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Synthesis of new ruthenium(II) complexes derived from labile nitrile ligands: an alternative route to the preparation of *trans*-dichlorotetrakis(diphenylphosphine)ruthenium(II)

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ABSTRACT

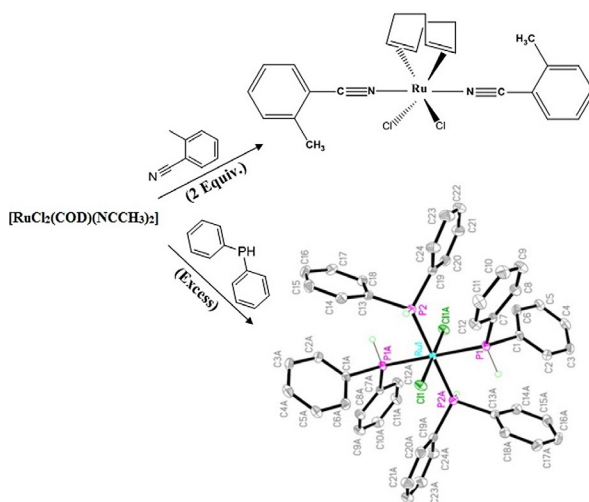
New ruthenium(II) complexes containing labile nitrile ligands have been prepared by treatment of either the polymer $[\{\text{RuCl}_2(\text{COD})\}_x]$ (COD = cycloocta-1,5-diene) (**1**) or its derivative $[\text{RuCl}_2(\text{COD})(\text{NCCH}_3)_2]$ (**2**) with the appropriate nitrile ligands in refluxing acetonitrile under argon. A new route to synthesis of *trans*-dichlorotetrakis(diphenylphosphine)ruthenium(II) (**7**) was also reported. A redetermination of the structure of **7** was undertaken and X-ray crystallographic data revealed that the complex crystallizes in the triclinic space group *P*-1 with unit cell dimensions $a = 12.7016(9) \text{ \AA}$, $b = 13.0847(10) \text{ \AA}$, $c = 14.1498(10) \text{ \AA}$, $\alpha = 101.46(3)^\circ$, $V = 2080.6(3) \text{ \AA}^3$, $Z = 2$ and $R = 0.0309$. Its polymorph **7'** was also obtained. The crystal structure of **4** was also determined. This complex crystallizes in the monoclinic space group *C2/c* with unit cell dimensions $a = 27.0510(3) \text{ \AA}$, $b = 11.0984(13) \text{ \AA}$, $c = 13.0450(16) \text{ \AA}$, $\alpha = 90^\circ$, $V = 3886.5(8) \text{ \AA}^3$, $Z = 8$ and $R = 0.0282$.

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1. Introduction

The ability to create coordination sites by the dissociation of weakly held ligands allows the metal center to interact with substrates; this is an important and necessary requirement for homogeneous catalysts to function at optimum capacity [1]. Coordinated acetonitriles [2] are labile in solution, thereby making their complexes convenient precursors to synthesis of other transition-metal compounds. In this regard, a general synthetic strategy to preparing nitrile containing ruthenium complexes has been developed [2]. The synthesis is based on the readily available polymeric species $[\{\text{RuCl}_2(\text{COD})\}_x]$ (**1**) which has attracted particular attention due to the lability of the η^4 -coordinated COD ligand [3]. The COD ligands in the polymer undergo exchange reactions under very mild conditions [4]. This property has been widely applied in numerous ligand-exchange processes and the polymer has been an ideal precursor for the synthesis of an extensive range of ruthenium(II) compounds [5–8]. The technique involves dissolving the polymer in refluxing acetonitrile to give a yellow solution after filtration, from which the product $[\text{RuCl}_2(\text{COD})(\text{NCCH}_3)_2]\cdot\text{NCCH}_3$ (**2**) crystallized out on cooling to 0°C after 24 h [9]. The polymer provides **2** with labile ligands that can easily be replaced by other ligands.

Isocyanides have been widely applied as ligands of transition metal complexes in the same manner as carbon monoxide due to the similarities in their electronic structures. Several metal complexes of this class of ligands have been reported as catalysts in some important reactions. Examples include the use of nickel(II) isocyanide complexes as catalysts in the presence of methylaluminoxane for polymerization of ethylene [10]. Hydrosilylation of alkene and styrene derivatives have been carried out in the presence of catalyst systems composed of organoiron(0) or (II) with isocyanides as auxiliary ligands [11]. Intramolecular silylation of C–C multiple bonds catalyzed by palladium-*tert*-alkyl isocyanide complexes have been reported [12]. The isocyanides have also been studied for their rich coordination chemistry [13].

Transition metal complexes of tris(4-fluorophenyl)phosphine derivatives have also been studied for their catalytic activities. A chiral lanthanum complex of 1,1'-bi-2-naphthol-tris(4-fluorophenyl)phosphine oxide was reported to have exhibited very high activity in the enantioselective epoxidation of conjugated enones [14(a)]. Also, in a recent report, a Au(I) complex of tris(4-fluorophenyl)phosphine has been applied as an excellent catalyst in the conversion of different alkynes into cyclic acetals [14(b)]. The catalytic properties of isocyanide ligands depend on the steric effect and electronic factors of the alkyl groups in their structure [12]. Therefore, we have chosen *tert*-butyl isocyanide and tris(4-fluorophenyl)phosphine as coordinating ligands to Ru(II) centers in the present study.

The use of **2** as a precursor to the synthesis of *trans*-dichlorobis(acetonitrile)bis(dimethylphenylphosphonite)ruthenium(II), a highly active transfer hydrogenation catalyst, has been recently reported by our group [15]. We now report the synthesis of other new ruthenium-organonitrile complexes derived from $[\{\text{RuCl}_2(\text{COD})\}_x]$ and a new convenient procedure for the preparation of *trans*-dichlorotetrakis(diphenylphosphine)ruthenium(II) using **2** as precursor.

2. Experimental

2.1. Materials and methods

The ruthenium trichloride hydrate was a commercial product from Acros Organics. All other reagents used were of analytical grade from Sigma-Aldrich and were used as received. The

methanol and ethanol used in the synthesis of the ruthenium complexes were freshly dried over 3 Å molecular sieves overnight followed by distillation under nitrogen. The other solvents were passed over a column of activated alumina just before use. $[\{\text{RuCl}_2(\text{COD})\}_x]$ [3], $[\text{RuCl}(\text{COD})(\text{NCCH}_3)_3][\text{PF}_6]$ [2] and **2** [9] were all prepared using literature procedures. Diphenylphosphine, tris(4-fluorophenyl)phosphine and *tert*-butyl isocyanide were purchased from Sigma-Aldrich. The reaction involving diphenylphosphine was carried out under a purified nitrogen atmosphere using standard Schlenk techniques. All other reactions were performed in air. Melting points were obtained on a Kofler microhotstage apparatus and were uncorrected. Infrared spectra were recorded on a Bruker Tensor 27 FTIR spectrophotometer at the Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, South Africa. NMR spectra were recorded on a Bruker Avance 300 MHz instrument at the Department of Chemistry, University of Connecticut, USA. NMR spectra were referenced internally to residual solvent resonances (^1H) or externally to 85% H_3PO_4 (^{31}P). Elemental analyses were determined at the Center for Nanotechnology, Department of Chemistry, Rhodes University, South Africa and at the Institute of Materials Science, University of Connecticut, USA. Single crystal X-ray diffraction data of **7** were collected with a Bruker APEX II CCD at the Small Molecule X-ray Crystallographic Facility, Department of Chemistry and Biochemistry, University of California, San Diego, USA. Furthermore, single crystal X-ray diffraction data of **4** and the polymorph of **7'** were collected with a Bruker APEX II CCD at the Department of Chemistry, University of Johannesburg.

2.2. Preparation of the ruthenium(II) complexes

2.2.1. Synthesis of bis(*o*-toluonitrile)dichloro(η^4 -1,5-cyclooctadiene)ruthenium(II) (**3**)

A 100 mL Erlenmeyer flask containing a magnetic stirring bar and fitted with a condenser was charged with **2** (0.16 g, 0.42 mmol) and *o*-toluonitrile (2 mL). To obtain complete dissolution, the reaction mixture was gently warmed. Ethanol (8 mL) was added to the solution, which was then heated under reflux for 45 min. The volume of the solution was then reduced to 3 mL by evaporation under reduced pressure. Addition of *n*-hexane (4 mL) and cooling to -20°C for 4 h gave the product as yellow precipitate. The precipitate was collected through filtration and dried under vacuum overnight to obtain a yellow powder. Yield 0.10 g, 45%; m.p. 190–194°C; ^1H NMR (CDCl_3) δ (ppm) 1.43 (6H, s, Me); 2.05 (4H, br, m, CH_2), 2.51 (4H, br, m, CH_2), 4.55 (4H, m, CH), 5.30 (CH_2Cl_2), 7.42 (4H, m, C_6H_4), 7.78 (4H, m, C_6H_4), IR $\nu(\text{CN})$ 2243 cm^{-1} . Elemental analysis for $\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{N}_2\text{Ru}$, Calcd (Found): C, 56.03 (56.25); H, 5.06 (5.34); N, 5.45 (5.71).

2.2.2. Synthesis of tris(acetonitrile)chloro(η^4 -1,5-cyclooctadiene)ruthenium(II) hexafluorophosphate (**4**)

A 50 mL Erlenmeyer flask containing a magnetic stirring bar and fitted with a reflux condenser was charged with **2** (0.16 g, 0.4 mmol) and acetonitrile (5 mL). A quantity of $\text{NH}_4[\text{PF}_6]$ (0.14 g, 0.8 mmol) in acetonitrile (2 mL) was added. The solution was heated under reflux for 15 min, cooled to room temperature, and filtered to remove precipitated NH_4Cl . The filtrate was concentrated under reduced pressure to a volume of 2 mL. Addition of ethanol (4 mL) and diethyl ether (8 mL) followed by cooling to -20°C for 2 h gave the product as yellow microcrystalline solid. Yield: 0.1316 g, 62%; m.p. 175–179°C; IR: 2994 (w); 2926 (w); 2859 (w); 2314 (w); 2163 (w); 2018 (w); 1452 (w); 1423 (m); 1338 (m); 1189 (w); 1039 (m); 998 (w); 831 (s); 558 (m); 484 (m); 380 (s). ^1H NMR (CDCl_3) δ (ppm): 1.53 (s, CH_3); 2.09 (m, CH_2); 2.42 (s, CH_2); 2.67

(s, CH_3); 4.50 (pt, CH); 4.66 (pt, CH_2). ^{13}C NMR (CDCl_3) δ (ppm): 4.90 (s, CH_3); 28.86 (s, CH_2); 29.27 (s, CH_2); 91.36 (s, CN); 95.89 (s, CN); 141.23 (s, CH_3). ^{31}P NMR (CDCl_3) δ (ppm): -144.40 (sp, PF_6). Elemental analysis for $\text{C}_{14}\text{H}_{21}\text{ClN}_3\text{F}_6\text{PRu}$, Calcd (Found): C, 32.79 (32.72); H, 4.13 (3.91); N, 8.19 (8.06).

2.2.3. Reaction of **4** with tris(4-fluorophenyl)phosphine

A 50 mL Erlenmeyer flask containing a magnetic stirring bar and fitted with a reflux condenser was charged with **4** (0.035 g, 0.07 mmol) and acetonitrile (10 mL). A quantity of tris(4-fluorophenyl)phosphine (0.13 g, 0.41 mmol) was added. The solution was heated under reflux for 1 h and allowed to cool to room temperature. The yellow solution was concentrated under reduced pressure to a volume of 2 mL. Addition of ethanol (5 mL) and diethyl ether (10 mL) followed by cooling to -20°C for 2 h gave **5** as pale yellow microcrystalline solids. Yield: 0.047 g, 51%; m.p. $162\text{--}164^\circ\text{C}$; IR: 3095 (w); 2360 (w); 2022 (w); 1589 (s); 1498 (s); 1396 (m); 1304 (m); 1238 (s); 1162 (s); 1091 (m); 1016 (m); 949 (w); 829 (s); 712 (m); 636 (m); 611 (w); 583 (w); 561 (m); 466 (m); 300 (m). ^1H NMR (CDCl_3) δ (ppm): 1.51 (s, CH_3); 1.93 (s, CH_3); 7.14 (t, C_6H_4); 7.72 (m, C_6H_4). ^{13}C NMR (CDCl_3) δ (ppm): 3.35 (s, CH_3); 115.64 (s, CN); 115.85 (Ar-CH); 127.71 (s, Ar-C-P); 136.23 (Ar-CH); 164.40 (s, Ar-C-F). ^{31}P NMR (CDCl_3) δ (ppm): -144.56 (sp, PF_6); 26.77 (s, $\text{P}(\text{FC}_6\text{H}_4)$). Elemental analysis for $\text{C}_{42}\text{H}_{33}\text{N}_3\text{ClF}_{12}\text{P}_3\text{Ru}$, Calcd (Found): C, 48.64 (48.45); H, 3.21 (3.45); N, 4.05 (4.08).

2.2.4. Reaction of **2** with *tert*-butylisocyanide

Tris(*tert*-butylisocyanide)acetonitriledichlororuthenium(II) (**6**) was prepared by heating a mixture of **2** (0.2 g, 0.5 mmol) and *tert*-butyl isocyanide (0.5 mL) in ethanol on a steam bath for 30 min. The yellow solution was collected and the solvent removed under reduced pressure to give a yellow solid. The yellow precipitate was collected through filtration, washed twice with ethanol and then recrystallized in the same solvent. Yield: 0.1773 g, 80%; mp $166\text{--}169^\circ\text{C}$; IR: 2985 (m); 2937 (w); 2362 (w); 2338 (w); 2125 (s); 1456 (m); 1401 (w); 1370 (m); 1237 (m); 1201 (s); 1043 (w); 928 (w); 720 (w); 564 (m); 549 (m); 470 (s); 462 (s); 455 (s); 379 (m); 300 (m); 234 (m). ^1H NMR (CDCl_3) δ (ppm): 1.52 (s, C_5H_9 , N, 27H), 1.97 (s, NCCH_3 , 3H). ^{13}C NMR (CDCl_3) δ (ppm): 30.99 (s); 56.64 (s). Elemental analysis for $\text{C}_{17}\text{H}_{30}\text{Cl}_2\text{N}_4\text{Ru}$, Calcd (Found): C, 44.15 (45.21); H, 6.49 (6.76); N, 12.12 (11.74).

2.2.5. Synthesis of dichlorotetrakis(diphenylphosphine)ruthenium(II) (**7**)

A weighed sample of diphenylphosphine (0.56 g, 3 mmol) was added to an acetonitrile (20 mL) solution of **2** (0.2 g, 0.5 mmol) and the mixture was heated under reflux for 19 h. The volume of the resulting yellow solution was reduced to 5 mL under reduced pressure and kept in the freezer for three weeks. A yellow crystalline precipitate was obtained. The yellow precipitate was collected through filtration and dried in the vacuum to give yellow powder of **7**. Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of ether into a dichloromethane solution. Yellow crystalline solids; Yield 0.1816 g, 40%; m.p. ($^\circ\text{C}$): decomp. >240 ; IR: 3055 (m); 2342 (m); 2157 (w); 1949 (w); 1572 (w); 1482 (m); 1434 (s); 1313 (m); 1281 (w); 1186 (m); 1154 (w); 1095 (m); 1069 (m); 1029 (w); 906 (w); 874 (s); 855 (m); 736 (s); 690 (s); 620 (w); 554 (w); 539 (w). ^1H NMR (CDCl_3) δ (ppm): 1.52 (s, H_2O); 6.94 (t, C_6H_5); 7.08 (t, C_6H_5); 7.30 (d, C_6H_5). ^{13}C NMR (CDCl_3) δ (ppm): 127.70 (s, C_6H_5); 128.70 (s, C_6H_5); 133.67 (s, C_6H_5). ^{31}P NMR (CDCl_3) δ (ppm): 19.50 (s, Ph_2PH). Elemental analysis for $\text{C}_{48}\text{H}_{44}\text{Cl}_2\text{P}_4\text{Ru}$, Calcd (Found): C, 62.84 (63.08); H, 4.80 (4.73).

2.2.6. X-ray diffraction analysis of **4** and **7**

A yellow crystal of **7** was mounted on a Cryoloop with Paratone-N oil and data were collected at 100 K on a Bruker Photon detector with Mo K α radiation. In addition, yellow cuboid crystals of **4** and **7'** were also mounted for analysis and data collected as mentioned for **7**. Data were corrected for absorption with SADABS [16] and structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full matrix least squares on F². Hydrogens on P were found from a Fourier difference map and refined isotropically with distances of 1.33(1) Å and –1.20 Ueq of the parent P. All other hydrogens were placed in calculated positions with appropriate riding parameters.

3. Results and discussion

The synthesis and crystal structure of **2** derived from the polymer $[\{\text{RuCl}_2(\text{COD})\}_x]$ was reported previously [9]. Complexes **3–7** were derived from **2** through ligand exchange of either the labile $\text{CH}_3\text{CN}/\text{COD}$ group or both with the appropriate ligand, except **5** that was prepared by the reaction of **4** with tris(4-fluorophenyl)phosphine. Sufficient evidence for *trans*-arrangement of the acetonitrile ligands in **2** was provided by both spectroscopic and X-ray diffraction analyses [2, 9]. It is therefore believed that the *o*-toluonitrile ligands in **3** are also in *trans*-positions (figure 1(a)). The same argument is used to assign *trans*-positions for the isocyanide ligands in **6** and diphenylphosphine in **7**. IR spectral data of **3** reported in the experimental section contain $\nu(\text{CN})$ bands which are to higher frequency than is observed

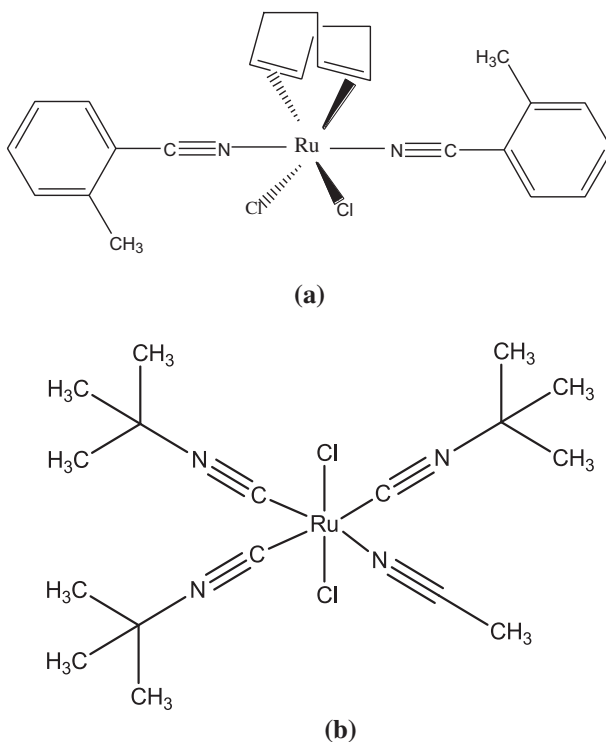


Figure 1. Chemical structures of the synthesized complexes: (a) **3**; (b) **6**.

in the free nitrile, in agreement with previous reports [2, 9, 17], suggesting coordination of the nitrile ligands to the ruthenium center through nitrogen [2, 9].

The two sets of *o*-toluonitrile ligands in **3** (figure 1(a)) are also believed to be *trans* to the chelating COD similar to the acetonitrile in **2**, which have been assigned by comparison to the IR spectrum of a similar compound in the literature [18]. The phenyl protons of the *o*-toluonitrile were observed between δ_{H} 7.2 and 7.7 ppm in the ^1H NMR spectrum of this complex. The CH_3 group protons appeared at δ_{H} 1.43 ppm as a singlet while the usual resonances of the cyclooctadiene protons were observed at δ_{H} 4.36 (CH) and 2.05 (CH_2) ppm. The singlet signal at δ_{H} 5.30 ppm is due to traces of DCM in the molecule. The ease with which the acetonitrile ligand in **2** can be replaced was also demonstrated when it was heated under reflux for 1 h in a *o*-toluonitrile-ethanol ($\text{CH}_3\text{C}_6\text{H}_4\text{CN}-\text{C}_2\text{H}_5\text{OH}$) mixture resulting in the replacement of both NCCH_3 ligands with $\text{CH}_3\text{C}_6\text{H}_4\text{CN}$ to form **3**. The labile nature of the nitrile ligands around these complexes demonstrate their usefulness as precursors to a range of ruthenium(II) complexes and this fact was investigated through the following reactions.

The known cationic salt **4** was prepared by reaction of **2** with a solution of NH_4PF_6 in acetonitrile under reflux for 15 min [2]. Compound **4** has spectroscopic (IR, ^1H , and ^{13}C NMR) assignment in agreement with literature reports [2]. The lability of the halide ligand is exhibited by precipitation of NH_4Cl from the reaction of **2** with NH_4PF_6 as described [2]. Treatment of the tris(acetonitrile) complex **4** with excess of tris(4-fluorophenyl)phosphine in acetonitrile under reflux for 1 h yielded a new complex **5** with the stoichiometry corresponding to $[\text{RuCl}(\text{NCCH}_3)_3(\text{P}(\text{4-FC}_6\text{H}_4)_3)_2][\text{PF}_6]$ ($\text{P}(\text{4-FC}_6\text{H}_4)_3 = \text{tris}(4\text{-fluorophenyl})\text{phosphine}$). This fluorophenyl-phosphine complex is characterized by disappearance of the cyclooctadiene signals both in its IR and NMR spectra and the appearance of phenyl protons at the expected region between δ_{H} 7.24 and 7.96 ppm in its ^1H NMR spectrum. The acetonitrile signal was observed at δ_{H} 1.93 ppm in the ^1H NMR spectrum of the complex. The ^{13}C -NMR spectral data of **5** (figure S3(d)) also support the proposed stoichiometry. The acetonitrile carbon signals were observed at δ_{C} 3.35 and 115.64 ppm, respectively, for CH_3 and CN while those due to coordinated tris(4-fluorophenyl)phosphine moiety were present at δ_{C} 115.85 and 136.23 ppm for aromatic CH, 127.71 ppm for aromatic CP and 164.40 ppm for aromatic CF [14(b)]. The coordinated $\text{P}(\text{4-FC}_6\text{H}_4)_3$ was observed as a single line at δ_{P} 26.77 ppm in the ^{31}P NMR spectrum of **5** (figure S3(c)) while the uncoordinated PF_6 appeared at δ_{P} -144.56 ppm as obtained for **4** (figure S2(c)).

Reaction of **2** with *tert*-butyl isocyanide under reflux in acetonitrile gave a compound with stoichiometry corresponding to $[\text{RuCl}_2(\text{t-BuNC})_3(\text{NCCH}_3)]$ (**6**) (figure 1(b)) which was characterized by both analytical and spectroscopic techniques. The characteristic isocyanide $\nu(\text{CN})$ band was observed at ν 2124 cm^{-1} in its IR spectrum. In the ^{13}C NMR spectrum of **6**, signal due to the tertiary carbon was observed at δ_{H} 56.64 ppm while the chemically equivalent methyl carbons were present at δ_{H} 30.99 ppm as a single line.

Complex **7** was prepared by a ligand-exchange reaction of **2** with excess molar equivalents of diphenylphosphine ligand. Suspension of **2** with diphenylphosphine in acetonitrile was stirred continuously at 78°C for 19 h to obtain an orange solution. The orange solution was reduced to half its original volume under reduced pressure and then stored in the freezer for at least two weeks, after which yellow crystalline solids precipitate. When reactions of **7** were performed with less than four molar equivalents of diphenylphosphine, a mixture of products, which could not be easily purified, was obtained. The structure of the chloroform

solvate of **7** has been reported but the synthetic procedure was not reported. Its analytical and spectroscopic data were also not previously reported [19].

The ^1H NMR spectrum of **7** displayed multiplet signals between δ_{H} 7.01 and 7.71 ppm attributable to protons on the diphenylphosphine ligands. In its ^{13}C NMR spectrum, resonances due to the aromatic carbons on diphenylphosphine were observed between δ_{C} 127.39 and 133.62 ppm as five distinct lines due to P–C being a doublet. The observed singlet at δ_{P} 19.50 ppm in the ^{31}P NMR spectrum of **7** suggests that the phosphorus atoms are in the same environment.

3.1. X-ray analysis of **4**

The yellow complex crystallized with a prism morphology in the monoclinic space group C2/c having eight molecules in the unit cell ($Z = 8$). The crystal structure shows three acetonitrile ligands coordinated to ruthenium, one axial and two equatorial, and a chloride *trans* to the axial acetonitrile ligand (figure 2). The equatorial coordinated nitrogen-donor ligand is *trans* to the cyclooctadiene ligand. Yellow needle-like crystals were obtained from addition of ethanol and diethyl ether to the reaction solution and placed in the refrigerator overnight. Table 2 shows selected bond lengths and angles of **4**, respectively. A similar complex was reported by Tubaro and co-workers [20]. However, the crystal system, monoclinic, of the complex obtained differed from that stated in the literature which is orthorhombic. The Ru–Cl bond of 2.4091(4) Å was identical to that reported, 2.4062(14). In addition, the Ru–N bond lengths observed, Ru1A–N1A 2.0686(16) Å and Ru1A–N3A 2.0450(15) Å, correspond with those in the

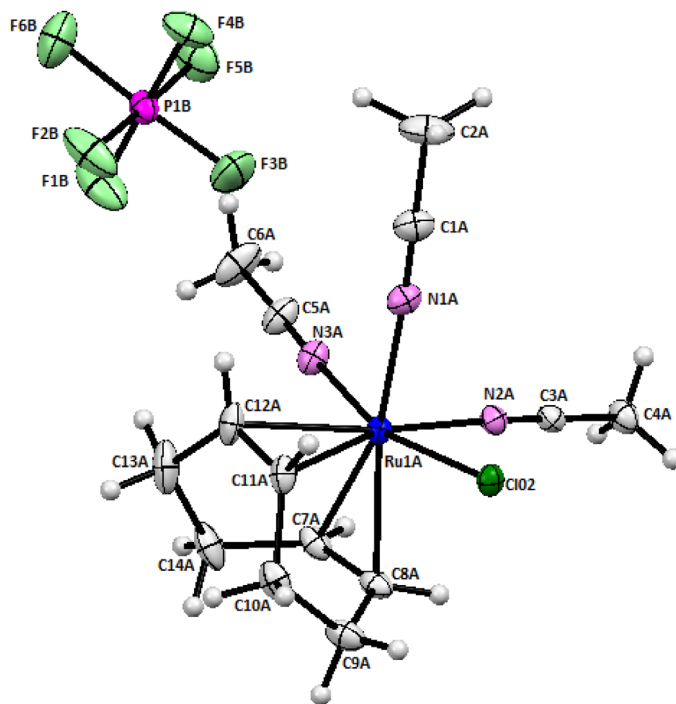


Figure 2. Molecular diagram of **4**, $[\text{RuCl}(1,5\text{-COD})(\text{NCCH}_3)_3]\text{PF}_6$.

literature, Ru1–N1 2.066(4) and Ru1–N3 2.045(4). However, Ru1A–N2A 2.0691(14) Å is slightly longer than that reported, Ru1–N2 2.044(4). The crystal structure of **4** shows a slight octahedral distortion as seen by the bond angle Cl02–Ru1A–N3A = 163.00(5).

3.2. X-ray analysis of **7**

Crystals of **7** suitable for X-ray diffraction studies were grown by slow evaporation of dichloromethane-methanol solution at room temperature. The ORTEP diagram with atom numbering scheme is presented in figure 3 while the details of the structural refinement are given in table 1. Selected bond lengths and angles are given in table 2. There are two half molecules of **7** located on inversion centers in the asymmetric unit with similar bond lengths and angles. For example, the Ru–P average bond distances in molecule 1 (shown in figure 2) are 2.3407(7) and 2.3606(7) Å compared to 2.3426(7) and 2.3446(6) Å for molecule 2. The Ru–Cl distances in molecule 1 are slightly shorter than in molecule 2. The octahedral environment of the ruthenium(II) center consists of four molecules of diphenylphosphine and two chloride ligands coordinated to ruthenium *trans* to each other in an almost ideal octahedral arrangement to Ru²⁺. The compound is monomeric with the equatorial plane occupied by four diphenylphosphine ligands coordinated through P while the two chloride ions occupy the axial positions. The mean Ru–P distance is 2.3506(7) Å while the P–C distances are 1.815(3)–1.836(3) Å.

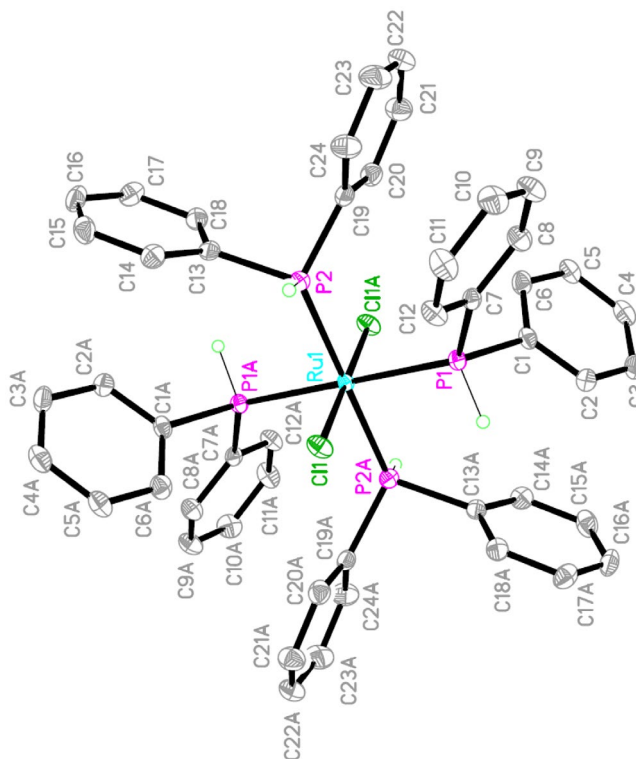


Figure 3. ORTEP diagram of one of the two crystallographically independent molecules of **7** showing atom-numbering scheme with thermal ellipsoids drawn at 50% probability level. Hydrogens are omitted for clarity except those on P which have been drawn with arbitrary radii.

Table 1. Summary of X-ray parameters for **4**, **7**, and **7'**, respectively.

	4	7	7'
Empirical formula	C ₁₄ H ₂₁ ClN ₃ F ₆ PRu	C ₄₈ H ₄₄ Cl ₂ P ₄ Ru	C ₄₈ H ₄₄ Cl ₂ P ₄ Ru
Formula weight (g.mol ⁻¹)	512.83	916.68	916.68
Temperature (K)	100	100	100
Wavelength (Å)	0.711 (Mo Kα)	0.694 (Mo Kα)	0.711 (Mo Kα)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P-1	P-1
Crystal size (mm)	0.38 × 0.24 × 0.17	0.20 × 0.18 × 0.10	0.27 × 0.18 × 0.15
Unit cell dimensions (Å, °)	<i>a</i> = 27.0510(3) <i>α</i> = 90 <i>b</i> = 11.0984(13) <i>β</i> = 97.08(3) <i>c</i> = 13.0450(16) <i>γ</i> = 90	<i>a</i> = 12.7016(9) <i>α</i> = 101.46(3) <i>b</i> = 13.0847(10) <i>β</i> = 95.51(3) <i>c</i> = 14.1498(10) <i>γ</i> = 113.07(3)	<i>a</i> = 10.0828(1) <i>α</i> = 71.03(3) <i>b</i> = 10.5026(1) <i>β</i> = 71.73(3) <i>c</i> = 11.6730(1) <i>γ</i> = 87.79(3)
Volume (Å ³)	3886.5(8)	2080.6(3)	1107.3(2)
<i>Z</i>	8	2	1
Density (calculated, mg.m ⁻³)	1.753	1.463	1.375
<i>F</i> (0 0 0)	2048	940	470
2 θ range collection (°)	3.034–66.3	2.35–25.41	3.89–61.32
Total reflections	44,323	25,102	23,433
Independent reflections	7402	7595	6838
Number of refined parameters	319	138	286
Goodness of fit on <i>F</i> ²	1.033	1.063	1.042
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0282, <i>wR</i> ₂ = 0.0703	<i>R</i> ₁ = 0.0309, <i>wR</i> ₂ = 0.0668	<i>R</i> ₁ = 0.0347, <i>wR</i> ₂ = 0.0837
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0324, <i>wR</i> ₂ = 0.0727	<i>R</i> ₁ = 0.0430, <i>wR</i> ₂ = 0.0711	<i>R</i> ₁ = 0.0442, <i>wR</i> ₂ = 0.0889
Largest diffraction peak and hole (e.Å ⁻³)	1.28/–0.58	0.89/–0.39	0.73/–0.23

Table 2. Selected bond lengths (Å) and angles (°) for **4**.

Ru1A–C102	2.409(4)	Ru1A–C7A	2.228(17)
Ru1A–N1A	2.069(16)	Ru1A–C8A	2.230(17)
Ru1A–N2A	2.069(14)	Ru1A–C11A	2.238(17)
Ru1A–N3A	2.045(15)	Ru1A–C12A	2.241(17)
C102–Ru1A–N3A	163.00(5)	C102–Ru1A–N2A	85.27(4)
C102–Ru1A–N1A	83.34(4)	N2A–Ru1A–N1A	92.12(6)

Average Ru–P bond distance of 2.3506(7) Å in **7** is slightly shorter than that reported for the chloroform solvate moiety [20]. The Ru–Cl bond length in molecule **1** is 2.4203(6) Å, significantly shorter than 2.4317(8) Å reported for Ru–Cl in the chloroform solvate of **7** but almost identical with Ru–Cl bond distance of 2.4315(6) Å found in molecule **2**. The crystal parameters of the polymorph **7'** are shown in table 1.

Supplementary material

CCDC 1517703, 1537045 and 885048 contains the supplementary crystallographic data for **4**, **7'** and **7**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. The IR and NMR (¹H, ¹³C and ³¹P) spectra of the complexes reported in this paper are available in the Electronic Supporting Information accompanying this article.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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