Reactions of Benzene–Ruthenium(II) Complexes with Pyrazoles. Possible Formation of Amidine Complexes $[Ru(\eta\text{-}C_6H_6)\{NH{=}CMe(R_2pz)\}(R_2Hpz)]^{2+}$ (R = H or Me, Hpz = Pyrazole)

Christopher J. Jones, Jon A. McCleverty,* and Anne S. Rothin
Department of Chemistry, The University, P. O. Box 363, Birmingham B15 2TT

In acetonitrile $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ reacted with pyrazole (Hpz), 3,5-dimethylpyrazole (Me_2Hpz), or with $K[HB(Me_2pz)_3]$ to give products assigned as the amidine complexes $[Ru(\eta\text{-}C_6H_6)\{NH{=}CMe(R_2pz)\}(R_2Hpz)]^{2+}$ (R = H or Me). In methanol, reactions with pyrazoles afforded $[Ru(\eta\text{-}C_6H_6)Cl(R_2Hpz)_2]^+$ (R = H or Me), but in benzene only $[Ru(\eta\text{-}C_6H_6)Cl_2(Me_2Hpz)]$ was formed. The complexes were characterised on the basis of spectroscopic studies.

It has been reported that whereas $[Ru(\eta\text{-}C_6H_6)\{RB(pz)_3\}]^+$ (R = H or pz; pz = $C_3H_3N_2$, pyrazolyl) are stable and can readily be isolated,[1,2] the related tris(3,5-dimethylpyrazolyl)-borate $\{[HB(Me_2pz)_3]^-\}$ analogue was unstable. The failure to obtain this last species was attributed, in part, to the apparent steric bulk of the heterocyclic ligand.[1] From our own extensive studies of molybdenum and tungsten complexes of $[HB(Me_2pz)_3]^-$,[3] we would fully accept that the ligand does impose severe steric constraints on the metal, but even so, surprisingly bulky ancillary ligands, *e.g.* the anions of 2,5-dimethylaniline, cyclohexylamine, and piperidine, can be accommodated within species such as $[Mo\{HB(Me_2pz)_3\}(NO)X(Y)]$(X = halide, Y = N-donor ligand). Consequently we felt that the failure to report that some product was formed in the reaction between $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ and $K[HB(Me_2pz)_3]$ was unusual and worthy of further investigation. At the least, we thought it possible that such a reaction might afford a convenient route to 'half-sandwich' tris(pyrazolyl)-borato-complexes of ruthenium.

Results and Discussion

Treatment of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with $K[HB(Me_2pz)_3]$ in acetonitrile, followed by addition of NH_4PF_6, afforded an air- and moisture-stable yellow crystalline solid in low yield. The i.r. spectrum of this compound showed that ν(BH) was absent [this appears at 2 400—2 500 cm^{-1} in typical $HB(Me_2pz)_3$ complexes], indicating that the tris(pyrazolyl)borato-ligand had broken up. However, the i.r. spectrum did contain absorptions typical of 3,5-dimethylpyrazole, as well as bands at 3 430 and 3 360 cm^{-1}, typical of ν(NH). Strong absorptions were also observed at 1 650 and 840 cm^{-1}, the latter due to ν(PF) of PF_6^-. The ^1H n.m.r. spectrum in $(CD_3)_2CO$ exhibited five resonances due to methyl protons (see Experimental section), two signals due to the proton at the C(4) position in 3,5-$Me_2C_3HN_2$, and a singlet due to $\eta\text{-}C_6H_6$. A broad resonance at δ *ca.* 11.12 may be assigned to an N–H proton, and on shaking with D_2O this signal disappeared. The ^{13}C n.m.r. spectrum in $(CD_3)_2CO$ exhibited 13 signals, five between 10 and 21 p.p.m. due to four inequivalent methyl groups and the C atom of the incorporated acetonitrile, a singlet at 88.5 p.p.m. due to $\eta\text{-}C_6H_6$, and two resonances at 108.5 and 115.2 p.p.m. due to inequivalent C(4) atoms in the pyrazolyl groups. The five remaining signals occur between 146 and 168 p.p.m. and must be due to the four C atoms of the pyrazolyl groups (*C*–Me) and the C atom of the incorporated acetonitrile, N*C*–Me. The ^{13}C n.m.r. spectrum of the analogous complex prepared by reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ and $K[HB(Me_2pz)]$ in CD_3CN revealed an identical spectrum with the exception that there were only *four* signals in the region 10—21 p.p.m., the resonance at δ = 20.99 p.p.m. for the non-deuteriated species probably being due to the methyl group of the incorporated acetonitrile.

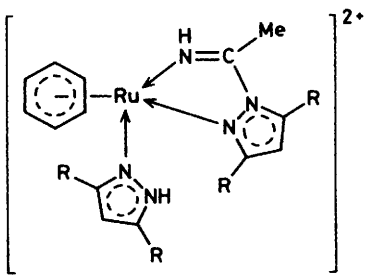

Figure. Proposed structure of $[Ru(\eta\text{-}C_6H_6)\{NH{=}CMe(R_2pz)\}(R_2Hpz)]^{2+}$

An initial consideration of the spectral and microanalytical data suggested that the complex was $[Ru(\eta\text{-}C_6H_6)(NCMe)(Me_2Hpz)_2][PF_6]_2$. However, there was no evidence for ν(CN) of a co-ordinated acetonitrile molecule, although it is known that this absorption is absent (or exceptionally weak) in $[Re(NCMe)(PPh_3)_2X_3]$ (X = Cl or Br).[4] However, if the species is as formulated above, the two pyrazole rings should be equivalent and should therefore give rise, in the ^1H n.m.r. spectrum, to two methyl-proton signals, making a total of three such resonances in the ratio 1:2:2. Similarly, there should be only one signal due to the equivalent C(4) protons. This is not what is actually observed, as described above. Furthermore, attempts to displace the putative NCMe ligand by PPh_3 were unsuccessful.

An alternative formulation for the complex could be as shown in the Figure (R = Me). This is consistent with the elemental analysis, with the observation of two ν(NH), and the strong absorption at 1 650 cm^{-1} (1 640 cm^{-1} for species obtained from CD_3CN) could be due to ν(C=N) of the amidine ligand NH=CMe(Me_2pz). Support for these assignments may be drawn from studies of $[ReCl_4\{NH{=}C(NHR')R\}_2]$ (R = Me, R' = *p*-MeC_6H_4, *p*-$EtO_2CC_6H_4$, or *m*-FC_6H_4; R = Ph, R' = *p*-$MeOC_6H_4$),[5] obtained by reaction of aromatic amines with $[ReCl_4(NCR)_2]$, which exhibited ν(C=N) at 1 600—1 650 cm^{-1}. The proposed structure (R = Me) is also consistent with five inequivalent methyl groups. Our observation of only one NH signal in the ^1H n.m.r. spectrum may be due either to slow exchange of hydrogen between two nitrogen sites, or due to differential ^{14}N quadrupole-broadening effects at one of the N atoms. It should be possible to use ^{13}C n.m.r. spectral information to determine whether the complex contains a co-

ordinated nitrile or the linkage –N=C<. However, there is very little ^{13}C n.m.r. spectral information on co-ordinated nitriles. The free ligand exhibits δ(NCR) in the range 115—125 p.p.m. [δ(MeCN) = 117.7 p.p.m.]. The ^{13}C n.m.r. spectrum of $[Re(CO)_5(NCMe)][PF_6]$[6] revealed δ(MeCN) = 128.1 p.p.m. (relative to $SiMe_4$) in CD_3CN [δ(CN) = 118.3 p.p.m.] and there was no evidence of exchange between co-ordinated and solvent nitrile. However, the ^{13}C n.m.r. spectrum of $[Ni(\eta^3\text{-}C_3H_4Me)(NCMe)_2]^+$ exhibited a broad signal at 118.6 p.p.m. due to rapid exchange between bound and free acetonitrile.[7] It is known that the C atom in the azomethine linkage usually exhibits δ = 150—160 p.p.m. The occurrence of five signals for our ruthenium complex in the range 146—168 p.p.m. would be consistent with the occurrence of one such bond in an amidine ligand, the other four signals being due, as mentioned, to the pyrazolyl *C*Me groups. We assume that such a ruthenium(II) complex would be six-co-ordinate, in common with most other $Ru(C_6H_6)^{2+}$ species.

We do not know how the $[HB(Me_2pz)_3]^-$ ligand is destroyed in reaction with $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$. However, it is known that, in acetonitrile, the areneruthenium complex exists as $[Ru(\eta\text{-}C_6H_6)Cl_2(NCMe)]$.[8] The formation of the amidine complex (R = Me) could therefore occur *via* attack by 3,5-dimethylpyrazole on the co-ordinated acetonitrile, the pyrazole being released in the decomposition of $[HB(Me_2pz)_3]^-$. This could partly account for the relatively low yield of the reaction. If this view is correct, then $[Ru(\eta\text{-}C_6H_6)Cl_2(NCMe)]$ should react directly with a pyrazole giving amidine species. We have confirmed this, reaction of the ruthenium species in acetonitrile with 3,5-dimethylpyrazole giving a compound identical to that formed from $[HB(Me_2pz)_3]^-$.

The reaction with pyrazole itself gave a mixture which could not be satisfactorily purified. However, its i.r. spectrum revealed bands at *ca.* 3 400 cm^{-1} [ν(NH)] and 1 660 cm^{-1} [ν(CN)], and the ^1H n.m.r. spectrum contained two signals due to η-C_6H_6 (probably two species in solution) and a singlet at δ 2.85 p.p.m. due to a methyl group. The intensities of the ^1H n.m.r. spectral signals varied after attempted recrystallisations, but it would appear that the assignment of the spectrum of the species shown in the Figure (R = H) would be as follows: δ = 9.03 [d, 1 H, H^3 or H^5 in $C_3H_3N_2$], 8.05 (d, similar), 7.90 (d, similar), 7.52 (d, similar), 6.92 (t, 1 H, H^4 in $C_3H_3N_2$), 6.55 (t, similar), 6.30 (s, 6 H, η-C_6H_6), and 2.85 p.p.m. (s, 3 H, CH_3).

These observations prompted our examination of the reactions between $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ and the pyrazoles in other solvents. Thus treatment of the arene complex with 3,5-dimethylpyrazole in methanol afforded orange $[Ru(\eta\text{-}C_6H_6)Cl(Me_2Hpz)_2]^+$, isolated as the PF_6^- salt. The i.r. spectrum of this compound exhibited ν(NH) at 3 350 and 3 320 cm^{-1}. At room temperature, the ^1H n.m.r. spectrum exhibited only one methyl signal (δ = 2.24 p.p.m., 12 H) instead of the two expected, one signal due to the proton at C(4) of the heterocyclic ring (intensity 2), and one signal due to the benzene protons. However, on cooling to −60 °C two methyl signals were resolved. This behaviour may be due to intermolecular exchange involving the pyrazole rings, or to intramolecular exchange or 'shuttling' of the H and Ru between each of the two pairs of N atoms, as is suggested to occur in $[RhCl(CO)(Me_2Hpz)]$.[9] The related pyrazole complex $[Ru(\eta\text{-}C_6H_6)Cl(Hpz)_2]^+$ was also prepared, the i.r. and ^1H n.m.r. spectra of which were consistent with our formulation.

Reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with 3,5-dimethylpyrazole in refluxing benzene resulted in bridge cleavage and formation of $[Ru(\eta\text{-}C_6H_6)Cl_2(Me_2Hpz)]$. The i.r. spectrum revealed ν(NH) at 3 270 cm^{-1}, and the ^1H n.m.r. spectrum, which clearly showed the inequivalence of the two methyl groups, provided no evidence for 'shuttling' of the H and the metal atom between the two N atoms.

Experimental

All reactions were carried out in purified and dried solvents under N_2. I.r. and ^1H n.m.r. spectra were recorded using PE 297, Varian HA100, and JEOL JMN-PMX60 spectrometers. Elemental analyses were determined by the Microanalytical Laboratory, Chemistry Department, University of Birmingham. Carbon-13 n.m.r. spectra were recorded at Warwick University on a Bruker WH 400 instrument by the S.E.R.C. High Field N.M.R. Service.

$[Ru(\eta\text{-}C_6H_6)\{NH{=}CMe(Me_2pz)\}(Me_2Hpz)][PF_6]_2$.—*Method* (1). A solution of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.50 g) and $K[HB(Me_2pz)_3]$ (0.75 g) in acetonitrile (30 cm^3) was refluxed for 5 min, cooled, and then filtered. The orange-yellow filtrate was evaporated to dryness, the residue was dissolved in water and re-filtered. The clear filtrate was then treated with an aqueous solution of NH_4PF_6 (0.50 g) and a yellow solid precipitated. This was filtered off and recrystallised from dichloromethane–acetone mixtures (1:1 v/v) and light petroleum (b.p. 60—80 °C) giving the *complex* as a bright yellow crystalline solid which was collected by filtration and dried *in vacuo* (yield 0.46 g, 33%) (Found: C, 30.9; H, 3.4; N, 10.0. $C_{18}H_{25}F_{12}N_5P_2Ru$ requires C, 30.8; H, 3.6; N, 10.0%).

Method (2). A mixture of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.30 g) and 3,5-dimethylpyrazole (0.36 g) in acetonitrile (40 cm^3) was refluxed for 10—15 min, cooled to room temperature, stirred for a further 1 h, and then filtered. To the orange filtrate was added an aqueous solution of NH_4PF_6 (1.0 g in 10 cm^3 water), which caused precipitation of a yellow solid. This was collected by filtration, dissolved in acetone, and the acetone solution dried over anhydrous $MgSO_4$ for 1 h. After removal of the $MgSO_4$ by filtration, the yellow solution was evaporated to dryness and the residue recrystallised from acetone–light petroleum (b.p. 40—60 °C)–diethyl ether mixtures. The yellow *complex* was dried *in vacuo* (0.41 g, 29%) (Found: C, 31.0; H, 3.6; N, 9.8. $C_{18}H_{25}F_{12}N_5P_2Ru$ requires C, 30.8; H, 3.6; N, 10.0%). I.r. spectrum (KBr disc): 3 430m, 3 360m, 3 175w, 3 120w, 2 940w, 1 650s, 1 580s, 1 482m, 1 442m, 1 420s, 1 390w, 1 380w, 1 360m, 1 300w, 1 260w, 1 182w, 1 135w, 1 105w, 1 060w, 1 040w, 995w, 840vs [ν(PF)], 740m, 695w, 655w, and 640w cm^{-1}. N.m.r. spectra $[(CD_3)_2CO]$: ^1H, δ = 2.21 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 2.93 (s, 3 H, CH_3), 3.02 (s, 3 H, CH_3), 6.05 (s, 1 H, CH of pyrazole), 6.43 (s, 6 H, C_6H_6), 6.61 (s, 1 H, CH of pyrazole), and 11.12 (br, 1 H, NH); ^{13}C, δ = 10.74 (CH_3), 13.95 (CH_3), 14.94 (CH_3), 16.86 (CH_3), 20.99 (CH_3), 88.49 (C_6H_6), 108.52 (CH), 115.15 (CH), 146.21 (*C*CH_3), 148.77 (*C*CH_3), 155.71 (*C*CH_3), 162.25 (*C*CH_3), and 167.30 p.p.m. (*C*CH_3).

$[Ru(\eta\text{-}C_6H_6)\{NH{=}C(CD_3)(Me_2pz)\}(Me_2Hpz)][PF_6]_2$.—This complex was prepared by Method (1) described for the acetonitrile-containing complex above using $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.5 g), $K[HB(Me_2pz)_3]$ (0.75 g) and CD_3CN (15 cm^3). The product was obtained as bright yellow microcrystals (yield 0.52 g, 37%) (Found: C, 30.5; H, 3.0; N, 10.1. $C_{18}H_{22}D_3F_{12}N_5P_2Ru$ requires C, 30.7; H, 3.1; N, 9.9%). N.m.r. spectra $[(CD_3)_2CO]$: ^1H, δ = 2.21 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 3.02 (s, 3 H, CH_3), 6.05 (s, 1 H, CH of pyrazole), 6.42 (s, 6 H, C_6H_6), 6.61 (s, 1 H, CH of pyrazole), and 11.16 (br, s, 1 H, NH); ^{13}C, δ = 10.74 (CH_3), 13.91 (CH_3), 14.94 (CH_3), 16.86 (CH_3), 88.48 (C_6H_6), 108.52 (CH), 115.13 (CH), 146.20 (*C*CH_3), 148.78 (*C*CH_3), 155.70 (*C*CH_3), 162.26 (*C*CH_3), and 167.28 p.p.m. (*C*CH_3).

$[Ru(\eta\text{-}C_6H_6)Cl(Me_2Hpz)_2][PF_6]$.—A mixture of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.50 g) and 3,5-dimethylpyrazole (0.80 g) was stirred in methanol (30 cm^3) for 3 h, the resulting solution being filtered. The filtrate was treated with NH_4PF_6 (1.0 g) and on vigorous shaking orange crystals formed. These were filtered off

and recrystallised from dichloromethane–methanol mixtures affording the *complex* as orange crystals (0.85 g, 77%) (Found: C, 34.6; H, 3.9; N, 10.3. $C_{16}H_{22}ClF_6N_4PRu$ requires C, 34.8; H, 4.0; N, 10.2%). I.r. spectrum (KBr disc): 3 350m, 3 320s, 3 160w, 3 120w, 2 945w, 1 572s, 1 465m, 1 440m, 1 420m, 1 410m, 1 380w, 1 275s, 1 155m, 1 042m, 1 025w, 982w, 910m, 840vs [ν(PF)], 740w, and 660w cm^{-1}. ^1H N.m.r. spectrum [$(CD_3)_2CO$]: δ = 2.24 (s, 12 H, CH_3), 6.09 (s, 2 H, CH of pyrazolyl), 6.20 (s, 6 H, C_6H_6), and 11.0 (br, 1 or 2 H, NH); at −60 °C, δ = 2.18 (s, 6 H, CH_3), 2.24 (s, 6 H, CH_3), 6.15 (s, 2 H, CH), 6.26 (s, 6 H, C_6H_6), and 11.22 p.p.m. (br, 1 or 2 H, NH).

$[Ru(\eta\text{-}C_6H_6)Cl(Hpz)_2][PF_6]$.—This complex was obtained in the same way as its 3,5-dimethylpyrazolyl analogue using $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.50 g) and pyrazole (0.58 g) (yield 0.65 g, 69%) (Found: C, 29.2; H, 2.7; Cl, 7.2; N, 11.5. $C_{12}H_{14}ClF_6N_4PRu$ requires C, 29.1; H, 2.9; Cl, 7.2; N, 11.3%). I.r. spectrum (KBr disc): 3 420s, 3 300s, 3 160m, 3 125m, 3 100s, 1 520m, 1 475s, 1 440s, 1 410s, 1 362s, 1 355s, 1 275m, 1 170m, 1 135s, 1 065vs, 915s, 840s [ν(PF)], 768s, 740m, and 685s cm^{-1}. ^1H N.m.r. spectrum [$(CD_3)_2CO$]: δ = 6.05 (s, 6 H, C_6H_6), 6.41 [t, 2 H, H on C(4) of pyrazole ring], 7.75 [d, 2 H, H on C(3) or C(5) of pyrazole ring], and 8.02 p.p.m. [d, 2 H, H on C(5) or C(3) of pyrazole ring].

$[Ru(\eta\text{-}C_6H_6)Cl_2(Me_2Hpz)]$.—The complex $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.50 g) and 3,5-dimethylpyrazole (0.58 g) were refluxed in benzene (30 cm^3) for 12 h and the mixture was then cooled and evaporated to dryness *in vacuo*. The resulting yellow-brown solid was recrystallised from chloroform–n-hexane mixtures to give the *complex* as brown crystals (0.42 g, 61%) (Found: C, 37.6; H, 4.1; N, 8.1. $C_{11}H_{14}Cl_2N_2Ru$ requires C, 38.2; H, 4.1; N, 8.1%). I.r. spectrum (KBr disc): 3 270s, 3 060m, 2 925w, 1 575s, 1 470w, 1 435s, 1 370m, 1 270s, 1 155m, 1 045m, 1 030m, 1 015w, 850s, 790s, 700w, and 660w cm^{-1}. ^1H N.m.r. spectrum [$(CD_3)_2CO$]: δ = 2.21 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 5.73 (s, 6 H, C_6H_6), 5.98 (s, 1 H, CH), and 10.80 p.p.m. (br, 1 H, NH).

Acknowledgements

We are grateful to the S.E.R.C. for a studentship and to Johnson Matthey PLC for a loan of $RuCl_3$.

References

1 D. J. O'Sullivan and F. J. Lalor, *J. Organomet. Chem.*, 1973, **57**, C58.
2 R. J. Restivo, G. Ferguson, D. J. O'Sullivan, and F. J. Lalor, *Inorg. Chem.*, 1975, **14**, 3046.
3 J. A. McCleverty, *Chem. Soc. Rev.*, 1983, **12**, 331.
4 G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 1967, 993.
5 G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 1968, 489.
6 M. J. Webb and W. A. G. Graham, *J. Organomet. Chem.*, 1975, **93**, 119.
7 D. Neibecker and B. Castro, *J. Organomet. Chem.*, 1977, **134**, 105.
8 R. A. Zelonka and M. C. Baird, *J. Organomet. Chem.*, 1972, **44**, 383 and ref. therein.
9 N. F. Borkett and M. I. Bruce, *J. Organomet. Chem.*, 1974, **65**, C57.

Received 26*th April* 1985; *Paper* 5/826