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Preparation and structure of new homochiral diazaphosphole ligands and their platinum(II) chloride complexes[1]

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Abstract

A new series of homochiral diazaphosphole ligands and their platinum complexes were prepared. © 1998 Elsevier Science Ltd. All rights reserved.

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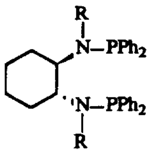
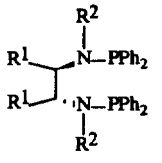
1. Introduction

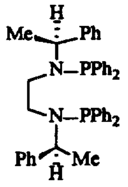
Asymmetric catalysis is recognized as one of the most efficient methods of preparing enantiomerically enriched organic compounds. The past two decades have seen rapid progress in the development of new ligands and complexes for asymmetric homogeneous catalysis.[2] One of the most successful classes of asymmetric reaction is homogeneous hydrogenation which has found several applications in industry.[3] In 1979, the first reports of cationic rhodium complexes of chiral phosphinamines **1–3** appeared.[4] These complexes were effective catalysts for the hydrogenation of acetamidoacrylates (dehydroaminoacids). Interestingly, in several of these phosphinamines (**1** and **2**), changing the nitrogen substituent from hydrogen to methyl resulted in increased enantioselectivity, but for the opposite enantiomer.



1a, R= H
1b, R = Me



2a, R^1 = Me, R^2 = H
2b, R^1 = Me, R^2 = Me
2c, R^1 = Ph, R^2 = H
2d, R^1 = Ph, R^2 = Me



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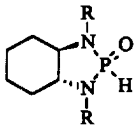

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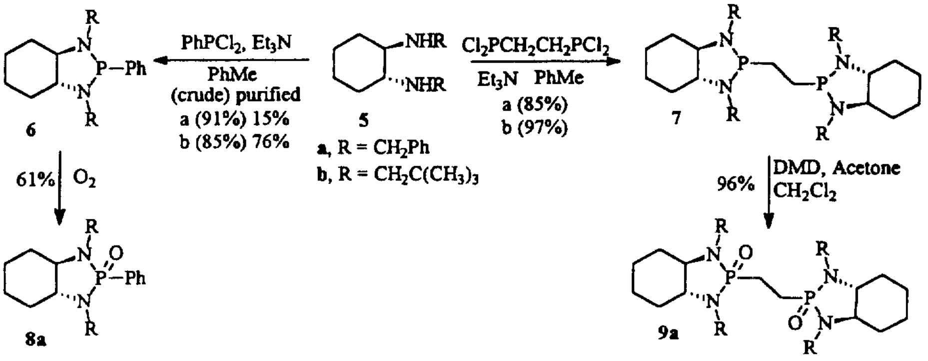
As part of an ongoing program investigating the use of chiral phosphorus compounds as reagents for asymmetric synthesis, we reported a method for the asymmetric synthesis of α-hydroxyphosphonic acids via the addition of chiral phosphorous acid diamides **4** to aldehydes.[5] The selectivity of these addition reactions was also critically dependent upon the nitrogen substituent and the diamides derived from N,N′ dibenzyl and dineopentyl cyclohexane-1,2-diamines were generally the most selective. These results were rationalized on the basis of the N-substituents adopting a preferred conformation. Thus, realizing the relationship of the phosphinamine ligands **1–3** and the diamides **4**, the ready availability of the optically pure diamines, and apparent ease of phosphinylation, we began to study diazaphospholes and aminophosphines[6] as economically viable chiral ligands for asymmetric catalysis. We now describe a versatile synthetic route to a new class of chiral diazaphosphole ligands based upon disubstituted cyclohexane-1,2-diamines.[7]

2. Results and discussion

trans-1,2-Cyclohexanediamine **1** was resolved using a variation of the method of Asperger and Liu,[8] which yielded both the R,R and S,S diamines as the tartrate salts. Treatment of a methanol slurry of the tartrate salt with a methanolic solution of potassium hydroxide (2 equiv.) followed by removal of the precipitated potassium tartrate salts by filtration, conveniently regenerated the pure diamine as a methanol solution. Addition of aldehydes to the cyclohexane-1,2-diamine solution gave the corresponding Schiff base, which was reduced with sodium borohydride to form the disubstituted diamines **5a** and **5b**.[5]

Reaction of the disubstituted diamines **5a** and **5b** with $PhPCl_2$ and Et_3N in toluene solution gave the diazaphospholes **6a** and **6b**, respectively (Scheme 1). Diazaphosphole **6b** was a colorless solid which was recrystallized to give crystals suitable for X-ray structure determination (see Fig. 1) and showed remarkable chemical stability, whereas **6a** was an oil which was rapidly hydrolyzed and oxidized in solution. Air oxidation of **6a** (during chromatography) gave the stable, crystalline diazaphosphole oxide **8a** for characterization.



Scheme 1.

In general, bidentate ligands have been more successful than monodentate ligands in asymmetric catalysis. A rigid and chiral environment around the phosphorus atoms should give rise to an effective asymmetric induction, therefore the synthesis of ethylene bridged bis-diazaphospholes was examined. Reaction of the diamines **5** with the commercially available 1,2-bis(dichlorophosphino)ethane and Et_3N in toluene gave the bis-diazaphospholes **7**. The bis-diazaphospholes **7** were oxidized with dimethyl dioxirane (DMD) to give the solid oxides **9** for characterization. Although the bis-diazaphospholes **7** were more reactive, and consequently less stable than the aryl phospholes **6**, again the nitrogen substituent

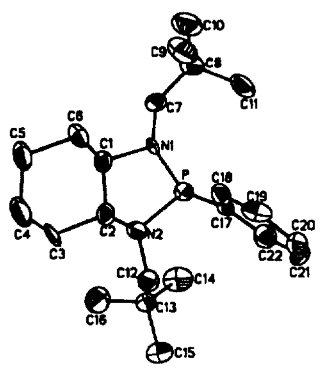
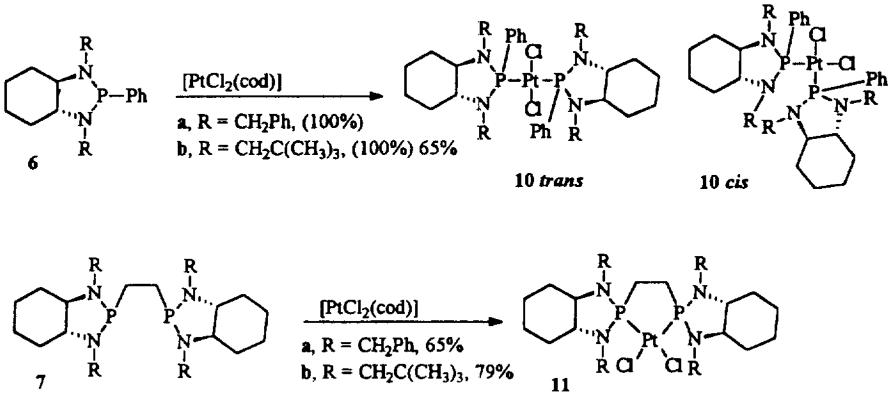


Fig. 1. The molecular structure of diazaphosphole ligand **6b** shown with 75% probability displacement ellipsoids (peripheral H atoms have been omitted for clarity)

contributed to the overall stability of the molecule. Whereas the N-neopentyl derivative could be purified on an alumina column, the N-benzyl derivative rapidly degraded and could not be used in any further reaction.[9]

To examine the complexing ability of the diazaphospholes and to obtain further structural information, the corresponding platinum complexes were prepared. Reaction of the diazaphospholes **6** with 0.5 equiv. of [PtCl$_2$(cod)] in CH$_2$Cl$_2$ solution gave the platinum complexes **10** (Scheme 2). The ^{31}P NMR spectrum of the N-benzyl derivative **10a** in benzene solution showed the presence of two interconverting complexes. The ^{1}J(Pt–P) couplings suggested that these were the *cis* and *trans* isomers. The ^{31}P NMR spectrum of the N-neopentyl derivative **10b** showed only one complex which was assigned as *trans* based on the ^{1}J(Pt–P) coupling. The complex **10b** was crystallized from THF/hexane giving crystals suitable for X-ray structure determination (Fig. 2). Reaction of the bis-diazaphosphole **7b** with [PtCl$_2$(cod)] in a 1:1 ratio gave the complex **11b**. Recrystallization of **11b** from THF/hexane also yielded crystals suitable for X-ray structure determination (Fig. 3).



Scheme 2.

The X-ray crystal structure of **6b** showed that the neopentyl groups are anti to each other and point to opposite sides of the plane from their adjacent methylene carbons. The five-membered ring formed by the P atom, the two N atoms and the carbons of the cyclohexane ring is puckered in a similar way to the analogous neopentyl-substituted phosphorous acid diamide.[10] The sum of the nitrogen bond angles, $\sum$N1=344.1(13)°, and $\sum$N2=339.9(13)°, indicates that their geometry is midway between planar and tetrahedral. The ligand in the platinum complex **10b** is structurally similar to the free ligand. The sum of the angles around the nitrogen atoms are $\sum$N1=341.6(16)° and $\sum$N2=344.8(16)°. The large neopentyl

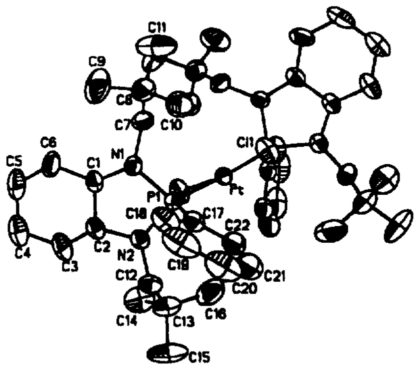


Fig. 2. The molecular structure of platinum complex **10b** shown with 50% probability displacement ellipsoids (peripheral H atoms have been omitted for clarity)

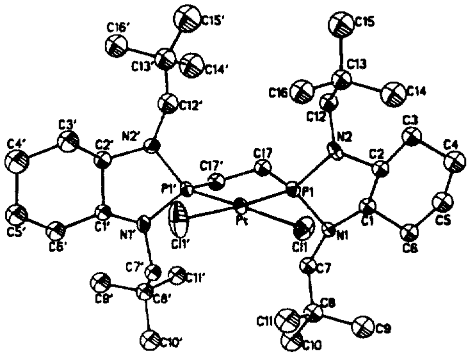


Fig. 3. The molecular structure of platinum complex **11b** shown with 75% probability displacement ellipsoids (peripheral H atoms have been omitted for clarity)

substituents on the same ligand are anti to each other, as in the free ligand. Steric demand is most likely the explanation for the complex adopting the *trans* geometry as well.

The X-ray structure of complex **11b** indicates that the substituents on the nitrogen atoms confer steric rigidity to the molecule by locking their position and, consequently, creating a good chiral environment around the phosphorus atoms. The substituents on the nitrogen atoms connected to the same cyclohexane ring are *cis* to each other and *trans* to the substituents on the pair of nitrogen atoms attached to the opposite cyclohexane ring. The coordination sphere of the Pt atom in **11b** is square planar with a slight tetrahedral distortion similar to that observed for other Pt(II) complexes.[11]

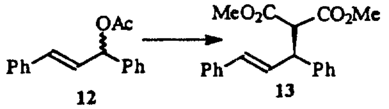
This distortion is indicated by a dihedral angle of 4.39° between the plane defined by Pt, P(1) and P(1′), and that defined by Pt, Cl(1) and Cl(1′), determined from the coordinates of the atoms. For N atoms (N1) and (N1′), the sum of their bond angles is $\sum N(1)=340.7(15)^\circ$ and $\sum N(1')=339.4(15)^\circ$, respectively. The geometries are approximately midway between tetrahedral and planar, in contrast to N atoms (N2) and (N2′) which have closer to planar geometry, [respectively, $\sum N(2)=358.1(15)^\circ$ and $\sum N(2')=355.6(16)^\circ$]. This feature may be explained by the observed relative position of the substituents on the N atoms connected to the same cyclohexane ring, that is, N(1) and N(2), N(1′) and N(2′), which are *cis* to each other and *trans* to the substituents on the pair of N atoms attached to the opposite cyclohexane ring. In the analogous monophosphine ligand, the substituents on the N atoms attached to the same cyclohexane ring were *trans* to each other, in their most sterically favorable spatial arrangement.

The application of the amino-phosphine ligands **6** and **7** in palladium-catalyzed asymmetric allylic alkylation was investigated. Although the alkylation reactions were not expected to proceed with

Table 1
Allylic alkylation of **12** using diazaphosphole ligands **6** and **7**

Entry	Ligand	Yield (%)	% E.e.	Config.
1	6a	80	21	(-)S
2	6b	57	25	(+)R
3	7b	19	4	(+)R

high enantiomeric excess, this reaction serves as a simple test of the ability of the ligands to form complexes in situ and then to influence the stereochemistry of the reaction. The palladium complex was formed in situ by mixing the ligand with $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$. Addition of 1,3-diphenyl-2-propenyl acetate **12** to the catalyst solution, followed by sodium dimethyl malonate afforded the allyl substituted product **13** (Table 1, Scheme 3). Interestingly, while the monophosphines resulted in an expected low enantioselectivity, the absolute configuration of the product **13** was the opposite for **6a** (predominantly S) and **6b** (predominantly R). It has recently been shown that an OMe group at the ortho position of the phenyl ring in related monophosphines results in increased enantioselectivity.[7b] The chelating ligand **7b** gave the malonate **13** in low yield and with low selectivity, probably due to the excessive steric bulk provided by the neopentyl groups.



1) 1 mol% $[Pd(C_3H_5)Cl]_2$
3 mol% Ligand
2) $CH_2(CO_2Me)_2$, base, r.t.

Scheme 3.

In summary, we have demonstrated that diazaphospholes can be prepared from diamines, and that they are able to form useful complexes. In addition, we have shown that the phosphorus atom can be sterically protected against unfavorable hydrolysis and oxidation reactions and that the exocyclic substituent on nitrogen can affect the configuration of the product formed in catalytic reactions.

3. Experimental section

^1H, ^{13}C and ^{31}P NMR spectra were recorded in C_6D_6 or CD_2Cl_2 solution on a Varian XL-300 spectrometer at 300, 75 and 121 MHz, respectively. The ^1H chemical shifts are reported in ppm relative to Me_4Si, ^{13}C chemical shifts are reported in ppm relative to the center line of C_6D_6 (128.0 ppm) or CD_2Cl_2 (54.0 ppm), and ^{31}P chemical shifts are reported relative to external H_3PO_4. Infrared spectra were recorded on a Perkin–Elmer 1600 series FTIR. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Optical rotations were determined on an Rudolph Research Autopol III polarimeter. Microanalyses were performed by Atlantic Microlab Inc. All reactions were carried out under an inert (argon) atmosphere, and all solvents were dried before use. Toluene and CH_2Cl_2 were distilled from CaH_2, THF and Et_2O were distilled from sodium–benzophenone ketyl, methanol was distilled from Mg and hexanes were distilled from Na. Triethylamine was distilled twice from KOH. Column chromatography was performed on neutral alumina (Fisher Scientific, Brockman Activity I, 80–200 mesh).

3.1. 2-Phenyl-2,3,3a,4,5,6,7,7a-octahydro-1,3-dibenzyl-1H-1,3,2-benzodiazaphosphole (**6a**)

To a stirred solution of (1R,2R)-N,N′-dibenzyl-1,2-cyclohexanediamine (1.05 g, 3.6 mmol) and Et_3N (1.46 g, 14.4 mmol) in toluene (12 mL) at 10°C was added $PhPCl_2$ (0.64 g, 3.6 mmol) dropwise. After the addition was complete, the resulting yellow solution was stirred overnight and monitored by TLC (alumina, hexanes:EtOAc=2:1). The reaction mixture was filtered through anhyd. $MgSO_4$, and then concentrated *in vacuo* to give a yellow oil (1.31 g, 91%, ≈60–70% pure). Column chromatography (neutral alumina, hexanes:EtOAc=2:1) gave the pure phosphine **6a** as a yellow oil (0.2 g, 15%). ^1H NMR (C_6D_6) δ 7.82 (m, 2H), 7.50 (m, 4H), 7.40–7.03 (m, 9H), 4.37 (dd, 1H, $J_{HH}=J_{HP}=14.6$ Hz), 4.22 (dd, 1H, $J_{HH}=J_{HP}=14.8$ Hz), 3.88 (dd, 1H, $J_{HH}=14.8$, $J_{HP}=12.4$ Hz), 3.55 (dd, 1H, $J_{HH}=14.8$, $J_{HP}=13.0$ Hz), 2.71 (m, 2H), 2.04 (m, 1H), 1.63–1.25 (m, 4H), 1.18–0.84 (m, 4H); ^{13}C NMR (C_6D_6) δ 131.6 (d, $^2J_{CP}=20.3$ Hz), 129.2–127.0 (m, aromatic carbons), 69.4 (d, $^2J_{CP}=4.2$ Hz), 66.4 (d, $^2J_{CP}=8.1$ Hz), 55.5 (d, $^2J_{CP}=32.6$ Hz), 49.6 (d, $^2J_{CP}=11.9$ Hz), 31.7, 30.7, 25.0, 24.9; ^{31}P NMR (C_6D_6) δ 109.9 ppm. Further elution (hexanes:EtOAc=2:1) gave 2-phenyl-2,3,3a,4,5,6,7,7a-octahydro-1,3-dibenzyl-1H-1,3,2-benzodiazaphosphole-2-oxide (**8a**) (0.8 g, 61%). Mp 125–126.4°C (C_6H_6–hexanes, white crystals); $[\alpha]_D$ −47.9 (c=1.11, C_6H_6); IR (KBr) 3100, 2940, 1654, 1560, 1495, 1357, 1207, 1120, 925, 852, 742 cm^{-1}; ^1H NMR (C_6D_6) δ 8.03 (m, 2H), 7.53 (d, 2H, $J=7.2$ Hz), 7.41 (d, 2H, $J=7.5$ Hz), 7.30–6.91 (m, 9H), 4.18 (dd, 1H, $J_{HH}=J_{HP}=15.9$ Hz), 4.10 (dd, 1H, $J_{HH}=15.9$, $J_{HP}=11.7$ Hz), 4.03 (dd, 1H, $J_{HH}=15.9$, $J_{HP}=8.7$ Hz), 3.20 (dd, 1H, $J_{HH}=15.9$, $J_{HP}=7.5$ Hz), 2.94 (m, 1H), 2.75 (m, 1H), 1.65 (m, 1H), 1.38 (m, 1H), 1.30 (m, 2H), 0.97–0.69 (m, 4H); ^{13}C NMR (C_6D_6) δ 140.8, 139.0, 133.3 (d, $^2J_{CP}=9.4$ Hz), 131.5, 129.0–127.1 (aromatic carbons), 66.5 (d, $^2J_{CP}=7.7$ Hz), 62.5 (d, $^2J_{CP}=6.7$ Hz), 47.6 (d, $^2J_{CP}=6.5$ Hz), 47.4 (d, $^2J_{CP}=3.3$ Hz), 30.4 (d, $^3J_{CP}=7.0$ Hz), 29.7 (d, $^3J_{CP}=9.1$ Hz), 24.6, 24.3; ^{31}P NMR (C_6D_6) δ 30.0 ppm; MS (EI/DIP) m/z (rel. intensity) 91 (100), 325 (37), 416 (M^+, 30). Anal. calcd for $C_{26}H_{29}N_2PO$: C, 74.96; H, 7.02. Found: C, 74.75; H, 7.13.

3.2. 2-Phenyl-2,3,3a,4,5,6,7,7a-octahydro-1,3-bis(2,2-dimethylpropyl)-1H-1,3,2-benzodiazaphosphole (**6b**)

To a solution of (1R,2R)-N,N′-bis(2,2-dimethylpropyl)-1,2-cyclohexanediamine (1.2 g, 4.8 mmol) and Et_3N (0.97 g, 9.6 mmol) in toluene (15 mL) at 10°C was added $PhPCl_2$ (0.86 g, 4.8 mmol) dropwise. The resulting yellow solution was stirred at room temperature for 3 h. The reaction mixture was then filtered through anhyd. $MgSO_4$ and concentrated *in vacuo* to give an off-white to yellow solid (1.45 g, 84%, 95% pure). Column chromatography (alumina, hexanes:EtOAc=2:1) gave the pure phosphine **6b** as a white solid (1.1 g, 76%). Mp 119.5–120°C (C_6H_6–hexanes, colorless plates); $[\alpha]_D$ −19.3 (c=1.05, C_6H_6). IR (KBr) 3100, 2945, 1475, 1360, 1207, 1140, 1008, 900, 747, 727, 702 cm^{-1}; ^1H NMR (C_6D_6) δ 7.84 (m, 2H), 7.30 (m, 2H), 7.27 (m, 1H), 3.27 (dd, 2H, $J_{HH}=J_{HP}=14.2$ Hz), 2.53–2.29 (m, 4H), 2.14–1.90 (m, 2H), 1.62–1.57 (m, 2H), 1.48–1.21 (m, 2H), 1.07 (s, 9H), 0.98 (brd s, 2H), 0.89 (s, 9H); ^{13}C NMR (C_6D_6) δ 132.5 (d, $^1J_{CP}=20.4$ Hz), 129.0–127.8 (m, aromatic carbons), 72.3 (d, $^2J_{CP}=4.6$ Hz), 66.7 (d, $^2J_{CP}=29.5$ Hz), 65.2 (d, $^2J_{CP}=7.9$ Hz), 55.4 (d, $^2J_{CP}=7.9$ Hz), 33.0, 32.5 (d, $^3J_{CP}=4.3$ Hz), 30.8 (d, $^3J_{CP}=2.4$ Hz), 28.9 (d, $^4J_{CP}=3.4$ Hz), 28.4, 25.4 25.3, 24.95, 24.90; ^{31}P NMR (C_6D_6) δ 119.1 ppm; MS (EI/DIP) m/z (rel. intensity) 57 (100), 303 (33), 42 (21). Anal. calcd for $C_{22}H_{37}N_2P$: C, 73.29; H, 10.34; N, 7.77. Found: C, 73.40; H, 10.38; N, 7.81.

3.3. *Bis-1,2-{2-[(1R,2R)-2,3,3a,4,5,6,7,7a-octahydro-1,3-dibenzyl-1H-1,3,2-benzodiazaphosphole]}ethane (**7a**)*

To a solution of (1R,2R)-N,N′-dibenzylcyclohexane-1,2-diamine (0.59 g, 1.99 mmol) and Et_3N (0.81 g, 8.0 mmol) in toluene (10 mL) at 10°C was added 1,2-bis(dichlorophosphino)ethane (0.23 g, 0.99 mmol) dropwise. The reaction mixture was stirred for 3 hours, then filtered through anhyd. $MgSO_4$. The solvent was evaporated *in vacuo* to give an unstable yellow solid (1.14 g, 85%). ^{31}P NMR (C_6D_6) δ 131.5 ppm. The crude phosphine **7a** (0.23 g, 0.34 mmol) was dissolved in CH_2Cl_2 (5 mL), and dimethyldioxirane (20.3 mL, 0.066 M in acetone) was added. Thin layer chromatography (alumina, CH_2Cl_2) indicated complete reaction after 15 min. The resulting solution was concentrated *in vacuo* to give bis-1,2-{2-[(1R,2R)-2,3,3a,4,5,6,7,7a-octahydro-1,3-dibenzyl-1H-1,3,2-benzodiazaphosphole-2 oxide]}ethane (**9a**) as a highly insoluble brown solid which could not be purified. ^{31}P NMR (C_6D_6) δ 42.5 ppm.

3.4. *Bis-1,2-{2-[(1R,2R)-2,3,3a,4,5,6,7,7a-octahydro-1,3-bis(2,2-dimethylpropyl)-1H-1,3,2-benzodiazaphosphole]}ethane (**7b**)*

To a solution of (1R,2R)-N,N′-bis (2,2-dimethylpropyl)-1,2-cyclohexanediamine (1.10 g, 4.32 mmol) and Et_3N (1.31 g, 13 mmol) in toluene (10 mL) at 10°C was added 1,2-bis(dichlorophosphino)ethane (0.50 g, 2.16 mmol) dropwise. The solution was stirred for 3 hours, then filtered through anhyd. $MgSO_4$ and concentrated *in vacuo* to give phosphine **7b** as a yellow solid (2.49 g, 97%, 90+% pure). ^1H NMR (C_6D_6) δ 3.19 (dd, 2H, $J_{HH}={}^3J_{HP}=13.7$ Hz), 3.02 (m, 2H), 2.69–2.63 (m, 4H), 2.53–2.21 (m, 8H), 2.11–1.85 (m, 4H), 1.59 (m, 4H), 1.20–0.98 (m, 4H), 1.05 (s, 18H), 1.00 (s, 18H); ^{31}P NMR (C_6D_6) δ 140.0 ppm. The crude phosphine **7b** (0.21 g, 0.358 mmol) was dissolved in CH_2Cl_2 (5 mL), and dimethyldioxirane (10.5 mL, 0.068 M in acetone) was added. Thin layer chromatography (alumina, CH_2Cl_2) indicated that the reaction was complete after 5 min. The resulting solution was concentrated *in vacuo* to give bis-1,2-{2-[(1R,2R)-2,3,3a,4,5,6,7,7a-octahydro-1,3-bis(2,2-dimethylpropyl)-1H-1,3,2-benzodiazaphosphole-2-oxide]}ethane (**9b**) as a brown solid (0.21 g, 96%). Mp 261–263.3°C (C_6H_6–hexanes, colorless crystals); $[\alpha]_D$ −88.8 (c=0.43, C_6H_6); IR (KBr) 2950, 1480, 1365, 1220, 1170, 1025, 805, 784 cm^{-1}; ^1H NMR (C_6D_6) δ 3.66–3.52 (m, 4H), 2.89–2.87 (m, 8H), 2.65–2.47 (m, 4H), 2.37–2.23 (m, 4H), 1.79–1.56 (m, 4H), 1.43–1.18 (m, 4H), 1.12 (s, 18H), 1.02 (s, 18H), 0.96–0.78 (m, 4H); ^{13}C NMR (C_6D_6) δ 66.1 (d, $^2J_{CP}=2.6$ Hz), 65.9 (d, $^2J_{CP}=4.4$ Hz), 57.4, 55.9, 32.8, 32.4, 31.3 (d, $^3J_{CP}=18$ Hz), 29.2, 28.9, 24.8, 22.1 (d, $^1J_{CP}=15.1$ Hz); ^{31}P NMR (C_6D_6) δ 44.7 ppm; MS (EI/DIP) m/z (rel. intensity) 57 (100), 569 (98), 43 (94), 460 (81). Anal. calcd for $C_{34}H_{68}O_2N_4P_2$: C, 65.14; H, 10.93; N, 8.94. Found: C, 65.02; H, 10.86; N, 8.87.

3.5. cis- *and* trans-*Dichloro-bis(2-phenyl-2,3,3a,4,5,6,7,7a-octahydro-1,3-dibenzyl-1H-1,3,2-benzodiazaphosphole) platinum (**10a**)*

The phosphine **6a** (0.72 g, 1.79 mmol) was dissolved in CH_2Cl_2 (10 mL), and $[PtCl_2(cod)]$ (0.33 g, 0.89 mmol) was added. The solvent was evaporated *in vacuo*, to give a yellow oil which was not further purified. ^{31}P NMR (CD_2Cl_2, 25°C) δ 82.0 ppm (brd), ($J_{P\text{-}Pt}=4598$ Hz), (−40°C) 84.2 ($J_{P\text{-}Pt}=4231$ Hz), 74.8 ($J_{P\text{-}Pt}=4502$ Hz).

3.6. trans-*Dichloro(2-phenyl-2,3,3a,4,5,6,7,7a-octahydro-1,3-bis(2,2-dimethylpropyl)-1H-1,3,2-benzodiazaphosphole)platinum (**10b**)*

The pure phosphine **6b** (0.10 g, 0.28 mmol) was dissolved in CH_2Cl_2 (2.5 mL) and $[PtCl_2(cod)]$ (0.052 g, 0.14 mmol) was added. The reaction occurred immediately. The solvent was evaporated *in vacuo*, and the resulting solid was recrystallized from THF/hexanes to give yellow crystals. The crystals were filtered, washed with hexanes, and dried *in vacuo* (0.1 g, 58%). Mp 247.3–248.3°C; $[\alpha]_D$ −73.4 (c=0.81, CH_2Cl_2); IR (KBr) 2953, 1478, 1434, 1109, 1065, 1015, 746, 695 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.97 (m, 2H), 7.42 (m, 3H), 4.51 (m, 1H), 3.18 (m, 1H), 2.64 (m, 2H), 2.34 (m, 2H), 2.15 (m, 1H), 2.0 (m, 1H), 1.80 (m, 2H), 1.33–1.27 (m, 2H), 1.00 (m, 2H), 0.99 (s, 9H), 0.80 (s, 9H); ^{13}C NMR (CD_2Cl_2) δ 134.3 (d, $^1J_{CP}$=5.6 Hz), 130.7, 126.9, 126.8, 126.7, 70.4, 67.5, 61.7, 57.4, 33.2 (d, $^3J_{CP}$=4.7 Hz), 32.8 (d, $^3J_{CP}$=3.6 Hz), 30.9, 29.4, 29.2, 25.0, 24.8; ^{31}P NMR (CD_2Cl_2) δ 103.2 ppm, (J_{P-Pt}=2917 Hz). Anal. calcd for $(C_{22}H_{37}N_2P)_2PtCl_2$: C, 53.54; H, 7.56; N, 5.68. Found: C, 53.44; H, 7.53; N, 5.71.

3.7. *Dichloro(bis-1,2-{2-[(1R,2R)-2,3,3a,4,5,6,7,7a-octahydro-1,3-dibenzyl-1H-1,3,2-benzodiazaphosphole]}ethane)platinum (**11a**)*

To a solution of the crude diphosphine **7a** (0.13 g, 0.20 mmol) in CH_2Cl_2 (8 mL) was added $[PtCl_2(cod)]$ (0.075 g, 0.20 mmol). The solvent was immediately evaporated *in vacuo* to give a yellow solid. Column chromatography (neutral alumina, CH_2Cl_2:Et_2O=1:1) afforded the pure complex **11a** (0.12 g, 65%). $[\alpha]_D$ −16.7 (c=0.06, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.36–7.18 (m, 4H), 7.12–7.00 (m, 6H), 4.79–4.53 (dd, 2H, $^3J_{HP}$=15 and 38 Hz), 4.30–3.63 (m, 2H), 3.40–3.32 (m, 1H), 3.11–2.95 (m, 1H), 2.40–2.11 (m, 2H), 1.74–1.68 (m, 4H), 1.43–0.98 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 140.2, 128.7, 128.6, 128.4, 128.2, 127.1, 126.9, 126.6, 76.7, 68.7, 65.7, 51.5, 48.2, 31.0, 29.4, 24.6, 24.1; ^{31}P NMR ($CDCl_3$) δ 124.5 ppm, (J_{P-Pt}=4368 Hz).

3.8. *Dichloro(bis-1,2-{2-[(1R,2R)-2,3,3a,4,5,6,7,7a-octahydro-1,3-bis(2,2-dimethylpropyl)-1H-1,3,2-benzodiazaphosphole]}ethane)platinum (**11b**)*

To a solution of the diphosphine **7b** (0.056 g, 0.094 mmol) in CH_2Cl_2 (3 mL) was added $[PtCl_2(cod)]$ (0.035 g, 0.094 mmol). The solvent was evaporated and the resulting yellow solid was chromatographed (neutral alumina, CH_2Cl_2:CH_3OH=9:1) to give the complex **11b** as a white solid (0.06 g, 79%). Mp softens at 185–185.6°C, melts at 355°C (THF/hexanes, colorless needles); $[\alpha]_D$ −10.28 (c=0.72, CH_2Cl_2); IR (KBr) 2950, 1654, 1560, 1466, 1364, 1183, 1095, 1010, 807, 776 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.70–3.58 (m, 2H), 3.38–3.23 (m, 2H), 3.13–3.05 (m, 2H), 2.94–2.92 (m, 2H), 2.80–2.68 (m, 4H), 2.25–2.07 (m, 4H), 1.94–1.76 (m, 8H), 1.68–1.55 (m, 4H), 1.53–1.18 (m, 4H), 1.03 (s, 18H), 0.98 (s, 18H); ^{13}C NMR (CD_2Cl_2) δ 68.5, 66.0, 59.2 (brd), 54.5 (brd), 33.8, 32.8, 32.7, 32.6 (brd), 29.9, 29.7, 25.2, 24.8; ^{31}P NMR (CD_2Cl_2) δ 130.8 ppm, (J_{P-Pt}=4339 Hz). Anal. calcd for $(C_{34}H_{68}N_4P_2)PtCl_2$: C, 47.44; H, 7.96; N, 6.51. Found: C, 47.39; H, 7.87; N, 6.37.

3.9. *Single crystal X-ray structure determination*

Data collection was performed using a Siemens R3 (for **6b** and **11b**) or Siemens P4RA (for **10b**) automated single crystal X-ray diffractometer using a graphite monochromated Mo-Kα radiation. Data reduction was carried out using XDISK for (**6b** and **11**)[12] and XSCANS (for **10b**).[13] Structure solution and least-squares refinement for all compounds were achieved by using SHELXTL plus.[14]

Crystal data and intensity data collection parameters, the final residual values and relevant structure refinement parameters, a complete list of bond distances and bond angles, positional and isotropic displacement coefficients for hydrogen atoms, a list of anisotropic displacement coefficients for the non-hydrogen atoms, and calculated and observed structure factors have been deposited in the Cambridge Crystallographic Data Base.

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