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Mono-, di- and tetranuclear rhodium(I) complexes of morpholine and *N*-methylpiperazine functionalized cyclodiphosph(III)azanes, *cis*-[(^{t}BuN-μ)$_2$(PNC$_4$H$_8$X)$_2$] (X = O, NMe)

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Abstract. The reactions of cyclodiphosphazanes, *cis*-[(^{t}BuN-μ)$_2$(PNC$_4$H$_8$O)$_2$] (**1**, R = NC$_4$H$_8$O; **2**, R = NC$_4$H$_8$NMe) (**2**) with [{RhCl(COD)}$_2$] and [{RhCl(CO)$_2$}$_2$] are described. The reactions of **1** or **2** with [{RhCl(COD)}$_2$] in 2:1 molar ratio yielded the mononuclear complexes [(COD)RhCl{(μ-N^{t}BuP)$_2$(NC$_4$H$_8$X)$_2$}] (**3**, X = O; **4**, X = NMe) in good yield. Treatment of one equivalent of [{RhCl(CO)$_2$}$_2$] with four equivalents of **1** or **2** produced the *trans*-[(CO)RhCl{(μ-N^{t}BuP)$_2$(NC$_4$H$_8$X)$_2$}$_2$] (**5**, X = O; **6**, X = NMe) complexes as pale yellow solids. On changing the molar ratio of [{RhCl(CO)$_2$}$_2$] and **1** or **2** from 1:4 to 1:1 resulted in the formation of tetranuclear complexes [{(CO)Rh(μ-Cl)(μ-N^{t}BuP)(NC$_4$H$_8$X)}$_4$] (**7**, X = O; **8**, X = NMe) under similar reaction conditions. The tetranuclear rhodium(I) complex **8** upon stirring with wet acetonitrile or in the presence of four equivalents of water at room temperature afforded a novel hydroxo bridged zwitterionic dirhodium(I) complex [{(ClRh(CO))$_2$(μ-OH)(MeNC$_4$H$_8$N)(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NHMe)}] (**9**). The crystal structures of **5**, **6** and **9** were established by single crystal X-ray diffraction studies.

Keywords. *Bis*(amido)cyclodiphosphazanes; rhodium(I); tetranuclear complexes; crystal structures; dirhodium(I) hydroxyl derivative; zwitterionic complex.

1. Introduction

Cyclodiphosphazanes constitute the major class of P–N compounds having alternate phosphorus and nitrogen atoms in their four-membered cyclic skeletons.[1] Recently, we have explored the transition metal chemistry, catalytic utility and the biological applications of cyclodiphosphazanes containing several hemilabile functionalities. Slight variations in the phosphorus substituents have brought significant changes in their coordinating abilities and resulted in the formation of novel complexes with totally different and interesting structural features, especially with late transition metals.[2] As an extension of our interest[3] and the interest of others[4] in cyclodiphosphazane system, we report in this paper rhodium(I) complexes of cyclodiphosphazanes appended with morpholine and *N*-methylpiperazine functionalities.

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2. Experimental

2.1 *General procedures*

All experimental manipulations were carried out under a dry nitrogen or argon atmosphere, using standard Schlenk techniques unless otherwise stated. Solvents were dried and distilled prior to use by conventional methods. *Cis*-[(^{t}BuN-μ)$_2$(PNC$_4$H$_8$O)$_2$] (**1**), *cis*-[(^{t}BuN-μ)$_2$(PNC$_4$H$_8$NMe)$_2$] (**2**),[5] [{RhCl(COD)}$_2$],[6] and [{RhCl(CO)$_2$}$_2$][7] were prepared according to the published procedures.

2.2 *Spectroscopy*

The ^{1}H and ^{31}P{^{1}H} NMR (δ in ppm) spectra were recorded on a Varian VXR 400 spectrometer operating at the appropriate frequencies using tetramethylsilane and 85% H_3PO_4 as internal and external references, respectively. Positive shifts lie downfield of the standard in all the cases. Microanalyses were carried out on a Carlo Erba Model 1106 elemental analyzer. IR spectra

were recorded on a Nicolet Impact 400 FT-IR instrument in KBr disk. Melting points of all compounds were determined on Veego melting point apparatus and were uncorrected.

2.3 *Synthesis of metal complexes*

*2.3a Synthesis of cis-[(COD)RhCl{(μ-N^{t}BuP)$_2$(NC$_4$H$_8$O)$_2$}] (**3**)*: A dichloromethane (5 mL) solution of [{Rh(μ-Cl)(COD)}$_2$] (0.044 g, 0.090 mmol) was added drop-wise to a well-stirred dichloromethane solution (5 mL) of **1** (0.068 g, 0.181 mmol) at room temperature. The stirring was continued at room temperature for 6 h. The yellow coloured solution was concentrated to 4 mL, layered with 2 mL of petroleum ether and stored at −25°C to afford **3** as a yellow crystalline compound. Yield: 73% (0.082 g). Mp: 212–214°C (dec). Anal. Cal. for $C_{24}H_{46}N_4O_2P_2RhCl$: C, 46.27; H, 7.44; N, 8.99%. Found: C. 46.35; H, 7.62; N, 8.93%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.31 (d, $J_{HH} = 4.2$ Hz, *CH*, 4H), 3.92-3.13 (m, CH_2, 32H), 2.45 (d, $J_{HH} = 4.8$ Hz, CH_2, 8H), 1.56 (s, ^{t}*Bu*, 36H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 94.2 (s), 89.8 (d, $^1J_{RhP} =$ 195 Hz).

*2.3b Synthesis of cis-[(COD)RhCl{(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NMe)$_2$}] (**4**)*: This was synthesized by a procedure similar to that of **3**, using **2** (0.045 g, 0.112 mmol) and [{Rh(μ-Cl)(COD)}$_2$] (0.027 g, 0.056 mmol). Yield: 76% (0.055 g). Mp: 216–218°C (dec). Anal. Cal. for $C_{26}H_{52}N_6P_2RhCl$: C, 48.11; H, 8.07; N, 12.94%. Found: C. 48.25; H, 8.38; N, 12.73%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.40 (d, $J_{HH} = 3.8$ Hz, *CH*, 4H), 3.78 – 3.12 (br s, CH_2, 16H), 2.44 (d, $J_{HH} = 4.2$ Hz, CH_2, 8H), 2.32 (s, *NMe*, 3H), 2.25 (s, *NMe*, 3H), 1.45 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 93.5 (s), 89.0 (d, $^1J_{RhP} = 197$ Hz).

*2.3c Synthesis of trans-[(CO)RhCl{(μ-N^{t}BuP)$_2$(NC$_4$H$_8$O)$_2$}] (**5**)*: To a stirred solution of **1** (0.057 g, 0.154 mmol) in dichloromethane (5 mL) added drop-wise a solution of [{Rh(μ-Cl)(CO)$_2$}$_2$] (0.015 g, 0.038 mmol) also in dichloromethane (5 mL). The clear yellow coloured solution was stirred at room temperature for 4 h. The solution was concentrated and layered with petroleum ether and stored at room temperature for 2 days to afford **5** as yellow crystalline compound. Yield: 88% (0.061 g). Mp: 208–210°C (dec). Anal. Cal. for $C_{33}H_{68}N_8O_5P_4RhCl$: C, 43.11; H, 7.45; N, 12.19%. Found: C. 43.27; H, 7.76; N, 12.23%. FT-IR (KBr disc): 1985 (s) cm^{-1} (ν_{CO}). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.61–3.11 (m, CH_2, 32H), 1.40 (s, ^{t}*Bu*, 36H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 99.8 (s), 90.8 (d, $^1J_{RhP} =$ 195 Hz).

*2.3d Synthesis of trans-[(CO)RhCl{(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NMe)$_2$}$_2$] (**6**)*: This was synthesized by a procedure similar to that of **5**, using **2** (0.066 g, 0.164 mmol) and [{Rh(μ-Cl)(CO)$_2$}$_2$] (0.016 g, 0.041 mmol). Yield: 78% (0.062 g). Mp: 232–234°C (dec). Anal. Cal. for $C_{37}H_{80}N_{12}OP_4RhCl$: C, 45.74; H, 8.30; N, 17.30%. Found: C. 45.76; H, 8.63; N, 17.03%. FT-IR (KBr disc): 1965 (s) cm^{-1} (ν_{CO}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 – 3.46 (m, CH_2, 32H), 2.34 (s, *NMe*, 6H), 2.22 (s, *NMe*, 6H), 1.76 (s, ^{t}*Bu*, 36H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, δ): 99.5 (s), 88.5 (d, $^1J_{RhP} = 180$ Hz).

*2.3e Synthesis of cis-[{(CO)Rh(μ-Cl)(μ-N^{t}BuP)(NC$_4$H$_8$O)}$_4$] (**7**)*: A dichloromethane (5 mL) solution of [{Rh(μ-Cl)(CO)$_2$}$_2$] (0.042 g, 0.109 mmol) was added drop-wise to a well-stirred solution of **1** (0.038 g, 0.109 mmol) in the same solvent (5 mL) at room temperature and the stirring was continued for 4 h. The solution was concentrated to 5 mL under reduced pressure, layered with 3 mL of petroleum ether, and placed at room temperature to get **7** as pale yellow crystalline compound. Yield: 85% (0.050 g). Mp: 208–210°C (dec). Anal. Cal. for $C_{36}H_{68}N_8P_4O_8Rh_4Cl_4$: C, 30.48; H, 4.83; N, 7.90%. Found: C. 30.26; H, 4.52; N, 7.83%. FT-IR (KBr disc): 2001 (s) cm^{-1} (ν_{CO}), 1975 (s) cm^{-1} (ν_{CO}). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.65 (br s, CH_2, 8H), 3.44 (br s, CH_2, 8H), 1.70 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 95.7 (d, $^1J_{RhP} =$ 221 Hz).

*2.3f Synthesis of cis-[{(CO)Rh(μ-Cl)(μ-N^{t}BuP)(NC$_4$H$_8$NMe)}$_4$] (**8**)*: This was synthesized by a procedure similar to that of **7**, using **2** (0.042 g, 0.104 mmol) and [{Rh(μ-Cl)(CO)$_2$}$_2$] (0.040 g, 0.104 mmol). Yield: 80% (0.047 g). Mp: 232–234°C (dec). Anal. Cal. for $C_{40}H_{80}N_{12}P_4O_4Rh_4Cl_4$: C, 32.67; H, 5.48; N, 11.43%. Found: C. 32.52; H, 5.32; N, 11.46%. FT-IR (KBr disc): 2072 (s) cm^{-1} (ν_{CO}), 1976 (s) cm^{-1} (ν_{CO}). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.24 (br s, CH_2, 16H), 2.45 (br s, CH_2 16H), 2.18 (s, *NMe*, 12H), 1.57 (s, ^{t}*Bu*, 36H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 94.8 (d, $^1J_{RhP} = 220$ Hz).

*2.3g Synthesis of cis-[{(ClRh(CO))$_2$(μ-OH)(MeNC$_4$H$_8$N)(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NHMe)}] (**9**)*: A dichloro-

methane (5 mL) solution of **8** (0.040 g, 0.035 mmol) was stirred in wet acetonitrile (5 mL) at room temperature. The stirring was continued for further 4 h. The reaction mixture was concentrated to 5 mL under reduced pressure and stored at room temperature for a day to get **9** as pale yellow crystalline compound. Yield: 65% (0.027 g). Mp: 176–178°C. Anal. Cal. for $C_{20}H_{42}N_6P_2O_3Cl_2Rh_2$: C, 31.89; H, 5.62; N, 11.16%. Found: C. 31.83; H, 5.32; N, 11.23%. FT-IR (KBr disc): 2072 (s) cm^{-1} (ν_{CO}), 1976 (s) cm^{-1} (ν_{CO}). ^1H NMR (400 MHz, $CDCl_3$, δ): 3.65 (br s, CH_2, 16H), 2.35 (br s, CH_2 16H), 2.15 (br s, *NMe*, 12H), 1.78 (br s, ^tBu, 36H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 90.8 (br s).

2.4 *X-ray crystallography*

A crystal of each of the compounds **5**, **6** and **9** suitable for X-ray crystal analysis was mounted in 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. Full spheres of data were obtained from three sets of 400 scans in ω (0.5° per scan) at $\varphi = 0$, 90 and 180° plus two sets of 800 scans in φ (0.45° per scan) at $\omega = -30$ and 210° all under the control of the APEX2[8] software packages. For **9**, in the final stages of refinement it became evident that the crystal was likely a merohedral twin and this was supported by the analysis performed by XPREP.[8] The raw data were reduced to F^2 values using the SAINT software[9] and global refinements of unit cell parameters using 5511–6856 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS[10] was used). The structures of **5** and **9** were solved by direct methods, whereas for **6** Patterson methods were employed, and refined by full-matrix least-squares procedures using the SHELXTL program package.[11] Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Pertinent crystallographic data and other experimental details are summarized in table 1. CCDC-838497 (**5**), 838498 (**6**) and 838499 (**9**) contain the supplementary crystallographic data for this paper. This can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic information for compounds **5**, **6** and **9**.

	5	**6**	**9**
Formula	$C_{33}H_{68}ClN_8O_5P_4Rh$	$C_{37}H_{80}Cl_5N_{12}OP_4Rh$	$C_{21}H_{44}Cl_2N_{6.50}O_4P_2Rh_2$
Fw	919.19	1113.17	790.29
Crystal system	Monoclinic	Triclinic	Tetragonal
Space group	C2/c (No. 15)	P-1 (No. 2)	I41/a (No. 88)
a, Å	24.262(2)	10.689(2)	18.7550(10)
b, Å	16.4130(10)	12.183(2)	18.7550(10)
c, Å	12.8244(8)	13.772(2)	36.310(4)
α, deg	90	77.775(2)	90
β, deg	111.6270(10)	85.009(2)	90
γ, deg	90	65.996(2)	90
V, $Å^3$	4747.3(6)	1601.2(5)	12772.0(17)
Z	4	1	16
ρ_{calc}, g cm^{-3}	1.286	1.154	1.644
μ (MoKα), mm^{-1}	0.594	0.610	1.338
F (000)	1936	584	6424
Crystal size mm	0.12 × 0.15 × 0.23	0.19 × 0.21 × 0.24	0.06 × 0.12 × 0.24
T, K	100	132	100
2θ range, deg	2.0, 28.3	1.5, 24.9	2.2, 26.9
Total no. reflns	41551	11453	101455
No. of indep. reflns	5927 ($R_{int} = 0.038$)	5511 ($R_{int} = 0.054$)	6856 ($R_{int} = 0.054$)
R1[a]	0.0265	0.0866	0.0326
wR_2^b	0.0689	0.2380	0.0793
GOF (F^2)	1.062	0.992	1.094

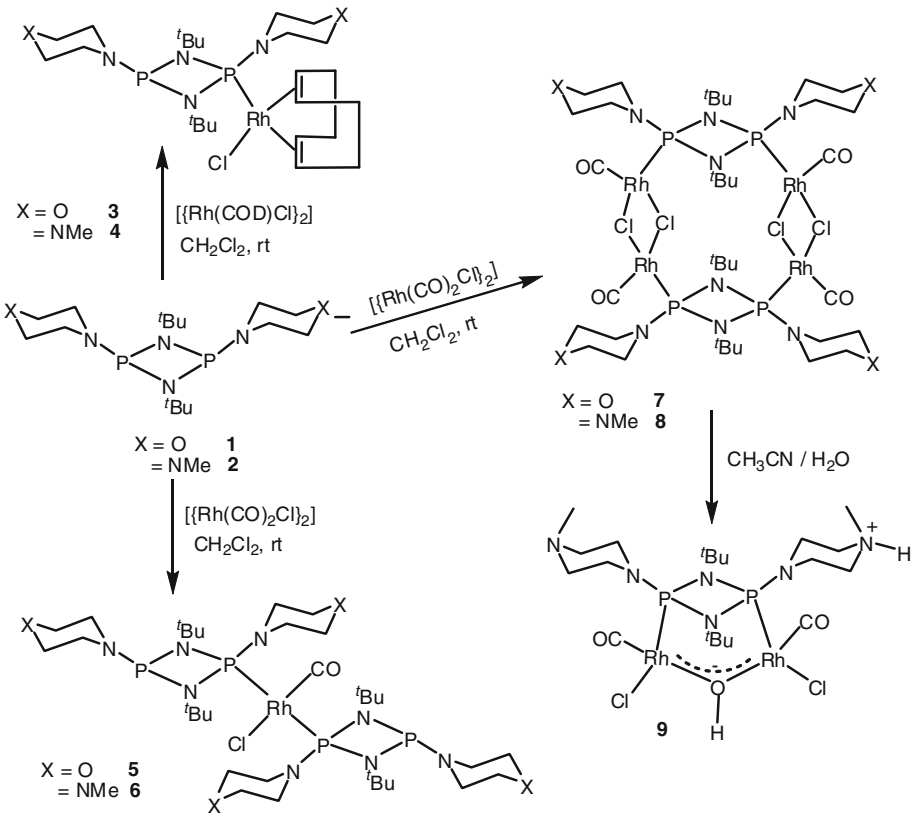
3. Results and discussion

The *bis*(amido)cyclodiphosphazane derivatives *cis*-[(^{t}BuN-μ)$_2$(PNC$_4$H$_8$O)$_2$] (**1**) and *cis*-[(^{t}BuN-μ)$_2$(PNC$_4$H$_8$NMe)$_2$] (**2**) were prepared by the reported procedure[5] and characterized by multinuclear NMR techniques. The ligands **1** and **2** are colourless crystalline solids and are moderately stable towards air and moisture, both in the solid state and in solution. The ^{31}P NMR spectra of **1** and **2** show single resonances at 92.8 and 91.4 ppm respectively.

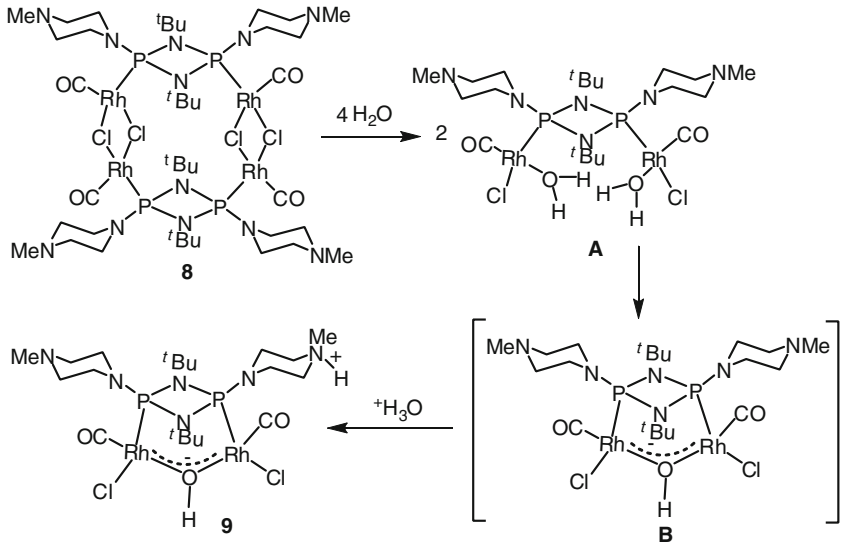
3.1 *Rhodium(I) complexes*

The reactions of **1** or **2** with [{ClRh(COD)}$_2$] in 2:1 molar ratio in dichloromethane afforded the mononuclear complexes [(COD)RhCl{(μ-N^{t}BuP)$_2$(NC$_4$H$_8$X)$_2$}] (**3**, X = O; **4**, X = NMe) with cyclodiphosphazanes showing monodentate mode of coordination (scheme 1). The ^{31}P NMR spectra of **3** and **4** show single resonances at 94.2 and 93.5 ppm for the uncoordinated phosphorus centres and the rhodium bound phosphorus centres appear as doublets centred at 89.8 and 89.0 ppm, respectively. The corresponding $^1J_{RhP}$ couplings are 195 and 197 Hz, respectively.

Treatment of one equivalent of [{RhCl(CO)$_2$}$_2$] with four equivalents of **1** or **2** produced the *trans*-[(CO)RhCl{(μ-N^{t}BuP)$_2$(NC$_4$H$_8$X)$_2$}$_2$] (**5**, X = O; **6**, X = NMe) rhodium(I) complexes as pale yellow solids. The ^{31}P NMR spectra of **5** and **6** show singlets at 99.8 and 99.5 ppm for the uncoordinated phosphorus centres and doublets centred at 90.8 and 88.5 ppm for the coordinated phosphorus centres with $^1J_{RhP}$ couplings of 195 and 180 Hz, respectively. The IR spectra of **5** and **6** show ν_{CO} at 1965 cm^{-1} and 1970 cm^{-1}, respectively. Similar reactions between [{RhCl(CO)$_2$}$_2$] and the ligands **1** or **2** in 1:1 molar ratio resulted in the formation of tetranuclear complexes [{(CO)Rh(μ-Cl)(μ-N^{t}BuP)(NC$_4$H$_8$X)}$_4$] (**7**, X= O; **8**, X= NMe). The tetrarhodium complexes **7** and **8** show doublets centred at 95.7 and 94.8 ppm in their ^{31}P NMR spectra with the $^1J_{RhP}$ couplings of 221 and 220 Hz, respectively. The IR spectrum of complex **7** shows ν_{CO} at 2001 cm^{-1} and 1975 cm^{-1} whereas **8** shows the same at 2010 cm^{-1} and 1985 cm^{-1}, which are consistent with the mutual *cis* orientations of CO and P atoms.[3e,3f]



Scheme 1. Rhodium(I) complexes of cyclodiphosphazanes **1** and **2**.



Scheme 2. Plausible mechanism for the formation of zwitterionic complex **9**.

The tetranuclear rhodium(I) complex **8** upon stirring with wet acetonitrile or in the presence of four equivalents of water at room temperature afforded a novel hydroxo bridged zwitterionic rhodium(I) complex [{(ClRh(CO))$_2$(μ-OH)(MeNC$_4$H$_8$N)(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NHMe)}] (**9**) as shown in scheme 1. The ^{31}P NMR spectrum of binuclear complex **9** shows a broad singlet centred at 90.8 ppm. A plausible mechanistic pathway for the formation of zwitterionic complex **9** is depicted in scheme 2. The cyclodiphosphazane **2** reacts with [{Rh(Cl)(CO)$_2$}$_2$] to form a tetrarhodium complex **8** which on reaction with four equivalents of water cleave the chloro bridges to form two equivalents of neutral rhodium(I) binuclear complex **A**. The complex **A** eliminates the hydronium ion (H_3O^+) to form a hydroxo-bridged [Rh(μ-OH)Rh] anionic complex **B**. The H_3O^+ quaternizes the NMe group of piperazine to form the binuclear zwitterionic complex **9**.

3.2 *Molecular structures of trans-[(CO)RhCl {(μ-N^{t}BuP)$_2$(NC$_4$H$_8$O)$_2$}$_2$] (**5**), trans-[(CO)RhCl {(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NMe)$_2$}$_2$] (**6**) and [{(ClRh(CO))$_2$ (μ-OH)(MeNC$_4$H$_8$N)(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NHMe)}] (**9**)*

Perspective views of the molecular structures of **5**, **6** and **9** with atom numbering schemes are shown in

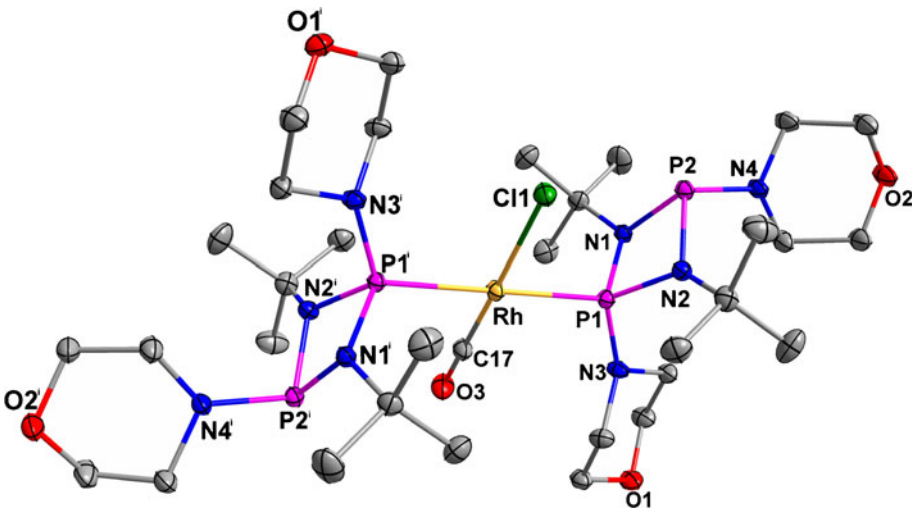


Figure 1. The molecular structure of *trans*-[(CO)RhCl{(μ-N^{t}BuP)$_2$(NC$_4$H$_8$O)$_2$}$_2$] (**5**). All hydrogen atoms were omitted for clarity. Thermal ellipsoids were drawn at 50% probability level.

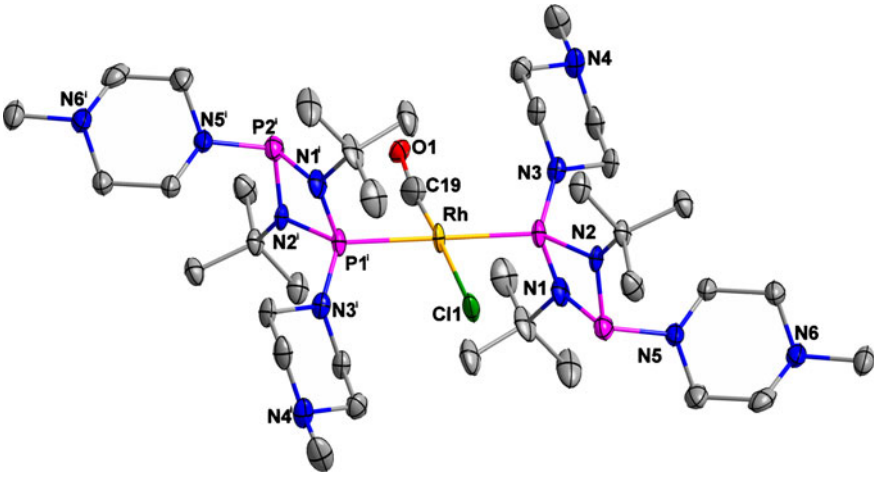


Figure 2. The molecular structure of *trans*-[(CO)RhCl{(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NMe)$_2$}$_2$] (**6**). All hydrogen atoms were omitted for clarity. Thermal ellipsoids were drawn at 30% probability level.

figures 1–3, respectively. The crystal data and the details of the structure determination are given in table 1. The selected bond lengths (Å) and bond angles (deg) are given in tables 2 and 3.

The yellow crystals suitable for single crystal X-ray diffraction study were obtained by slow evaporation of dichloromethane-petroleum ether solution of **5** at room temperature. The asymmetric unit contains one half of the molecule **5** due to the crystallographically imposed C_2 symmetry. The rhodium atom with a distorted square planar geometry is located on an inversion centre with the chloride and the carbonyl ligands showing

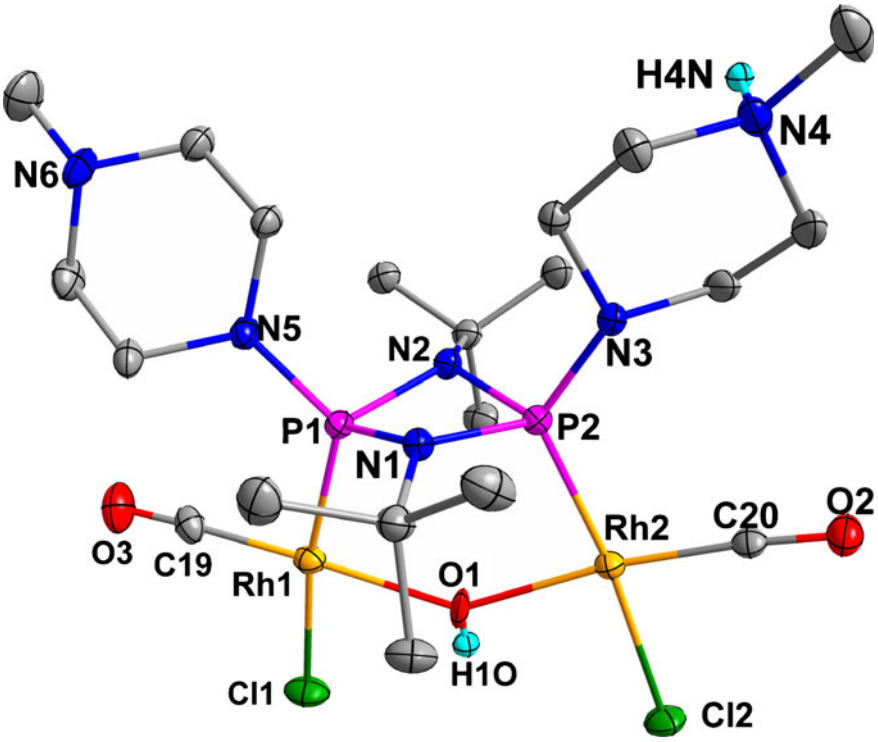


Figure 3. The molecular structure of [(ClRh(CO))$_2$(μ-OH){(MeNC$_4$H$_8$N)(μ-N^{t}BuP)$_2$(NC$_4$H$_8$NHMe)}] (**9**). All hydrogen atoms (except H1O and H4N), solvated water and acetonitrile molecules were omitted for clarity. Thermal ellipsoids were drawn at 50% probability level.

Table 2. Selected bond lengths (Å) and bond angles (deg) for complexes **5** and **6**.

Bond lengths (Å)		Bond angles (deg)	
		Complex **5**	
Rh–Cl1	2.3953(15)	Cl1-Rh-P1	93.06(3)
Rh–P1	2.3227(4)	Cl1-Rh -C17	176.17(12)
Rh–C17	1.755(5)	P1-Rh-C17	87.90(12)
P1–N1	1.6903(12)	P1-Rh-P1^{i}	180.00
P1–N2	1.6963(13)	Rh-P1-N1	114.17(4)
P1–N3	1.6689(13)	Rh-P1-N2	120.77(4)
O3–C17	1.160(7)	Rh-P1-N3	114.99(5)
O1–C10	1.4271(18)	N1-P1-N2	82.49(6)
O1–C11	1.424(2)	N1-P1-N3	107.49(6)
		N1-P2-N2	79.74(6)
		N1-P2-N4	108.92(6)
		Complex **6**	
Rh–Cl1	2.391(6)	Cl1-Rh-P1	87.52(18)
Rh–P1	2.3186(19)	Cl1-Rh-C19	174.8(10)
Rh–C19	1.813(17)	P1-Rh-P1^{i}	180.00
P1–N1	1.678(7)	P1-Rh-C19	92.5(9)
P1–N2	1.699(6)	Cl1-Rh-P1^{i}	92.48(18)
P1–N3	1.652(6)	Rh-P1-N1	114.2(2)
O1–C19	1.148(17)	Rh-P1-N2	121.4(2)
		Rh–P1-N3	114.0(2)
		N1–P1-N2	82.2(3)
		N1–P1-N3	108.5(3)
		N1–P2-N2	80.6(3)

slight disorder. The *trans*-P1-Rh-P1^{i} bond angle is perfectly linear (180°), while the *trans*-Cl1-Rh-C17 angle is 176.17(12)°. The *cis*-Cl1-Rh-P1 and *cis*-C17-Rh-P1 bond angles are 93.06(3)° and 92.10(12)°, respectively. The P_2N_2 rings are highly puckered and the dihedral angle over P2-N1-P1-N2 is 15.387(58)°.

Slow evaporation of dichloromethane-petroleum ether solution of **6** afforded single crystals suitable for X-ray diffraction study. The complex **6** is isostructural with **5** and crystallizes in triclinic crystal system with *P*-1 (No. 2) space group. The trends of bond lengths and bond angles found in **6** are similar to those in **5**.

Crystals suitable for X-ray diffraction study were obtained by slow evaporation of dichloromethane and acetonitrile solution of **9** at room temperature. The zwitterionic complex **9** crystallizes in tetragonal crystal system, whose asymmetric unit contains one molecule of metal complex, one molecule of water and a distorted acetonitrile molecule as solvent of crystallization. The two rhodium centres are linked *via* bridging hydroxo group to form a puckered six-membered dinuclear

Table 3. Selected bond lengths (Å) and bond angles (deg) for complex **9**.

Bond lengths (Å)		Bond angles (deg)	
Rh1–Cl1	2.3825(12)	Cl1-Rh1-P1	171.15(5)
Rh1–P1	2.2075(12)	Cl1-Rh1-O1	82.39(11)
Rh1–O1	2.124(3)	Cl1-Rh1-C19	90.91(16)
Rh1–C19	1.795(5)	P1-Rh1-O1	89.06(11)
Rh2–Cl2	2.4010(12)	Cl2-Rh2-P2	173.61(5)
Rh2–P2	2.2030(12)	Cl2-Rh2-O1	85.43(11)
Rh2–O1	2.145(3)	Cl2-Rh2-C20	87.92(13)
Rh2–C20	1.792(4)	P2-Rh2-O1	88.57(11)
P1–N1	1.722(4)	O1-Rh2-C20	173.12(16)
P1–N2	1.700(4)	Rh1-O1-Rh2	142.1(2)
P1–N5	1.650(4)		

metallacycle. The $[(CO)ClRh(\mu\text{-}OH)Rh]^{-}$ anionic moiety was neutralized by the $[\text{-}NC_4H_8NHMe]^{+}$ cationic counterpart to make a rare zwitterionic rhodium(I) complex containing bridging cyclodiphosphazane ligand. The two rhodium(I) atoms are in distorted square planar geometry being bound to one phosphorus atom, chlorine atom, one carbon atom of CO and an oxygen atom of the bridging hydroxo group. The *trans* angles around the rhodium vary from 171.15(5)° (Cl1-Rh1-P1) to 173.16(5)° (Cl2-Rh2-P2), whereas the *cis* angles range from 82.39(11)° (Cl1-Rh1-O1) to 98.00(13)° (P2-Rh2-C20), which indicate the distorted nature of the square planar geometry around the rhodium centres. The Rh1-O1-Rh2 bond angle is 142.1(2)°. The Rh–O bond distances (Rh1-O, 2.124(3) Å) are slightly longer than the same present in the neutral complex $[\{(COD)Rh(\mu\text{-}OH)\}_2]$ (Rh-O, 2.082(4) Å).[12] The Rh-P bond lengths (Rh1-P1, 2.2075(12) Å; Rh2-P2, 2.2030(12) Å) are almost similar but are shorter than the same found in the corresponding *trans* mononuclear complex **6** (Rh-P1, 2.3186(19) Å), which is expected due to the increase in the back-bonding as a result of *cis* arrangements CO/P ligands. The Rh1-Cl1 and Rh2-Cl2 bond lengths are 2.3825(12) Å and 2.4010(12) Å, respectively.

4. Conclusion

The *bis*(amino)cyclodiphosphazane ligands show flexible coordination behaviour with the rhodium(I) precursors which lead to the isolation of mono-, di-, and tetranuclear complexes. In mononuclear complexes the ligands exhibit monodentate mode of coordination, whereas in di- and tetranuclear complexes, bridged bidentate mode of coordination was observed. The tetranuclear complex **8** on exposure to wet acetonitrile hydrolyses the Rh–Cl bonds to give a hydroxo-species which is the first example of its kind containing cyclodiphosphazane ligands. Utilization of these metal complexes as catalysts in various organic transformations is the active part of interest in our laboratory.

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References

1. (a) Balakrishna M S, Eisler D J and Chivers T 2007 *Chem. Soc. Rev*. **36** 650; (b) Briand G G, Chivers T and Krahn M 2002 *Coord. Chem. Rev*. **233–234** 237; (c) Stahl L 2000 *Coord. Chem. Rev*. **210** 203; (d) Balakrishna M S, Reddy V S, Krishnamurthy S S, Nixon J F and Laurent St J C T R B 1994 *Coord. Chem. Rev*. **129**, 1
2. (a) Chandrasekaran P, Mague J T, Venkateswaran R and Balakrishna M S 2007 *Eur. J. Inorg. Chem*. 4988; (b) Chandrasekaran P, Mague J T and Balakrishna M S 2005 *Inorg. Chem*. **44** 7925; (c) Chandrasekaran P, Mague J T and Balakrishna M S 2008 *Polyhedron* **27** 80; (d) Suresh D, Balakrishna M S and Mague J T 2008 *Dalton Trans*. 3272
3. (a) Balakrishna M S, Venkateswaran R and Mague J T 2009 *Inorg. Chem*. **48** 1398; (b) Chandrasekaran P, Mague J T and Balakrishna M S 2009 *Dalton Trans*. 5478; (c) Suresh D, Balakrishna M S, Rathinasamy K, Panda D and Mobin S M 2008 *Dalton Trans*. 2812; (d) Chandrasekaran P, Mague J T and Balakrishna M S 2006 *Inorg. Chem*. **45** 5893; (e) Chandrasekaran P, Mague J T and Balakrishna M S 2006 *Inorg. Chem*. **45** 6678; (f) Chandrasekaran P, Mague J T and Balakrishna M S 2005 *Organometallics* **24** 3780; (g) Suresh D, Balakrishna M S and Mague J T 2007 *Tetrahedron Lett*. **48** 2283; (h) Chandrasekaran P, Mague J T and Balakrishna M S 2007 *Tetrahedron Lett*. **48** 5227; (i) Balakrishna M S, Chandrasekaran P and Venkateswaran R 2007 *J. Organomet. Chem*. **692** 2642; (j) Balakrishna M S 2010 *J. Organomet. Chem*. **695** 925; (k) Balakrishna M S, Suresh D, Rai A, Mague J T and Panda D 2010 *Inorg. Chem*. **49** 8790; (l) Mohanty S and Balakrishna M S 2010 *J. Chem. Sci*. **122** 137
4. (a) Rama Suresh R and Kumara Swamy K C 2009 *Tetrahedron Lett*. **50** 6004; (b) Kumara Swamy K C, Bhuvan Kumar N N, Balaraman E and Pavan Kumar K V P 2009 *Chem. Rev*. **109** 2551; (c) Bhuvan Kumar N N and Kumara Swamy K C *Tetrahedron Lett*. **49** 7135; (d) González-Calera S, Eisler D J, Morey J V, McPartlin M, Singh S and Wright D S 2008 *Angew. Chem. Int. Ed*. **47** 1111; (e) Lief G R, Moser D F, Stahl L and Staples R J 2004 *J. Organomet. Chem*. **689** 1110
5. Balakrishna M S, Suresh D and Mague J T 2010 *Eur. J. Inorg. Chem*. 4201
6. Giordano G and Crabtree R H 1990 *Inorg. Synth*. **28** 88
7. McCleverty J A and Wilkinson G 1990 *Inorg. Synth*. **28** 84
8. APEX2 Version 2.1–4, Bruker–AXS 2006 Madison WI
9. SAINT Versions 7.03 and 7.34A Bruker–AXS 2004–2006 Madison WI
10. Sheldrick G W SADABS Versions 2.05 and 2007/4 2002 2007 University of Göttingen Germany
11. (a) Sheldrick G W TWINABS 2002 2007 University of Göttingen Germany; (b) SHELXTL Version 6.10 2000 Bruker–AXS Madison WI.
12. Suarez A, Mendez-Rojas M A and Pizanno A 2002 *Organometallics* **21** 4611