19.54, 18.03, 17.98, 13.82; δ_P (121.5 MHz) 72.86 (S=P), 5.72 ($P(C_{alk})_2$); m/z (FAB+) 339.2 (100%, (M+H)); Found (FAB+) 339.1469; $C_{18}H_{29}P_2S$ (M+H), requires 339.1465; $[\alpha]_D^{20}=-140$ ($CHCl_3$, c 0.5). And *bis-sulfide* (53 mg, 18%) as a colourless solid; mp 258–259°C; R_f (5:1, petrol:EtOAc) 0.25; ν_{max} (film) 3053, 2962, 2925, 1456; δ_H (300 MHz) 7.67–7.59 (2H, m), 7.56–7.50 (2H, m), 3.54–3.42 (2H, m), 2.88–2.77 (2H, m), 2.59–2.43 (2H, m), 2.16–1.95 (4H, m), 1.50–1.38 (2H, m), 1.34 (6H, dd, $J=16.6$ and 6.8), 0.99 (6H, dd, $J=20.0$ and 7.5); δ_C (75.5 MHz) 135.90, 135.82, 135.06, 134.98, 132.94, 132.81, 131.69, 130.56, 130.45, 130.40, 130.36, 130.25, 42.05, 42.03, 41.32, 41.30, 33.39, 33.36, 32.65, 32.62, 30.40, 30.35, 30.29, 29.87, 29.80, 29.70, 29.59, 29.53, 20.60, 12.04; δ_P (121.5 MHz) 74.48 (2×S=P); m/z (FAB+) 371.1 (85%, (M+H)); found 371.1181; $C_{18}H_{29}P_2S_2$ (M+H), requires 371.1186; $[\alpha]_D^{20}=-44$ ($CHCl_3$, c 0.5).

4.5. (*R*,*R*)-[5-(Diphenyl-phosphinothioylmethyl)-2,2-dimethyl-[1,3]dioxolan-4-yl-methyl]-diphenyl-phosphane and (*R*,*R*)-4,5-*bis*-(diphenyl-phosphinothioylmethyl)-2,2-dimethyl-[1,3]dioxolane (Table 1, entry 4)

Sulfur (6.2 mg, 0.19 mmol) was added to a stirring solution of (*R*,*R*)-DIOP (80 mg, 0.16 mmol) in degassed benzene (3 mL). The resulting solution was heated to reflux for 2.5 h before being allowed to cool to rt. The solvent was removed in vacuo and the resulting residue was purified via flash chromatography (gradient elution, 10:1–5:1, petrol:EtOAc) to yield in order of elution, (*R*,*R*)-DIOP (21 mg, 26%) as a colourless solid. And *mono-sulfide* **6** (20 mg, 24%) as a

colourless solid; mp 128–130°C; R_f (5:1, petrol:EtOAc) 0.39; ν_{max} (film) 3055 (C_{ar}-H), 2986, 2930, 1437, 1102; δ_H (300 MHz) 7.89–7.73 (4H, m), 7.50–7.38 (10H, m), 7.33–7.30 (6H, m), 4.38–4.29 (1H, m), 3.89–3.85 (1H, m), 2.92–2.81 (1H, m), 2.55 (1H, m), 2.37–2.34 (2H, m), 1.26 (3H, s), 1.21 (3H, s); δ_C (75.5 MHz) 138.41, 133.25, 129.99, 132.68, 132.43, 131.73, 131.59, 130.98, 130.84, 128.83, 128.64, 128.50, 128.47, 128.41, 128.37, 128.28, 128.11, 109.42, 79.62, 79.46, 79.27, 77.20, 76.86, 76.73, 37.24, 36.74, 31.56, 31.36, 27.02, 26.00; δ_P (121.5 MHz) 40.89 (S=PPh_2), −21.66 (PPh_2); m/z (FAB+) 531.2 (100%, (M+H)); Found (FAB+) 531.1686; $C_{31}H_{33}O_2P_2S$ (M+H) requires 531.1677. $[\alpha]_D^{20}=-18$ ($CHCl_3$, c 1.7). And *bis-sulfide* (20 mg, 27%) as a colourless solid; mp 179–180°C; R_f (5:1, petrol:EtOAc) 0.25; ν_{max} (film) 3055, 2986, 2934, 1436, 1103; δ_H (300 MHz) 7.89–7.73 (8H, m), 7.49–7.37 (12H, m), 4.46–4.35 (2H, m), 2.94–2.84 (2H, m), 2.61–2.51 (2H, m), 1.11 (6H, s); δ_C (75.5 MHz) 134.39, 133.36, 133.30, 132.27, 132.06, 131.97, 131.92, 131.75, 131.71, 131.35, 131.18, 131.04, 129.16, 129.00, 128.67, 128.50, 109.80, 77.83, 77.63, 76.79, 76.76, 76.61, 36.43, 35.68, 27.16; δ_P (121.5 MHz) 41.29 (2×S=PPh_2); m/z (FAB+) 563.2 (100%, (M+H)), 531.2 ((M+H) – S); Found (FAB+) 563.1405; $C_{31}H_{33}O_2P_2S_2$ (M+H), requires 653.1397. $[\alpha]_D^{20}=+13$ ($CHCl_3$, c 0.6).

4.6. Reduction of disulfide

$LiAlH_4$ (22 mg, 0.852 mmol) was added to a solution of BINAP bis sulfide (50 mg, 0.073 mmol) in freshly distilled THF (0.5 mL) and the reaction was stirred at reflux for 16 h. The reaction mixture was then cooled to 0°C and 40 μL of H_2O was slowly added, followed by 40 μL of 15% NaOH, and another 120 μL of H_2O. The heterogeneous mixture was stirred for 30 min, filtered and the solid washed with Et_2O. The filtrate was evaporated to dryness in vacuo. Purification by flash chromatography (10:1 hexane:ethyl acetate) yielded BINAP (39 mg, 86% yield) as a white solid.

4.7. Preparation of Pd complex 8

Mono sulfide **5** (70 mg, 0.21 mmol) was added to a solution of $[Pd(dmba)(\mu\text{-}Cl)]_2$ (57 mg, 0.1 mmol) in CH_2Cl_2 (6 mL) at ambient temperature. The mixture was stirred for 30 min, filtered, and the volatiles evaporated to leave a pale green powder, which was washed with diethyl ether (2 mL) and pentane (2×3 mL) and dried under vacuum. Crystallisation form CH_2Cl_2/hexane produced pale green prisms suitable for X-ray diffraction study (102 mg, 80%); mp 199°C; ν_{max} (cm^{-1}, KBr) 3046, 2923, 2863, 1624, 1577, 1560, 1448, 1376, 1290, 1251, 1112, 1040, 1006, 989, 926, 844, 742, 675, 578, 561, 473; δ_H (300 MHz) 8.326–8.26 (1H, m), 7.99 (1H, t, $J=6.4$), 7.86 (1H, t, $J=7.0$), 7.81–7.74 (1H, m), 7.09 (1H, d, $J=7.2$), 6.99 (1H, t, $J=7.1$), 6.87–6.78 (2H, m), 4.66 (1H, d, $J=13.2$), 3.56–3.44 (2H, m), 3.24–3.08 (2H, m), 3.00 (2H, Br s), 2.81–2.68 (1H, m), 1.84–2.68 (10H, m), 1.52–1.84 (2H, m), 1.42 (3H, dd, $J=6.6$, 18.6), 0.85–1.02 (9H, m); δ_H (300 MHz, $^1H\{^{31}P\}$) 8.33 (1H, d, $J=7.7$), 7.99 (1H, t, $J=7.7$), 7.86 (1H, t, $J=7.5$), 7.77 (1H, d, $J=7.7$), 7.09 (1H, d, $J=7.3$), 6.99 (1H, dt, $J=6.9$, 1.5), 6.87–6.79 (2H, m), 4.66 (1H, d, $J=13.0$), 3.56–3.43 (2H, m), 3.22–3.08 (2H, m), 2.98 (2H, br s), 1.87–2.74 (10H, m), 1.74 (1H, dq, $J=5.0$, 13.0), 1.66–1.58 (1H, m), 1.42 (3H, d, $J=6.9$), 0.93 (9H, app d, $J=6.9$); δ_C (75.5 MHz) 157.9, 148.3, 135.1, 134.9, 133.5, 131.2, 126.9, 125.6, 124.3, 73.7, 49.2, 48.6, 38.9, 37.6, 37.2, 34.8, 33.1, 30.5, 22.0, 20.2, 20.0, 15.3, 14.3; δ_P (121.5 MHz) 71.2 (d, $J=15.8$), 66.2 (d, $J=15.8$). Anal. calcd for $C_{25}H_{36}ClNP_2PdS$: C, 52.77; H, 6.56; N, 2.28; found: C, 52.8; H, 6.58; N, 2.28.

Crystal data for **8**: yellow orange rhombohedron, crystal dimensions 0.45×0.4×0.3 mm, empirical formula $C_{27}H_{40}ClNP_2PdS$, $F_w=614.45$, monoclinic, space group $P2_1$, $a=10.0000(1)$, $b=14.2690(2)$, c 10.1270(1) Å, $\beta=102.45(5)°$, $V=1411.04(3)$ Å^3, $Z=2$, $\rho_{calcd}=1.446$ g cm^{-3}. Data collection: $T=150(2)$ K, Nonius Kappa CCD, $3.23°\leq\theta\leq33.74°$, ($\lambda$(MoK$_\alpha$)=0.71073 Å, $\mu=0.956$ mm^{-1}), 42476 reflections collected, 11057 unique ($R_{int}=0.033$). Solution and refinement with WinGX-1.64.04,[17] leading to a final $R_1(I>2\sigma(I))=0.0241$, $wR_2=0.0567$, $GOF=1.056$, absolute structure factor $\chi^{18}=-0.030(12)$, max./min. residual electron density 0.62/−1.32 e Å^{-3}.

The phosphacyclopentane ligands are disordered in their conformation with consequences to groups directly attached to the rings. A split atom model was successfully employed for these groups leading to a ratio of 1:1 for S(1), S(1A) and C(13–18), C(13A–18A) and a ratio of 2:1 for C(4), C(4A) and C(6), C(6A).

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