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Journal of Organometallic Chemistry 568 (1998) 13–20

Journal of Organo metallic Chemistry

Synthesis, characterization, reactivity and structure of some mono and binuclear (η^6-*p*-cymene)ruthenium(II) complexes

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Received 14 October 1997

Abstract

Reactions of $[\{Ru(\eta^6\text{-}C_{10}H_{14})Cl_2\}_2]$ ($\eta^6\text{-}C_{10}H_{14}$ = *p*-cymene $H_3C\text{–}C_6H_4\text{–}CH(CH_3)_2$) with 4-cyanopyridine (referred hereafler as CNPy) in 1:1 and 1:2 molar ratios in dichloromethane yields the binuclear complex $[\{Ru(\eta^6\text{-}C_{10}H_{14})Cl_2\}_2(\mu\text{-CNPy})]$ and the mononuclear complex $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(CNPy)]$. The latter complex further reacts with $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ and $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl]$ to give 4-cyanopyridine bridged complexes $[Cl_2(\eta^6\text{-}C_{10}H_{14})Ru(\mu\text{-CNPy})Ru(\mu^6\text{-}C_6Me_6)Cl_2]$ and $[Cl_2(\eta^6\text{-}C_{10}H_{14})Ru(\mu\text{-CNPy})Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$. The complex $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(CNPy)]$ also undergoes metathetical reactions with EPh_3 (E = P, As or Sb) to give complexes with the general formulations $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(EPh_3)]$, however its reaction with diphenylphosphinomethane (dppm) in a 1:1 ratio gives the mononuclear complex $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(dppm)]$ in which the dppm ligand is present in uncommon coordination mode (η^1-dppm). The reaction products have been characterized by microanalyses and spectroscopic studies (IR, ^{1}H-, ^{13}C-, ^{31}P-NMR). The structure of $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(CNPy)]$ [$a = 10.984(1)$, $b = 14.052(1)$, $c = 12.189(1)$ Å; $\beta = 114.810(1)°$; $V = 1707.8(4)$ Å^3; $D_{calc} = 1.596$ g cm^{-3}; monoclinic $P2_1/c$; $Z = 4$] and confirmation of uncommon coordination mode of dppm, in $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(dppm)]$ [$a = 11.504(3)$, $b = 19.532(3)$, $c = 15.942(3)$ Å; $\beta = 96.08(2)°$; $V = 3562(2)$ Å^3; $D_{calc} = 1.446$ g cm^{-3}; monoclinic $P2_1/n$; $Z = 4$] has been determined by X-ray crystallography.

Keywords: Arene–ruthenium complexes; Mononuclear complexes; Bridged ruthenium complexes; Metathetic reactions

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1. Introduction

Synthesis and characterization of arena–ruthenium complexes have drawn special attention owing to their catalytic potential and their use as precursors for the synthesis of Ru(0) and Ru(II) complexes ([1]a–g). In this regard, the *p*-cymene complex $[\{Ru(\eta^6\text{-}C_{10}H_{14})Cl_2\}_2]$ has been very important. Reactions of this molecule with a variety of Lewis bases, monodentate ligands, chiral bidentate ligands, aminoacids, peptides and nucleobases have been studied extensively [2–9]. However, its reactions with simple organonitriles viz. 4-cyanopyridine, 1,4-dicyanobenzene, 1,4-piperazinedicarbonitrile, tetracyanoethylene, etc., possessing two or more donor sites, have not been studied despite detailed reports concerning complexes of these ligands with a number of metal ions ([10]a–k). As a continuation of our studies on these systems ([11]a–c), we thought it worth while to make a detailed study of the reactivity of $[\{Ru(\eta^6\text{-}C_{10}H_{14})Cl_2\}_2]$ with 4-cyanopyridine. Our prime concern in undertaking this study was (a) to investigate relative donor capabilities of the two

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PII S0022-328X(98)00571-3

donor sites in the formation of mononuclear and/or, polynuclear complexes, (b) to investigate the possibility of formation of (η^6-$C_{10}H_{14}$) containing ruthenium(II) bi- and/or polynuclear bridged complexes. In this paper we report the reproducible synthesis and characterization of mononuclear pyridine N-bound complex [Ru(η^6-$C_{10}H_{14}$)Cl_2(CNPy)] and binuclear complex [{Ru(η^6-$C_{10}H_{14}$)Cl_2}$_2$(μ-CNPy)], in which the ligand 4-cyanopyridine serves as a bridge to two Ru(II) centers through its nitrile nitrogen, along with a few other related complexes. We also present the X-ray crystal structure of [Ru(η^6-$C_{10}H_{14}$)Cl_2(CNPy)] and confirm the presence of dppm ligand in an unusual coordination mode in the complex [Ru(η^6-$C_{10}H_{14}$)Cl_2(dppm)] for the first time by X-ray analysis.

2. Experimental

Analytical or chemically pure grade reagents were used throughout. All the reactions were carried out 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. Triphenylphosphine, triphenylarsine, triphenylstibine, hexamethylbenzene, dicyclopentadiene, ammonium hexafluorophosphate and $RuCl_3 \cdot xH_2O$ (Aldrich) were used as-received.

The starting complexes [{Ru(η^6-$C_{10}H_{14}$)Cl_2}$_2$], [{Ru(η^6-C_6Me_6)Cl_2}$_2$] and [Ru(η^5-C_5H_5)$(PPh_3)_2$Cl] were prepared following the literature procedures [12,13]. Melting points of the complexes were recorded by a Jyoti melting point apparatus in air. Microanalyses were performed by the microanalytical laboratory of R.S.I.C., Central Drug Research Institute, Lucknow. IR spectra in the range 4000–200 cm^{-1} in KBr pellets, ^1H-, ^{13}C- and ^{31}P-NMR with tetramethylsilane as the internal standard were recorded with a Perkin-Elmer 577 Bruker WM-400 MHz and Bruker DRX-300 MHz spectrometers. X-ray single crystal diffraction data for the complex [Ru(η^6-$C_{10}H_{14}$)Cl_2(CNPy)] were obtained on a Siemens P4 diffractometer and for the complex [Ru(η^6-$C_{10}H_{14}$)Cl_2(dppm)] on an AFC6S-Rigaku diffractometer.

2.1. Preparation of [Ru(η⁶-C₁₀H₁₄)Cl₂(CNPy)] **1**

[{Ru(η^6-$C_{10}H_{14}$)Cl_2}$_2$] (612 mg, 1.0 mmol) dissolved in dichloromethane (50 ml) was treated with 4-cyanopyridine (208 mg, 2.0 mmol) and the solution was heated under reflux for 1 h. The orange–red solution was cooled to r.t., filtered through celite and evaporated to dryness under reduced pressure. The solid residue was washed several times with petroleum ether, crystallized from dichloromethane–petroleum ether and dried in vacuum. Yield 655 mg (80%); m.p. 200°C; Anal. Calc. for $C_{16}Cl_2H_{18}N_2Ru$: C, 46.82; H, 4.39; N, 6.82; Cl, 10.72. Found: C, 46.7; H, 4.29; N, 6.62; Cl, 10.80; IR (KBr) 2039 cm^{-1} (νC≡N); ^1H-NMR ($CDCl_3$): δ 9.35 (d, αH–CNPy), 7.32 (d, βH–CNPy), 5.2–5.5 (AB pattern, C_6H_4), 2.90 (m, $CH(CH_3)_2$), 1.63 (s, C–CH_3), 1.57 (d, CH (CH_3)$_2$); $^{13}C\{^1H\}$-NMR ($CDCl_3$): 151.1 (αC–CNPy), 128.32 (βC–CNPy), 125.81 (γC–CNPy), 119.25 (C≡N, CNPy), 104.52 (C–$CHMe_2$), 96.4 (C–CH_3), 83.03 and 80.45 (C_6H_4), 30.76 ($CH(CH_3)_2$), 22.26 ($CH(CH_3)_2$), 18 27 (C–CH_3).

2.2. Preparation of [{Ru(η⁶-C₁₀H₁₄)Cl₂}₂(μ-CNPy)] **(2)**

This compound was prepared following the above procedure except that [{Ru(η^6-$C_{10}H_{14}$)Cl_2}$_2$] and 4-cyanopyridine were taken in 1:1 molar ratio. The compound separated as red–brown needles. Yield 65%: m.p. 175°C (decom.); Anal. Calc. for $C_{26}C_{14}H_{32}N_2Ru_2$: C, 43.58; H, 4.47; N, 3.91; Cl, 16.83. Found: C, 43.72; H, 4.25; N, 3.86; Cl, 20.52; IR (KBr) 2229 cm^{-1} (νC≡N); ^1H-NMR ($CDCl_3$): δ 9.30 (d, αH–CNPy), 7.54 (d, βH–CNPy), 5.36–5.60 (m, C_6H_4), 3.00 (m, $CH(CH_3)_2$), 1.863 (s, C–CH_3), 1.43 (m, $CH(CH_3)_2$); $^{13}C\{^1H\}$-NMR ($CDCl_3$): 156.1 (αC–CNPy), 129 (βC–CNPy), 125.9 (γC–CNPy), 121.7 (C≡N, CNPy), 104.0 (C–$CHMe_2$), 97.6 (C–CH_3), 89.6, 89.5, 82.9, 81.7, 81.4, 81.2, 80.5 (C_6H_4), 30.7, 30.4 ($CH(CH_3)_2$), 22.2, 22.1 ($CH(CH_3)_2$), 18.2, 15.7 (C–CH_3).

2.3. Preparation of [Ru(η⁶-C₁₀H₁₄)Cl₂(PPh₃)] **(3)**

To a suspension of **1** (410 mg, 1.0 mmol) in methanol (25 ml), triphenylphosphine (263 mg, 1.0 mmol) was added and the solution was heated under reflux. The suspension slowly dissolved and a bright red crystalline compound started separating from the solution. It was cooled to r.t. and the crystals were separated by filtration. These were washed several times with methanol, diethylether and dried in vacuum. Yield 70%; m.p. 245°C (decom.); Anal. Calc. for $C_{28}C_{12}H_{29}PRu$: C, 59.05; H, 5.09; Cl, 12.47. Found: C, 59.32; H, 5.25; Cl, 12.20; ^1H-NMR ($CDCl_3$): δ 7.22–7.93 (br, m, Ar PPh_3), 5.00–5.25 (AB pattern, C_6H_4). 2.84 (m, $CH(CH_3)_2$), 1.86 (s, C–CH_3), 1.06 (d, $CH(CH_3)_2$).

2.4. Preparation of [Ru(η⁶-C₁₀H₁₄Cl₂(AsPh₃)] **(4)**

This compound was obtained in the form of red microcrystals following the above procedure for **3** starting from **1** and triphenylarsine. Yield 60%; m.p. 195°C; Anal. Calc. for $AsC_{28}Cl_2H_{29}Ru$: C, 54.90; H, 4.74; Cl, 11.60. Found: C, 54.92; H, 4.54; Cl, 11.22; ^1H-NMR ($CDCl_3$): δ 7.2–7.8 (br, m, Ar $AsPh_3$), 5.12–5.36 (AB pattern, C_6H_4), 2.92 (m, $CH(CH_3)_2$), 1.84 (s, C–CH_3), 1.21 (d, $CH(CH_3)_2$).

2.5. Preparation of [Ru(η^6-$C_{10}H_{14}$)Cl_2($SbPh_3$)] (***5***)

This compound was also prepared following the procedure used for **3** starting from **1** and triphenylstibine. It separated out as red crystals. Yield 60%; m.p. 180°C (decom.); Anal. Calc. for $C_{28}Cl_2H_{29}RuSb$: C, 50.98; H, 4.40; Cl, 10.77. Found: C, 51.02; H, 4.22; Cl, 11.22; ^{1}H-NMR ($CDCl_3$): δ 7.25–7.82 (br, m, Ar $SbPh_3$), 5.20–5.32 (AB pattern, C_6H_4), 2.86 (m, $CH(CH_3)_2$), 1.86 (s, C–CH_3), 1.16 (d, $CH(CH_3)_2$).

2.6. Preparation of [Ru(η^6-$C_{10}H_{14}$)Cl_2(dppm)]·CH_2Cl_2 (***6***)

To a suspension of [Ru(η^6-$C_{10}H_{14}$)Cl_2(CNPy)] (205 mg, 0.5 mmol) in methanol (25 ml), 1,2-bis(-diphenylphosphino)methane (142 mg, 0.5 mmol) was added and the solution was heated to reflux for 1 h. The deep red solution thus obtained was cooled to r.t., filtered to remove any solid residue and rotaporated. The residue was washed several times with petroleum ether, extracted with dichloromethane and filtered. The dichloromethane extract was layered with light petroleum ether (40–60°C) and left for slow crystallization. Red needle-shaped crystals separated. These were filtered, washed several times with petroleum ether and dried under vacuum. Yield 65%: m.p. 158°C Anal. Calc. for $C_{36}Cl_4H_{38}P_2Ru$: C, 55.74; H, 4.65, Cl, 18.32. Found: (C, 55.82; H. 4.62; Cl, 18.75; ^{1}H-NMR ($CDCl_3$): δ 6.99–7.95 (br, m, Ar $Ph_2PCH_2PPh_2$), 5.14, 5.32 (AB pattern, C_6H_4), 3.40–3.44 (dd, $Ph_2PCH_2PPh_2$), 248 (m, $CH(CH_3)_2$), 1.87 (s, C–CH_3), 0.76 (d, $CH(CH_3)_2$); ^{13}C{^{1}H}-NMR ($CDCl_3$): 128.1–138.2 (Ar $Ph_2PCH_2PPh_2$), 107.6 (C–$CHMe_2$), 93.7 (C-CH_3), 90.3 and 85.6 (C_6H_4) 54.5 ($Ph_2PCH_2PPh_2$), 29.9 ($CH(CH_3)_2$), 21.2 ($CH(CH_3)_2$), 17.7 (C–CH_3); ^{31}P{^{1}H}-NMR ($CDCl_3$): 26.1 (dd Ru-bound P of $Ph_2PCH_2PPh_2$) − 27.6 (d Pendant P of $Ph_2PCH_2PPh_2$).

2.7. Preparation of [Cl_2(η^6-$C_{10}H_{14}$)Ru(μ-CNPy) Ru(η^6-C_6Me_6)Cl_2] (7)

[{Ru(η^6-C_6Me_6)Cl_2}$_2$] (334 mg, 0.5 mmol) was added to a suspension of [Ru(η^6-$C_{10}H_{14}$)Cl_2(CNPy)] (410 mg 1.0 mmol) in methanol (40 ml) and heated under reflux for ca. 5 h. After cooling to r.t., the orange solution was filtered to remove any solid residue. The filtrate was concentrated to ca. 15 ml under reduced pressure and left for slow crystallization. After a few hours, a golden red microcrystalline compound separated out from the solution. It was filtered, washed several times with, methanol, diethylether and dried under vacuum. Yield 45%; m.p. 195°C (decom); Anal. Calc. for $C_{28}Cl_4H_{36}N_2Ru_2$: C, 45.16; H, 4.83; N, 3.76; Cl, 19.09. Found: C, 44.82; H, 4.87; N, 3.42; Cl, 19.22; IR (KBr) 2230 cm^{-1} (νC≡N); ^{1}H-NMR ($CDCl_3$): δ 9.33 (αH–CNPy), 7.50 (βH–CNPy), 5.22–5.50 (AB pattern C_6H_4), 2.99 (m $CH(CH_3)_2$), 2.15 (s, CH_3 of C6$(CH_3)_6$), 1.65 (s, C–CH_3), 1.24 (d, $CH(CH_3)_2$).

2.8. Preparation of [Cl_2(η^6-$C_{10}H_{14}$)Ru(μ-CNPy) Ru(η^5-C_5H_5)(PPh_3)$_2$]PF_6 (***8***)

[Ru(η^5-C_5H_5)(PPh_3)$_2$Cl] (250 mg, 0.34 mmol) in methanol (20 ml) was treated with $AgPF_6$ (85 mg, 0.33 mmol) and the solution was stirred at r.t. for 0.5 h. It was centrifuged to remove the white precipitate of AgCl and the yellow/orange filtrate was treated with [Ru(η^6-$C_{10}H_{14}$)Cl_2(CNPy)] (125 mg, 0.33 mmol). It was stirred at r.t. Slowly, a brown microcrystalline compound separated. It was filtered, washed several times with methanol, diethylether and dried in vacuum. Yield 65%; m.p. 225°C; Anal. Calc. for $C_{57}Cl_4H_{53}N_2P_2Ru_2$: C, 54.97; H, 4.25; N, 2.29. Found: C, 54.82; H, 4.46; N, 1.84; IR (KBr) 2226 cm^{-1} (νC≡N); ^{1}H-NMR (Acetone-d$_6$): δ 9.20 (αH–CNPy), 7.25–7.85 (br, m, βH–CNPy and Ar PPh_3), 5.32, 5.84 (AB pattern C_6H_4), 4.6 (s, (C_5H_5), 2 89 (m, $CH(CH_3)_2$), 2.16 (s, C–CH_3), 1.25 (d, $CH(CH_3)_2$).

2.9. X-ray diffraction studies

Data collection, crystal and refinement parameters are given in Table 1. Atomic co-ordinates and selected bond lengths and angles are given in Table 2. ORTEP views for **1** and **6** are given in Figs. 1 and 2, respectively.

Table 1
Crystal data for **1** and **6**

	1	**6**
Formula	$C_{16}H_{18}Cl_2N_2Ru$	$C_{36}H_{38}Cl_4P_2Ru$
Formula weight	410.3	775.5
Color, habbit	Red, irregular	Red, irregular
Crystal system	monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.984(1)	11.504(3)
b (Å)	14.052(1)	19.532(3)
c (Å)	12.189(1)	15.942(3)
β (°)	114.810(0)	96.08(2)
V (Å^3)	1707.8(4)	3562(2)
Z	4	4
D_{calc} (g cm^{-3})	1.596	1.446
Absorption coeff. (cm^{-1})	12.25	8.46
Reflections collected	3155	5645
Independent reflections	2997 (R_{int} = 0.146)	5418 (R_{int} = 0.085)
Observed reflections	2339	3507
GOF	1.33	1.96

Table 2
Selected bond lengths (Å) and angles (°) with estimated S.D. in parentheses for **1** and **6**

1		**6**	
Bond lengths (Å)			
Ru(1)–Cl(1)	2.405(2)	Ru(1)–Cl(1)	2.409(2)
Ru(1)–Cl(2)	2.404(2)	Ru(1)–Cl(2)	2.414(2)
Rr(1)–N(1)	2.127(6)	Ru(1)–P(1)	2.348(2)
Ru(1)–C(8)	2.173(7)	Ru(1)–C(1)	2.226(8)
Ru(1)–C(9)	2.176(7)	Ru(1)–C(2)	2.184(8)
Ru(1)–C(10)	2.197(8)	Ru(1)–C(3)	2.149(8)
Ru(1)–C(11)	2.219(7)	Ru(1)–C(4)	2.200(9)
Ru(1)–C(12)	2.178(7)	Ru(1)–C(5)	2.239(9)
Ru(1)–C(13)	2.121(7)	Ru(1)–C(6)	2.248(9)
C(1)–N(1)	1.136(16)		
Bond angles (°)			
Cl(1)–Ru(1)–Cl(2)	88.0(1)	Cl(1)–Ru(1)–Cl(2)	89.05(8)
Cl(1)–Ru(1)–N(1)	85.3(1)	Cl(1)–Ru(1)–P(1)	84.26(8)
Cl(2)–Ru(1)–N(1)	87.0(1)	Cl(2)–Ru(1)–P(1)	86.64(8)
C(9)–C(8)–C(14)	121.5(7)		
C(13)–C(8)–C(14)	120.1(8)		
C(10)–C(11)–C(15)	118.2(7)		
C(12)–C(11)–C(15)	123.2(6)		

2.9.1. Complex *1*

Diffraction data for **1** were collected from red irregular crystals of dimensions 0.48 × 0.32 × 0.18 mm, in ω scan mode (2θ range from 3.0 to 50.0°). Intensities were measured by 2θ-ω scan method using Mo-K_α radiation ($\lambda = 0.71073$). A variable scan speed between 4.00 and 100.0° min^{-1} in ω was used. Throughout the data collection, intensities of three standard reflections were measured every 297 reflections as a check of the stability of the crystal. A total of 3155 reflections ($2\theta < 50.0°$) were measured and out of these, 2339 reflections with $F > 4.0\sigma(F)$ were used in solution and struture refinement.

The structure was solved by direct methods with SIR-92 [14] and refined by block-matrix least-square procedures using SHEXTL [15]. All the non-hydrogen atoms were refined with anisotropic thermal parameters by a full-matrix least-square method. Positions of the hydrogen atoms were calculated at the ideal positions and were not refined. The function minimized was $\Sigma\, w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) - 0.0008F^2$ resulting in $R = 0.0649$, $wR = 0.1766$ and $S = 1.33$.

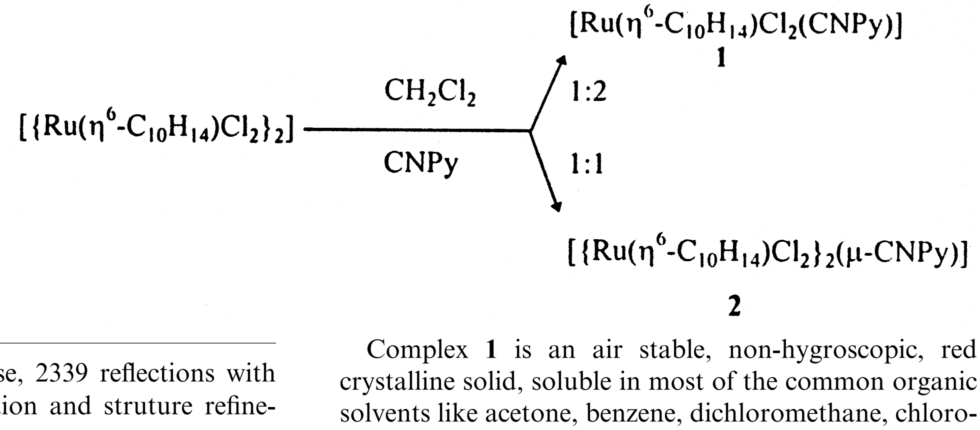
2.9.2. Complex *6*

Diffraction data for **6** were collected from red irregular crystals of dimensions 0.28 × 0.12 × 0.35 mm in ω-2θ scan mode (2θ range from 5.0 to 50.0°) using Mo–K_α radiation ($\lambda = 0.71073$) at a speed of 4.0° min^{-1} in ω. Throughout the data collection, intensities of three standard reflections were measured every 100 reflections as a check of the stability of the crystal. A total of 5645 reflections (5418 unique) were measured.

The structure was solved by the Patterson method and refined by block-matrix least-square procedures using 3507 reflections with $I > 3.0\sigma(I)$. All the non-hydrogen atoms were refined with anisotropic thermal parameters by a full-matrix least-square method. Position of the hydrogen atoms were calculated at the ideal positions and were not refined. The function minimized was $\Sigma\, w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F)$. Final values of $R = 0.051$ $wR = 0.067$ and $S = 1.96$ were obtained. All calculations for data reduction, structure solution and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Technologia de la Universidad de Cadiz, using the TEXSAN [16] software system.

3. Results and discussion

The reaction of $[\{Ru(\eta^6\text{-}C_{10}H_{14})Cl_2\}_2]$ with 4-cyanopyridine in dichloromethane in 1:1 and 1:2 molar ratios gives the mononuclear complex **1** and the binuclear complex **2** in quantitative yields.



Complex **1** is an air stable, non-hygroscopic, red crystalline solid, soluble in most of the common organic solvents like acetone, benzene, dichloromethane, chloroform, dimethylformamide and dimethylsulfoxide; slightly soluble in methanol, ethanol and insoluble in diethylether and petroleum ether. Its IR spectrum showed the $\nu(C{\equiv}N)$ of the co-ordinated CNPy at 2239 cm^{-1}. In the ^{1}H-NMR spectrum, the arene (η^6-$C_{10}H_{14}$) signals were observed at δ 1.32 (d), 2.18 (s), 2.92 (sp), 5.25, 5.49 ppm (AB pattern) and the α and β protons of the CNPy resonated at δ 9.38 and 7.35 ppm. The arene

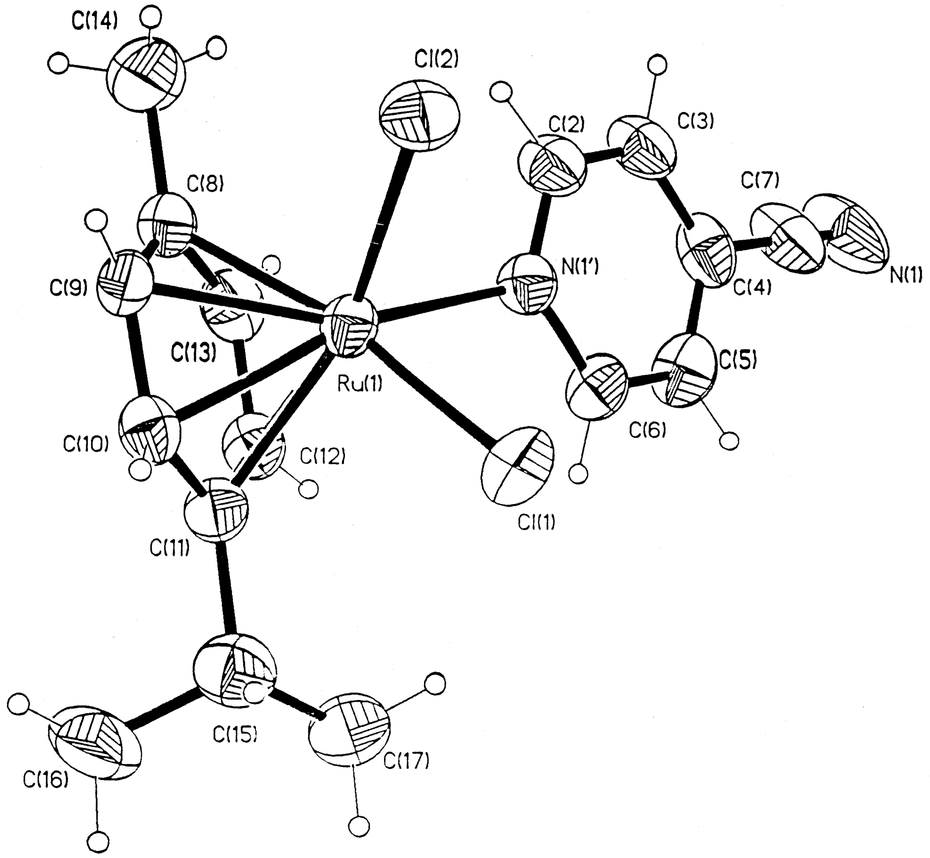


Fig. 1. ORTEP drawing of [Ru(η^6-$C_{10}H_{14}$)Cl_2(CNPy)] (**1**) with 50% probability thermal ellipsoids.

protons and 4-cyanopyridine (α and β) protons exhibited a downfield shift as compared with that in the precursor complex [{Ru(η^6-$C_{10}H_{14}$)Cl_2}$_2$] [12] and in the free ligand 4-cyanopyridine ([17]a,b). The $^{13}C\{^1H\}$-NMR spectrum of **1** follows the trends observed in the ^1H-NMR spectrum, with the nitrile carbon of the CNPy resonating at lowfield (δ 119.25 ppm) as compared with that in the free ligand (δ 116 ppm). The IR, ^1H and $^{13}C\{^1H\}$ spectral data of **1** strongly suggested the linkage of the CNPy with the metal center ruthenium, through its aromatic ring nitrogen ([18]a–f). It was further confirmed by single crystal X-ray analysis. It is worth noting that due to the presence of the pendant nitrile group in **1**, it could be used as a metallo-ligand or as synthon for the synthesis of homo/heterobimetallic complexes. The IR spectra of **2** showed a band assignable to v(C≡N) at 222 cm^{-1}. This band exhibited a decrease in the position of nitrile stretching frequency ν(C≡N) as compared with that in **1** (2239 cm^{-1}) and free ligand (2242 cm^{-1}). In the ^1H-NMR spectra of **2** splitted resonances were observed in the same region as that for **1** (δ 9.30, 7.54, 5.36–5.60, 2.34–3.00, 1.86–2.18, 1.30–1.43 ppm). Both, the arene (η^6-$C_{10}H_{14}$) and 4-cyanopyridine (α and β) protons exhibited a downfield shift relative to those in complex **1** and free ligand. The splitting of the signals is not unexpected and it could result from the difference in the local electron density on the (η^6-$C_{10}H_{14}$) protons, which could arise from the nature of M–L bonding of the two Ru(II) centers (one bonded to an aromatic nitrogen atom and the other bonded to the nitrile nitrogen atom). In the $^{13}C\{^1H\}$-NMR spectrum of **2**, the nitrile carbon atom resonated at lowfield (δ 121.5 ppm) as compared with that in **1** (δ 119.25 ppm) and free ligand (δ 116 ppm). On comparison with the elemental and spectral data of **2** with **1** it was elucidated that it is a binuclear complex, in which the CNPy acts as a bridge between two Ru(II) centers. Treatment of an equimolar amount of complex **1** with EPh_3 (E = P, As, Sb) gave brick-red to red-brown crystalline complexes **3**, **4** or **5**. The IR spectra of these complexes did not show any band in the nitrile stretching frequency region assignable to ν(C≡N), however, they exhibited characteristic bands due to EPh_3. In the ^1H-NMR spectra of **3**, **4** or **5**, signals due to the arene (η^6-$C_{10}H_{14}$) and EPh_3 were observed; however, resonances corresponding to α and β protons of CNPy were absent. It therefore suggested that, in the presence of good Lewis bases like EPh_3, the ligand CNPy gets substituted to give metathetical products **4**, **5** or **6**. Further support of this view point comes from the reaction of **1** with a bidentate phosphine such as dppm, yielding complex **6**. The IR spectrum of **6** did not show any band assignable

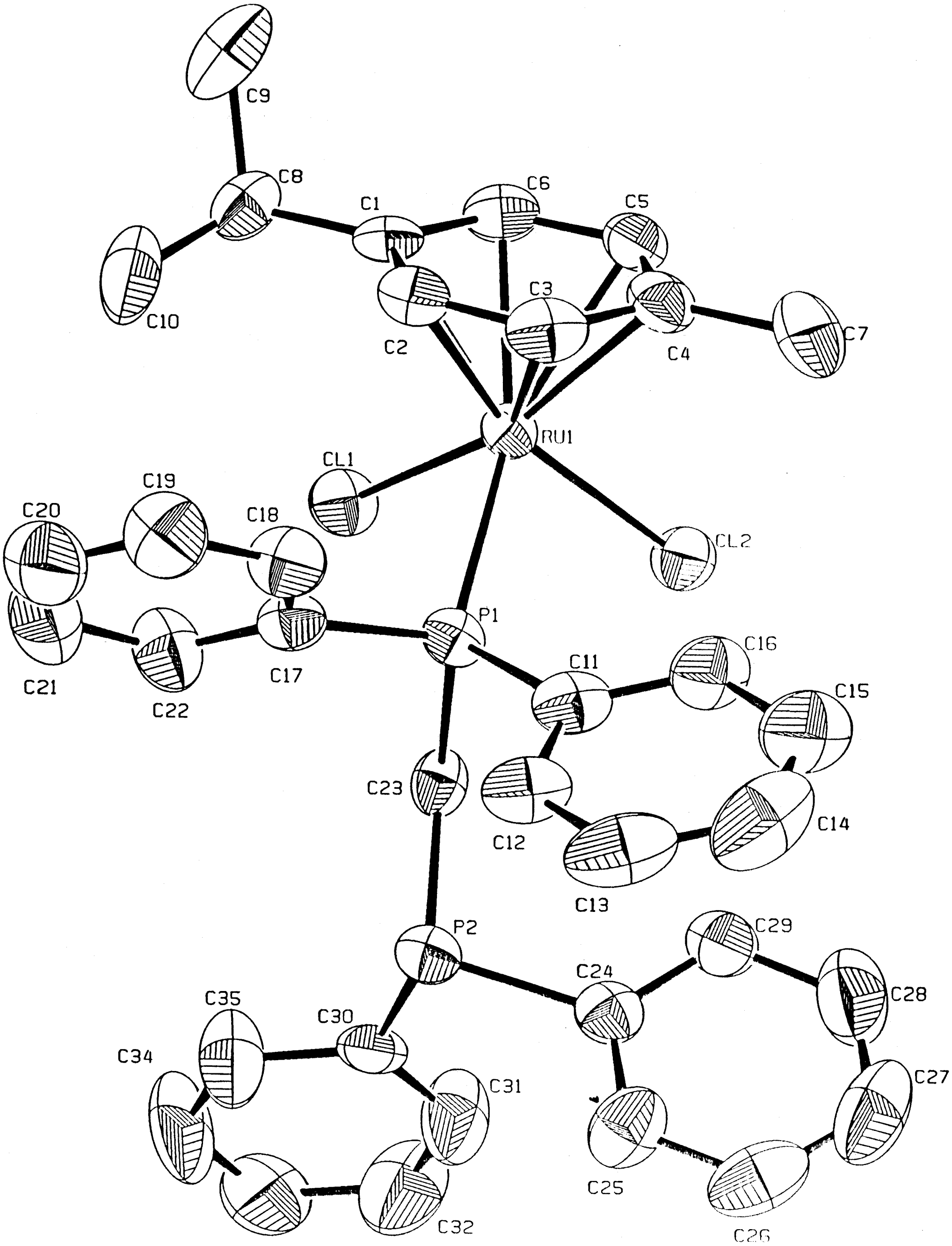


Fig. 2. ORTEP drawing of [Ru(η^6- $C_{10}H_{14}$)Cl_2(dppm)] (**6**) with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

to ν(C≡N). The ^{1}H-NMR spectra of the complex displayed aromatic resonances overlapping between δ 7.61–6.99 ppm along with the resonances due to the arene (η^6-$C_{10}H_{14}$). However, signals assignable to α and β photons of CNPy were not observed. In the $^{13}C\{^1H\}$-NMR spectrum of **6**, signals assignable to aromatic and methylene carbons of dppm, and those for arene (η^6-$C_{10}H_{14}$) were observed in their usual positions, signals corresponding to α, β and γ carbons of CNPy were not observed. The $^{31}P\{^1H\}$-NMR spectrun of **6** exhibited two separated peaks at δ -27.6 (d) and 26.1 (dd) ppm, suggesting that the two phosphorus nuclei of the dppm ligand are present in different chemical environments. The peak at δ 26.1 ppm has been assigned to the ruthenium-bound phosphorus atom, while the one at δ -27.6 ppm to the pendant phosphorus [19,20]. These data suggested (i) the formation of **6** takes place by substitution of CNPy in **1** by dppm and (ii) dppm acts as monodentate ligand in the complex. The unusual binding mode of the dppm ligand in **1** has been confirmed by single crystal X-ray analysis. It is one of the few examples of ruthenium complexes in which dppm is in uncommon monodentate binding mode ([21]a–f). Complex **6** therefore, represents a unique opportunity of behaving as a metallo-ligand and as a synthon for the development of homo/heterobimetallic systems.

The presence of a pendant nitrile group in **1** prompted us to exploit the nucleophilicity of this group in the synthesis of binuclear complexes. Basically, treatment of **1** with $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ resulted in the formation of golden red, shiny crystalline complex **7** and with $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Cl]$ in the presence of $[PF_6]^-$ gave a cationic red-brown complex $[Cl_2(\eta^6\text{-}C_{10}H_{14})Ru(\mu\text{-}CNPy)Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]PF_6$ **8**. The analytical and spectral data of **7** and **8** corresponds to CNPy bridged binuclear complexes.

3.1. Crystal structures of $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(CNPy)]$ (1) and $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(dppm)]\cdot CH_2Cl_2$ (6)

Both complexes adopted a typical 'piano-stool' geometry with the tetrahedral arrangement of the *p*-cymene and the other three ligands about the metal center ruthenium. These have a similar arrangement to that of $[Ru(\eta^6\text{-}C_{10}H_{14})RuCl_2(MePPh_2)]$ and $[Ru(\eta^6\text{-}C_{10}H_{14})RuCl(pz)_2]PF_6$ ([22]a,b). For both compounds, the *p*-cymene rings are planar with mean deviation from the planes of 0.0087 and 0.0082 Å, respectively. The ruthenium to carbon distances in **1** are almost equal, with an average Ru–C = 2.177(7) Å [range 2.121(7)–2.219(7) Å] with an exception of Ru–C(11) which is slightly larger [2.219(7) Å] compared with the others. In **6**, all the Ru–C distances are almost equal with an average Ru–C 2.207(9) Å [range 2.149(8)–2.248(9) Å]. The Ru–C distances of 1.6539 Å in **1** and 1.6947 Å are very close to those reported for other Ru(II) arene complexes ([23]a–c), but for **1** it is shorter than the average of 1.678 Å.

The C–C bond lengths in the *p*-cymene ring are equal in both complexes, as well as there are no alternate short and long bond lengths. It indicates that there are no localization and shows no trends associated with non-planarity of the arene ring. The Ru–Cl(1) and RuCl(2) distances in **1** are 2.405(2) and 2.404(2) Å, respectively, and in 6, 2.409(2) and 2 414(2) Å, respectively. These bond lengths are shorter than the average bond length of 2.429 Å in other Ru(II) complexes ([24]a–c).

The ligand 4-cyanopyridine in **1** is planer. The Ru–N(1) distance is 2.127(6) Å which is comparable with the Ru–N distance in the pyrazine complex $[Ru(\eta^6\text{-}C_{10}H_{14})(pz)_2Cl][PF_6]$ ([22]b) and 3-aminopyrazole complexes $[Cl_2(\eta^6\text{-}C_6H_6)Ru(\mu_3\text{-}3ampzH)Ru(\eta^6\text{-}C_6H_6)Cl_2$, $[\{Cl)\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)(\mu_3\text{-}3ampzH)Ru(\eta^6\text{-}C_6H_6)\}_2]^{2+}$ and related complexes [25]. However, it is slightly larger than Ru–N bond length in the 4-MePy complex $[Ru(\eta^6\text{-}C_6H_6)(L\text{–}L)(2\text{-}MePy)][PF_6]$ [26],1, and in octahedral complexes like $[Ru(NH_3)_5(pz)](BF_4)_2$ and $[Ru(NH_3)_5(pz)](CF_3SO_3)2\cdot H_2O$ [27]. The nitrile C≡N bond length is 1.136(16) Å which is very close to the one characteristic for sp-N bond type and comparable with the one reported for CH_3CN complexes $[Ru(\eta^6\text{-}C_6H_6)(CH_3CN)_3]^{2+}$ and $[Ru(\eta^5\text{-}C_5H_5)(CH_3CN)_3]^{2+}$ [28].

The Ru–P(1) distance in **6** is 2.348(2) Å which is close to Ru–P distances in $[Ru(\eta^5\text{-}C_5H_5)(\eta^1\text{-dppm})_2Cl]$ and other related systems [19,20].

4. Conclusions

In the present study, we have developed two systems, complex **1** and **6**, bearing pendant donor groups. These systems therefore, behave as metallo-ligands and as synthons, these are potential precursors for the synthesis of homo/heterobimetallic complexes. Works on the synthesis of homo/heterobimetallic complexes starting from both complexes is in progress.

Acknowledgements

Thanks are due to the Council of Scientific and Industrial Research, New Delhi and the Director CSMCRI, Bhavnagar for financial assistance (HRDG-01(1375)/95/EMR-II). The Head, Department of Chemistry for extending facilities, The Head, R.S.I.C. CDRI, Lucknow for providing spectral and analytical data and Professor U.C. Agawala for his helpful suggestions and encouragement.

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