New Piano-stool Ruthenium(II) Complexes of Benzene and Bidentate/Tridentate Nitrogen-donor Ligands: Synthesis and Characterization†

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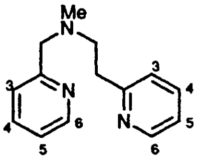
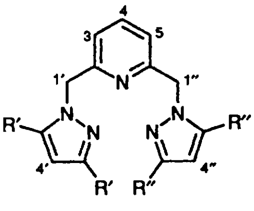
New piano-stool ruthenium(II) complexes, $[Ru(\eta^6\text{-}C_6H_6)L^1]^{2+}$, $[Ru(\eta^6\text{-}C_6H_6)(L^2)Cl]^+$, $[Ru(\eta^6\text{-}C_6H_6)(L^3)Cl]^+$, $[Ru(\eta\text{-}C_6H_6)(L^4)Cl]^+$ and $[Ru(\eta^6\text{-}C_6H_6)(L^5)Cl]^+$ have been isolated as their hexafluorophosphate salts by bridge-cleavage reactions of $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ in methanol with the potentially tri- and bi-dentate nitrogen-containing ligands [2-(2-pyridyl)ethyl](2-pyridylmethyl)methylamine (L^1), 2,6-bis(pyrazol-1-ylmethyl)pyridine (L^2) and its tetramethyl-substituted derivative (L^3), 2-(pyrazol-1-ylmethyl)pyridine (L^4) and its dimethyl derivative (L^5). The structures of these compounds in MeCN solution have been elucidated by ^1H NMR spectroscopy. The complex $[Ru(\eta^6\text{-}C_6H_6)L^1][PF_6]_2$ has been characterized by single-crystal X-ray crystallography: triclinic, space group $P\bar{1}$ (no. 2), $a = 7.790(3)$, $b = 10.039(3)$, $c = 16.679(5)$ Å, $\alpha = 88.31(2)$, $\beta = 83.15(3)$, $\gamma = 77.19(3)°$ and $Z = 2$. The structure has been refined to an R factor of 0.063 based on 5330 observed reflections. Average Ru–C and Ru–N (two types) bond lengths are 2.202(6) and 2.114(5) and 2.170(5) Å respectively.

Benzene complexes of ruthenium(II) are well known[1] but the corresponding half-sandwich or piano-stool complexes $[Ru(\eta^6\text{-}C_6H_6)L_3]^{z+}$ or $[Ru(\eta^6\text{-}C_6H_6)L(L')]^+$ or $[Ru(\eta^6\text{-}C_6H_6)L'']^+$ (L = mono-, L′ = bi- and L″ = tri-dentate ligand, z = 0–2) have been studied only occasionally.[2–8]

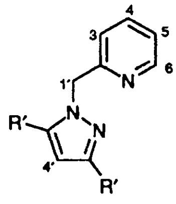
Mann and co-workers[9] reported a class of piano-stool cyclopentadienyl complexes using pyrazolylborates as tridentate nitrogen-donor ligands. However, there is no report in the literature of the existence of piano-stool complexes of $Ru^{II}(\eta^6\text{-}C_6H_6)$ containing pyridine as part of the tridentate donor ligands. Herein we report the syntheses and characterization of cationic piano-stool compounds of ruthenium(II) with benzene and a variety of tri- and bi-dentate nitrogen-containing ligands.



L1



L^2 R′ = R″ = H
L^3 R′ = R″ = Me



L^4 R′ = H
L^5 R′ = Me

Experimental

Materials.—All chemicals and reagents were obtained from commercial sources and used as received, unless otherwise stated. The compound $RuCl_3{\cdot}3H_2O$ and tetrabutylammonium perchlorate were purified/synthesized as before.[10,11] [2-(2-Pyridyl)ethyl](2-pyridylmethyl)methylamine (L^1), 2,6-bis(pyrazol-1-ylmethyl)pyridine (L^2), 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L^3), 2-(pyrazol-1-ylmethyl)pyridine (L^4) and 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L^5) were prepared as described.[10c,12–14] Acetonitrile, methanol and diethyl ether were purified as reported previously.[10] The starting complex $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ was synthesised by literature procedures.[5a,15]

Syntheses of Ruthenium Complexes.—All the complexes were synthesized by bridge cleavage of $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ with compounds L^1–L^5, in methanol at room temperature. Details are, therefore, given for a representative complex.

$[Ru(\eta^6\text{-}C_6H_6)L^1][PF_6]_2$ **1**. To a methanolic solution (40 cm³) of L^1 (0.45 g, 1.0 mmol) was added solid $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ (0.5 g, 1.0 mmol). The mixture was stirred for 12 h at room temperature and the yellow solution thus obtained was then filtered. The desired complex which precipitated as a yellow microcrystalline solid upon dropwise addition of a saturated solution of NH_4PF_6 was filtered off, washed with cold methanol and finally dried *in vacuo*. It was recrystallized from hot methanol (0.2 g, yield 72%), m.p. 210–220 °C (Found: C, 34.8; H, 3.50; N, 6.20. Calc. for $C_{20}H_{23}F_{12}N_3P_2Ru$: C, 34.5; H, 3.30; N, 6.00%). Molar conductance, Λ_M (MeCN, 298 K) = 300 Ω^{-1} cm² mol⁻¹. UV/VIS spectrum (in MeCN): λ/nm (ε/dm³ mol⁻¹ cm⁻¹) 267 (9030) and 363 (710). Cyclic voltammetry (in MeCN): reductive response, E_{pc} (cathodic peak potential) at −1.12 V.

$[Ru(\eta^6\text{-}C_6H_6)(L^2)Cl]PF_6$ **2**: m.p. 180 °C (decomp.) (Found: C, 37.9; H, 3.00; N, 11.20. Calc. for $C_{19}H_{19}ClF_6N_5PRu$: C, 38.1; H, 3.20; N, 11.70%). Molar conductance, Λ_M (MeCN, 298 K) = 138 Ω^{-1} cm² mol⁻¹. UV/VIS spectrum (in MeCN): λ/nm (ε/dm³ mol⁻¹ cm⁻¹): 274 (5800), 327(sh) (900) and 407 (400). Cyclic voltammetry (in MeCN): reductive responses (E_{pc}) at

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

-1.15 and -1.44 V; oxidative response, E_{pa} (anodic peak potential) at 1.78 V.

$[Ru(\eta^6\text{-}C_6H_6)(L^3)Cl]PF_6$ **3**: m.p. 210 °C (decomp.) (Found: C, 41.9; H, 3.90; N, 10.40. Calc. for $C_{23}H_{27}ClF_6N_5PRu$: C, 42.2; H, 4.10; N, 10.70%). Molar conductance, Λ_M (MeCN, 298 K) = 130 Ω^{-1} cm^2 mol^{-1}. UV/VIS spectrum (in MeCN): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 276 (7450), 330 (sh) (1150) and 412 (570). Cyclic voltammetry (in MeCN): reductive responses (E_{pc}) at -1.06 and -1.30 V.

$[Ru(\eta^6\text{-}C_6H_6)(L^4)Cl]PF_6$ **4**: m.p. 200 °C (decomp.) (Found: C, 34.4; H, 3.00; N, 7.90. Calc. for $C_{15}H_{15}ClF_6N_3PRu$: C, 34.7; H, 2.95; N, 8.10%). Molar conductance, Λ_M (MeCN, 298 K) = 134 Ω^{-1} cm^2 mol^{-1}. UV/VIS spectrum (in MeCN): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 261 (4050), 287 (sh) (3200) and 408 (360). Cyclic voltammetry (in MeCN): reductive responses (E_{pc}) at -1.10, -1.20 and -1.62 V.

$[Ru(\eta^6\text{-}C_6H_6)(L^5)Cl]PF_6$ **5**: m.p. 250 °C (decomp.) (Found: C, 36.9; H, 3.20; N, 7.50. Calc. for $C_{17}H_{19}ClF_6N_3PRu$: C, 37.3; H, 3.40; N, 7.70%). Molar conductance, Λ_M (MeCN, 298 K) = 135 Ω^{-1} cm^2 mol^{-1}. UV/VIS spectrum (in MeCN): λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 261 (4900), 290 (sh) (3400) and 409 (380). Cyclic voltammetry (in MeCN): reductive responses (E_{pc}) -1.14 and -1.26 V.

Physical Measurements.—Conductivity measurements were done with an Elico Type CM-82T conductivity bridge (Hyderabad, India) with solute concentrations of *ca*. 1.0×10^{-3} mol dm^{-3}. Spectroscopic measurements were made using the following instruments: IR (KBr, 4000–600 cm^{-1}), Perkin Elmer 1320; electronic, Perkin Elmer Lambda-2; ^{1}H NMR (in CD_3CN), Brüker WM-400 (400 MHz) spectrometer (Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow, India) using $SiMe_4$ as internal standard.

Cyclic voltammetric measurements were made using a PAR model 370 electrochemistry system: 174 A polarographic analyser, 175 universal programmer and RE 0074 *x–y* recorder. Potentials are reported at 298 K referenced to a saturated calomel electrode (SCE) and are uncorrected for the junction contribution. A planar Beckman model 39273 platinum inlay electrode was used as the working electrode. The details of the cell configuration were as described before.[11,12]

Crystal Structure Determination of $[Ru(\eta^6\text{-}C_6H_6)L^1][PF_6]_2$.—*Crystal data*. $C_{20}H_{23}F_{12}N_3P_2Ru$, M = 696.42, triclinic, space group $P\bar{1}$ (no. 2), a = 7.790(3), b = 10.039(3), c = 16.679(5) Å, α = 88.31(2), β = 83.15(3), γ = 77.19(3)°, U = 1262.8 Å^3, Z = 2, D_c = 1.83 g cm^{-3}, D_m = 1.82 g cm^{-3}, $F(000)$ = 690, λ(Mo-Kα) = 0.710 73 Å, μ = 8.4 cm^{-1}. Crystal dimensions: *ca*. $0.30 \times 0.45 \times 0.45$ mm.

Data collection and processing. Yellowish block crystals of $[Ru(\eta^6\text{-}C_6H_6)L^1)(PF_6]_2$ were obtained by slow evaporation of a methanolic solution and one was mounted on a glass fibre. Diffracted intensities were collected [scan mode ω–2θ, scan rate 1–3° min^{-1} (in ω), scan width $(0.90 + 0.34 \tan\theta)°$, graphite-monochromated Mo-Kα radiation] at 296 K in the range $2.8 \leqslant 2\theta \leqslant 55°$, on an Enraf-Nonius CAD-4 diffractometer (University of Louisville). Data were corrected for Lorentz polarization effects and an empirical absorption correction based on ψ scans was applied. Relative transmission coefficients ranged from 0.937 to 0.999 (average 0.973). A secondary extinction correction was applied.[16] Of the 6026 reflections collected, 5764 were unique, of which 5330 satisfying the relation $I \geqslant 3\sigma(I)$ were used for the structure solution.

Structure analysis and refinement. The position of the Ru atom was located from a Patterson map and the remaining non-hydrogen atoms emerged from a series of Fourier difference maps. The hydrogen atoms were located and added to the structure-factor calculations but their positions were not refined. All refinements were performed by full-matrix least-squares procedure, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weighting function applied in the final cycles was that of Killean and Lawrence[17] with $w = [\sigma(F) + (0.002F)^2 + 3.0]^{-1}$. Final agreement factors were $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ = 0.063 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ = 0.069 for 332 parameters. The maximum and minimum peaks in the final Fourier difference map corresponded to 1.00 and 0.00 e Å^3. All computations were performed on a VAX-11/750 computer by using the MOLEN (Enraf-Nonius) programs.[18] Atomic scattering factors, corrected for anomalous dispersion effects, were taken from ref. 19.

Both the hexafluorophosphate anions were found to be disordered. For each P atom twelve positions could be located as possible F positions. The occupancy of each disordered F atom was constrained to 0.5. With this model the structure converged to the observed R values. The final atomic coordinates are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Syntheses and Selected Properties.—The present $Ru(\eta^6\text{-}C_6H_6)^{2+}$ complexes were obtained from the reaction of $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ with tridentate/bidentate compounds L^1–L^5, in methanol at room temperature. This synthetic method involves *in situ* use of $[Ru(\eta^6\text{-}C_6H_6)(MeOH)_3]$; analogous reagents were previously shown[7b] to be highly efficient synthetic precursors for the synthesis of many arene–ruthenium complexes. The yellow salts **1**–**5** were isolated in 70–80% yield by the addition of NH_4PF_6. These new compounds are air stable and soluble in most polar organic solvents. We have used acetonitrile in our solution studies, in which complex **1** behaves as a 1:2 electrolyte whereas **2**–**5** are 1:1 electrolytes.[20] Microanalytical and solution electrical conductivity data (Experimental section) support the formulations of these new compounds. Interestingly, in complexes **2** and **3** the potentially tridentate ligands L^2 and L^3 act in a bidentate manner with a dangling arm (see below). To confirm this we synthesized complexes **4** and **5** using bidentate ligands L^4 and L^5 having only one pyrazole group attached to a pyridine ring at the 2 position. Presumably, the meridional co-ordination mode of L^2 (ref. 21) and L^3 limits formation of the tridentate ligand co-ordination products.

The absorption spectral features of these compounds are straightforward (Experimental section). We assign the short-wavelength band(s) in the region 260–290 nm to π–d transitions and the longer-wavelength band(s) in the region 325–420 nm to symmetry-forbidden d–d transitions.[5e,22]

Structures of the Complexes.—(*a*) ^{1}*H NMR spectra*. The ^{1}H NMR spectra of representative compounds **3** and **5** are shown in Fig. 1. The data (Table 2) support the expected 'piano-stool' structure of these compounds. For a representative compound **1** the structure has been confirmed by X-ray crystallography (see below). The proton resonances of **1**–**5** were assigned based on the available ^{1}H NMR spectral results for the free ligands[10b,c,12–14] and those for related compounds.[8,9,23] The spectra of these compounds are consistent with the presence of a benzene ligand and tri- (L^1) or bi-dentate (L^2–L^5) ligands. In the spectra of these compounds the benzene resonance always appears as a sharp singlet.

A few comments regarding the ^{1}H NMR spectral data for complex **1** are in order. The NCH_2 protons (associated with the pyridine ring which provides a five-membered chelate ring) give rise to an AB quartet, which confirms the presence of two diastereotopic protons, axial and equatorial. However, the NCH_2CH_2 protons exhibit two sets of multiplets.

Bidentate pyridylpyrazole binding in complexes **2** and **3** is consistent with the appearance of two sets of pyrazole ring protons/methyl groups for ligands L^2 and L^3. One set was shifted from the free-ligand positions and the other set was not

Table 1 Fractional atomic coordinates for non-hydrogen atoms in $[Ru(\eta^6\text{-}C_6H_6)L^1][PF_6]_2$ **1** with estimated standard deviations (e.s.d.s) in parentheses.

Atom	*x*	*y*	*z*
Ru	0.171 44(5)	0.238 27(4)	0.250 55(3)
P(1)	0.084 0(3)	0.234 4(2)	0.919 6(1)
P(2)	0.980 5(3)	0.236 9(2)	0.593 6(1)
F(11)	0.111(1)	0.089 0(9)	0.878 2(5)
F(12)	−0.114(1)	0.269(1)	0.901 5(6)
F(13)	0.152(1)	0.302(1)	0.839 3(7)
F(14)	0.289(1)	0.194 5(8)	0.934 0(5)
F(15)	0.056(2)	0.380(1)	0.956 0(7)
F(16)	0.027(1)	0.171(1)	1.002 3(7)
F(11B)	−0.092(2)	0.193(2)	0.962(1)
F(12B)	0.198(3)	0.109(2)	0.962(1)
F(13B)	−0.034(3)	0.364(2)	0.885(1)
F(14B)	0.087(2)	0.140(1)	0.845 1(7)
F(15B)	0.089(2)	0.320(1)	0.999 2(8)
F(16B)	0.252(2)	0.273(2)	0.872(1)
F(21)	1.109(1)	0.177 5(9)	0.513 8(6)
F(22)	0.871(1)	0.306(1)	0.670 4(6)
F(23)	0.869(1)	0.310(1)	0.527 1(7)
F(24)	1.051(1)	0.366(1)	0.603 0(7)
F(25)	1.108(1)	0.138(1)	0.646 7(7)
F(26)	0.889(1)	0.112(1)	0.596 0(6)
F(21B)	0.220(2)	−0.298(1)	0.358 7(9)
F(22B)	0.075(2)	−0.360(2)	0.466(1)
F(23B)	0.138(2)	−0.140(2)	0.439 4(9)
F(24B)	−0.155(2)	−0.160(1)	0.454 6(9)
F(25B)	−0.135(2)	−0.317(2)	0.388(1)
F(26B)	−0.014(3)	−0.147(2)	0.329(1)
N(1)	0.362 9(7)	0.065 0(5)	0.195 7(3)
N(2)	0.349 3(6)	0.338 6(5)	0.182 4(3)
N(3)	0.333 8(6)	0.237 8(5)	0.344 6(3)
C(1)	0.292(1)	−0.055 3(7)	0.177 7(6)
C(2)	0.429(1)	0.121 5(9)	0.113 9(5)
C(3)	0.458 0(8)	0.261 4(9)	0.121 7(4)
C(4)	0.362(1)	0.466 2(7)	0.193 7(6)
C(5)	0.490(1)	0.521 9(9)	0.143 6(6)
C(6)	0.594(1)	0.442(1)	0.085 4(6)
C(7)	0.581(1)	0.312(1)	0.074 0(5)
C(8)	0.519(1)	0.020 1(8)	0.238 3(6)
C(9)	0.469(1)	0.003 8(8)	0.328 1(5)
C(10)	0.445 4(8)	0.129 8(7)	0.371 6(4)
C(11)	0.316 0(9)	0.357 9(8)	0.383 9(5)
C(12)	0.404(1)	0.372(1)	0.448 0(6)
C(13)	0.515(1)	0.261(1)	0.473 5(6)
C(14)	0.542 5(9)	0.139 4(9)	0.436 1(5)
C(15)	−0.059 8(8)	0.344 0(7)	0.332 2(4)
C(16)	−0.057 7(8)	0.202 2(7)	0.333 0(4)
C(17)	−0.053 6(7)	0.135 8(7)	0.261 1(5)
C(18)	−0.048 5(8)	0.208 2(7)	0.186 8(4)
C(19)	−0.046 5(8)	0.346 8(7)	0.186 1(4)
C(20)	−0.054 1(8)	0.415 9(7)	0.259 7(4)

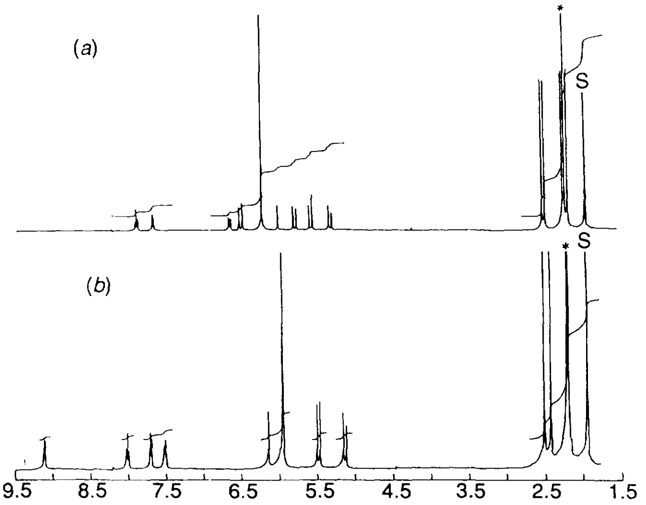

Fig. 1 Proton NMR spectra of (*a*) $[Ru(\eta^6\text{-}C_6H_6)(L^3)Cl]PF_6$ and (*b*) $[Ru(\eta^6\text{-}C_6H_6)(L^5)Cl]PF_6$ in CD_3CN in the region δ 1.5–9.5 (peaks for the solvent and the water present therein are marked by S and * respectively)

significantly shifted, confirming the inequivalence of the two pyrazole arms attached to the pyridine ring. This second set of features is consistent with a 'dangling' pyrazole ring. For **2**–**5** we observe, as for **1**, an AB quartet for each CH_2 protons. The ^1H NMR spectra (Table 2) of **4** and **5** augment our assignments for **2** and **3**.

(*b*) *Crystallographic characterization of* $[Ru(\eta^6\text{-}C_6H_6)L^1][PF_6]_2$. A view of the cation is shown in Fig. 2, with the atomic numbering scheme. Selected bond distances and angles are given in Table 3. The overall co-ordination geometry at the ruthenium atom can be described as a 'piano-stool'. The central atom is bound to L^1, through a tertiary amine nitrogen N(1) and two pyridine nitrogens N(2) and N(3). The bite angle of the L^1 ligand produces an average N–Ru–N angle of 84.7(2)°, only slightly distorted from 90°. The two Ru–N(py) distances are smaller than Ru–N(amine). Moreover, of the two Ru-N(py) distances that of the pyridine ring which affords a six-membered chelate ring is longer (0.03 Å) than the one which give rise to a five-membered chelate ring. Additionally, the ruthenium atom is bound to the benzene ring with Ru–C bond distances ranging from 2.185(6) to 2.209(6) Å and the benzene ring centroid to Ru distance of 1.697 Å is in good agreement with those of other benzene–ruthenium structures.[2,3,7a,8,24] The average C–C distance in the planar benzene ring is 1.403 Å.

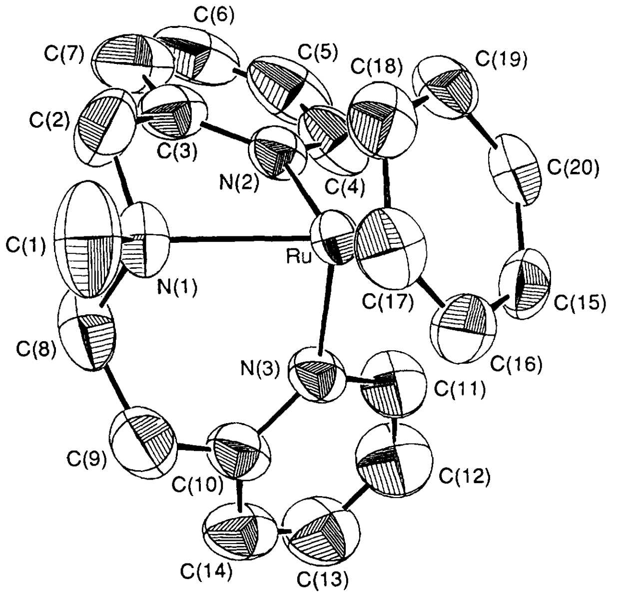

Fig. 2 The molecular structure of $[Ru(\eta^6\text{-}C_6H_6)L^1][PF_6]_2$ **1** showing the atomic labelling scheme

Cyclic Voltammetry.—In acetonitrile solution complexes **1**–**5** exhibit irreversible reduction(s) (E_{pc} = −1.06 to −1.62 V *vs.* SCE) at a platinum working electrode (scan rate 100 mV s^{-1}). Complex **2** shows an additional oxidative response at a very positive potential (E_{pa} = 1.78 V *vs.* SCE). The lack of facile

Table 2 Proton NMR data (δ)[a]

Compound	C_6H_6	H^3	H^4	H^5	H^6	$R^{3'}$	$H^{4'}$
1	6.10 (s)	7.47 (d) $J(H^3H^4)$ = 8.2	7.42 (t) 7.62 (t) $J(H^3H^4)$, $J(H^4H^5)$ = 8.2	7.94 (t) 8.02 (t) $J(H^4H^5)$, $J(H^5H^6)$ = 8.2	9.00 (d) 9.30 (d) $J(H^5H^6)$ = 8.2	3.57 (s)[b]	—
2	6.14 (s)	7.60 (m)[e]	7.87 (t) $J(H^3H^4)$, $J(H^4H^5)$ = 8.2	6.95 (d) $J(H^4H^5)$ = 8.2	—	8.00 (d) $J(H^{3'}H^{4'})$ = 2.1	6.56 (t) $J(H^{3'}H^{4'})$, $J(H^{4'}H^{5'})$ = 2.1
3	6.18 (s)[e]	7.64 (d) $J(H^3H^4)$ = 7.4	7.85 (t) $J(H^3H^4)$, $J(H^4H^5)$ = 7.4	6.60 (d) $J(H^4H^5)$ = 7.4	—	2.47 (s)	6.18 (s)[e]
4	5.94 (s)	7.63 (d) $J(H^3H^4)$ = 7.4	8.00 (t) $J(H^3H^4)$, $J(H^4H^5)$ = 7.4	7.50 (t) $J(H^4H^5)$, $J(H^5H^6)$ = 7.4	9.10 (d) $J(H^5H^6)$ = 7.4	7.90 (d)[e] $J(H^{3'}H^{4'})$ = 3.5	6.50 (t) $J(H^{3'}H^{4'})$, $J(H^{4'}H^{5'})$ = 3.5
5	5.98 (s)	7.70 (d) $J(H^3H^4)$ = 7.4	8.02 (t) $J(H^3H^4)$, $J(H^4H^5)$ = 7.4	7.52 (t) $J(H^4H^5)$, $J(H^5H^6)$ = 7.4	9.11 (d) $J(H^5H^6)$ = 7.4	2.45 (s)	6.15 (s)

Compound	$R^{5'}$	$R^{3''}$	$H^{4''}$	$R^{5''}$	$CH^{1'}_2$	$CH^{1''}_2$
1	—	—	—	—	4.08 (ABq)[c] $J = 16$ 3.26, 2.92 (m)[d]	—
2	7.91 (d) $J(H^{4'}H^{5'})$ = 2.1	7.76 (d) $J(H^{3''}H^{4''})$ = 2.1	6.40 (t) $J(H^{3''}H^{4''})$, $J(H^{4''}H^{5''})$ = 2.1	7.60 (m)[e]	5.60 (ABq) $J = 15$	6.30 (ABq) $J = 15$
3	2.50 (s)	2.18 (s)	5.98 (s)	2.24 (s)	5.40 (ABq) $J = 15$	6.10 (ABq) $J = 15$
4	7.90 (d)[e] $J(H^{3'}H^{4'})$ = 3.5	—	—	—	5.50 (ABq) $J = 15$	—
5	2.53 (s)	—	—	—	5.32 (ABq) $J = 15$	—

[a] Spectra taken in CD_3CN solution relative to $SiMe_4$; s = Singlet, d = doublet, t = triplet, m = multiplet, ABq = AB quartet; *J* values in Hz. [b] R =NMe. [c] NCH_2. [d] NCH_2CH_2. [e] Overlapped.

Table 3 Selected bond distances (Å) and angles (°) in $[Ru(\eta^6-C_6H_6)L^1][PF_6]_2$ **1**

Ru–N(1)	2.170(5)	Ru–N(2)	2.098(5)
Ru–N(3)	2.129(6)	Ru–C(15)	2.209(6)
Ru–C(16)	2.209(6)	Ru–C(17)	2.208(7)
Ru–C(18)	2.200(7)	Ru–C(19)	2.185(6)
Ru–C(20)	2.203(6)	C(15)–C(16)	1.420(1)
C(16)–C(17)	1.380(1)	C(18)–C(19)	1.390(1)
C(15)–C(20)	1.390(1)	C(17)–C(18)	1.420(1)
C(19)–C(20)	1.420(1)		
N(1)–Ru–N(2)	79.5(2)	N(1)–Ru–N(3)	89.6(2)
N(2)–Ru–N(3)	85.1(2)	C(15)–C(16)–C(17)	119.6(6)
C(16)–C(17)–C(18)	120.3(6)	C(17)–C(18)–C(19)	119.9(7)
C(18)–C(19)–C(20)	119.9(6)	C(15)–C(20)–C(19)	119.6(6)
C(16)–C(15)–C(20)	120.6(6)		

redox transformations of these ruthenium(II) complexes could be attributed to the π-back-bonding behaviour of the arene ligands.[7b]

Conclusion

The present work demonstrating reactions between potentially tridentate/bidentate nitrogen-containing ligands with pyridine as donor sites and the dimer $[\{Ru(\eta^6-C_6H_6)Cl_2\}_2]$ affording piano-stool complexes should considerably open up the area to further development. To the best of our knowledge the present crystal structure is the first within the family of piano-stool complexes of $Ru(\eta^6-C_6H_6)^{2+}$ with pyridine-containing tridentate ligands. Aside from their piano-stool structures, these compounds also seemed interesting because they offer an opportunity to investigate reactions of aromatic molecules co-ordinated to metal ions in relatively high oxidation states. Such studies are in progress.

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