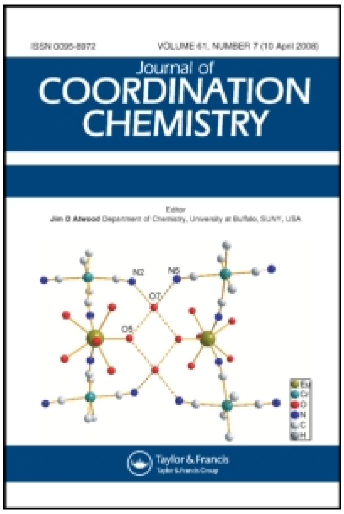

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Synthesis, Characterization and Molecular Structure of a new (?^{6}-*P*-Cymene) Ruthenium(II) Amidine Complex, [(?^{6}-*P*-Cymene)Ru{NH=C(Me)3,5-Dmpz}(3,5-Hdmpz)](BF$_4$)$_2$·H$_2$O

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SYNTHESIS, CHARACTERIZATION AND MOLECULAR STRUCTURE OF A NEW (η^6-*p*-CYMENE) RUTHENIUM(II) AMIDINE COMPLEX, [(η^6-*p*-CYMENE)Ru{NH=C(Me)3,5-dmpz}(3,5-Hdmpz)]$(BF_4)_2 \cdot H_2O$

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A new arene ruthenium(II) complex [(η^6-*p*-cymene)Ru(L)(3,5-Hdmpz)]$(BF_4)_2 \cdot H_2O$ (L = 1-methylcarbaldimino-3,5-dimethylpyrazole; 3,5-Hdmpz = 3,5-dimethylpyrazole) has been synthesized. The ligand L has been generated *in situ* through the condensation of 3,5-dimethylpyrazole and acetonitrile in the presence of [{(η^6-*p*-cymene)$RuCl_2$}$_2$]. The complex [(η^6-*p*-cymene)Ru{NH=C(Me)3,5-dmpz}(3,5-Hdmpz)]$(BF_4)_2 \cdot H_2O$ crystallizes in monoclinic space group $P2_1/c$, $a = 10.943(2)$, $b = 26.394(7)$, $c = 11.502(1)$ Å, $\beta = 115.43(1)°$, $V = 3000.1(19)$ Å^3 and $Z = 4$. The compound has been characterized by FTIR, ^{1}H NMR, 2D-COSY NMR spectroscopy and a single-crystal X-ray diffraction study.

Keywords: Ruthenium; Cymene; 3,5-Dimethylpyrazole; Amidine; X-ray structure

INTRODUCTION

Arene ruthenium(II) complexes with a three-legged piano stool structure have attracted much interest in recent years owing to their role in catalysis [1–5]. Reactions between free nitriles and nucleophiles such as amines, alcohols and water usually proceed in presence of a Lewis acid or base [6–9]. However, compounds with coordinated nitriles react with those nucleophiles without the help of a Lewis acid or base [10]. A review article by Michelin *et al.* [11] presents comprehensive details of the reactions of coordinated transition metal nitriles. Ruthenium amidine complexes have been prepared from reactions of nitriles coordinated to metals with amines, pyrazoles etc. [4,12,13]. During an investigation of the reactivity of the (η^6-*p*-cymene)ruthenium(II) complex, we found that nucleophiles such as 3,5-dimethylpyrazole are inserted in the coordinated

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acetonitrile to give a stable (η^6-*p*-cymene)ruthenium amidine complex, viz [(η^6-*p*-cymene)Ru(L)(3,5-Hdmpz)]$(BF_4)_2 \cdot H_2O$ (L = 1-methylcarbaldimino-3,5-dimethylpyrazole). This complex was characterized by a single-crystal X-ray analysis.

EXPERIMENTAL

All chemicals used were of reagent grade. All reactions were carried out in purified and dried solvents. IR spectra were recorded using a Perkin-Elmer 983 spectrophotometer. Microanalyses were carried out at RSIC, NEHU, Shillong. ^{1}H NMR and 2D-COSY experiments were recorded on a Brucker ACF 300 spectrometer. [{(η^6-*p*-cymene)$RuCl_2$}$_2$] was prepared according to the literature procedure [14]. 3,5-Dimethylpyrazole was prepared by the condensation of acetylacetone and hydrazine hydrate.

Preparation of [(η^6-*p*-cymene)Ru{(HN=C(Me)3,5-dmpz}(3,5-Hdmpz)]$(BF_4)_2 \cdot H_2O$

A mixture of [{(η^6-*p*-cymene)$RuCl_2$}$_2$] (0.1 g, 0.16 mmol) and 3,5-dimethylpyrazole (0.08 g, 0.83 mmol) in acetonitrile (20 mL) was refluxed for 20 min. The solution was cooled and stirred for 1 h at room temperature and then filtered. To the yellow filtrate, NH_4BF_4 (0.25 g, 3.0 mmol) was added with stirring for 15 min. The solvent was evaporated in a water bath, when an oily mass was separated out. The oily mass was dissolved in dichloromethane and hexane was added for precipitation. The crude mass obtained was washed several times with dry diethylether and dried under vacuum. The compound was recrystallized from dichloromethane–hexane (1 : 3 v/v) by the slow diffusion method. A yellow crystalline solid separated out which was collected by filtration and dried *in vacuo*.

Yield: 0.055 g (52.9%). Anal. Calcd. for $C_{22}H_{33}N_5B_2F_2Ru$(%): C, 41.4; H, 5.1; N, 11.0 (Found: C, 40.9; H, 5.0; N, 10.9. IR (cm^{-1}, KBr pellet): 3450(br), 3060(s), 1655(s), 1480(s), 1435(m), 1196(s), 1177(s), 1136(s), 1096(s), 1026(s), 996(m), 837(m), 827(m), 796(s), 745(s), 721(s), 706(s), 516(s), 505(s). ^{1}H NMR (ppm, $CDCl_3$): 1.02(d), 1.06(d), 1.82(s), 2.14(s), 2.32(s), 2.57(sept.), 2.58(s), 2.83(s), 3.04(s), 5.90(s), 5.56(d), 6.41(s), 6.53(d), 11.38(s), 10.89(s).

Crystal Structure Determination of [(η^6-*p*-cymene)Ru{(HN=C(Me)3,5-dmpz}-(3,5-Hdmpz)]$(BF_4)_2 \cdot H_2O$

Suitable crystals for X-ray analysis were grown by diffusion of hexane into a dichloromethane solution. A yellow crystal of suitable size was mounted on a Nonius MACH3 diffractometer equipped with graphite-monochromatized Mo Kα ($\lambda = 0.70930$ Å) radiation at of 293 K for cell determination and intensity data collection. Unit cell parameters were derived and refined by using 25 centred reflections in the θ range 5–12. Crystal data collection parameters are summarized in Table I. All crystallographic calculations were performed using Maxus [15] software. The structure was solved by direct methods [16]. Refinement was by full-matrix least squares based on F^2 using SHELXL-93 [17]. All reflections were used during refinement (F^2 values that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + 0.0516P^2 + 9.8409P]$ where $P = (F_o^2 + 2F_o^2)/3$. Lorentz and polarization

TABLE I Crystal data and structure refinement for $[(\eta^6\text{-}p\text{-cymene})Ru\{NH=C(Me)3,5\text{-}dmpz\}(3,5\text{-}Hdmpz)](BF_4)_2 \cdot H_2O$.

Empirical formula	$C_{22}H_{33}B_2F_8N_5ORu$
Formula weight	658.22
Temperature (K)	293(2)
Wavelength (Å)	0.70930
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions (Å,°)	$a = 10.9430(16)$
	$b = 26.394(7)$ $\beta = 115.434(10)$
	$c = 11.5020(13)$
Volume (Å^3)	3000.1(9)
Z, Calculated density (Mg/m^3)	4, 1.457
Absorption coefficient (mm^{-1})	0.596
F (000)	1336
Crystal size (mm)	0.4 × 0.35 × 0.30 mm
θ Theta range for data collection (°)	1.54 to 24.93
Index ranges	$0 \le h \le 12$, $0 \le k \le 31$, $-13 \le l \le 12$
Reflections collected/unique	4715/4715
Completeness to 2θ (°,%)	24.93; 87.4
Max. and min. transmission	1.000 and 0.987
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4715/0/388
Goodness-of-fit on F^2	1.064
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0603$, $wR_2 = 0.1675$
R indices (all data)	$R_1 = 0.0713$, $wR_2 = 0.1786$
Largest diff. peak and hole	0.841 and -0.854 eÅ^{-3}

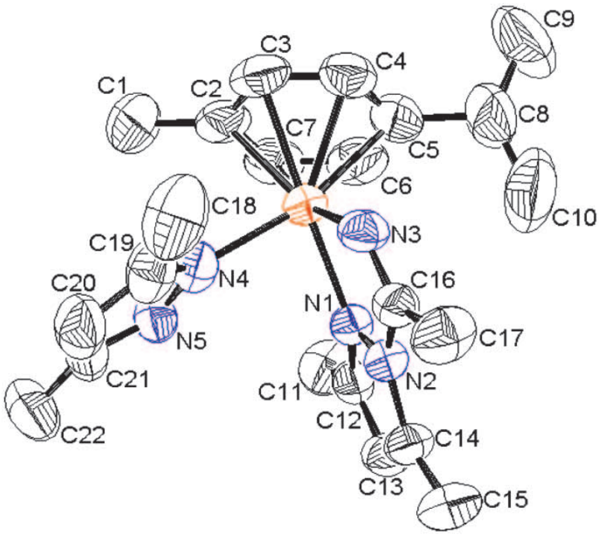

FIGURE 1 ORTEP diagram of the complex with 30% probability thermal ellipsoids. BF_4 is omitted for clarity.

corrections were applied. An empirical absorption correction was employed by using psi-scans where the maximum and minimum transmission factors were 1.000 and 0.987, respectively. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a 'riding' model. Refinement converged to $R_1 = 0.0603$ and $wR_2 = 0.1675$ for 4715 reflections for which $I > 2\sigma(I)$ and $R_1 = 0.0713$, $wR_2 = 0.1786$, GOF = 1.064 for all non-zero reflections and 398 variables [18]. Figure 1 is an

TABLE II Bond lengths [Å] and angles [°] for $[(\eta^6\text{-}p\text{-cymene})\text{Ru}\{\text{NH}=\text{C(Me)3,5-dmpz}\}(\text{3,5-Hdmpz})](\text{BF}_4)_2\cdot\text{H}_2\text{O}$

Ru(1)–N(3)	2.045(6)	Ru(1)–N(1)	2.092(5)
Ru(1)–N(4)	2.123(6)	Ru(1)–C(6)	2.179(8)
Ru(1)–C(4)	2.183(7)	Ru(1)–C(3)	2.194(7)
Ru(1)–C(7)	2.200(9)	Ru(1)–C(5)	2.210(7)
Ru(1)–C(2)	2.232(7)	N(1)–C(12)	1.329(8)
N(1)–N(2)	1.382(7)	N(2)–C(16)	1.389(7)
N(2)–C(14)	1.390(7)	N(3)–C(16)	1.262(7)
N(4)–C(19)	1.330(9)	N(4)–N(5)	1.366(7)
N(5)–C(21)	1.344(9)	C(2)–C(7)	1.378(13)
C(2)–C(3)	1.438(12)	C(3)–C(4)	1.416(12)
C(4)–C(5)	1.379(12)	C(5)–C(6)	1.409(13)
C(6)–C(7)	1.407(13)	C(12)–C(13)	1.399(10)
C(13)–C(14)	1.353(10)	C(19)–C(20)	1.406(12)
C(20)–C(21)	1.356(13)		
N(3)–Ru(1)–N(1)	74.3(2)	N(3)–Ru(1)–N(4)	87.5(2)
N(1)–Ru(1)–N(4)	83.6(2)	C(12)–N(1)–N(2)	106.1(5)
C(12)–N(1)–Ru(1)	139.5(4)	N(2)–N(1)–Ru(1)	114.0(3)
N(1)–N(2)–C(16)	115.5(4)	C(16)–N(3)–Ru(1)	121.7(4)
C(19)–N(4)–N(5)	106.5(6)	C(19)–N(4)–Ru(1)	134.4(5)
N(5)–N(4)–Ru(1)	119.1(4)	C(7)–C(2)–Ru(1)	70.6(5)
C(3)–C(2)–Ru(1)	69.6(4)	C(1)–C(2)–Ru(1)	128.5(6)
N(3)–C(16)–N(2)	114.0(5)		

ORTEP [19] representation of the molecule with 30 % probability thermal ellipsoids displayed. Table II lists selected bond lengths and angles.

RESULTS AND DISCUSSION

Treatment of $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2]$ with 3,5-dimethylpyrazole in acetonitrile, followed by addition of NH_4BF_4, afforded an air-stable yellow crystalline solid in moderate yield. Microanalytical data suggested that the air-stable complex obtained is $[(\eta^6\text{-}p\text{-cymene})\text{Ru}\{(\text{HN}=\text{C(Me)(3,5-dmpz)})\}(\text{3,5-Hdmpz})](\text{BF}_4)_2$. The *in situ* formation of the ligand 1-methylcarbaldimino-3,5-dimethylpyrazole presumably takes place by the condensation of 3,5-dimethylpyrazole with acetonitrile activated by $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2]$ complex.

The IR spectrum of the complex shows a characteristic absorption at $1655\,\text{cm}^{-1}$ due to $\nu_{(\text{CN})}$ of the amidine ligand [NH = C(Me)dmpz]. A broad band is also observed at $3450\,\text{cm}^{-1}$ due to $\nu_{(\text{NH})}$ of 3,5-dimethylpyrazole and/or amidine ligand [13]. Besides these strong absorptions, bands at 1096, 796 and $516\,\text{cm}^{-1}$ are also observed due to ν_1, ν_2 and ν_3 modes of ionic BF_4^- [20].

The ^{1}H NMR spectrum of the complex suggests the presence of *p*-cymene, 3,5-dimethylpyrazole and 1-methylcarbaldimino-3,5-dimethylpyrazole (L) ligands in a 1 : 1 : 1 ratio. The methyl groups of the isopropyl group of the *p*-cymene ligand exhibits two sets of doublets in the range δ 1.00–1.07 due to loss of planarity of the benzene ring due to sterically bulky ligands coordinated to ruthenium and a septet at δ 2.57 is observed. The arene ring protons appear as two AB quartets in the range δ 6.39–6.54 [21]. Six singlets of equal intensity in the range δ 1.82–3.03 are observed due to the methyl protons of the *p*-cymene, 3,5-dimethylpyrazole and the amidine ligands. The singlets were assigned tentatively for *p*-cymene at δ 2.14, amidine at δ 1.82

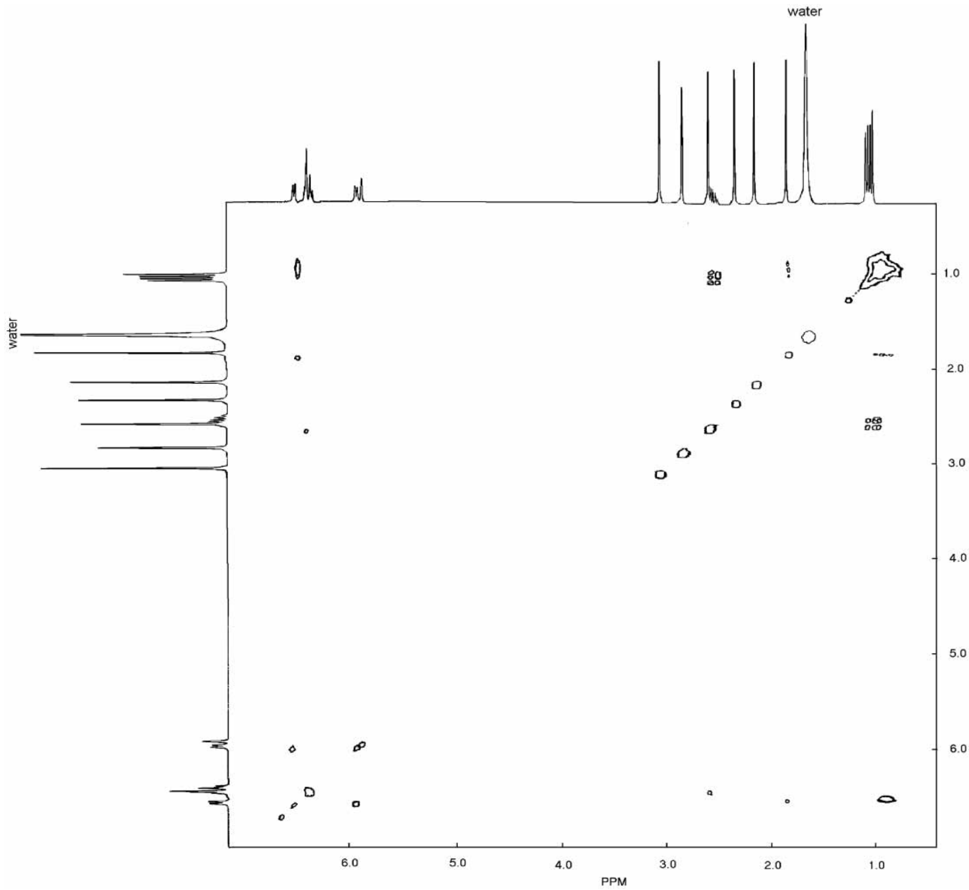

FIGURE 2 2D-COSY spectrum of the complex.

(N = CCH_3), δ 2.83 and 3.04 (dmpz), and 3,5 dimethylpyrazole at δ 2.32 and 2.58, respectively. The methylenic protons of the ligand (L) and coordinated 3,5-dimethylpyrazole show two singlets in the region δ 5.90–6.43. Two singlets in the region δ 10.89–11.38 indicate the presence of NH protons of amidine ligand and coordinated 3,5-dimethylpyrazole [10]. The data suggest a bidentate chelating mode of bonding of the amidine ligand through the nitrogens of the pyrazole and the imino group.

The 2D-COSY spectrum of the complex (Fig. 2) shows coupling between the –CH of the isopropyl group at δ 2.57 with the methyl protons observed as two doublets at δ 1.00–1.07 of the isopropyl group of the *p*-cymene ligand. Long-range coupling between the protons of the phenyl group at δ 6.54–6.52 and the –CH proton of the isopropyl group was also observed at δ 2.57. There is also coupling between the methyl protons of the imine group of the amidine ligand at δ 1.82 with the methyl protons of the isopropyl group of *p*-cymene.

A plausible mechanism for the reaction involves initial coordination of both 3,5-dimethylpyrazole and acetonitrile to [{(arene)$RuCl_2$}$_2$] and formation of the monomeric cationic complex [{(η^6-*p*-cymene)Ru(Cl)(CH_3CN)(3,5-Hdmpz)]$^+$, followed by condensation to form a C–N linkage by nucleophilic attack of 3,5-dimethylpyrazole at the nitrile carbon of acetonitrile. However, it is known that individual arene ruthenium acetonitrile complexes [(arene)$RuCl_2$(NCMe)] [22, 23] and an arene ruthenium 3,5-dimethylpyrazole complex [(arene)$RuCl_2$(3,5-Hdmpz)] [13] have been synthesized by the reaction of [{(arene)$RuCl_2$}$_2$] with acetonitrile and 3,5-dimethylpyrazole in benzene. Hence, for closely related reactions a mechanism of this kind has been reported [22].

To confirm the solid-state structure, a single crystal X-ray study has been carried out. The ruthenium atom is coordinated to a *p*-cymene ring, 3,5-dimethylpyrazole and an amidine ligand. The geometry around the metal atom can be regarded as distorted octahedral if the η^6-cymene group is assumed to occupy three facially coordinated positions. The Ru–C bonds of the arene ring are in the range 2.179(8)–2.232(7) Å (mean 2.20 Å). The arene rings are essentially planar, showing a maximum deviation of 0.04 Å from the mean plane [21]. The carbon atoms attached to methyl, Ru–C(2) (2.232 Å), and isopropyl groups, Ru–C(5) (2.210 Å), have metal-to-carbon bond lengths a little longer than the other four metal-to-carbon bonds (av. 2.189 Å) of the *p*-cymene group. Ru–N bonds are in the range 2.045 Å to 2.123 A°. Ru–N(1) (2.092 Å) and Ru–N(3) (2.045 Å) bond lengths are almost equal, owing to the formation of a five-membered chelated ring through the N(1) and N(3) atoms of the amidine ligand. The average bond distance for Ru–N(1) and Ru–N(3) (2.068 Å) is slightly shorter than Ru–N(4) (2.123 Å) of the 3,5-dimethylpyrazole ligand. The bond length of particular significance is the amidine C=N bond, C(16)–N(3), (1.262 Å). This is significantly shorter than the average C–N bond distances (1.359 Å) in the pyrazole ring and C(16)–N(2)(1.359 Å), indicating its pronounced double bond character. The compound has one water molecule per formula unit, which is hydrogen bonded to N(5)–H(105), and F(3) of BF_4, and F(1) of the same BF_4 ion is hydrogen bonded to H(103)–N(3) of another molecule. The net result is that two molecules of the complex are linked by hydrogen bonds through BF_4 and H_2O molecules in continuous fashion. Selected bond lengths and bond angles are presented in Table II.

Acknowledgments

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Supplementary Data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 198417. Copies of the 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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[18] $R_1 = \Sigma\|F_0| - |F_c\|/\Sigma|F_o|$; $wR_2 = \{\Sigma w(F_0^2 - F^2c)^2/\Sigma w(F_o^2)^2\}^{1/2}$; $\mathrm{GOF} = \{\Sigma w(F_0^2 - F^2c)^2/(n-p)\}^{1/2}$ where n = number of reflections and p = the number of parameters refined.

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