

Chemistry of ruthenium(II) complexes of the tridentate NNS donor methyl 2-pyridyl ketone 4-(4-tolyl)thiosemicarbazone. Isolation and structural characterisation of a novel ruthenium(II) complex containing a co-ordinated imine of an α -N heterocyclic ketone

Milan Maji,^a Madhumita Chatterjee,^a Saktiprosad Ghosh,^{*a} Shyamal Kumar Chattopadhyay,^b Bo-Mu Wu^c and Thomas C. W. Mak^c

^a Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

^b Department of Chemistry, Bengal Engineering College (Deemed University), Howrah 711103, India

^c Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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A series of ruthenium(II) complexes of the NNS donor ligand methyl 2-pyridyl ketone 4-(4-tolyl)thiosemicarbazone (HL) has been synthesized using $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$: $[\text{Ru}(\text{HL})_2][\text{ClO}_4]_2$ **1**, $[\text{Ru}(\text{L})(\text{PPh}_3)_2\text{Cl}]$ **2**, $[\text{Ru}(\text{HL})(\text{PPh}_3)_2\text{Cl}]\text{Cl}$ **3**, $[\text{Ru}(\text{HL})(\text{PPh}_3)_2\text{Cl}]\text{PF}_6$ **4**, $[\text{Ru}(\text{L})(\text{PPh}_3)(\text{bpy})]\text{PF}_6$ **5**, $[\text{Ru}(\text{L})(\text{PPh}_3)(\text{dppe})]\text{PF}_6$ **6**, $[\text{Ru}(\text{HL})(\text{PPh}_3)(\text{pic})]\text{PF}_6$ **7** and $[\text{Ru}(\text{HL})(\text{PPh}_3)(\text{mpi})]\text{Cl}_2$ **8** [where bpy = 2,2'-bipyridine, dppe = 1,2-bis(diphenylphosphino)ethane, Hpic = pyridine-2-carboxylic acid, mpi = methyl(2-pyridyl)methyleneimine]. Chemical and electrochemical studies have been carried out. Structures of the compounds **3**· CH_2Cl_2 **3** and **8**· CH_2Cl_2 · $3\text{H}_2\text{O}$ have been determined by single crystal X-ray diffraction. The thione form of the ligand (HL) is chelated to the ruthenium centre through the pyridine nitrogen, imine nitrogen and the thione sulfur atom. The existence of a new unstable ligand methyl(2-pyridyl)-methyleneimine (mpi) co-ordinated to Ru^{II} through the pyridine and imine nitrogen atoms was confirmed from the crystal structure of compound **8**.

The chemistry of ruthenium bound to nitrogen–sulfur donor ligands has evinced considerable interest in recent years primarily due to their ability to form complexes with unusual stereochemistry,¹ uncommon co-ordination number,^{2,3} interesting electronic structure and bonding situations and with intricate electron-transfer characteristics.^{4,5} Thiosemicarbazides and thiosemicarbazones constitute an important class of nitrogen–sulfur donor ligands, because of their highly interesting chemical^{5–9} and biological properties.¹⁰ As a part of our programme to investigate ruthenium complexes of thiosemicarbazides and thiosemicarbazones in general, we undertook the study of ruthenium complexes of methyl 2-pyridyl ketone 4-(4-tolyl)thiosemicarbazone (HL). During the course of our investigations we came across two very interesting phenomena. (1) Under certain reaction conditions Ru^{II} -catalysed reductive cleavage of the hydrazinic N–N bond of the thiosemicarbazone moiety occurred. Such reductive cleavage is rather common in the molybdenum complexes of hydrazine,¹¹ but never observed previously in the metal complexes of thiosemicarbazides and thiosemicarbazones. (2) We isolated and structurally characterised the first metal complex of the imine of a 2(N)-heterocyclic ketone, *i.e.* a ruthenium(II) complex of methyl(2-pyridyl)-methyleneimine formed during the process mentioned earlier. Most ketone imines ($\text{HN}=\text{CR}^1\text{R}^2$) are unstable at room temperature¹² and are found to react with some metal ions as a monodentate ligand through the imine nitrogen or as an exobidentate ligand bridging two metal ion centres through its deprotonated iminate nitrogen. However, no report on a metal complex containing a co-ordinated imine of a 2(N)-heteroaromatic ketone has appeared previously. This paper reports the results of our studies on several ruthenium complexes involving HL as well as the complex $[\text{Ru}(\text{HL})(\text{PPh}_3)(\text{mpi})]\text{Cl}_2$ containing methyl(2-pyridyl)methyleneimine (mpi). Structures of two complexes, $[\text{Ru}(\text{HL})(\text{PPh}_3)_2\text{Cl}]\text{Cl} \cdot \text{CH}_2\text{Cl}_2$

and $[\text{Ru}(\text{HL})(\text{PPh}_3)(\text{mpi})]\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, are described and discussed.

Experimental

Materials and instrumentation

Elemental analysis were performed with a Perkin-Elmer 240 CHN analyser. Those of complexes **3** and **8** were before crystallisation. The IR and electronic spectra were recorded on a Perkin-Elmer 783 spectrophotometer (as KBr disks) and on a Shimadzu UV-VIS recording spectrophotometer respectively. Solution conductances were measured on a Systronics direct reading conductivity meter (model 304) and magnetic susceptibility (at room temperature) was determined with a PAR vibrating sample magnetometer using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. The NMR spectra were recorded on a Bruker 300 MHz spectrometer using SiMe_4 as an internal standard. Electrochemical data were collected with a BAS CV-27 and a BAS model X-Y recorded at 298 K. Cyclic voltammetry experiments were carried out with platinum working and auxiliary electrodes and a Ag–AgCl reference electrode.

The compound $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was obtained from Arora Matthey (Calcutta, India) and 2-acetylpyridine from Aldrich. 4-(4-Tolyl)thiosemicarbazide¹⁰ and $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ ¹³ were prepared according to published procedures. Acetonitrile (pure) obtained from E. Merck (India) was freshly distilled over calcium hydride for electrochemical experiments. Other reagents were used without further purification.

Preparations

Methyl 2-pyridyl ketone 4-(4-tolyl)thiosemicarbazone (HL). 4-(4-Tolyl)thiosemicarbazide (2.42 g, 0.02 mol) was dissolved in ethanol (100 cm^3) by heating and 2-acetylpyridine (3.62 g,

0.02 mol) was added. The mixture was stirred for 45 min. Then acetic acid (2 cm³) was added and stirred again for 3 h. The product was filtered off, washed with water and diethyl ether and dried. The yield was 90%. ¹H NMR (CDCl₃, room temperature): δ 9.32 (s, 1 H, NH), 8.88 (s, 1 H, NH), 8.76 (d), 8.61 (d), 8.01 (d), 7.87 (t), 7.74 (t), 7.56 (t), 7.37 (t), 7.31 (t), 7.19 (t), 2.49 (s, 3 H, CH₃) and 2.36 (s, 3 H, CH₃).

[Ru(HL)₂][ClO₄]₂ 1. CAUTION! perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of compound should be prepared, and handled with caution.

The ligand (HL) (568 g, 0.2 mmol) was suspended in methanol (30 cm³) and RuCl₃·xH₂O (261 mg, 0.2 mmol) dissolved in methanol (25 cm³) was added drop by drop. The mixture was stirred for 3 h. It was filtered and the filtrate concentrated to about 10 cm³ using a rotary evaporator. An aqueous solution of lithium perchlorate was added to the concentrated solution and the desired compound precipitated. It was washed with water followed by diethyl ether and dried over fused calcium chloride (Found: C, 41.03; H, 3.60; N, 12.90. Calc. for C₃₀H₃₂Cl₂N₈O₈RuS₂: C, 41.47; H, 3.69; N, 12.90%). Conductance in CH₃CN (*A_M*): 230 Ω⁻¹ cm² mol⁻¹. Electronic spectrum in CH₃CN [$\lambda_{\max}/\text{nm}(10^3\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1})$]: 650 (2.536), 382 (86.032), 255 (100.9) and 210 (151.58).

[Ru(L)(PPh₃)₂Cl] 2, [Ru(HL)(PPh₃)₂Cl]Cl 3 and [Ru(HL)(PPh₃)₂Cl]PF₆ 4. The ligand (HL) (71 mg, 0.25 mmol) was dissolved in ethanol (20 cm³) and [Ru(PPh₃)₃Cl₂] (240 mg, 0.25 mmol) added. The mixture was refluxed for 4 h under dry nitrogen, then cooled. The solid product (**2**) was filtered off, washed with ether and dried in a calcium chloride desiccator. The filtrate was concentrated in a rotary evaporator to about 10 mL. Compound **4** was isolated by adding saturated aqueous ammonium hexafluorophosphate to the concentrated solution. It was filtered off, washed thoroughly with water and then with ether and finally dried over fused calcium chloride. Alternatively, the chloride compound **3** was obtained by concentrating the filtrate to about 10 mL and adding ether. The solid separated was filtered off, washed thoroughly with ether and recrystallised from dichloromethane (Found: C, 64.63; H, 4.78; N, 6.01. Calc. for C₅₁H₄₅ClN₄P₂RuS **2**: C, 64.86; H, 4.77; N, 5.93%). Conductance in CH₃CN (*A_M*): 15.4 Ω⁻¹ cm² mol⁻¹. Electronic spectrum in CH₃CN [$\lambda_{\max}/\text{nm}(10^3\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1})$]: 580 (0.9007), 481 (2.256), 398 (9.760), 376 (11.192), 274 (11.870) and 215 (40.85) (Found: C, 62.67; H, 4.83; N, 5.59. Calc. for C₅₁H₄₆Cl₂N₄P₂RuS **3**: C, 62.45; H, 4.69; N, 5.71%). Conductance in CH₃CN 123.09 Ω⁻¹ cm² mol⁻¹. Electronic spectrum in CH₃CN [$\lambda_{\max}/\text{nm}(10^3\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1})$]: 478 (0.3218), 445 (9.381), 402 (10.67), 378 (12.58) and 210 (73.15). ¹H NMR (CDCl₃, room temperature): δ 12.16 (s, 1 H, NH), 11.12 (s, 1 H, NH), 8.76 (d), 7.41 (m), 7.36 (t), 7.24 (m), 7.06 (t), 6.79 (t), 2.31 (s, 3 H, CH₃) and 2.16 (s, 3 H, CH₃) (Found: C, 56.27; H, 4.34; N, 5.19. Calc. for C₅₁H₄₆ClF₆N₄P₃RuS **4**: C, 56.17; H, 4.22; N, 5.14%). Conductance in CH₃CN 153.24 Ω⁻¹ cm² mol⁻¹. Electronic spectrum in CH₃CN [$\lambda_{\max}/\text{nm}(10^3\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1})$]: 478 (0.3712), 442 (11.37), 403 (16.15), 362 (12.37), 265 (35.41) and 212 (52.27).

[Ru(L)(PPh₃)(bpy)]PF₆ 5. The complex [Ru(L)(PPh₃)₂Cl] (119 mg, 0.12 mmol) was dissolved in dichloromethane (20 cm³). 2,2'-Bipyridine (219.5 mg, 0.12 mmol) followed by methanol (25 cm³) was added. The mixture was refluxed for 8 h. After cooling the solution was concentrated in a rotary evaporator to about 10 cm³. Compound **5** was isolated by adding saturated aqueous ammonium hexafluorophosphate to the concentrated solution. The precipitated compound was filtered off, washed thoroughly with distilled water and dried over fused calcium chloride. It was then washed with ether and dried (Found: C, 54.93; H, 4.29; N, 9.1. Calc. for C₄₃H₃₈F₆N₆P₂RuS:

C, 54.49; H, 4.01; N, 8.87%). Conductance in CH₃CN 125.21 Ω⁻¹ cm² mol⁻¹. Electronic spectrum in CH₃CN [$\lambda_{\max}/\text{nm}(10^3\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1})$]: 456 (8.01), 376 (15.59), 296 (28.57) and 209 (81.19).

[Ru(L)(PPh₃)(dppe)]PF₆ 6. The complex [Ru(L)(PPh₃)₂Cl] (120 mg, 0.12 mmol) was dissolved in dichloromethane (20 cm³). 1,2-Bis(diphenylphosphino)ethane (49 mg, 0.12 mmol) was added followed by methanol (25 cm³). The mixture was refluxed for 8 h then concentrated in a rotary evaporator. The compound was isolated by adding an aqueous solution of ammonium hexafluorophosphate. It was filtered off, washed with water and dried over fused calcium chloride. The dry compound was finally washed with ether and dried (Found: C, 60.13; H, 4.67; N, 4.59. Calc. for C₅₉H₅₄F₆N₄P₄RuS: C, 59.54; H, 4.54; N, 4.71. Conductance in CH₃CN 127.10 Ω⁻¹ cm² mol⁻¹. Electronic spectrum in CH₃CN [$\lambda_{\max}/\text{nm}(10^3\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1})$]: 481 (0.820), 424 (5.94), 373 (11.91), 261 (21.75) and 216 (45.96).

[Ru(HL)(PPh₃)(pic)]PF₆ 7. The complex [Ru(L)(PPh₃)₂Cl] (120 mg, 0.12 mmol) was dissolved in dichloromethane (20 cm³). Pyridine-2-carboxylic acid (16 mg, 0.12 mmol) was added, followed by methanol (25 cm³). The mixture was refluxed for 8 h (Hpic) then concentrated in a rotary evaporator. Compound **7** was isolated by adding an aqueous solution of ammonium hexafluorophosphate. It was filtered off, washed thoroughly with water and dried over calcium chloride. The dry compound was washed again with ether and dried (Found: C, 50.8; H, 4.03; N, 4.75. Calc. for C₃₉H₃₄F₆N₅O₂P₂RuS: C, 51.26; H, 3.72; N, 7.67%). Conductance in CH₃CN 139.30 Ω⁻¹ cm² mol⁻¹. Electronic spectrum in CH₃CN [$\lambda_{\max}/\text{nm}(10^3\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1})$]: 577 (0.811), 481 (4.82), 376 (21.93), 256 (23.09) and 220 (54.13).

[Ru(HL)(PPh₃)(mpi)]Cl 8. The complex [Ru(L)(PPh₃)₂Cl] (120 mg, 0.12 mmol) was dissolved in ethanol (40 cm³) and a sixfold excess of ligand (HL) (0.72 mmol) added. The mixture was refluxed for 24 h then cooled and filtered. The filtrate was evaporated to dryness. The solid residue was stirred with *n*-hexane to wash out excess of ligand and triphenylphosphine, filtered off, dried and recrystallised from a mixture of dichloromethane and *n*-hexane. The components in the filtrate were separated by column chromatography using neutral silica gel. The first component was triphenylphosphine eluted with light petroleum (bp 60–80 °C), the middle fraction was *N*-(*p*-tolyl)thiourea and the last fraction with the ligand (HL) eluted with 10% ethyl acetate in light petroleum (Found: C, 57.21; H, 4.62; N, 10.38. Calc. for C₄₀H₃₉Cl₂N₆PRuS **8**: C, 57.28; H, 4.65; N, 10.02%). Conductance in CH₃CN 210.00 Ω⁻¹ cm² mol⁻¹. Electronic spectrum in CH₃CN [$\lambda_{\max}/\text{nm}(10^3\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1})$]: 464 (3.469), 378 (10.94), 317 (15.65), 260 (20.94) and 216 (45.96). ¹H NMR (CDCl₃, room temperature): δ 12.25 (s, 1 H, NH), 8.14 (d), 8.04 (t), 7.87 (q), 7.6 (m), 7.3 (s), 7.05 (d), 6.66 (s), 2.31 (s, 3 H, CH₃) and 2.35 (s, 3 H, CH₃) (Found: C, 57.68; H, 5.93; N, 17.03. Calc. for *N*-(*p*-tolyl)thiourea (C₈H₁₀N₂S): C, 57.83; H, 6.02; N, 16.87%). IR in CHCl₃: ν(NH) 3400, 3380, ν(SH) 2420, ν(C–S) 840 cm⁻¹. ¹H NMR (CDCl₃, room temperature): δ 8.62 (d, 1 H, Ph), 8.24 (d, 1 H, Ph), 7.77 (t, 1 H, Ph), 7.31 (t, 1 H, Ph) and 3.37 (s, 3 H, CH₃).

X-Ray crystallography

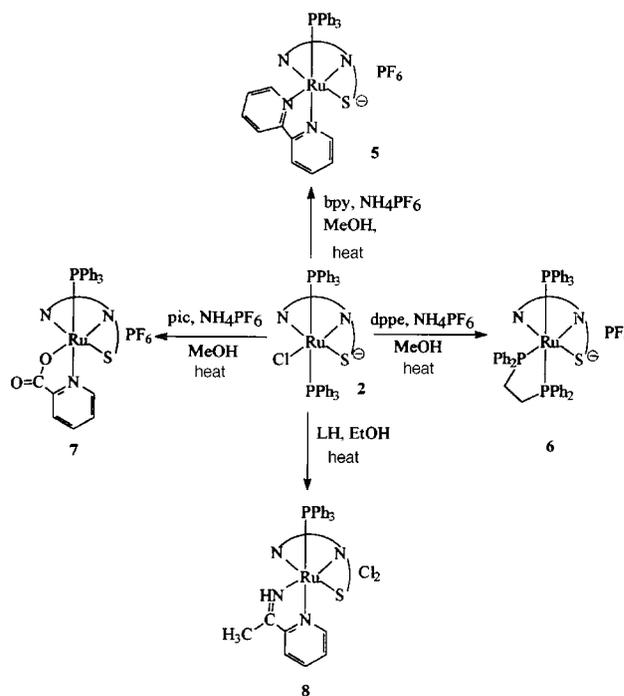
Brown prismatic crystals were grown by the slow diffusion of *n*-hexane into dichloromethane solution of complexes **3** and **8** at room temperature. Single crystals 0.15 × 0.19 × 0.20 and 0.10 × 0.20 × 0.40 mm were chosen for diffraction study respectively. Crystal data are in Table 1. Intensity data were collected at 294 K on a MSC/Rigaku-IIC imaging plate diffractometer using graphite-monochromatized Mo-Kα ($\lambda = 0.71073$

Å) radiation from a rotating anode generator. For **3** a total of 15190 reflections were collected, with 5221 independent reflections ($R_{\text{int}} = 6.44\%$).¹⁴ For complex **8**, 8178 ($R_{\text{int}} = 0.00$) unique data were collected. The intensities were corrected for Lorentz-polarisation effects and absorption using the ABSCOR program.¹⁵ The structure of **3** and **8** were solved by Patterson methods and direct methods respectively. All non-hydrogen atoms were refined anisotropically by full matrix least squares, with a riding model for hydrogen atoms, using the SHELXTL PLUS (PC Version) package.¹⁶ For compound **3** with 2966 [$F > 6.0\sigma(F)$] observed reflections, refinement converged with $R_f = 0.042$ and $R' = 0.049$. Largest difference peak and hole are 0.83 and $-0.93 \text{ e } \text{Å}^{-3}$ respectively. For compound **8** with 6127 observed reflection ($|F_o| \geq 6\sigma|F_c|$), refinement converged with $R_f = 0.072$ and $R' = 0.078$. Largest difference peak and hole are 0.95 and $-0.93 \text{ e } \text{Å}^{-3}$ respectively. Selected bond lengths and bond angles are given in Table 2.

CCDC reference number 186/1231.

Results and discussion

Reaction of ruthenium chloride with HL affords the bis chelate complex $[\text{Ru}(\text{HL})_2][\text{ClO}_4]_2$ **1**. The compound is diamagnetic and behaves as a 1:2 electrolyte in acetonitrile solution. Previous works¹⁷⁻¹⁹ with thiosemicarbazones of 2-acetylpyridine have established that the ligand behaves as a planar NNS donor, co-ordinating through the pyridine nitrogen, the imine nitrogen and the thione sulfur atom. The IR spectrum of compound **1** indicates a similar co-ordination behaviour of the ligand. Thus **1** may be considered as a ruthenium(II) bis chelate, where each tridentate NNS ligand occupies a meridional plane. Reaction of (HL) with $[\text{Ru}(\text{PPh}_3)_2\text{Cl}_2]$ in refluxing ethanol leads to the isolation of the monochelates $[\text{Ru}(\text{L})(\text{PPh}_3)_2\text{Cl}]$ **2** and $[\text{Ru}(\text{HL})(\text{PPh}_3)_2\text{Cl}]\text{X}$ [$\text{X} = \text{Cl}$ **3** or PF_6 **4**]. The neutral complex **2** separated out from the reaction mixture, whereas the cationic complexes [**3** and **4**] were isolated from the mother-liquor by addition of the appropriate anion. Compounds **2** and **3/4** can easily be converted into each other by the addition of acid and base respectively. Crystal structure analysis of **3** established that in the distorted octahedral complex the two triphenylphosphine moieties are *trans* to each other, while the three NNS donor points of the ligand and the co-ordinated chloride constitute the equatorial square plane. The electronic spectrum of the bulk compound **3** in acetonitrile is identical to that of the crystals dissolved in the same solvent, indicating that the bulk compound is the *trans* isomer. The ready interconversion of **2** and **3** and very similar IR and electronic spectra suggest that the *trans* structure also prevails in **2**. The steric repulsion between the two bulky triphenylphosphine moieties, as well as the *p*-tolyl moiety of the ligand leads to the formation of only the *trans* compounds. When compound **2** is dissolved in acetonitrile the co-ordinated chloride is solvolyzed and the resulting solution behaves as a 1:1 electrolyte. However, compounds **3** and **4** did not suffer such a change. It is well known that Ru^{II} , a low spin d^6 system, undergoes substitution by a dissociative mechanism.²⁰ Complex **2** being neutral, can dissociate the chloride ion much more easily than **3** and **4** which are monocationic. Such an effect of the overall charge of the complex unit on the dissociation of chloride ion is well documented.²¹ Compound **2** reacts with bidentate donors like bipyridine (bpy) and dppe to give $[\text{Ru}(\text{L})(\text{PPh}_3)(\text{bpy})]\text{PF}_6$ **5** and $[\text{Ru}(\text{L})(\text{PPh}_3)(\text{dppe})]\text{PF}_6$ **6** (Scheme 1). However, reaction with Hpic produces $[\text{Ru}(\text{HL})(\text{PPh}_3)(\text{pic})]\text{PF}_6$ **7** in which the ligand is present in its protonated form, picolinic acid displaying its usual behaviour by acting in the monoanionic bidentate fashion. The proton dissociated from picolinic acid appears to transform the deprotonated ligand into its protonated form. A very interesting reaction took place when compound **2** was refluxed with an excess of ligand HL. From the reaction medium it was possible to isolate the complex $[\text{Ru}(\text{HL})(\text{PPh}_3)(\text{mpi})]\text{Cl}_2$ **8**, in which the



Scheme 1

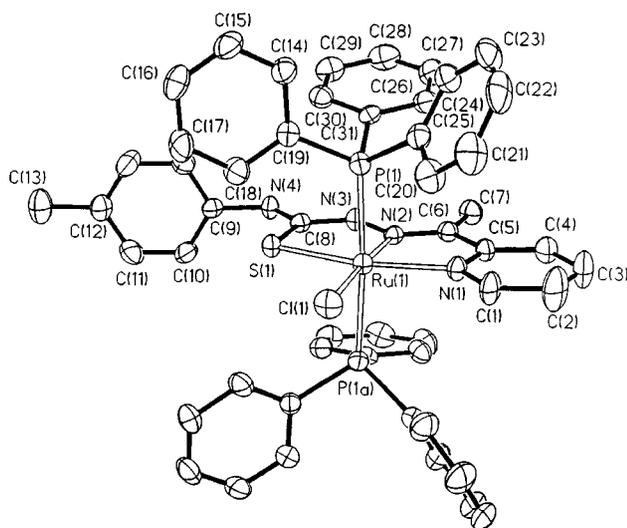
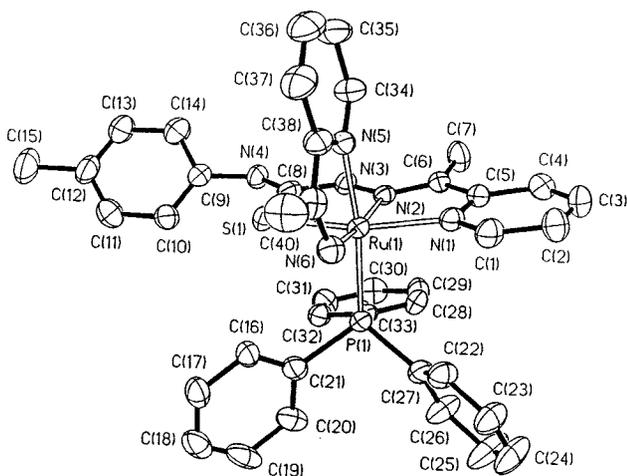
ligand HL is in its protonated form while the imine (mpi) retains its neutral (non-deprotonated) form. Though a number of diphenylmethylenimine complexes are reported in the literature involving a variety of co-ordination modes, no $[\alpha(\text{N})\text{-heterocyclic}]\text{methyleneimine}$ complexes have been reported to date. To our knowledge this is the first report of an $[\alpha(\text{N})\text{-heterocyclic}]\text{iminato}$ complex which has been fully characterised by X-ray crystallography. The formation of the imine complex from the thiosemicarbazone may be visualised to proceed *via* a two-electron reductive cleavage of the hydrazinic N–N bond of the thiosemicarbazone by the ruthenium(II) acceptor centre in **2**. The resulting ruthenium(IV) complex could be reduced subsequently by the triphenylphosphine or by the excess of ligand present in the system. If the ligand plays the role of reductant, it should be converted into the *N*-(4-tolyl)thiourea. The latter is actually isolated from the reaction medium and identified by its characteristic NMR and IR spectra and elemental analysis. The two-electron reductive cleavage of the N–N bond is one of the elementary reaction steps in the reduction of nitrogen to ammonia. Examples of such reductive cleavage are abundant in molybdenum complexes of hydrazine.¹⁰ It is also known that diphenylmethylenimine complexes may be generated by the reaction of an appropriate precursor metal complex and azines like $\text{Ph}_2\text{C}=\text{N}=\text{N}=\text{CPh}_2$. However, this is the first report of the generation of an imine complex by such cleavage of the N–N bond of a thiosemicarbazone co-ordinated to a metal centre.

Structures of complexes **3** and **8**

In both complexes **3** and **8** the ligand occupies a meridional plane co-ordinating through pyridine nitrogen [N(1)], imine nitrogen [N(2)] and the thiolate sulfur [S(1)] atom. Along with these three donor atoms a chlorine [Cl(1)] atom in **3** (Fig. 1) and an imine nitrogen [N(6)] in **8** (Fig. 2) complexes a square plane around the metal ion. The Ru–Cl(1) distance (2.459 Å) in **3** is somewhat long {*cf.* Ru–Cl distance of 2.387 Å in $[\text{Ru}(\text{PPh}_3)_2\text{Cl}_2]$ ¹³}. Two *trans* triphenylphosphine groups in **3** and one triphenylphosphine and one pyridine nitrogen [N(5)] of methyl-(2-pyridyl)methyleneimine ion **8** complete the octahedron. It is worthwhile to make a comparison of structures of **3** and **8** with that of $[\text{Ru}(\text{L}')(\text{PPh}_3)_2]\text{ClO}_4$ **9**; [L' = monoanion of 2,6-diacetylpyridine 4-(4-tolyl)thiosemicarbazone].⁶ The *trans* triphenyl-

Table 1 Crystal data for [Ru(HL)(PPh₃)₂Cl]Cl·CH₂Cl₂ **3** and [Ru(HL)(PPh₃)(mpi)]Cl₂·CH₂Cl₂·3H₂O **8**

| Formula | C ₅₂ H ₄₈ Cl ₄ N ₄ P ₂ RuS | C ₄₁ H ₄₇ Cl ₄ N ₆ O ₃ PRuS |
|---|---|--|
| <i>M</i> | 1065 | 977.7 |
| Space group | <i>Pnma</i> | <i>P1</i> |
| <i>a</i> /Å | 19.279(4) | 11.286(1) |
| <i>b</i> /Å | 15.947(3) | 13.629(1) |
| <i>c</i> /Å | 15.752(3) | 16.109(2) |
| <i>α</i> /° | | 98.36 |
| <i>β</i> /° | | 97.19 |
| <i>γ</i> /° | | 109.02(1) |
| <i>V</i> /Å ³ | 4843(2) | 2277.99(11) |
| <i>Z</i> | 4 | 2 |
| <i>F</i> (000) | 2184 | 1000 |
| <i>D</i> _c /g cm ⁻³ | 1.462 | 1.424 |
| <i>R</i> | 0.0418 | 0.072 |
| <i>R</i> ' | 0.0493 | 0.078 |

**Fig. 1** Perspective view of the [Ru(HL)(PPh₃)₂Cl]⁺ cation of [Ru(HL)(PPh₃)₂Cl]Cl·CH₂Cl₂ with atom labelling.**Fig. 2** Perspective view of the [Ru(HL)(PPh₃)(mpi)]²⁺ cation of [Ru(HL)(PPh₃)(mpi)]Cl₂·CH₂Cl₂·3H₂O with atom labelling.

phosphine groups in **3** have identical Ru–P bond lengths (2.399 Å). These bonds are longer than reported (2.370, 2.373 Å) for *trans*-[Ru(L')(PPh₃)₂]ClO₄ but similar to that observed in [Ru(CO)(C₂HN₂S₃)₂(PPh₃)₂]²² (2.397 Å, 2.399 Å). However, the Ru–P bond lengths in both **3** and **9** are longer than that observed in **8** (2.334 Å), the latter being on the shorter side of the range normally observed for Ru–P bonds.²³ Again, in the 2-acetylpyridine Schiff base complexes **3** and **8**, the Ru–N (py) distances are larger than the Ru–N (imine) distances, but in 2,6-

Table 2 Selected bond distances (Å) and angles (°) for [Ru(HL)(PPh₃)₂Cl]Cl·CH₂Cl₂ **3** and [Ru(HL)(PPh₃)(mpi)]Cl₂·CH₂Cl₂·3H₂O **8**

| | | | |
|-------------------|----------|------------------|-----------|
| Ru(1)–N(1) | 2.085(5) | Ru(1)–N(1) | 2.092(6) |
| Ru(1)–N(2) | 1.984(5) | Ru(1)–N(2) | 1.991(5) |
| Ru(1)–S(1) | 2.386(2) | Ru(1)–S(1) | 2.358(2) |
| Ru(1)–P(1) | 2.399(1) | Ru(1)–P(1) | 2.334(2) |
| Ru(1)–P(1A) | 2.399(1) | Ru(1)–N(5) | 2.110(6) |
| Ru(1)–Cl(1) | 2.459(2) | Ru(1)–N(6) | 2.075(7) |
| C(6)–N(2) | 1.304(7) | C(6)–N(2) | 1.336(8) |
| N(2)–N(3) | 1.383(7) | N(2)–N(3) | 1.371(9) |
| N(3)–C(8) | 1.359(7) | N(3)–C(8) | 1.347(8) |
| C(8)–S(1) | 1.707(6) | C(8)–S(1) | 1.698(7) |
| C(8)–N(4) | 1.334(8) | C(8)–N(4) | 1.344(11) |
| C(5)–C(6) | 1.462(9) | C(5)–C(6) | 1.478(12) |
| N(4)–C(9) | 1.416(8) | N(4)–C(9) | 1.418(9) |
| N(1)–Ru(1)–N(2) | 77.4(2) | N(1)–Ru(1)–N(2) | 78.0(2) |
| N(1)–Ru(1)–S(1) | 160.8(1) | N(1)–Ru(1)–S(1) | 161.1(2) |
| N(1)–Ru(1)–Cl(1) | 99.0(1) | N(1)–Ru(1)–N(6) | 98.7(3) |
| N(2)–Ru(1)–Cl(1) | 176.4(1) | N(2)–Ru(1)–N(6) | 169.5(2) |
| N(2)–Ru(1)–S(1) | 83.3(1) | N(2)–Ru(1)–S(1) | 83.4(2) |
| Cl(1)–Ru(1)–S(1) | 100.2(1) | N(6)–Ru(1)–S(1) | 98.9(2) |
| P(1)–Ru(1)–N(1) | 91.9(1) | P(1)–Ru(1)–N(1) | 97.0(2) |
| P(1)–Ru(1)–N(2) | 91.9(1) | P(1)–Ru(1)–N(2) | 92.0(2) |
| P(1)–Ru(1)–S(1) | 88.7(1) | P(1)–Ru(1)–S(1) | 87.3(1) |
| P(1)–Ru(1)–Cl(1) | 88.2(1) | P(1)–Ru(1)–N(6) | 98.3(2) |
| P(1)–Ru(1)–P(1A) | 175.2(1) | P(1)–Ru(1)–N(5) | 171.6(1) |
| P(1A)–Ru(1)–N(1) | 91.9(1) | N(5)–Ru(1)–N(1) | 90.4(2) |
| P(1A)–Ru(1)–N(2) | 91.9(1) | N(5)–Ru(1)–N(2) | 93.5(2) |
| P(1A)–Ru(1)–S(1) | 88.7(1) | N(5)–Ru(1)–S(1) | 87.0(2) |
| P(1A)–Ru(1)–Cl(1) | 88.2(1) | N(1)–Ru(1)–N(6) | 76.5(2) |
| C(5)–C(6)–N(2) | 112.5(5) | C(5)–C(6)–N(2) | 110.8(6) |
| | | C(38)–C(39)–N(6) | 115.3(7) |

diacetylpyridine monothiosemicarbazone complex **9** the opposite trend is observed.⁶ In **9** the Ru–N (py) distance is appreciably shorter than the normally observed value and the Ru–N (py) distances increase in the order **9** < **3** < **8**. The Ru–N(2) (imine) distances are slightly shorter than the Ru–N(1) (py) distances, but they follow the same order, *e.g.* **9** < **3** < **8**. The Ru–S(1) distances are normal, but they follow an order opposite to that of the Ru–N(1) distances, *e.g.* **9** > **3** > **8**. The C(8)–S(1) distances in all the three compounds are similar (1.69–1.71 Å) and close to the C=S distances observed in the free thiosemicarbazides and thiosemicarbazones.^{24,25} Again, though the imine C(6)–N(2) distances are close to their expected values, both the C(8)–N(3) bond distances in the thiosemicarbazone moiety are appreciably shorter than the C–N single bond distance. The C(8)–N(4) distance in **8** is shorter than the C(8)–N(3) distance, but in complex **9** the opposite is true. Similarly the N(2)–N(3) distances in all the complexes are appreciably shorter than that reported for free thiosemicarbazide or for hydrazine.^{23,24} It has been suggested that in thiosemicarbazides and thiosemicarbazones there is an extensive π delocalisation over the entire chain, so that none of the bonds can be considered a true single or double bond. Rheingold and co-workers⁹ proposed that, even in deprotonated thiosemicarbazones, the iminothiolate sulfur S(1) undergoes rehybridisation to sp² and the lone pair on the p orbital can participate in conjugation with the imine moiety. Such extensive π delocalisation within the ligand moiety coupled with the π backbonding from the metal is responsible for the apparent anomalies in bond distances mentioned above.

Electrochemistry

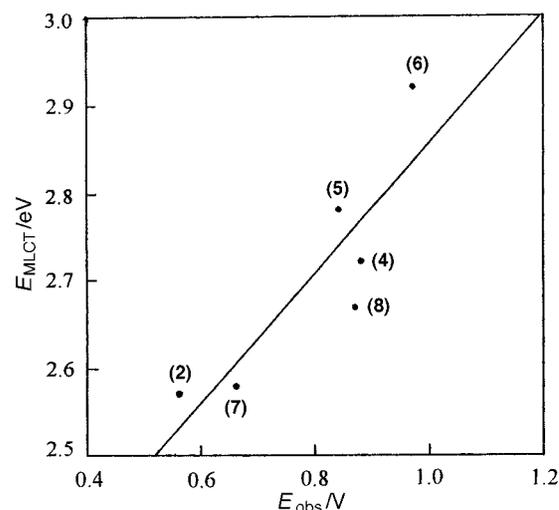
The electrochemical data for the complexes are given in Table 3. The electrochemistry of the complexes is dominated by a reversible Ru^{II}–Ru^{III} oxidation. Peak potential separations between anodic and cathodic peaks, $E_{pa} - E_{pc}$, vary between 60 and 90 mV and are virtually independent of scan rate. These peak separations, though larger than the ideal Nernstian value of 59 mV, are commonly observed for this type of com-

Table 3 Cyclic voltammetric data^a of the complexes in acetonitrile at 298 K

| Compound | E_i/V ($\Delta E_p/mV$) | | Donor sites ^b |
|--|-----------------------------|------------|------------------------------------|
| | Oxidation | Reduction | |
| 1 [Ru(HL) ₂][ClO ₄] ₂ | 0.005(90) | | N ₄ S ₂ |
| 2 [Ru(L)(PPh ₃) ₂ Cl] | 0.36(75) | | N ₂ P ₂ S'Cl |
| 3 [Ru(HL)(PPh ₃) ₂ Cl]Cl | 0.65(60) | | N ₂ P ₂ S'Cl |
| 4 [Ru(HL)(PPh ₃) ₂ Cl]PF ₆ | 0.70(60) | | N ₂ P ₂ S'Cl |
| 5 [Ru(L)(PPh ₃)(bpy)]PF ₆ | 0.65(60) | -1.42(100) | N ₄ PS' |
| 6 [Ru(L)(PPh ₃)(dppe)]PF ₆ | 0.77(80) | | N ₂ P ₃ S' |
| 7 [Ru(HL)(PPh ₃)(pic)]PF ₆ | 0.47(60) | | N ₃ PSO |
| 8 [Ru(HL)(PPh ₃)(mpi)]Cl ₂ | 0.67(60) | -1.56(80) | N ₄ PS |

^a Conditions: supporting electrolyte, NEt₄ClO₄ (0.1 M); working electrode, platinum; reference electrode, Ag-AgCl; solute concentration, 10⁻³ M. E_i is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials; $\Delta E_p = E_{pa} - E_{pc}$; $I_{pc}/I_{pa} = 1$, and scan rate = 50 mV s⁻¹.
^b S refers to thiocarbonyl sulfur and S' to thiolato sulfur.

plexes.^{6,26,27} In most of the cases no well defined peaks are observed at the cathodic side of the cyclic voltammograms. This is probably due to the reduction of the ligand followed by decomposition of the resultant complex. For complexes **5** and **8** a reductive couple observed around -1.5 V may be ascribed to a ligand (bipyridine/mpi) centered reduction.²⁸ It may be noted that in this study we have extensively varied the co-ordination environment around the ruthenium(II) acceptor centre employing a variety of nitrogen, sulfur, phosphorus, oxygen and chloride donors. So, it is worthwhile to follow the trend in the variation of Ru^{III}-Ru^{II} potential with the change of donor environment around the metal ion, particularly because such studies are rather scanty.²⁹ It is well established that such potentials are affected by both the nature of the donor sets as well as the overall charge of the complex, the latter being the dominating factor. So, a meaningful correlation is possible only when one compares complexes having identical charges. Thus, we may compare the $E_{Ru(III)/Ru(II)}$ of Ru(bpy)₃²⁺ (1.38 V, N₆ donors) with that of [Ru(HL)₂]²⁺ (-0.005 V, N₄S₂ donors) and conclude that replacement of two pyridine nitrogens by two thiocarbonyl sulfurs has stabilised the Ru^{III} by 1.43 V. This may be rationalised by referring to the higher polarisability and poorer π -accepting capability of the thiocarbonyl sulfur compared to pyridyl nitrogen, and both the factors tend to stabilise the ruthenium(III) state. Again, we can compare the Ru^{III}-Ru^{II} potential of the complex [Ru(L)(PPh₃)₂Cl] (0.36 V, N₂P₂S'Cl donors) with that of [Ru(bpy)₂Cl₂] (0.34 V, N₄Cl₂ donors); in this case the replacement of two pyridine nitrogens and a chloride by two phosphorus and a thiolato donor set keeps the potential almost unaltered. Though thiolato ligands are known to be efficient in stabilising higher (III and IV) oxidation states of ruthenium, in the present case that effect is compensated by the introduction of two phosphine donors, which are even more efficient in stabilising ruthenium(II) than the pyridine nitrogens. Similarly one can compare the series of five monocationic complexes [Ru(HL)(PPh₃)₂Cl]-Cl (0.65 V, N₂P₂S'Cl donors), [Ru(HL)(PPh₃)₂Cl]PF₆ (0.70 V, N₂P₂S'Cl donors), [Ru(L)(PPh₃)(bpy)]PF₆ (0.65 V, N₄PS' donors), [Ru(L)(PPh₃)(dppe)]PF₆ (0.77 V, N₂P₃S' donors) and [Ru(HL)(PPh₃)(pic)]PF₆ (0.47 V, N₃PSO donors) and conclude that the presence of bipyridine nitrogen or imine nitrogen as well as phosphine donors tends to stabilise the ruthenium(II) state, whereas thiolato and carboxylato donors stabilise the ruthenium(III) state. One may also compare the $E_{Ru(III)/Ru(II)}$ values of [Ru(bpy)₂(SPh)₂] (-0.28 V, N₄S₂⁻ donors)²⁹ and [Ru(bpy)₂(pybt)]⁺ [0.32 V, N₅S⁻ donors; pybt = 2-(2-pyridyl)benzenethiolate]²⁸ with those of thiolato complexes reported in this paper and conclude that the benzenethiolato group is more efficient in stabilising Ru^{III} than the iminethiolates described in this paper, a fact which correlates

**Fig. 3** Plot of E_{MLCT} versus Ru^{III}-Ru^{II} potential (E_{obs} , on NHE scale).

well with the lower basicity of the latter as described by Rheingold and co-workers.⁹

Electronic spectra

The electronic spectra of low-spin d⁶ complexes are generally dominated by metal to ligand charge transfer in the visible region.³⁰⁻³² As most of the complexes discussed in this work are of C_s or lower symmetry all the d orbitals are non-degenerate. So, a number of MLCT transitions are expected. However, due to the small energy separation between some of these d orbitals, as well as poor overlap between them and the excited state orbitals, some of the expected MLCT transitions may not be resolved. In general, all the complexes exhibit two well resolved MLCT transitions around 420-480 (band I) and 373-378 nm (band II). When the energy of band I is plotted against $E_{Ru(III)/Ru(II)}$ a nice linear correlation $E_{MLCT} = 1.18 E_{Ru(III)/Ru(II)} + 2.42$ is obtained (Fig. 3). Besides, for some of the complexes, there is an additional low energy band at 480-580 nm (band III). While bands I and III are substituent dependent, II is unaffected by substituents. The two highest energy bands at 260-290 and 210-220 nm are probably due to intraligand transitions.

¹H NMR spectra

The ¹H NMR spectrum of the ligand (HL) exhibits signals at δ 2.49 (3 H) and 2.35 (3 H) which are assigned to the CH₃ group of the *p*-tolyl moiety and that attached to the imine moiety of the ligand. The signals at δ 9.32 (1 H) and 8.9 (1 H) are due to NH protons and all aromatic protons exhibit signals in the region δ 7.19-8.61.³³ For complex **3** the signal of the CH₃ group attached to the imine moiety was shifted upfield to δ 2.16, whereas the CH₃ proton signal of the *p*-tolyl moiety remains unaffected at δ 2.31. The NH proton signals are at δ 12.16 and 11.12. The aromatic protons are observed between δ 6.8 and 8.76. Compound **8** exhibits three CH₃ proton signals at δ 2.31 (3 H), 2.35 (3 H) and 2.46 (3 H). The signal at δ 2.35 is due to the CH₃ group of the *p*-tolyl residue. One NH signal is observed at δ 12.25. The broken organic fragment isolated from the reaction mixture [N-(*p*-tolyl)thiourea] exhibits a signal at δ 3.37 due to the CH₃ group³³ of the tolyl part. The phenyl protons are observed between δ 7.3 and 8.62. The NH proton signals are not observed and similar observations were reported³⁴ previously in the case of N-(*p*-nitrophenyl)thiourea.

Conclusion

This paper describes the ruthenium(II) complexes of methyl 2-pyridyl ketone 4-(4-tolyl)thiosemicarbazone, in which the

ligand behaves either as a monoanionic tridentate NNS donor (thioenol form) or as a neutral tridentate NNS donor (thione form). The pH-dependent interconversion of the compounds $[\text{Ru}(\text{L})(\text{PPh}_3)_2\text{Cl}]$ and $[\text{Ru}(\text{HL})(\text{PPh}_3)_2\text{Cl}]\text{Cl}$ is a manifestation of thione–thioenol tautomerisation of the co-ordinated ligand. Formation of the compound $[\text{Ru}(\text{HL})(\text{PPh}_3)(\text{mpi})]\text{Cl}_2$ from the complex $[\text{Ru}(\text{L})(\text{PPh}_3)_2\text{Cl}]$ is an extremely interesting manifestation of the unusual reactivity of the co-ordinated thiosemicarbazone moiety. The complex $[\text{Ru}(\text{HL})(\text{PPh}_3)(\text{mpi})]\text{Cl}_2$, produced through reductive cleavage of the hydrazinic N–N bond of the thiosemicarbazone ligand, is the first structurally characterised metal complex of an imine of a heterocyclic ketone. The crystal structure of the compound $[\text{Ru}(\text{HL})(\text{PPh}_3)_2\text{Cl}]\text{Cl}\cdot\text{CH}_2\text{Cl}_2$ has been of great help in understanding the rather unusual chemical reaction leading to the formation of $[\text{Ru}(\text{HL})(\text{PPh}_3)(\text{mpi})]\text{Cl}_2$.

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