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Short-bite Chiral Diphosphazanes Derived From (S)-α-Methyl Benzyl Amine and Their Pd, Pt and Rh Metal Complexes

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Abstract: New chiral diphosphazane ligands of the type $Ph_2PN(S^*CHMePh)PYY'$ {YY'= Ph_2 (**2**), $O_2C_6H_4$ (**3**); Y= Ph, Y'= Cl {**4a** (*SS*), **4b** (*SR*)}, $N_2C_3HMe_2$-*3,5* {**5a** (*SR*), **5b** (*SS*)} are synthesised starting from a chiral aminophosphine, $Ph_2PNH(S^*CHMePh)$ (**1**). The structure of one of the diastereomer **5a** has been confirmed by single crystal X-ray diffraction {Orthorhombic system, $P2_12_12_1$; a=10.456 (4), b=15.362 (7), c=17.379 (6) Å, Z=4}. Transition metal mononuclear complexes $[Rh\{\eta^2\text{-}(Ph_2P)_2N(S^*CHMePh)\}_2]^+(BF_4)^-$ (**6**), $[PdCl_2\{\eta^2\text{-}(Ph_2P)_2N(S^*CHMePh)\}]$ (**7**) and $[PtCl_2\{\eta^2\text{-}(Ph_2P)_2N(S^*CHMePh)\}]$ (**8**) have also been synthesised. The structure of the palladium complex **7** is solved by X-ray crystallography {Orthorhombic system, $P2_12_12_1$; a=8.746 (2), b=18.086 (2), c=20.811 (3) Å, Z=4}. All these compounds are characterised by micro analyses, IR and NMR spectroscopic data.

INTRODUCTION

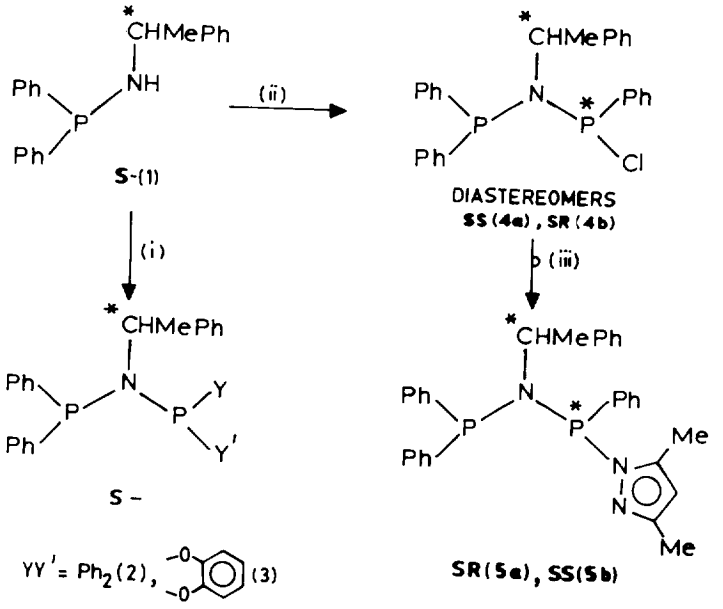
Heterofunctional ligands containing soft and hard donor sites are expected to be efficient ligands for various types of transition metal catalytic transformations.[1] Studies on chiral heterofunctional ligands is growing rapidly in recent years, e.g., a hybrid phosphine-phosphite ligand, (*R*)-(*2*-(diphenylphosphino)-*1,1'*-binaphthalen-*2'*-yl)-((*S*)-*1,1'*- binaphthalen-*2,2'*-yl)phosphite called as *RS*-BINAPHOS,[2] aminophosphine phosphinite ligand [(*5S*)-(+)-N- dicyclopentylphosphino)-*5*-(dicyclopentylphosphinoxymethyl)-*2*- pyrrolidinone],[3] P..O chelating ligand (*R*)-*2*-(diphenylphosphino)- *2'*-methoxy-*1,1'*-binaphthyl called as (*R*)-MOP,[4] a P..N chelating ligand cyclopentadienyl-(*7*-dimethylamino-*1*-diphenylphosphino-*4,5,6,7*-tetrahydroindenyl)iron.[5] Synthetic methodology adopted for chiral heterofunctional ligands is quite tedious involving many steps and the yield of the final product is generally poor. In recent years considerable work has been carried out on short-bite diphosphazane ligands of the type X_2PNRPX_2.[6] These diphosphazane ligands have attracted much attention because of the ease of their syntheses, high thermal stability and their ability to stabilize bimetallic and polymetallic complexes.[6,7] The substituents on the phosphorus atoms of diphosphazanes can be varied readily thereby allowing the possibility to create chiral centre on phosphorus and also to functionalize side groups.[6] Although symmetrically substituted diphosphazanes have been studied extensively, studies on unsymmetrical and chiral diphosphazanes are sparse.[8-10] Continuing

our interest in the synthesis of heterofunctional diphosphazane ligands[11] and their organometallic chemistry,[12] we report here the syntheses of new optically active diphosphazane ligands and some of their transition metal complexes.

RESULTS AND DISCUSSION

Chiral Diphosphazane Ligands

Syntheses. Chiral diphosphazane ligands of the type $Ph_2PN(S\text{-}{}^*CHMePh)PYY'$ {where $YY'=Ph_2$ (**2**), $O_2C_6H_4$ (**3**). Y= Ph; Y'= Cl {**4a**(*SS*), **4b**(*SR*)}, $N_2C_3HMe_2$-*3,5* {**5a**(*SR*), **5b**(*SS*)} are prepared by simple condensation reactions involving a chiral aminophosphine {$Ph_2PNH(S\text{-}{}^*CHMePh)$ (**1**)} and a chlorophosphine. This is illustrated in Scheme 1. The reaction of $PPhCl_2$ with the chiral aminophosphine **1** gives the diastereomers $Ph_2PN(S\text{-}{}^*CHMePh)PPhCl$ {**4a** (*SS*), **4b** (*SR*)}. Chiral induction is observed during the formation of the chiral phosphorus centre leading to a diastereomeric excess of 11.1% in the products. This is measured from the relative integrated intensities of the ^{31}P NMR signals of the *SS* and *SR* diastereomers(4:5). The chloro diphosphazanes{**4a** (*SS*), **4b** (*SR*)} is derivatised using dimethyl pyrazole to obtain a heterofunctional chiral diphosphazane ligand $Ph_2PN(S\text{-}{}^*CHMePh)PPh(N_2C_3HMe_2\text{-}3,5)$ {**5a** (*SR*), **5b** (*SS*)} possessing two phosphorus and one nitrogen coordination sites. It is well known that nucleophilic substitution reaction at the optically active P(III) centre takes place with almost complete inversion of configuration at phosphorus.[13] Hence, it is reasonable to assume that the displacement of chloride from the diphosphazane {**4a** (*SS*), **4b** (*SR*)} by pyrazolyl ion occurs with inversion of configuration at phosphorus.



Scheme 1. (i) ClPYY'; (ii) $PPhCl_2$; (iii) $N_2C_3HMe_2$-*3, 5*

The individual diastereomers {**5a** (*SR*), **5b** (*SS*)} are separated by fractional crystallisation. The less abundant *SR* diastereomer is more stable to air than the *SS* diastereomer.

Spectroscopic aspects. The ^{1}H NMR spectra of the chiral diphosphazane ligands $Ph_2PN(S\text{-}^*CHMePh)$-PYY'{Y=Y'=Ph (**2**); YY'=$O_2C_6H_4$ (**3**); Y=Ph, $N_2C_3HMe_2$- *3,5* (**5a,b**)} show a doublet for the methyl protons; the methine proton appears as a multiplet (compounds **2**, **5a** or **5b**) or doublet of quartets (compound **3**) owing to coupling to methyl protons and adjacent phosphorus nuclei. The diastereomers **5a** and **5b** show different resonances for the methyl group on the chiral carbon as well for the pyrazolyl methyl groups. The ^{1}H NMR spectrum of the diasteromeric mixture is shown in Fig.1. The ^{31}P resonances of the diastereomers **4a**, **4b** or **5a**, **5b** are different and appear as two AX patterns. The relative integrated intensities of the two sets of peaks directly gives the ratio of the diastereomers.

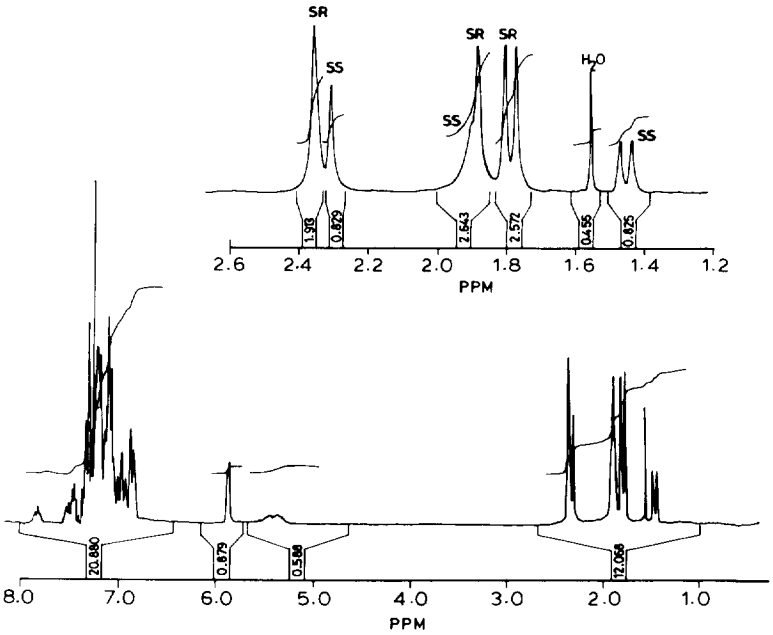


Fig.1. The ^{1}H NMR spectrum of diastereomeric mixture of $Ph_2PN(^*CHMePh)^*PPh(N_2C_3HMe_2$-*3, 5*) {**5a** (*SR*), **5b** (*SS*)}

X-ray crystal structure of SR-{$Ph_2PNH(S\text{-}^*CHMePh)^*PPh(N_2C_3HMe_2$-3,5)} (**5a**). A perspective view of the molecule is shown in Fig.2 and selected structural parameters are listed in Table 1. The configuration of the chiral diphosphazane can be assigned easily by applying Cahn, Ingold and Prelog rules.[14] The configuration of the chiral carbon is *S*- and the configuration of the phosphorus can be assigned as *R*-. The geometry around the phosphorus atoms and nitrogen atom are respectively, trigonal pyramidal and almost planar. The substituents on the PPh_2 phosphorus atom is *trans* to

the α-methyl benzyl group whereas the PYY′ substituents are *cis* oriented. A similar C_s type of conformation is observed for $Ph_2PN(Pr^i)PPh_2$[8] and $Ph_2P(S)N(Pr^i)PPh(N_2C_3HMe_2\text{-}3,5)$[11] where a bulky group is present on the nitrogen atom.

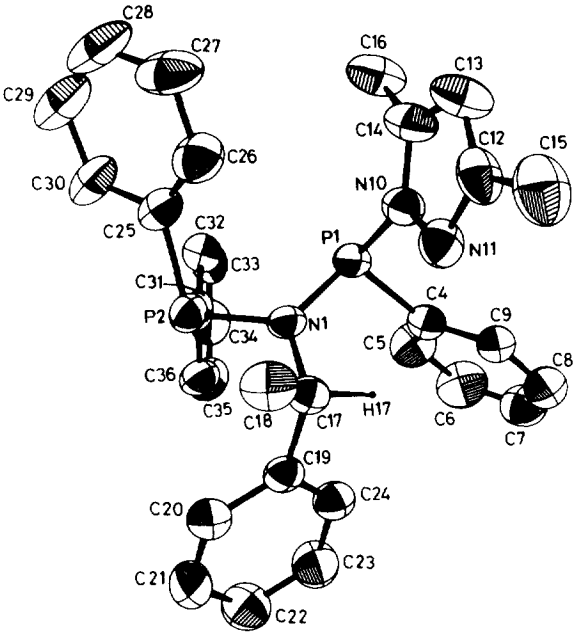


Fig.2. The molecular structure of *SR*-$Ph_2PN(^*CHMePh)^*PPh(N_2C_3HMe_2\text{-}3,5)$ (**5a**)

Two different P-N bond lengths are observed; the one connected to the PYY′ segment {$PPh(N_2C_3HMe_2\text{-}3,5)$} is shorter (1.694 Å) than the other P-N bond length connected to the PPh_2 centre (1.727 Å). This difference presumably arises as a result of the increased π-bonding in the P(1)-N(1) segment where an electron withdrawing substituent ($N_2C_3HMe_2\text{-}3,5$) is present as observed in the case of $Ph_2PN(Pr^i)P(O_2C_6H_4)$.[15] The P-N-P angle is 120.0°.

The geometry around the nitrogen atom of the pyrazolyl group connected to phosphorus is also planar but this P-N bond(1.753Å) is longer than the P-N bond of the P-N-P segment(≈ 1.711Å).

Rhodium, Palladium and Platinum complexes of $(Ph_2P)_2N(S\text{-}^*CHMePh)$ (**2**) *$[Rh\{\eta^2\text{-}(Ph_2P)_2N(S\text{-}^*CHMePh)\}_2]^+(BF_4)^-$* (**6**). The reaction of $[Rh(COD)_2]^+(BF_4)^-$ with the chiral diphosphazane $(Ph_2P)_2N(S\text{-}^*CHMePh)$ (**2**) in the ratio 1:2 gives the bis-chelate complex, $[Rh\{\eta^2\text{-}(Ph_2P)_2N(S\text{-}^*CHMePh)\}_2]^+(BF_4)^-$ (**6**) (Scheme 2). The same complex is obtained even when the ratio of the Rh to diphosphazane is 1:1. This shows the pronounced tendency for these diphosphazanes to form chelate complexes. This complex is characterized by elemental analyses, IR, ^1H and ^{31}P NMR spectroscopic studies. The Fab-mass spectrum of **6** shows the parent ion peak at

m/z 1081 which corresponds to the cationic rhodium bis-chelate diphosphazane species, $[Rh\{\eta^2\text{-}(Ph_2P)_2N(S\text{-}^*CHMePh)\}_2]^+$.

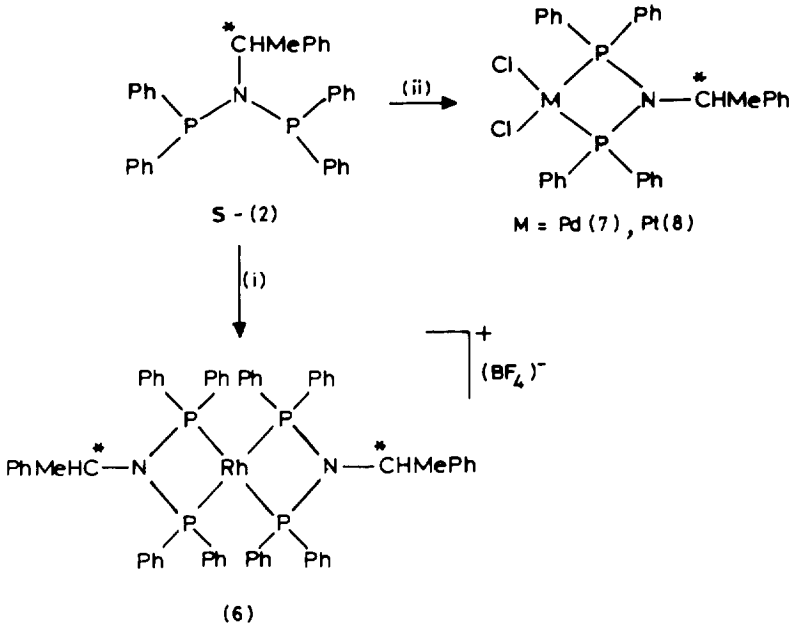
Table 1. Selected Bond Distances (Å) and Bond Angles (°) in (*SR*)-$Ph_2PN(^*CHMePh)$-$^*PPh(N_2C_3HMe_2\text{-}3,5)$ (**5a**) and $[PdCl_2\{\eta^2\text{-}(Ph_2P)_2N(S\text{-}^*CHMePh)\}].CH_2Cl_2$(**7**).

Bond distances (Å)		Bond angles (°)	
(a) (*SR*)-$Ph_2PN(^*CHMePh)^*PPh(N_2C_3HMe_2\text{-}3,5)$ (**5a**)			
P1 - N1	1.694 (2)	N1 - P1 - N10	104.7 (1)
P1 - C4	1.830 (3)	N1 - P1 - C4	105.3 (1)
P1 - N10	1.753 (3)	C25 - P2 - C31	103.3 (2)
P2 - N1	1.727 (2)	N1 - P2 - C31	102.5 (1)
P2 - C25	1.820 (3)	N1 - P2 - C25	104.9 (1)
P2 - C31	1.837 (3)	P1 - N1 - P2	120.0 (1)
N1 - C17	1.503 (4)	P2 - N1 - C17	115.1 (2)
		P1 - N1 - C17	124.8 (2)
(b) $[PdCl_2\{\eta^2\text{-}(Ph_2P)_2N(S\text{-}^*CHMePh)\}].CH_2Cl_2$ (**7**)			
Pd1 - Cl1	2.376 (3)	P1 - Pd1 - P2	71.5 (1)
Pd1 - Cl2	2.365 (4)	Cl2 - Pd1 - P2	96.1 (1)
Pd1 - P1	2.212 (2)	Cl2 - Pd1 - P1	166.9 (1)
Pd1 - P2	2.211 (3)	Cl1 - Pd1 - P2	167.5 (1)
P1 - N1	1.700 (7)	Cl1 - Pd1 - P1	96.5 (1)
P1 - C1	1.806 (10)	Cl1 - Pd1 - Cl2	96.2 (1)
P1 - C7	1.779 (8)	Pd1 - P1 - N1	95.5 (3)
P2 - N1	1.718 (7)	Pd1 - P2 - N1	94.9 (3)
P2 - C13	1.809 (9)	P1 - N1 - P2	98.2 (4)
P2 - C19	1.764 (9)	P2 - N1 - C25	131.6 (6)
N1 - C25	1.482 (11)	P1 - N1 - C25	130.2 (6)

The ^1H NMR spectrum of **6** shows a doublet at 0.99 ppm for the methyl group on the chiral carbon and the methine proton signal is a multiplet. These peaks are slightly shielded in comparison to the free ligand **2**. The phosphorus resonance is observed at 71 ppm as a doublet with a Rh-P coupling of 121 Hz. This value of $^1J_{RhP}$ is less than that observed for similar type of Rh cationic diphosphazane complexes.[16] The signal is deshielded to the extent of 18.8 ppm when compared to the chemical shift for the ligand.

cis-$[MCl_2\{\eta^2\text{-}(Ph_2P)_2N(S\text{-}^*CHMePh)\}]$ {*M = Pd* (**7**), *Pt* (**8**)}. Reaction of $[MCl_2(COD)]$ (M = Pd or Pt) with 1:1 molar proportion of $(Ph_2P)_2N(S\text{-}^*CHMePh)$ (**2**) in dichloromethane at ambient temperature gives complexes of the type *cis*- $[MCl_2\{\eta^2\text{-}(Ph_2P)_2N(S\text{-}^*CHMePh)\}]$ {M = Pd (**7**) or Pt (**8**)} (Scheme 2). The same complex is obtained even when the metal to ligand ratio is 1:2. Both the palladium and platinum complexes are air-stable solids with high melting points(>200°C). The

reaction of *trans*- $[PdCl_2(PhCN)_2]$ with the diphosphazane ligand also yields the same *cis*-chelate complex.



Scheme 2. (i) $[Rh(COD)]^+(BF_4)^-$; (ii) $[MCl_2(COD)]$ (M = Pd or Pt)

The infra red spectra of **7** and **8** show two distinct bands for ν_{M-Cl} in the region 280 - 310 cm^{-1} as observed in case of similar diphosphazane complexes.[6] In the ^1H NMR spectra, the methyl protons are shielded by about 0.5 ppm in comparison to the free ligand. The ^{31}P NMR spectra of these complexes shows a singlet resonance and are considerably shielded compared to that of the free ligand. The same type of shielding effect is observed for diphosphazane complexes $[PdCl_2\{\eta^2\text{-}((PhO)_2P)_2NR\}]$ (R=Me, Ph)[17] and $[PdCl_2\{\eta^2\text{-}(Ph_2P)_2NPr^i\}]$.[18] The $^1J_{PtP}$ coupling for **8** is 3284 Hz which is nearly the same as that observed for the diphosphazane complex $[PtCl_2\{\eta^2\text{-}(Ph_2P)_2NPr^i\}]$ (3280 Hz).[18]

X-ray crystal structure of $[PdCl_2\{\eta^2\text{-}(Ph_2P)_2N(S\text{-}^*CHMePh)\}].CH_2Cl_2$ (**7**). A perspective view of the molecule is shown in Fig.3 and Selected structural parameters are listed in Table 1. The diphosphazane ligand is coordinated in a chelating fashion. The P1-N1-P2 bond angle(98.2°) is considerably less than the tetrahedral or trigonal angle. The chelate bite angle (P1-Pd-P2 = 71.5°) shows much distortion from the value expected(90°) for a square-planar configuration. This bite angle is much shorter than that observed in the case of $[PdCl_2\{\eta^2\text{-}(R)\text{-BINAP}\}]$[19] (92.7°) where a seven membered chelate ring is present. In spite of the strained geometry of the four-membered

chelate ring, the planarity around the nitrogen atom of the P-N-P skeleton is retained. The geometry around the phosphorus atom is tetrahedral. The mean Pd-P(2.21 Å), P-N(1.71 Å)

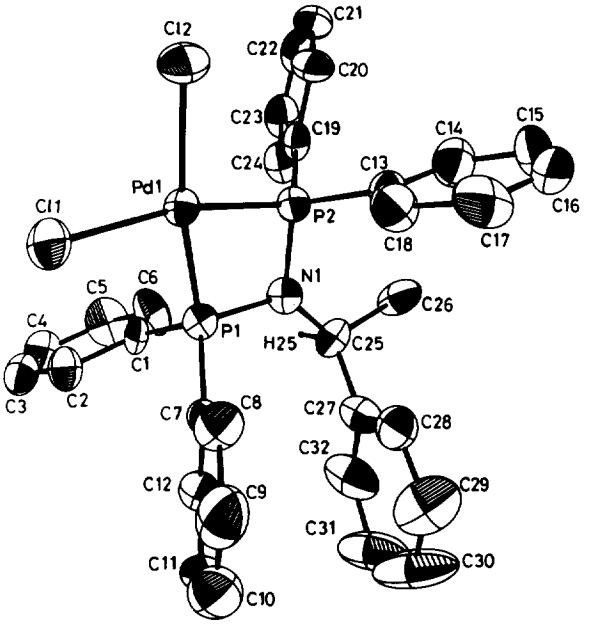


Fig.3. The molecular structure of $[PdCl_2\{\eta^2\text{-}(Ph_2P)_2N(S\text{-}^*CHMePh)\}].CH_2Cl_2$ (**7**)

bond lengths and the P-N-P bond angle(98.2°) are comparable to the corresponding values observed for other structurally characterised palladium diphosphazane complexes.[20]

EXPERIMENTAL

General

All experimental manipulations were performed under an atmosphere of dry nitrogen in a vacuum system or in Schlenk apparatus. All solvents were purified by conventional procedures and freshly distilled prior to use. The transition metal precursor complexes, $[Rh(COD)_2]^+(BF_4)^-$,[21] *cis*-$[MCl_2(COD)]$ (M=Pd, Pt)[22,23] and *trans*-$[MCl_2(PhCN)_2]$[24] were prepared and purified by published procedures. Micro analyses, FAB-Mass, IR and NMR spectra were recorded as reported previously.[12a] Optical rotations were measured using JASCO DIP-370 Digital polarimeter equipped with a sodium lamp at 22°C.

$Ph_2PNH(S\text{-}^*CHMePh)$ (**1**). (Following a slight modification of the literature procedure[25]). A solution of PPh_2Cl(3.6 mL, 0.02 mol) in 30 mL of toluene was added dropwise to (*S*)-α-methyl benzyl

amine (2.6 mL, 0.02 mol) and triethylamine (4.2 mL, 0.03 mol) in 30 mL of toluene at 0°C. The mixture was stirred for 1 h; the colorless precipitate of triethylamine hydrochloride was filtered off. The filtrate containing Ph_2PNH(*S*-*CHMePh) was used as such for the next step.

*$(Ph_2P)_2N$(S-*CHMePh)* (**2**).
A short note has appeared on the synthesis of racemic $(Ph_2P)_2N$(*CHMePh) but no experimental or spectroscopic data was reported.[26]

Triethylamine (4.2 ml, 0.03 mol) was added to the filtrate containing Ph_2PNH(*S*-*CHMePh) (**1**) (0.02 mol, see above), followed by the dropwise addition of PPh_2Cl (3.6 ml, 0.02 mol) in toluene (20 mL) at 0°C. The mixture was stirred for 8 h at ambient temperature. The amine hydrochloride was filtered off and the filtrate was passed through a short silica gel column and eluted with toluene/petrol (1:1) mixture (30 mL). Solvent was removed *in vacuo* from the eluent to obtain a viscous oil. This oil was dissolved in methanol and cooled to 0°C overnight to obtain colorless crystals of the title compound. Yield: 7.25 g, 74%. Mp. 122-123°C; Anal. Calcd for $C_{32}H_{29}N_1P_2$: C, 78.5; H, 5.9; N, 2.9 %. Found: C, 79.6; H, 6.3; N, 3.2 %. IR (Nujol, cm^{-1}): 1086 (m), 1071 (m), 1029 (w), 1017 (w), 939 (m), 864 (s), 741 (s), 693 (s), 669 (w). ^1H NMR ($CDCl_3$, ppm): 7.4-7.1 (m, 25H, aryl protons), 4.7 (m, 1H, CH-*CHMePh), 1.58 (d, $^3J_{HH}$=7.1 Hz, 3H, CH_3-*CHMePh). ^{31}P NMR (CH_2Cl_2, ppm): 52.2 (br). $[\alpha]_D$= -113.4 (c 2.77, CH_2Cl_2).

*Ph_2PN(S-*CHMePh)$P(O_2C_6H_4)$* (**3**). The procedure was similar to the preparation of **2**; *1,1'*-phenylene phosphoro chloridite (2.6 ml, 0.02 mol) was used instead of PPh_2Cl. Yield: 6.21 g, 70%. Mp. 76-77°C; Anal. Calcd for $C_{26}H_{23}NO_2P_2$: C, 70.4; H, 5.2; N, 3.2 %. Found: C, 70.2; H, 4.9; N, 3.3 %. IR (Nujol, cm^{-1}): 1338 (w), 1236 (s), 1095 (w), 1080 (w), 1053 (m), 1032 (w), 987 (s), 885 (m), 858 (w), 819 (s), 780 (w), 741 (s), 723 (m), 690 (s). ^1H NMR ($CDCl_3$, ppm): 7.6-6.8 (m, 19H, aryl protons), 4.47 (dq, 1H, CH-*CHMePh), 1.63 (d, $^3J_{HH}$=6.9 Hz, 3H, CH_3-*CHMePh). ^{31}P NMR (CH_2Cl_2, ppm): 151.1 (d), 31.4 (d), $^2J_{PP}$=30 Hz. $[\alpha]_D$= -216.5 (c 2.31, CH_2Cl_2).

*Ph_2PN(*CHMePh)*PPhCl* {**4a**(*SS*), **4b**(*SR*)}. A solution of $PPhCl_2$ (2.7 ml, 0.02 mol) in 20 ml of toluene was added dropwise to a solution of Ph_2PNH(*S*-*CHMePh) (**1**) (0.02 mol) and triethylamine in 30 ml of toluene at 0°C. The mixture was stirred at ambient temperature for 8 h. Triethylamine hydrochloride was filtered off. The filtrate was passed through a short silica gel column and eluted with toluene/petrol (1:1) mixture (30 mL). Solvent was removed *in vacuo* to obtain a viscous oil containing the diastereomers *SS* (**4a**) and *SR* (**4b**) in the ratio 4:5 alongwith minor impurities. ^{31}P NMR (C_6H_6): *SS* (**4a**) = 126.0(d), 46.1(d), $^2J_{PP}$=35 Hz; *SR* (**4b**) = 128.4(bs), 46.1(d); $^2J_{PP}$ = 35 Hz. The diastereomers were not separated and the viscous oil was used as such for subsequent reaction.

$Ph_2PN(^*CHMePh)^*PPh(N_2C_3HMe_2$-3,5) {*SR*-**5a** *SS*-**5b**}. A solution of $Ph_2PN(^*CHMePh)^*PPhCl$ (**4a** and **4b**; 4:5 mixture) (see above) in 30 mL of toluene was added dropwise to a solution of *3,5*-dimethyl pyrazole (1.92 g, 0.02 mol) and triethylamine (4.2 mL, 0.03 mol) in 20 mL of toluene at 0°C. The mixture was stirred at ambient temperature for 24 h. Triethylamine hydrochloride was filtered off. The filtrate was passed through a short silica gel column and eluted with toluene/petrol (1:1) mixture (30 mL). Solvent was removed *in vacuo* to obtain a viscous oil containing both diastereomers **5a** and **5b** in the same ratio 4:5. The total yield was 5.58 g, 55%. The viscous oil obtained was dissolved in petrol and cooled to 0°C overnight to obtain air-stable colourless crystals of the *SR* diastereomer (**5a**) (yield: 2.45 g). The *SS* diastereomer (**5b**) was air-sensitive and was isolated as an oil. Attempts to crystallize **5b** were unsuccessful. The analytical and spectroscopic data for **5a** and **5b** are given below.

(*SR*)-$Ph_2PN(^*CHMePh)^*PPh(N_2C_3HMe_2$-*3,5*) (**5a**) : Mp. 160°C; Anal. Calcd for $C_{31}H_{31}N_3P_2$: C, 73.4; H, 6.2; N, 8.3 %. Found: C, 73.7; H, 5.8; N, 8.1 %. IR (Nujol, cm^{-1}): 1555 (w), 1306 (w), 1126 (m), 1094 (w), 1077 (w), 1049 (m), 1018 (w), 961 (s), 868 (s), 776 (m), 744 (s), 698 (s), 532 (w), 504 (m), 482 (w), 456 (w). ^1H NMR ($CDCl_3$, ppm): 7.4-6.8 (m, 20H, aryl protons), 5.87 (bs, 1H, CH-pyrazolyl), 5.41 (m, 1H, CH-*CHMePh), 2.35 (s, 3H, CH_3-pyrazolyl), 1.88 (s, 3H, CH_3-pyrazolyl), 1.78 (d, $^3J_{HH}$=6.7 Hz, 3H, CH_3-*CHMePh). ^{31}P NMR (CH_2Cl_2, ppm): 67.5 (d), 47.2 (b), $^2J_{PP}$=32 Hz. $[\alpha]_D$= -163.8 (c 1.92, CH_2Cl_2).

(*SS*)-$Ph_2PN(^*CHMePh)^*PPh(N_2C_3HMe_2$-*3,5*) (**5b**): ^1H NMR ($CDCl_3$, ppm): 7.8-6.8 (m, 20H, aryl protons), 5.86 (bs, 1H, CH-pyrazolyl), 5.6 (m, 1H, CH-*CHMePh), 2.30 (s, 3H, CH_3-pyrazolyl), 1.89 (s, 3H, CH_3-pyrazolyl), 1.45 (d, $^3J_{HH}$=7.0 Hz, 3H, CH_3-*CHMePh). ^{31}P NMR (CH_2Cl_2, ppm): 65.2 (d), 49.1 (d), $^2J_{PP}$=33 Hz.

$[Rh\{\eta^2$-$(Ph_2P)_2N(S$-$^*CHMePh)\}_2]^+(BF_4)^-$ (**6**). A solution of the chiral diphosphazane ligand $(Ph_2P)_2N(S$-*CHMePh) (**2**)(0.196 g, $4x10^{-4}$ mol) in 10 mL of dichloromethane was added dropwise to the CH_2Cl_2 solution containing $[Rh(COD)_2]^+BF_4^-$ {$2x10^{-4}$ mol; which is obtained by stirring $[Rh(COD)Cl_2]_2$(0.049 g, $1x10^{-4}$ mol) and NH_4BF_4 (0.063 g, $6x10^{-4}$ mol) in CH_2Cl_2 (25 mL) for 24 h at 25°C followed by filtration}. The solution was stirred for 30 mins and the solvent was removed *in vacuo* to obtain an oily residue. The residue was washed twice with hot petrol to remove cyclooctadiene and the excess of diphosphazane ligand. The resultant residue was crystallised from CH_2Cl_2-petrol (3:1) mixture (10 mL) to obtain an yellow crystalline solid. (Yield: 0.164 g; 70%). Mp. 243°C; Anal. Calcd for $C_{64}H_{58}BF_4N_2P_4Rh$: C, 65.8; H, 5.0; N, 2.4 %. Found: C, 64.4; H, 4.9; N, 2.1 %. IR (Nujol, cm^{-1}): 1439 (m), 1098 (s), 1059 (s), 965 (w), 860 (m), 744 (m), 695 (s), 525 (m), 504 (m), 488 (m), 425 (w). ^1H NMR ($CDCl_3$, ppm): 7.5-6.5 (m, 50H, aryl protons), 4.3 (m, 2H, CH-*CHMePh), 0.99 (d, $^3J_{HH}$=7.0 Hz, 6H, CH_3-*CHMePh). ^{31}P NMR (CH_2Cl_2, ppm): 71 (d, $^1J_{RhP}$=121 Hz). FAB Mass spectral data: m/z=1081, $[Rh\{(Ph_2P)_2N(S$-$^*CHMePh)\}_2]^+$. $[\alpha]_D$ = -19 (c 1,CH_2Cl_2).

*cis-[MCl$_2${η^2-(Ph$_2$P)$_2$N(S-*CHMePh)}] {M = Pd* (**7**), *Pt* (**8**)}. A mixture of [MCl$_2$(COD)] (M = Pd, 0.057 g; or M = Pt, 0.075 g. 2x10^{-4} mol) and (Ph$_2$P)$_2$N(*S*-*CHMePh) (0.098 g, 2x10^{-4} mol) was dissolved in CH_2Cl_2 (10 mL) and stirred at 25°C for 10 min. Evaporation of the solvent *in vacuo* yields an oily residue which was washed twice with hot petrol to remove cyclooctadiene and crystallized from CH_2Cl_2- petrol (3:1) mixture (10 mL) to obtain the pure title complex. The yield, melting point, micro analyses, optical rotation and spectroscopic data for **7** and **8** are given below.

Compound **7** was also obtained by adopting similar procedure, starting from *trans*-[PdCl$_2$(PhCN)$_2$] (0.077 g, 2x10^{-4} mol) and (Ph$_2$P)$_2$N(*S*-*CHMePh) (0.098 g, 2x10^{-4} mol).

cis-[PdCl$_2${η^2-(Ph$_2$P)$_2$N(*S*-*CHMePh)}].CH_2Cl_2 (**7**): Yield: 0.126 g, 84%. Mp. 241°C (with dec.). Anal. Calcd for $C_{33}H_{31}Cl_4NP_2Pd$: C, 52.7; H, 4.2; N, 1.9 %. Found: C, 53.2; H, 4.4; N, 2.3 %. IR (Nujol, cm^{-1}): 1438 (s), 1204 (m), 1102 (s), 1034 (m), 872 (s), 751 (s), 721 (m), 695 (s), 539 (m), 498 (s), 301 (w), 285 (w). ^{1}H NMR ($CDCl_3$, ppm): 8.1-6.6 (m, 25H, aryl protons), 5.3 (s, 2H, CH_2Cl_2), 4.65 (m, 1H, CH-*CHMePh), 1.06 (d, $^3J_{HH}$=7.0 Hz, 3H, CH_3-*CHMePh). ^{31}P NMR (CH_2Cl_2, ppm): 33.3 (s). $[\alpha]_D$= -6 (c 2, CH_2Cl_2).

cis-[PtCl$_2${η^2-(Ph$_2$P)$_2$N(*S*-*CHMePh)}] (**8**): Yield: 0.133 g, 88%. Mp. 245°C (with dec.). Anal. Calcd for $C_{33}H_{29}Cl_2NP_2Pt$: C, 50.9; H, 3.9; N, 1.9 %. Found: C, 49.5; H, 3.3; N, 1.6 %. IR (Nujol, cm^{-1}): 1435 (s), 1100 (m), 864 (s), 752 (s), 722 (m), 695 (s), 517 (m), 497 (m), 306 (w), 281 (w). ^{1}H NMR ($CDCl_3$, ppm): 8.0-6.7 (m, 25H, aryl protons), 4.55 (m, 1H, CH-*CHMePh), 1.03 (d, $^3J_{HH}$=7.0 Hz, 3H, CH_3-*CHMePh). ^{31}P NMR (CH_2Cl_2, ppm): 18.9 ($^1J_{PtP}$ = 3284 Hz). $[\alpha]_D$= -5 (c 2, CH_2Cl_2).

*X-ray crystal structure determinations of (SR)- Ph$_2$PN(*CHMePh)*PPh(N$_2$C$_3$HMe$_2$-3,5) (5a) and cis*-[PdCl$_2${η^2-(Ph$_2$P)$_2$N(*S*-*CHMePh)}].CH_2Cl_2 (**7**)

The crystal in each case was coated with paraffin oil to protect it from atmospheric air and moisture. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu-Kα radiation for **5a** and Mo-Kα radiation for **7** as described in our previous publication.[12a] The structures were solved by Direct method for **5a** or by Patterson method for **7** using SHELXS-86 program.[27] Refinements were carried out using SHELX-76 program.[28] Hydrogen atoms were located from difference Fourier maps; all non-hydrogen atoms were refined anistropically and hydrogen atoms refined isotropically. For **7**, all non-hydrogen atoms except those of the lattice held solvent(CH_2Cl_2) were refined anisotropically; the solvent molecule showed disorder and hence was refined only isotropically. Crystal data and details pertinent to each structure determination are given in Table 2. The final atomic coordinates with equivalent isotropic thermal parameters are deposited as supplementary material.

Table 2. Crystal Data and Intensity Collection Parameters for (*SR*)-$Ph_2PN(^*CHMePh)$-$^*PPh(N_2C_3HMe_2$-*3,5*) (**5a**) and $[PdCl_2\{\eta^2$-$(Ph_2P)_2N(S$-$^*CHMePh)\}].CH_2Cl_2$(**7**).

	5a	**7**
Formula	$C_{31}H_{31}N_3P_2$	$C_{33}H_{31}Cl_4NP_2Pd$
Molecular weight	507.6	751.79
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Z	4	4
a, Å	10.456(4)	8.746 (2)
b, Å	15.362 (7)	18.086 (2)
c, Å	17.379 (6)	20.811 (3)
V, $Å^3$	2791.6	3291.8
Radiation (graphite monochromator)	Cu-Kα(1.542 Å)	Mo-Kα(0.7107 Å)
Linear abs.coeff., μ, cm^{-1}	14.92	9.44
Temperature (°C)	20	20
Scan technique	$\omega/2\theta$	$\omega/2\theta$
2θ range (°)	2-100	2-50
Total number of reflections	2392	3439
Unique reflections	2357	3263
Observed reflections	2241 $\{F_o>5\sigma(F_o)\}$	2795 $\{F_o>5\sigma(F_o)\}$
R[a]	0.044	0.054
R_w[b]	0.047	0.062
Residual peak in final diff. map, $e/Å^3$	0.23	1.21
$(\Delta/\sigma)_{max}$	0.038	0.143

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; w for **5a**= $1.0000/(\sigma^2(F)+0.032366F^2)$ and for **7**=$1.0000/(\sigma^2(F)+0.006453F^2)$.

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REFERENCES

1. Bader, A.; Lindner, E. *Coord. Chem. Rev.*, **1991**, *108*, 27.
2. Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem., Soc.*, **1993**, *115*, 7033.
3. Roucoux, A.; Agbossou, F.; Mortreux, A.; Petit, F. *Tetrahedron: Asymmetry*, **1993**, *4*, 2279.
4. Hayashi, T. *et al.*, *J. Am. Chem. Soc.*, **1994**, *116*, 775.
5. Jedlicka, B.; Kratky, C.; Weissensteiner W.; Widhalm M. *J. Chem. Soc., Chem. Commun.*, **1993**, 1329.

6. Balakrishna, M.S.; Reddy, V.S.; Krishnamurthy, S.S.; Nixon, J.F.; Burckett St.Laurent, J.C.T.R. *Coord. Chem. Rev.*, **1994**, *129*, 1.

7. King, R.B. *Acc. Chem. Res.*, **1980**, *13*, 243.

8. Keat, R.; Manojlovic-Muir, L.; Muir, K.W.; Rycroft, D.S. *J. Chem Soc.,Dalton Trans.*, **1981**, 2192.

9. Prout, T.R.; Imiolczyk, T.W.; Haltiwanger, R.C.; Hill, T.G.; Norman, A.D. *Inorg. Chem.*, **1992**, *31*, 215.

10. Lednor, P.W.; Beck, W.; Fick, H.G.; Zippel, H. *Chem. Ber.*, **1978**, *111*, 615.

11. Babu, R.P.K.; Aparna, K.; Krishnamurthy, S.S.; Nethaji, M. *Phosphorus, Sulfur, Silicon* (In press).

12. (a) Babu, R.P.K.; Krishnamurthy, S.S.; Nethaji, M. *J. Organomet. Chem.*, **1993**, *454*, 157. (b) Babu, R.P.K.; Krishnamurthy, S.S. *Proc. Indian Acad. Sci. (Chem. Sci.)*, **1994**, *106*, 37.

13. Mikolajczyk, M. *Pure and Appl. Chem.*, **1980**, *52*, 959.

14. Cahn, R.S.; Ingold, S.C.; Prelog, V. *Angew. Chem. Int. Ed. Engl.*, **1966**, *5*, 385.

15. Babu, R.P.K.; Krishnamurthy, S.S.; Nethaji, M. *Heteroatom Chem.*, **1991**, *2*, 477.

16. Mague, J.T.; Lloyd, C.L.; *Organometallics*, **1988**, *7*, 983.

17. Balakrishna, M.S.; Krishnamurthy, S.S.; Murugavel, R.; Mathews, I.I.; Nethaji, M. *J. Chem. Soc., Dalton Trans.*, **1993**, 477.

18. Prakasha, T.K.; *Transition Metal Organometallic Complexes and related derivatives of bis(diphenylphosphino)isopropylamine and 1,3,2λ^3,4λ^3-diazadiphosphetidines*, Ph.D., Thesis, Indian Institute of Science, Bangalore, India, **1990**.

19. Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T.; Nishioka, E.; Yanagi, K.; Moriguchi K. *Organometallics*, **1993**, *12*, 4188.

20. Browning, C.S.; Farrar, D.H.; Frankal, D.C.; *Acta. Crystallogr.*, **1992**, *C48*, 806.

21. Schrock, R.R.; Osborn, J.A. *J. Am. Chem. Soc.*, **1971**, *93*, 3089.

22. Drew, D.;Doyle, J.R.; *Inorg. Synth.*, **1972**, *13*, 52.

23. Drew, D.;Doyle, J.R.; *Inorg. Synth.*, **1972**, *13*, 48.

24. Doyle, J.R.; Slade, P.E., Jonassen, H.B. *Inorg. Synth.*, **1960**, *6*, 218.

25. Brunner, H.; Doppelberger, *Chem. Ber.*, **1978**, *111*, 673.

26. Clemens, D.F.; Smith, R.B.; Dickinson, J.G. *Canad. J. Chem.*, **1973**, *51*, 3187.

27. Sheldrick, G.M. *SHELXS86*, Program for crystal structure solution, University of Gottingen, Germany **1986**.

28. Sheldrick, G.M. *SHELX76*, Program for crystal structure refinement, University of Cambridge, UK **1976**.

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