

## Organometallic ammine complexes: the preparation and X-ray crystal structures of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{NH}_3)]\text{PF}_6$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})(\text{NH}_3)]\text{PF}_6$

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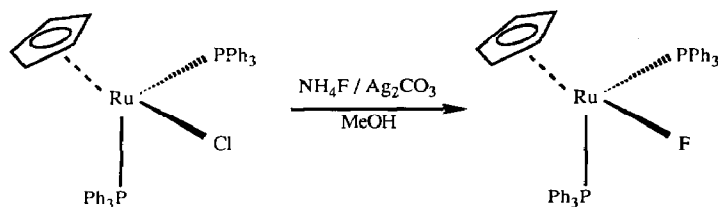
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### Abstract

Reaction of the neutral chloro-complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}]$  (**1**) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})\text{Cl}]$  (**2**) with ammonium hexafluorophosphate gives the ammonia cations  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{NH}_3)]\text{PF}_6$  (**3**) and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})(\text{NH}_3)]\text{PF}_6$  (**4**). The crystal structures of **3** and **4** have been determined, and the  $^{15}\text{NH}_3$  isotopomers prepared to facilitate spectroscopic studies. The nature of the product from the reaction of **1** and  $\text{NH}_4\text{F}$  in the presence of a halide ion trap has been established.

### Introduction

The use of halide ion acceptors such as ammonium ion to drive the ionisation of metal halide complexes to completion is well established in both coordination and organometallic chemistry. Thallium or silver salts are also useful for this purpose, and our initial interest was in using this route to prepare the ruthenium fluoro complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{F}]$  from **1** and a suitable fluoride salt.



This reaction has been reported by Bruce, who used silver carbonate and ammonium fluoride in wet methanol [1]. A pale yellow product was isolated which was reported to be unstable in solution. The absence of a resonance in its 94.1 MHz  $^{19}\text{F}$  spectrum and the absence of coupling between fluorine and any other nucleus in

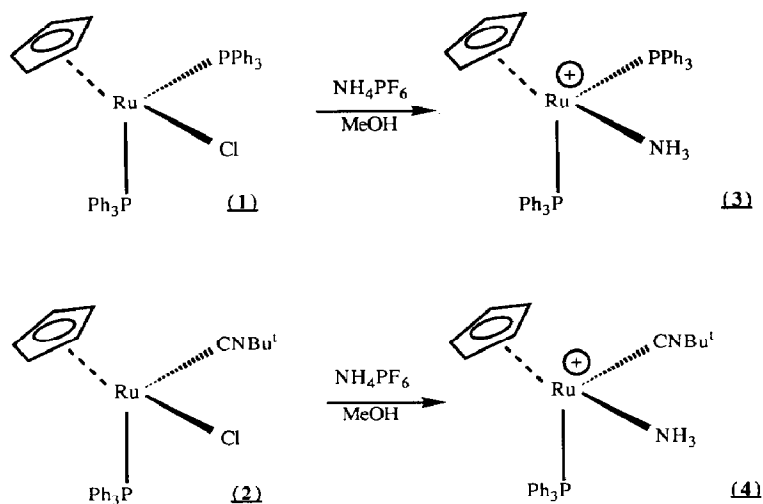
the molecule were puzzling features of this compound. There appear to be only isolated examples of late organometallic fluorides, amongst which the best studied are the stable *trans*-[Rh(PPh<sub>3</sub>)<sub>2</sub>(CO)F] [2,3] and the less stable iridium analogue [3]. A preliminary search of the CAS database revealed no other examples of stable organometallic fluorides containing carbocyclic ligands of the late transition metal series (Fe to Ni), so the report of [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>F] was of considerable interest to us. Since we desired this fluoride for spectroscopic studies related to our work on haloalkanes as ligands in organometallic chemistry we decided to investigate its preparation and properties [4].

## Results and discussion

Addition of **1** to a solution of NH<sub>4</sub>F in methanol at 60 °C followed by Ti<sub>2</sub>CO<sub>3</sub> gave a yellow solid and solution. Removal of the solvent, extraction, and crystallisation gave a yellow microcrystalline solid. The <sup>1</sup>H NMR spectrum of this solid in CDCl<sub>3</sub> contained a singlet at δ 4.43 assignable to a cyclopentadienyl ligand and a broad resonance at δ 2.07, in addition to a broad resonance for the triphenylphosphine ligand. The infrared spectrum of the solid contained bands between 3600 and 3300 cm<sup>-1</sup> indicative of N–H stretching modes. The <sup>19</sup>F NMR spectrum was recorded in CDCl<sub>3</sub> at both 84.6 and 282.41 MHz; a broad resonance at δ –153.4 (ω<sub>1/2</sub> 80 Hz) was seen at the higher frequency, but no signal was observable at the lower frequency. The latter result is in agreement with that obtained by Bruce at 94.1 MHz [1]. Free fluoride ion resonates at ca. δ –123 in aqueous solution and its <sup>19</sup>F NMR chemical shift is very solvent dependent [5]; we have obtained a value of δ –130.3 (ω<sub>1/2</sub> 150 Hz) for a solution of (Et<sub>3</sub>BzNF) in CDCl<sub>3</sub>. The <sup>19</sup>F spectroscopic results suggest the existence of an exchange process involving free ionic fluoride and an ion pair. A fresh nitromethane solution of the solid had a conductivity of 62 cm<sup>2</sup>Ω<sup>-1</sup>mol<sup>-1</sup>, compared with a value of 84 cm<sup>2</sup>Ω<sup>-1</sup>mol<sup>-1</sup> for an equivalent solution of [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>(CN<sup>t</sup>Bu)]PF<sub>6</sub>. We believe that the correct formulation of this product is as [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)]F, and not as the simple fluoride [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>F]. The unstable product prepared by Bruce [1] has a cyclopentadienyl resonance at δ 4.56 in its <sup>1</sup>H NMR spectrum and contained no nitrogen; this material is likely to be authentic [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>F] (consistent with the elemental analysis), but we could not isolate it under our experimental conditions. It is difficult to see why there should be a difference in the behaviour of thallium and silver salts in this simple metathetical exchange reaction. Treatment of **1** with lithium fluoride in hot methanol led to recovery of the starting material.

Anion exchange with potassium hexafluorophosphate in acetone or direct synthesis as above using NH<sub>4</sub>PF<sub>6</sub> in place of NH<sub>4</sub>F gave the salt [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)]PF<sub>6</sub> (**3**), which has been fully characterised spectroscopically and crystallographically. In particular the infrared spectrum of **3** contains bands at 3583, 3348 and 1619 cm<sup>-1</sup> characteristic of an ammine ligand. The <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> contains a singlet at δ 4.36 due to the cyclopentadienyl ligand and a broad signal at δ 2.03 assignable to the ammine ligand, while the <sup>19</sup>F NMR spectrum consists solely of a doublet at δ –70.1 (*J* = 713 Hz) for the PF<sub>6</sub><sup>-</sup> ion.

The related compound [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)(CN<sup>t</sup>Bu)(NH<sub>3</sub>)]PF<sub>6</sub> (**4**) was prepared in a similar manner from [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)(CN<sup>t</sup>Bu)Cl] (**2**). The ammine ligand



bands appear at 3376, 3301 and  $1621\text{ cm}^{-1}$  in the infrared spectrum of **4**, and the  $^1\text{H}$  NMR spectrum of **4** contained a broad resonance at  $\delta$  1.75 for this ligand. These parameters for **3** and **4** can be compared with those reported for two similar ammine complexes,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{dppe})(\text{NH}_3)]\text{PF}_6$  [6] and  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2(\text{NH}_3)]\text{BPh}_4$  [7] which have bands assigned to  $\nu(\text{NH})$  at 3350, 3285 and 3328,  $3269\text{ cm}^{-1}$  respectively. Bands at 1611 and  $1287\text{ cm}^{-1}$  are assigned to  $\delta(\text{NH}_3)_{\text{asym.}}$  and  $\delta(\text{NH}_3)_{\text{sym.}}$ , respectively, for the latter compound. The ammine proton signals appear at  $\delta$  0.75 and  $\delta$  3.10 in the  $^1\text{H}$  NMR spectrum of these compounds in  $(\text{CD}_3)_2\text{CO}$ .

The (ammine- $^{15}\text{N}$ ) analogues of **3** and **4**, namely **3- $^{15}\text{N}$**  and **4- $^{15}\text{N}$** , were prepared by use of  $^{15}\text{NH}_4\text{Cl}$  (98% enriched) and  $\text{KPF}_6$  in place of  $\text{NH}_4\text{PF}_6$ . Multinuclear NMR spectroscopic studies revealed several interesting parameters, for which comparisons are difficult due to a paucity of literature data [8]. The  $^1\text{H}$  NMR spectrum of **3- $^{15}\text{N}$**  contained a doublet of triplets for the ammine ligand ( $J(^{15}\text{N}-^1\text{H}) = 69.3$ ,  $J(^{31}\text{P}-^1\text{H}) = 2.9\text{ Hz}$ ). Attempts to measure a secondary isotopic shift between **3** and **3- $^{15}\text{N}$**  were hampered by the flattened top of the  $^{14}\text{NH}_3$  peak in **3** under high resolution conditions, but a value of  $0.000 \pm 0.004\text{ ppm}$  was determined, a value in order with prediction [9]. The  $^{15}\text{N}\{^1\text{H}\}$  NMR spectrum of **3- $^{15}\text{N}$**  consisted of a triplet at  $\delta$   $-446.1$  ( $J(^{31}\text{P}-^{15}\text{N}) = 2.9\text{ Hz}$ ); the coupling constant was confirmed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. Corresponding data were obtained from studies of **4- $^{15}\text{N}$**  in solution. Interestingly we could not observe the ammine ligand resonance for either **3** or **4** by  $^{14}\text{N}\{^1\text{H}\}$  NMR spectroscopy, and so the linewidth must be  $> 3\text{ KHz}$  at room temperature for these compounds. Few nitrogen chemical shifts have been reported for ammine ligands bonded to transition metals, most of the reports involving redetermination of the value of  $\delta$   $-430 \pm 10$  found by Herbison-Evans and Richards for the aqueous ion  $\{\text{Co}(\text{NH}_3)_6\}^{3+}$  [10]. Yamatera et al. found that  $^{59}\text{Co}-^{15}\text{N}$  coupling could be resolved for this symmetrical ion and reported an accurate  $^{15}\text{N}$  chemical shift of  $\delta$   $-423.4$  for a  $0.3\text{ M}$  solution [11]. The asymmetry of **3** and **4** and their  $^{15}\text{N}$  isotopomers precluded similar observations of coupling to  $^{99}\text{Ru}$  or  $^{101}\text{Ru}$  or, indeed, observation of any  $^{14}\text{N}$  signals. Values of

$^2J(^{31}\text{P}-^{15}\text{N})$  have been reported for a number of square planar complexes of Au [12], Pd [13], and Pt [14] with phthalimido, thiocyanato, and nitro ligands. The general finding is that the *trans* coupling is 40–95 Hz and the *cis* coupling ranges from 2–7 Hz. The values of  $^2J(^{31}\text{P}-^{15}\text{N})$  found here fit this pattern. The values of  $^1J(^1\text{H}-^{15}\text{N})$  for  $3\text{-}^{15}\text{N}$  and  $4\text{-}^{15}\text{N}$  are comparable with those for ammonium ion (73.2 Hz) rather than ammonia (61.2 Hz), and illustrate that the bonding between nitrogen and ruthenium in these compounds is entirely of the  $\sigma$  donor type, a point confirmed by the crystal structures.

The reaction chemistry of **3** and **4** has proved rather limited. Thus treatment of dichloromethane solutions with the base 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) led to recovery of starting material. This reagent has been used to deprotonate cationic osmium complexes of phosphine ( $\text{PH}_3$ ) to give phosphido complex [15]. Presumably the lack of  $d_\pi\text{-}p_\pi$  bonding in these metal ammine complexes reduces the acidity of the ligand hydrogens. Carbon monoxide does not displace ammonia from **3** and **4** at pressures up to 7 atmospheres. This reaction does not provide a route to carbamoyl complexes ( $\text{M-C[O]NH}_2$ ) to complement that involving the reactions of metal carbonyl cations with liquid ammonia reported by Behrens [16].

#### *X-ray structure of 3*

Yellow blocks were obtained by crystallisation from a dichloromethane-diethyl ether solution. A suitable crystal was mounted on a glass fibre with epoxy resin. Precession photographs and intensity data were collected on a Nicolet R3m/V diffractometer using graphite monochromatized  $\text{Mo-K}_\alpha$  X-rays.

*Crystal data.*  $\text{C}_{41}\text{H}_{38}\text{F}_6\text{NP}_3\text{Ru}$ ,  $M = 852.7$ , orthorhombic, space group  $Pna2_1$ ,  $a$  14.278(4),  $b$  14.427(6),  $c$  18.775(6) Å,  $U = 3868(2)$  Å<sup>3</sup>,  $D_c$  1.46 g cm<sup>-3</sup> for  $Z = 4$ .  $F(000) = 1736$ ,  $\mu(\text{Mo-K}_\alpha)$  5.77 cm<sup>-1</sup>,  $T$  23°C, crystal size 0.35 × 0.30 × 0.25 mm. Cell dimensions were obtained from 36 centred reflections with  $2\theta$  values from 16 to 28°. Intensity data in the range  $3 < 2\theta < 55^\circ$  were collected using a  $\theta\text{-}2\theta$  scan technique. The intensities of three reflections measured periodically showed a decrease of less than 1% over the data collection. An empirical absorption correction was applied using an azimuthal scan technique. A total of 6395 reflections were collected of which 5937 were independent, and 4171 for which  $I > 3\sigma(I)$  were used in the refinement. The structure was solved by standard heavy atom routines and refined by full matrix least squares methods. All non-hydrogen atoms with the exception of the fluorine atoms of the  $\text{PF}_6^-$  group were given anisotropic temperature factors. Hydrogen atoms were placed in the model at calculated positions but were not refined, an N–H bond length of 0.90 Å was assumed together with tetrahedral symmetry at nitrogen. The  $\text{PF}_6^-$  group was disordered and was modelled as two constructed octahedra around a common phosphorus atom (P(3)) with occupancies of 56% and 44%. The P–F bond length was fixed at 1.585 Å in the final cycles of refinement. All the phenyl rings were refined with geometrical and planarity restraints. The highest peak in the final difference map was 1.24 eÅ<sup>3</sup> and associated with the  $\text{PF}_6^-$  group. At convergence  $R = 5.26\%$  and  $R_w = 6.80\%$   $w = [\sigma^2(F) + 0.0008F^2]^{-1}$ ,  $S = 1.65$  for a data/parameter ratio 11.7:1,  $\Delta/\sigma < 0.04$ . The Rogers  $\eta$ -test [17] was used to confirm the absolute structure and converged at 1.01(16) for the coordinates given in Table 1.

Calculations were performed using SHELXTL-PLUS on a MICROVAXII. The final positional parameters are given in Table 1, and selected bond lengths and angles in

Table 1

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **3**

	x	y	z	$U_{\text{eq}}^a$
Ru(1)	2360(1)	1683(1)	0	42(1)
N(1)	1013(4)	2367(4)	184(4)	50(2)
C(1)	3445(7)	2296(7)	-714(7)	64(4)
C(2)	3137(7)	2962(7)	-264(7)	60(4)
C(3)	3356(8)	2679(8)	453(8)	79(5)
C(4)	3773(8)	1813(8)	402(7)	63(4)
C(5)	3846(8)	1552(7)	-316(8)	62(4)
P(1)	1993(2)	721(2)	959(2)	44(1)
C(12)	2949(5)	534(3)	2275(4)	62(4)
C(13)	3243	854	2940	90(5)
C(14)	3119	1782	3124	85(5)
C(15)	2699	2392	2643	73(4)
C(16)	2404	2072	1979	57(3)
C(11)	2529	1144	1795	51(3)
C(22)	443(4)	1024(4)	1891(3)	60(3)
C(23)	-501	961	2074	69(4)
C(24)	-1131	525	1616	78(5)
C(25)	-816	153	973	69(4)
C(26)	128	216	789	62(4)
C(21)	758	652	1248	53(3)
C(32)	1775(4)	-1201(4)	1169(5)	91(6)
C(33)	2086	-2117	1153	152(10)
C(34)	2970	-2326	880	113(7)
C(35)	3544	-1618	624	86(5)
C(36)	3234	-701	640	63(4)
C(31)	2350	-493	913	53(3)
P(2)	1738(2)	918(1)	-995(2)	46(1)
C(42)	3192(5)	-353(5)	-1192(4)	75(4)
C(43)	3911	-787	-1570	91(5)
C(44)	4096	-528	-2272	110(7)
C(45)	3563	163	-2596	112(7)
C(46)	2845	596	-2219	77(5)
C(41)	2659	338	-1517	59(3)
C(52)	1031(3)	-903(4)	-802(5)	68(4)
C(53)	320	-1562	-739	94(5)
C(54)	-614	-1297	-816	101(6)
C(55)	-838	-373	-957	100(6)
C(56)	-127	285	-1020	68(4)
C(51)	807	20	-942	51(3)
C(62)	746(6)	1386(4)	-2244(4)	77(4)
C(63)	316	1994	-2726	102(6)
C(64)	350	2947	-2601	94(5)
C(65)	794	3292	-1996	88(5)
C(66)	1215	2685	-1514	64(4)
C(61)	1191	1732	-1638	57(3)
P(3)	1219(1)	5225(2)	155(2)	60(1)
F(1C)	246	5020	529	150(6)
F(2C)	756	6051	-275	109(4)
F(3C)	1484	5919	778	145(6)
F(4C)	1683	4399	586	94(4)
F(5C)	955	4530	-467	127(5)
F(6C)	2193	5430	-218	115(5)

Table 1 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}^a$
F(1D)	2074	4903	633	130(7)
F(2D)	1856	5999	-196	152(8)
F(3D)	1526	4516	-445	117(6)
F(4D)	582	4451	507	109(5)
F(5D)	912	5935	756	78(4)
F(6D)	364	5547	-322	123(6)

<sup>a</sup> Equivalent isotropic *U* defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor.

Table 2. A complete table of bond lengths and angles and lists of thermal parameters and structure factors are available from the authors.

### *X-ray structure of 4*

Yellow blocks were obtained by crystallisation from a dichloromethane-diethyl ether solution. A suitable crystal was mounted on a glass fibre with epoxy resin. Precession photographs and intensity data were collected on a Nicolet R3m/V diffractometer using graphite monochromatized Mo- $K_{\alpha}$  X-rays.

*Crystal data.*  $C_{28}H_{32}F_6N_2P_2Ru$ ,  $M = 673.6$ , monoclinic, space group  $P2_1/c$ ,  $a$  9.867(2),  $b$  17.935(4),  $c$  17.537(4) Å,  $\beta$  90.14(2)°,  $U = 3103(1)$  Å<sup>3</sup>,  $D_c$  1.44 g cm<sup>-3</sup> for  $Z = 4$ .  $F(000) = 1368$ ,  $\mu(\text{Mo-}K_{\alpha})$  6.50 cm<sup>-1</sup>,  $T$  23°C, crystal size 0.40 × 0.20 × 0.20 mm. Cell dimensions were obtained from 45 centred reflections with  $2\theta$  values from 10 to 29°. Intensity data in the range  $3 < 2\theta < 55^\circ$  were collected using a  $\theta$ - $2\theta$  scan technique. The intensities of three reflections measured periodically showed a decrease of less than 1% over the data collection. An empirical absorption correction was applied using an azimuthal scan technique. A total of 7792 reflections were collected of which 7142 were independent, and 4995 for which  $I > 2\sigma(I)$  were used in the refinement. The structure was solved by standard heavy atom routines and refined by full matrix least squares methods. All non-hydrogen atoms were given anisotropic temperature factors. Hydrogen atoms were placed in the model at calculated positions but were not refined, an N-H bond length of 0.90 Å was assumed together with tetrahedral symmetry at nitrogen. The highest peak in the final difference map was 0.59 eÅ<sup>-3</sup> and associated with the PF<sub>6</sub><sup>-</sup> group. At convergence  $R$ ,  $R_w = 5.18\%$  with unit weights,  $S = 1.77$  for a data/parameter ratio 14.2:1,  $\Delta/\sigma < 0.038$ .

Calculations were performed using SHELXTL-PLUS on a MICROVAXII. The final positional parameters are given in Table 3, and selected bond lengths and angles are

Table 2

Selected bond lengths (Å) and bond angles (°) for 3

Ru(1)-C(1)	2.231(11)	Ru(1)-C(2)	2.209(10)
Ru(1)-C(3)	2.194(12)	Ru(1)-C(4)	2.162(11)
Ru(1)-C(5)	2.210(12)	Ru(1)-N(1)	2.190(6)
Ru(1)-P(1)	2.333(3)	Ru(1)-P(2)	2.345(3)
N(1)-Ru(1)-P(1)	87.1(2)	N(1)-Ru(1)-P(2)	90.3(2)
P(1)-Ru(1)-P(2)	104.4(1)		

Table 3

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 4

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Ru(1)	1227(1)	1022(1)	2119(1)	52(1)
C(1)	202(8)	1041(8)	3209(4)	131(5)
C(2)	-394(8)	1540(5)	2756(6)	107(4)
C(3)	-987(6)	1200(6)	2168(5)	105(4)
C(4)	-760(8)	461(6)	2219(6)	123(4)
C(5)	7(9)	318(6)	2877(8)	142(5)
N(2)	1649(4)	529(2)	1022(2)	65(2)
P(1)	3356(1)	722(1)	2540(1)	51(1)
C(11)	3350(5)	-109(3)	3142(3)	63(2)
C(12)	3619(6)	-78(4)	3919(3)	85(3)
C(13)	3452(9)	-699(6)	4371(5)	120(4)
C(14)	3033(9)	-1354(6)	4064(6)	131(5)
C(15)	2773(8)	-1406(4)	3290(5)	113(4)
C(16)	2914(6)	-786(3)	2835(4)	84(2)
C(21)	4614(5)	538(3)	1793(3)	52(2)
C(22)	5271(6)	-124(3)	1668(3)	70(2)
C(23)	6213(7)	-194(4)	1096(4)	91(3)
C(24)	6520(6)	392(4)	641(4)	86(3)
C(25)	5881(6)	1057(4)	744(3)	86(3)
C(26)	4922(6)	1137(3)	1321(3)	76(2)
C(31)	4285(5)	1418(3)	3102(3)	56(2)
C(32)	3612(6)	2040(3)	3373(3)	69(2)
C(33)	4341(7)	2584(4)	3769(3)	89(3)
C(34)	5696(7)	2504(4)	3897(4)	98(3)
C(35)	6359(6)	1875(5)	3651(3)	94(3)
C(36)	5653(5)	1336(4)	3250(3)	78(2)
C(6)	1831(5)	1972(3)	1724(3)	58(2)
N(1)	2108(5)	2553(3)	1490(3)	70(2)
C(7)	2284(7)	3297(3)	1199(4)	78(2)
C(71)	2886(9)	3773(4)	1806(5)	127(4)
C(72)	3184(10)	3229(5)	527(5)	159(5)
C(73)	924(9)	3576(4)	956(6)	157(5)
P(2)	137(2)	8432(1)	711(1)	72(1)
F(1)	-434(9)	8341(5)	1502(3)	243(5)
F(2)	657(6)	7623(2)	695(3)	168(3)
F(3)	-1238(5)	8214(3)	843(4)	173(3)
F(4)	-395(5)	9261(2)	710(3)	155(3)
F(4)	1517(5)	8704(3)	1030(4)	179(3)
F(6)	635(6)	8551(4)	-100(3)	185(3)

<sup>a</sup> Equivalent isotropic *U* defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor.

Table 4

Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for 4

Ru(1)–C(1)	2.165(8)	Ru(1)–C(2)	2.162(8)
Ru(1)–C(3)	2.210(6)	Ru(1)–C(4)	2.211(8)
Ru(1)–C(5)	2.196(11)	Ru(1)–N(2)	2.158(4)
Ru(1)–P(1)	2.290(1)	Ru(1)–C(6)	1.934(5)
C(6)–N(1)	1.152(7)	N(1)–C(7)	1.439(7)
N(2)–Ru(1)–P(1)	90.7(1)	N(2)–Ru(1)–C(6)	89.0(2)
P(1)–Ru(1)–C(6)	92.3(1)	Ru(1)–C(6)–N(1)	175.7(5)
C(6)–N(1)–C(7)	173.2(5)		

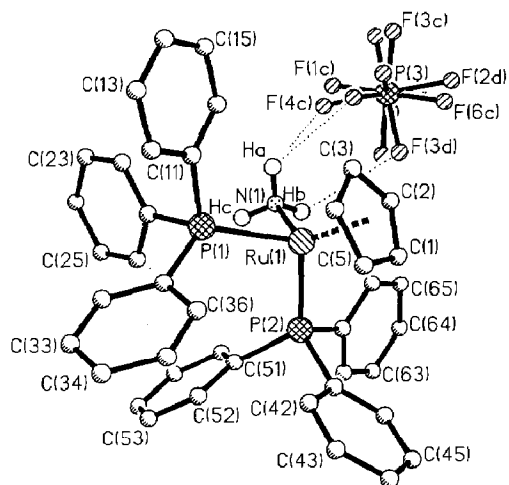


Fig. 1. Proposed molecular structure of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{NH}_3)]\text{PF}_6$  (**3**).

given in Table 4. A complete table of bond lengths and angles and lists of thermal parameters and structure factors are available from the authors.

#### Discussion of the solid state structures of **3** and **4**

The molecular structure of **3** and of the cation present in **4** are shown in Fig. 1 and 2 respectively. Both cations show pseudo-octahedral coordination geometry at the ruthenium atom, with the cyclopentadienyl group occupying three sites in a *fac*-arrangement. The ruthenium to ammine nitrogen bond lengths are 2.190(6) and 2.158(4) Å for **3** and **4**, respectively. Comparison with other Ru<sup>II</sup> ammine structures shows a range of values for this parameter, viz: in  $[\text{Ru}(\text{NH}_3)_6](\text{I})_2$  2.144(4) Å [18], in  $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{BF}_4$  2.11 Å [19], and in  $[\text{Ru}(\text{NH}_3)_5(\eta^2\text{-fumaric acid})](\text{S}_2\text{O}_6) \cdot 2\text{H}_2\text{O}$  2.143(6) to 2.154(5) [20]. Orpen et al. [21] give a mean value of 2.150(12) Å for

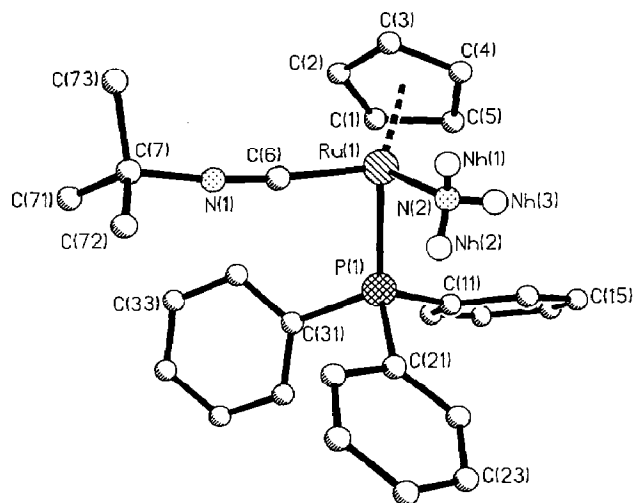


Fig. 2. Proposed molecular structure of the cation in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})(\text{NH}_3)]\text{PF}_6$  (**4**).



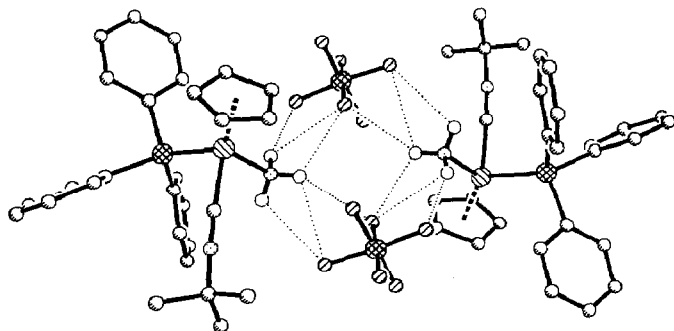


Fig. 3. Proposed molecular structure of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}^t\text{Bu})(\text{NH}_3)]\text{PF}_6$  (**4**) showing a symmetry related pair of molecules.

this bond length in their tabulation of the Cambridge Crystallographic data base. Thus the bond in **3** is quite long, whereas that in **4** is normal. It seems reasonable to account for these data by considering the steric compression at the metal centre in **3** relative to **4**; indeed, the ruthenium phosphine bond lengths in **3** (2.333(3) and 2.345(3) Å) are also longer than that in **4** (2.290(1) Å). While it is the case that **4** contains a good  $\pi$ -acceptor ligand in  $^t\text{BuNC}$  relative to  $\text{PPh}_3$  in **3**, which may account for some bond shortening in **4**, it would be premature to suggest an electronic rationalisation.

Figure 3 shows the complete structure of **4**, in particular the hydrogen bonding between the ammine ligand and the hexafluorophosphate anion. Contacts range from 2.56 to 2.87 Å in **3**, while the remarkable double bridging network found for **4** contains contacts from 2.42 to 2.94 Å. The lack of disorder of the  $\text{PF}_6^-$  group in **4** is undoubtedly due to this extensive network of bonds. The large difference in stretching frequencies  $\nu(\text{NH})$ , between **3** and **4** (3583 vs. 3376  $\text{cm}^{-1}$ ) may also be explained by this difference in degree of hydrogen bonding.

## Experimental

All reactions and preparations were carried out under nitrogen by standard Schlenk-tube techniques. Tetrahydrofuran was dried over sodium benzophenone ketyl and distilled prior to use. Diethyl ether and light petroleum ether (b.p. 40–60 °C) were dried over sodium wire and distilled. Dichloromethane was dried over phosphorus pentoxide and distilled. All other solvents were used as supplied. Reactions performed at > 1 atm pressure were carried out in Fischer-Porter bottles. Infrared spectra were recorded on a Perkin-Elmer 710 FTIR instrument. Nuclear magnetic resonance spectra were recorded on Perkin-Elmer R32 (90 MHz,  $^1\text{H}$ ; 84.6 MHz,  $^{19}\text{F}$ ) and Bruker AC300 (300.13 MHz,  $^1\text{H}$ ; 282.41 MHz,  $^{19}\text{F}$ ; 121.49 MHz,  $^{31}\text{P}$ ; 75.47 MHz,  $^{13}\text{C}$ ; 30.41 MHz,  $^{15}\text{N}$ ) spectrometers. The  $^{15}\text{N}$  spectra were referenced to neat  $\text{CH}_3\text{NO}_2$  at 298 K;  $\delta = 10.136767$  MHz [22]. Elemental analyses were by Butterworth Laboratories, London. Fast Atom Bombardment (FAB) mass spectra were obtained on a Kratos Concept S1 spectrometer. The chloro-compounds **1** and **2** were prepared as described previously [23].

$$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{NH}_3)]\text{PF}_6 \text{ (3)}$$

A suspension of **1** (0.3 g, 0.41 mmol),  $\text{NH}_4\text{PF}_6$  (0.2 g, 1.23 mmol), and thallium(I) carbonate (0.28 g, 0.60 mmol) in methanol (40  $\text{cm}^3$ ) was stirred at 60 °C for 16 h. Removal of the solvent under reduced pressure and crystallization of the residue from dichloromethane-diethyl ether (1 : 3) gave fine yellow needles, yield 0.17 g (48%). (Found: C, 57.77; H, 4.42; N, 1.76.  $\text{C}_{41}\text{H}_{38}\text{F}_6\text{N}_3\text{Ru}$  calcd.: C, 57.75; H, 4.49; N, 1.64%). IR (Nujol):  $\nu_{\text{max}}$  3583m, 3348w and 1619w  $\text{cm}^{-1}$  (NH);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.37 and 7.27 (m, 30H, Ph), 4.36 (s, 5H,  $\text{C}_5\text{H}_5$ ), 2.03 (bd.s, 3H,  $\text{NH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  136.2–128.3 (m, Ph), 81.6 (s,  $\text{C}_5\text{H}_5$ ) ppm;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  45.3 ppm;  $^{19}\text{F}$  NMR ( $9\text{CDCl}_3$ ):  $\delta$  -70.06 (d,  $J(\text{PF})$  713 Hz,  $\text{PF}_6$ ) ppm; MS (FAB): 708 ( $M - \text{PF}_6$ ).

Compound **3**- $^{15}\text{N}$  was prepared similarly using  $^{15}\text{NH}_4\text{Cl}$  (0.15 g) and  $\text{KPF}_6$  (0.20 g) in place of  $\text{NH}_4\text{PF}_6$ .  $^1\text{H}$  NMR ( $[\text{CD}_3]_2\text{CO}$ ):  $\delta$  4.49 (s, 5H,  $\text{C}_5\text{H}_5$ ), 2.83 (dt, 3H,  $J(\text{NH})$  69.3,  $J(\text{PH})$  2.9 Hz,  $\text{NH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $[\text{CD}_3]_2\text{CO}$ ):  $\delta$  137.0 ( $[\text{AXX}']$ ,  $\text{C}_{\text{ipso}}$ ), 134.2 (br,  $\text{C}_{\text{ortho}}$ ), 130.8 (s,  $\text{C}_{\text{para}}$ ), 129.2 (br,  $\text{C}_{\text{meta}}$ ), 82.2 (s,  $\text{C}_5\text{H}_5$ ) ppm;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $[\text{CD}_3]_2\text{CO}$ ):  $\delta$  46.0 (d,  $J(\text{PN})$  2.9 Hz) ppm;  $^{15}\text{N}\{^1\text{H}\}$  NMR ( $[\text{CD}_3]_2\text{CO}$ ):  $\delta$  -446.1 (d,  $J(\text{PN})$  2.9 Hz) ppm.

$$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)(\text{CN}'\text{Bu})(\text{NH}_3)]\text{PF}_6 \text{ (4)}$$

A mixture of **2** (0.40 g, 0.73 mmol),  $\text{NH}_4\text{PF}_6$  (0.25 g, 1.54 mmol), and thallium(I) carbonate (0.50 g, 1.07 mmol) in methanol (40  $\text{cm}^3$ ) was stirred at 60 °C for 18 h. Removal of the solvent under reduced pressure and crystallisation from dichloromethane-diethyl ether (1 : 3) gave pale yellow needles, yield 0.45 g (91%). (Found: C, 50.06; H, 4.77; N, 4.26.  $\text{C}_{28}\text{H}_{32}\text{F}_6\text{N}_2\text{P}_2\text{Ru}$  calcd.: C, 49.93; H, 4.79; N, 4.16%). IR (Nujol):  $\nu_{\text{max}}$  3376m, 3301w and 1621w (NH), 2126s (CN)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.42 and 7.23 (m, 15H, Ph), 4.67 (s, 5H,  $\text{C}_5\text{H}_5$ ), 1.75 (bd.s, 3H,  $\text{NH}_3$ ), 1.21 (s, 9H,  $\text{CMe}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  134.1 (d,  $J(\text{PC})$  44 Hz,  $\text{C}_{\text{ipso}}$ ), 133.2 (d,  $J(\text{PC})$  11 Hz  $\text{C}_{\text{ortho}}$ ), 130.4 (s,  $\text{C}_{\text{para}}$ ), 128.8 (d,  $J(\text{PC})$  10 Hz,  $\text{C}_{\text{meta}}$ ), 81.4 (s,  $\text{C}_5\text{H}_5$ ), 30.6 (s,  $\text{CMe}_3$ ) ppm;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  58.8 ppm; MS (FAB): 529 ( $M - \text{PF}_6$ ).

The isotopomer **4**- $^{15}\text{N}$  was prepared similarly by using  $^{15}\text{NH}_4\text{Cl}$  (0.15 g) and  $\text{KPF}_6$  (0.20 g) in place of  $\text{NH}_4\text{PF}_6$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  4.73 (s, 5H,  $\text{C}_5\text{H}_5$ ), 1.75 (dd, 3H,  $J(\text{NH})$  70.2,  $J(\text{PH})$  2.8 Hz,  $\text{NH}_3$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  134.6 (d,  $J(\text{PC})$  44 Hz,  $\text{C}_{\text{ipso}}$ ), 133.7 (d,  $J(\text{PC})$  11 Hz,  $\text{C}_{\text{ortho}}$ ), 131.0 (s,  $\text{C}_{\text{para}}$ ), 129.2 (d,  $J(\text{PC})$  10 Hz,  $\text{C}_{\text{meta}}$ ), 81.7 (s,  $\text{C}_5\text{H}_5$ ), 58.2 (s,  $\text{CMe}_3$ ), 30.8 (s,  $\text{CMe}_3$ ) ppm;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  58.8 (d,  $J(\text{PN})$  2.2 Hz) ppm;  $^{15}\text{N}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -446.1 (d,  $J(\text{PN})$  2.2 Hz) ppm.

$$[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{NH}_3)]\text{F}$$

Methanol (40  $\text{cm}^3$ ) was saturated with ammonium fluoride at 60 °C, solid **1** (0.5 g, 0.69 mmol.) was added with stirring followed by thallium(I) carbonate (0.52 g, 1.1 mmol). The reactants were stirred at 60 °C for 5 min, after which a white precipitate and a yellow solution were present. The hot supernatant solution was filtered into a stirred aqueous solution of ammonium fluoride (2.0 g in 20  $\text{cm}^3$ ). The pale yellow precipitate was rapidly washed with methanol (3  $\text{cm}^3$ ) and diethyl ether (5  $\text{cm}^3$ ) and dried in vacuo, yield 0.25 g (50%). IR (Nujol):  $\nu_{\text{max}}$  3563m, 3346w and 1617w (NH)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.38 and 7.20 (m, 30H, Ph), 4.43 (s, 5H,  $\text{C}_5\text{H}_5$ ), 2.07 (bd.s, 3H,  $\text{NH}_3$ ) ppm;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -153.4 ( $\omega_{1/2}$  = 80 Hz) ppm.

The compound was also prepared by the method described for **3** involving ammonium fluoride, and recrystallised from dichloromethane-light petroleum ether to give yellow crystals.

The conductivity of a  $4.3 \times 10^{-3} M$  solution in nitromethane was  $62 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$  compared with a value of  $84 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$  for a  $4.9 \times 10^{-3} M$  solution of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2(\text{CN}^t\text{Bu})]\text{PF}_6$  at  $22^\circ \text{C}$ .

#### *Secondary isotopic shift determination for 3 and 3-<sup>15</sup>N*

An equimolar solution of **3** and **3-<sup>15</sup>N** was prepared in  $\text{CD}_2\text{Cl}_2$  (15 mM in each). The  $^1\text{H}$  NMR spectrum of the mixture was measured six times during 2 h with the sample in the probe kept at  $298 \pm 0.5 \text{ K}$ . The spectral resolution was 0.076 Hz/pt. Resolution enhancement was used to improve the chemical shift determinations and the relative shift was measured between the two triplets of **3-<sup>15</sup>N** and **3**. After averaging the six measurements:  $\sigma_{\text{H}}^{\text{S}}(^{15}\text{NH}_3) - \sigma_{\text{H}}^{\text{S}}(^{14}\text{NH}_3) = 0.000 \pm 0.004 \text{ ppm}$ .

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