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Di- and tetranulcear Ru^{II} complexes of phenylene-1,4-diaminotetra(phosphonite), p-$C_6H_4[N\{P(OC_6H_4OMe\text{-}o)_2\}_2]_2$ and their catalytic investigation towards transfer hydrogenation reactions

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ABSTRACT

The stoichiometric reaction of phenylene-1,4-diaminotetra(phosphonite), p-$C_6H_4[N\{P(OC_6H_4OMe\text{-}o)_2\}_2]_2$ ($P_2N\Phi NP_2$) (**1**) with $[RuCl_2(p\text{-cymene})]_2$ in acetonitrile produces *cis,cis*-$[\{RuCl_2(CH_3CN)_2\}_2(P_2N\Phi NP_2)]$ (**2**), whereas the similar reaction of **1** with $[RuCl_2(p\text{-cymene})]_2$ in THF medium affords a *tri*-chloro-bridged tetrametallic complex, $[\{(\eta^6\text{-}p\text{-cymene})Ru_2(\mu_2\text{-}Cl)_3Cl\}_2(P_2N\Phi NP_2)]$ (**3**) irrespective of the stoichiometry and reaction conditions. The formation and structure of complexes **2** and **3** are assigned through various spectroscopic and micro analysis data. The molecular structure of **2** is confirmed by single crystal X-ray diffraction study. The catalytic activities of complexes **2** and **3** have been investigated in transfer hydrogenation reactions.

1. Introduction

The design and synthesis of phosphine ligands has been an active field of research over several years as their metal complexes play a major role in various organic transformation reactions [1]. Particularly, aminophosphines (phosphines having P–N bonds) have generated considerable interest because of their easier synthetic methodologies which facilitate tuning of steric and electronic properties around phosphorus centers [2]. A variety of aminophosphines can be readily prepared by treating primary or secondary amines with halo phosphines (Eq. (1)).

$$\underset{x=0-3}{R_xPCl_{(3-x)}} + (3-x)\underset{y=1\text{ or }2}{R'_yNH_{(3-y)}} \xrightarrow{(3-x)Et_3N} R_xP(NR')_{(3-x)} + (3-x)Et_3N\cdot HCl \quad (1)$$

Although these reactions look simple the choice of the product formation depends heavily on the reaction conditions and stoichiometry. Often the reactions lead to the formation of a mixture of products which can not be separated through conventional column chromatography other than fractional crystallization or distillation methods. We have a long standing interest in designing aminophosphine ligands appended with additional hetero-donor atoms to explore their transition metal chemistry and catalytic applications [3]. Recently, we have utilized a "short-bite" aminobis(phosphine), $PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2$ in combination with various pyridyl ligands to make several multinuclear mixed ligand complexes including 2D and 3D coordination polymers [4]. We have also reported the synthesis of Pd^{II}, Pt^{II}, Rh^{I} and Group 11 complexes, and catalytic applications of a tetraphosphonite, p-$C_6H_4[N\{P(OC_6H_4OMe\text{-}o)_2\}_2]_2$ (**1**) (hereafter referred as $P_2N\Phi NP_2$) [5]. As a part of our interest in the transition metal chemistry of cyclic and acyclic diphosphazane ligands [6] and their catalytic applications [7], we describe herein the coordinating behavior of $P_2N\Phi NP_2$ (**1**) towards Ru^{II} derivative and their utility in transfer hydrogenation reactions.

2. Experimental section

2.1. General procedures

All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use [8]. Compounds p-$C_6H_4[N\{P(OC_6H_4OMe\text{-}o)_2\}_2]_2$ [5c] and $[RuCl_2(p\text{-cymene})]_2$ [9] were prepared according to the published procedures. Other chemicals were obtained from commercial sources and purified prior to use.

2.2. Instrumentation

The ^1H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were recorded using VXR 400 spectrometer operating at the appropriate frequencies

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using TMS and 85% H_3PO_4 as internal and external references, respectively. The microanalyses were performed using Carlo Erba Model 1112 elemental analyzer. The melting points of compounds were observed in capillary tubes and are uncorrected.

2.3. Synthesis of cis,cis-[{$RuCl_2(CH_3CN)_2$}$_2$($P_2N\Phi NP_2$)] (**2**)

A solution of [Ru(η^6-cymene)Cl_2]$_2$ (0.023 g, 0.038 mmol) in acetonitrile (5 mL) was added dropwise to a solution of **1** (0.046 g, 0.038 mmol) also in acetonitrile (20 mL). The reaction mixture was allowed to stir at room temperature for 4 h. The resulting solution was concentrated to 4 mL and stored at room temperature for 3 days to give pale yellow crystals of **2**. Yield: 81% (0.053 g), m.p.: 202–204 °C (dec). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.22–6.72 (m, 36H, ArH), 3.50 (s, 24H, OCH_3), 2.06 (s, 12H, CH_3CN). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6): δ 101.6 ppm (br s). Anal. Calc. for $C_{70}H_{72}N_6O_{16}P_4Ru_2Cl_4$ (1721.20): C, 48.85; H, 4.22; N, 4.88. Found: C, 48.30; H, 3.80; N, 4.20%.

2.4. Synthesis of [{(η^6-p-cymene)Ru_2(μ_2-Cl)$_3$Cl}$_2$($P_2N\Phi NP_2$)] (**3**)

A mixture of [Ru(η^6-cymene)Cl_2]$_2$ (0.065 g, 0.106 mmol) and **1** (0.064 g, 0.053 mmol) in THF (15 mL) was stirred under reflux condition for 5 h. It was cooled to room temperature and concentrated to 5 mL under vacuum. Keeping this solution at −30 °C for several days afforded red crystals of **3**. Yield: 76% (0.087 g), m.p.: 198–200 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–6.13 (m, 36H, ArH), 5.54 (d, $J_{H,H}$ = 5.6 Hz, 4H, cymene Ph), 5.41 (d, 4H, cymene Ph), 3.81 (s, 24H, OCH_3), 2.59 (sep, 2H, CH), 1.69 (s, 6H, CH_3), 1.04 ppm (d, $J_{H,H}$ = 7.2 Hz, 12H, $C(CH_3)_2$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 110.1 ppm (s). Anal. Calc. for $C_{82}H_{88}N_2O_{16}P_4Ru_4Cl_8$ (2169.38): C, 45.40; H, 4.09; N, 1.29. Found: C, 45.46; H, 4.58; N, 1.45%.

2.5. General procedure for the transfer hydrogenation reactions

In a dry two-necked round bottom flask under an atmosphere of nitrogen were placed appropriate amount of catalyst (0.2 or 1 mol%) in 2-propanol (5 mL) and it was stirred at room temperature for 15 min. Acetophenone (0.1 g, 0.832 mmol) was added to the mixture and stirred for another 15 min at room temperature. A 2-propanol solution of sodium isopropoxide (10 mol%) (prepared by the dissolution of metallic sodium into the hot 2-propanol) was then added and the resulting mixture was refluxed under an atmosphere of nitrogen and the course of the reaction was monitored by GC analysis. After completion of the reaction, the solvent was removed. The residual mixture was diluted with H_2O and Et_2O (10 mL each), washed with brine and extracted with Et_2O (2 × 6 mL). The combined organic fractions were dried ($MgSO_4$), stripped of the solvent and the residue was redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GC analysis. Conversions were calculated relative to acetophenone as an internal standard.

2.6. X-ray crystallography

A crystal of the compound **2** 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 collected using a combination of three sets of 400 scans in ω (0.5° per scan) at φ = 0°, 90° and 180° plus two sets of 800 scans in φ (0.45° per scan) at ω = −30° and 210° under the control of the SMART software package [10]. The raw data were reduced to F^2 values using the SAINT+ software [11] and global refinements of unit cell parameters using 5662 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 crystal deterioration during the data collection (SADABS [12a] and TWINABS [12b]). The structures was solved by Patterson methods and refined by full-matrix least-squares procedures using the SHELXTL program package [13]. 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.

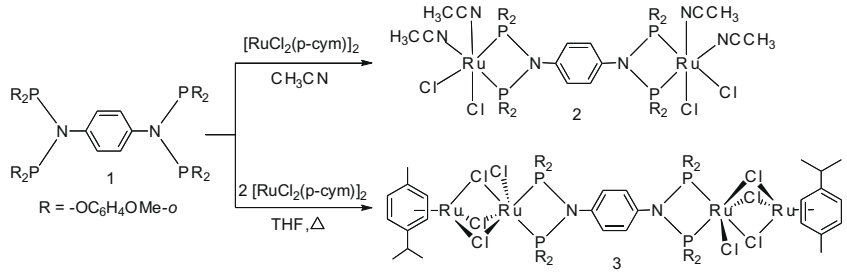
3. Results and discussion

The tetraphosphonite **1** has been prepared by the reaction of *p*-C_6H_4[$N(PCl_2)_2$]$_2$ with 4 equiv. of 2-(methoxy)phenol in presence of triethylamine [5c]. This novel tetradenate ligand can be compared to two 4,4′-bipyridines fused sideways to form a bis-chelating ligand yet with four tunable phosphorus atoms. This type of systems can facilitate the formation of several multinuclear complexes and we have explored their versatile coordination chemistry. In this paper, we describe the synthesis of di- and tetranuclear Ru^{II} complexes of **1** (Scheme 1).

The stoichiometric reaction of **1** with [$RuCl_2$(*p*-cymene)]$_2$ in acetonitrile afforded the dinuclear complex, *cis*,*cis*-[{$RuCl_2(CH_3CN)_2$}$_2$($P_2N\Phi NP_2$)] (**2**) in good yield. Compound **2** is a pale yellow micro crystalline solid and partially soluble in dimethyl sulfoxide. Similarly, the compound **1** reacts with [$RuCl_2$(*p*-cymene)]$_2$ in 1:2 mole ratio in THF to form a *tri*-chloro-bridged tetrametallic complex, [{(η^6-*p*-cymene)Ru_2(μ_2-Cl)$_3$Cl}$_2$($P_2N\Phi NP_2$)] (**3**) as an orange crystalline solid. Recently, we reported the synthesis and crystal structure of a similar *tri*-chloro-bridged bimetallic complex, [(η^6-*p*-cymene)Ru_2(μ_2-Cl)$_3$Cl{PhN(P(OC_6H_4OMe-*o*)$_2$)$_2$}] with a bisphosphonite ligand, PhN(P(OC_6H_4OMe-*o*)$_2$)$_2$ [6d] and this method provides an efficient way to make this kind of systems without going through multi step synthesis [14]. The ^{31}P NMR spectra of complexes **2** and **3** show single resonances at 101.6 and 110.1 ppm, respectively. The ^{1}H NMR spectrum of complex **2** shows a singlet at 2.06 ppm corresponding to the acetonitrile group and the *p*-cymene protons of **3** appear as two doublets at 5.41 and 5.54 ppm with a $J_{H,H}$ coupling of 5.6 Hz. The isopropyl methyl protons appear as a doublet centered at 1.04 ppm with a $J_{H,H}$ coupling of 7.2 Hz and the CH proton appears as a multiplet centered at 2.59 ppm. The ^{1}H NMR and analytical data are consistent with the proposed structures of **2** and **3**.

3.1. The crystal and molecular structure of **2**

Perspective view of the molecular structure of compound **2** with atom numbering scheme is shown in Fig. 1. Crystal data and the details of the structure determination are given in Table 1, while selected bond lengths and bond angles are given in Table 2. Crystals of **2** suitable for X-ray diffraction analysis were grown by keeping the saturated acetonitrile solution of **2** at room temperature for several days. Compound **2** is a bimetallic Ru^{II} derivative and ruthenium adopts an approximate octahedral geometry, with the corners being occupied by two chlorines, two nitrogens and two phosphorus atoms of tetraphosphazane **1** in *cis* passion. The P1–N1 and P2–N2 bond distances are 1.694(5) and 1.680(5) Å, respectively, whereas, the Ru1–P1 and Ru1–P2 distances are 2.218(2) and 2.212(2) Å, respectively. Due to the formation of strained four-membered chelate ring the P–N–P angle of the free ligand shrinks from 115.25(9)° to 98.2(3)° [5c]. The bite angle created by the chelating ligand P1–Ru–P2 with Ru center is 70.27(7)°. In **2**, the bridging phenylene ring makes a dihedral angle of 53.30° (P1–N1–C2–C1) with the plane of the P–N–P skeletons. Orientation of the phenylene ring with respect to P–N–P skeleton varies depending upon the choice of



Scheme 1.

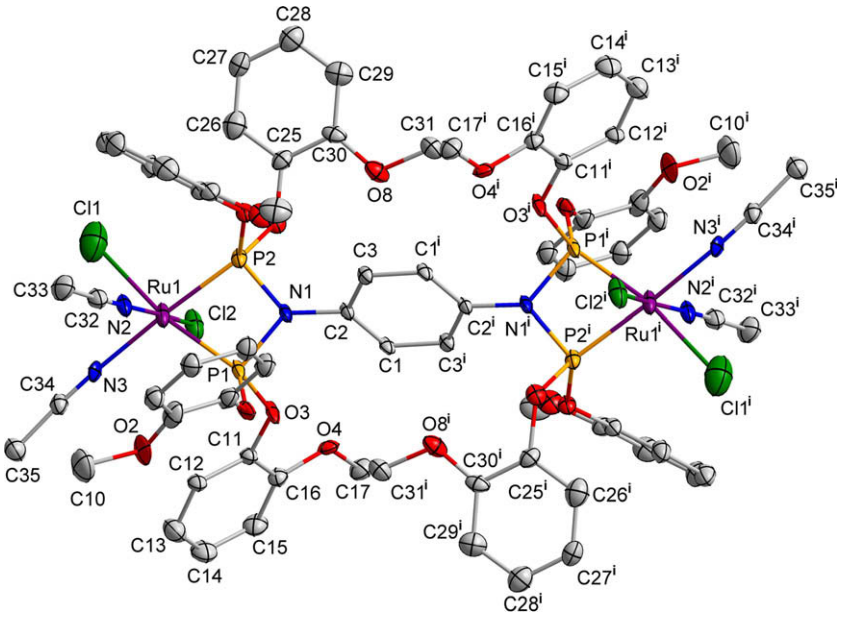


Fig. 1. Molecular structure of **2**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Crystallographic information for compound **2**.

	2
Empirical formula	$C_{70}H_{72}Cl_4N_6O_{18}P_4Ru_2$
Formula weight	1753.16
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	9.7505(9)
b (Å)	11.9710(10)
c (Å)	17.8465(2)
α (°)	88.2790(10)
β (°)	86.3570(10)
γ (°)	88.9130(10)
V (Å^3)	2077.7(3)
Z	1
ρ_{calc} (g cm^{-3})	1.401
μ (Mo Kα) (mm^{-1})	0.635
F (0 0 0)	894
Crystal size (mm)	0.03 × 0.07 × 0.16
T (K)	100
2θ Range (°)	1.1–26.4
Total number of reflections	16641
Number of independent reflections	8398 [R_{int} = 0.039]
Goodness-of-fit (GOF) (F^2)	1.07
R_1[a]	0.0727
wR_2[b]	0.2176

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

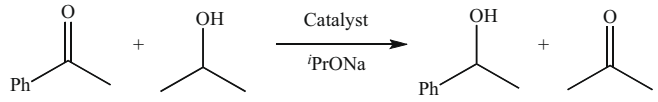
[b] $R_w = \left[\sum w(F_o^2 - F_c^2) / \sum w(F_o^2)^2\right]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2]$ where $P = \left(F_o^2 + 2F_c^2\right)/3$.

Table 2
Selected bond distances and bond angles for complex **2**.

Bond distances (Å)		Bond angles (°)	
Complex ***2***			
P1–N1	1.694(5)	P1–N1–P2	98.2(3)
P2–N1	1.680(5)	P1–Ru1–P2	70.27(7)
Ru1–P1	2.218(2)	Cl1–Ru1–Cl2	86.06(11)
Ru1–P2	2.212(2)	Cl1–Ru1–P1	169.01(10)
Ru1–N2	2.034(7)	Cl1–Ru1–P2	100.04(9)
Ru1–N3	2.088(9)	Cl2–Ru1–P1	88.65(8)
Ru1–Cl1	2.443(4)	Cl2–Ru1–P2	89.69(7)
Ru1–Cl2	2.384(2)	N2–Ru1–N3	89.8(4)
P1–O1	1.613(5)	P2–Ru1–N3	173.9(3)
P1–O3	1.601(5)	P1–Ru1–N3	107.9(3)
P2–O5	1.604(5)	Cl2–Ru1–N2	171.95(16)
P2–O7	1.605(5)	Cl2–Ru1–N3	84.4(3)
N1–C2	1.439(8)	Cl1–Ru1–N2	87.55(19)

metal to which it is coordinated. In free ligands the bridging phenylene ring is almost perpendicular to the P–N–P skeleton, where as its platinum and rhodium square planar complexes have almost parallel alignment of phenylene ring with the P–N–P skeletons [5a,c]. The structurally characterized Group 11 metal complexes of **1** show perpendicular alignment [5b]. At this moment, the conformational preference of tetraphosphazane ligand **1** towards different metals is not fully understood.

Table 3
Transfer hydrogenation reactions of acetophenone.



Entry	Catalyst	Conditions[a]	Conversion (%)[b]	TON[c]
1	**2** (1 mol%)	^{i}PrONa (10 mol%), reflux, 22 h	99	99
2	**3** (0.2 mol%)	^{i}PrONa (10 mol%), reflux, 5 h	100	500
3	**3** (1 mol%)	^{i}PrONa (10 mol%), 30 °C, 24 h	19	19

[a] Acetophenone (0.1 g, 0.832 mmol), ^{i}PrONa (10 mol%), catalyst (0.2–1 mol%), ^{i}PrOH (5 mL).
[b] Conversion to coupled product determined by GC, based on acetophenone; average of two runs.
[c] Defined as mol product per mol of catalyst.

3.2. Transfer hydrogenation reactions

The catalytic transfer hydrogenation of ketones has emerged as a useful and convenient method to prepare secondary alcohols by avoiding the use of molecular hydrogen and pressure apparatus [15]. Recently we have shown that di-, tetra- and polynuclear rhodium(I) complexes of **1** serve as good catalysts for the transfer hydrogenation reactions of ketones into their respective alcohols [5a]. As a preliminary investigation we have scanned the catalytic activities of complexes **2** and **3** for the reduction of acetophenone using 2-propanol as a hydrogen source in the presence of a base. The catalytic reactions were carried out with 0.1 g of acetophenone in 5 mL of 2-propanol in the presence of 0.2 or 1 mol% of the catalyst and 10 mol% of sodium 2-propoxide as a promoter under refluxing conditions. The progress of the reaction was monitored by gas chromatography and representative catalytic data are given in Table 3. For example, acetophenone is reduced to 1-phenylethanol in the presence of sodium 2-propoxide with 100% conversion in 2-propanol under refluxing conditions with 0.2 mol% of catalyst **3** within 5 h (Table 3, entry 2). The reactions are slow at room temperature but proceed at good rates at refluxing conditions (Table 3, entry 3). In the absence of base, no conversion was observed and conversion rates were increased with increasing concentration of base [16]. However, under similar catalytic reaction condition significant amount of conversion was observed with $[RuCl_2(p\text{-cymene})]_2$ (1 mol%) for the reduction of acetophenone into 1-phenylethanol with 10 mol% of ^{i}PrONa which is much better than that of **2**. The lower catalytic activity of **2** may be due to its poor solubility in 2-propanol compared to $[RuCl_2(p\text{-cymene})]_2$.

4. Conclusion

Tetraphosphazane **1** readily reacts with $[RuCl_2(p\text{-cymene})]_2$ to afford di- and tetranuclear Ru^{II} complexes depending upon the stoichiometry and reaction conditions. Complexes **2** and **3** show moderate to good catalytic activities towards the reduction of acetophenone to 1-phenylethanol using 2-propanol as a hydrogen source. Compound **2** is a potential precursor for the synthesis of multinuclear Ru^{II} complexes due to the presence of weakly coordinating solvent molecules in it. Further, these complexes are promising catalysts for various organic transformations. The work in this direction is in progress.

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Appendix A. Supplementary material

CCDC 732606 contains the supplementary crystallographic data for complex **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.07.002.

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