

Synthesis and characterization of some mono and binuclear ($\eta^3:\eta^3\text{-C}_{10}\text{H}_{16}$) containing ruthenium(IV) complexes. Crystal structure of $[\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{CNPy})]$

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Abstract

Reaction of $[\{\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2]$ with 4-cyanopyridine (referred hereafter as (CNPy) in dichloromethane in 1:2 and 1:1 molar ratio gives mononuclear complex $[\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{CNPy})]$ (**1**) and binuclear complex $[\{\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\}_2(\mu\text{-CNPy})]$ (**2**) in quantitative yield. The mononuclear complex **1** reacts further with the chloro bridged arene Ru(II) complexes $[\{\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\mu\text{-Cl})\text{Cl}\}_2]$, $[\{\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})(\mu\text{-Cl})\text{Cl}\}_2]$, $[\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\mu\text{-Cl})\text{Cl}\}_2]$ and the rhodium complex $[\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-Cl})\text{Cl}\}_2]$, to form Ru(IV)–Ru(II) or Ru(IV)–Rh(III) binuclear complexes, in which the respective metal centers are bridged by a 4-cyanopyridine ligand. The reaction products have been characterized by microanalyses and spectroscopic studies (IR, ¹H-, ¹³C-NMR and FAB mass spectra). The structure of the complex $[\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{CNPy})]$ has been confirmed by single-crystal X-ray analysis. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ru(IV) complexes; 2,7-Dimethyloctadienediyl; 4-Cyanopyridine; Metallo-ligand; Synthone

1. Introduction

Organometallic compounds of ruthenium in high formal oxidation states and possible application of such compounds in homogeneous catalysis are rather interesting [la–c]. In this regard Ru(IV) dimeric chloro bridged bis-allyl complex $[\{\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2]$ have drawn special attention [2a–g]. Its reaction with a variety of Lewis-bases and coordinating solvents to form mononuclear complexes $[\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{CNPy})]$ has been taken up extensively [3a–d]. However, there are only a few reports dealing with the dimeric complexes [4a–c]. Literature further reveals that the reactivity of $[\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{CNPy})]$ with potential bridging organonitriles having two or more donor sites, viz. 4-cyanopyridine, 1,4-dicyanobenzene, 1,4-piperazinedicarbonitrile, 1,4-dicyanotrans-2-butene etc., have not been examined despite detailed reports concerning complexes of these ligands with a number of

metal ions [5a–g]. In view of the potential synthetic importance of $[\{\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2]$, and because of our continuing interest in structurally related arene ruthenium complexes $[\{\text{Ru}(\eta^6\text{-arene})\text{Cl}(\mu\text{-Cl})\}_2]$, we have started a systematic study on the reactivity of $[\{\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2]$ with organonitriles.

Our prime concern in undertaking this study was (a) to investigate relative donor capabilities of the donor sites in the 4-cyanopyridine molecule in the formation of mono or binuclear complexes, (b) to investigate the possibility of formation of homo or hetero bimetallic mixed valence bridged complexes containing 2,7-dimethyloctadienediyl ($\eta^3:\eta^3\text{-C}_{10}\text{H}_{16}$) group as a spectator ligand. We describe herein the characterized mono and binuclear complexes obtained by the interaction of $[\{\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2]$ with 4-cyanopyridine and the application of the resulting mononuclear complex $[\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{CNPy})]$ in the synthesis of Ru(IV)–Ru(II) or Ru(IV)–Rh(III) 4-cyanopyridine bridged complexes $[\{\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\text{Ru}(\mu\text{-CNPy})\text{Ru}(\eta^6\text{-arene})\text{Cl}_2(\eta^6\text{-arene})]$ ($\eta^6\text{-arene}$ = benzene, *p*-cymene or hexamethylbenzene). Also, we present herein the single-

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crystal X-ray structure of the complex $[\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{CNPy})]$.

2. Experimental

2.1. Materials

Analytically or chemically pure grade reagents were used throughout. All the synthetic manipulations were performed under nitrogen atmosphere. The solvents were dried and distilled by standard procedures before use. 4-Cyanopyridine (Aldrich) was purified from hot 90% ethanol prior to its use. Hydrated ruthenium(III) chloride, isoprene, 1,3-cyclohexadiene, hexamethylbenzene, pentamethylcyclopentadiene (all Aldrich) and α -phellandrene (Fluka) were used as received without further purification. The complexes $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2]$, $[\{\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\mu\text{-Cl})\text{Cl}\}_2]$, $[\{\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})(\mu\text{-Cl})\text{Cl}\}_2]$, $[\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\mu\text{-Cl})\text{Cl}\}_2]$, $[\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-Cl})\text{Cl}\}_2]$ were prepared and purified following the literature procedures [3c,7,8].

2.2. Physical measurements

The melting points of the complexes were recorded on a Jyoti melting point apparatus in air. Micro-analytical data of the complexes were obtained from R.S.I.C., Central Drug Research Institute, Lucknow. IR spectra (Nujol mull) of the complexes were recorded on Shimadzu 8201PC spectrophotometer. ^1H - and ^{13}C -NMR spectra in CDCl_3 with tetramethylsilane as the internal standard, were recorded on a Bruker-DRX-300 NMR instrument. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature (r.t.) and *m*-nitrobenzyl alcohol was used as the matrix. The X-ray single-crystal diffraction data for the complex $[\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{CNPy})]$ were obtained on a Nonius MACH3 diffractometer.

2.3. Syntheses

2.3.1. Preparation of $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{CNPy})\}]$ (**1**)

A solution of $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2]$ (308 mg, 0.5 mmol.) in dichloromethane (25 ml) was treated with 4-cyanopyridine (104 mg, 1.0 mmol.). The resulting orange–red solution was stirred at r.t. for 1 h then filtered through celite and evaporated to dryness under reduced pressure. The orange–red powder thus obtained was extracted with dichloromethane. The dichloromethane extract was layered with light petroleum ether (40–60°) and left for slow crystalliza-

tion. After a couple of days, shiny golden crystals separated. These were filtered, washed a couple of times with light petroleum ether and dried under vacuum; yield 380 mg (95%). M.p. 180°C. Anal. Calc. for $\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Ru}$: C, 46.60; H, 4.85; N, 6.79. Found: C, 46.67; H, 5.01; N, 6.73%. IR (Nujol). 2240 cm^{-1} .

2.3.2. Preparation of $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\}_2(\mu\text{-CNPy})]$ (**2**)

It was prepared following the above procedure starting from $[\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2]$ and 4-cyanopyridine in 1:1 molar ratio. The complex separated as red–brown crystalline solid; yield, (85%). M.p. 250°C. Anal. Calc. for $\text{C}_{26}\text{H}_{36}\text{Cl}_4\text{N}_2\text{Ru}_2$: C, 433.3; H, 5.00; N, 3.85. Found: C, 43.20; H, 5.16; N, 3.92%. IR (Nujol): 2253 cm^{-1} .

2.3.3. Preparation of $[\{\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\text{Ru}(\mu\text{-CNPy})\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2]$ (**3**)

Complex **1** (206 mg, 0.5 mmol) dissolved in dichloromethane (25 ml) was treated with $[\{\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\mu\text{-Cl})\text{Cl}\}_2]$ (125 mg, 0.25 mmol) and heated under reflux for about 4 h. The resulting red–brown solution was filtered through celite and was evaporated to dryness under vacuum. The solid mass obtained was extracted with dichloromethane, filtered and saturated with light petroleum ether. After a couple of hours a brown microcrystalline product separated. It was filtered, washed with petroleum ether and dried under vacuum; yield (75%). Anal. Calc. for $\text{C}_{22}\text{H}_{26}\text{C}_4\text{N}_2\text{Ru}_2$: C, 39.87; H, 3.92; N, 4.22. Found: C, 39.67; H, 3.98; N, 4.02%. IR (Nujol): 2262 cm^{-1} .

2.3.4. Preparation of $[\{\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\text{Ru}(\mu\text{-CNPy})\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})\text{Cl}_2]$ (**4**)

This complex was prepared starting from complex **1** and $[\{\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})(\mu\text{-Cl})\text{Cl}\}_2]$ in a 2:1 molar ratio following the above procedure. It was separated as a red–brown crystalline solid; yield (75%). Anal. Calc. for $\text{C}_{26}\text{H}_{34}\text{Cl}_4\text{N}_2\text{Ru}_2$: C, 43.45; H, 4.73; N, 33.89. Found: C, 42.23; H, 5.02; N, 3.82%. IR (Nujol): 2258 cm^{-1} .

2.3.5. Preparation of $[\{\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\text{Ru}(\mu\text{-CNPy})\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2]$ (**5**)

It was prepared from the reaction of the complex **1** with $[\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\mu\text{-Cl})\text{Cl}\}_2]$ in a 2:1 molar ratio following the above procedure. It was separated as dark tan crystals; yield (70%). Anal. Calc. for $\text{C}_{28}\text{H}_{38}\text{Cl}_4\text{N}_2\text{Ru}_2$: C, 45.06; H, 5.09; N, 3.75. Found: C, 45.02; H, 5.12; N, 33.82%. IR (Nujol): 2255 cm^{-1} .

2.3.6. Preparation of $[\{\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2\text{Ru}(\mu\text{-CNPy})\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]$ (**6**)

It was prepared following the above procedure starting from complex **1** with $[\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-Cl})\text{Cl}\}_2]$ in

a 2:1 molar ratio. The red–brown complex was obtained in more than a 70% yield. Anal. Calc. for $C_{26}H_{35}Cl_4N_2RhRu$: C, 43.27; H, 4.85; N, 3.88. Found: C, 42.97; H, 4.82; N, 86%. IR (Nujol): 2252 cm^{-1} .

2.4. X-ray structure of $[Ru(\eta^3\text{-}\eta^3\text{-}C_{10}H_{16})Cl_2(CNPy)]$ (**1**)

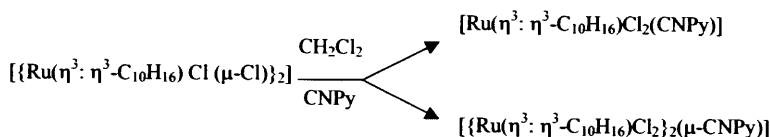
Single crystals of $[Ru(\eta^3\text{-}\eta^3\text{-}C_{10}H_{16})Cl_2(CNPy)]$ (**1**) were grown from dichloromethane/petroleum ether at r.t. Crystals suitable for X-ray diffraction studies were chosen from the crop of crystals obtained and mounted on a Nonius MACH3 diffractometer (graphite monochromatized Mo– K_α radiation) for the cell determination and intensity data collection. The unit cell parameters were derived and refined by using randomly selected reflections in the θ range 8–11. The structures were solved by direct methods and refined by using MAXUS (1999), SHELX-97 methods, respectively, [9a–c]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

2.5. Crystal data for complex **1**

$C_{16}H_{20}Cl_2N_2Ru_1$, $M = 41231$, Triclinic, $P\bar{1}$, $a = 8.598(3)$, $b = 10.889(2)$, $c = 20.848(2)$ Å, $\alpha = 74.891(12)$, $\beta = 833.161(14)$, $\gamma = 66.816(18)^\circ$, $U = 17331.9$ Å³, $D_{\text{calc}} = 1.581$ Mg m⁻³, $Z = 4$, $F(000) = 832$, $\lambda = 0.71073$ Å, $\mu = 1.208$ mm⁻¹, total/unique reflections = 6296/6071 [$R_{\text{int}} = 0.0120$], $T = 293$ K, θ range = $1.01\text{--}24.92^\circ$, Final R [$I > 2\sigma(I)$]: $R_1 = 0.0332$, $wR_2 = 0.899$, R_1 (all data): $R_1 = 0.03380$, $wR_2 = 0.097$.

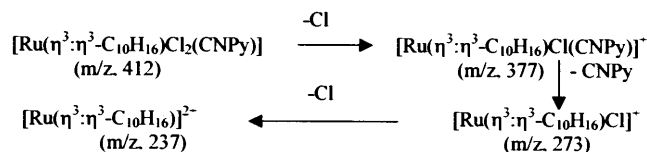
3. Results and discussion

Reaction of the chloro-bridged dimeric complex $[Ru(\eta^3\text{-}\eta^3\text{-}C_{10}H_{16})(\mu\text{-Cl})Cl]_2$, with 4-cyanopyridine at r.t. in dichloromethane in a 1:2 and 1:1 molar ratio rapidly leads in the formation of the mononuclear $[Ru(\eta^3\text{-}\eta^3\text{-}C_{10}H_{16})Cl_2(CNPy)]$ (**1**) and binuclear complex $[Ru(\eta^3\text{-}\eta^3\text{-}C_{10}H_{16})Cl_2]_2(\mu\text{-CNPy})$ (**2**) in a quantitative yield according to the following scheme:



These are air stable, non-hygroscopic micro-crystalline solids soluble in common organic solvents viz., dichloromethane, chloroform, dimethyl-sulfoxide, dimethylformamide, acetonitrile slightly soluble in benzene, methanol, ethanol and insoluble in diethyl ether

and petroleum ether. Analytical data of the complex **1** is in good agreement with our formulation. The FAB mass spectra of the complex **1** displayed the following fragmentation pattern, which strongly supported our formulation of the complex.



The IR spectrum of complex **1** displayed a sharp band at 2240 cm^{-1} corresponding to $\nu(C\equiv N)$. The position of this band remained practically unaltered, as compared to that in the free ligand (2242 cm^{-1}). It therefore, indicated linkage of the ligand 4-cyanopyridine, through pyridine ring nitrogen. Further support for the bonding through pyridine ring nitrogen is shown by the shifts in the position of pyridine ring vibrations in the region $1600\text{--}1400\text{ cm}^{-1}$ having contributions from $\nu(C\text{--}C)$ and $\nu(C\text{--}N)$ towards high wave numbers [10]. The ¹H-NMR spectrum of complex **1** (Table 1) displayed resonances at δ 9.48 (*d*, 2H, 6.33 Hz), 7.56 (*d*, 2H, 63 Hz), 5.31 (*m*, 4H), 4.58 (*s*, 4H), 4.48 (*s*, 4H), 3.06 (*m*, 4H) and 2.40 (*s*, 6H) ppm corresponding, to the coordinated 4-cyanopyridine and 2,7-dimethyloctadienediyl ligand. The presence of only two terminal allyl singlets (δ 4.58 and 4.48 ppm) and a single methyl resonance (δ 2.40 ppm) in the ¹H-NMR spectrum indicated chemical equivalence of the two allyl moieties in complex **1**. It is consistent with the one found in simple adducts of the complex $[Ru(\eta^3\text{-}\eta^3\text{-}C_{10}H_{16})(\mu\text{-Cl})Cl]_2$ containing equatorially coordinated monodentate ligands [3]. The ¹³C{¹H}-NMR spectrum of complex **1** exhibited resonances at δ 156.1, 131.7, 125.3, 121.7, 116.6, 96.3, 79.5, 36.0 and 21.1 ppm corresponding to the carbons of coordinated 4-cyanopyridine and 2,7-dimethyloctadienediyl. It followed the trends observed in ¹H-NMR spectrum and further indicated chemical equivalence of the allyl groups of the 2,7-dimethyloctadienediyl ligand in complex **1**. The nitrile carbon of the cyanopyridine ligand resonated at δ 117.6 ppm. It displayed a downfield as compared to that in the free ligand (116.0 ppm). The

analytical and spectral (IR, ¹H, ¹³C{¹H}) data of complex **1** strongly indicated linkage of the cyanopyridine ligand through its pyridine ring nitrogen. This observation is consistent with the earlier reports [11a–e]. Linkage of the cyanopyridine through aromatic ring

Table 1
¹H-NMR spectral data of the complexes

Sample number	Complex	Terminal allyl	Internal allyl	–CH ₂ –	Me	Arene	Others
1	[Ru(η ³ :η ³ -C ₁₀ H ₁₆)Cl ₂ (CNPy)]	4.58 (<i>s</i> , 4H)	5.31 (<i>m</i> , 4H)	3.06 (<i>m</i> , 4H)	2.40 (<i>s</i> , 6H)		9.48 (<i>d</i> , 2H, 6.3 Hz); 7.56 (<i>d</i> , 2H, 6.3 Hz)
2	[{Ru(η ³ :η ³ -C ₁₀ H ₁₆)Cl ₂ } ₂ (μ-CNPy)]	4.48 (<i>s</i> , 4H) 4.74 (<i>m</i>)	5.33 (<i>m</i>)	3.03 (<i>m</i>)	2.43 (<i>s</i>)		9.5 (<i>d</i> , 2H, 6.8 Hz); 7.52 (<i>d</i> , 2H, 6.8 Hz)
3	[Ru(η ³ :η ³ -C ₁₀ H ₁₆)Cl ₂ (μ-CNPy) Ru(η ⁶ -C ₆ H ₆)Cl ₂]	4.49 (<i>m</i>) 4.72 (<i>s</i> , 4H)	5.02 (<i>m</i> , 4H)	3.07 (<i>m</i> , 4H)	2.30 (<i>s</i> , 6H)	5.95 (<i>s</i> , 6H)	8.28 (<i>d</i> , 2H, 6.5 Hz)
4	[Ru(η ³ :η ³ -C ₁₀ H ₁₆)Cl ₂ (μ-CNPy) Ru(η ⁶ -C ₁₀ H ₁₄)Cl ₂]	3.85 (<i>s</i> , 4H) 4.84 (<i>s</i> , 2H);	5.17 (<i>m</i> , 4H)	3.06 (<i>m</i> , 4H)	2.38 (<i>s</i> , 6H)	5.59–5.33 (AB, 4H, 6.8 Hz); 2.92 (<i>sep</i> , 1H, 6.8 Hz); 2.13 (<i>s</i> , 3H); 1.25 (<i>dd</i> , 6H, 6.8 Hz)	9.47 (<i>d</i> , 2H, 6.2 Hz); 7.584 (<i>d</i> , 2H, 6.2 Hz)
5	[Ru(η ³ :η ³ -C ₁₀ H ₁₆)Cl ₂ (μ-CNPy) Ru(η ⁶ -C ₆ Me ₆)Cl ₂]	4.53 (<i>s</i> , 2H) 4.86 (<i>s</i> , 2H);	5.19 (<i>m</i> , 4H)	3.09 (<i>m</i> , 4H)	2.46 (<i>s</i> , 6H)	2.12 (<i>s</i> , 18H)	8.65 (<i>d</i> , 2H, 5.4 Hz); 7.92 (<i>d</i> , 2H, 5.4 Hz)
6	[Ru(η ³ :η ³ -C ₁₀ H ₁₆)Cl ₂ (μ-CNPy) Rh(η ⁵ -C ₅ Me ₅)Cl ₂]	4.48 (<i>s</i> , 2H) 4.86 (<i>s</i> , 2H)	5.26 (<i>m</i> , 4H)	3.08 (<i>m</i> , 4H)	2.36 (<i>m</i> , 4H)	1.65 (<i>s</i> , 15H)	8.88 (<i>d</i> , 2H, 5.8 Hz); 7.96 (<i>d</i> , 2H, 5.8 Hz)
		4.32 (<i>s</i> , 2H)					

nitrogen has further been confirmed by single-crystal X-ray diffraction studies. The nitrile group in this complex is present as a pendant group, due to the presence of the pendant nitrile group, the molecule therefore offers an unique opportunity of behaving as a metallo-ligand or as a synthon in the synthesis of homo- or hetero- bimetallic mixed valence complexes.

The IR spectrum of complex **2** displayed a sharp band at 2224 cm^{-1} corresponding to $\nu(\text{C}\equiv\text{N})$. It showed an increase in the nitrile stretching frequency as compared to that in complex **1** or the free cyanopyridine ligand (2242 cm^{-1}). It suggested coordination of the nitrile group with the metal center and poor π back donation from ruthenium to the π^* orbitals of the nitrile group. The $^1\text{H-NMR}$ spectrum of complex **2** showed doubling of the signals in the same region as that for complex **1**. It displayed broad multiplets corresponding to the terminal allyl protons and internal allyl protons while the remaining 2,7-dimethyloctadienediyl protons gave two sets of resonances (Table 1). The doubling of the signals is not unexpected, it could result from the difference in the local electron density on the ($\eta^3:\eta^3\text{-C}_{10}\text{H}_{16}$) protons, which could arise from the nature of M–L bonding of the two Ru(IV) centers (one bonded to an aromatic nitrogen atom and the other bonded to the nitrile nitrogen atom). On comparison with the elemental and spectral data of complex **1** it was elucidated that complex **2** is a binuclear complex in which two Ru(IV) centers are bridged by a 4-cyanopyridine ligand.

The mononuclear complex **1** reacts further with the complexes [$\{\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\mu\text{-Cl})\text{Cl}\}_2$], [$\{\text{Ru}(\eta^6\text{-C}_{10}\text{H}_{14})(\mu\text{-Cl})\text{Cl}\}_2$], [$\{\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\mu\text{-Cl})\text{Cl}\}_2$] and [$\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-Cl})\text{Cl}\}_2$] to form Ru(IV)–Ru(II) or Ru(IV)–Rh(III) binuclear complexes **3–6**. The elemental data

for the complexes **3–6** are in excellent agreement with our formulation. The FAB mass spectra for one of the representative complex, **3** is shown in Fig. 1. In the FAB mass spectra of the complexes **3–6** exhibited peaks were observed at m/z values 661, 718, 746 and 718, respectively. The presence of these peaks in the FAB mass spectra of the respective complexes strongly supported the binuclear nature of these complexes. The IR spectra of the complexes show a sharp band in the nitrile stretching frequency region ($2256\text{--}2262\text{ cm}^{-1}$) corresponding to $\nu(\text{C}\equiv\text{N})$. It exhibited a shift towards the high wave number side as compared to that in complex **1**. The shift of the band at 2240 cm^{-1} to a higher wave number implies direct coordination of the ruthenium in complexes **3–5** or rhodium in complex **6** with the nitrogen atom of the pendant nitrile group in complex **1**. Furthermore, the shift also indicates poor back bonding from ruthenium or rhodium into π^* orbitals of the nitrile group. The analytical and spectral data IR, $^1\text{H-NMR}$ (Table 1) **3–6** correspond to cyanopyridine bridged binuclear complexes in which the respective metal centers are bridged by the 4-cyanopyridine ligand.

Reactions of the complex [$\text{Ru}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\mu\text{-Cl})\}_2$] with 1,4-dicyanobenzene (DCB), 1,4-piperidine-carbonitrile (PPd), 1,4-piperazinedicarbonitrile (PPd) and 1,4 dicyanotrans-2-butene (DCBT) under varying reaction conditions have also been carried out. The reaction of [$(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{RuCl}(\mu\text{-Cl})\}_2$] with PPd gave a mononuclear complex however, its reaction with DCBT gave only a binuclear complex.

Detailed work dealing with the synthesis and characterization of homo or heterometallic binuclear complexes using complex **1** and other related mononuclear complexes as a metallo-ligand is in progress.

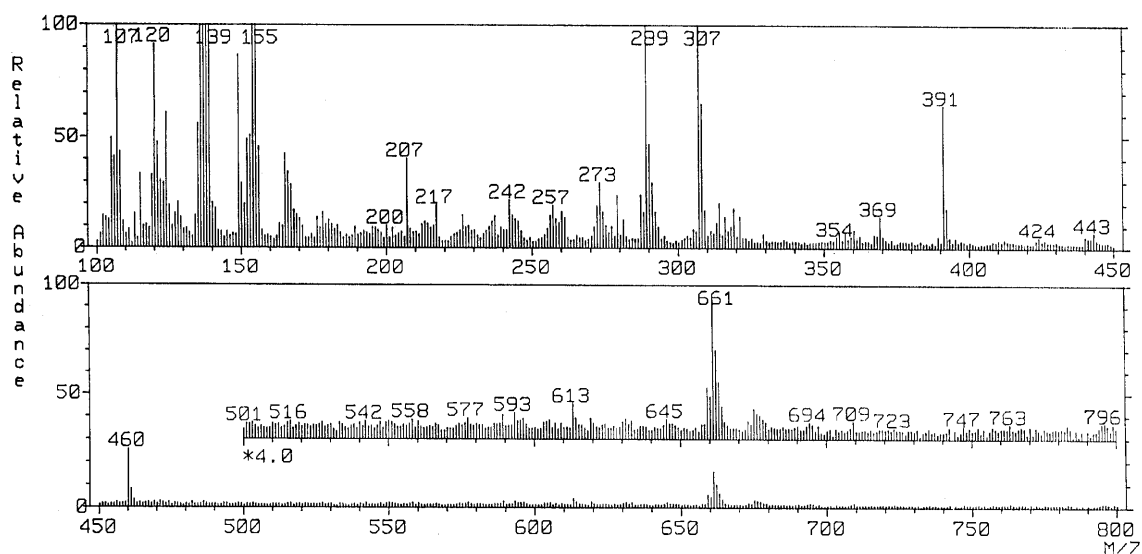


Fig. 1. FAB mass spectra of the complex **3**.

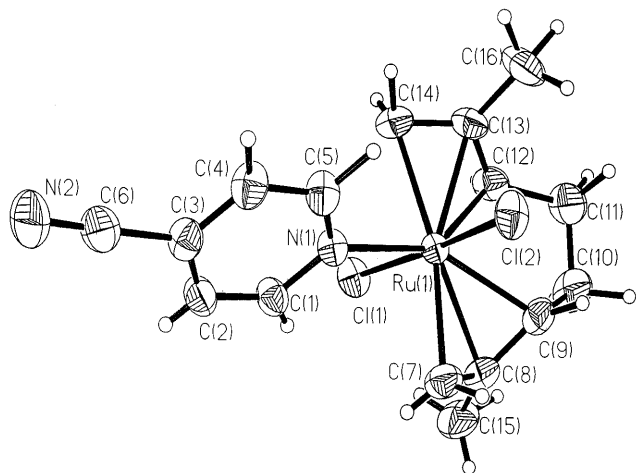


Fig. 2. An ORTEP view of the complex 1.

Table 2
Selected bond lengths (Å) and bond angles (°) for the complex 1^a

Ru(1)–N(1)	2.210(3)	N(2)–C(6)	1.133(6)
Ru(1)–Cl(7)	2.218(4)	C(7)–C(8)	1.403(6)
Ru(1)–C(8)	2.281(4)	C(8)–C(9)	1.404(6)
Ru(1)–C(9)	2.250(4)	C(8)–C(15)	1.513(6)
Ru(1)–C(12)	2.228(4)	C(9)–C(10)	1.506(6)
Ru(1)–C(13)	2.279(4)	C(10)–C(11)	1.502
Ru(1)–C(14)	2.232(4)	C(11)–C(12)	1.520
Ru(1)–Cl(2)	2.4133(11)	C(12)–C(13)	1.415(6)
Ru(1)–Cl(1)	2.4197(11)	C(13)–C(14)	1.408(6)
Ru(1)–D(1)	2.0328	C(13)–C(16)	1.491(6)
Ru(1)–D(2)	2.0190	Ru(2)–N(3)	2.202(3)
Ru(2)–C(23)	2.227(4)	Ru(2)–C(24)	2.285(4)
Ru(2)–C(25)	2.241(4)	Ru(2)–C(28)	2.242(4)
Ru(2)–C(29)	2.282(4)	Ru(2)–C(30)	2.210(4)
Ru(2)–Cl(3)	2.4027(13)	Ru(2)–Cl(4)	2.4308(13)
N(1)–Ru(1)–Cl(2)	85.62(8)	C(9)–C(8)–C(15)	124.0(4)
N(1)–Ru(1)–Cl(1)	86.24(8)	C(8)–C(9)–C(10)	124.1(4)
Cl(2)–Ru(1)–Cl(1)	171.85(3)	C(11)–C(10)–C(9)	105.4(4)
C(7)–Ru(1)–C(9)	63.82(15)	C(10)–C(11)–C(12)	105.5(4)
C(12)–Ru(1)–C(14)	64.80(14)	C(12)–C(13)–C(16)	123.5(4)
N(1)–Ru(1)–D(1)	114.35	C(14)–C(13)–C(12)	115.6(4)
N(1)–Ru(1)–D(2)	112.54	C(14)–C(13)–C(16)	120.6(4)
D(1)–Ru(1)–D(2)	133.11	N(3)–Ru(2)–Cl(3)	86.59(8)
C(7)–C(8)–C(9)	114.6(4)	N(3)–Ru(2)–Cl(4)	86.97(8)
C(7)–C(8)–C(15)	121.2(4)	Cl(3)–Ru(2)–Cl(4)	173.56(4)

^a D(1) and D(2) are centers of mass of the atoms C(7), C(8), C(9) and C(12), C(13), C(14), respectively.

3.1. Single-crystal X-ray structure of complex 1

The structure of complex 1 has been confirmed by single-crystal X-ray analysis. The crystal structure determination revealed the presence of two independent molecules in unit cell. However, both the molecules are structurally identical and for clarity only one is shown in Fig. 2. Selected bond lengths and angles are recorded in Table 2.

The coordination geometry about the ruthenium atom is distorted trigonal bipyramid. The ligand 4-cyanopyridine is coordinated with the metal center through its pyridine ring nitrogen atom, which occupies an equatorial position along with the allyl groups. Both the allyl groups of the 2,7-dimethyloctadienediyl ligand are η^3 -bound to the ruthenium atom with the Ru–C distances in the range [2.219(4)–2.281(4)] Å. The C–C distances and the internal C–C–C bond angles within the allyl groups are (1.45 Å, mean) and (115.1°, mean), respectively. These values are consistent with those reported for transition metal η^3 coordination [12a–b]. Arrangement of the 2,7-dimethyloctadienediyl group, which has a local C_2 symmetry is similar to that in the precursor complex [$\{Ru(\eta^3:\eta^3-C_{10}H_{16})Cl(\mu-Cl)\}_2$] and its PF_3 adduct [$\{Ru(\eta^3:\eta^3-C_{10}H_{16})Cl_2(PF_3)\}$] [13]. The methyl substituents C(15) and C(16) showed deviation from the allyl plane towards the ruthenium center by 3.4(4) and 4.0(4)°, respectively. This observation is consistent with the earlier report [2a]. The two chloro ligands are *trans* disposed [Cl(1)–Ru(1)–Cl(2), 171.85(3)] and occupy axial sites. The Ru(1)–Cl(1) and Ru(1)–Cl(2) distances are 2.4197(11) and 2.4133(11) Å, respectively. These are almost equal and comparable to Ru–Cl distances in the other related complexes [2a–c,4c].

The ligand 4-cyanopyridine is planar and inclined at an angle of 35.32° to the plane of metal ion Ru(1) and the two chloro ligands Cl(1) and Cl(2). The Ru(1)–N(1) bond length is 2.210(3) Å which is comparable to Ru–N in other related systems [2d,4c,14]. The nitrile bond length N(2)–C(6) in complex 1 is 1.1333(6) Å, which is very close to the one characteristic for sp³-N bond type and comparable with the CH_3CN complexes [$\{Ru(\eta^6-C_6H_6)(CH_3CN)_3\}^{2+}$, [$\{Ru(\eta^5-C_5H_5)(CH_3CN)_3\}^{2+}$] and closely related 4-cyanopyridine complex [$\{Ru(\eta^6-C_{10}H_{14})Cl_2(CNPy)\}$] [15a,b,6f].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 41431 for compound 1. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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