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Synthesis and characterization of ruthenium(II) complexes with polypicolylamine ligands

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Abstract

A series of ruthenium(II) complexes of polypicolylamine ligands have been prepared. The reaction of $Ru(PhCN)_4Cl_2$ with the tridentate ligand *N*,*N*-bis(2-pyridylmethyl)aniline (phdpa) followed by precipitation with PF_6^- salts affords the complex, $[Ru(phdpa)_2](PF_6)_2$. The crystal structure of $[Ru(phdpa)_2](PF_6)_2$ shows that the ligand coordinates in a facial mode, with sp^3-nitrogens located *cis* to each other. The reaction of $Ru(dmso)_4Cl_2$ with the tetradentate ligand tris(2-pyridylmethyl)amine (tpa) in ethanol yielded the (Cl, N_{amine})-*trans* $[Ru(tpa)(dmso)Cl](PF_6)$ complex which was characterized by X-ray crystallography. $[Ru(tpa)(dmso)Cl](PF_6)$ reacts with bipyridine, tpa and tricyanomethane anion (tcm) affording the $[Ru(tpa)(bipy)](PF_6)_2$, $[Ru(tpa)_2](PF_6)_2$ and $Ru(tpa)(tcm)_2$ complexes, respectively. The structures of $[Ru(tpa)(bipy)](PF_6)_2$ and $Ru(tpa)(tcm)_2$ show that tpa acts as a tetradentate ligand, while in $[Ru(tpa)_2](PF_6)_2$ it is tridentate, facially coordinated, with one non-coordinated pyridine.

Keywords: Ruthenium(II) complexes; Polypicolylamine ligands; Tricyanomethane anions; X-ray crystallography

1. Introduction

Polydentate ligands containing 2-pyridylmethyl or 2-pyridylethyl fragments attached to a tertiary nitrogen atom contain both σ-donor and π-acceptor binding sites. Thus ligands of this class (e.g. tris(2-pyridylmethyl)amine, tpa, or *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine, tpen) are capable of stabilizing both high- and low-oxidation states in their metal complexes. A number of topologies for complexes of this class of ligand are known, e.g. strapped dinuclear complexes with different ligands functionalities capping different metals [1] and encapsulated, semi-cage mononuclear complexes [2]. The studied systems include copper [3] and iron complexes [4] as models for dioxygen activation centers, spin-crossover iron(II) complexes [5] and polynuclear complexes of manganese with a high-oxidation state [6].

Complexes of second- and third-row transition metals with this class of ligand are less known. Sasaki and co-workers obtained rhenium complexes of tpa showing that the ligand may be either tetradentate or tridentate with one uncoordinated pyridylmethyl arm [7]. A significant interest has centered around the catalytic properties of high-valent ruthenium complexes. Che and co-workers obtained the Ru(III) complex of tris[2-(2-pyridyl)ethyl]amine which was shown to undergo oxidation to a Ru(III) complex of bis(2-(2-pyridyl)(2-hydroxy-2-(2-pyridylethyl)]amine [8]. The latter complex was used to prepare a rare mono-oxoruthenium(V) complex, which was found to be an active oxidant capable of oxidizing C–H bonds [9,10]. The Ru(III)

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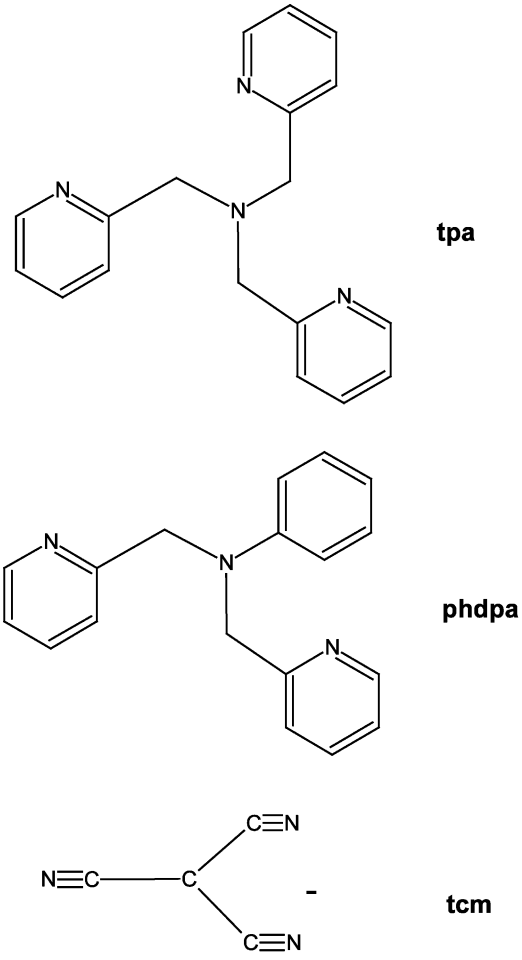
complex of the related *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)ethylenediamine was shown to be an efficient catalyst for electrochemical oxidation of alcohols and tetrahydrofuran [11]. The reaction proceeds via a Ru(V)-oxo species and allowed the normally complicated electrooxidation of methanol [12]. There have been several reports of ruthenium complexes containing tetradentate tpa or a homologue. Kojima reported the structure of [Ru(III)(tpa)Cl_2]Cl and its catalytic activity in the oxidation of alcohols [13]. Subsequently, Yamaguchi et al. reported the synthesis of [Ru(tpa)(dmso)Cl]PF_6, which was obtained as a mixture of two possible isomers, differing in their mutual orientation of sp^3-nitrogen and coordinated chlorine; the crystal structure of *cis*-(N_{sp^3},Cl)–[Ru(tpa)(dmso)Cl]PF_6 was reported [14]. Kojima et al. described related ruthenium complexes of tpa and its 5-methyl substituted homologue and their catalytic activity in hydrocarbon oxygenation [15]. Reaction between tpa or its 5-methyl substituted analogue with *cis*-Ru(dmso)$_4Cl_2$ lead solely to formation of the *trans*-(N_{sp^3},Cl)–[Ru(L)(dmso)Cl]$^+$ complexes (L = tpa, tris(5-methyl-2-pyridylmethyl)amine). The structures of the dinuclear [Ru(II)(L)Cl]$_2$(ClO_4)$_2$ and mononuclear [Ru(III)(L)(Cl_2)](ClO_4), have also been determined. Recently Kojima and Matsuda reported that reaction of tris(3-methyl-2-pyridylmethyl)amine (3-Metpa) with $RuCl_3$ yields the chiral Ru(3-Metpa)$_2$(PF_6)$_2$ complex [16].

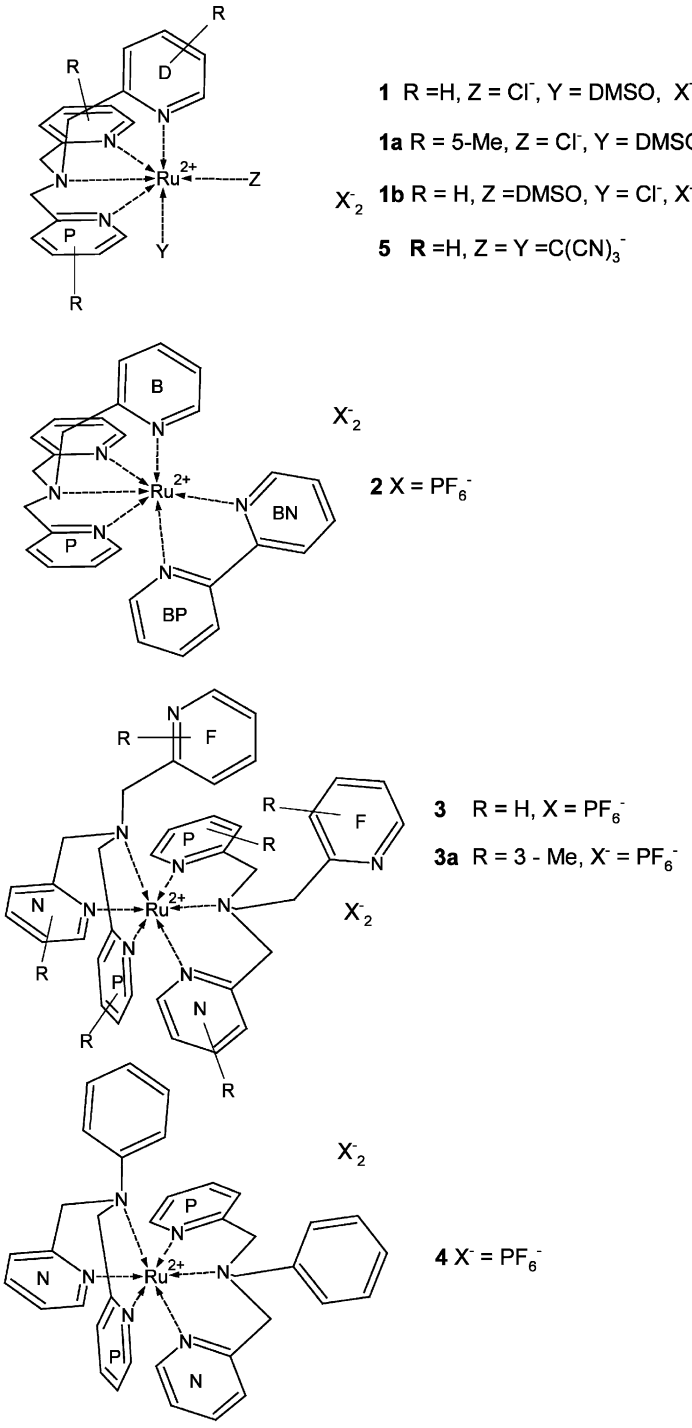
The work described here is a further investigation of ruthenium chemistry of tpa and related ligands. As the Ru(tpa)$^{2+}$ moiety seems to be a promising building block for constructing supramolecular arrays, the substitution reactions of [Ru(tpa)(dmso)Cl]$^+$ were investigated. It was found that the dmso and chlorine ligands may be replaced by monodentate or, bidentate ligands as well as by another tpa ligand. For comparison, a complex comprising of 2-pyridylmethyl units and a tertiary nitrogen from the tridentate phdpa ligand have been obtained. The complexes were characterized by X-ray crystallogrpahy. Both tetradentate and tridendate coordination modes for tpa are found. The ligands are depicted in Scheme 1. The obtained complexes and their homologues obtained by others are depicted in Scheme 2 together with notation for the chemically distinct pyridine rings.



Scheme 1.

2. Experimental

IR spectra were measured as KBr discs using a Hitachi 270-30 IR spectrometer. UV–Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. EI mass spectra were recorded on a Varian MAT311A spectrometer, FAB mass spectrometry was carried out on a Kratos MS50TC instrument and Electrospray Ionization mass spectra (ESMS) were obtained using a Finnigan TSQ 710 instrument with a combined electrospray and atmospheric pressure chemical ionization source using acetonitrile solutions. NMR spectra were recorded on Bruker AC 250 and APS 500 MHz spectrometers. The signals were assigned on the basis of 2D COSY and NOESY experiments. Elemental analyses were carried out at the microanalytical laboratory of the H.C. Ørsted Institute, Copenhagen. Cyclic voltammograms were measured using a locally constructed three-electrode potentiostat using acetonitrile solutions containing Bu_4NPF_6 (0.1 M) and a scan rate of 0.100 V s^{-1}. The working electrode was a BAS platinum electrode, the auxiliary electrode was a platinum wire and the reference a BAS Ag–AgCl electrode (calibrant, ferrocene–ferrocenium at 450 mV). Literature preparations were used for Ru(dmso)$_4Cl_2$ [17], Ru(PhCN)$_4Cl_2$ [18], *N*,*N*-bis(2-pyridylmethyl)aniline (phdpa) [19] and potassium tricyanomethanate [20].



Scheme 2.

2.1. *trans-(Cl, N_{amine})-[Ru(tpa)(dmso)Cl](PF$_6$) (1)*

Tpa (433 mg 1.49 mmol) and $Ru(dmso)_4Cl_2$ (711 mg,1.47 mmol) were heated in absolute ethanol (350 ml) under reflux for 3 h. The solvent was removed and the residual oil dissolved in 20 ml of water. A saturated solution of NH_4PF_6 was added. The resulting precipitate was filtered off, washed with water and dried in vacuo. The product recrystallized from dichloromethane (15 ml) by slow diffusion of diethylether into the solution, which was protected from light. Brown crystals of the product were collected after few days and dried in

vacuo. Yield: 790 mg (82%). Found: C, 36.73; H, 3.67; N, 8.45. $C_{20}H_{24}F_6N_4PSOClRu$ requires: C, 36.85; H, 3.72; N, 8.62%.

FAB MS: *m/z* 505 ($[Ru(tpa)(dmso)Cl]^+$), 427 ($[Ru(tpa)Cl]^+$), 391 ($[Ru(tpa)]^+$) UV–Vis (CH_2Cl_2) 364 nm (10300), 314 nm (6600); $E^\circ = 0.664$ V. ^{1}H NMR (d-6 acetone, 500 MHz) δ 9.81 (d, 1H, $J = 5.7$ Hz, $6H^D$), 8.85 (d, 2H, $J = 5.5$ Hz, $6H^P$), 7.92 (td, 2H, $J = 7.8$, 1.5 Hz, $H4^P$), 7.79 (td, 1H, $J = 7.8$, 1.6 Hz, $H4^D$), 7.63 (dm, 1H, $J = 7.9$ Hz, $H3^P$), 7.45 (m, H3, $H5^P$ and $H5^D$), 7.31 (dm, 1H, $J = 7.3$ Hz, $H3^D$), 5.54 (d, 2H, $J = 15.1$ Hz, CH_{2A}^P), 4.94 (d, 2H, $J = 15.1$ Hz, CH_{2B}^P), 4.82 (s, 2H, CH_2^D).

2.2. *[Ru(tpa)(bipy)](PF$_6$)$_2$·0.5(CH$_3$)$_2$CO (**2**)*

Complex (**1**) (200 mg, 0.308 mmol) and 2,2′-bipyridine (49 mg, 0.31 mmol) were heated in 15 ml of ethylene glycol at 120 °C for 3 h. Stirring was continued overnight at ambient temperature. Subsequently 15 ml of water was added followed by addition of 1 g of NH_4PF_6 in a minimal amount of water. The red precipitate was filtered off, washed with cold water and dried on air.

Chromatographic purification was performed following the method of Belser et al. [21] using thick-layer silica gel plates and NaCl:water:methanol (1:6:12) as eluent. The crude complex was dissolved in a small amount of acetone and placed on a plate. Thick-layer chromatography was performed using the above eluent in a closed vessel protected form light, yielding the separation of several crops. The plates were dried in air and silica gel containing the main orange crop was scratched off. The silica gel was placed in a small column and eluted with a 5% solution of NH_4PF_6 in a 9:1 mixture of acetone and water. Evaporation of acetone yielded the red precipitate that was washed with cold water and dried in air. The subsequent recrystallization from acetone–diethyl ether yielded red crystals. Yield: 160 mg (62%). Found: C, 40.57; H, 3.28; N, 9.84. $C_{29.5}H_{29}F_{12}N_6P_2O_{0.5}$ requires: C, 40.88; H, 3.37; N, 9.69%. UV spectrum (MeCN) 420 nm (9400), 370 nm (10 800), 292 nm (27 200), $E^\circ = 0.77$, 0.97 V. Mass spectrum: FAB, *m/z* 693 ($[Ru(tpa)(bipy)](PF_6)^+$), 548 ($Ru(tpa)(bipy)^+$).

^{1}H NMR (d-6 acetone, 500 MHz) δ 9.94 (1H, ddd, $J = 5.7$,1.4, 0.7 Hz, $H6^{BN}$), 9.52 (1H, ddd, $J = 5.8$, 1.4, 0.7 Hz, $H6^{BP}$), 9.41 (ddd, 1H, $J = 5.9$, 1.4, 0.7 Hz, $H6^B$), 8.81 (ddd, 1H, $J = 8.1$, 1.4, 0.8 Hz, $H3^{BN}$), 8.69, (ddd, 1H, $J = 8.1$, 1.5, 0.7 Hz, $H3^{BP}$), 8.38 (ddd, 1H, $J = 8.1$, 7.6, 1.4 Hz, $H4^{BN}$), 8.12 (ddd, 1H, $J = 7.6$, 5.7, 1.4 Hz, $H5^{BN}$), 7.99 (ddd, 2H, $J = 5.6$, 1.5, 0.7 Hz, $H6^P$), 7.81 (dd, 1H, $J = 7.7$, 1.4 Hz, $H4^B$), 7.75 (dd, 2H, $J = 7.8$, 1.6 Hz, $H4^P$), 7.61 (ddd, 1H, $J = 7.5$, 5.8, 1.5 Hz, $H5^{BP}$), 7.57 (ddd, 2H, $J = 7.0$, 1.5, 0.7 Hz, $H3^P$), 7.56 (ddd, 1H, $J = 7.8$, 1.5, 0.8 Hz, $H3^B$), 7.44 (ddd, 1H, $J = 7.6$, 5.8, 1.5 Hz, $H5^B$), 7.14 (ddd, 2H, $J = 7.6$, 5.6, 1.5 Hz, $H5^P$), 5.90 (d, 2H, $J = 17.1$ Hz, CH_{2A}^N), 5.45 (d, 2H, $J = 17.1$ Hz, CH_{2B}^N), 5.04 (s, 2H, CH_2^B).

2.3. *[Ru(tpa)$_2$](PF$_6$)$_2$·CH$_2$Cl$_2$ (**3**)*

Complex (**1**) (363 mg, 0.5 mmol) and tpa (145 mg, 0.5 mmol) were heated at 120 °C in ethylene glycol (10 ml) with stirring over 4 h. Water (10 ml) was added to the cooled solution and 1 g of NH_4PF_6 dissolved in a minimal amount of water was added. The resulting yellow precipitate was filtered off, washed with water and dried in vacuo. Chromatographic separation on silica gel plates and subsequent workup of the yellow crop were performed as described for [Ru(tpa)(bipy)](PF_6)$_2$. Recrystallization from CH_2Cl_2–ligroine (light protected) yielded the product as yellow crystals, 180 mg (37%). Found: C, 42.14; H, 3.73; N, 10.69. $C_{37}H_{38}F_{12}N_8Cl_2Ru$ requires: C, 42.05; H, 3.62; N, 10.60%. FAB MS, *m/z*: 827 ($[Ru(tpa)_2](PF_6)^+$), 681 ($[Ru(tpa)_2]^+$). UV–Vis (MeCN) 368 nm (6700), $E^\circ = +0.88$ V. ^{1}H NMR (d-6 acetone, 500 MHz) δ 8.96 (d, 2H, $J = 5.7$ Hz, $H6^N$) 8.76 (d, 2H, $J = 5.3$ Hz, $H6^P$), 8.74 (ddd, 2H, $J = 4.8$ Hz, $H6^F$), 7.91 (dd, 2H, $J = 7.7$, 1.8 Hz, $H4^F$), 7.87 (dd, 2H, $J = 7.7$, 1.2 Hz, $H4^N$), 7.82 (dd, 2H, $J = 7.8$, 1.4 Hz, $H4^P$), 7.69 (4H, d, $J = 7.7$ Hz, $H3^N + H3^F$), 7.51 (2H, ddd, $J = 7.6$, 4.8, 1.0 Hz, $H5^F$), 7.41, (d, 2H, $J = 7.7$ Hz, $H3^P$), 7.38 (apt, 2H, $J = 6.7$ Hz, $H5^N$), 7.33 (apt, 2H, $J = 6.6$ Hz, $H5^P$), 5.79(d, 2H $J =$ 18.3 Hz, CH_{2A}^P), 5.35 (d, 2H, $J = 13.3$ Hz, CH_{2A}^N), 5.00 (d, 2H, $J = 15.6$ Hz, CH_{2A}^F), 4.63 (d, 2H $J = 18.3$ Hz, CH_{2B}^P), 4.62 (d, 2H, $J = 15.6$ Hz, CH_{2B}^F), 4.47 (d, 2H, $J = 13.3$ Hz, CH_{2B}^N).

2.4. *[Ru(phdpa)$_2$](PF$_6$)$_2$·2CH$_2$Cl$_2$ (**4**)*

Phdpa (57.8 mg, 210 mmol) and $Ru(PhCN)_4Cl_2$ (50 mg, 83.9 mmol) were heated in ethanol (100 ml) under reflux and under Ar for 48 h. The yellow solution was evaporated to dryness and the remainder was dissolved in water (10 ml). The crude product was precipitated by addition of a saturated aqueous solution of NH_4PF_6. Purification was achieved by column chromatography on silica gel (acetonitrile:saturated aqueous KNO_3:-water, 14:2:1). After addition of a saturated aqueous solution of NH_4PF_6 the product was allowed to stand for 7 days, then recrystallized from benzene–dichloromethane (1:1) to give yellow crystals. Yield: 29.8 mg, 32%. Found: C, 41.29; H, 3.39; N, 7.49. $C_{38}H_{38}N_4Cl_4P_2F_{12}Ru$ requires: C, 41.06; H, 3.45; N, 7.56%. MS (FAB, *m/z*): 797 ($[Ru(phdpa)_2PF_6]^+$, 100%), 651 ($[Ru(phdpa)_2–H]^+$, 45%), 376 ($[Ru(phdpa)\text{-}H]^+$, 48). $E^\circ = 1.234$ V. UV–Vis (MeCN): 249 nm (24 790), 359 nm (12 910), 377 nm (12 600). ^{1}H NMR (d-6 acetone, 500 MHz), δ 9.65 (d, 2H, $J = 5.3$ Hz, $H6^N$), 8.71 (dd, 2H, $J = 5.5$, 0.7 Hz, $H6^P$), 8.13 (td, 2H, $J = 7.7$,

1.4 Hz, $H4^N$), 7.95 (m, 2H, $H5^P$), 7.85 (td, 2H, $J = 7.7$, 1.5 Hz, $H4^P$), 7.57 (d, 2H, $J = 6.8$ Hz, $H3^N$), 7.55 (m, 2H, $H5^N$), 7.37 (d, 2H, $J = 7.8$ Hz, $H3^P$), 7.12 (br, 6H, ph−H3+H4), 6.86 (br, 4H, ph−H2), 5.06 (d, 2H, $J =$ 14.7 Hz, CH_{2A}^P), 4.86 (d, 2H, $J = 14.7$ Hz, CH_{2B}^P), 4.65 (AB, 4H, $J = 18.1$ Hz, CH_2^N).

2.5. Ru(tpa)(tcm)$_2$·CH$_3$OH·1/2H$_2$O (5)

Compound **1** (145 mg, 0.24 mmol) and 34 mg of potassium tricyanomethanate (0.51 mmol) were suspended in 25 ml of methanol and refluxed for 3 days. The solution was concentrated to approximately 10 ml and the resulting yellow precipitate was collected, passed through a column (Al_2O_3, 4% v/v MeOH in CH_2Cl_2) and recrystallized from MeOH–Et_2O. Yield: 20 mg (14%). Found: C, 52.90; H, 3.52; N, 22.90. $C_{27}H_{23}N_{10}O_{1.5}Ru$ requires: C, 52.85; H, 3.77; N, 22.80%. MS (ESI, *m/z*): 573 (MH^+), 482 ($Ru(tpa)(tcm)^+$), UV–Vis (MeCN) 379 nm (11620), 330sh nm (8755).

^{1}H NMR (d-6 acetone, 300 MHz) δ 9.07 (d, 1H, $J =$ 5.3 Hz, $6H^D$), 8.73 (dm, 2H, $J = 4.1$ Hz, $6H^P$), 7.87 (td, 2H, $J = 7.8$, 1.6 Hz, $H4^P$), 7.67 (td, 1H, $J = 8.0$, 1.6 Hz, $H4^D$), 7.61 (d, 2H, $J = 8.0$ Hz, $H3^P$) 7.43 (m, 3H, $H5^N$ and $H5^D$), 7.22 (d, 1H, $J = 8.0$ Hz, $H3^D$), 5.22, 5.13 (4H, $J_{AB}^2 = 15.2$ Hz, CH_2^P), 4.95 (s, 2H, CH_2^P).

2.6. X-ray crystallography

Single crystals were grown from dichloromethane–diethyl ether for [Ru(tpa)dmsoCl]PF_6 (**1**), from acetone–diethyl ether for [Ru(tpa)(bipy)]$(PF_6)_2$·0.5$(CH_3)_2CO$ (**2**), from dichloromethane–ligroine for $[Ru(tpa)_2](PF_6)_2$·0.5CH_2Cl_2 (**3**) and from benzene–dichloromethane for $[Ru(phdpa)_2](PF_6)_2$·2CH_2Cl_2 (**4**). For Ru(tpa)$(tcm)_2$·CH_3OH (**5**) they were grown from methanol. Crystal data and details of the refinements are given in Table 1. Data for **1**, **2** and **3** were collected on a Siemens SMART diffractometer with a CCD area detector, data for **4** were collected on a Huber four-circle diffractometer and data for **5** a Nonius Kappa CCD. For **1** the crystal was cooled to 120 K using a cryostream nitrogen gas cooler system [22], for **5** the crystal was cooled to 150 K using an Oxford Cryostream cooling device, the other data sets were obtained at room temperature. Programs used for data collection, data reduction and absorption correction were SMART [23], SAINT [23] and SADABS [24] for **1**, **2** and **3**, and KRYSTAL [25] for **4**. The structures were solved by direct methods, using SHELXS86 [26] for **1** and SIR92 [27] for **2**, **3**, and **4**. Structures were refined on *F* using the modification of ORFLS [28] in KRYSTAL, hydrogen atoms were kept fixed in calculated positions with C–H = 0.95 Å and with $U_{iso} = 1.2U_{eq}$ for the atoms to which they were attached. Atomic scattering factors were from ref [29]. For **5** the structure was solved using Patterson techniques [30] and from subsequent Fourier difference syntheses. The structure was refined on F^2 using SHELX [31]. All non-hydrogen atoms were refined freely with anisotropic displacement parameters. The majority of hydrogen atoms were located in the Fourier difference maps, but were placed in idealized positions and allowed to ride on the relevant non-hydrogen atom. For the methanol solvent molecule in the lattice it was necessary to let the torsion of the methyl group adjust to the residual electron density, while the hydroxyl-hydrogen was placed in the optimum position for hydrogen bonding.

3. Results and discussion

3.1. Synthesis

The reaction of tpa with Ru(dmso)$_4Cl_2$ in ethanol followed by precipitation as the PF_6^- salt gives the *trans*-(N_{sp^3},Cl)–[Ru(tpa)(dmso)Cl](PF_6) complex **1**. The same geometry of cation has been reported by Kojima et al. in a perchlorate salt for the 5-Me substituted analogue **1a** [15a]. In our case the yield was significantly higher (82 vs. 45%). Both Kojima et al. [15a] and we obtained solely the *trans*-(N_{sp^3},Cl)-isomer, contrary to the report of Yamaguchi et al. [14] who obtained a mixture of **1** and the *trans*-(N_{sp^3}, DMSO)-isomer **1b**. The $[Ru(phdpa)_2](PF_6)_2$ complex (**4**) was obtained by reaction of the tridentate ligand with Ru(PhCN)$_4Cl_2$ in ethanol followed by chromatography and recrystallization.

Complex **1** is a convenient starting material for synthesis of $[Ru(tpa)(L)]^{2+}$ (L = bipyridine, tpa) complexes. The synthetic route involved the reaction of **1** with the appropriate ligand in ethylene glycol at 120 °C, followed by chromatography and recrystallization. $[Ru(tpa)_2](PF_6)_2$ (**3**) and Ru[(tpa)(bipy)]$(PF_6)_2$ (**2**) were isolated in 40–60% yield. The homologue of $[Ru(tpa)_2](PF_6)_2$, namely $[Ru(3\text{-}Metpa)_2](PF_6)_2$ (**3a**) was recently obtained by Kojima and Matsuda [16] by means of reaction of the ligand with $RuCl_3$ in MeOH in the presence of NEt_3. In contrast, the tpa and 5-Metpa ligands under the same conditions yielded the dinuclear bis-μ-chloro Ru(II) dinuclear complexes [15a,15c]. Our protocol also allows the complex for the tpa ligand bearing no methyl substituents to be obtained.

3.2. Molecular structures

The molecular structures of five complexes, i.e. [Ru(tpa)(dmso)Cl](PF_6) (**1**), [Ru(tpa)(bipy)]$(PF_6)_2$·0.5$(CH_3)_2CO$ (**2**), $[Ru(tpa)_2](PF_6)_2$·CH_2Cl_2 (**3**), $[Ru(phdpa)_2](PF_6)_2$·2CH_2Cl_2 (**4**) and Ru(tpa)$(tcm)_2$]·CH_3OH (**5**), were determined by X-ray crystallography.

Table 1
Crystallographic data for [Ru(tpa)dmsoCl](PF$_6$) (**1**), [Ru(tpa)(bipy)](PF$_6$)$_2$·0.5(CH$_3$)$_2$CO (**2**), Ru(tpa)$_2$](PF$_6$)$_2$·0.5CH$_2$Cl$_2$ (**3**), [Ru(phdpa)$_2$](PF$_6$)$_2$·2CH$_2$Cl$_2$ (**4**) and [Ru(tpa)(tcm)$_2$] (**5**)

	1	**2**	**3**	**4**	**5**
Formula	$C_{20}H_{24}ClF_6N_4OPRuS$	$C_{29.5}H_{29}F_{12}N_6O_{0.5}P_2Ru$	$C_{36.5}H_{37}ClF_{12}N_8P_2Ru$	$C_{38}H_{38}Cl_4F_{12}N_6P_2Ru$	$C_{27}H_{22}N_{10}Ru$
Formula weight	649.98	866.65	1014.27	1111.65	603.62
Crystal symmetry	orthorhombic	monoclinic	orthorhombic	monoclinic	triclinic
Space group	$Pna2_1$ (No. 33)	$P2_1/a$ (No. 14)	$Fdd2$ (No.43)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	17.4325(8)	17.0849(2)	25.635(1)	19.294(3)	9.9626(2)
b (Å)	15.5659(5)	18.7370(3)	65.860(2)	11.239(2)	10.7637(2)
c (Å)	18.2731(8)	21.5670(4)	10.0376(4)	22.810(3)	12.4740(2)
α (°)					84.6414(12)
β (°)	90.0	94.264(1)	90.0	117.570(8)	89.4673(11)
γ (°)					87.3582(8)
V (Å^3)	4958.5(4)	6884.9(1)	16947(1)	4385(1)	1330.36(4)
Z	8	8	16	4	2
μ (Mo Kα) (mm^{-1})	0.956	0.647	0.600	0.763	0.630
T (K)	120	295	295	295	150
Reflections measured (R_{int})	62 981 (0.049)	46 857 (0.043)	42 723 (0.045)	4344 (0.024)	30 705 (0.0473)
Number of unique reflections	14 422	17 383	11 003	4049	9666
Number of observed reflections	12 776 [$I > 2.5\sigma(I)$]	11 043 [$I > 3\sigma(I)$]	6527 [$I > 3\sigma(I)$]	2685 [$I > 3\sigma(I)$]	7592 [$I > 2\sigma(I)$]
$R(F)$ observed reflections	0.032	0.057	0.052	0.047	0.0378
$wR_2(F)$ observed reflection	0.038	0.076	0.059	0.057	0.0852

Selected bond lengths and angles are listed in Table 2. The molecules are depicted in Figs. 1–5.

In all five structures Ru(II) coordinates to six atoms in an approximately octahedral configuration. Complex **1** crystallizes with two almost identical molecules in the asymmetric unit. The ruthenium atom is coordinated to all four nitrogen atoms of tpa, the chlorine atom is located *trans* to the sp^3-nitrogen and the dmso molecule is coordinated by its sulfur atom. The overall structure of the complex is similar to the cation in **1a** [15a] revealing the *trans* orientation of the chlorine atom and sp^3 nitrogen atom. The pyridines of the tpa ligand fall into two categories: two of them (denoted P) are coordinated *trans* to each other, while the third one (denoted D) is coordinated *trans* to the dmso molecule. Consequently, the dipicolylamine (dpa) linkage involving two P pyridines coordinates meridionally, while that involving one of the P pyridines and the D pyridine coordinates facially. The comparison of the structure of **1** with those of **1a** [15a] and **1b** [14] reveals pronounced differences in Ru–N$_{sp^3}$ bond lengths, varying from 2.062(4) Å for **1a** to 2.093(3) Å for **1b**, that for **1** revealing the intermediate values of 2.082 and 2.080 Å, for two independent molecules. The Ru–N$_{py}$ distances

Table 2
Selected bond distances for [Ru(tpa)dmsoCl](PF$_6$)$_2$ (**1**), [Ru(tpa)(bipy)](PF$_6$)·0.5(CH$_3$)$_2$CO (**2**), [Ru(tpa)$_2$](PF$_6$)$_2$·0.5CH$_2$Cl$_2$ (**3**), [Ru(phdpa)$_2$](PF$_6$)$_2$·2CH$_2$Cl$_2$ (**4**) and [Ru(tpa)(tcm)$_2$] (**5**)

	1	**1**	**2**	**2**	**3**	**4**	**5**
Ru–N(sp^3)	2.082(3) [a]	2.080(2) [a]	2.086(4) [b]	2.103(4) [b]	2.172(5)	2.205(4)	2.068(3)
					2.146(5)	2.205(4)	
Ru–py *trans* to py	2.087(3)	2.079(2)	2.100(4)	2.086(5)	2.058(5)	2.087(4)	2.0732(15)
	2.093(2)	2.060(2)	2.059(4)	2.052(4)	2.049(5)	2.087(4)	2.0522(15)
Ru–py *trans* to bipy			2.097(4)	2.109(4)			
Ru–bipy *trans* to py			2.115(4)	2.099(4)			
Ru–py *trans* to S	2.101(2)	2.099(2)					
Ru–py *trans* to N(sp^3)			2.076(4) [c]	2.074(4) [c]	2.087(5)	2.076(4)	
					2.085(5)	2.076(4)	
Ru–py *trans* to NC(sp)							2.0563(14)
Ru–S	2.251(1)	2.258(1)					
Ru–Cl	2.430(1)	2.420(1)					
Ru–NC(sp)							2.0336(16)
							2.0328(15)

[a] N *trans* to Cl.
[b] N *trans* to bipy.
[c] bipy *trans* to N(sp^3).

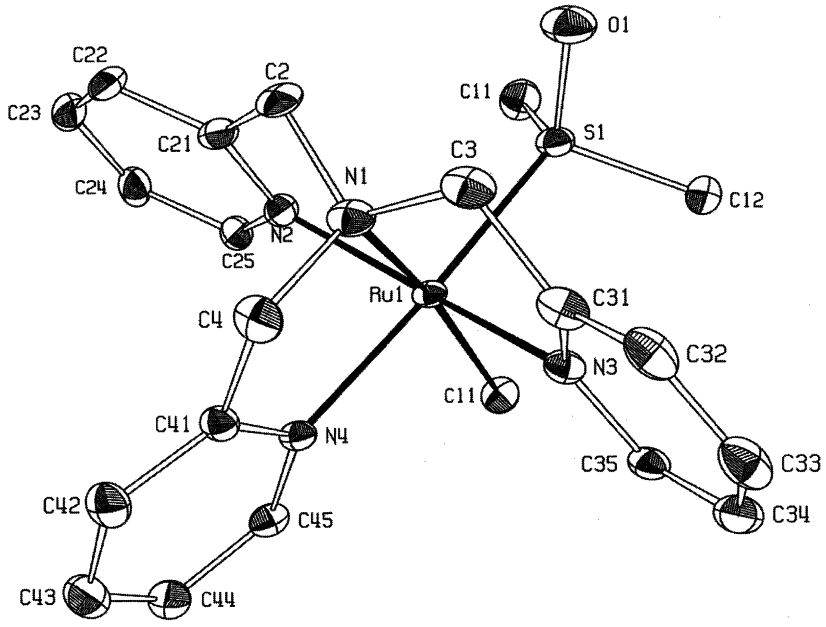


Fig. 1. Molecular representation of **1**.

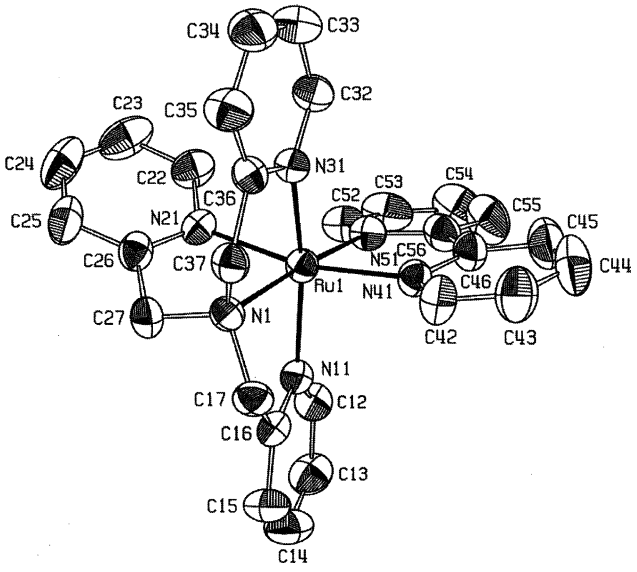


Fig. 2. Molecular representation of **2**.

for pyridines coordinated *trans* to dmso in *trans* [Cl, N_{sp^3}] isomers (D) are significantly larger than for that coordinated *trans* to Cl^- in *trans* [dmso, N_{sp^3}] isomer **1b** (2.099–2.104 vs. 2.062 Å, respectively) reflecting the effect of π-back bonding from Ru center to the S=O moiety (cf. Ref. [15a]). For all three structures the geometry around the ruthenium atom is significantly distorted from octahedral: the Ru–N_{py} distances for P pyridines differ significantly in each molecule (2.087 and 2.093 [2.079 and 2.060] Å for **1**, 2.066 and 2.090 Å for **1a** and 2.079 and 2.091 Å for **1b** [14]. Additionally the N_{py}–Ru–N_{py} angles involving P (meridionally disposed) pyridines are 162.8(1)° (163.6(1)°), 162(1)° and 160.1(1)°, respectively.

Complex **2** crystallizes with two crystallographically independent molecules in the asymmetric unit, which also contains one molecule of acetone. The tpa ligand is tetradentate, with the bipyridine ligand completing the coordination sphere. Again there are two types of pyridines in the tpa ligand, coordinated either *trans* to each other or *trans* to a bipyridine pyridine. The complex has approximate mirror symmetry with the ruthenium atom, the bipyridine, the sp^3-nitrogen atom and a pyridine group lying in the plane. The Ru–N_{bipy} bond *trans* to the sp^3-nitrogen atom is significantly shorter than that *trans* to the pyridine nitrogen atom. Both molecules show deviations from mirror symmetry, there are significant differences in the Ru–N_{py} tpa pyridines across the mirror plane (Table 2). The coordination about the Ru(II) atom is significantly distorted from octahedral; the N_{py}–Ru–$N_{py'}$ and N_{py}–Ru–N_{bipy} angles being 162.3(2)° and 166.6(2)°, respectively, for molecule **1** and 162.2(2)° and 168.0(2)° for molecule **2**.

The structures of **3** and **4** are very similar, three nitrogen-atoms of each ligand, an sp^3-nitrogen atom and two pyridine ones are coordinated to the ruthenium atom. So in the case of the bis–tpa complex one pyridine of each ligand is uncoordinated. The ligands coordinate facially with sp^3-nitrogens located *cis* to each other, so that the cation in **3** has approximate twofold symmetry. Complex **4**, which is on a crystallographic twofold axis, necessarily has exact twofold symmetry. The analogous structure was recently established for the related $[Ru(etdpa)_2]$ $(PF_6)_2$ etdpa = *N*,*N*-bis(2-pyridylmethy-

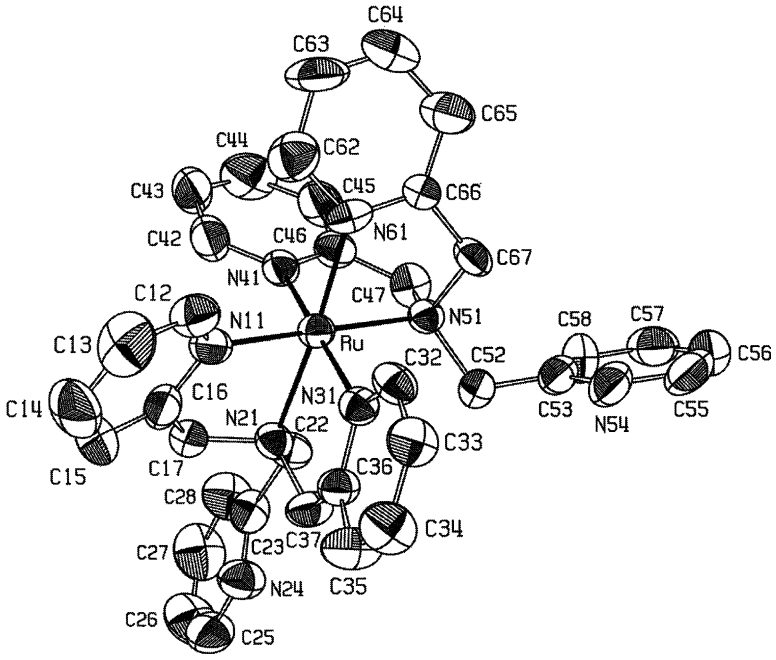


Fig. 3. Molecular representation of **3**.

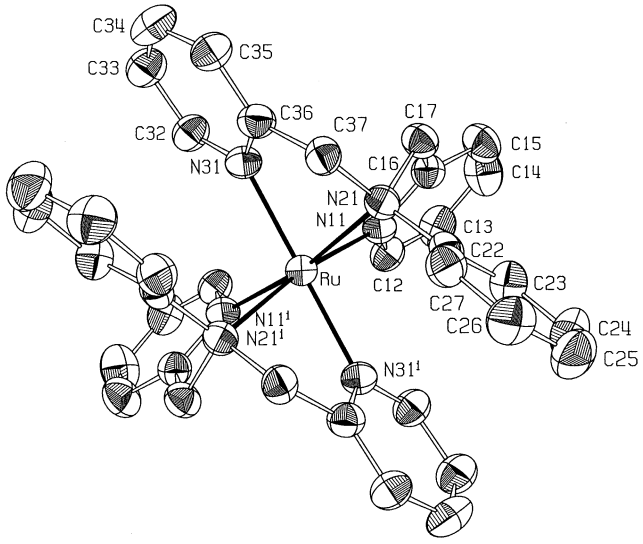


Fig. 4. Molecular representation of **4**.

l)ethylamine [32]. Complex **3b** crystallizes with half a dichloromethane molecule in the asymmetric unit and **4** has one dichloromethane in the asymmetric unit, i.e. two solvent molecules per cation. The coordination about the Ru(II) atom in **4** is slightly distorted octahedral with N_{py}–Ru–$N_{py'}$ 168.0(2)° and N_{py}–Ru–N_{sp^3} 170.8(2)°. The octahedron in **3** is more regular with N_{py}–Ru–$N_{py'}$ being 174.5(2)° and 174.8(2)°.

The N_{sp^3}–Ru bonds are slightly shorter than the corresponding bonds in **4**, the difference may be due to the electron withdrawing effect of the phenyl group attached to the tertiary nitrogen atom of phdpa. This difference is even more pronounced if **4** and $[Ru(etdpa)_2]^{2+}$ are compared (N_{sp^3}–Ru distances 2.139(3) and 2.148(4) Å for the latter [31]). It is noteworthy that the coordination mode established for $[Ru(tpa)_2]^{2+}$ was recently observed in an $[Fe(tpa)_2]^{2+}$ complex [33].

A comparison of structure of **3** with that of the 3-methyl substituted homologue $Ru(3\text{-}Metpa)_2(PF_6)_2$ (**3a**) [16] reveals that both molecules have essentially the same structure, the most pronounced difference concerning the Ru–N_{sp^3} bond lengths that differ significantly for **3** (see Table 2).

The structure of $[Ru(tpa)(tcm)_2]$ (**5**) reveals a pseudo-octahedral coordination around the ruthenium with a tetradentate tpa ligand. The planes of tricyanomethanide (tcm) ligands are mutually orthogonal with an interplane angle of 86.00(3)°. The Ru–N–C angles for the coordinated tcm ligand decline slightly from 180°, more so at N412 than at N512 (171.56(15)° and 175.51(15)°, respectively).

The tcm ligands are essentially threefold symmetric with all C–C bonds in the range 1.402(3)–1.412(3) Å and C–N bonds in the range 1.147(2)–1.155(3) Å.

Because of this equivalence, there is no evidence for an anionic contribution to the metal–ligand bonding, but the shortness of the Ru–N bonds is consistent with the presence of metal-to-ligand π-back bonding.

Again, as in the case of **1** and **2** a significant difference is seen in Ru–N distances for P pyridines (those coordinated *trans* to each other), being 2.0732(15) and 2.0522(15) Å. This is accompanied by a N_{py}–Ru–N_{py} angle of 163.50(6)°. The hydrogen bond between one of

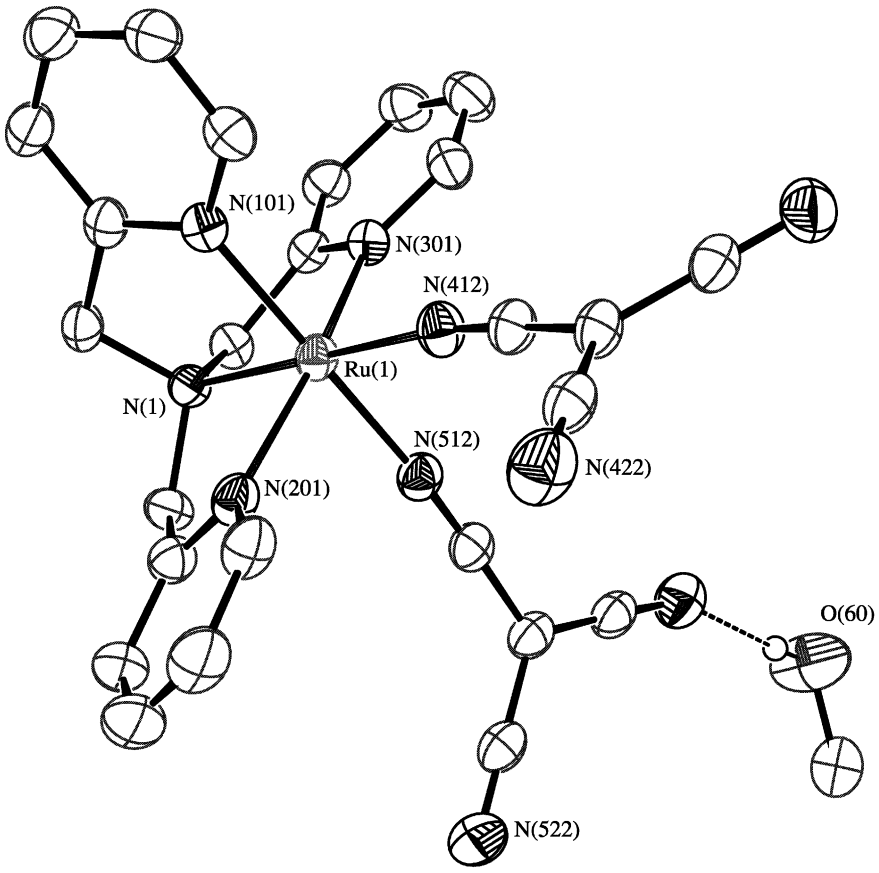


Fig. 5. Molecular representation of **5**.

the cyano nitrogens and the OH group of solvated methanol is noteworthy. It reveals the donor–acceptor distance of 2.843 Å and D–H–A angle of 174° and can thus be considered a strong H-bond.

The available structural data on tcm complexes show that the ligand typically coordinates using three or two of its cyanide donors giving rise to polymeric structures [34].

Examples of mono-coordination are more rare [35]. The complex **5** may be compared with the $Ru(II)(PPh_3)_2(Cp)(tcm)$ system [35c]. In both cases threefold symmetry of the mono-coordinating tcm is observed, the Ru–N bond length for $Ru(II)(PPh_3)_2(Cp)(tcm)$ (2.071(6) Å) being slightly shorter than that for **5**.

A comparison of the structures presented here and those in refs. [14–16,32] shows a marked difference in $Ru–N_{sp^3}$ bond lengths between the complexes with tpa coordinating as a tetradentate ligand and those where one pendant arm is uncoordinated. The bond lengths for the former lie in the range 2.037(6)–2.103(4) Å, while for the latter they vary from 2.146(5) to 2.205(4) Å. The effect of shortening the N_{sp^3}–metal bond on going from tetradentate to tridentate tpa coordination was also observed for tpa oxorhenium(V) complexes for which it changes from 1.86 to 2.33 Å [7]. Another geometrical parameter that changes markedly on going from the tetradentate to tridentate coordination mode of tpa is the valency angle defined by the ruthenium and pyridines coordinated *trans* to each other (P pyridines). For the complexes with tetracoordinating pyridine this angle is in the range 160°–166°, while for those with tridentate coordination it is in the range 174°–176°. Complex **4** is a borderline case (vide supra). Hence it seems that although the strong π-back bonding from ruthenium to pyridines favors the tetracoordinating mode of tpa bonding, simultaneously it brings about steric strain by both dragging the sp^3-nitrogen closer to the metal ion and incorporating the meridionally coordinated dpa fragment. With two fused five-member chelate rings disposed merdionally a significant deviation of the $N_{py}–Ru–N_{py}$ angle from 180° occurs leading to a distortion of the octahedral geometry. Both factors increasing the steric strain are removed when one of the pyridines involved in the meridionally coordinated dpa moiety dissociates and facial coordination of dpa occurs. This is well illustrated by the case of formation of **3** from **1**: upon substitution of $[Ru(tpa)(dmso)Cl]^+$ by an additional tpa ligand, one of the pyridines disposed merdionally (P pyridines) undergoes dissociation leading to $[Ru(tpa)_2]^{2+}$. However, the use of terpyridine as the second ligand in a heteroleptic complex enforces mer-

idional coordination of the dpa unit of the tpa ligand [36].

There are two possible structures of $[Ru(tpa)_2]^{2+}$ and $[Ru(Rdpa)_2]^{2+}$ complexes with both ligands coordinating facially with its dpa unit, differing in mutual orientation of the amine nitrogens. Apart from the respective *cis*-orientation resulting in C_2 symmetry of the complex, that has been established, the centerosymmetric isomer with tertiary nitrogens located *trans* to each other can be envisaged. The *trans* effect of a σ-donating sp^3 nitrogen seems to be the likely case for the higher stability of the complex with tertiary nitrogens located *cis* to each other [16].

4. Supplementary material

Atomic coordinates, bond distances and angles are available 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), CCDC reference numbers are 189689–189693 for compounds **1**–**5**.

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