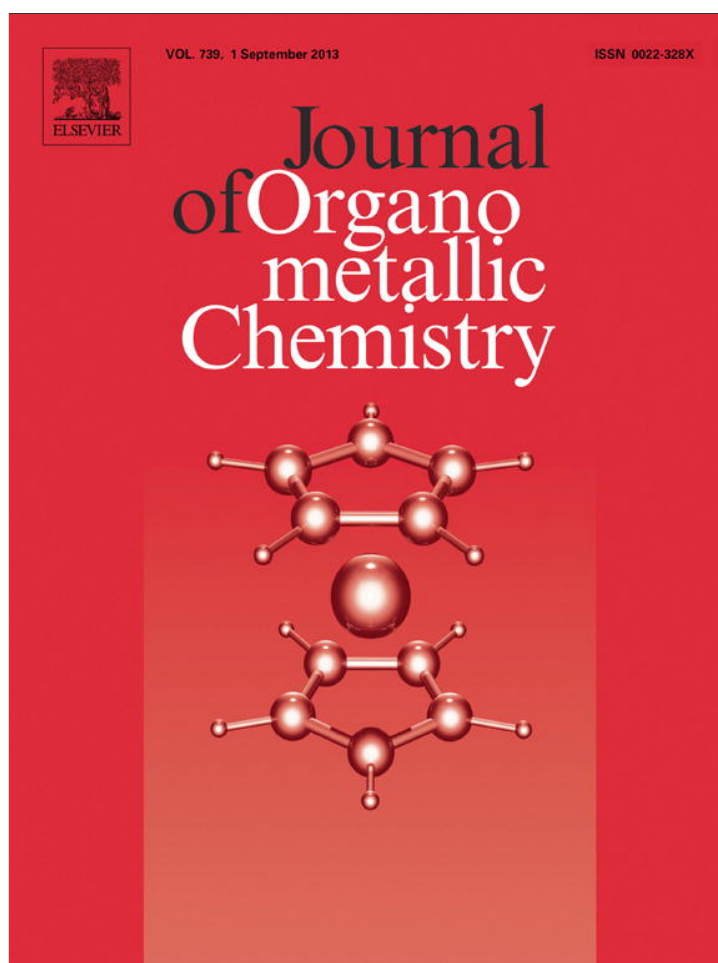


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Syntheses and X-ray crystal structures of two ruthenium(II) complexes derived from acetonitrile and dimethylphenylphosphonite

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ABSTRACT

The ruthenium acetonitrile complex $[\text{RuCl}_2(\text{NCCH}_3)_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2]$ (**1**) and the stable salt $[\text{Ru}(\text{CH}_3\text{CN})_4\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2][\text{BF}_4]_2$ (**2**) have been prepared from $[\text{RuCl}_2(\text{NCCH}_3)_2(\text{COD})]$ and the salt $[\text{Ru}(\text{COD})(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ respectively. The two compounds have been characterized by IR, microanalytical, NMR measurements and single-crystal X-ray diffraction studies. The ruthenium in both compounds has almost ideal octahedral coordination geometry. One of the complexes, $[\text{RuCl}_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2(\text{NCCH}_3)_2]$ (**1**) has shown significant catalytic activity for the transfer hydrogenation of simple ketones while the other, $[\text{Ru}\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ (**2**) did not show any catalytic activity for this reaction.

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1. Introduction

The polymer $[\{\text{RuCl}_2(\text{COD})\}_x]$ has been often applied as a useful synthetic precursor to a wide range of ruthenium compounds in the past [1–3]. This compound is highly insoluble in most organic solvents; therefore reactions with it are usually carried out under extreme conditions which require filtration steps, long reaction times etc [1] and often give products in moderate to low yields [4]. Its suspensions in methanol or ethanol have however been found to react rapidly with hydrazines to produce clear solutions from which cationic ruthenium(II) salts were isolated in quantitative yield on addition of suitable counter anions [1]. Such derivatives of the polymer contain labile hydrazine groups in solution making them ideal precursors for the synthesis of an extensive range of ruthenium(II) salts [1,5]. Treatment of the polymer $[\{\text{RuCl}_2(-\text{COD})\}_x]$ with acetonitrile at reflux also produced a soluble acetonitrile solvate compound $[\text{RuCl}_2(\text{NCCH}_3)_2(\text{COD})]$ which has a great potential as precursor for ruthenium compounds [6–12]. A range of useful organometallic compounds have been prepared using this soluble precursor, in particular, compounds with medicinal and

biological activities have been reported [13–19]. The use of this derivative as a precursor to ruthenium organometallic compounds has not been given prominent attention despite its great potential, probably due to low yields. We have recently reported an efficient synthetic procedure for $[\text{RuCl}_2(\text{COD})(\text{NCCH}_3)_2]$ [20]. Transition metal complexes with coordinated phosphinite and phosphonite ligands have remained one of the most studied systems. This is attributed to their simple synthetic methods, versatile coordination behavior and more importantly their wide applications as catalysts for several organic functional groups transformations [21,22]. Ruthenium complexes with phosphinite and phosphonite ligands in particular have been reported as being very active catalysts in the transfer of hydrogen from alcohols in the form of hydrides to ketones [23]. Metal complexes with chiral bidentate ligands are the most frequently used in the transfer hydrogenation reactions [24] with those ligands containing nitrogen as donor atoms exhibiting greater catalytic activity [25,26]. Since the monodentate ligands are less expensive and more readily available than most chiral bidentate ligands, we hereby report our findings in the reactivity of ruthenium starting materials $[\text{RuCl}_2(-\text{COD})(\text{CH}_3\text{CN})_2]$ and $[\text{Ru}(\text{COD})(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ with the monodentate dimethylphenylphosphonite ligand $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$, data on the catalytic activity of the resulting complexes in the transfer hydrogenation of ketones are also presented.

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2. Experimental

2.1. General comments

All manipulations were performed using standard Schlenk-tube techniques under an atmosphere of purified nitrogen. All solvents were purified by standard procedures [27]. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was purchased from Acros Organics. Dimethylphenylphosphonite and acetonitrile were commercially obtained from Aldrich. The starting materials $[\{\text{RuCl}_2(\text{COD})\}_x]$ [3], $[\text{RuCl}_2(\text{COD})(\text{NCCH}_3)_2]$ [20] and $[\text{Ru}(\text{COD})(\text{NCCH}_3)_4][\text{BF}_4]_2$ [28] were synthesized according to literature methods. Elemental analyses were performed with an Elementar Vario EL analyzer at the Institute of Materials Science, University of Connecticut. High-resolution ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shifts were calibrated to solvent peaks, which are reported relative to TMS. ^{31}P NMR chemical shifts were measured relative to 85% H_3PO_4 . GC–MS analyses were performed on Agilent 5975 Series MSD and 7820A GC System. All reported yields in transfer hydrogenation experiments are GC yields and were averages of at least two runs.

2.2. Preparations

2.2.1. $[\text{RuCl}_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2(\text{NCCH}_3)_2]$ (**1**)

In a 100 mL Schlenk flask, $[\text{RuCl}_2(\text{COD})(\text{NCCH}_3)_2]$ (0.20 g, 0.5 mmol) and $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ (0.18 g, 1 mmol) were dissolved in 20.0 mL of acetonitrile and the orange solution was stirred at 78 °C for 19 h during which time a bright yellow solution formed. The solution was reduced in volume to 5 mL under vacuum and kept at 0 °C for three weeks to obtain yellow crystalline solids. Yield 76%; mp 282–301 °C; ^1H NMR (CD_2Cl_2) δ (ppm) 1.85 (s, 6H, CH_3), 3.83 (s, 12H, OCH_3), 7.47–7.92 (m, 10H, C_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2), δ (ppm) 3.50 (s, CH_3), 53.01 (s, OCH_3), 128.09 (s, CN), 130.23–131.30 (m, C_6H_5); $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2), δ 154.81; IR (KBr) $\nu(\text{CN})$ 2279 cm^{-1} , $\nu(\text{Ru}-\text{P})$ 526 cm^{-1} . Elemental analysis for $\text{C}_{20}\text{H}_{28}\text{Cl}_2\text{N}_2\text{O}_4\text{P}_2\text{Ru}$, calcd. (found): C, 40.30 (40.40); H, 5.29 (4.71); N, 4.71 (4.71).

2.2.2. $[\text{Ru}\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ (**2**)

$[\text{Ru}(\text{COD})(\text{NCCH}_3)_4][\text{BF}_4]_2$ (0.20 g, 0.37 mmol) and dimethoxyphenylphosphine (0.14 g, 0.75 mmol) were dissolved in 15.0 mL of acetonitrile and the yellow mixture was refluxed for 12 h. The volume was reduced to 5 mL and kept at 0 °C for two weeks. The white precipitate obtained was collected by filtration, dried in the vacuum and recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution to give colorless prisms. Yield 70%; mp 225–228 °C; ^1H NMR (CD_2Cl_2) δ (ppm) 2.27 (s, 12H, CH_3), 3.86 (s, 12H, OCH_3), 7.66–7.69 (m, 10H, C_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2), δ (ppm) 3.74 (s, CH_3), 127.58 (s, CN), 129.50–132.20 (m, C_6H_5); $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2), δ 151.07 (s, $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$); IR (KBr) $\nu(\text{CN})$ 2081 cm^{-1} , $\nu(\text{Ru}-\text{P})$ 529 cm^{-1} . Elemental analysis for $\text{C}_{24}\text{H}_{34}\text{P}_2\text{O}_4\text{N}_4\text{B}_2\text{F}_8\text{Ru}$, calcd. (found): C, 36.97 (37.15); H, 4.37 (4.42); N, 7.19 (7.28).

2.3. General procedure for the transfer hydrogenation study

A published procedure was adopted [29] for the transfer hydrogenation studies of **1** and **2** as described here for **1**. The ruthenium complex **1** (0.004 mmol) was placed in a 50 mL flask containing 15 mL of 2-propanol as solvent, and 5 mL of a NaOH (0.096 mol/L) solution in 2-propanol was added as a co-catalyst. The mixture was then freed from oxygen by three freeze-thaw cycles. Subsequently the flask was filled with argon and the ketone (5.0 mmol) was added. The reaction mixture was vigorously stirred at 82 °C for 4 h. During the transfer hydrogenation, samples were taken from the reaction mixture at regular interval of 30 min

to check the conversion. The samples were inserted by a special glass syringe into a gas chromatograph and the reaction products were compared with authentic samples. The results of the catalytic reactions are collected in Table 2.

2.4. X-ray diffraction measurements

Crystals of **1** and **2** were mounted on a Cryoloop with Paratone-N oil and data were collected at 90 K with a Bruker APEX II CCD using Mo K alpha radiation. Data were corrected for absorption with SADABS [30] and the structures solved by direct methods. All non-hydrogen atoms were refined anisotropically by full matrix least squares on F^2 . Hydrogen atoms on acetonitrile were found from a Fourier difference map and were then fixed in position with suitable riding parameters. Hydrogen atoms on phosphorus atoms were found from a Fourier difference map and were refined isotropically with distances of 1.33(1) angstroms and -1.20 Ueq of parent P atom. All other hydrogen atoms were placed in calculated positions with appropriate riding parameters.

3. Results and discussion

3.1. Structural characterization of $[\text{RuCl}_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2(\text{NCCH}_3)_2]$ (**1**)

Complex **1** was obtained in good yield from a ligand exchange reaction of $[\text{RuCl}_2(\text{COD})(\text{NCCH}_3)_2]$ with 2 M equivalents of the $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ ligand. The physical properties and elemental analysis of the complex are given in the experimental section. Once isolated, the complex was found to be relatively stable in air over a period of two weeks and was therefore stored in an inert atmosphere. The complex is soluble in CHCl_3 , CH_2Cl_2 , DMF and DMSO solvents but not in methanol, ethanol, hexane, pentane, THF and ether.

The IR spectrum of complex **1** has characteristic $\nu(\text{CN})$ bands at 2279 cm^{-1} in the region higher in frequency than in the free nitrile (2248 cm^{-1}) [31], as expected for coordination through the nitrile nitrogen atom [7]. Absence of COD protons at the expected regions in both compounds suggests that the COD ligand was substituted in preference to the acetonitrile in contrast to literature report [5]. The ^1H NMR spectrum of **1** displays singlets at 3.83 and 1.8 ppm which are assigned to the protons on the methoxy groups on $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ and acetonitrile methyl groups respectively. The resonances attributable to the protons on the phenyl groups on $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ were observed between 7.47 and 7.92 ppm. The ^{13}C NMR spectrum of **1** consist of lines at 3.50 ppm assigned to the methyl groups on the acetonitrile while lines for CN were present at 128.09 ppm and aromatic carbons on $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ were observed between 130 and 131 as multiplets. Appearance of a singlet at 154.81 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** is indicative of equivalent phosphorus of the two $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ ligands. The ^{31}P chemical shift of free $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ have been reported at $\delta +161.7$ [32] and $+165.09$ ppm [33]. The ^{31}P NMR signal in the complex **1** is $\delta +154.81$ ppm, the coordination shift is between 8 and 11 units upfield when the free $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ becomes coordinated in the $[\text{RuCl}_2(\text{NCCH}_3)_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2]$ complex. The integration ratios in the ^1H NMR of **1** combined with the elemental analysis data support the stoichiometry $[\text{RuCl}_2(\text{NCCH}_3)_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2]$.

3.2. Structural characterization of $[\text{Ru}\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2(\text{NCCH}_3)_4][\text{BF}_4]_2$ (**2**)

The cationic tetrakisacetonitrile complex $[\text{Ru}(\text{CH}_3\text{CN})_4\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2][\text{BF}_4]_2$ (**2**) has been obtained in 70% isolated yield by the reaction of $[\text{Ru}(\text{CH}_3\text{CN})_4(\text{COD})][\text{BF}_4]_2$ with $\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5$ in

CH₃CN at 78 °C. Compound **2** was isolated as air-stable colorless solid and has been characterized by means of standard spectroscopic techniques (IR and ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR) as well as elemental analysis. The IR spectrum of **2** contained weak $\nu(\text{CN})$ absorption bands at 2081 cm⁻¹. In the ¹H NMR spectrum of **2**, proton resonances for hydrogen atoms attached to the methoxy groups of P(OCH₃)₂C₆H₅ were observed at 3.86 ppm while the resonances attributable to the acetonitrile methyl groups appeared at 2.27 ppm. The phenyl proton resonances in the complex were observed between 7.66 and 7.69 ppm as multiplets. This is also supported by the ¹³C{¹H}NMR data giving rise to a single line at 3.74 ppm attributable to the CH₃CN methyl carbons and a multiplet of resonance between 129 and 132 ppm for the phenyl rings on P(OCH₃)₂C₆H₅. The resonance of the nitrile group is found at 127.58 ppm, compared to 116.92 ppm in free CH₃CN [34]. The signal attributable to the two equivalent phosphorus atoms in **2** was observed at 151.07 ppm in the ³¹P NMR spectrum. The coordination shift when compared to the ³¹P chemical shift of the free P(OCH₃)₂C₆H₅ at δ +161.7 [32] or +165.09 ppm [33] is between 11 and 14 units upfield when the free P(OCH₃)₂C₆H₅ become coordinated in the [Ru(NCCH₃)₄(P(OCH₃)₂C₆H₅)₂][BF₄]₂ complex. All data are in agreement with the proposed stoichiometry.

3.3. X-ray analysis of **1** and **2**

Crystals suitable for X-ray structural analysis have been obtained for complexes **1** and **2** by slow evaporation of dichloromethane-methanol (1:3) solution of the complexes at room temperature. The molecular structures of complexes **1** and **2** are shown in Figs. 1 and 2. Crystal data and structure refinement details are presented in Table 1 while the selected bond distances and bond angles of both complexes are listed as footnotes to each figure.

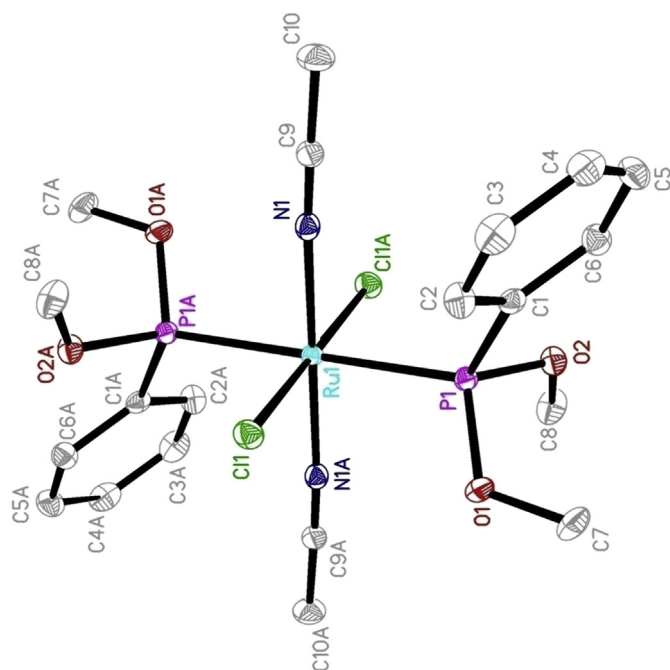


Fig. 1. ORTEP diagram of [RuCl₂(P(OCH₃)₂C₆H₅)₂(NCCH₃)₂] (**1**) with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)–N(1) 2.023 (2), Ru(1)–N(2) 2.023(2), Ru(1)–P(1) 2.3321(6), P(1)–O(1) 1.6118(17), P(1)–C(1) 1.823 (2), Ru(1)–Cl(1) 2.4091(6), N(1)–Ru(1)–N(1A) 180.0, N(1A)–Ru(1)–P(1A) 88.63 (5), N(1)–Ru(1)–P(1) 91.37(5), N(1)–Ru(1)–Cl(1) 89.26(5), P(1)–Ru(1)–Cl(1) 87.29(2), N(1)–Ru(1)–Cl(1) 90.74(5), O(2)–P(1)–O(1) 105.16(9).

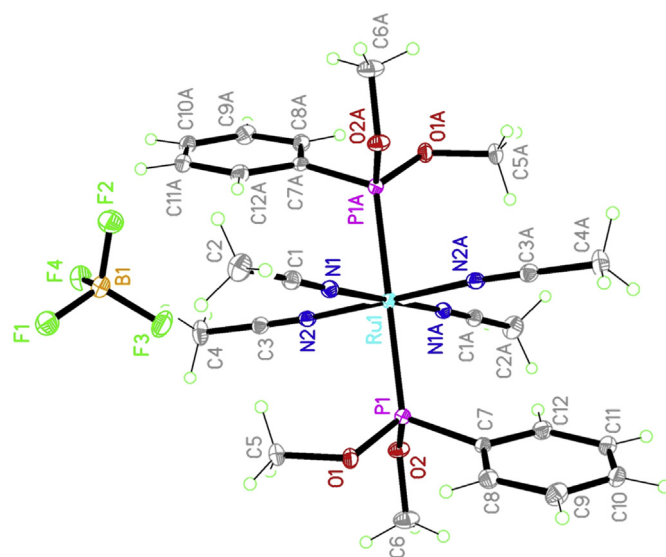


Fig. 2. ORTEP diagram of [Ru(NCCH₃)₄(P(OCH₃)₂C₆H₅)₂][BF₄]₂ (**2**) with ellipsoids drawn at 50% probability. One of the BF₄ counterion has been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)–N(1) 2.0347(14), Ru(1)–N(2) 2.0226(14), Ru(1)–P(1) 2.3535(4), P(1)–O(2) 1.5981(12), P(1)–C(1) 1.8074(16), N(2A)–Ru(1)–N(2) 180.00(6), N(2)–Ru(1)–N(1) 89.35(5), N(2)–Ru(1)–P(1) 89.87(4), N(1)–Ru(1)–P(1A) 88.26(4), N(1)–Ru(1)–P(1) 90.13(4), O(2)–P(1)–O(1) 106.79(6).

The crystal structure of **1** (Fig. 1) consists of a mononuclear [RuC₂₀H₂₈Cl₂N₂O₄P₂] unit. Ru²⁺ has an octahedral geometry with the equatorial plane occupied by N1, N1A, P1 and P1A from two CH₃CN and two P(OCH₃)₂C₆H₅, and the axial positions are completed by Cl1, Cl1A from the chlorides. The two Cl ligands in **1** are bound to the ruthenium center in *trans* positions, forming angle 180.00(3)°. The other two ligands, CH₃CN and P(OCH₃)₂C₆H₅ are also bound to the ruthenium center in similar fashion with angles of 180.00(11) and 180.00(3)° respectively. The angles around the Ru

Table 1
Summary of X-ray parameters for compounds **1** and **2**.

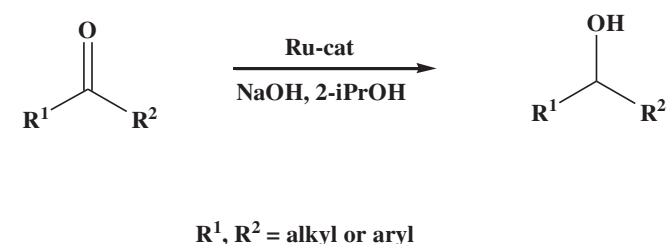
	1	2
Formula	C ₂₀ H ₂₈ Cl ₂ N ₂ O ₄ P ₂ Ru	C ₂₄ H ₃₄ B ₂ F ₈ N ₄ O ₄ P ₂ Ru
Mol wt	594.35	779.18
Cryst syst	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n
T (K)	100(2)	100(2)
a (Å)	12.4227(11)	8.4490(10)
b (Å)	8.3978(8)	11.2854(10)
c (Å)	12.7477(13)	17.1068(10)
α (deg)	90	90
β (deg)	110.507(3)	98.305(4)
γ (deg)	90	90
V (Å ³)	1245.6(2)	1614.0(5)
Z	2	2
D _{calcd} (Mg/m ³)	1.585	1.603
μ(Mo Kα) mm ⁻¹	1.001	0.668
F(000)	604	788
Range θ, deg	2.84–26.38	2.56–26.38
No. of rflns	10,607	14,884
No. of indep rflns	2521	3309
No. of refined params	138	209
R1 (I > 2σ(I))	R1 = 0.0323	R1 = 0.0210
wR2	wR2 = 0.0841	wR2 = 0.0495
R indices (all data)	R1 = 0.0339	R1 = 0.0248
	wR2 = 0.0856	wR2 = 0.0517
GOF	1.074	1.024
Max peak, e Å ⁻³	0.940	0.439
CCDC no.	873004	884044

atom are all close to 90° in line with the octahedral coordination arrangement. Bond distances found in this structure correspond to related values from other similar structures. The average C–C bond distance of 1.391(3) Å and C–C–C bond angles of 120° in the two phenyl rings in the structure are within the accepted values of 1.394 Å and 120° for phenyl rings [35]. The average Ru–P bond length of 2.3316(6) Å is slightly shorter than the sum of their covalent radii (2.51 Å) which indicates a strong mutual attraction between Ru and P [36]. Mean P–O and O–C distances are 1.6121(16) and 1.444(3) Å respectively and are normal and requires no comment [36]. The average Ru–Cl bond length in **1** (2.4090(5) Å) is shorter than the values previously reported for a related octahedral complex [29].

The asymmetric unit of complex **2** comprises half the molecule with the ruthenium atom situated on a center of symmetry. The X-ray crystal structure shows (Fig. 2) four CH₃CN and two P(OCH₃)₂C₆H₅ ligands coordinated in an almost ideal octahedral arrangement to the central Ru²⁺ cation. The cation within **2** is monomeric, the equatorial plane is occupied by four CH₃CN ligands coordinated through the nitrogen atoms while the two coordinated P-bonded P(OCH₃)₂C₆H₅ molecules occupy axial positions. The mean Ru–P distance is 2.3535(4) Å while the P–O distances range between 1.5981(12)–1.6042(12) Å. Average Ru–N bond distance of 2.02865 Å in **2** is somewhat shorter than in the parent acetonitrile species [28]. Associated with the Ru cation are two essentially tetrahedral BF₄ counter ions (only one illustrated). The geometry of the counter ions is in agreement with that found in other structures [37] but no interactions were found between these ions and the ruthenium(II) core.

3.4. Catalytic transfer hydrogenation reactions

The simple synthetic routes to the isolated complexes prompted us to investigate their catalytic activity in the transfer hydrogenation of ketones (Scheme 1). The ruthenium complex **1** showed remarkable performance in the conversion of both aliphatic and aromatic ketones to alcohols and the results are presented in Table 2. The complex efficiently catalyzed the reduction of ethyl methyl ketone and hexanone to their corresponding alcohols with 99.5 and 97% conversion respectively. The conversion in case of both acetophenone and cyclohexanone was 100%. No transfer hydrogenation was observed in the absence of base, suggesting loss of the chlorides to form a reactive dihydride species in a similar fashion to the formation of RuH₂(PPh₃)₂(cydn) reported by Morris et al. [38]. Therefore, it is believed that the base facilitated the formation of a ruthenium alkoxide by abstracting the proton from the alcohol and subsequently the alkoxide underwent β-elimination to give the active species, ruthenium hydride [39]. The ketone then coordinates to the hydride-ruthenium intermediate which eventually led to the alcohol formation [40–45]. Complex **1** however, showed no activity toward the hydrogenation of nitrobenzene after 48 h, therefore no further attempt was made to hydrogenate compounds with similar functional groups.



Scheme 1. Transfer hydrogenation reactions.

Table 2
Catalytic transfer hydrogenation of ketones catalyzed by complex **1**.

Entry	Substrate	Product	Yield (%)
1.			99.5
2.			97
3.			100
4.			100

Experimental conditions: ketone, 5 mmol; NaOH, 0.096 mol; catalyst loading, 0.004 mmol; 2-propanol, 15 mL; temp, 82 °C; time, 4 h. Yields were determined by GC–MS and related to the unreacted ketone.

The activity of complex **2** was also investigated under the same conditions as complex **1** but **2** showed no activity toward the transfer hydrogenation of any of the ketones even at an extended time of 24 h. This gives further support to the assertion that an active dihydride species RuH₂(NCCH₃)₂{P(OCH₃)₂C₆H₅}₂ formed by complex **1** through the loss of the two chlorides is likely to be the true catalyst. The different catalytic performances of the two complexes may therefore be due to the different coordination environments around the metal centers.

The results obtained in this study are similar to those reported by Wills and co-workers with the complex [{P(OC₁₀H₆)₂C₆H₄Br}₂·RuCl₂(DPEN)] (DPEN = diphenylethylenediamine) for the transfer hydrogenation of acetophenone [24(b)]. Using the complex at 50 bar hydrogen pressure and S/C ratio of 2000, acetophenone was fully reduced in less than 4 h. The new catalyst system does not require the presence of molecular hydrogen to function; the hydrogen is rather transferred in form of hydride from isopropanol to the ketones as proposed above. In another report, a Ru complex containing BINOL-derived monodentate diphosphonite ligand [{P(OC₁₀H₆)₂]₂C₁₅H₁₂O] was reported to efficiently catalyze the asymmetric transfer hydrogenation of both aryl/alkyl and alkyl/alkyl ketones [46]. However, the simple synthetic route and price affordability will place this new catalyst system a better candidate for asymmetric transfer hydrogenation of ketones.

The new catalyst system is also very effective and fast, achieving 100% yield in 4 h for acetophenone, there is therefore no problem of chiral resolution of products with this new catalyst system.

4. Conclusions

The reaction of the ruthenium(II)-organonitrile precursor [RuCl₂(COD)(NCCH₃)₂] or [Ru(COD)(NCCH₃)₄][BF₄]₂ with dimethylphenylphosphonite gave new acetonitrile–Ru(II) complexes. The complexes were isolated as air and moisture stable solids and have been characterized by IR and NMR spectroscopic techniques, elemental analyses and X-ray crystal structure analyses. One of the

complexes showed significant activity toward the transfer hydrogenation of simple ketones.

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Appendix A. Supplementary material

CCDC 873004 (1) and 884044 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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