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Chiral "P–N–P" ligands, $(C_{20}H_{12}O_2)PN(R)PY_2$ [R = $CHMe_2$, Y = C_6H_5, OC_6H_5, OC_6H_4-4-Me, OC_6H_4-4-OMe or OC_6H_4-4-^{t}Bu] and their allyl palladium complexes ☆

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Abstract

Chiral "P–N–P" ligands, $(C_{20}H_{12}O_2)PN(R)PY_2$ [R = $CHMe_2$, Y = C_6H_5 (**1**), OC_6H_5 (**2**), OC_6H_4-4-Me (**3**), OC_6H_4-4-OMe (**4**) or OC_6H_4-4-^{t}Bu (**5**)] bearing the axially chiral 1,1′-binaphthyl-2,2′-dioxy moiety have been synthesised. Palladium allyl chemistry of two of these chiral ligands (**1** and **2**) has been investigated. The structures of isomeric η^3-allyl palladium complexes, $[Pd(\eta^3\text{-}1,3\text{-}R'_2\text{-}C_3H_3)\{\kappa^2\text{-(racemic)-}(C_{20}H_{12}O_2)PN(CHMe_2)PY_2\}](PF_6)$ (R′ = Me or Ph; Y = C_6H_5 or OC_6H_5) have been elucidated by high field two-dimensional NMR spectroscopy. The solid state structure of $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)\{\kappa^2\text{-}(racemic)\text{-}(C_{20}H_{12}O_2)PN(CHMe_2)PPh_2\}](PF_6)$ has been determined by X-ray crystallography. Preliminary investigations show that the diphosphazanes, **1** and **2** function as efficient auxiliary ligands for catalytic allylic alkylation but give rise to only moderate levels of enantiomeric excess.

Keywords: Chiral "P–N–P" ligands; η^3-allyl palladium complexes; NMR spectroscopy; X-ray crystal structure; allylic alkylation

1. Introduction

There is considerable interest in the design and synthesis of new trivalent chiral phosphorus ligands in view of their applications in enantioselective catalysis, which has developed in recent years as a topic of fundamental importance [1]. Diphosphazanes constitute a class of versatile short-bite bidentate phosphorus-donor ligands based on the "P–N–P" framework that have engendered a varied and extensive transition metal organometallic chemistry [2]. An attractive feature of diphosphazane ligands is that "chirality" can be incorporated at the phosphorus centres as well as at the substituents attached to the nitrogen or to the two phosphorus atoms. There are only a few reports on chiral diphosphazanes and their transition metal complexes [2a,3–6]. As a part of our ongoing investigations on the organometallic chemistry of diphosphazane ligands, we had reported the synthesis and dynamic behaviour of allyl palladium complexes of a range of diphosphazane and diphosphazane monosulfide ligands [7]. The chemistry of η^3-allyl palladium(II) complexes is a topic of considerable importance in view of the various dynamic processes observed in these systems and also their potential applications in asymmetric synthesis [8,9]. Herein, we report the design and synthesis of several chiral diphosphazane ligands based on the "P–N–P" backbone bearing C_2-symmetric [1,1′-binaphthyl]-2,2′-dioxy moiety and the

☆ Organometallic chemistry of diphosphazanes – Part 21; for part 20, see [6d].

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reactivity of some of these chiral diphosphazane ligands with η^3-allyl palladium dimers. The results of high-field two-dimensional NMR studies on the resulting η^3-allyl palladium complexes of chiral diphosphazanes are reported. Preliminary experiments have been carried out to probe the utility of some of these ligands in palladium catalysed alkylation reactions. A part of this work has been reported in a Conference Proceedings [6a].

2. Experimental

2.1. Materials and general procedures

All reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures [10] and distilled under nitrogen prior to use. The synthesis of (*racemic*)-1,1′-binapthyl-2,2′-diol [11] and its resolution [12] were carried out as described in the literature. The chloro-bridged allyl palladium dimers, $[Pd(\eta^3\text{-}1,3\text{-}Me_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ [13] and $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ [14] were prepared according to the literature procedures. The NMR spectra were recorded at 25 °C using Bruker AMX-400 MHz and Bruker ACF-200 MHz spectrometers. Chemical shifts downfield from the reference standard were assigned positive values. Optical rotations were measured on a Jasco DIP-370 digital polarimeter. Elemental analyses were carried out using a Perkin–Elmer 2400 CHN analyser.

2.2. (Racemic, R or S)-($C_{20}H_{12}O_2$)PN($CHMe_2$)PPh_2 (1)

The ligand, *racemic*-($C_{20}H_{12}O_2$)PN($CHMe_2$)PPh_2 (**1**) was prepared by a slight modification of the procedure previously described [15]. The phosphoro chloridite (*racemic*)-($C_{20}H_{12}O_2$)PCl was prepared [16] by the reaction of PCl_3 with (*racemic*)-1,1′-binaphthyl-2,2′-diol in toluene at −78 °C in the presence of Et_3N and was treated with $Ph_2PNH(CHMe_2)$ in toluene to obtain *racemic* – ($C_{20}H_{12}O_2$)PN($CHMe_2$)PPh_2 (**1**) (yield 50%). In the same way, (*R* or *S*)-($C_{20}H_{12}O_2$)PN($CHMe_2$)PPh_2 was prepared by starting from (*R* or *S*)-($C_{20}H_{12}O_2$)PCl. $^{31}P\{^1H\}$ NMR (81.0 MHz, toluene): 28.5 (d, ^2J(P,P) = 25.8 Hz); 148.3 (d). $[\alpha]_D^{25} = -161.5°$ (c = 1.0, CH_2Cl_2) for (*R*)-($C_{20}H_{12}O_2$)PN($CHMe_2$)PPh_2 and $[\alpha]_D^{25} = +166.0°$ (c = 1.0, CH_2Cl_2) for (*S*)-($C_{20}H_{12}O_2$) PN($CHMe_2$)PPh_2.

2.3. (Racemic, R or S)-($C_{20}H_{12}O_2$)PN($CHMe_2$)P-(OC_6H_5)$_2$ (2)

A solution of (*racemic*, *R* or *S*)-($C_{20}H_{12}O_2$)PCl (0.01 mol) in 30 cm^3 toluene was added drop-wise at 0 °C to a 30 cm^3 toluene solution of Me_2CHNH_2 (2.6 cm^3, 0.03 mol). The reaction mixture was warmed to 25 °C and stirred for 6 h. The precipitate of $Me_2CHNH_2 \cdot HCl$ was filtered off and the solvent removed under reduced pressure to obtain a pale yellow viscous oil. This oil was dissolved in 30 cm^3 of toluene and PCl_3 (1.0 cm^3, 0.012 mol) in 20 cm^3 toluene was added drop-wise to it at 0 °C in the presence of Et_3N (2.1 cm^3, 0.015 mol). The reaction mixture was warmed to 25 °C and stirred for 12 h. The precipitate of $Et_3N \cdot HCl$ was filtered off and solvent was evaporated to dryness under reduced pressure to obtain ($C_{20}H_{12}O_2$)PN($CHMe_2$)PCl_2 as a yellow viscous oil [$^{31}P\{^1H\}$ NMR (81.0 MHz, toluene): 157.3 (d, ^2J(P,P) = 12.0 Hz); 169.4 (d)]. A solution of this oil in 30 cm^3 toluene was added drop-wise to a mixture of phenol (1.880 g, 0.02 mol) and Et_3N (4.2 cm^3, 0.03 mol) in 30 cm^3 toluene at 0 °C. The reaction mixture was stirred for 12 h at 25 °C; the resulting $Et_3N \cdot HCl$ was removed by filtration and the filtrate was evaporated to dryness to give a light yellow foamy solid. This solid was loaded over a silica gel column and chromatographed (~400 cm^3 of a 1:1 mixture (v/v) benzene/hexane (b.p. 40–60 °C) was used as eluant) to obtain the title compound **2** as a colourless solid after evaporation of the eluant. Yield: 52%. Anal. Calc. for $C_{35}H_{29}P_2NO_4$: C, 71.3; H, 4.9; N, 2.4. Found: C, 70.8; H, 5.0; N, 2.0%. M.p.122–123 °C. The NMR data for (*racemic*)-($C_{20}H_{12}O_2$)PN($CHMe_2$)P(OC_6H_5)$_2$ are given here. ^1H NMR (200 MHz, $CDCl_3$): 4.32 (m, *CH*–$CHMe_2$); 1.61 (d, ^3J(H,H) = 6.8 Hz, CH_3–$CHMe_2$); 1.45 (d, ^3J(H,H) = 6.8 Hz, CH_3–$CHMe_2$). $^{31}P\{^1H\}$ NMR (81.0 MHz, toluene): 156.4 (d, ^2J(P,P) = 56.3 Hz); 136.2 (d). $[\alpha]_D^{25} = -274.0°$ (c = 1.0, CH_2Cl_2) for (*R*)-($C_{20}H_{12}O_2$) PN($CHMe_2$)P(OC_6H_5)$_2$ and $[\alpha]_D^{25} = +231.0°$ (c = 1.0, CH_2Cl_2) for (*S*)-($C_{20}H_{12}O_2$)PN-($CHMe_2$)P(OC_6H_5)$_2$.

2.4. (Racemic)-($C_{20}H_{12}O_2$)PN($CHMe_2$)P(OC_6H_4-4-Me)$_2$ (3)

The ligand was prepared following the same procedure as described for **2** using 4-methyl phenol (1.842 g, 0.02 mol). The title compound could not be isolated in a pure form owing to its high sensitivity to air and moisture. ^1H NMR (200 MHz, $CDCl_3$): 4.28 (m, *CH*–$CHMe_2$); 2.34, 2.23 (s, CH_3-OC_6H_4-4-Me); 1.57, 1.46 (d, ^3J(H,H) = 6.4 Hz, CH_3–$CHMe_2$). $^{31}P\{^1H\}$ NMR (81.0 MHz, toluene): 158.4 (d, ^2J(P,P) = 56.6 Hz); 137.2 (d).

2.5. (Racemic)-($C_{20}H_{12}O_2$)PN($CHMe_2$)P(OC_6H_4-4-OMe)$_2$ (4)

The ligand was prepared following the same procedure as described for **2** using 4-methoxy phenol (2.482 g, 0.02 mol). Yield: 54%. Anal. Calc. for $C_{37}H_{33}P_2NO_6$: C, 68.4; H, 5.1; N, 2.2. Found: C, 68.7; H, 5.1; N, 2.1%. M.p. 121–122 °C. ^1H NMR (200 MHz, $CDCl_3$): 4.23 (m, *CH*–$CHMe_2$); 3.80, 3.71 (s, CH_3-OC_6H_4-4-OMe);

1.56, 1.44 (d, ^3J(H,H) = 6.9 Hz, CH_3–CHMe$_2$). ^{31}P{^{1}H} NMR (81.0 MHz, toluene): 155.7 (d, ^2J(P,P) = 64.5 Hz); 138.3 (d).

2.6. (Racemic, R or S)-($C_{20}H_{12}O_2$)PN(CHMe$_2$)P-(OC$_6$H$_4$-4-^{t}Bu)$_2$ (5)

The ligand was prepared following the same procedure as described for **2** using 4-tert-butyl phenol (3.020 g, 0.02 mol). Yield: 55%. Anal. Calc. for $C_{43}H_{45}P_2NO_4$: C, 73.6; H, 6.4; N, 2.0. Found: C, 73.5; H, 6.4; N, 1.8%. M.p.124–125 °C. The NMR data for (*racemic*)-($C_{20}H_{12}O_2$)PN(CHMe$_2$)P(OC$_6$H$_4$-4-^{t}Bu)$_2$ are presented here. ^{1}H NMR (200 MHz, CDCl$_3$): 4.28 (m, CH–CHMe$_2$); 1.59 (d, ^3J(H,H) = 7.0 Hz, CH_3–CHMe$_2$); 1.43 (d, ^3J(H,H) = 6.8 Hz, CH_3–CHMe$_2$); 1.35 (s, CH_3–^{t}Bu); 1.24 (s, CH_3–^{t}Bu). ^{31}P{^{1}H} NMR (81.0 MHz, toluene): 155.9 (d, ^2J(P,P) = 63.7 Hz); 136.4 (d). $[\alpha]_D^{25} = -162.0°$ (c = 1.0, CH_2Cl_2) for (*R*)-($C_{20}H_{12}O_2$)PN(CHMe$_2$)P(OC$_6$H$_4$-4-^{t}Bu)$_2$ and $[\alpha]_D^{25} = +146.0°$ (c = 1.0, CH_2Cl_2) for (*S*)-($C_{20}H_{12}O_2$)PN(CHMe$_2$)P(OC$_6$H$_4$-4-^{t}Bu)$_2$.

2.7. [Pd(η^3-1,3-Me$_2$-C_3H_3){κ^2-(racemic)-($C_{20}H_{12}O_2$)-PN(CHMe$_2$)PPh$_2$}](PF$_6$) (6)

A mixture of 0.042 g (0.99×10^{-4} mol) of [Pd(η^3-1,3-Me$_2$-C_3H_3)(μ-Cl)]$_2$, 0.033 g (2.02×10^{-4} mol) of NH_4PF_6 and 0.115 g (2.06×10^{-4} mol) of (*racemic*)-($C_{20}H_{12}O_2$)PN(CHMe$_2$)PPh$_2$ was dissolved in 20 cm^3 of acetone. The solution was stirred for 1 h at 25 °C and the white precipitate formed during the reaction was filtered off. The resulting filtrate was concentrated under reduced pressure to 10 cm^3 and the solution was layered by adding 10 cm^3 of hexane (b.p. 40–60 °C) to yield colourless crystals. Yield: 90%. Anal. Calc. for $C_{40}H_{38}F_6P_3O_2NPd$: C, 53.4; H, 4.3; N, 1.6. Found: C, 55.2; H, 4.5; N, 1.5%. M.p. 165–167 °C dec. Major isomer **6a**: ^{1}H NMR (400 MHz, CDCl$_3$): 5.26 (t, ^3J(H,H) = 11.8 Hz, H$_c$); 4.50 (m, H$_a$ and H$'_a$); 1.64 (m, CH_3-allyl); 0.83 (m, CH_3-allyl). ^{13}C NMR (100.6 MHz, CDCl$_3$): 120.6 (br.d, ^2J(P,C) = 12.5 Hz, central allyl carbon); 89.8 (dd, ^2J(P,C)$_{trans}$ = 29.3 Hz, ^2J(P,C)$_{cis}$ = 16.7 Hz, terminal allyl carbon); 85.9 (dd, ^2J(P,C)$_{trans}$ = 47.3 Hz, ^2J(P,C)$_{cis}$ = 8.4 Hz, terminal allyl carbon); 18.7 (br.s, CH_3-allyl); 18.5 (br.s, CH_3-allyl). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): 59.0 (d, ^2J(P,P) = 64.6 Hz); 113.4 (d). Minor isomer **6b**: ^{1}H NMR (400 MHz, CDCl$_3$): 5.93 (t, ^3J(H,H) = 12.0 Hz, H$_c$); 4.10 (m, H$_a$); 3.94 (m, H$'_a$); 1.75 (m, CH_3-allyl); 1.30 (m, CH_3-allyl). ^{13}C NMR (100.6 MHz, CDCl$_3$): 121.8 (br.d, ^2J(P,C) = 14.0 Hz, central allyl carbon); 92.2 (dd, ^2J(P,C)$_{trans}$ = 29.1 Hz, ^2J(P,C)$_{cis}$ = 17.0 Hz, terminal allyl carbon); 84.1 (dd, ^2J(P,C)$_{trans}$ = 46.5 Hz, ^2J(P,C)$_{cis}$ = 8.2 Hz, terminal allyl carbon); 19.1 (br.s, CH_3-allyl); 18.8 (br.s, CH_3-allyl). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): 57.7 (d, ^2J(P,P) = 58.1 Hz); 114.2 (d).

2.8. [Pd(η^3-1,3-Ph$_2$-C_3H_3){κ^2-(racemic)-($C_{20}H_{12}O_2$)-PN(CHMe$_2$)PPh$_2$}](PF$_6$) (7)

The title complex was prepared by the same procedure as that for **6**. Crystals suitable for X-ray crystallography were grown from toluene/hexane (5:1 v/v) mixture. Yield: 78%. Anal. Calc. for $C_{50}H_{42}F_6P_3O_2NPd$: C, 60.0; H, 4.2; N, 1.4. Found: C, 60.6; H, 3.9; N, 1.2%. M.p. 193–195 °C dec. Major isomer **7a**: ^{1}H NMR (400 MHz, CDCl$_3$): 6.41 (m, H$_c$); 5.85 (m, H$_a$); 5.75 (m, (m, H$'_a$). ^{13}C NMR (100.6 MHz, CDCl$_3$): 114.9 (dd, ^2J(P,C) = 17.4 and 9.7 Hz, central allyl carbon); 93.2 (dd, ^2J(P,C)$_{trans}$ = 28.3 Hz, ^2J(P,C)$_{cis}$ = 16.5 Hz, terminal allyl carbon); 89.2 (dd, ^2J(P,C)$_{trans}$ = 43.1 Hz, ^2J(P,C)$_{cis}$ = 8.1 Hz, terminal allyl carbon). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): 57.9 (d, ^2J(P,P) = 115.3 Hz); 110.7 (d). Minor isomer **7b**: ^{1}H NMR (400 MHz, CDCl$_3$): 6.95 (m, H$_c$); 5.59 (m, H$_a$); 5.17 (m, H$'_a$). ^{13}C NMR (100.6 MHz, CDCl$_3$): 113.5 (dd, ^2J(P,C) = 16.7 and 9.2 Hz, central allyl carbon); 96.0 (dd, ^2J(P,C)$_{trans}$ = 27.5 Hz, ^2J(P,C)$_{cis}$ = 17.1 Hz, terminal allyl carbon); 86.8 (dd, ^2J(P,C)$_{trans}$ = 43.2 Hz, ^2J(P,C)$_{cis}$ = 8.0 Hz, terminal allyl carbon). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): 56.8 (d, ^2J(P,P) = 122.1 Hz); 109.8 (d).

2.9. [Pd(η^3-1,3-Ph$_2$-C_3H_3){κ^2-(racemic)-($C_{20}H_{12}O_2$)-PN(CHMe$_2$)P(OC$_6$H$_5$)$_2$}](PF$_6$) (8)

The title complex was prepared by the same procedure described above for **6**. Yield: 65%. Anal. Calc. for $C_{50}H_{42}F_6P_3O_4NPd$: C, 58.1; H, 4.1; N, 1.4. Found: C, 58.0; H, 4.4; N, 1.2%. M.p. 170–172 °C dec. Major isomer **8a**: ^{1}H NMR (400 MHz, CDCl$_3$): 6.24 (m, H$_c$); 5.52 (m, H$_a$ and H$'_a$). ^{13}C NMR (100.6 MHz, CDCl$_3$): 114.7 (t, ^2J(P,C) = 15.4 Hz, central allyl carbon); 96.4 (dd, ^2J(P,C)$_{trans}$ = 38.2 Hz, ^2J(P,C)$_{cis}$ = 11.8 Hz, terminal allyl carbon); 89.9 (dd, ^2J(P,C)$_{trans}$ = 36.0 Hz, ^2J(P,C)$_{cis}$ = 14.4 Hz, terminal allyl carbon). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): 110.8 (d, ^2J(P,P) = 58.5 Hz); 115.5 (d). Minor isomer **8b**: ^{1}H NMR (400 MHz, CDCl$_3$): 6.62 (m, H$_c$); 5.50 (m, H$'_a$); 4.88 (m, H$_a$). ^{13}C NMR (100.6 MHz, CDCl$_3$): 113.0 (t, ^2J(P,C) = 14.3 Hz, central allyl carbon); 95.6 (dd, ^2J(P,C)$_{trans}$ = 32.9 Hz, ^2J(P,C)$_{cis}$ = 14.4 Hz, terminal allyl carbon); 90.6 (dd, ^2J(P,C)$_{trans}$ = 39.8 Hz, ^2J(P,C)$_{cis}$ = 13.8 Hz, terminal allyl carbon). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): 110.5 (d, ^2J(P,P) = 66.9 Hz); 114.9 (d).

2.10. General procedure for palladium-catalysed allylic alkylation

The ligand (2.5 mol%) and [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ (1 mol%) were dissolved in 4 cm^3 of degassed (by three freeze, pump and thaw cycles) CH_2Cl_2. A solution of (*racemic*)-1,3-diphenyl-2-propenyl acetate (I) (1×10^{-3} mol), in 2 cm^3 CH_2Cl_2, was added followed by dimethyl

malonate (2×10^{-3} mol), N,O-bis(trimethylsilyl)acetamide (2×10^{-3} mol) and a catalytic amount (2 mol%) of KOAc. The mixture was stirred at 25 °C for 24 h and the reaction was monitored by TLC. A saturated aqueous solution of NH_4Cl (10 cm^3) was added to the reaction mixture and the organic part was extracted with diethyl ether (10×3 cm^3). The ether extract was filtered over activated celite, washed with water (3×10 cm^3) and dried over anhydrous Na_2SO_4. Solvent was removed from the ether extract under reduced pressure and the crude product was purified by column chromatography over silica gel [eluant: hexane/ethyl acetate, 9:1 (v/v)]. The optical rotation was measured for the product, PhCH=CH–CHPh{$CH(CO_2Me)_2$} (II) and the enantiomeric excess (*ee*) was calculated from the optical rotation value using the literature data [17].

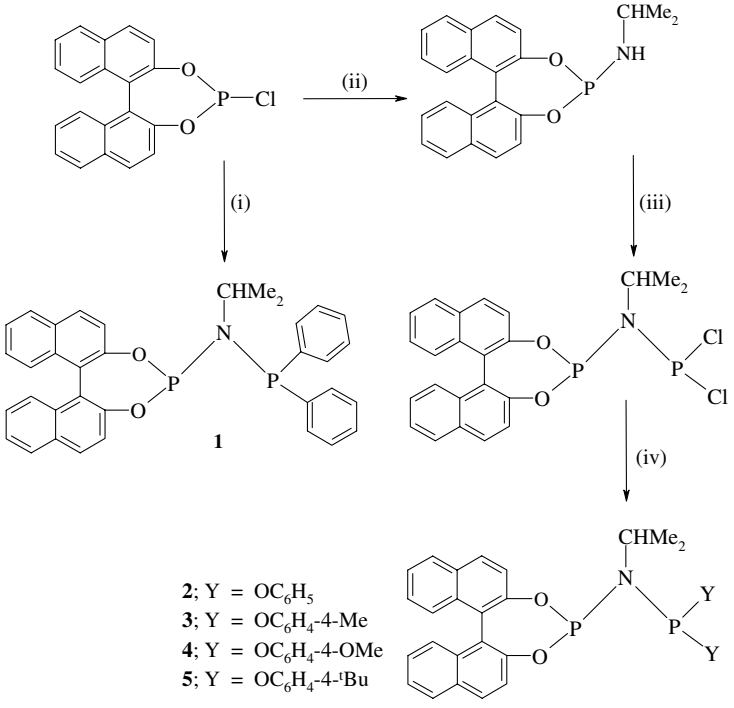
2.11. X-ray crystallography

Crystal data for **7a** were collected from shock-cooled, oil coated crystals on a BRUKER-APEX diffractometer with a D8 goniometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$Å) equipped with a low temperature device in omega-scan mode at 173(2)K [18]. The data was integrated with SAINT [19] and an empirical absorption correction was applied [20]. The structure was solved by direct methods (SHELXS-97) [21] and refined by full-matrix least squares methods against F^2 (SHELXL-97) [22]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 times the U_{eq} value of the parent $C(sp^2)$ atom and 1.5 times the U_{eq} value of the parent $C(sp^3)$ atom, respectively. The disorder of the hexafluorophosphate moiety was refined using distance and similarity restraints.

3. Results and discussion

3.1. Synthesis of ligands

The optically pure unsymmetrical diphosphazane ligand, (*R* or *S*)-$(C_{20}H_{12}O_2)PN(CHMe_2)PPh_2$ (**1**) has been prepared following the procedure adopted previously for the synthesis of (*racemic*)-$(C_{20}H_{12}O_2)PN(CHMe_2)$-$PPh_2$ [15] by the reaction of the aminophosphane, $Ph_2PNH(CHMe_2)$ with 1,1′-binaphthyl-2,2′phosphoro chloridite, (*R* or *S*)-$(C_{20}H_{12}O_2)PCl$ in the presence of Et_3N (Scheme 1). Unsymmetrical diphosphazane ligands of the general formula, (*racemic*)-$(C_{20}H_{12}O_2)PN$ $(CHMe_2)PY_2$ [Y = OC_6H_5 (**2**), OC_6H_4-4-Me (**3**), OC_6H_4-4-OMe (**4**) or OC_6H_4-4-^{t}Bu (**5**)] have been prepared as shown in Scheme 1. The reaction of (*racemic*)-$(C_{20}H_{12}O_2)PCl$ with Me_2CHNH_2 in toluene gives



(i) $Ph_2PNH(CHMe_2)$, Et_3N, toluene, 12 h; (ii) Me_2CHNH_2, toluene, 6 h; (iii) PCl_3, Et_3N, toluene, 12 h; (iv) YH, Et_3N, toluene, 12 h.

Scheme 1.

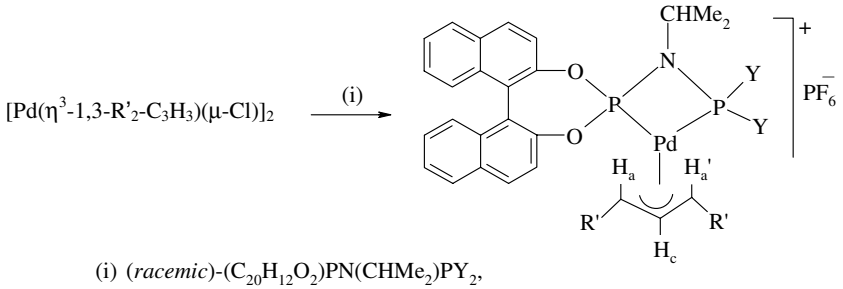
the amino derivative, (*racemic*)-($C_{20}H_{12}O_2$)PNH-($CHMe_2$) which is treated with PCl_3 in the presence of Et_3N to yield (*racemic*)-($C_{20}H_{12}O_2$)PN($CHMe_2$)PCl_2. Subsequent derivatisation with various phenols gives the unsymmetrically substituted diphosphazane ligands **2**–**5**.

The ligands **1**–**5** are characterized by ^1H and $^{31}P\{^1H\}$ NMR spectra. The $^{31}P\{^1H\}$ NMR spectra display an AX pattern; the doublet in the range 148–159 ppm is assigned to the –P($O_2C_{20}H_{12}$) phosphorus nucleus in these ligands. The resonance at 28.5 ppm is assigned to the –PPh_2 phosphorus nucleus in ligand **1**. The PY_2 phosphorus in ligands **2**–**5** resonates as a doublet in the range 136–139 ppm.

3.2. Reactions of *1* and *2* with chloro-bridged allyl palladium dimers

The cationic η^3-allyl palladium complexes **6**–**8** have been prepared by the treatment of the chlorodimer, $[Pd(\eta^3-1,3-R'_2-C_3H_3)(\mu-Cl)]_2$ (R′ = Me or Ph) with the appropriate diphosphazane ligand, (*racemic*)-($C_{20}H_{12}O_2$)PN($CHMe_2$)PY_2 [Y = C_6H_5 (**1**) or Y = OC_6H_5 (**2**)] in the presence of NH_4PF_6 as shown in Scheme 2. The $^{31}P\{^1H\}$ NMR spectra of these complexes reveal the presence of two diastereomers in solution; two sets of AX patterns are observed in each case. The –PPh_2 phosphorus chemical shifts (56.8–59.0 ppm) lie very much down field as compared to that of the free ligand (**1**) and the magnitude of the coordination shift $\Delta\delta$ [$\Delta\delta = \delta$ (complex)$-\delta$ (free ligand)] is in the range 28.3–30.5 ppm. On the other hand, the phosphonite phosphorus [$-P(OC_6H_5)_2$ or $-P(O_2C_{20}H_{12})$] chemical shifts (109.8–114.2 ppm) lie up-field as compared to the free ligands (**1** and **2**); the $\Delta\delta$ values are in the range −25.4 to −41.5 ppm. The ^{13}C NMR spectra of **6**–**8** also indicate the presence of two diastereomers; two sets of allyl ^{13}C resonances are observed in each case. The central allyl carbon resonance for the two diastereomers appears as two separate signals at 113.0–121.8 ppm. The terminal allyl carbon resonances appear as doublet of doublets owing to coupling with the two different phosphorus nuclei present in the molecule. The terminal allyl carbon resonance *trans* to $-P(O_2C_{20}H_{12})$ gives rise to a signal at 89.8–96.4 ppm for these isomers. The other terminal allyl carbon at the *trans* position with respect to the $-PY_2$ (Y = C_6H_5 or OC_6H_5) group resonates at 84.1–90.6 ppm.

Three different allylic arrangements (*syn*/*syn*-, *syn*/*anti*-, and *anti*/*anti*-) are possible for the 1,3-disubstituted allyl complexes (**6**–**8**), depending on the orientation of the two substituents (Me or Ph) with respect to the central allyl proton H_c [7b]. In addition, diastereomers can arise owing to different face coordination of the allyl moiety with the palladium centre [7c]. We performed detailed two-dimensional NMR studies ($^1H-^1H$ DQF COSY, $^1H-^1H$ NOESY and $^1H-^1H$ ROESY) to ascertain the allylic arrangement in these complexes and their structures in solution. The COSY experiment clearly shows that the minor isomer **6b** contains two *anti* allylic protons at 3.94 ppm (H'_a) and 4.10 ppm (H_a) which are strongly coupled (^3J (H,H) = 12.0 Hz which is typical for *anti* coupling) to the central allyl proton indicating that the two allyl methyl groups are situated in a *syn* position with respect to the central allyl proton H_c. For the major isomer **6a**, the resonances of the allylic protons H_a and H'_a overlap with each other at 4.50 ppm thus making their structural assignment difficult from the COSY spectrum. However, the $^1H-^1H$ NOESY spectrum unequivocally establishes a *syn*/*syn*- arrangement of the two allyl methyl groups in the major isomer **6a**. The $^1H-^1H$ NOESY spectrum shows two strong cross-peaks arising from the central allyl proton H_c to both the allyl-methyl protons in the isomer **6a** and **6b** supporting their *syn*/*syn*- allylic arrangements. The $^1H-^1H$ NOESY spectrum shows an NOE contact between the H'_a and ortho phenyl proton on the –PPh_2 group for the major isomer **6a** but no such NOE contact is observed for the minor isomer **6b**. On the basis of this observation, the two isomers are formulated as shown in Fig. 1. The diastereomers arise because of dif-



(i) (*racemic*)-($C_{20}H_{12}O_2$)PN($CHMe_2$)PY_2, NH_4PF_6, acetone, 1 h

6; R' = Me, Y = C_6H_5
7; R' = Ph, Y = C_6H_5
8; R' = Ph, Y = OC_6H_5

Scheme 2.

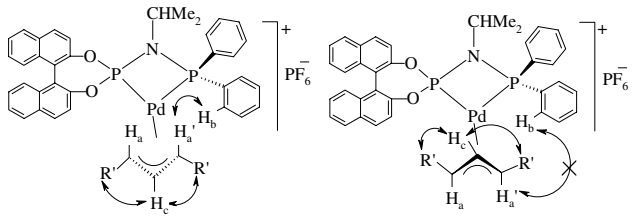


Fig. 1. The two diastereomers of 1,3-disubstituted allyl palladium complex, $[Pd(\eta^3\text{-}1,3\text{-}R'_2\text{-}C_3H_3)\{\kappa^2\text{-}(racemic)\text{-}(C_{20}H_{12}O_2)PN(CHMe_2)PPh_2\}](PF_6)$ [R′ = Me (**6**) or Ph (**7**)] observed in solution.

ferent allyl face coordination to the palladium centre as we have observed in our previous studies [7c]. Similar results are obtained for the 1,3-diphenyl-allyl complex **7**, which exists as a mixture of two diastereomers in the ratio 8:1 as revealed by its $^{31}P\{^1H\}$ NMR spectrum. The $^1H-^1H$ COSY spectrum suggests *syn*/*syn*- allylic arrangement in both the diastereomers of **7**. The $^1H-^1H$ NOESY spectrum of **7** (shown in Fig. 2) displays a selective cross-peak between the *anti* allyl proton H'_a and ortho-phenyl proton (H_b) of the $-PPh_2$ group for the major diastereomer **7a**; for the minor diastereomer **7b** no such NOE contact between H'_a and ortho-phenyl proton of the $-PPh_2$ group is observed. The reaction of optically pure diphosphazane ligand, (*R* or *S*)-$(C_{20}H_{12}O_2)PN(CHMe_2)PPh_2$ with the 1,3-diphenyl-allyl dimer, $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ also results in two isomers whose NMR spectra are identical to the diastereomers (**7a** and **7b**) obtained with (*racemic*)-$(C_{20}H_{12}O_2)PN(CHMe_2)\text{-}PPh_2$.

The reaction of the diphosphonite diphosphazane ligand, (*racemic*)-$(C_{20}H_{12}O_2)PN(CHMe_2)P(OC_6H_5)_2$ with the 1,3-dimethyl-allyl dimer, $[Pd(\eta^3\text{-}1,3\text{-}Me_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ yields a light yellow complex which turns into a black mass over a period of few hours. By contrast, the reaction of the same ligand with the 1,3-diphenyl-allyl dimer, $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)(\mu\text{-}Cl)]_2$ gives an allyl complex, $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)\{\kappa^2\text{-}(racemic)\text{-}(C_{20}H_{12}O_2)PN(CHMe_2)P(OC_6H_5)_2\}](PF_6)$ (**8**), which is stable to air and moisture. The stability of **8** is presumably due to mesomeric electron release from the phenyl groups into the allyl moiety. NMR spectroscopic data reveal that **8** exists as a mixture of two isomers (**8a**, **8b**) in solution in the ratio 6:1 and their structures are similar to those of **6a**/**6b** and **7a**/**7b** (Fig. 1).

3.3. Solid state structure of $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)\{\kappa^2\text{-}(racemic)\text{-}(C_{20}H_{12}O_2)PN(CHMe_2)PPh_2\}](PF_6)$ (**7a**)

A crystallographic study has been carried out for the complex **7a**. The details of the crystal data are presented in Table 1. The solid state structure consists of only the major isomer **7a** as shown in Fig. 3. The molecule crystallises with one molecule of solvent toluene in the unit cell. The two terminal Pd–C(allyl) bond distances *trans* to $-PPh_2$ and *trans* to $-P(O_2C_{20}H_{12})$ are 2.220(3) and 2.183(3) Å, respectively, which fall within the range of the terminal Pd–C(alllyl) bond distances observed for other structurally characterised allyl palladium complexes bearing a bidentate phosphorus ligand [23]. The geometry around palladium is distorted square planar. The P(1)–Pd(1)–P(2) bond angle is $70.4(1)^0$ which

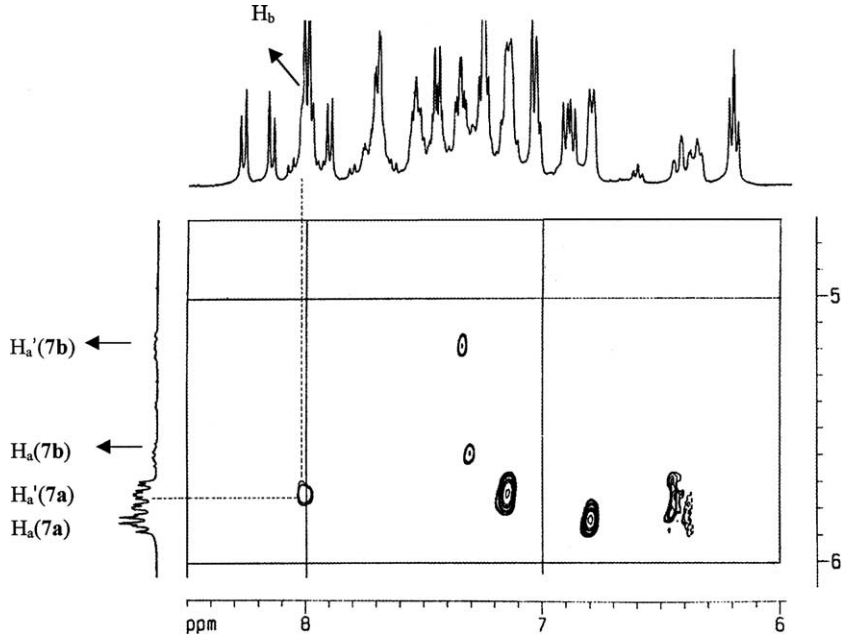


Fig. 2. The $^1H-^1H$ NOESY (400 MHz, $CDCl_3$) spectrum of $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{-}C_3H_3)\{\kappa^2\text{-}(racemic)\text{-}(C_{20}H_{12}O_2)PN(CHMe_2)PPh_2\}](PF_6)$ (**7**) displaying selective NOE cross-peak between H'_a and the ortho-phenyl proton (H_b) on the $-PPh_2$ group in the major diastereomer **7a**.

Table 1
Crystal data and structure refinement for [Pd(η^3-1,3-Ph_2-C_3H_3){κ^2-(*racemic*)-($C_{20}H_{12}O_2$)PN($CHMe_2$)PPh_2}](PF_6) (**7a**)

Identification code	**7a**
Empirical formula	$C_{50}H_{42}F_6P_3O_2NPd$ + 0.59 C_7H_8
Formula weight	1056.12
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	12.9498(11)
b (Å)	28.617(2)
c (Å)	13.0417(11)
β (°)	93.3430(10)
Volume ($Å^3$)	4824.8(7)
Z	4
Density (calculated) (mg/m^3)	1.454
Absorption coefficient (mm^{-1})	0.550
F(000)	2157
Crystal size (mm^3)	$0.40 \times 0.35 \times 0.05$
Theta range for data collection (°)	1.42–26.44
Index ranges	$-16<=h<=16$, $0<=k<=35$, $0<=l<=16$
Reflections collected	51,332
Independent reflections	10,063 [R_{int} = 0.0348]
Completeness to theta = 26.44°	98.6%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10063/282/522
Goodness-of-fit on F^2	1.077
Final *R* indices [$I > 2\text{sigma}(I)$]	R_1 = 0.0417, wR_2 = 0.1004
R indices (all data)	R_1 = 0.0500, wR_2 = 0.1051
Largest different peak and hole ($e Å^{-3}$)	1.834 and −0.646

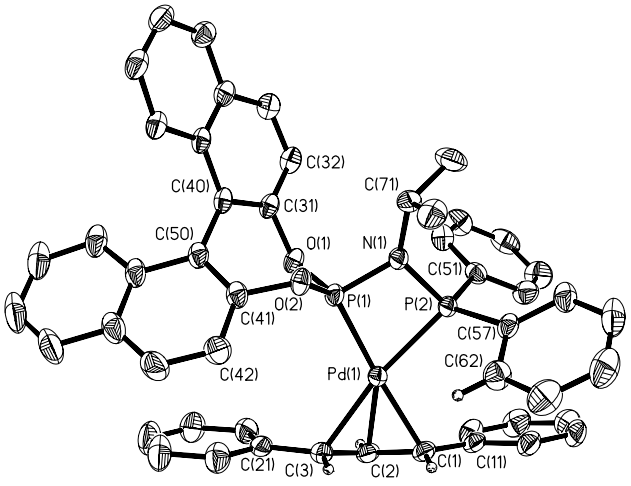
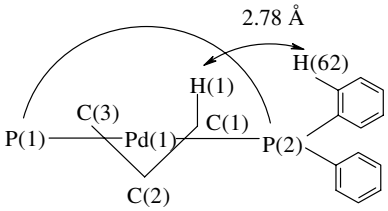


Fig. 3. The molecular structure of [Pd(η^3-1,3-Ph_2-C_3H_3){κ^2-(*racemic*)-($C_{20}H_{12}O_2$)PN($CHMe_2$)PPh_2}] (**7a**) in the solid state; hexafluorophosphate, lattice held toluene and hydrogen atoms [except H(1), H(2), H(3) and H(62)] are omitted for the sake of clarity.

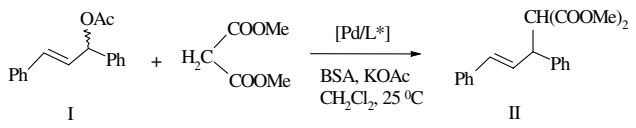
deviates very much from the ideal value. The allyl plane formed by C(1), C(2) and C(3) atoms is not coplanar with the coordination plane formed by P(1)–Pd(1)–P(2); the two planes are inclined at an angle of 62.1^0. The structure can be best described as shown below:



The P(1)–Pd(1)–P(2) plane is considered as the reference plane for this description. The central allyl carbon lies below this plane and the two terminal allyl carbon C(1) and C(3) lie above with respect to such a plane. The phenyl groups on the –PPh_2 groups are not symmetrically placed with respect to the coordination plane formed by P(1)–Pd(1)–P(2). The *ortho*-phenyl proton H(62) on one of these phenyl groups is close to the *anti* allylic proton H(1). From X-ray data, the estimated distance between H(62) and H(1) is 2.78 Å. This short distance is reflected in the NOE interaction between these protons in the major isomer **7a**.

3.4. Catalytic allylic alkylation reactions

The catalytic activity of the chiral diphosphazane ligands **1** and **2** has been tested in allylic alkylation reactions of the symmetrically substituted substrate, (*racemic*)-1,3-diphenyl-2-propenyl acetate (I) (Scheme 3) using dimethyl malonate anion as the nucleophile. The reaction is found to be complete within 24 h as shown by the ^1H NMR spectrum of the reaction mixture. The enantiomeric excess (*ee*) values and the configuration of the alkylated product are listed in Table 2. These "P–N–P" ligands give rise to only moderate levels of asymmetric induction. The *ee* values do not reflect the diastereomeric ratio observed for the two isomers of the η^3-1,3-diphenyl allyl palladium complexes, **7** and **8** (8:1 and 6:1 respectively), presumably because attack *trans* to the two different phosphorus atoms would lead to different product configurations.



L*= chiral diphosphazane ligand
BSA = N,O-bis(trimethylsilyl)acetamide

Scheme 3.

Table 2
Results of catalytic allylic alkylation reactions of a symmetrically substituted substrate (*racemic*)-1,3-diphenyl-2-propenyl acetate using chiral diphosphazane ligands

Entry	Diphosphazane ligand (L*)	Enantiomeric excess[a] (%)	Absolute configuration
(1)	(*R*)-$(C_{20}H_{12}O_2)PN(CHMe_2)PPh_2$	44	*S*
(2)	(*S*)-$(C_{20}H_{12}O_2)PN(CHMe_2)PPh_2$	40	*R*
(3)	(*R*)-$(C_{20}H_{12}O_2)PN(CHMe_2)P(OC_6H_5)_2$	27	*S*
(4)	(*S*)-$(C_{20}H_{12}O_2)PN(CHMe_2)P(OC_6H_5)_2$	20	*S*

[a] The enantiomeric excess (*ee*) is calculated from the optical rotation value using the literature data [17]; the values are accurate to ±5%.

4. Conclusions

A facile synthetic route for chiral and unsymmetrical bidentate phosphorus ligands based on the "P–N–P" motif and bearing 1,1′-binaphthyl-2,2′-dioxy moiety has been developed. The reactivity of some of these ligands towards η^3-allyl palladium dimers has been investigated. The structures of η^3-allyl palladium complexes have been probed by two-dimensional NMR techniques and X-ray crystal structure analysis. These chiral phosphorus ligands and their transition metal complexes would be potentially useful in enantioselective catalysis.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-230791. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

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