J. Chem. Sci. Vol. 127, No. 6, June 2015, pp. 979–986. © Indian Academy of Sciences.
DOI 10.1007/s12039-015-0865-3

A mixed-valent cyclodiphosphazane: Transition metal chemistry and *cis/trans* isomerisation

GUDDEKOPPA S ANANTHNAG[a], JOEL T MAGUE[b] and MARAVANJI S BALAKRISHNA[a,*]

[a]Phosphorus Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

[b]Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, USA

e-mail: krishna@chem.iitb.ac.in; msb_krishna@iitb.ac.in

MS received 12 December 2014; revised 22 January 2015; accepted 24 January 2015

Abstract. The hydrolysis of *cis*-{ClP(μ-N^{t}Bu)$_2$P(NH^{t}Bu)} (**1**) produced a mixed P^{III}/P^V derivative of cyclodiphosphazane, *cis*-{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H} (**2**). The treatment of **2** with elemental selenium resulted in the formation of the monoselenide, *trans*-{(^{t}BuNH)P(Se)(μ-N^{t}Bu)$_2$P(O)H} (**3**) in good yield. The reactions of two equivalent of **2** with [Pd(μ-Cl)(η^3-C$_3$H$_5$)]$_2$ or [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ in dichloromethane afforded corresponding mononuclear complexes, [(η^3-C$_3$H$_5$)PdCl{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H}] (**4**) and [((η^6-*p*-cymene)RuCl$_2$){(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H}] (**5**). The treatment of **2** with M(COD)Cl$_2$ (M = Pd and Pt) in dichloromethane at room temperature gave [MCl$_2$\{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H\}$_2$] (**6** M = Pd; **7** M = Pt) in good yield. Owing to the *cis/trans* isomerisation of the cyclodiphosphazane rings, the complexes **6** and **7** exist as a mixture of two isomers. Various NMR spectroscopic techniques were employed for structural elucidation. The molecular structures of **5** and **7** were established by single crystal X-ray crystallographic studies.

Keywords. Cyclodiphosphazanes; *cis/trans* isomerisation; NMR studies; complexes

1. Introduction

Cyclodiphosphazanes or diazadiphosphetidines are a major class of cyclic phosphorus-nitrogen compounds.[1,2] They find applications in various fields such as coordination chemistry,[3–8] in anti-tumour studies[9,10] and in catalytic organic transformations.[11–13] The dichlorocyclodiphosphazanes, *cis*-{ClP(μ-NR)}$_2$, have been effectively explored as building blocks in the synthesis of a large range of phosphorus-nitrogen macrocycles.[14–20] Cyclodiphosphazanes can exist as *cis* and *trans* isomers in solution as well as in the solid state (chart 1, A and B).[2] The ring conformations of these isomers can be established by single crystal X-ray diffraction studies or by ^{31}P NMR data, where the *cis* isomers show upfield chemical shifts compared to the *trans* analogues.[21] The *cis/trans* interconversion in solution is observed for several cyclodiphosphazanes. The interconversion can proceed through edge (N) or vertex (P) inversion.[22]

The *cis* cyclodiphosphazanes act as versatile bridging ligands for the construction of polynuclear metalomacrocycles, or one- (1D), two- (2D), and three-dimensional (3D) coordination polymers and their transition metal chemistry has been extensively studied.[23–25] The coordination chemistry of the *trans* isomer has been much less studied.[26–29] Recently we explored the coordination chemistry of acyclic dimers of cyclodiphosphazanes derived from *cis*-{ClP(μ-N^{t}Bu)$_2$P(NH^{t}Bu)}.[14,30,31] Hydrolysis of the P–Cl bond in *cis*-{ClP(μ-N^{t}Bu)$_2$P(NH^{t}Bu)} to produce *cis*-{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H} was reported by Wright and co-workers,[32] while a similar compound was accidentally isolated by Kumaraswamy and co-workers.[33] Herein we report transition metal chemistry and *cis/trans* isomerisation of *cis*-{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H}.

2. Experimental

2.1 *General procedures*

All manipulations were performed using standard vacuum-line and Schlenk techniques under nitrogen atmosphere unless otherwise stated. All the solvents were purified by conventional methods[34] and distilled prior to use. The compounds, *cis*-{ClP(μ-N^{t}Bu)$_2$P(NH^{t}Bu)},[35] [Pd(μ-Cl)(η^3-C$_3$H$_5$)]$_2$,[36] [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$,[37] Pd(COD)Cl$_2$,[38] and Pt(COD)Cl$_2$,[38] were prepared according to the published procedures. Other chemicals were obtained from commercial sources and purified before use.

*For correspondence

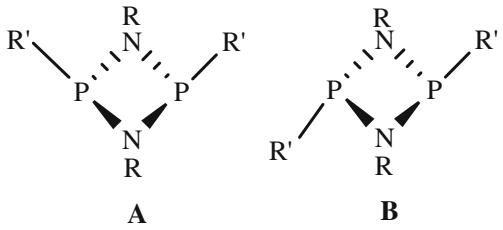


Chart 1. *Cis* and *trans*-cyclodiphosphazanes.

2.2 *Instrumentation*

The NMR spectra were recorded at the following frequencies: 400 MHz (^{1}H), 162 MHz (^{31}P), 100 MHz (^{13}C) and 107.5 MHz (^{195}Pt) using Varian VXR 400, Bruker AV 400 or AV 500 spectrometers. The ^{13}C, ^{31}P and ^{195}Pt NMR spectra were acquired using broad-band proton decoupling. The spectra were recorded in $CDCl_3$ solutions with $CDCl_3$ as an internal lock; chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in ppm downfield from TMS, used as internal standard. The chemical shifts of ^{31}P and ^{195}Pt NMR spectra are referred to 85% H_3PO_4 (in D_2O) and K_2PtCl_6 (in D_2O), respectively, used as an external standard. Microanalyses were performed using a Carlo Erba Model 1112 elemental analyzer. Mass spectra were recorded using Waters Q-Tof micro (YA-105). The melting points were observed in capillary tubes and are uncorrected.

2.3 *Synthesis of cis-{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H} (**2**)*[32]

A solution of *cis*-{ClP(μ-N^{t}Bu)$_2$P(NH^{t}Bu)} (**1**) (1.1 g, 3.528 mmol) in THF (20 mL) was added dropwise to a solution of water (0.064 g, 3.528 mmol) and triethylamine (0.54 mL, 0.39 g, 3.88 mmol) also in THF (20 mL) at –78°C. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed under vacuum and the residue obtained was dissolved in toluene (30 mL) and filtered. The filtrate was concentrated to 10 mL under reduced pressure and stored at –20°C to yield analytically pure product of **2**. Yield: 66% (0.68 g). M.p.: 161–164°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, 1H, $^{1}J_{PH}$ = 586 Hz, $^{3}J_{PH}$ = 3.1 Hz, PH), 3.13 (d, 1H, $^{2}J_{PH}$ = 6.2 Hz, NH), 1.44 (s, 18H, μ-N^{t}Bu), 1.16 (s, 9H, ^{t}BuNH). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 73.6 (br s), –7.2 (d, $^{2}J_{PP}$ = 8.1 Hz, P=O). ^{13}C{^{1}H}: δ 52.1 (d, $^{2}J_{PC}$ = 7.5 Hz), 51.9 (d, $^{2}J_{PC}$ = 14.5 Hz), 32.7 (d, $^{3}J_{PC}$ = 9.7 Hz), 31.5 (t, $^{3}J_{PC}$ = 4.6 Hz).

2.4 *Synthesis of cis-{(^{t}BuNH)P(Se)(μ-N^{t}Bu)$_2$P(O)H} (**3**)*

A mixture of **2** (0.1 g, 0.341 mmol) and elemental selenium (0.027 g, 0.342 mmol) in toluene (20 mL) was refluxed for 6 h. The solution was cooled to room temperature, filtered through Celite and the solvent removed under vacuum to obtain **3** as an off-white crystalline solid. Analytically pure **3** was obtained by recrystallising the crude product from toluene. Yield: 98% (0.124 g). M.p.: 212–215°C (dec). HRMS (Calcd. for M+H $C_{12}H_{29}N_3OP_2Se$): 374.1029. Found: 374.1045. Anal. Calcd. for $C_{12}H_{29}N_3OP_2Se$: C, 38.71; H, 7.85; N, 11.29. Found: C, 38.44; H, 7.73; N, 11.32. IR (KBr, ν/cm^{-1}): 3165 (br, m, N–H str.), 2396 (m, P–H str.), 1262 (s), 1196 (s, P–O str.), 1071(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, $^{1}J_{PH}$ = 628 Hz, $^{3}J_{PH}$ = 8.5 Hz, PH, 1H), 3.66 (d, $^{2}J_{PH}$ = 15.0 Hz, NH, 1H), 1.60 (s, ^{t}Bu, 18H), 1.48 (s, ^{t}Bu, 9H). ^{31}P{^{1}H}NMR (162 MHz, $CDCl_3$): δ 20.9 (s, $^{1}J_{SeP}$ = 876 Hz, P=Se), –12.4 (d, $^{2}J_{PP}$ = 22.7 Hz, P=O).

2.5 *Synthesis of [(PdCl(η^3-C$_3$H$_5$))$_2${(^{t}BuNH)P(μ-N^{t}Bu)$_2$ P(O)H}] (**4**)*

A solution of [Pd(μ-Cl)(η^3-C$_3$H$_5$)]$_2$ (0.025 g, 0.0683 mmol) in dichloromethane (10 mL) was added to a solution of **2** (0.04 g, 0.1364 mmol) in the same solvent (5 mL) at room temperature. After 4 h, the volume of the solvent was reduced to 2 mL, the solution was layered with 4 mL of petroleum ether and kept at −20°C for 24 h to obtain **4** as an analytically pure yellow solid. Yield: 83% (0.054 g). M.p.: 245°C (dec). Anal. Calcd. for $C_{15}H_{34}ClN_3OP_2Pd$: C, 37.83; H, 7.20; N, 8.82. Found: C, 37.19; H, 6.60; N, 8.45. IR (KBr, ν/cm^{-1}): 3219 (br, m, N–H str.), 2352 (m, P–H str.), 1265 (s), 1202 (s, P–O str.), 1062 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, $^{1}J_{PH}$ = 605.5 Hz, $^{3}J_{PH}$ = 7.5 Hz, PH, 1H), 5.55 (m, CH, 1H), 5.26 (d, $^{2}J_{PH}$ = 28.8 Hz, NH, 1H), 4.62 (t, J = 8.4 Hz, CH, 1H), 3.56 (t, J = 13.6 Hz, CH, 1H), 3.26 (d, J = 6.0 Hz, CH, 1H), 2.74 (d, J = 12.0 Hz, CH, 1H), 1.54 (s, ^{t}Bu, 9H), 1.43 (d, J = 13.4 ^{t}Bu, 18H). ^{31}P{^{1}H}NMR (162 MHz, $CDCl_3$): δ 54.9 (s, P–Pd), –13.4 (s, P=O). ^{31}P NMR (162 MHz, $CDCl_3$): δ 54.9 (s, P–Pd), –13.4 (d, $^{1}J_{PH}$ = 606 Hz, P=O). MS (EI): m/z = 440.12 [M–Cl]$^{+}$.

2.6 *Synthesis of [((η^6-p-cymene)RuCl$_2$)$_2${(^{t}BuNH) P(μ -N^{t}Bu)$_2$P(O)H}] (**5**)*

A solution of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.024 g, 0.0392 mmol) in dichloromethane (10 mL) was added to a solution of **2** (0.023 g, 0.0784 mmol) in the same solvent (10 mL) at room temperature. The reaction mixture was stirred for 4 h, the solvent volume was reduced to 2 mL under vacuum, and the solution layered with 4 mL of diethyl ether and kept in −20°C for 24 h

to afford analytically pure red crystals of **5**. Yield: 77% (0.036 g). M.p.: 198°C (dec) Anal. Calcd. for $C_{22}H_{43}Cl_2N_3OP_2Ru{\cdot}2CH_2Cl_2$: C, 37.47; H, 6.16; N, 5.46. Found: C, 37.23; H, 6.10; N, 5.64. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, $^1J_{PH}$ = 604 Hz, $^3J_{PH}$ = 11.2 Hz, PH, 1H), 5.66 (d, $^3J_{HH}$ = 6.0 H, CH, 2H), 5.35 (s, CH_2Cl_2, 4H), 5.08 (d, $^3J_{HH}$ = 6.0 Hz, CH, 2H), 4.09 (d, $^2J_{PH}$ = 22.0 Hz, NH, 1H), 3.13 (p, $^3J_{HH}$ = 6.8 Hz, CH, 1H), 2.18 (s, CH_3, 3H) 1.63 (s, ^{t}Bu, 18H), 1.38 (s, ^{t}Bu, 9H), 1.36 (d, $^3J_{HH}$ = 6.8 Hz, $C(CH_3)_2$, 6H). ^{31}P{^{1}H}NMR (162 MHz, $CDCl_3$): δ 62.7 (d, $^2J_{PP}$ = 16.8 Hz, P–Pd), −6.4 (d, P=O). MS (EI): m/z = 564.2 $[M–Cl]^+$.

2.7 *Synthesis of [$PdCl_2${(^{t}BuNH)P(μ-N^{t}Bu)$_2$ P(O)H}$_2$] (**6**)*

A solution of $Pd(COD)Cl_2$ (0.0204 g, 0.0716 mmol) in dichloromethane (5 mL) was added to a solution of **2** (0.042 g, 0.1432 mmol) in the same solvent (5 mL) at room temperature. The resultant yellow solution was stirred for 4 h and all the volatiles were removed under reduced pressure to yield **6** as yellow crystalline solid. The complex **6** was recrystallized from a mixture of dichloromethane and petroleum ether to obtain analytically pure crystals. Yield: 84% (0.046 g). M.p.: 230–232°C. Anal. Calcd. for $C_{24}H_{58}Cl_2N_6O_2P_4Pd$: C, 37.73; H, 7.65; N, 11.00. Found: C, 37.68; H, 7.34; N, 10.89. IR (KBr, ν/cm^{-1}): 3242 (m, NH, str), 2972 (m), 2392 (s, PH, str), 1266 (m), 1200 (m, P=O, str). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dt, $^1J_{PH}$ = 651 Hz, J = 4.4 Hz, PH, 2H), 7.59 (dt, $^1J_{PH}$ = 650 Hz, J = 4.4 Hz, PH, 2H), 5.41 (t, J = 14.4 Hz, NH, 2H), 5.24 (t, J = 14.4 Hz, NH, 2H), 1.62 (s, ^{t}Bu, 72H), 1.45 (s, ^{t}Bu, 36H). ^{31}P{^{1}H}NMR (162 MHz, $CDCl_3$): δ 40.92 (unresolved t, P–Pd), 40.86 (unresolved t, P–Pd), –6.5 (t, J = 4 Hz, P=O), −6.8 (s, J = 5.9 Hz, P=O). ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.9 (s, P–Pd), –6.5 (d, $^1J_{PH}$ = 652 Hz, P=O), –6.8 (d, $^1J_{PH}$ = 651 Hz, P=O). MS (EI): m/z = 765.2 $[M+H]^+$.

2.8 *Synthesis of [$PtCl_2${(^{t}BuNH)P(μ -N^{t}Bu)$_2$ P(O)H}$_2$] (**7**)*

A dichloromethane solution (5 mL) of $Pt(COD)Cl_2$ (0.0191 g, 0.0511 mmol) was added to a solution of **2** (0.03 g, 0.1023 mmol) in the same solvent (5 mL) at room temperature. The reaction mixture was stirred for 4 h and all the volatiles were removed under reduced pressure to obtain an off-white residue. The residue obtained was re-dissolved in dichloromethane (2 mL), layered with petroleum ether (4 mL) and stored at −20°C for 24 h to obtain **7** as analytically pure white crystalline solid. Yield: 81% (0.035 g). M.p.: >275°C. Anal. Calcd. for $C_{24}H_{58}Cl_2N_6O_2P_4Pt{\cdot}CH_2Cl_2$: C, 32.03; H, 6.45; N, 8.96. Found: C, 32.11; H, 6.37; N, 8.61. IR (KBr, ν/cm^{-1}): 3254 (m, NH, str), 2971 (m), 2390 (s, PH, str), 1266 (m), 1203 (m, P=O, str). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dt, $^1J_{PH}$ = 650 Hz, $^3J_{PH}$ = 4.4 Hz, PH, 2H), 7.51 (dt, $^1J_{PH}$ = 648 Hz, $^3J_{PH}$ = 4.4 Hz, PH, 2H), 5.51 (s, CH_2Cl_2, 2H), 5.46 (t, J = 13.2 Hz, NH, 2H), 5.29 (t, J = 13.2 Hz, NH, 2H), 1.62 (s, ^{t}Bu, 72H), 1.46 (s, ^{t}Bu, 36H). ^{31}P{^{1}H}NMR (162 MHz, $CDCl_3$): δ 36.7 (t, J = 6.5 Hz, $^1J_{PtP}$ = 3379 Hz, P–Pt), –3.9 (t, J = 8.3 Hz, $^3J_{PtP}$ = 77.1 Hz, P=O), −4.4 (t, J = 6.2 Hz, $^3J_{PtP}$ = 83.3 Hz, P=O). ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.7 (br s, $^1J_{PtP}$ = 3382 Hz, P–Pt), –3.9 (m, $^1J_{PH}$ = 648 Hz, P=O), −4.4 (m, P=O). ^{195}Pt{^{1}H}NMR (107.5 MHz, $CDCl_3$): δ –3872 (t, $^1J_{PtP}$ = 3381 Hz), –3859 (t, $^1J_{PtP}$ = 3402 Hz). MS (EI): m/z = 875.25 $[M+Na]^+$.

2.9 *X-ray Crystallography*

A crystal of the compound **5** suitable for X-ray crystal analysis was mounted on a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of the Bruker APEX CCD diffractometer. A full sphere of data was collected using 3 sets of 400 frames, each of width 0.5° in ω, collected at φ = 0.00, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ, collected at ω = −30.00 and 210.00° using the *APEX2*[39] program suite. A crystal of **7** was mounted on a glass fibre using epoxy glue and placed on a Rigaku Saturn724 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). For **5**, the raw data were reduced to F^2 values using the *SAINT* software,[39] while for **7**, the images were processed with the *CrystalClear* program (Expert 2.1 b24). Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (*SADABS*[39]). Both the structures were solved by direct methods (*SHELXS*[40]) and refined by full-matrix least-squares procedures on F^2 using *SHELXL*[40] (SHELXTL program package.[39] Hydrogen atoms attached to carbon were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Those attached to nitrogen were placed in locations derived from a difference map and also included as riding contributions as for the others. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon for phenyl hydrogen and 1.5 times for $C(CH_3)_3$. Crystallographic

data (excluding structures factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1000229 (compound **5**) and 1000230 (compound **7**).

3. Results and Discussion

Hydrolysis of *cis*-{ClP(μ-N^{t}Bu)$_2$P(NH^{t}Bu)} (**1**) with one equivalent of degassed water in the presence of triethylamine at –78°C resulted in the formation of a mixed-valent derivative *cis*-{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H} (**2**), as shown in scheme 1. Because of the interference of adventitious water, **2** is an undesired product in many reactions involving **1**. The compound **2** is air and moisture stable and obtained as an analytically pure white solid after recrystallisation from toluene. The reaction of **2** with elemental selenium in toluene resulted in the formation of the monoselenide, *trans*-{(^{t}BuNH)P(Se)(μ-N^{t}Bu)$_2$P(O)H} (**3**) along with a small amount of *cis* isomer **3a**. The ^{31}P{^{1}H}NMR spectrum of **3** showed two doublets at 20.9 ppm and −12.4 ppm with a $^2J_{PP}$ coupling of 22.7 Hz.[41,42] The signal at 20.9 ppm having characteristic selenium satellite peaks with a $^1J_{SeP}$ coupling of 876 Hz was assigned to the P(Se) centre. The ^{1}H NMR spectrum of **3** showed a doublet of doublets for the PH proton with a large $^1J_{PH}$ coupling (628 Hz) and a relatively small $^3J_{PH}$ coupling (8.5 Hz). The coupling constants are larger than those observed for **2** ($^1J_{PH}$ = 586 Hz and $^3J_{PH}$ = 3.1 Hz). The large $^1J_{PH}$ coupling in the ^{1}H NMR spectrum of **3** confirms the presence of the P(O)H rather than the POH tautomer in solution. The structure and molecular composition of compound **3** was further confirmed by mass spectrometry and elemental analysis.

The reaction of two equivalent of **2** with [Pd(μ-Cl)(η^3-C$_3$H$_5$)]$_2$ in dichloromethane gave [(η^3-C$_3$H$_5$)PdCl{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H}] (**4**). The ^{31}P{^{1}H}NMR spectrum of **4** recorded in CDCl$_3$ showed two singlets for coordinated phosphorus and P(O) atoms, at 54.9 and −13.4 ppm, respectively. The spectral assignments for compound **4** were confirmed by a proton-coupled ^{31}P NMR spectrum in which the signal at −13.4 ppm splits into a doublet with a $^1J_{PH}$ coupling of 606 Hz. The ^{1}H NMR spectrum confirms the presence of a coordinated allyl group. All the five protons of the allyl fragment

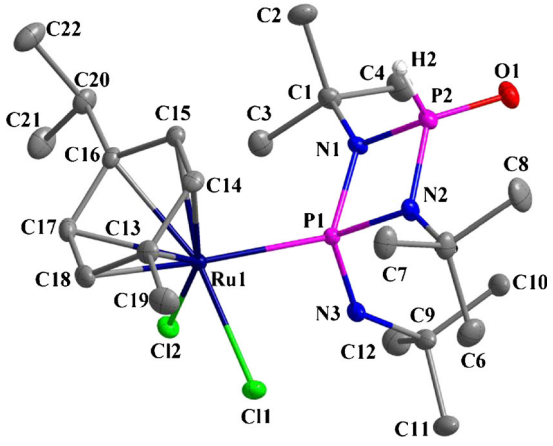
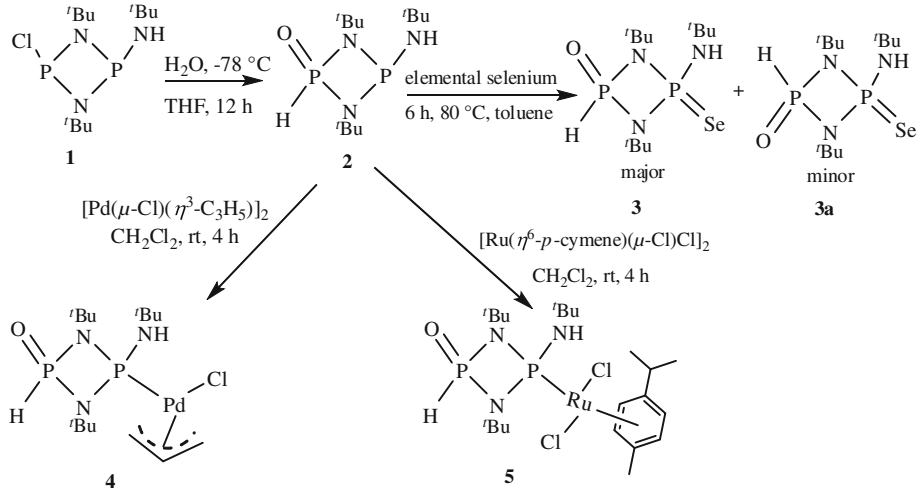


Figure 1. The molecular structure of [(η^6-*p*-cymene)RuCl$_2${(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H}] (**5**). All hydrogen atoms except H(P) and lattice solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances [Å]: Ru1–Cl1, 2.4224(12); Ru1–Cl2, 2.4154(12); Ru1–P1, 2.3892(12); P2–O1, 1.4736(16); P1–N2, 1.7358(19); P1–N3, 1.6320(17); P2–N1, 1.6627(18); P2–N2, 1.6754(18). Selected bond angles [°]: Cl1–Ru1–Cl2, 86.37(1); Cl1–Ru1–P1, 84.54(2); Cl2–Ru1–P1, 88.26(1); N1–P1–N2, 81.20(8); N1–P2–N2, 84.83(8).



Scheme 1. Synthesis and reactivity of *cis*-{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H} (**2**).

appear distinctly in the ^{1}H NMR spectrum of **4**. The ^{1}H NMR data indicate the allyl group (η^3-C_3H_5) is rigidly coordinated to the metal centre and all the four terminal *syn* and *anti* protons remain non-equivalent on NMR time scale.

The reaction of **2** with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ afforded [((η^6-*p*-cymene)RuCl$_2$){(^{t}BuNH)P(μ-N^{t}Bu)$_2$ P(O)H}] (**5**) in moderate yield. The ^{31}P{^{1}H} NMR spectrum of **5** showed two doublets centered at 62.7 and −6.4 ppm, with a $^2J_{PP}$ coupling of 16.8 Hz. The mass spectrum of **5** showed base peak at 564.2 corresponding to the [M–Cl]$^+$ ion. Further, the structure of **5** is established by a single-crystal X-ray diffraction study.

Slow diffusion of petroleum ether into a chloroform solution of **5** led to the formation of crystals suitable for X-ray diffraction studies.[43] The coordination geometry around the ruthenium center in **5** is typical pseudo-octahedral (figure 1) with a three-legged piano-stool arrangement having ligand **2** acting as a monodentate ligand. The Ru–P1 bond distance is 2.3892(12) Å and Ru–C bond distances range from 2.205(2) to 2.262(2) Å with an average bond distance of 2.236 Å, which is slightly longer than that of [(η^6-*p*-cymene)RuCl$_2$\{(*o*-MeOC$_6$H$_4$O)P(μ-N^{t}Bu)\}$_2$\}AuCl].[44] The P2–O1 bond distance in **5** [1.474(2) Å] is similar to that of **2** [1.468(2) Å], whereas the P2–H2 bond distance in **5** [1.26(2) Å] is shorter than that of the free ligand **2** [1.35(2) Å].[32]

The steric and electronic aspects of the coordinating ligands dictate the conformations of d^8 square planar complexes. The bulky ligands generally confer *trans* configuration, whereas the strong σ-donor ligands impose *cis* conformation around the metal center due to the *trans* influence.[45–47] The reaction of **2** with M(COD)Cl$_2$ (M = Pd and Pt) can give six possible conformational and geometrical isomers, as both the cyclodiphosphazane as well as the metal center can adopt *cis* and *trans* conformations (chart 2). The treatment of **2** with M(COD)Cl$_2$ (M = Pd and Pt) in 2:1 ratio in dichloromethane at room temperature resulted in the formation of [MCl$_2$\{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H\}$_2$] (**6** M = Pd; **7** M = Pt) as shown in scheme 2. In both the complexes, the metal centres adopt *trans* geometry as established by the X-ray analysis of **7**. The microanalytical data of both **6** and **7** support 1:2 ratio of metal to ligand in the isolated products. The evidence for the formation of complexes also comes from mass spectral data, where both **6** and **7** show the molecular ion peaks, at 765.2 [M+H]$^+$ and 875.2 [M+Na]$^+$, respectively. To assign the geometry of the cyclodiphosphazanes in **6** and **7**, both 1D and 2D NMR studies were carried out.

The ^{31}P{^{1}H} and ^{1}H NMR spectra of complexes **6** and **7** recorded in CDCl$_3$ at room temperature are similar, which confirm that the structures of both the complexes in solution are essentially the same. The ^{31}P{^{1}H}NMR spectrum of the palladium complex **6** shows two unresolved triplets centred at 40.92 and 40.86 ppm and two set of triplets centered at −6.5 and −6.8 ppm with couplings of 4.0 and 5.9 Hz in a ∼2:3 ratio, respectively, as shown in figure 2. The ^{31}P{^{1}H}NMR spectrum of platinum complex **7** showed three triplets at 36.7, −3.9 and −4.4 ppm. The signal at 36.7 ppm with a $^1J_{PtP}$ coupling of 3379 Hz was assigned to the coordinated phosphorus. In the ^{1}H coupled ^{31}P NMR spectra of **6** and **7**, only the upfield signals split into two sets of resonances with large $^1J_{PH}$ values. This observation confirms that the upfield signals are due to the phosphorus atom directly attached to hydrogen. Based on ^{31}P NMR integration, it is clear that the two products in **6** exist in ∼3:2 ratios. No interconversion was observed on keeping the solution of complex **6** in CDCl$_3$ for 24 h at room temperature.

The ^{1}H NMR spectrum of **6** showed complex splitting patterns due to the presence of two isomers. Two overlapping doublets of triplets centered at 7.62 and 7.59 ppm are observed for the PH protons ($|^1J_{PH}|$ = 651 Hz, $|J|$ = 4.4 Hz), the NH protons appear as triplets centred at 5.41 and 5.24 ppm (∼3:2 ratio) with a coupling of $|J|$ = 14.4 Hz. The observed multiplicity is probably due to the long range coupling between NH and PH protons. The ^{1}H–^{1}H COSY spectrum indicates that the triplet at 5.41 ppm (NH) is correlated with the doublet of triplets at 7.62 ppm (PH). Similarly, the triplet at 5.24 ppm (NH) is correlated with the doublet of triplets at 7.59 ppm (PH). Furthermore, in the ^{31}P–^{1}H HSQC experiment (figure 3), the triplets at 7.62

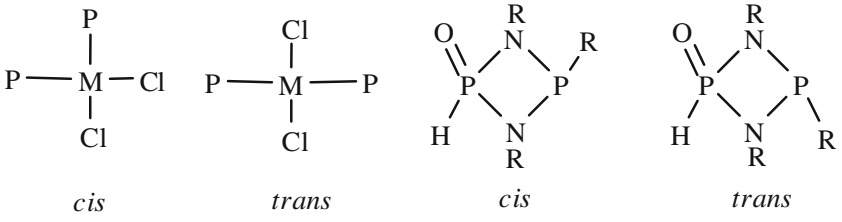
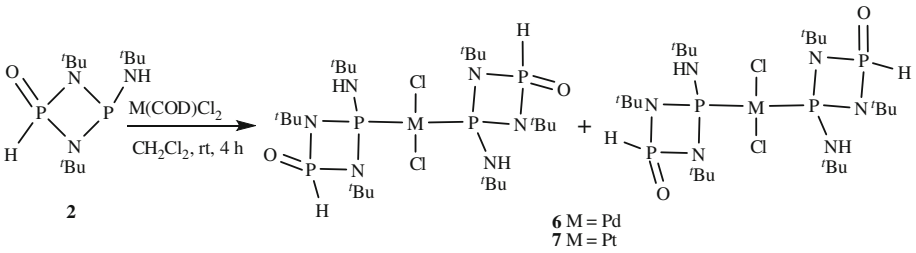


Chart 2. Possible isomers of **6** and **7**.



Scheme 2. Pd(II) and Pt(II) complexes of *cis*-{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H} (**2**).

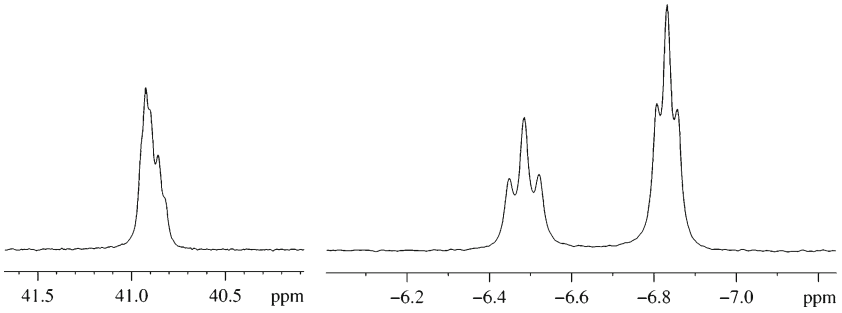


Figure 2. The ^{31}P{^{1}H}NMR spectrum [PdCl$_2$\{(^{t}BuNH)P(μ-N^{t}Bu)$_2$P(O)H\}$_2$] (**6**).

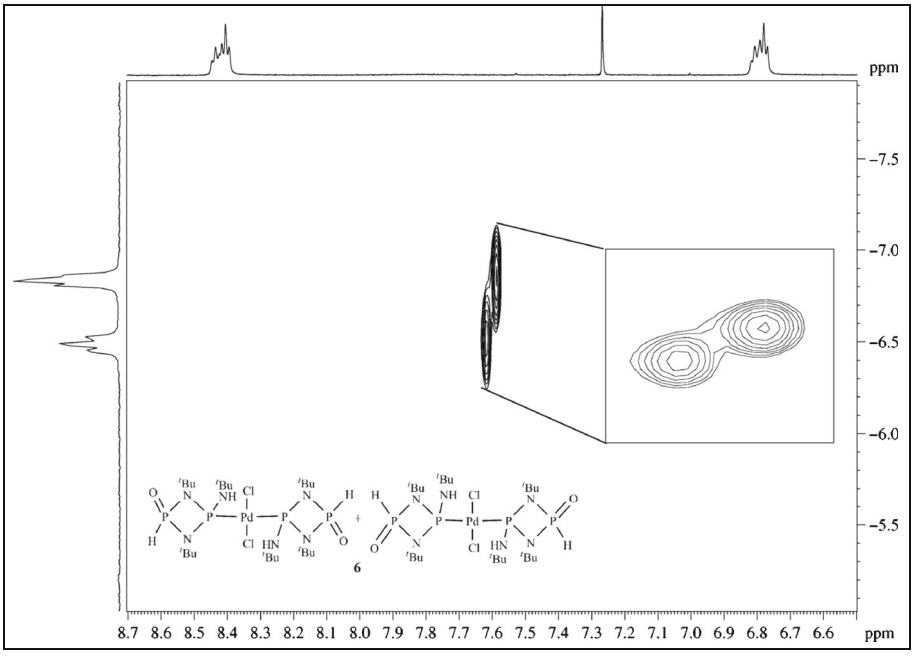


Figure 3. ^{31}P–^{1}H HSQC spectrum of **6** recorded in CDCl$_3$.

and 7.59 ppm showed correlation with the phosphorus signals at −6.5 and −6.8 ppm, respectively. The ^{195}Pt{^{1}H}NMR spectrum of **7** showed two overlapping triplets with similar coupling constants, at –3872 ($^1J_{PtP}$ = 3380 Hz) and −3859 ($^1J_{PtP}$ = 3402 Hz). This obeservation clearly indicates the presence of two different species in solution.

The X-ray structure of **7** confirms the *trans* geometry around the square planar platinum centre as shown in figure 4. Both the cyclodiphosphazane rings in **7** assume the *trans* conformation in the solid state. Because of the steric bulk, the vector Cl1–Pt1–Cl1^i is tilted away from exocyclic nitrogen, and the acute bond angle Cl1–Pt1–P1 is 87.10(2)°. The Pt1–P1 [2.3062(8) Å] and Pt1-Cl1 [2.3116(7) Å] bond distances for **7** are comparable to the Pt−P [2.2447(13) Å] and Pt−Cl [2.3254(15) Å] bond lengths of the complex [(PtCl$_2$)$_2$\{^{t}BuNP(OC$_6$H$_4$PPh$_2$-*o*)\}$_2$.[48] The P–O bond lengths in **7** [1.467(2) Å]

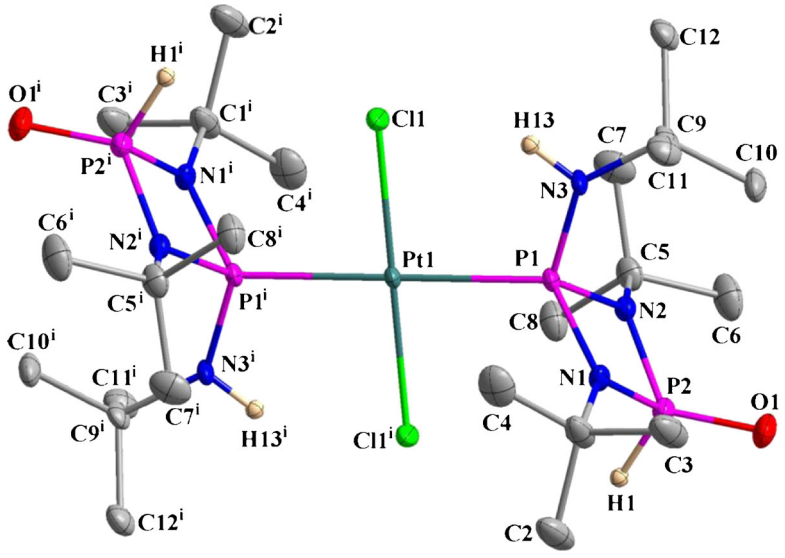


Figure 4. The molecular structure of $[PtCl_2\{(^tBuNH)P(\mu\text{-}N^tBu)_2P(O)H\}_2]$ (**7**). All hydrogen atoms except H(P) and H(N) and all lattice solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances [Å]: Pt1–P1, 2.3062(8); Pt1–Cl1, 2.3116(7); Pt1–Cl1^i, 2.3116(7); P2–O1, 1.467(2); P1–N2, 1.7006(19); P1–N3, 1.621(2); P2–N1, 1.6669(19); P2–N2, 1.672(2); P2–H1, 1.29(3). Selected bond angles [°]:Cl1–Pt1–P1, 87.10(2); Cl1–Pt1–P1^i, 92.90(2N1–P1–N2, 82.39(9).

and **2** [1.468(2) Å] are nearly identical. The exocyclic and endocyclic P–N bond distances in **7** are shorter than that found in **2**, but follow the same trend.[32] In general, the exocyclic P–N distances are shorter and comparable with typical P–N distances observed in both cyclic and acyclic diphosphazanes[49] and P–N bond distances associated with P^V centers are shorter than that of P^{III} centers in cyclodiphosphazanes.

4. Conclusions

The reactivity and transition metal chemistry of a mixed-valent cyclodiphosphazane derivative, *cis*-$\{(^tBuNH)P(\mu\text{-}N^tBu)_2P(O)H\}$ (**2**), has been studied. The compound **2** exists purely as the *cis* isomer in both solution and solid states but exhibits *cis/trans* isomerisation when coordinated to metal centres. The reaction of **2** with palladium(II) and platinum(II) precursors yielded a mixture of two isomers. In both the complexes **isomers**, the two cyclodiphosphazane rings adopt *cis/cis* and *trans/trans* conformations, but the mixed *cis/trans* conformation was not observed. The presence of two conformations of the cyclodiphosphazane rings was established by NMR spectroscopy and single crystal X-ray diffraction studies.

Supplementary Information

NMR spectra for compounds **3**–**7** are provided. The electronic supplementary information can be seen at www.ias.ac.in/chemsci. Crystallographic data for compounds **5** and **7** has been deposited at the Cambridge Crystallographic Data Centre with CCDC no. 1000229 (compound **5**) and 1000230 (compound **7**). These data can be obtained free of charge at www.ccdc.cam.ac.ul/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

We are grateful to the Science & Engineering Research Board, New Delhi, India. for financial support of this work through grant No.SB/S1/IC-08/2014. GSA thanks CSIR, New Delhi, for Senior Research Fellowship (SRF). We also thank the Department of Chemistry Instrumentation Facilities, IIT Bombay, for spectral and analytical data. JTM thanks the Louisiana Board of Regents for the purchase of the CCD diffractometer and the Chemistry Department of Tulane University for support of the X-ray laboratory.

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43. Crystal data for **5**: $C_{22}H_{43}Cl_2N_3OP_2Ru$, fw = 599.50, Orthorhombic, *Pna21* (No. 33), a = 13.383(6) Å, b = 16.425(7) Å c = 12.607(6) Å V = 2771(2) Å^3, Z = 4, ρ_{calc} = 1.437 gcm^{-3}, μ (MoK$_\alpha$) = 0.893 mm^{-1}, F(000) = 1248, S = 1.03, T = 100 K. A total of 45,206 reflections were processed; of which, 7,190 were unique (R_{int} = 0.063). The final wR value was 0.0592 (all data) and R = 0.024 [I > 2r(I)]. Crystal data for **7**: $C_{24}H_{58}Cl_2N_6O_2P_4Pt$, fw = 852.62, Monoclinic, *P21/n* (No. 14), a = 9.2580(15) Å, b = 8.7540(14) Å c = 22.885(4) Å, β = 98.053(2) [°], V = 1836.4(5) Å^3, Z = 2, ρ calc = 1.542 gcm^{-3}, μ (MoK$_\alpha$) = 4.170 mm^{-1}, F(000) = 864, S = 1.02, T = 100 K. A total of 12941 reflections were processed; of which, 3,178 were unique (R_{int} = 0.025). The final wR value was 0.0431 (all data), R = 0.0175 [I > 2r(I)]
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