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Ligand ambivalence in pallada(platina)cyclic complexes of a rigid phosphine

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Palladium(II) and platinum(II) complexes of a chiral pentacyclic phosphine, (1*S*, 4*R*, 4a*S*, 5a*R*, 6*R*, 9*S*, 9a*S*, 10a*R*)-4,6,11,11,12,12-hexamethyl-10-phenyl-dodecahydro-1,4:6,9-dimethano-phenoxaphosphinine (phenop), show diverse structures dependent upon the chosen metal-containing starting material and reaction conditions. With palladium acetate, a *P*,*C*-cyclometallated dimeric complex $[Pd(\mu\text{-}\kappa^2\text{-OAc})(\mu\text{-}\kappa^1\text{-OAc})(\kappa P,\kappa C^{14}\text{-phenop})]_2$, **4**, is obtained through metallation at the C(14) methyl to form a six-membered chelate. The acetato bridged dimer is readily converted to the halo-bridged species $[Pd(\mu\text{-X})(\kappa P,\kappa C^{14}\text{-phenop})]_2$, where X is chloride (**5**) or bromide (**6**). Reaction of one equivalent of phenop with $Pd(COD)Cl_2$ or Na_2PdCl_4 gives a different phosphapalladacycle dimer $[Pd(\mu\text{-Cl})(\kappa P,\kappa C^{8}\text{-phenop})]_2$, **7**, with a five-membered chelate and metallation at the C(8) methylene carbon. The analogous platinum derivative $[Pt(\mu\text{-Cl})(\kappa P,\kappa C^{8}\text{-phenop})]_2$, **8**, is obtained from the 1 : 1 reaction of phenop and K_2PtCl_4. An unusual ligand–ligand coupled product, **9**, has been isolated in low yield from the reaction of phenop and $Pd(COD)Cl_2$. The zerovalent $Pd(\kappa P\text{-phenop})_2$, **10**, and a monodentate silver(I) derivative, $[Ag(\kappa P\text{-phenop})(CF_3SO_3)]$, **11**, have also been prepared. These new complexes have been fully characterised by spectroscopic and other techniques including single crystal X-ray structure determinations of phenop, **7**–**9** and **11**.

Introduction

Heterocyclic phosphorus chemistry has been a highly active research field as demonstrated in a recent collection of monographs.[1] Unsaturated systems predominate, although a wide range of saturated systems from 3-membered phosphiranes to large-ring multiheteroatom species are known.[2] The coordination chemistry of small-ring unsaturates, especially the phospholes, has been exploited by, amongst others, Mathey,[3] Nelson[4] and Leung.[5] These workers and their groups have highlighted the rich chemistry that is possible with these heterocycles particularly for making other phosphines by controlled additions to coordinated phospholes. Mathey and coworkers have also contributed hugely to the development of the saturated systems, whilst Wild[2] (phosphiranes, phosphepanes and higher members), Marinetti[6] (asymmetric phosphetanes and others), Grützmacher[7] (stable, fused-ring phosphiranes) and Pringle[8] (various) have all made significant additions to the area especially regarding the complexation chemistry of such donors. The discovery of the highly successful DuPHOS[9] family of ligands in metal-based asymmetric hydrogenation brought the phospholanes to the attention of a wider audience and the chemistry of this ring size and smaller rings has benefitted. However, the next largest member, the six-membered phosphinane class, has received little to no attention. We and others have recently sought to address this oversight with the synthesis of chiral phosphinane[10] and oxaphosphinane[11,12] derivatives.

We are interested in developing chiral monophosphines with superstructures derived from readily available 'chiral-pool' precursors and employing them as ligands for broad-range catalytic application. To this end, we recently reported the stereoselective synthesis of the oxaphosphinane derivative (1*S*, 4*R*, 4a*S*, 5a*R*, 6*R*, 9*S*, 9a*S*, 10a*R*)-4,6,11,11,12,12-hexamethyl-10-phenyl-dodecahydro-1,4:6,9-dimethano-phenoxaphosphinine, phenop (Fig. 1) and a complex with palladium(II) acetate.[12] The impetus for such work stems from the knowledge that many organic transformations catalysed by metal–phosphine complexes are extremely sensitive to the steric and electronic nature of the phosphine, and that bulky, electron-rich phosphines are often more effective ligands than those that are poor σ-bases and/or are sterically slight. This disparity is no more evident than in the field of C–C and C–heteroatom coupling chemistry where little to no catalytic activity is observed for palladium based systems using, for example, trialkylphosphines where the alkyl groups are small (methyl, ethyl) but efficient systems result when using tri-*tert*-butyl-, tricyclohexylphosphine or mixed 1-adamantyl(*tert*-butyl)phosphines.[13–15] Moreover, in the newly developing field of alkyl–alkyl Suzuki coupling, extreme ligand sensitivity is observed, so that, of the twelve or so phosphines tested by Fu and co-workers, only tricyclohexylphosphine, and to a lesser extent tri(2-propyl)phosphine and tricyclopentylphosphine, gave the desired product; tri-*tert*-butylphosphine was ineffective.[16] This highlights a recurring theme: that for selected organic transformations catalysed by transition metal–phosphine complexes, a narrow steric and/or electronic 'window' of activity exists, such that only a very limited number of ligands are effective. For C–C coupling reactions performed at high temperatures and/or over extended periods of time, cyclometallated-phosphine complexes have often proved to be more efficient catalysts then simple P-bound phosphine complexes.[17] The cyclometallated species appear to act as precatalysts for the active species, hence their advantage as more robust catalyst reservoirs. The ready availability of a large number of chiral phosphines meant the transition from achiral C–C coupling to asymmetric variants was an inevitable one. However, to date, surprisingly little has been reported on asymmetric Suzuki, and to a lesser extent, Heck couplings catalysed by phosphine–metal complexes, cyclometallated or otherwise. This paper extends the initial studies of the chemistry of phenop to include other palladium derivatives, platinum and silver complexes and report an unusual ambidenticity in the formation of *P*,*C* chelates in the palladium(II) complexes.

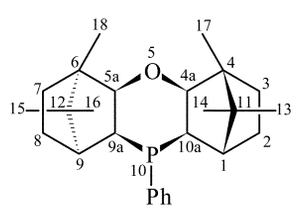

Fig. 1 Structure and numbering of phenop.

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Experimental

General

The complexes were synthesised under nitrogen using standard Schlenk line techniques. All solvents were freshly distilled from sodium (toluene, 40/60 petroleum ether), sodium/benzophenone (diethyl ether, tetrahydrofuran) or calcium hydride (acetonitrile, ethanol) under nitrogen before use. The ^{31}P NMR spectra were recorded on a Jeol Eclipse 300 spectrometer operating at 121.7 MHz and referenced to 85% H_3PO_4 (δ = 0 ppm). ^{1}H (400.13 or 300 MHz) and ^{13}C (100 or 75.6 MHz) NMR spectra were obtained on Bruker DPX400 and Jeol Eclipse 300 spectrometers and are referenced to tetramethylsilane (δ = 0 ppm). Mass-spectra were obtained on a VG Fisons Platform II spectrometer. Microanalyses were performed by Warwick Analytical Service Ltd. Optical rotations were acquired on an Optical Activity Instruments polarimeter. All other chemicals were of reagent grade and were used as supplied unless otherwise stated.

X-Ray crystallography

The X-ray intensity data for the free ligand phenop, and the metal complexes **7**–**9** and **11** were recorded on a Bruker Nonius kappa CCD area detector at 150 K using monochromated Mo-Kα radiation (λ = 0.71073 Å). The unit cell parameters for each compound were initially determined from the reflections in a ϕ range of 10°, and finally refined using all the observed reflections in the data set. Data collection and processing were carried out by using the programs COLLECT[18] and DENZO.[19] Empirical absorption corrections were applied to all data sets using multiple and symmetry-related data measurements *via* the program SORTAV.[20] The structures were solved by direct methods (SHELXS-96)[21] and refined on F_o^2 by full-matrix least-squares (SHELXL-97)[22] using all the unique data. In each case, the non-hydrogen atoms were all refined anisotropically. The crystal lattice of **7** contained voids with several low electron density peaks suggesting that there were some disordered solvent species (acetone). These did not fit into a readily recognisable geometry; however, eight such sites, two oxygens and six carbons, each with occupancy 0.25, were included in the SHELXL-97 refinement, with ISOR = 0.005 restraint. Compound **8** also contained a half occupied 0.5 acetone per asymmetric unit showing expected geometry; four sites for these atoms (three carbons and one oxygen) were refined with occupancy 0.5, C–C distance fixed at 1.52 Å and an ISOR = 0.003 restraint. Complex **9** contained a total of two toluene solvent molecules per complex unit at four sites (one fully occupied, one half occupied and two quarter occupied). These solvent molecules were idealised (C–C = 1.39, phenyl–CH_3 = 1.52 Å) and refined with ISOR = 0.01 restraint. The hydrogen atoms of the disordered acetone in **7** were ignored; all other hydrogen atoms in the four compounds were included in calculated positions (riding model). The final values of the Flack parameter[23] −0.05(10) (phenop), −0.08(3) (**7**), −0.006(12) (**8**), −0.06(4) (**9**) and −0.02(4) (**11**) were all 0 within the limits of error, and this indicated that the absolute stereochemistry has been determined correctly in each case. The crystal data and refinement details are summarised in Table 1. All structures have been reproduced using ORTEP.[24]

CCDC reference numbers 213238–213242.

See http://www.rsc.org/suppdata/dt/b3/b307070k/ for crystallographic data in CIF or other electronic format.

Preparations

(1*R*,1′*R*,3*S*,3′*S*)-3,3′-(phenylphosphoryl)bis(1,7,7-trimethylbicyclo[2.2.1]heptan-2-one. To a solution of 1*R*-camphor (10 g, 65.7 mmol) in THF (250 ml) at −78 °C was added a solution of n-BuLi in hexane (28 ml of 2.5 M, 70 mmol) *via* syringe. The mixture was stirred at −78 °C for 1 h, then allowed to slowly warm to room temperature and stirred for a further 0.5 h at RT. The mixture was cooled back to −78° and a solution of dichlorophenylphosphine (4.4 ml, 32.4 mmol) in THF (20 ml) added dropwise with stirring. After stirring at low temperature for 2 h, the solution was allowed to warm slowly to RT, stirred overnight, subsequently quenched with water (5 ml) and taken to dryness at the pump. The residue was dissolved in methanol (300 ml) and oxidised by the dropwise addition of H_2O_2 (10 ml of 30% solution) with ice cooling. After stirring overnight, the excess hydrogen peroxide was destroyed by the addition of a saturated aqueous solution of sodium sulfite (30 ml) and the methanol removed *in vacuo*. The resultant gummy aqueous residue was partitioned between dichloromethane (200 ml) and water (200 ml) and the organic phase isolated and dried ($MgSO_4$). After filtering off the $MgSO_4 \cdot xH_2O$, the volatiles were removed *in vacuo* to give a white solid that could be recrystallised from petroleum ether if required. Yield = 12 g (87%). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz) δ 30.8 ppm. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 (2H, t br, *J* 10.1 Hz), 7.5–7.4 (4H, m), 4.58 (1H, ddd, *J* 26.6, 4.0, 2.4 Hz), 3.95 (1H, ddd, *J* 14.1, 4.2, 2.2 Hz), 2.63 (1H, t, *J* 3.9 Hz), 2.05 (1H, m), 1.88 (1H, t, *J* 4.0 Hz), 1.77 (1H, m), 1.60 (2H, m), 1.30 (2H, m), 0.93 (3H, s), 0.92 (3H, s), 0.91 (3H, s), 0.90 (3H, s), 0.86 (3H, s), 0.84 (3H, s), 0.54 (1H, m) ppm. ^{13}C DEPT NMR ($CDCl_3$, 100 MHz) δ 215.0 (s, CO), 213.5 (d, *J* 4.0 Hz, CO), 132.6 (d, *J* 34.3 Hz, *ipso*-Ph), 132.4 (s, *p*-Ph), 131.8 (d, *J* 9.8 Hz, *o*-Ph), 129.0 (d, *J* 10.1 Hz, *m*-Ph), 60.2 (s, C), 60.0 (d, *J* 3.2 Hz, C), 53.5 (d, *J* 78.8 Hz, CH), 52.8 (d, *J* 79.3 Hz, CH), 47.6 (d, *J* 1.5 Hz, C), 47.5 (d, *J* 1.7 Hz, C), 46.3 (d, *J* 1.6 Hz, CH), 45.9 (d, *J* 1.6 Hz, CH), 29.8 (s, CH_2), 29.3 (s, CH_2), 23.5 (d, *J* 10.0 Hz, CH_2), 23.3 (d, *J* 13.3 Hz, CH_2), 19.7 (s, CH_3), 19.5 (s, CH_3), 18.9 (s, CH_3), 18.7 (s, CH_3), 10.1 (s, CH_3), 9.9 (s, CH_3) ppm. *Anal.*: Calc. for $C_{26}H_{35}O_3P$: C, 73.20; H, 8.29%. Found: C, 73.2; H, 8.3%. $[\alpha]_D$ = + 24.7° (*c* = 0.6, CH_2Cl_2). Mpt = 135–7 °C (dec).

It is noteworthy that, although the *endo*,*endo*-isomer was always obtained as the major product, small amounts of the *endo*,*exo*-form were observed occasionally; this had no bearing on the subsequent chemistry and the ultimate synthesis of phenop.

(1*S*, 4*R*, 4a*S*, 5a*R*, 6*R*, 9*S*, 9a*S*, 10a*R*)-4,6,11,11,12,12-hexamethyl-10-phenyl-dodecahydro-1,4:6,9-dimethano-phenoxaphosphinine oxide (phenop oxide). (1*R*,1′*R*,3*S*,3′*S*)-3,3′-(phenylphosphoryl)bis(1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (10 g) was dissolved in 2% aq. ethanol and reduced by the portionwise addition of solid sodium borohydride (4 g in total) at 50°. The reduction was monitored by ^{31}P{^{1}H} NMR and was deemed complete when the signal for the starting material at δ_P 30.8 ppm had disappeared (1–2 days, occasionally longer). Excess borohydride was digested by the addition of saturated ammonium chloride, the mixture reduced to small volume (~50 ml) and partitioned between dichloromethane (200 ml) and water (200 ml). The organic phase was isolated, washed with water (2 × 100 ml), dried over $MgSO_4$ and all volatiles removed to give a white solid. This solid consisted of all possible isomers of the diol. This mixture was then refluxed in toluene (200 ml) containing *para*-toluenesulfonyl chloride (5 g) for 24 h. On return the light-brown solution was cooled to RT, concentrated to small volume (40 ml), diluted with CH_2Cl_2 (200 ml) and washed thoroughly with water (100 ml), 10% NaOH solution (100 ml) and water (100 ml) again. After drying, the solvents were removed to give the desired product. If oily, the compound could be encouraged to crystallise by stirring with 40/60 petroleum ether. Recrystallisation was effected from hot toluene. Yield = 5 g (52%). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz) δ 26.2 ppm. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80 (2H, m, *o*-Ph), 7.50 (3H, m, *m*-Ph, *p*-Ph), 3.63 (1H, dd obs, H5a), 3.61 (1H, dd, *J* 7.5, 4.0 Hz, H4a), 3.00 (1H, m, *endo*-H8), 2.33 (1H, m, H9a), 2.27 (1H, dd, *J* 8.1, 3.8 Hz, H1), 2.04 (1H, m, *endo*-H7), 2.00

Table 1 Crystal data and structure refinement for phenop, **7**–**9** and **11**

	Phenop	**7**	**8**	**9**	**11**
Empirical formula	$C_{26}H_{37}OP$	$C_{52}H_{72}O_2P_2Cl_2Pd_2\cdot 0.5(C_3H_6O)$	$C_{52}H_{72}O_2P_2Cl_2Pt_2\cdot 0.5(C_3H_6O)$	$C_{52}H_{68}O_2P_2Cl_2Pd_2\cdot 2(C_7H_8)$	$C_{54}H_{74}O_8P_2S_2F_6Ag_2$
Formula weight	396.53	1103.78	1281.16	1254.97	1306.93
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	*P*2(1)2(1)2(1)	*P*2(1)	*P*2(1)	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)
a/Å	7.57200(10)	10.3021(2)	10.3287(2)	15.8838(4)	16.6065(2)
b/Å	10.3049(2)	22.5573(4)	22.5278(5)	17.5364(5)	17.2601(2)
c/Å	28.3367(6)	12.4212(2)	12.4452(3)	25.2450(8)	20.6222(3)
β/°		101.0630(8)	101.0500(11)		101.0500(11)
U/Å^3	2211.08(7)	2832.89(9)	2842.10(11)	7031.9(3)	5910.94(13)
Z	4	2	2	4	4
Reflections collected, independent	14316, 4712	24754, 9970	11276, 7768	29630, 13557	43065, 11592
R_{int}	0.0560	0.0549	0.0501	0.0623	0.0619
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0446, 0.1011	0.0438, 0.1065	0.0494, 0.1330	0.0593, 0.1501	0.0598, 0.1463
All data R_1, wR_2	0.0620, 0.1113	0.0549, 0.1233	0.0542, 0.1513	0.0924, 0.1697	0.0902, 0.1646

(1H, t, *J* 4.4 Hz, H9), 2.00 (1H, m obs, H10a), 1.80 (2H, m, *exo*-H2), 1.56 (1H, dt, *J* 15.0, 2.6 Hz, *exo*-H3), 1.48 (1H, m, *exo*-H8), 1.33 (3H, s), 1.24 (1H, m, *exo*-H7), 1.13 (1H, m, *endo*-H3), 0.99 (3H, s), 0.92 (3H, s), 0.91 (1H, m obs, *endo*-H2), 0.89 (3H, s), 0.86 (3H, s), 0.83 (3H, s) ppm. ^{13}C DEPT NMR ($CDCl_3$, 75.6 MHz) *δ* 137.7 (d, *J* 98.1 Hz, *ipso*-Ph), 130.8 (d, *J* 8.1 Hz, *o*-Ph), 130.8 (obs, *p*-Ph), 128.5 (d, *J* 10.4 Hz, *m*-Ph), 89.8 (d, *J* 5.8 Hz, C4a), 85.1 (d, *J* 3.5 Hz, C5a), 50.2 (s, C), 49.7 (s, C), 48.1–47.2 (obs, 2 × C, 1 × CH), 46.0 (d, *J* 2.3 Hz, CH), 38.5 (s, CH), 37.6 (s, CH), 33.9 (s, CH_2), 31.2 (d, *J* 12.7 Hz, CH_2), 26.9 (s, CH_2), 22.3 (s, CH_3), 21.8 (s, CH_3), 21.4 (d, *J* 3.5 Hz, CH_2), 19.0 (s, CH_3), 18.9 (s, CH_3), 14.1 (s, CH_3), 11.2 (s, CH_3) ppm. *Anal.*: Calc. for $C_{26}H_{37}O_2P$: C, 75.68; H, 9.06%. Found: C, 76.1; H, 9.1%. $[a]_D$ = + 29.4° (*c* = 1.64, $CHCl_3$). Mpt > 300 °C.

(1*S*, 4*R*, 4a*S*, 5a*R*, 6*R*, 9*S*, 9a*S*, 10a*R*)-4,6,11,11,12,12-hexamethyl-10-phenyl-dodecahydro-1,4:6,9-dimethano-phenoxaphosphinine (phenop). A solution of phenop oxide (5 g, 12.12 mmol) in toluene (100 ml) containing trichlorosilane (10 ml) was refluxed under nitrogen for 18 h. After cooling, the mixture was hydrolysed carefully by the dropwise addition of 25% aq. NaOH with ice-cooling. The organic layer was washed with degassed water (2 × 50 ml) then dried over $MgSO_4$. After filtering, the solvent was removed *in vacuo* and the oily residue crystallised from ethanol. Yield = 4.56 g (95%). ^{31}P{^{1}H} NMR (C_6D_6, 121.7 MHz) *δ* −36 ppm. ^{1}H NMR (C_6D_6, 300 MHz) *δ* 7.47 (2H, m, *o*-Ph), 7.2–7.0 (3H, m, *p*-Ph, *m*-Ph), 3.44 (1H, dt, *J* 9.6, 1.5, 1.5 Hz, H5a), 3.28 (1H, d, *J* 7.9 Hz, H4a), 2.73 (1H, m, *endo*-H8), 2.48 (1H, m, H9a), 2.20 (1H, m, *endo*-H7), 1.95 (1H, dd, *J* 7.6, 5.9 Hz, H10a), 1.87 (1H, dd, *J* 6.3, 4.0 Hz, H1), 1.72 (1H, t, *J* 4.4 Hz, H9), 1.67 (3H, d, *J* 1.4 Hz, H14), 1.67 (2H, m obs, *exo*-H2, *exo*-H8), 1.48 (1H, m, *exo*-H3), 1.28 (1H, m, *exo*-H7), 1.06 (3H, s), 1.0 (2H, m obs, *endo*-H2, *endo*-H3), 0.97 (3H, s), 0.85 (3H, s), 0.84 (3H, s), 0.83 (3H, s) ppm. ^{13}C NMR (C_6D_6, 100 MHz) *δ* 143.0 (d, *J* 24.0 Hz, *ipso*-Ph), 130.0 (d, *J* 17.4 Hz, *o*-Ph), 127.2 (d, *J* 4.8 Hz, *m*-Ph), 126.4 (s, *p*-Ph) 88.3 (s, C4a), 84.1 (d, *J* 1.5 Hz, C5a), 48.6 (d, *J* 18.5 Hz, C1), 48.3 (s, C), 48.0 (s, C), 47.9 (d, *J* 14.4 Hz, C9), 46.8 (s, C), 45.7 (d, *J* 4.6 Hz, C), 43.7 (d, *J* 17.2 Hz, C10a), 39.9 (d, *J* 12.5 Hz, C9a), 33.6 (s, C3), 29.1 (d, *J* 8.3 Hz, C2), 26.6 (s, C7), 23.2 (d, *J* 31.0 Hz, C8), 21.3 (d, *J* 24.1 Hz, C14), 20.9 (s, CH_3), 18.8 (s, CH_3), 17.4 (s, CH_3), 12.9 (s, CH_3), 10.4 (s, CH_3) ppm. *Anal.*: Calc. for $C_{26}H_{37}OP$: C, 78.73; H, 9.42%. Found: C, 78.4; H, 9.3%. $[a]_D$ = + 40.6° (*c* = 1, $CHCl_3$). Mpt = 102–3 °C.

***cis*-[Pd$_2$(μ-κ^1-OAc)(μ-κ^2-OAc)(κ*P*,κ*C*^{14}-phenop)$_2$], 4.** The compound was prepared as before.[12] ^{31}P{^{1}H} NMR (C_6D_6, 121.7 MHz, 55 °C) *δ* 16.7 ppm. ^{1}H NMR (C_6D_6, 300 MHz, 55 °C) *δ* 7.84 (4H, t, *J* 8.5 Hz, *o*-Ph), 7.2–7.0 (6H, m, *p*-Ph, *m*-Ph), 4.47 (2H, m, *endo*-H8), 3.27 (2H, dd, *J* 8.9, 1.5 Hz, H5a), 3.20 (2H, t, *J* 7.2 Hz, H4a), 2.93 (2H, dd, *J* 8.8, 5.2 Hz, H14), 2.75 (2H, dd, *J* 8.8, 4.3 Hz, H14), 2.46 (2H, m, H9a), 2.38 (2H, m, *endo*-H7), 2.03 (8H, br, H1, CH_3CO_2), 1.75 (2H, br, H9), 1.61 (2H, dd, *J* 10.7, 7.2 Hz, H10a), 1.7–1.4 (4H, m obs, *exo*-H2, *exo*-H8), 1.48 (2H, m, *exo*-H3), 1.26 (2H, m, *exo*-H7), 1.03 (12H, s, H13, H17), 1.02 (4H, m obs, *endo*-H2, *endo*-H3), 0.88 (6H, s, H18), 0.78 (6H, s, H15), 0.66 (6H, s, H16) ppm. ^{13}C DEPT NMR (C_6D_6, 75.6 MHz, 55 °C) *δ* 134.5 (d, *J* 55 Hz, *ipso*-Ph), 132.4 (d, *J* 13.7 Hz, *o*-Ph), 129.7 (s, *p*-Ph), 128.3 (d, *J* 9.2 Hz, *m*-Ph), 88.0 (d, J 4.6 Hz, C4a), 83.9 (s, C5a), 56.8 (d, *J* 13.9 Hz, C1), 50.2 (s, C), 50.0 (d, *J* 1.5 Hz, C), 49.7 (s, C), 47.2 (obs, C), 47.2 (s, C9), 40.6 (d, *J* 32.3 Hz, C9a), 39.0 (d, *J* 34.6 Hz, C10a), 35.1 (s, C3), 27.3 (obs, 3 × CH_2), 24.5 (obs, CH_2, CH_3CO_2), 25.5 (d, *J* 13.2 Hz, C8), 24.5 (t, *J* 7.5 Hz, C14), 19.9 (s, C13), 19.4 (s, C15), 18.2 (s, C16), 13.7 (s, C18), 11.9 (s, C17) ppm. All other data were as reported previously.[12]

***cis*-[Pd(μ-Cl)(κ*P*,κ*C*^{14}-phenop)]$_2$, 5.** To a solution of **4** (100 mg, 8.9 × 10^{-5} mol) in dichloromethane (5 ml) was added an excess of tetraethylammonium chloride (100 mg, 3.60 × 10^{-4} mol) and the solution stirred for 12 h. On return the solution was washed with water (2 × 10 ml), dried over $MgSO_4$ and filtered. Volatiles were removed under reduced pressure and the resultant solid residue crystallised from acetone at 4 °C as pale yellow crystals. Yield = 89 mg (96%). ^{31}P{^{1}H} NMR (C_6D_6, 121.7 MHz) *δ* 18.2 ppm. ^{1}H NMR (C_6D_6, 300 MHz) *δ* 7.76 (4H, t, *J* 8.2 Hz, *o*-Ph), 7.17 (4H, obs, *m*-Ph), 7.06 (2H, t, *J* 9.0 Hz, *p*-Ph), 4.87 (2H, br, *endo*-H8), 3.20 (2H, d br, *J* 8.4 Hz, H5a), 3.11 (2H, dd, *J* 9.2, 4.1 Hz, H14), 3.06 (2H, t, *J* 7.1 Hz, H4a), 2.86 (2H, t, *J* 9.2 Hz, H14), 2.66 (2H, br, H9a), 2.45 (2H, br, *endo*-H7), 2.10 (2H, br, H9), 1.99 (2H, br, H1), 1.6–1.2 (10H, br), 0.99 (12H, s), 0.95 (12H, s), 1.0–0.8 (4H, obs), 0.68 (6H, s) ppm. ^{13}C DEPT NMR ($CDCl_3$, 100 MHz) *δ* 135.6 (d, *J* 42.7 Hz, *ipso*-Ph), 132.5 (d, *J* 9.2 Hz, *o*-Ph), 129.8 (s, *p*-Ph), 128.0 (d, *J* 9.2 Hz, m-Ph) 87.7 (s, C4a), 83.4 (s, C5a), 57.7 (d, *J* 11.5 Hz, C1), 50.8 (s, C), 49.9 (s, C), 49.6 (s, C), 47.7 (d, *J* 11.0 Hz, C), 47.5 (s, C9), 40.9 (d, *J* 31.2 Hz, C9a), 37.6 (d, *J* 35.8 Hz, C10a), 35.0 (s, C3), 29.2 (s, C14), 27.2 (d, *J* 15.0 Hz, C2), 26.9 (s, C7), 24.2 (d, *J* 15.0 Hz, C8), 20.2 (s, CH_3), 19.7 (s, CH_3), 18.9 (s, CH_3), 14.1 (s, CH_3), 12.3 (s, CH_3) ppm. *Anal.*: Calc. for $C_{52}H_{72}O_2P_2Cl_2Pd_2$: C, 58.10; H, 6.77%. Found: C, 57.3; H, 6.7%. $[a]_D$ = + 3.6° (*c* = 2.8, $CHCl_3$). Mpt = 185 °C (dec).

***cis*-[Pd(μ-Br)(κ*P*,κ*C*^{14}-phenop)]$_2$.0.25n-Bu$_4$NBr, 6.** This compound was prepared in a similar manner to **5** except using n-Bu_4NBr. Yield of yellow solid (recrystallised from acetone) = 85%. *Anal.*: Calc. for $C_{56}H_{81}O_2P_2N_{0.25}Br_{2.25}Pd_2$: C, 54.03; H, 6.57; N, 0.28%. Found: C, 54.6; H, 6.9; N, 0.29%. The included n-Bu_4NBr could be removed by dissolution of the solid in CH_2Cl_2 and washing with water. The following spectroscopic and other data are for the salt-free complex. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz) *δ* 20.4 ppm. ^{1}H NMR ($CDCl_3$, 300 MHz)

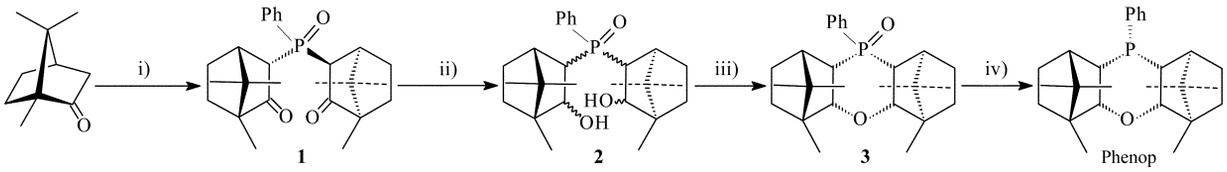
δ 7.73 (4H, br, *o*-Ph), 7.33 (6H, br, *m*-Ph, *p*-Ph), 4.18 (2H, br, *endo*-H8), 3.44 (2H, t, *J* 6.9 Hz, H4a), 3.44 (2H, obs, H5a), 2.92 (2H, br, H9a), 2.81 (2H, dd, *J* 8.9, 5.2 Hz, H14), 2.54 (2H, t, *J* 8.9 Hz, H14), 2.12 (2H, dd, *J* 7.5, 4.2 Hz, H1), 2.00 (2H, m, *endo*-H7), 1.78 (2H, dd, *J* 10.7, 7.1 Hz, H10a), 1.9–0.9 (14H, m), 0.95 (6H, s), 0.85 (12H, s), 0.82 (12H, s) ppm. ^{13}C DEPT NMR ($CDCl_3$, 100 MHz) δ 137.0 (d, *J* 42.1 Hz, *ipso*-Ph), 132.0 (d, *J* 10.4 Hz, *o*-Ph), 129.6 (s, *p*-Ph), 128.1 (d, *J* 10.4 Hz, *m*-Ph) 87.7 (s, C4a), 83.2 (s, C5a), 58.6 (d, *J* 15.0 Hz, C1), 51.0 (s, C), 50.1 (s, C), 49.9 (s, C), 47.8 (s, C9), 47.7 (s, C), 40.9 (d, *J* 31.2 Hz, C9a), 38.1 (d, *J* 34.7 Hz, C10a), 35.0 (s, C3), 30.3 (s, C14), 27.3 (d, *J* 15.0 Hz, C2), 24.3 (d, *J* 11.5 Hz, C8), 20.2 (s, CH_3), 19.7 (s, CH_3), 19.1 (s, CH_3), 13.9 (s, CH_3), 12.4 (s, CH_3) ppm. MS (APCI): 1083 (70%), [**6** − Br]$^+$. $[a]_D$ = + 11.8° (*c* = 3.3, CH_2Cl_2). Mpt = 160–5° (dec).

***trans*-[Pd(μ-Cl)(κ*P*,κ*C*^{8}-phenop)]$_2$·0.5(C_3H_6O), 7.** A mixture of Pd(1,5-cyclooctadiene)Cl_2 (200 mg, 0.70 mmol) and phenop (300 mg, 0.76 mmol) in methanol (12 ml) was refluxed for 14 h with stirring. During this time a white microcrystalline solid deposited. After cooling to room temperature and then 4 °C overnight, the solid was filtered off, washed sparingly with cold methanol and air-dried. The complex could be recrystallised from acetone as colourless blocks. Yield = 350 mg (93%). ^{31}P{^{1}H} NMR (C_6D_6, 121.7 MHz) δ 42.8s ppm. ^{1}H NMR (C_6D_6, 300 MHz) δ 8.11 (4H, m, *o*-Ph), 7.10 (6H, m, *p*-Ph, *m*-Ph), 3.85 (2H, m, *exo*-H8), 3.64 (2H, dd, *J* 9.2, 7.0 Hz, H5a), 3.22 (2H, d, *J* 6.9 Hz, H4a), 2.70 (2H, dd, *J* 7.6, 2.9 Hz, H1), 2.55 (2H, ddd, *J* 15.0, 8.5, 1.5 Hz, *endo*-H7), 2.47 (6H, s, H14), 2.30 (2H, m, H9a), 1.90 (2H, dd obs, *J* 6.9 Hz, H10a), 1.89 (2H, t, *J* 5.0 Hz, H9), 1.78 (2H, m, *exo*-H7), 1.60 (2H, m, *exo*-H2), 1.43 (2H, dt, *J* 12.4, 2.5 Hz, *endo*-H2), 1.09 (6H, s), 0.98 (6H, s), 0.97 (2H, m obs, H3), 0.96 (6H, s), 0.72 (6H, s), 0.70 (2H, m obs, H3), 0.69 (6H, s) ppm. ^{13}C DEPT NMR (C_6D_6, 100 MHz) δ 135.6 (d, *J* 37.1 Hz, *ipso*-Ph), 133.1 (d, *J* 12.6 Hz, *o*-Ph), 130.1 (s, *p*-Ph), 128.5 (d, *J* 10.2 Hz, *m*-Ph), 87.9 (s, C4a), 85.1 (s, C5a), 61.0 (d, *J* 12.7 Hz, C9), 51.7 (d, *J* 2.5 Hz, C8), 50.1 (s, C), 49.6 (s, C), 48.4 (d, *J* 20.4 Hz, C10a), 48.4 (s, C), 46.8 (s, C1), 45.2 (d, *J* 26.0 Hz, C), 43.5 (d, *J* 35.5 Hz, C9a), 36.7 (s, C7), 33.8 (s, C3), 31.3 (d, *J* 11.3 Hz, C2), 25.1 (s, C14), 22.1 (s, CH_3), 21.2 (s, CH_3), 19.2 (s, CH_3), 13.6 (s, CH_3), 11.5 (s, CH_3) ppm. *Anal.*: Calc. for $C_{53.5}H_{75}O_{2.5}P_2Cl_2Pd_2$: C, 58.20; H, 6.86%. Found: C, 57.7; H, 6.9%. $[a]_D$ = − 2.4° (*c* = 0.15, CH_2Cl_2). Mpt = 235–7 °C (dec). MS (APCI): 1039 (100%), [**7** − Cl]$^+$. It should be noted that small amounts of a secondary species (presumably the *cis*-isomer) were often observed in solution by ^{31}P{^{1}H} NMR (δ = 41.8 ppm), but these always constituted less than 10% of the total. Details for the isolation of **9**: When **9** was detected in the reaction mixture (δ_P = 2.5 ppm) after isolating **7**, the solution was taken to dryness and **9** was isolated from the residue as pale yellow blocks by crystallisation from toluene in air. Yield = 4 mg (1%). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz) δ 2.5s ppm. ^{1}H NMR (C_6D_6, 300 MHz) δ 7.99 (4H, *o*-Ph), 7.38 (4H, *m*-Ph), 7.21 (2H, *p*-Ph), 4.12 (2H, d, *J* 5.7 Hz, H4a), 4.03 (2H, m, *endo*-H7), 3.41 (2H, d, *J* 7.0 Hz, H5a), 3.34 (2H, m), 2.40 (2H, d, *J* 3.8 Hz, H9), 2.35 (2H, m), 2.00 (2H, m), 1.75 (2H, m), 1.61 (6H, s), 1.52 (6H, s), 1.33 (6H, s), 0.97 (6H, s), 0.94 (6H, s), 0.85 ppm. MS(APCI): 1035 (100%), [**9** − Cl]$^+$.

***trans*-[Pt(μ-Cl)(κ*P*,κ*C*^{8}-phenop)]$_2$·0.5(C_3H_6O), 8.** A suspension of Na_2PtCl_4 (98 mg, 2.56 × 10^{-4} mol) and phenop (105 mg, 2.65 × 10^{-4} mol) in n-butanol (15 ml) was refluxed with stirring for 24 h. The initially insoluble platinum salt dissolved during this time with the formation of a light-brown solution. After cooling, the solution was filtered and concentrated to small volume (3 ml). Cooling at 4 °C overnight led to the precipitation of a colourless, crystalline solid. Filtered off solid and washed sparingly with n-butanol. Recrystallisation was effected from acetone. Yield = 150 mg (94%). ^{31}P{^{1}H} NMR (C_6D_6, 121.7 MHz) δ 24.4s ($^1J_{Pt-P}$ = 5529 Hz), ppm. ^{1}H NMR (C_6D_6, 300 MHz) δ 8.06 (4H, *o*-Ph), 7.05 (6H, *p*-Ph, *m*-Ph), 3.64 (2H, dd, *J* 8.8, 7.0 Hz, H5a), 3.28 (2H, dd, *J* 7.1, 1.8 Hz, H4a), 3.11 (2H, m, *exo*-H8), 2.60 (2H, dd, *J* 8.1, 3.3 Hz, H1), 2.51 (6H, s, H14), 2.50 (2H, m obs, *endo*-H7), 2.27 (2H, m, H9a), 2.04 (2H, dd, *J* 12.7, 7.1 Hz, H10a), 1.78 (2H, t, *J* 7.0 Hz, H9), 1.5–1.3 (6H, m), 1.09 (6H, s), 1.01 (6H, s), 0.95 (6H, s), 0.81 (6H, s), 0.77 (6H, s), 1.1–0.7 (4H, m obs) ppm. ^{13}C DEPT NMR ($CDCl_3$, 100 MHz) δ 134.5 (d, *J* 54.3 Hz, *ipso*-Ph), 132.9 (d, *J* 10.9 Hz, *o*-Ph), 130.3 (s, *p*-Ph), 128.4 (d, *J* 11.0 Hz, *m*-Ph), 88.2 (s, C4a), 85.0 (s, C5a), 61.1 (d, *J* 8.7 Hz, C9), 49.6 (s, C), 49.5 (s, C), 48.2 (s, C), 46.7–46.4 (obs, C1, C8, C10a), 44.3 (d, *J* 19.6 Hz, C), 42.3 (d, *J* 43.9 Hz, C9a), 36.8 (s, C7), 33.8 (s, C3), 31.6 (d, *J* 12.1 Hz, C2), 25.5 (s, C14), 22.2 (s, CH_3), 21.5 (s, CH_3), 19.5 (s, CH_3), 13.6 (s, CH_3), 11.5 (s, CH_3) ppm. *Anal.*: Calc. for $C_{53.5}H_{75}O_{2.5}P_2Cl_2Pt_2$: C, 50.15; H, 5.91%. Found: C, 50.4; H, 6.0%. $[a]_D$ = + 54.0° (*c* = 0.64, CH_2Cl_2). Mpt = 250–5 °C (dec). MS (APCI): 1218 (100%), [**8** − Cl]$^+$. As for the palladium derivative, a minor species was observed in solution (^{31}P{^{1}H} NMR, d = 23.9 ppm) and believed to be the *cis*-isomer.

Pd(κ*P*-phenop)$_2$·C_7H_8, 10. A solution of phenop (235 mg, 5.93 × 10^{-4} mol) and (η^5-Cp)Pd(η^3-C_3H_5) (63 mg, 2.96 × 10^{-4} mol) in toluene (20 ml) was heated at 75° with stirring for 3 h. After cooling, the solution was filtered and concentrated to small volume (~ 5 ml). After diluting with MeOH (10 ml), the solution was stored at −35° whereupon the desired compound crystallised. The pale yellow crystals were isolated by filtration. Yield = 222 mg (76%). The toluene of crystallisation could be removed by pumping *in vacuo* if so desired. ^{31}P{^{1}H} NMR (C_6D_6, 121.7 MHz) δ −7.2 ppm. ^{1}H NMR (C_6D_6, 400 MHz) δ 7.84 (2H, m, *o*-Ph), 7.17 (4H, t, *J* 7.2 Hz, *m*-Ph), 7.07 (2H, t, *J* 7.2 Hz, *p*-Ph), 4.54 (2H, m, *endo*-H8), 3.44 (2H, d, *J* 9.3 Hz, H5a), 3.33 (2H, d, *J* 7.2 Hz, H4a), 2.63 (2H, m, H9a), 2.51 (2H, dd, *J* 8.4, 3.0 Hz, H1), 2.25 (2H, m, *endo*-H7), 2.13 (2H, m, H10a), 1.95 (6H, s, H14), 1.76 (6H, m br, *exo*-H2, *exo*-H8, H9), 1.50 (2H, m, *exo*-H3), 1.35 (2H, m, *exo*-H7), 1.08 (6H, s, H17), 1.08 (4H, m obs, *endo*-H2, *endo*-H3), 0.97 (6H, s, H18), 0.95 (6H, s, H13), 0.88 (6H, s, H15), 0.78 (6H, s, H16) ppm. ^{13}C DEPT NMR (C_6D_6, 100 MHz) δ 146.6 (t, *J* 10 Hz, *ipso*-Ph), 131.9 (t, *J* 8.2 Hz, *o*-Ph), 128.0 (s, *m*-Ph), 127.7 (s, *p*-Ph), 89.8 (s, C4a), 84.7 (s, C5a), 51.6 (t, *J* 7.2 Hz, C1), 49.6 (s, C), 49.3 (m obs, C), 49.2 (s, C9), 48.2 (s, C), 46.9 (d, *J* 3.4 Hz, C), 45.2 (t, *J* 5.5 Hz, C10a), 40.4 (t, *J* 8.6 Hz, C9a), 34.4 (s, C3), 30.7 (t, *J* 5.8 Hz, C2), 27.8 (s, C7), 25.5 (t, *J* 13.2 Hz, C8), 24.5 (t, *J* 7.5 Hz, C14), 22.3 (s, C13), 19.8 (s, C15), 18.5 (s, C16), 14.3 (s, C18), 11.5 (s, C17) ppm. *Anal.*: Calc. for $C_{59}H_{82}O_2P_2Pd$: C, 71.45; H, 8.35%. Found: C, 71.8; H, 8.2%. MS (APCI): 522 (40%), [**10** − phenop + NH_4^+].

[Ag(κ*P*-phenop)(CF_3SO_3)]$_2$, 11. A solution of Ag(CF_3SO_3) (91 mg, 3.53 × 10^{-4} mol) and phenop (140 mg, 3.53 × 10^{-4} mol) were stirred in diethyl ether (15 ml) in the absence of light for 24 h. On return, the solution was diluted with 40/60 petroleum ether (15 ml) and left at −30 °C overnight. The resultant crystals were filtered off and dried at the pump. Yield = 140 mg (61%). A second crop was obtained on further cooling of the solution. Yield = 50 mg (22%). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz) δ −12.1d ($^1J_{Ag-P}$ = 763 Hz, $^1J_{Ag-P}$ = 879 Hz) ppm. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55 (2H, m), 7.47 (3H, m), 3.56 (2H, dd, *J* 7.7, 1.5 Hz), 2.83 (1H, br), 2.42 (1H, m), 2.28 (1H, m), 2.08 (1H, dd, *J* 11.4, 3.8 Hz), 1.90 (4H, m), 1.62 (1H, m), 1.52 (3H, d, 3.5 Hz), 1.33 (1H, m), 1.15 (2H, m), 0.98 (3H, s), 0.95 (3H, s), 0.93 (9H, s), 0.92 (3H, s) ppm. ^{13}C DEPT NMR ($CDCl_3$, 100 MHz) δ 135.5 (d, *J* 33 Hz, C), 131.7 (d, *J* 16 Hz, CH), 130.9 (s, CH), 129.6 (d, *J* 10 Hz, CH), 89.5 (s, CH), 84.2 (s, CH), 51.2 (d, *J* 9 Hz, CH), 49.7 (s, C), 48.7 (s, C), 47.6 (s, CH), 47.4 (s, C), 43.7 (d, *J* 16 Hz, CH), 39.4 (d, *J* 22 Hz, CH), 33.8 (s, CH_2), 30.8 (d, *J* 14 Hz, CH_2), 27.3 (s, CH_2), 23.9 (d, *J* 23 Hz, CH_2), 23.2 (d, *J* 14 Hz, CH_3), 21.6 (s, CH_3), 19.7 (s, CH_3), 18.7 (s, CH_3), 13.9 (s, CH_3), 11.1 (s, CH_3) ppm.



Scheme 1 (i) nBuLi, 0.5 $PhPCl_2$, H_2O_2, 87%; (ii) $NaBH_4$, 93%; (iii) TsCl, 52%; (iv) $HSiCl_3$, 93%.

$^{31}P\{^1H\}$ NMR (C_6D_6, 121.7 MHz) δ −16.4d ($^1J_{Ag-P}$ = 730 Hz, $^1J_{Ag-P}$ = 843 Hz) ppm. ^1H NMR (C_6D_6, 300 MHz) δ 7.43 (4H, dd, *J* 8.0, 7.1 Hz, *o*-Ph), 7.17 (4H, m, *m*-Ph), 7.08 (2H, t, *J* 7.4 Hz, *p*-Ph), 3.20 (2H, d, *J* 9.0 Hz, H5a), 3.05 (2H, d, *J* 7.4 Hz, H4a), 2.48 (4H, m, *endo*-H8, H9a), 2.03 (2H, dd, *J* 10.5, 2.9 Hz, H1), 1.94 (2H, m, *endo*-H7), 1.9–1.5 (6H, m), 1.61 (6H, d, *J* 3.0 Hz, H14), 1.35 (2H, m, *exo*-H3), 1.22 (2H, m, *exo*-H7), 0.9–0.7 (4H, obs, *endo*-H2, *endo*-H3), 0.89 (6H, s), 0.86 (6H, s), 0.83 (6H, s), 0.76 (6H, s), 0.67 (6H, s) ppm. ^{13}C DEPT NMR (C_6D_6, 100 MHz) δ 136.8 (d, *J* 33.5 Hz, *ipso*-Ph), 131.7 (d, *J* 16.2 Hz, *o*-Ph), 130.1 (s, *p*-Ph), 129.1 (d, *J* 9.8 Hz, *m*-Ph), 89.2 (s, C4a), 84.1 (s, C5a), 50.2 (d, *J* 9.2 Hz, C1), 49.4 (s, C), 48.6 (s, C), 47.6 (s, C9), 47.0 (d, *J* 7.5 Hz, C), 43.9 (d, *J* 16.2 Hz, C10a), 39.0 (d, *J* 21.9 Hz, C9a), 33.8 (s, C3), 30.4 (d, *J* 12.7 Hz, C2), 27.2 (s, C7), 23.6 (d, *J* 23.1 Hz, C8), 23.0 (d, *J* 12.7 Hz, C14), 21.3 (s, CH_3), 19.4 (s, CH_3), 18.2 (s, CH_3), 13.7 (s, CH_3), 11.0 (s, CH_3) ppm. *Anal.*: Calc. for $C_{27}H_{37}O_4PF_3SAg$: C, 49.62; H, 5.72%. Found: C, 49.6; H, 5.7%. $[\alpha]_D$ = +24.3° (*c* = 1.9, CH_2Cl_2). Mpt = 135–7°. MS (APCI): 505 (50%), [**11** − CF_3SO_3]$^+$.

Results and discussion

The synthesis of phenop is highlighted in Scheme 1. The protocol presented here is more reliable than the previously reported route[12] that has, since the original preparation, proven to be poorly reproducible with highly variable yields for a number of the synthetic steps. Unlike the earlier synthesis, here the diketophosphine is not isolated but oxidised immediately to give the phosphine oxide **1** which is obtained as a mixture of *exo*,*endo* (minor) and *endo*,*endo* (major) isomers that can be separated by fractional cystallisation from 40/60 petroleum ether. Often, only the *endo*,*endo*-isomer is isolated. Sodium borohydride reduction of either isomer gives essentially the same diastereomeric mixture of the diol precursor **2**; no one isomer was dominant, although the actual proportion of each did vary from one batch to another. Indeed, if no effort is made to isolate the diastereomeric ketones the same mixture (containing at least four isomers) of diols, **2**, is obtained on reduction. No attempt was made to isolate this diastereomeric mixture of diols and after reflux with 2 mol equivalents of *para*-toluenesulfonyl chloride in toluene the oxide of the desired ligand (**4**) was obtained in 52% yield. Phenop was produced after exhaustive reduction of the oxide **3** using trichlorosilane. The reduction is slow, presumably as a consequence of the steric bulk about the phosphorus centre, and the oxide requires refluxing with excess trichlorosilane in toluene for 24 to 48 h.

Aside from the reproducibility of this procedure, a further advantage is the fact that no separation of diastereomeric mixtures is required at any stage as the cyclisation to give **3** produces but a single isomer of phenop oxide, determined previously to be the (1*S*, 4*R*, 4a*S*, 5a*R*, 6*R*, 9*S*, 9a*S*, 10a*R*) form. The formation of the oxaphosphinane ring is likely to proceed through an initial dehydration reaction to give a phosphine oxide species with a single remaining alcohol functionality and a vinyl group α to the P=O function on the other bicyclic unit. This compound is thus set up for an internal Michael type addition of the alcohol oxygen to the vinyl β carbon giving **3**. The fact that the stereochemistry is *endo*,*exo*- in **3** suggests that the cyclisation is stereoselective, with residual *exo*-orientated alcohol groups adding to the alkenic β-carbon from the *endo*-face and *vice versa*. Such a mechanism explains why the initial stereochemistry of the diol is not critical and that a single isomer of **3** can be obtained in >50% yield from the diastereomeric mixture of diols.

The structure of phenop is shown in Fig. 2. The structure is very similar to that of the previously reported phosphine oxide **3**, and it is clear that the chiral integrity of the compound is retained upon reduction. The phosphorus centre in phenop is described as pseudochiral because, although two of the substituents are constitutionally equivalent, they have the opposite chirality; one α-carbon (C1) is *S* while the other (C12) is *R*. The ligand is readily recrystallised from alcohols and is air-stable in the solid-state. As emphasised previously, the central six-membered ring is fixed in the boat conformation as dictated by the rigid nature of the ligand. This introduces the notion of possible coordination of the oxygen of the oxaphosphinane ring to give bidentate or hemilabile P∧O chelates. This is unlikely here because of steric impedance by a methyl group and a dimethylene bridge, but may be feasible for a related ligand derived from norcamphor; this is currently under investigation in our laboratories. The NMR spectra of phenop accord with the X-ray structure, and pertinent resonances are presented in Table 2. Full assignments (with respect to the labelling scheme in Fig. 1), as deduced from ^1H, $^1H\{^{31}P\}$, ^1H-^1H-COSY, 2D-NOESY, ^1H-^{13}C HMQC and where necessary ^1H-^{13}C HMBC NMR techniques appear in the Experimental. The H4a and H5a protons of phenop are distinguished by the presence of a four-bond coupling for the latter (a 'W' relation to *exo*-H7) that is absent for the former, whilst the H1 and H9 protons are distinguished by the presence or absence of a coupling to their neighbouring methine protons H10a and H9a, respectively. Unlike in the ^1H NMR spectrum of phenop oxide, there is no discernible $^3J_{H-P}$ coupling for the methine protons H4a and H5a in the corresponding spectrum of phenop. Contact deshielding leads to the *endo*-H7, *endo*-H8 and the C14 protons being observed downfield of the other methylene and methyl resonances. It is also noteworthy that the C14 methyl is coupled to the phosphorus (*J* = 1.4 Hz). Although the coupling constant is small, it is unlikely to occur *via* a through-bond mechanism (the two nuclei are separated by five bonds in an orientation that disfavours long-range coupling) and is considered to result from through-space coupling. The P–C14 separation is only 3.41 Å in the crystal. In addition, the *endo*-H8 hydrogen that resides in close proximity to the phosphorus shows a greater J_{H-P} coupling of 6.5 Hz. Neither of these couplings are

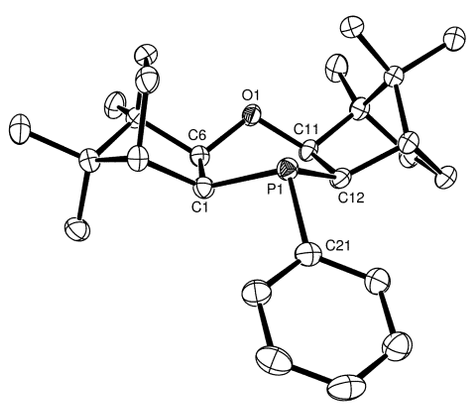


Fig. 2 ORTEP[24] representation of phenop.

Table 2 Selected NMR data for the compounds

Complex[a]								
Assignment	Phenop	**4**	**5**	**6**[b]	**7**	**8**	**10**	**11**
^{31}P	−36.0	16.7	18.2	20.4	42.8	24.4	−7.2	−16.4
H1	1.87dd (6.3, 4.0)	2.03obs	1.99br	2.12dd (7.5, 4.2)	2.70dd (7.6, 2.9)	2.60dd (8.1, 3.3)	2.51dd (8.4, 3.0)	2.03dd (10.5, 2.9)
H4a	2.28d (7.9)	3.20t (7.2)	3.06t (7.1)	3.44t (6.9)	3.22d (6.9)	3.28dd (7.1, 1.8)	3.33d (7.2)	3.05d (7.4)
H5a	3.44d (9.6, 1.5, 1.5)	3.27dd (8.9, 1.5)	3.20d br (8.4)	3.44obs	3.64dd (9.2, 7.0)	3.64dd (8.8, 7.0)	3.44d (9.3)	3.20d (9.0)
endo-H8	2.73m	4.47m	4.87br	4.18br			4.54m	obs
exo-H8	obs	obs	obs	obs	3.85m	3.11m	obs	obs
H9	1.72t (4.4)	1.75br	2.10br	obs	1.89t (5.0)	1.78t (7.0)	1.76obs	obs
H9a	2.48m	2.46m	2.66br	2.92br	2.30m	2.27m	2.63m	obs
H10a	1.95dd (7.6, 5.9)	1.61dd (10.7, 7.2)	obs	1.78dd (10.7, 7.1)	1.90dd obs (6.9)	2.04dd (12.7, 7.1)	2.13m	
H14	1.67d (1.4)	2.93dd (8.8, 5.2)	3.11dd (9.2, 4.1)	2.81dd (8.9, 5.2)	2.47s	2.51s	1.95s	1.61d (3.0)
		2.75dd (8.8, 4.3)	2.86t (9.2)	2.54t (8.9)				
C8	23.2d (31.0)	obs	24.2d[b] (15.0)	24.3d (11.5)	51.7d (2.5)	obs[b]	25.5t (13.2)	23.6d (23.1)
C14	21.3d (24.1)	obs	29.2s[b]	30.3s	25.1s	25.5s[b]	24.5t (7.5)	23.0d (12.7)

[a] In C_6D_6 unless otherwise stated. [b] In $CDCl_3$. Values in brackets are the coupling constants in Hertz. s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad, obs = obscured.

observed for phenop oxide reflecting the through space influence of the lone pair.

It has been shown that the reaction of phenop with palladium(II) acetate gives a cyclometallated dimer, [Pd(μ-κ^2-OAc)(μ-κ^1-OAc)(κ*P*,κ*C*^{14}-phenop)]$_2$, **4**, where the site of metallation is an *exo*-methyl, namely the C14 carbon centre of Fig. 1.† The bridging acetates can be replaced by chloride or bromide by simple metathesis in dichloromethane to give the corresponding halide bridged dimers [Pd(μ-X)(κ*P*,κ*C*^{14}-phenop)]$_2$, **5** (X = Cl) and **6** (X = Br), with the same structure as the acetate. Such an assignment is based on spectroscopic data, where the C14 methyl doublet at δ = 21.3 ppm in the ^{13}C{^{1}H} NMR spectrum of phenop is lost in the corresponding spectrum of the complexes and replaced by an extra CH_2 resonance as a result of metallation of the said methyl (Table 2). The extra methylene is a singlet in the ^{13}C{^{1}H} NMR showing no through-metal coupling to the phosphorus. A similar situation is observed in the ^{1}H NMR where only three singlets are present for the methyl groups of **5** and **6** (two sets of two being coincident). Most of the resonances in the ^{1}H NMR spectrum of **4** are broadened at room temperature, but become well-resolved at higher temperature. The methylene protons of the coordinated carbon are diastereotopic and are observed as distinct doublets of doublets when the ^{1}H NMR spectrum of **4** is run at 55 °C in C_6D_6 (Table 2). These protons have a geminal coupling constant of 8.8 Hz and each couples further to the phosphorus nucleus with $^3J_{P-H}$ of 5.2 and 4.3 Hz, respectively. Although some of the resonances in the ^{1}H NMR spectra of *cis*-[Pd(μ-Cl)(κ*P*,κ*C*^{14}-phenop)]$_2$, **5**, and *cis*-[Pd(μ-Br)(κ*P*,κ*C*^{14}-phenop)]$_2$, **6**, were broadened at room temperature, most of the relevant signals were resolved and assignments could be made at this temperature (Table 2). The broadening in the NMR spectra of **4** was interpreted[12] as resulting from inversion through the diacetate bridge as noted in related *N*,*C* systems.[25] Such a process may explain the slightly broadened spectra of **5** and **6**, but low temperature studies were precluded by the poor solubility of the compounds. Aside from the loss of a methyl signal and the presence of the extra CH_2 protons in the ^{1}H NMR spectrum of **4**, **5** and **6**, other significant differences between the ^{1}H NMR spectra of these complexes and the uncoordinated ligand include a downfield shift for the *endo*-H8 to δ values > 4 ppm as opposed to 2.73 ppm for the free ligand and the presence of a J_{P-H4a} coupling in the ^{1}H NMR spectra of the complexes. The downfield shift of the *endo*-H8 proton may reflect its position over the metal in the complexes; in the crystal structure of **4** it resides over the palladium at a distance of 2.466 Å. The coupling of H4a to the ^{31}P nucleus is unique to these P∧C14 chelated complexes.

When Pd(1,5-COD)Cl$_2$ or Na$_2$PdCl$_4$ is reacted with 1 mol equivalent of phenop, the compound *trans*-[Pd(μ-Cl)(κ*P*,κ*C*^{8}-phenop)]$_2$, **7**, is obtained in high yield. The crystal structure of the complex is shown in Fig. 3 with selected bond lengths and angles presented in Table 3. Remarkably, the phenop ligands in this dimeric species have metallated at a different site to that observed for the acetate complex; a methylene carbon of one of the flanking six-membered carbocyclic rings, *i.e.* C8 (see Fig. 1), as opposed to the *exo*-methyl C14. The overall structure is a butterfly with the chorides as a hinge as seen in most palladium dimers of this type. The smallest chelate is now five-membered as opposed to six-membered in **4**, **5** and **6**. The average Pd–P bond length (2.208 Å) in **7** is relatively short, but longer than that observed in **4** (2.197 Å) as are the Pd–C bonds (av. 2.052 Å compared to 2.033 Å);[12] they do, however, accord with literature values for related cyclopalladated complexes.[26] The Pd–Cl bonds *trans* to the cyclometallated carbons are longer than those *trans* to the phosphorus donors and it is clear that the

† The superscript on the κC in the formula indicates the site of metallation, in this case the C14 carbon, with respect to the numbering in Fig. 1.

Table 3 Selected bond lengths (Å) and angles (°) for the complexes

7		**8**		**9**		**11**	
Pd(1)–C(1)	2.049(5)	Pt(1)–C(1)	2.068(12)	Pd(1)–P(1)	2.3131(19)	Ag(1)–P(1)	2.360(2)
Pd(1)–Cl(1)	2.4185(16)	Pt(1)–Cl(1)	2.407(3)	Pd(1)–C(14)	2.138(6)	Ag(1)–O(1)	2.252(6)
Pd(1)–P(1)	2.2083(16)	Pt(1)–P(1)	2.182(4)	Pd(1)–C(40)	2.286(7)	Ag(1)–O(4)	2.314(10)
Pd(1)–Cl(2)	2.5010(14)	Pt(1)–Cl(2)	2.510(3)	Pd(1)–C(41)	2.100(7)	Ag(2)–P(2)	2.389(2)
Pd(2)–C(27)	2.054(6)	Pt(2)–C(27)	2.046(14)	Pd(1)–Cl(1)	2.3641(18)	Ag(2)–O(2)	2.376(8)
Pd(2)–Cl(1)	2.4988(15)	Pt(2)–Cl(1)	2.509(3)	Pd(2)–P(2)	2.323(2)	Ag(2)–O(5)	2.547(7)
Pd(2)–P(2)	2.2067(17)	Pt(2)–P(2)	2.180(4)	Pd(2)–C(14)	2.282(7)		
Pd(2)–Cl(2)	2.4135(16)	Pt(2)–Cl(2)	2.404(3)	Pd(2)–C(40)	2.134(6)		
				Pd(2)–C(15)	2.090(7)		
				Pd(2)–Cl(2)	2.3559(18)		
				C(14)–C(15)	1.454(9)		
				C(14)–C(40)	1.517(9)		
				C(40)–C(41)	1.464(9)		
C(1)–Pd(1)–P(1)	81.37(17)	C(1)–Pt(1)–P(1)	83.2(4)	C(14)–Pd(1)–P(1)	84.81(19)	P(1)–Ag(1)–O(1)	143.9(2)
C(1)–Pd(1)–Cl(1)	91.20(17)	C(1)–Pt(1)–Cl(1)	91.1(4)	C(14)–Pd(1)–C(40)	39.9(2)	P(1)–Ag(1)–O(4)	134.2(3)
Cl(1)–Pd(1)–Cl(2)	86.26(5)	Cl(1)–Pt(1)–Cl(2)	84.40(12)	C(40)–Pd(1)–C(41)	38.7(2)	O(1)–Ag(1)–O(2)	80.3(4)
Cl(2)–Pd(1)–P(1)	101.80(5)	Cl(2)–Pt(1)–P(1)	101.96(12)	Cl(1)–Pd(1)–C(41)	96.3(2)	P(2)–Ag(2)–O(2)	145.5(2)
C(27)–Pd(2)–P(2)	82.24(19)	C(27)–Pt(2)–P(2)	83.4(4)	Cl(1)–Pd(1)–P(1)	103.63(7)	P(2)–Ag(2)–O(5)	119.4(4)
C(27)–Pd(2)–Cl(2)	91.48(18)	C(27)–Pt(2)–Cl(2)	92.0(4)	C(40)–Pd(2)–P(2)	84.62(19)	O(2)–Ag(2)–O(5)	85.8(5)
Cl(1)–Pd(2)–Cl(2)	86.41(5)	Cl(1)–Pt(2)–Cl(2)	84.47(12)	C(14)–Pd(2)–C(40)	40.0(2)		
Cl(1)–Pd(2)–P(2)	100.52(6)	Cl(1)–Pt(2)–P(2)	100.88(13)	C(14)–Pd(2)–C(15)	38.5(2)		
				Cl(2)–Pd(2)–C(15)	96.11(19)		
				Cl(2)–Pd(2)–P(2)	104.17(7)		

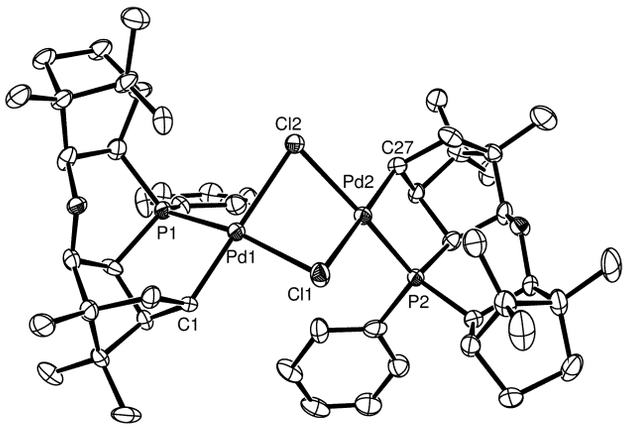


Fig. 3 Molecular structure of **7**.

trans influence of the alkyl donor is greater than that of the phosphine. Unlike **4**, the phosphorus donors (and the metallated carbons) in **7** are orientated *trans*- with respect to the Pd–Pd axis. The P–Pd–C bond angles in **7** average 81.8° as compared to 86.7° in **4**, consistent with the smaller chelate ring size of the former. As for *cis*-[Pd(μ-κ^1-OAc)(μ-κ^2-OAc)-(κ*P*,κ*C*^{14}-phenop)]$_2$ (**4**), two new chiral centres are generated stereoselectively on formation of *trans*-[Pd(μ-Cl)(κ*P*,κ*C*^{8}-phenop)]$_2$ (**7**). The stereogenic phosphorus centres in **7** have the absolute configuration *R*, and the C8 carbons (labelled C1 and C27 in Fig. 3), which also become chiral on metallation (coordination) have the *S* stereochemistry. In **4** the stereogenic phosphorus is *S* and the second new chiral centre that is generated on cyclometallation, the tertiary carbon C11, is also *S*. Ambivalence over the site of C–H activation in palladacycles has been observed previously in nitrogen donor systems,[27] but to our knowledge this is the first example of such ambidenticity in *P*,*C*-chelates and the first where such discretion can generate two different diastereomers. The platinum analogue of **7**, namely **8**, is isolated in excellent yield (94%) after refluxing a suspension of Na_2PtCl_4 with one mol equivalent of phenop in n-butanol. The structure (Fig. 4, Table 3) is analogous to the palladium complex **7**.

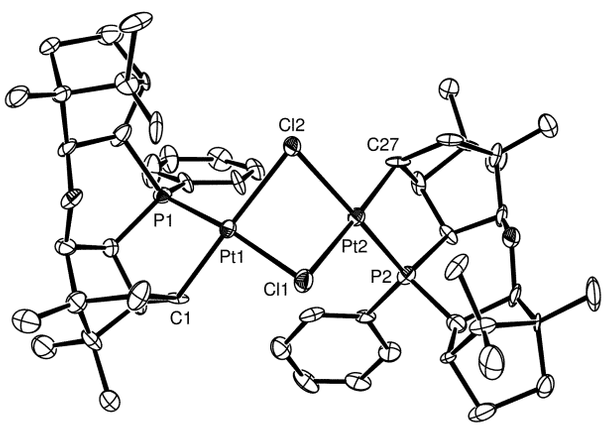


Fig. 4 Molecular structure of **8**.

The different site of metallation produces fused six- and seven-membered chelates in **4**, **5** and **6**, and fused five- and seven-membered chelates in **7**. This generates quite distinct ^{31}P chemical shifts for the two sets of complexes (Table 2), where the former have δ_P values around 20 ppm and the latter a δ_P of 42 ppm; this downfield shift is consistent with the presence of a five-membered chelate in **7** as opposed to the six-membered palladacycle in **4**–**6**. The ^{31}P{^{1}H} NMR spectrum of the Pt(II) dimer **8** shows a singlet at 24.4 ppm (this is, as expected, upfield of the palladium analogue) and two satellites from the 33% of platinum-195 in the sample with a $^1J_{P-Pt}$ coupling constant of 5529 Hz.

The *exo*-H8 proton resonance shifts downfield when its carbon is bound to palladium and/or platinum as observed in the ^{1}H NMR spectra of **7** and **8**. The named proton is seen as a multiplet at δ 3.85 (**7**) and 3.11 ppm (**8**) that shows no observable coupling to ^{31}P. The cyclometallated carbon is observed as a doublet at δ = 51.7 ppm with $^2J_{C-P}$ = 2.5 Hz in the ^{13}C{^{1}H} NMR spectrum of *trans*-[Pd(μ-Cl)(κ*P*,κ*C*^{8}-phenop)]$_2$, **7**, but is obscured in the ^{13}C{^{1}H} NMR spectrum of the corresponding platinum complex. No interconversion of **5**⟶**7** or *vice versa* was observed on heating the complexes to 120 °C and the different sites of metallation are likely to be the result of kinetic factors. We are currently seeking simple P-bound complexes of phenop with palladium halides and actetates in an effort to identify the contributing factors.

Although the complex *trans*-[Pd(μ-Cl)(κ*P*,κ*C*^{8}-phenop)]$_2$, **7**, is obtained in good yield from either Pd(1,5-COD)Cl$_2$ or Na_2-$PdCl_4$, ^{31}P{^{1}H} NMR analysis of the reaction mixtures did, on occasion, reveal the presence of several minor species, one of which was isolated pure and its structure determined by X-ray crystallography as shown in Fig. 5. Like the previous structures (Fig. 3, ref. 12), the compound is a dimer, however here the secondary ligands (chlorides) are not bridging but bound as simple terminal donors at single metal sites. Instead, the two phenop ligands have coupled through the C8 carbons (refer to Fig. 1 for assignments) to form a new C–C bond connecting the two ligands. These carbons (denoted C14 and C40 in Fig. 5) form the dimeric bridge by binding both palladium centres while the C15 and C41 carbons each coordinate a single Pd(II); this is the only example where C–H activation at the C7 carbons has occurred (Fig. 1). The bridging carbons are those that are cyclometallated in the non-coupled product (Fig. 3). This C_4 link does not appear to be a butendiyl of the classical type because each of the C–C bond lengths are 1.50 ± 0.05 Å indicating essentially single carbon–carbon bonds throughout the link. Unfortunately, this compound was only isolated in very low yield on one occasion and it was only possible to acquire some basic spectroscopic data (^{31}P, ^{1}H NMR) and a mass spectrum in addition to the X-ray structure. It is included here as an example of a ligand–ligand coupled product that may have relevance to other P∧C cyclometallates that are used as catalysts.

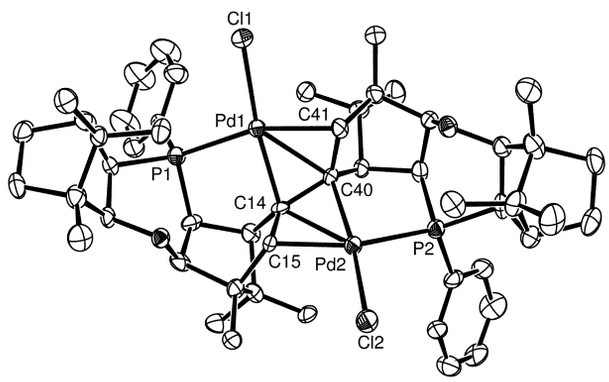
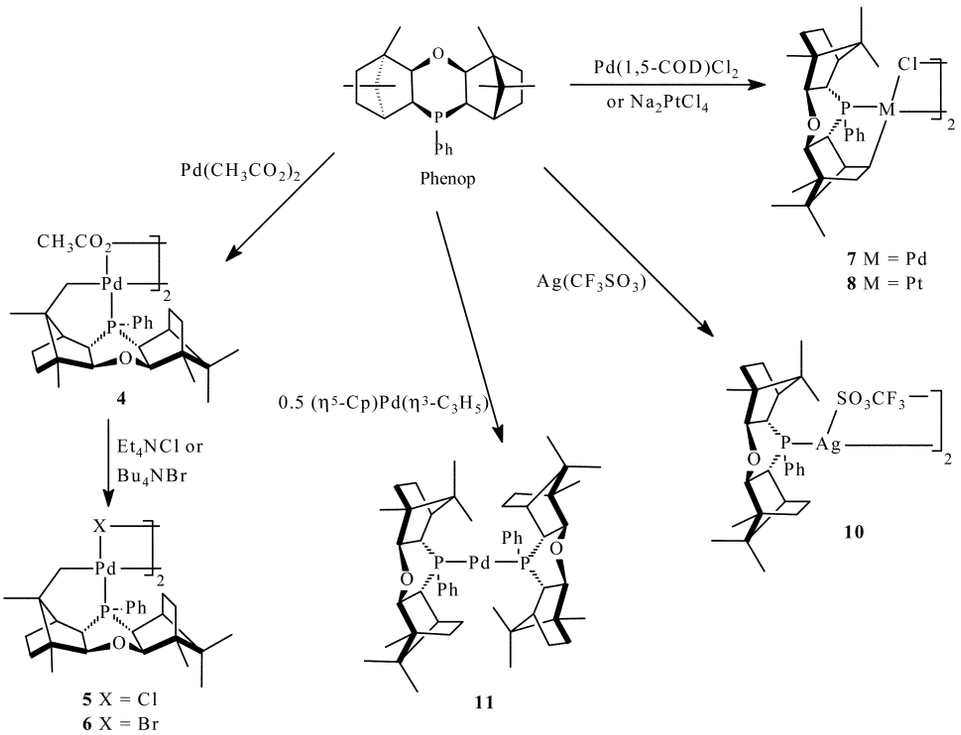


Fig. 5 Molecular structure of **9**.

The reaction of 2 mol of phenop with (η^5-Cp)Pd(η^3-C_3H_5) in toluene generates the zerovalent bis(phosphine) complex Pd(κ*P*-phenop)$_2$, **10**, in excellent yield. The compound is readily recrystallised from toluene/methanol mixtures as pale yellow to golden brown crystals. However, the crystals were solvent-dependent aggregates that precluded any single crystal X-ray analysis. The ^{31}P{^{1}H} NMR spectrum of the complex is the expected singlet whilst the ^{1}H NMR spectrum, which is well resolved at room temperature, shows the *endo*-H8 and the H14 protons shifted to low field (see above). The *ortho*-phenyl



Scheme 2

protons show two couplings to phosphorus and appear as a multiplet in the normal ^{1}H NMR spectrum that collapses to a doublet in the ^{1}H{^{31}P} NMR spectrum. Similarly, a number of the carbon resonances occur as virtual triplets in the ^{13}C{^{1}H} NMR spectrum of **10**, with a long range $^{6}J_{C-P}$ coupling of 7.5 Hz being observed for the C14 carbon. The presence of these couplings in the ^{13}C NMR spectrum reflects the *trans* arrangement of the phosphines in this bis(phenop)Pd complex. The complex is air-stable in the solid state, with no visible decomposition being observed over several days.

Addition of 1 mol equivalent of phenop to a diethyl ether solution of silver(I) triflate gives the dimeric species [Ag(κ*P*-phenop)(CF_3SO_3)]$_2$, **11**, as the only isolable complex. The compound was isolated as small well-formed colourless crystals that showed little tendency to decompose in light in the solid-state, but proved to be slightly sensitive to decomposition in solution when left exposed to light. The dimeric structure of the complex is shown in Fig. 6 with selected bond lengths and angles collected in Table 3. The structure consists of two three-coordinate silver(I) centres with trigonal planar geometry (sum of angles about silver are 358.4 and 350.8°, respectively) bridged by two μ-κ^2-CF_3SO_3 ligands. The geometry about the Ag(2) centre is considerably more distorted then that around the Ag(1) ion, with a difference in the two Ag(2)–O bond lengths of 0.172 Å. The Ag–P bond lengths lie in the range observed for a number of related systems.[28] The phenop ligands are clearly bound as monodentates through the phosphorus donors, with both carbon centres that cyclometallate in the two distinct sets of palladium(II) complexes in close proximity to the silver centre with average distances of Ag ··· C8 = 3.49 and Ag ··· C14 = 3.21 Å.‡ The latter is just within the sum (3.29 Å) of the van der Waals radius of a methyl group and the ionic radius of a silver(I) ion.[29] The Ag ··· H distance to the fixed *endo*-H8 hydrogen averages as 2.54 Å. The ^{31}P{^{1}H} NMR spectrum of **11** consists of two doublets through coupling to the two nuclei of the metal with the one-bond ^{109}Ag–^{31}P doublet having a larger value (843 Hz) compared to the ^{107}Ag–^{31}P coupling constant (730 Hz) by virtue of its greater gyromagnetic ratio. Unlike a number of related complexes,[30] these individual coupling constants and the resultant two doublet pattern is clear in the ^{31}P{^{1}H} NMR spectrum of **11** at room temperature; others typically show an averaged broad singlet at this temperature, although the couplings are clear in the ^{31}P{^{1}H} NMR spectrum of [Ag($^{t}Bu_3P$)$_2$].[31] The ^{1}H NMR of **11** is, however, slightly broadened at room temperature. The spectrum of the complex is quite different in $CDCl_3$ compared to C_6D_6 suggesting that different species are dominant in these two solvents; spectroscopic data for **11** in both solvents are included in the Experimental, but complete assignments have only been made for the complex in C_6D_6. The coordination chemistry of phenop is summarised in Scheme 2.

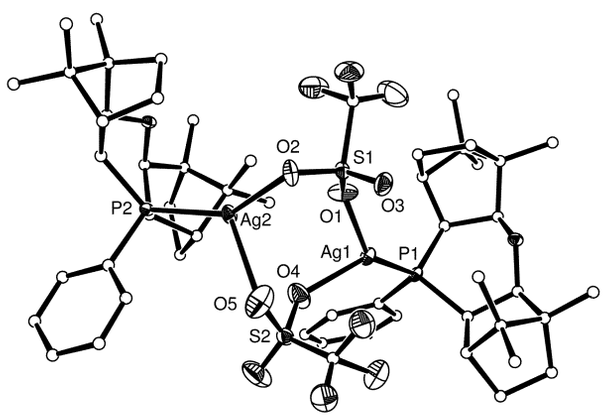


Fig. 6 Molecular structure of **11**.

Preliminary efforts to extend the coordination chemistry to nickel(II) have proved fruitless. No reaction was observed when two mol equivalents of ligand were added to [Ni(H_2O)$_6$]Cl_2 or anhydrous $NiCl_2$ in ethanol. In all cases, no distinct colour change was observed and only uncoordinated ligand was seen in solution by ^{31}P{^{1}H} NMR; indeed, the ligand could be recovered intact from the solutions on work-up. In addition, no reaction was observed when two mol equivalents of phenop were refluxed with [(1,5-COD)RhCl]$_2$ in ethanol or n-butanol and the starting materials were again recovered intact.

‡ The labelling reported here is with respect to the scheme of Fig. 1 and not to the actual carbon labelling of the crystal structure. This is for comparison with the other structures and solution studies (NMR).

In conclusion, the rigid, bulky tertiary phosphine phenop has been prepared by an improved method and its complexation chemistry with a number of metal ions examined. Simple monodentate P-bound complexes have been obtained with Pd(0) and Ag(I). For palladium(II), the nature of the complexes depends on the choice of starting compound and reaction conditions with $Pd(OAc)_2$ giving a six-membered P∧C chelate through metallation at an *exo*-methyl and $Pd(1,5\text{-}COD)Cl_2$ producing a cyclometallated five-membered P∧C chelate through C–H activation at a ring methylene. New chiral centres are generated stereoselectively in both these systems. Work on assessing the use of the ligand in asymmetric catalysis and extending the coordination chemistry is currently in progress and will be presented in due course.

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