Synthesis, *X*-Ray Structure, and Nuclear Magnetic Resonance (^1H and ^{13}C) Studies of Ruthenium(II) Complexes containing Pyrazolyl Ligands†

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The synthesis and n.m.r. spectra (^1H and ^{13}C) are reported for 24 *p*-cymeneruthenium complexes belonging to one of the following families: [Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)X] (**3**)—(**9**), [Ru(MeC$_6$H$_4$-Pr^i-*p*)(acac)L]BF$_4$ (**10**)–(**17**), [Ru(MeC$_6$H$_4$Pr^i-*p*)ClL$_2$]BF$_4$ (**19**)—(**22**), and [Ru(MeC$_6$H$_4$-Pr^i-*p*)L$_3$][BF$_4$]$_2$ (**23**), [Ru(MeC$_6$H$_4$Pr^i-*p*)XL$_2$]BF$_4$ (**24**), and [Ru(MeC$_6$H$_4$Pr^i-*p*)X$_2$L] (**25**), where X = Br, I, N$_3$, pz, mpz, dmpz, or idz, and L = pyridine, PPh$_3$, CNBu^t, P(OMe)$_3$, Hpz (pyrazole), Hmpz (3-methylpyrazole), Hdmpz (3,5-dimethylpyrazole), and Hidz (indazole) for complexes (**3**)—(**17**), and only azoles (pyrazoles and indazole) for the remaining ones. Crystals of [Ru(MeC$_6$H$_4$Pr^i-*p*)(pz)(Hpz)$_2$]BF$_4$ are monoclinic, space group $P2_1/c$, with a = 9.882 6(2), b = 13.966 3(3), c = 31.690 2(15) Å, β = 94.650(3)°, and Z = 8. The structure was determined by *X*-ray diffraction and refined to R = 0.045 (R' = 0.036). There are two crystallographic units, each having an intramolecular hydrogen bond between a pyrazole and a pyrazolate ring, and another between the other pyrazole ligand and the BF$_4$ anion. The n.m.r. data (δ and J) of the azole complexes were carefully determined and are thoroughly discussed.

The aim of the present work was to obtain a better knowledge of the structure of *p*-cymeneruthenium(II) complexes containing pyrazole (Hpz) and indazole ligands. It was the result of the conjunction of, at least, four different problems: (*i*) the geometry of the pyrazolylruthenium(II) complexes in comparison with previous results;[1–6] (*ii*) the conformation about the *p*-cymene–metal bond,[5–12] which has gained in interest with the determination of rotational barriers about the arene–metal bond, both of electronic[13] and steric origin;[14,15] (*iii*) the assignment and determination of chemical shifts (^1H and ^{13}C) and coupling constants (^1H–^1H and ^1H–^{13}C) of pyrazoles and indazoles, a question that we have thoroughly studied for the free ligands[16–24] and for some complexes (Rh and Ir);[25,26] (*iv*) the network of hydrogen bonds in pyrazole crystals and its dynamic consequences, both in free ligands[27,28] and in complexes (Ir).[29]

Results and Discussion

Neutral Complexes.—Reaction of compound (**1**)[30] with an excess of Na(acac)·nH$_2$O (acac = acetylacetonate) in acetone gives the β-diketonato-complex (**2**) in which the ruthenium-bonded chlorine can be displaced by bromide, iodide, azide (on reaction with NH$_4$Br, NaI, or NaN$_3$, respectively), or pyrazolate (pz), 3-methylpyrazolate (mpz), 3,5-dimethylpyrazolate (dmpz), and indazolate (idz) (on reaction with the appropriate diazole and KOH) (Scheme 1) The new complexes (**2**)—(**9**) were characterized on the basis of elemental analysis (Table 1) and ^1H n.m.r. (see below) and i.r. spectroscopies.

Their i.r. spectra showed the presence of two ν(CO) bands at *ca.* 1 600 and 1 550 cm^{-1} assignable to bidentate O-bonded acac groups[31] and an intense band at 2 050 cm^{-1} for complex (**5**) corresponding to the azide group.[32] No reaction was observed between (**2**) and NaF, NaO$_2$CMe, or NaO$_2$CH, the chlororuthenium complex (**2**) being recovered unchanged from the reaction medium. On the other hand, the interaction between (**2**) and NaCN or NaSCN gave a mixture of products which we have not been able to separate or characterize.

Cationic Complexes.—When the β-diketonato-complex (**2**) was treated with silver tetrafluoroborate in acetone chloride was removed and the addition of neutral carbon, nitrogen, or phosphorus donor ligands gave cationic complexes of general formula [Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)L]BF$_4$ [L = pyridine (py) (**10**), PPh$_3$ (**11**), CNBu^t (**12**), P(OMe)$_3$ (**13**), Hpz (**14**), Hmpz (**15**), Hdmpz (**16**), or Hidz (**17**)] (Scheme 1). This preparative method is comparable to the two-step synthetic route developed by Maitlis and co-workers[31] for the preparation of cationic pentamethylcyclopentadienylrhodium(III) complexes [Rh(C$_5$Me$_5$)(acac)L]$^+$ from [Rh(C$_5$Me$_5$)Cl(acac)]. Nevertheless, all attempts to isolate the intermediate dimeric complex [{[Ru(MeC$_6$H$_4$Pr^i-*p*)]$_2$(μ-acac)}$_2$][BF$_4$]$_2$, related to the pentamethylcyclopentadienylrhodium analogue,[31] were unsuccessful.

The cationic compounds (**10**)—(**17**) could also be prepared by treating, in acetone, complex (**2**) with the corresponding ligand L and subsequent addition of NaBF$_4$. Complexes (**11**) and (**16**) were prepared by this alternative route and, for L = Hpz, the intermediate chloride cationic complex [Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(Hpz)]Cl (**18**) was isolated and characterized. Acetone solutions of complex (**2**), which contained 1 equivalent of Hpz, were conductors and their conductivity increased when more Hpz was added showing that the equilibrium (1) was operative.

$$[\mathrm{Ru(MeC_6H_4Pr^i\text{-}}p\mathrm{)Cl(acac)}] + \mathrm{Hpz} \rightleftharpoons [\mathrm{Ru(MeC_6H_4Pr^i\text{-}}p\mathrm{)(acac)(Hpz)}]^+ + \mathrm{Cl}^- \quad (1)$$

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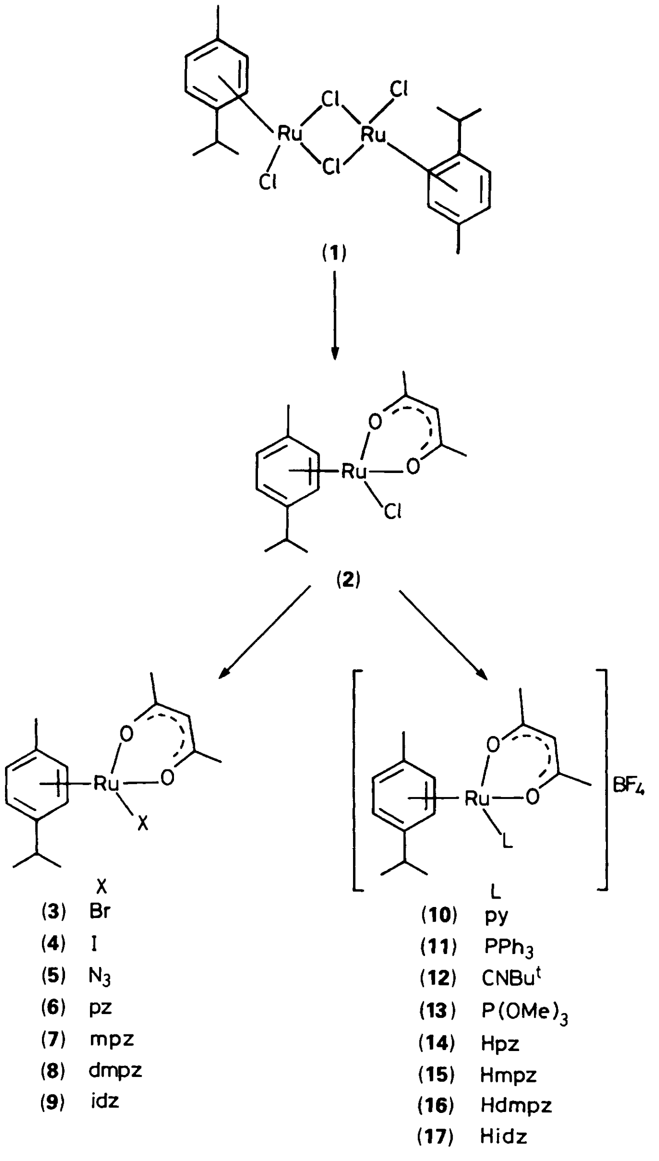
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme 1.

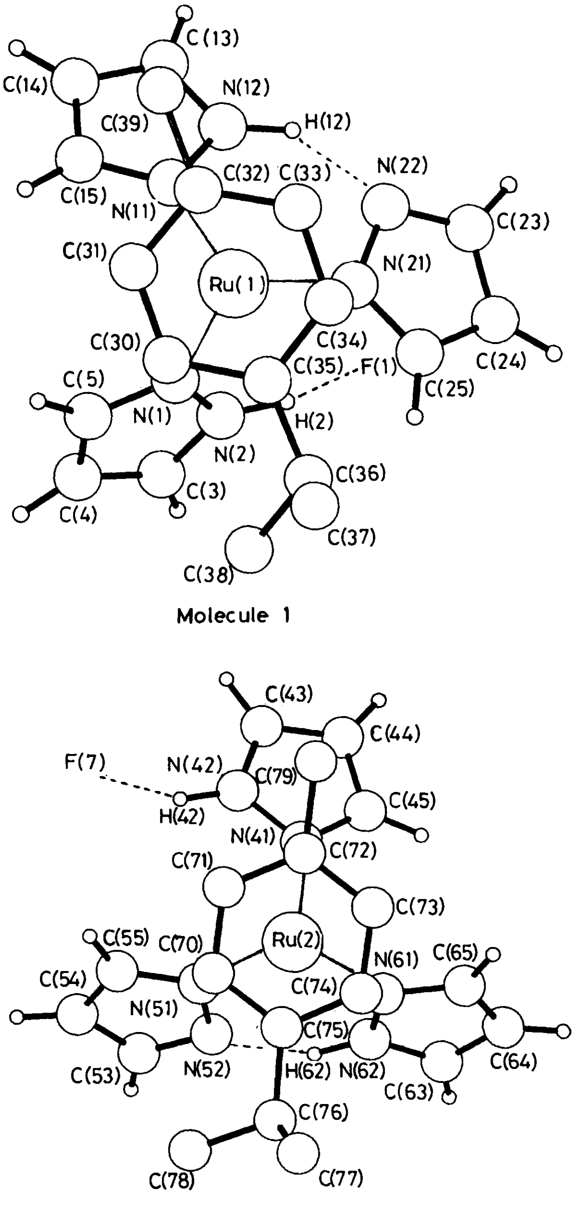


Figure. Projection on the *p*-cymene ring plane of both molecules of complex (**24**) (W. D. S. Motherwell and W. Clegg, PLUTO, A program for plotting crystal and molecular structures, Cambridge University, 1978)

On the other hand, cationic complexes of general formula $[Ru(MeC_6H_4Pr^i\text{-}p)Cl(L)_2]BF_4$ [L = Hpz (**19**), Hmpz (**20**), Hdmpz (**21**), or Hidz (**22**)] were prepared by treating methanolic suspensions of the binuclear complex $[\{Ru(MeC_6H_4Pr^i\text{-}p)Cl\}_2(\mu\text{-}Cl)_2]$ with an excess of the corresponding diazole and $NaBF_4$.[33–35] Alternatively, we have prepared complex (**19**) by treating, in methanol, the acetylacetonate complex (**2**) with HBF_4 in the presence of 2 equivalents of Hpz or the neutral dichloride $[Ru(MeC_6H_4Pr^i\text{-}p)Cl_2(Hpz)]$[5] with $AgBF_4$ and Hpz. Most probably, both reactions proceed *via* the intermediate cation $[Ru(MeC_6H_4Pr^i\text{-}p)Cl(Hpz)(MeOH)]^+$. Recently, Werner and co-workers[33,36] reported the preparation of related cationic phosphine complexes of the type $[Ru(arene)Cl(PR_3)(Me_2CO)]^+$.

The new cationic complexes (**10**)—(**22**) were characterized on the basis of elemental analysis (Table 1) and n.m.r. (see below) and i.r. spectroscopies. Their i.r. spectra show the presence of the unco-ordinated BF_4 anion (bands at *ca.* 1 100 and 520 cm^{-1}). In particular, the acetylacetonate complexes show two bands between 1 520 and 1 625 cm^{-1} and the diazole complexes (**14**)—(**22**) present an intense ν(NH) band in the 3 250—3 400 cm^{-1} region. In addition, the chloride diazole complexes (**18**)—(**22**) show a medium-intensity very broad ν(NH) band centred at *ca.* 2 800 cm^{-1} which suggests that a strong N–H···Cl association is operating in the solid state[37] (Table 1). As expected, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of complexes (**11**) and (**13**) consist of one singlet at δ 52.3 and 127.7 p.p.m., respectively.[38]

All the chloride ligands present in the binuclear complex $[\{Ru(MeC_6H_4Pr^i\text{-}p)Cl\}_2(\mu\text{-}Cl)_2]$ could be removed by addition of $AgBF_4$ in a polar solvent such as acetone. Further addition of Hpz gave the tris(pyrazole) derivative $[Ru(MeC_6H_4Pr^i\text{-}p)(Hpz)_3][BF_4]_2$ (**23**), related to the previously reported pentamethylcyclopentadienylrhodium-(III) and -iridium(III) complexes $[M(C_5Me_5)(Hpz)_3][BF_4]_2$.[29,39] Treatment of compound (**23**), in acetone, with equimolar amounts of methanolic KOH afforded $[Ru(MeC_6H_4Pr^i\text{-}p)(pz)(Hpz)_2]BF_4$ (**24**) which, in turn, could be further deprotonated by addition of a second

Table 1. Analytical[a] and physical data for the new complexes

Complex		Analysis (%)						
		C	H	N	Colour	ν(CO)[b]/cm^{-1}	ν(NH)[b]/cm^{-1}	Yield (%)
(2)	[Ru(MeC$_6$H$_4$Pr^i-*p*)Cl(acac)]	48.6	5.7	—	Orange	1 575, 1 525	—	70
		(48.7)	(5.7)					
(3)	[Ru(MeC$_6$H$_4$Pr^i-*p*)Br(acac)]	43.3	5.4	—	Orange	1 600, 1 550	—	70
		(43.5)	(5.1)					
(4)	[Ru(MeC$_6$H$_4$Pr^i-*p*)I(acac)]	39.1	4.5	—	Dark red	1 600, 1 550	—	81
		(39.0)	(4.6)					
(5)	[Ru(MeC$_6$H$_4$Pr^i-*p*)N$_3$(acac)]	47.9	5.6	11.6	Orange	1 625, 1 575	—	79
		(47.9)	(5.6)	(11.1)				
(6)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(pz)(acac)]	53.5	6.0	6.9	Orange	1 600, 1 550	—	73
		(53.8)	(6.0)	(7.0)				
(7)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(mpz)(acac)]	54.6	6.4	6.8	Orange	1 575, 1 525	—	62
		(54.8)	(6.3)	(6.7)				
(8)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(dmpz)(acac)]	55.0	6.6	6.2	Orange	1 600, 1 550	—	40
		(55.9)	(6.6)	(6.5)				
(9)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(idz)(acac)]	58.0	6.0	6.1	Yellow	1 600, 1 550	—	63
		(58.5)	(5.8)	(6.2)				
(10)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(py)]BF$_4$	47.5	5.4	2.7	Yellow	1 570, 1 520	—	66
		(48.0)	(5.2)	(2.8)		1 600s [ν(C=N), py]		
(11)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(PPh$_3$)]BF$_4$	58.2	5.7	—	Yellow	1 575, 1520	—	71,86[c]
		(58.0)	(5.3)					
(12)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(CNBu^t)]BF$_4$	46.6	6.2	2.9	Yellow	1 625, 1560	—	78
		(47.0)	(6.0)	(2.8)		2 200vs [ν(C≡N)]		
(13)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(acac){P(OMe)$_3$}]BF$_4$	39.4	5.6	—	Yellow	1 600, 1 550	—	75
		(39.6)	(5.5)					
(14)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(Hpz)]BF$_4$	43.9	5.6	5.7	Yellow	1 600, 1 550	3 300s	70
		(44.2)	(5.2)	(5.7)				
(15)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(Hmpz)]BF$_4$	44.9	5.7	5.9	Yellow	1 600, 1 550	3 400s	63
		(45.3)	(5.4)	(5.6)				
(16)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(Hdmpz)]BF$_4$	45.8	5.5	5.4	Yellow	1 575, 1 525	3 300s	80, 72[c]
		(46.4)	(5.6)	(5.4)				
(17)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(Hidz)]BF$_4$	48.7	5.2	5.2	Yellow	1 580, 1 540	3 250s	84
		(49.0)	(5.2)	(5.0)				
(18)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)(Hpz)]Cl	49.3	6.0	6.5	Yellow	1 600, 1 550	3 200—2 200m	47
		(49.4)	(5.7)	(6.4)				
(19)	[Ru(MeC$_6$H$_4$Pr^i-*p*)Cl(Hpz)$_2$]BF$_4$	39.0	4.5	11.3	Yellow	—	3 320s	62
		(38.9)	(4.5)	(11.3)			3 100—2 500m	
(20)	[Ru(MeC$_6$H$_4$Pr^i-*p*)Cl(Hmpz)$_2$]BF$_4$	41.0	5.4	10.6	Orange	—	3 300s	59
		(41.4)	(5.0)	(10.7)			3 100—2 500m	
(21)	[Ru(MeC$_6$H$_4$Pr^i-*p*)Cl(Hdmpz)$_2$]BF$_4$	43.8	5.9	10.2	Orange	—	3 250s	43
		(43.7)	(5.5)	(10.2)			3 100—2 500m	
(22)	[Ru(MeC$_6$H$_4$Pr^i-*p*)Cl(Hidz)$_2$]BF$_4$	48.0	4.6	9.1	Yellow	—	3 300s	67
		(48.5)	(4.4)	(9.4)			3 100—2 500m	
(23)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(Hpz)$_3$][BF$_4$]$_2$	36.9	4.5	13.7	Yellow	—	3 350(br)	84
		(37.2)	(4.3)	(13.7)				
(24)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(pz)(Hpz)$_2$]BF$_4$	43.8	5.1	16.2	Yellow	—	3 360(br)	81
		(43.4)	(4.8)	(16.0)			3 200—2 500m	
(25)	[Ru(MeC$_6$H$_4$Pr^i-*p*)(pz)$_2$(Hpz)]·H$_2$O	50.0	5.7	18.1	Yellow	—	3 100—2 200m	72
		(50.0)	(5.3)	(18.4)				

[a] Required values are given in parentheses. [b] In Nujol mulls. All ν(CO) bands are very strong. [c] Prepared from complex (2), Hdmpz, and NaBF$_4$.

equivalent of KOH, giving rise to [Ru(MeC$_6$H$_4$Pr^i-*p*)(pz)$_2$(Hpz)] (**25**). These complexes have been characterized by analytical and i.r. measurements (Table 1), n.m.r. studies, and by determination of the *X*-ray structure of (**24**) (see below).

Crystal Structure of [Ru(MeC$_6$H$_4$Pr^i-*p*)(pz)(Hpz)$_2$]BF$_4$ (**24**).—There are two independent molecules in the unit cell. The projections of each molecule on the plane of the *p*-cymene ring are shown in the Figure, together with the numbering system. One molecule is twisted with respect to the other by 120°. The ruthenium atom has a distorted octahedral co-ordination (see Table 2). One of the *p*-cymene rings could be considered as planar, the maximum deviation of the carbon atoms from the mean plane being 0.006(6) Å, in contrast with the other one [maximum deviation is −0.039(8) Å] which adopts an envelope conformation. In the planar *p*-cymene ring, the range of C–C distances is 1.402(9)—1.415(9) Å while in the non-planar one the range is wider [1.407(10)—1.437(9) Å] the largest corresponding to the bond with the largest torsion. With regard to the benzene ring, the isopropyl groups are unsymmetrical in molecules 1 and 2. Table 3 lists eight compounds found in the Cambridge Structural Data Base[40] with the torsion angles, which define the positions of the isopropyl groups together with the relative positions of the three substituents on the metal with respect to the *p*-cymene ring. Among all these compounds, the values of the angles involving the 6—7 bond oscillate between 15 and 112° with the exception of one molecule of [Ru$_2$(MeC$_6$H$_4$Pr^i-*p*)$_2$Cl$_3$]BPh$_4$.[12] It may be worthy of note that the range for the 14–11–G–3 torsion angles is 0—60°, molecules 1 and 2 having the lowest values.

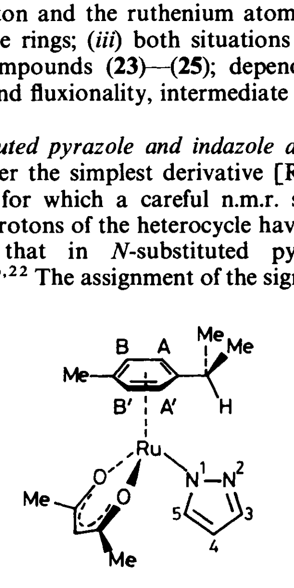
Comparison between the structure of compound (**24**) and those of other pyrazoleruthenium complexes[1–6] shows that the Ru–N(*il*)(pz) (*i* = 0,1,2,4,5, or 6) distances are within the literature range (2.070—2.228 Å) and the bonds around that nitrogen are planar. However, the characteristic of those complexes is that the RuNN angle is much lower than the RuNC angle, as shown by the ranges 114.1—122.3 *vs.* 130.5—138.5°; this is not entirely followed in the case of compound (**24**) where RuNN is only slightly lower (122.3—126.1°) than RuNC (127.4—131.4°).

Finally, in compound (**24**) there is an intramolecular hydrogen bond between the NH of one of the pyrazoles (Hpz) and the pyrazolate ring (pz)[N(12)–H(12) ··· N(22)]. The NH of the second Hpz ring is engaged in an intermolecular hydrogen bond with the BF_4 anion [N(2)–H(2) ··· F(1)]. A comparable situation is found in the other independent crystallographic molecule [N(62)–H(62) ··· N(52) and N(42)–H(42) ··· F(7)]. In previous work[29] we determined the structure of $[Ir(C_5Me_5)(dmpz)_2(Hdmpz)]$, the only hydrogen bond observed being the intramolecular one, Hdmpz ··· dmpz. Very likely, in the corresponding ruthenium derivative $[Ru(MeC_6H_4Pr^i\text{-}p)(pz)_2(Hpz)]$ (**25**) there would be a Hpz ··· pz intramolecular hydrogen bond. The presence of a coordinated metal allows for situations concerning intramolecular hydrogen bonds that cannot be found in free NH pyrazoles, where only linear polymers or cyclic dimers, trimers, and tetramers have been observed.[28,41] When discussing the n.m.r. spectra of ruthenium pyrazole complexes it will be necessary to bear in mind these possibilities.

N.M.R. Studies.—Non-pyrazole derivatives. We have gathered in Table 4 the proton chemical shifts (the isopropyl coupling constant is between 6.8 and 7.0 Hz) for these compounds, which will not be discussed further.

Pyrazole and indazole derivatives. As discussed in the Introduction, the problem of assigning unambiguously the proton and carbon signals of these heterocycles is by no means banal. Three situations are to be considered: (*i*) the ligand is substituted at only one nitrogen, *e.g.* as in compounds (**6**)—(**9**); in this case the problem is similar to that of classical pyrazole derivatives, where the substituent R is a non-metal residue; (*ii*) the ligand is substituted at both nitrogen atoms, *e.g.* as in compounds (**14**)—(**17**) and (**19**)—(**22**); this case is more difficult since the problem requires one to determine to which nitrogen atom are the proton and the ruthenium atom bound in pyrazole and indazole rings; (*iii*) both situations (*i*) and (*ii*) are present, as in compounds (**23**)—(**25**); depending on prototropic exchange and fluxionality, intermediate behaviours will be observed.

(*i*) *Monosubstituted pyrazole and indazole derivatives* (**6**)—(**9**). Let us consider the simplest derivative $[Ru(MeC_6H_4Pr^i\text{-}p)(pz)(acac)]$ (**6**), for which a careful n.m.r. study has been carried out. The protons of the heterocycle have been assigned using the rule that in *N*-substituted pyrazoles, $J(H^4\text{-}H^5) > J(H^3H^4)$.[16,22] The assignment of the signal at δ 7.607 to H^3 and that at 6.584 to H^5 is confirmed by the observation of a slight broadening of H^3 due to the quadrupolar relaxation of N^2.[22] A heteronuclear two-dimensional experiment (^1H–^{13}C) (vertical lines in Table 5) has been used to assign the signals of C^{3-5} in the ^{13}C spectrum. For compound (**6**), as with other neutral pyrazoles bearing different substituents on the nitrogen,[23,24] $^1J(C^5) > {}^1J(C^3)$ and $^2J(C^5) > {}^3J(C^5)$. Reciprocally, the assignment of the *p*-cymene signals in the ^{13}C n.m.r. spectrum (the more deshielded CH is *ortho* to the methyl group)[*] allows, through the two-dimensional experiment, the assignment of the protons of the AA′BB′ system.



(**6**)

A comparison of the pyrazole signals of compound (**6**) with those of 1-methylpyrazole[16,21–24] shows that in the ^1H n.m.r. spectrum the only signal significantly affected is that of H^5 ($\Delta\delta = \delta_{Me} - \delta_{Ru} = +0.77$); this deshielding is difficult to interpret, due to the proximity of the other ligands. In the ^{13}C n.m.r. spectrum C^4 is shielded ($\Delta\delta = +3.1$ p.p.m.) and C^5 deshielded ($\Delta\delta = -4.7$ p.p.m.), whereas C^3 remains unaffected. More significant is the fact that all the ^1J coupling constants decrease ($\Delta J = J_{Me} - J_{Ru} \approx 4.7$ Hz), thus attaining lower values than ever observed for pyrazoles. As electron-withdrawing *N*-substituents increase ^1J values whereas electron-releasing substituents produce the opposite effect, the above result demonstrates a considerable donation of electrons from ruthenium to pyrazole.

The ^1H n.m.r. spectra of compounds (**7**) and (**8**), more routinely recorded, are useful to determine the structure of (**7**): the signal at δ 6.48 clearly belongs to H^5, thus the compound is a 3-methylpyrazole derivative. The comparison of pyrazole proton chemical shifts in compounds (**6**)—(**8**), on the one hand, and in 1-methyl-, 1,3-dimethyl-, and 1,3,5-trimethyl-pyrazole,[16] on the other, shows that the substituent chemical shift (s.c.s.) produced by the *C*-methyl groups is very similar which, in turn, confirms the 3-position of the methyl group in compound (**7**). The shift of the signals of the *p*-cymene part in compound (**8**), mainly the methyl and the BB′ protons, is, probably, a consequence of a conformational change in the other ligands, induced by the 5-methyl pyrazole substituent.

The compound $[Ru(MeC_6H_4Pr^i\text{-}p)(idz)(acac)]$ is a mixture of two isomers (**9a**) and (**9b**) whose proportions depend on the purification procedure [we have observed mixtures comprised between 53—47 and 23—77% of (**9a**)—(**9b**)]. the first one is a 1*H*-indazole and the second one is a 2*H*-indazole derivative.

The assignment of signals and of the isomeric structure was performed simultaneously through a careful ^1H and ^{13}C n.m.r. study, which comprised two-dimensional correlation spectroscopy (COSY) homo-(^1H–^1H) and hetero-nuclear (^1H–^{13}C) experiments, nuclear Overhauser effect (n.O.e.) differential spectra, analysis of the proton spectra by means of the PANIC

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[*] Although the ^{13}C n.m.r. spectrum of *p*-cymene has been described twice (F. Bohlmann, R. Zeisberg, and E. Klein, *Org. Magn. Reson.*, 1975, 7, 426; Y. Kusuyama, C. Dyllick-Brenzinger, and J. D. Roberts, *ibid.*, 1980, 13, 372) we have carried out a careful ^1H and ^{13}C n.m.r. study of this ligand in $CDCl_3$. Through selective irradiations and two-dimensional (COLOC) experiments the following chemical shifts have been unambiguously assigned: ^1H, 2.289 (Me), 1.221 ($CHMe_2$) and 2.844 (CH) (J = 6.91 Hz) (Pr^i), 7.083 (s) (four aromatic protons); ^{13}C, 20.95 (Me), 24.11 (Me), 33.75 (CH) (Pr^i), 135.11 (CMe), 129.02 (C_A), 126.30 (C_B), and 145.88 p.p.m. (CPr^i). In the coupled ^{13}C spectrum the four aromatic carbons are readily distinguished, and their appearance is maintained for the complexes: CMe and CPr^i appear as complex multiplets, but the former is narrower and higher; C_A *ortho* to the methyl group appears as a doublet of quintuplets since ^3J[H (aromatic)] ≈ ^3J(H of Me), whereas C_B *ortho* to the isopropyl group appears as a doublet of triplets since ^3J[H (aromatic)] ≈ ^3J(H of Pr^i). As can be seen, complexation shifts all signals to higher field, aromatic protons by ≈1.5 and aromatic carbons by ≈40 p.p.m.

Table 2. Selected geometrical features of complex (**24**) (distances in Å, angles in °)

Ru(1)–N(1)	2.100(5)	Ru(2)–N(41)	2.108(5)	N(1)–Ru(1)–G(1)	129.8(2)	N(41)–Ru(2)–G(2)	128.4(2)
Ru(1)–N(11)	2.109(5)	Ru(2)–N(51)	2.101(5)	N(11)–Ru(1)–G(1)	127.0(2)	N(51)–Ru(2)–G(2)	127.9(2)
Ru(1)–N(21)	2.095(5)	Ru(2)–N(61)	2.096(5)	N(21)–Ru(1)–G(1)	125.7(2)	N(61)–Ru(2)–G(2)	126.0(2)
Ru(1)–G(1)*	1.689(3)	Ru(2)–G(2)*	1.684(3)	N(1)–Ru(1)–N(11)	83.9(2)	N(41)–Ru(2)–N(51)	85.0(2)
N(1)–N(2)	1.359(7)	N(41)–N(42)	1.350(7)	N(1)–Ru(1)–N(21)	86.9(2)	N(41)–Ru(2)–N(61)	84.1(2)
N(11)–N(12)	1.331(7)	N(51)–N(52)	1.352(7)	N(11)–Ru(1)–N(21)	89.9(2)	N(51)–Ru(2)–N(61)	91.4(2)
N(21)–N(22)	1.360(7)	N(61)–N(62)	1.341(7)				

Torsion angles

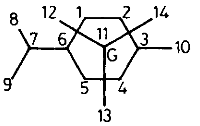
C(30)–C(35)–C(36)–C(37)	−87.3(8)	C(70)–C(75)–C(76)–C(77)	−107.4(7)
C(30)–C(35)–C(36)–C(38)	37.9(9)	C(70)–C(75)–C(76)–C(78)	18.7(9)
N(1)–Ru(1)–G(1)–C(35)	51.4(4)	N(41)–Ru(2)–G(2)–C(75)	177.1(3)
N(11)–Ru(1)–G(1)–C(35)	168.3(3)	N(51)–Ru(2)–G(2)–C(75)	58.6(3)
N(21)–Ru(1)–G(1)–C(35)	−69.3(3)	N(61)–Ru(2)–G(2)–C(75)	−68.4(3)

Hydrogen contacts

N(2) ··· F(1)	2.817(7)	N(42) ··· F(7)	2.842(8)
N(2)–H(2)	0.9(1)	N(42)–H(42)	0.9(1)
N(2)–H(2) ··· F(1)	132(9)	N(42)–H(42) ··· F(7)	149(9)
N(12) ··· N(22)	2.603(8)	N(62) ··· N(52)	2.580(7)
N(12)–H(12)	1.0(1)	N(62)–H(62)	1.1(1)
N(12)–H(12) ··· N(22)	154(10)	N(62)–H(62) ··· N(52)	148(11)

* G(i) (i = 1 or 2) are the centroids of the six-membered ring.

Table 3. Torsion angles (°) through the 6—7 bond and metal–p-cymene centroids (G)



Complex	1–6–7–8	1–6–7–9	12–11–G–3	13–11–G–3	14–11–G–3
$[Ru(MeC_6H_4Pr^i\text{-}p)Cl(pyz)_2]PF_6$[7]	−43.1	79.0	−130.2	106.5	−14.1
$[Ru(MeC_6H_4Pr^i\text{-}p)Cl_2(PPh_2CH_2SiMe_2OH)]$[8]	−106.3	16.8	−138.4	97.9	−20.6
$[Ir(CO)Cl_2(PEt_2)_2(\mu\text{-}PF_2)RuCl_2(MeC_6H_4Pr^i\text{-}p)]$[9]	−95.5	19.5	−144.1	92.8	−23.8
$[\{Os(MeC_6H_4Pr^i\text{-}p)Cl\}_2Cl_2]$[10]	−40.5	85.9	−136.3	100.6	−23.9
$[Os(MeC_6H_4Pr^i\text{-}p)(Me_2SO)Cl_2]$[11]	−15.1	111.9	−157.1	83.3	−36.9
$[Ru_2(MeC_6H_4Pr^i\text{-}p)_2Cl_3]BPh_4$ (Molecule a)[12]	175.9	57.2	−166.7	75.3	−44.7
$[Ru_2(MeC_6H_4Pr^i\text{-}p)Cl_3]BPh_4$ (Molecule b)[12]	−101.0	25.9	−166.2	74.2	−46.5
$[\{Ru(MeC_6H_4Pr^i\text{-}p)\}_2(pz)_2(OH)]BPh_4$[6]	−79.9	44.2	−164.8	77.7	−48.5
$[Ru(MeC_6H_4Pr^i\text{-}p)(\mu\text{-}Cl)_2(\mu\text{-}pz)Rh(tfbb]$[5]*	−78.0	47.5	−165.8	72.1	−49.8
Present work (Molecule 1)	−107.4	18.7	−121.4	111.6	−2.9
Present work (Molecule 2)	−87.3	37.9	−128.6	110.7	−11.7

* tfbb = tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene.

Table 4. Proton n.m.r. chemical shifts (relative to $SiMe_4$) of non-pyrazolic ruthenium–p-cymene complexes (solvent $CDCl_3$)

	p-Cymene			Acetylacetonate		
Compound	Me	Pr^i	AA′BB′	Me	CH	Other ligands
(**2**)	2.22	1.27, 2.83	5.29	1.94	5.11	
(**3**)	2.27	1.31, 2.90	5.33	1.96	5.16	
(**4**)	2.26	1.31, 2.90	5.38	1.93	5.21	
(**5**)	2.20	1.31, 2.80	5.26	1.98	5.14	
(**10**)	2.03	1.27, 2.75	5.52	1.92	4.99	8.39 ($H^{2,6}$), 7.48 ($H^{3,5}$), 7.85 (H^4), py
(**11**)	1.80	1.21, 2.55	5.41	1.69	4.83	7.47, PPh_3
(**12**)	2.09	1.23, 2.65	5.74	1.91	5.26	1.48, $CNBu^t$
(**13**)	2.06	1.22, 2.60	5.81	1.93	5.35	3.68, J_{HP} = 11.5 Hz, $P(OMe)_3$

routine implemented on the Bruker instrument, and first-order analysis of the coupled ^{13}C n.m.r. spectra. This and the fact that the signals of both isomers are of different intensities allows the assignment of all carbons and protons. The PANIC analyses were adjusted till a root-mean-square (r.m.s.) error of 0.048 (**9a**) and 0.049 (**9b**) and the most relevant n.O.e. effects were observed between H^3 and H^4 for both isomers. Comparison of the data in Table 5 with those for the corresponding N-methylindazoles[17,20,22,24] leaves no doubt concerning the isomeric structure. The most characteristic parameters of (**9a**) are the chemical shift of C^3 (133.8 p.p.m.) and the $^3J(C^3H^4)$ coupling constant (2.1 Hz) (132.4 p.p.m. and 2.5 Hz for 1-methylindazole),[24] whereas for the 2-substituted isomer, $\delta(C^3)$ = 128.4 p.p.m. and $^3J(C^3H^4) \approx 0$ Hz (for 2-methylindazole[24] the

Table 5. N.m.r. chemical shifts (relative to $SiMe_4$) and coupling constants (Hz) of $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)L]$ (L = a pyrazolate) complexes (solvent $CDCl_3$)*

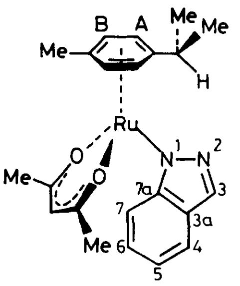
Compound and nucleus	*p*-Cymene			Acetylacetonate			Azole	
	Me	Pr^i	Aromatic	Me	CH	CO		
(**6**) ^1H	2.020	1.224 (Me) 2.749 (CH) $J = 6.93$	5.24 (AA′) 5.51 (BB′) $J_{AB} = 6.08$	1.910	5.116	—	7.607 (H^3) 6.035 (H^4) 6.584 (H^5)	$^3J(H^3H^4) = 1.67$ $^3J(H^4H^5) = 1.89$ $^4J(H^3H^5) = 0.62$
^{13}C	17.21	22.23 (Me) 30.42 (CH)	97.57 (CMe) 80.88 (C_A) 84.36 (C_B) 100.05 (CPr^i)	27.15	99.06	186.83	139.14 (C^3) 102.02 (C^4) 134.19 (C^5)	$^1J(C^3H^3) = 178.8$ $^2J(C^3H^4) = {}^3J(C^3H^5) = 6.5$ $^1J(C^4H^4) = 170.7$ $^2J(C^4H^3) = {}^2J(C^4H^5) = 10.4$ $^1J(C^5H^5) = 179.7$ $^2J(C^5H^4) = 7.6$ $^3J(C^5H^3) = 5.0$
(**7**) ^1H	1.97	1.20 (Me) 2.73 (CH) $J = 6.9$	5.24 (AA′) 5.50 (BB′) $J_{AB} = 6.0$	1.88	5.09	—	2.32 (Me^3) 5.78 (H^4) 6.48 (H^5)	$^3J(H^4H^5) = 1.79$
(**8**) ^1H	1.74	1.23 (Me) 2.77 (CH) $J = 7.1$	5.07 (AA′) 5.51 (BB′) $J_{AB} = 5.7$	1.86	4.92	—	2.24 (Me^3) 5.52 (H^4) 2.17 (Me^5)	
(**9a**) ^1H	1.75	1.27 (Me) 2.82 (CH) $J = 6.96$	5.17 (AA′) 5.52 (BB′) $J_{AB} = 6.02$	1.80	4.76	—	8.069 (H^3) 7.612 (H^4) 6.826 (H^5) 6.994 (H^6) 7.518 (H^7)	$^5J(H^3H^7) = 1.02$ $^3J(H^4H^5) = 8.01$ $^4J(H^4H^6) = 1.08$ $^5J(H^4H^7) = 1.05$ $^3J(H^5H^6) = 6.67$ $^4J(H^5H^7) = 0.98$ $^3J(H^6H^7) = 8.53$
^{13}C	17.51	22.46 (Me) 30.69 (CH)	98.98 (CMe) 79.63 (C_A) 84.30 (C_B) 101.75 (CPr^i)	26.68	98.98	186.54	133.83 (C^3) 125.17 (C^{3a}) 118.89 (C^4) 116.87 (C^5) 121.60 (C^6) 113.61 (C^7) 149.24 (C^{7a})	$^1J(C^3H^3) = 182.8$ $^3J(C^3H^4) = 2.1$ $^1J(C^4H^4) = 158.2$ $^3J(C^4H^6) = 7.9$ $^1J(C^5H^5) = 157.5$ $^3J(C^5H^7) = 7.0$ $^1J(C^6H^6) = 154.9$ $^3J(C^6H^4) = 8.7$ $^1J(C^7H^7) = 159.8$ $^3J(C^7H^5) = 7.2$
(**9b**) ^1H	1.94	1.22 (Me) 2.73 (CH) $J = 6.94$	5.26 (AA′) 5.55 (BB′) $J_{AB} = 5.94$	1.91	5.01	—	7.297 (H^3) 7.533 (H^4) 6.809 (H^5) 7.007 (H^6) 7.740 (H^7)	$^5J(H^3H^7) = 0.92$ $^3J(H^4H^5) = 8.16$ $^4J(H^4H^6) = 1.10$ $^5J(H^4H^7) = 1.01$ $^3J(H^5H^6) = 6.60$ $^4J(H^5H^7) = 0.86$ $^3J(H^6H^7) = 8.50$
^{13}C	17.30	22.28 (Me) 30.46 (CH)	98.98 (CMe) 80.55 (C_A) 84.89 (C_B) 100.65 (CPr^i)	27.06	99.24	187.02	128.36 (C^3) 122.71 (C^{3a}) 117.34 (C^4) 118.70 (C^5) 121.29 (C^6) 115.97 (C^7) 151.28 (C^{7a})	$^1J(C^3H^3) = 184.5$ $^1J(C^4H^4) = 157.4$ $^3J(C^4H^6) = 7.7$ $^1J(C^5H^5) = 157.4$ $^3J(C^5H^7) = 7.1$ $^1J(C^6H^6) = 156.3$ $^3J(C^6H^4) = 8.2$ $^1J(C^7H^7) = 158.2$ $^3J(C^7H^5) = 7.1$

* Vertical lines correspond to two-dimensional (^1H–^{13}C) correlations (COSY experiments).

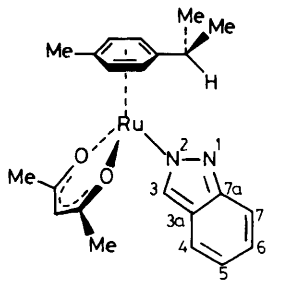
corresponding values are 123.1 p.p.m. and ≈0 Hz). A systematic comparison of the spectral characteristics (^1H and ^{13}C) of the pairs compound (**9a**)–1-methylindazole and (**9b**)–2-methylindazole yields, for the heterocyclic part, values comparable with those previously reported for (**6**)–1-methylpyrazole: the nuclei closer to the substituent [C^{7a} in (**9a**) and C^3 and H^3 in (**9b**)] are the most sensitive to the comparison ($\Delta\delta$ and ΔJ). Signals (^1H and ^{13}C) due to positions 5 and 6 in both isomers are shifted to high field [$\Delta\delta(^1H) \approx 0.27$, $\Delta\delta(^{13}C) \approx 2.8$ p.p.m.]; this reflects a modification of the electronic distribution in indazoles due to the ruthenium atom. Finally, we have recorded a spectrum of an initial 53–47% mixture of (**9a**)–(**9b**); after several days in $CDCl_3$ solution (**9a**) remained unaltered (52%) but (**9b**) slowly decomposed (31%).

(*ii*) *Disubstituted derivatives containing only one azole ligand* (**14**)—(**17**). Since these compounds have both nitrogens of the azole ligand substituted, it is necessary to define which is N^1 and which N^2. We have represented below the numbering and the canonical form chosen.

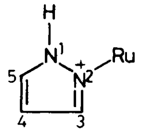
The spectral characteristics of compounds (**14**)—(**17**) are gathered in Table 6. In the case of pyrazoles, the crucial experiment was carried out on a 75–25% mixture of (**15a**) and



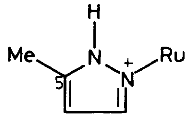
(9a)



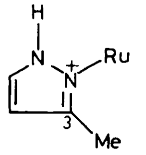
(9b)



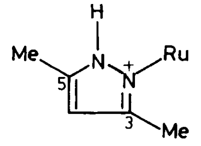
(14)



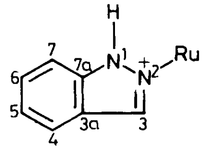
(15a)



(15b)



(16)



(17)

(15b). N.O.e. difference spectra were recorded for both NH signals; irradiation of the most intense (δ 11.48) produces an enhancement of the *C*-methyl signal, whereas irradiation of the weaker NH (11.06) increases the signal of a CH at 7.63. This demonstrates that the most abundant isomer is **(15a)** and that the signal at δ 7.63 belongs to H^5 of the minor isomer **(15b)**. Taking into account the well known effects of the *C*-methyl groups in pyrazoles,[16] the assignment of H^3 and H^5 in compound **(14)** is straightforward. Similarly, a n.O.e. experiment carried out with the indazole derivative **(17)** shows that the NH (δ 12.00) is close to the proton at δ 7.832 and far from the proton at δ 7.680 (with a multiplicity characteristic of H^3). This experiment demonstrates that the NH proton is on N^1 and that the signal at δ 7.832 belongs to H^7.

The values of the chemical shifts and coupling constants in Table 6 were obtained through a series of experiments such as NH selective decoupling [^1H and ^{13}C of **(14)**, **(15a)**, **(15b)**, and **(17)**], C–Me selective decoupling [^1H of **(15a)** and **(15b)**], homonuclear COSY [^1H of **(17)**], heteronuclear COSY [^1H and ^{13}C of **(14)** and **(17)**, see vertical lines in Table 6], and iterative analysis of the proton spectrum [compound **(17)**, r.m.s. = 0.041].

The most interesting fact of Table 6 is that couplings with NH can be observed both in ^1H and ^{13}C n.m.r. spectra. Due to prototropic exchange, *N*-unsubstituted pyrazoles and indazoles do not show couplings with NH, with very few exceptions.[19,20] In protonated pyrazolium and indazolium salts pure sulphuric acid is required to observe these couplings.[18] Here, for the first time, a complete collection of such couplings has been determined. They are summarized in Scheme 2.

Some of them are similar to those previously reported,[18–20] but others are original such as the couplings measured for compound **(17)**, $^4J(H^1H^3)$ and $^3J(C^3H^1)$, and, particularly, the zigzag coupling between H^1 and H^5 (0.9 Hz) which is the counterpart of the well known $^5J(H^3H^7)$ coupling for indazoles.[17,20]

Other coupling constants that deserve comment are $^3J(H^3H^4)$ and $^3J(H^4H^5)$, 2.2 and 2.6 Hz respectively, for compounds **(14)**, **(15a)**, and **(15b)**. Based on the relationship between coupling constants and bond orders that holds in neutral pyrazoles,[16,22] the structure of the ligands is represented with single C^3C^4 and double C^4C^5 bonds. A significant ^{13}C–^1H coupling is $^3J(C^3H^4)$ = 2.1 Hz for compound **(17)**, which is identical to that measured for compound **(9a)** (Table 5) [this coupling being absent in **(9b)**] and seems to be characteristic of an indazole structure with a single bond between C^3 and C^{3a}.

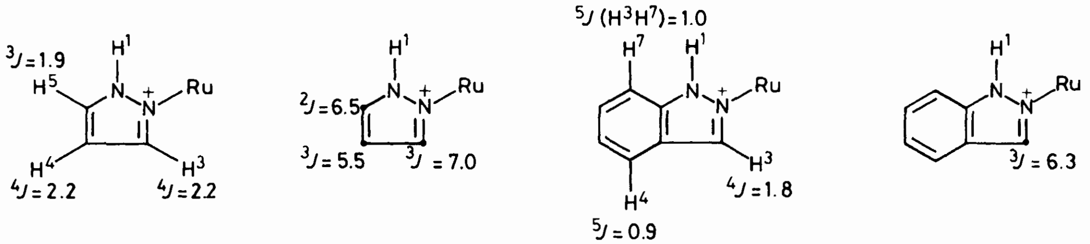
Finally, we will make some comparisons in order to reveal the electronic structure of the pyrazole ligands. As we have pointed out before, the s.c.s. induced by the *C*-methyl groups in compounds **(14)**, **(15a)**, **(15b)**, and **(16)** are very similar to those observed for *N*-methylpyrazoles in CF_3CO_2H (pyrazolium cations).[16] When pyrazoles and indazoles, on the one hand, and pyrazolium and indazolium quaternary salts, on the other, are compared the main changes observed in the n.m.r. spectra are: (*a*) protons H^3 and H^5 are shifted downfield by about δ 1.3 and proton H^4 by about 0.8;[42] (*b*) $^3J(H^3H^4)$ and $^3J(H^4H^5)$ increase from about 2.2 Hz for pyrazole to 3.0 Hz for 1,2-dimethylpyrazolium cation;[42] (*c*) the ^{13}C chemical shifts of CH groups are unaffected or only slightly affected;[43] (*d*) the $^1J(^{13}C$–$^1H)$ coupling constants increase considerably, between 10 and 15 Hz.[43] For analogous compounds of Tables 5 (pyrazolates) and 6 (pyrazoles), all those observations are valid but always weaker: protons are shifted downfield between δ 0.2 and 0.6; ^1H–^1H coupling constants increase from about 1.8 to about 2.4 Hz; ^{13}C chemical shifts for a given position (*with the numbering used at the beginning of this section*) are relatively unaffected; the ^1J coupling constants increase between 8 and 10 Hz, remaining smaller than the couplings observed for quaternary salts (near 200 Hz). A difficulty arises from the fact that compounds of the [$Ru(MeC_6H_4Pr^i$-*p*)(acac)L] (L = a pyrazolate) series have the ruthenium on N^1 [save **(9b)**] whereas those of the [$Ru(MeC_6H_4Pr^i$-*p*)(acac)L]BF_4 (L = a pyrazole) series have the ruthenium on N^2. However, the conclusion is clear: in the second group, the pyrazole ligand behaves as an attenuated azolium cation. Here also the donation of electrons from the ruthenium to the heterocycle somewhat compensates its electron deficiency.

(*iii*) *Disubstituted derivatives containing two azole ligands* **(19)**—**(22)**. These salts of general formula [$Ru(MeC_6H_4Pr^i$-*p*)$Cl(L)_2$]BF_4 (L = a pyrazole) are similar to those previously discussed, but the presence of two azole ligands can complicate the discussion, even though for all compounds only one series of signals is observed for both rings (^1H and ^{13}C n.m.r.). The results obtained from the n.m.r. spectra [through PANIC analysis in the case of compound **(22)**, ^1H n.m.r.] are gathered in Table 7.

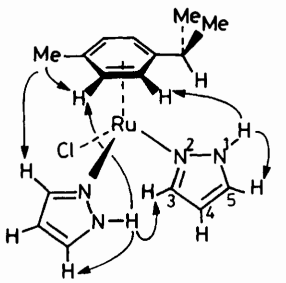
Assignment problems have been solved by techniques similar to those previously discussed. From a large number of experiments only three points will be noted.

(*a*) The couplings with NH^1 (^1H and ^{13}C) are more difficult to observe than in the preceding series. Thus, compound **(22)** shows totally uncoupled spectra or residual couplings depending on the solvent and the concentration. The values for this compound, $^5J(H^1H^4)$ = 0.68 Hz and $^3J(C^3H^1)$ = 5.4 Hz, could be slight underestimates.

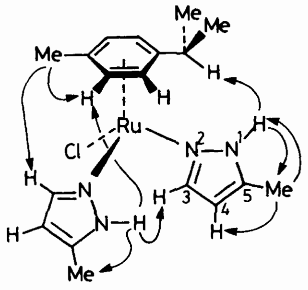
(*b*) Amongst the n.O.e. experiments we have selected (and represented below) the most significant results obtained with pyrazole derivatives. There are several inter-ring n.O.e. enhancements that can be used for conformational purposes (always keeping in mind that the rotations about the *p*-cymene– and the pyrazole–ruthenium bonds are almost free). For instance, there is an averaged conformation where the NH of one pyrazole is close to the H^3 of the other; both aromatic protons (AA′BB′ system) are close to the NH groups and the *C*-methyl group of the *p*-cymene is close to H^3. A rapid



Scheme 2.



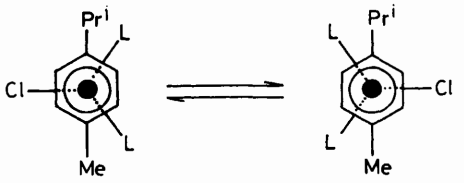
(19)



(20)

equilibrium between the following two conformations could account for these effects.

(*c*) Indazole derivative (**22**) has a structure similar to that of (**17**), *i.e.* it is a 1*H*-indazole co-ordinated to the ruthenium by the N^2 nitrogen. The coupling constants (Table 7) and the n.O.e. experiments leave no doubt about its structure. In particular n.O.e.s are observed within one indazole ring between H^1 and H^7 and between H^3 and H^4 and inter-ring between H^1 and H^3.



(19a) **(19b)**

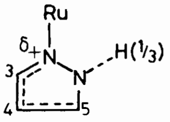
(20a) **(20b)**

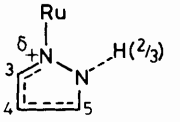
L = a pyrazolate

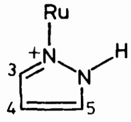
We cannot hide the fact that there are some problems in this series which appear when the results of Table 6 and 7 are compared. An examination of $^1J(^1H-^{13}C)$ coupling constants shows that, in general, they are larger for $[Ru(MeC_6H_4Pr^i\text{-}p)Cl(L)_2]BF_4$ (L = a pyrazole) (Table 7) than for $[Ru(MeC_6H_4Pr^i\text{-}p)(acac)L]BF_4$ (Table 6). From the preceding discussion, it follows that the azoles in the former are more 'cationic' than in the latter. However, this is not so for the C^5 of pyrazole complexes (**19**) and (**14**) [$^1J(C^5H^5)$ = 190.7 and 193.5 Hz]. We have no explanation for this anomaly; maybe the positive charge, which we continue to locate on N^2, is somewhat different in the two kinds of complexes.

(*iv*) *Derivatives containing one, two, or three pyrazole ligands* (**23**)—(**25**). It is better to discuss these three compounds in the order $[Ru(MeC_6H_4Pr^i\text{-}p)(pz)_2(Hpz)]$ (**25**), $[Ru(MeC_6H_4Pr^i\text{-}p)(pz)(Hpz)_2]BF_4$ (**24**), and $[Ru(MeC_6H_4Pr^i\text{-}p)(Hpz)_3][BF_4]_2$ (**23**) corresponding to the increase in overall positive charge. Remember that the crystal structure of (**24**) shows an intramolecular N–H • • • N bond between one of the Hpz and pz.

We will omit the technical details of the assignments since they are similar to those used for the preceding compounds. The $^1H-^1H$ coupling constants of the pyrazoles (Table 8) correspond to iterative analyses (PANIC, r.m.s. = 0.03) of NH decoupled spectra. However, coupling with NH cannot be measured (^1H and ^{13}C n.m.r. spectroscopy). The numbering of the pyrazole ring atoms in these compounds which contain both neutral pz–Ru and cationic Hpz–Ru is the same as in compounds (**14**) and (**19**), *i.e.* C^3 near the ruthenium.







(25) **(24)** **(23)**

Taking compound (**6**) (Table 5) as a model of pz and compound (**19**) (Table 7) as a model of Hpz, the n.m.r. data for compounds (**25**) ($\frac{2}{3}$pz–$\frac{1}{3}$Hpz), (**24**) ($\frac{1}{3}$pz–$\frac{2}{3}$Hpz), and (**23**) (Hpz) can be estimated. Comparison of these values with the experimental data of Table 8 shows a reasonable agreement for ^{13}C, $^1J(^{13}C-^1H)$, and $^3J(^1H-^1H)$, larger differences being observed for compound (**23**). The chemical shifts of protons H^3 and H^5 are too sensitive to the ring-current effects of the neighbouring pyrazoles to be compared. Particularly striking is the value of $\delta(H^3)$ 6.81 for (**23**) when this proton appears at δ 8.11 for compound (**19**). It is worthy of note that the three H^3 protons (Table 8) appear slightly broadened compared with the corresponding H^5 protons.

Conclusion

Pyrazoles are one of the most popular ligands in organometallic chemistry[22,44,45] and n.m.r., ^1H and ^{13}C, is the standard technique used to establish the structures of the resulting complexes. The present paper shows that even in the most favourable cases, when the metal does not produce a broadening of the signals with loss of the $^1H-^1H$ couplings, and when an *X*-ray determination supports the proposed structure, the assignment of n.m.r. signals is by no means trivial.

On the other hand, the present careful n.m.r. study has shed light on the structures of the complexes in solution. In our case

Table 6. N.m.r. chemical shifts (relative to SiMe$_4$) and coupling constants (Hz) of [Ru(MeC$_6$H$_4$Pr^i-*p*)(acac)L]BF$_4$ (L = a pyrazole) complexes (solvent CDCl$_3$)[a]

Compound and nucleus	*p*-Cymene			Acetylacetonate			Azole	
	Me	Pr^i	Aromatic	Me	CH	CO		
(14) ^{1}H	2.019	1.221 (Me)	5.46 (AA′)	1.925	5.016	—	7.143 (H^3)	$^3J(\mathrm{H^3H^4}) = 2.22$[b]
		2.698 (CH)	5.64 (BB′)				6.288 (H^4)	$^3J(\mathrm{H^4H^5}) = 2.62$[b]
		$J = 6.95$	$J_{AB} = 6.29$				7.809 (H^5)	$^4J(\mathrm{H^3H^5}) = 0.77$[b]
							11.92 (NH^1)	
^{13}C	17.34	22.08 (Me)	99.98 (CMe)	26.85	99.16	187.70	140.05 (C^3)	$^1J(\mathrm{C^3H^3}) = 189.6$
		30.62 (CH)	80.24 (C$_A$)					$^2J(\mathrm{C^3H^4}) = {}^3J(\mathrm{C^3H^5}) = {}^3J(\mathrm{C^3H^1}) = 7.3$
			84.36 (C$_B$)				106.54 (C^4)	$^1J(\mathrm{C^4H^4}) = 180.7$
			101.60 (CPr^i)					$^2J(\mathrm{C^4H^3}) = {}^2J(\mathrm{C^5H^3}) = 7.6$
								$^3J(\mathrm{C^4H^1}) = 5.3$
							133.42 (C^5)	$^1J(\mathrm{C^5H^5}) = 193.5$
								$^2J(\mathrm{C^5H^4}) = 7.6$
								$^3J(\mathrm{C^5H^3}) = {}^2J(\mathrm{C^5H^1}) = 6.2$
(15a) ^{1}H	1.98	1.17 (Me)	5.44 (AA′)	1.88	4.99	—	6.90 (H^3)	$^3J(\mathrm{H^3H^4}) = 2.2$, $^5J(\mathrm{H^3H^5}) = 0.5$ (Me)
		2.65 (CH)	5.61 (BB′)				5.97 (H^4)	$^4J(\mathrm{H^4H^5}) = 0.75$ (Me)
		$J = 6.9$	$J_{AB} = 6.2$				2.35 (Me)	$^4J(\mathrm{H^1H^3}) = 2.2$, $^4J(\mathrm{H^1H^4}) = 2.1$
							11.48 (NH^1)	
^{13}C	17.17	21.96 (Me)	99.82 (CMe)	26.73	98.97	187.40	140.39 (C^3)	$^1J(\mathrm{C^3H^3}) = 188.5$
		30.46 (CH)	79.96 (C$_A$)					$^2J(\mathrm{C^3H^4}) = {}^3J(\mathrm{C^3H^1}) = 7.2$
			84.26 (C$_B$)				105.98 (C^4)	$^1J(\mathrm{C^4H^4}) = 179.01$
			101.21 (CPr^i)					$^2J(\mathrm{C^4H^3}) = 9.1$, $^3J(\mathrm{C^4H^5}) = 3.6$ (Me)
								$^3J(\mathrm{C^4H^1}) = 5.7$
							144.24 (C^5)	$^2J(\mathrm{C^5H^4}) = {}^3J(\mathrm{C^5H^3}) = {}^2J(\mathrm{C^5Me}) =$
								$^2J(\mathrm{C^5H^1}) = 6.5$
							10.52 (Me)	$^1J = 129.8$
(15b) ^{1}H	1.98	1.17 (Me)	5.41 (AA′)	1.89	4.95	—	2.30 (Me^3)	$^4J(\mathrm{H^3H^4}) = 0.5$ (Me), $^5J(\mathrm{H^3H^5}) = 0.5$ (Me)
		2.70 (CH)	5.61 (BB′)				6.07 (H^4)	$^3J(\mathrm{H^4H^5}) = 2.6$, $^4J(\mathrm{H^1H^4}) = 2.2$
		$J = 6.9$	$J_{AB} = 6.2$				7.63 (H^5)	$^3J(\mathrm{H^1H^5}) = 1.9$
							11.06 (NH^1)	
^{13}C	17.43	21.96 (Me)	99.75 (CMe)	26.52	98.97	187.40	151.46 (C^3)	$^3J(\mathrm{C^3H^1}) = 6.5$
		30.46 (CH)	80.07 (C$_A$)				13.01 (Me)	$^1J = 128.5$
			84.26 (C$_B$)				106.74 (C^4)	$^1J(\mathrm{C^4H^4}) = 176$
			101.58 (CPr^i)				133.19 (C^5	$^1J(\mathrm{C^5H^5}) = 190.9$
								$^2J(\mathrm{C^5H^4}) = {}^2J(\mathrm{C^5H^1}) = 7.1$
(16) ^{1}H	1.87	1.17 (Me)	5.43 (AA′)	1.89	4.96	—	2.23 (Me^3)	
		2.74 (CH)	5.66 (BB′)				5.82 (H^4)	
		$J = 7.0$	$J_{AB} = 6.3$				2.28 (Me^5)	
(17) ^{1}H	2.02	1.23 (Me)	5.56 (AA′)	1.95	5.01	—	7.680 (H^3)	$^5J(\mathrm{H^3H^7}) = 0.98$, $^3J(\mathrm{H^4H^5}) = 8.30$
		2.73 (CH)	5.72 (BB′)				7.635 (H^4)	$^4J(\mathrm{H^4H^6}) = 0.95$, $^5J(\mathrm{H^4H^7}) = 0.94$
		$J = 6.93$	$J_{AB} = 6.25$				7.128 (H^5)	$^3J(\mathrm{H^5H^6}) = 6.89$, $^4J(\mathrm{H^5H^7}) = 0.88$
							7.339 (H^6)	$^3J(\mathrm{H^6H^7}) = 8.62$
							7.832 (H^7)	
							12.00 (NH^1)	$^4J(\mathrm{H^1H^3}) = 1.84$, $^5J(\mathrm{H^1H^4}) = 0.91$
^{13}C	17.32	22.07 (Me)	100.33 (CMe)	26.88	99.30	187.77	135.45 (C^3)	$^1J(\mathrm{C^3H^3}) = 192.1$, $^3J(\mathrm{C^3H^4}) = 2.1$
		30.61 (CH)	80.53 (C$_A$)				122.01 (C^{3a})	$^3J(\mathrm{C^3H^1}) = 6.3$
			84.68 (C$_B$)				119.87 (C^4)	$^1J(\mathrm{C^4H^4}) = 163.5$, $^3J(\mathrm{C^4H^6}) = 7.8$
			101.89 (CPr^i)				122.13 (C^5)	$^1J(\mathrm{C^5H^5}) = 161.1$, $^3J(\mathrm{C^5H^7}) = 7.5$
							128.47 (C^6)	$^1J(\mathrm{C^6H^6}) = 156.3$, $^3J(\mathrm{C^6H^4}) = 8.0$
							111.48 (C^7)	$^1J(\mathrm{C^7H^7}) = 167.7$, $^3J(\mathrm{C^7H^5}) = 7.5$
							141.90 (C^{7a})	

[a] Vertical lines correspond to two-dimensional (^{1}H–^{13}C) correlations (COSY experiments). [b] Couplings determined after NH irradiation; the three protons are coupled with the NH, but the coupling constants cannot be measured.

it was demonstrated that: (*i*) all the complexes have structures related to that of **(24)**; (*ii*) in solution there is a rapid prototropy when there is more than one azole present in the molecule which prevents the measurement of couplings with NH; (*iii*) pyrazole ligands are best represented as 1*H*-azoles co-ordinated through the N^2 lone pair than as protonated 2-substituted azoles; (*iv*) contrary to the solid state (Table 3), in solution there is a free rotation about the *p*-cymene–ruthenium bond even if all the conformers are not equally populated; (*v*) the conformation of the azole is strongly dependent on the nature of the complex, in particular for compounds of the last family [see (*iv*) above] it depends on the possibility [**(24)** and **(25)**] or not [**(23)**] of intramolecular hydrogen bonds.

Experimental

Synthesis.—[Ru(MeC$_6$H$_4$Pr^i-*p*)Cl(acac)] **(2)**. A suspension of [{Ru(MeC$_6$H$_4$Pr^i-*p*)Cl}$_2$(μ-Cl)$_2$] **(1)** (1.00 g, 1.63 mmol) and

Table 7. N.m.r. chemical shifts (relative to $SiMe_4$) and coupling constants (Hz) of $[Ru(MeC_6H_4Pr^i\text{-}p)Cl(L)_2]BF_4$ (L = a pyrazole) complexes (solvent $CDCl_3$)[a]

Compound and nucleus	*p*-Cymene			Azole	
	Me	Pr^i	Aromatic		
(19) ^1H	1.794	1.093 (Me)	5.851 (AA′)	8.114 (H^3)	$^3J(H^3H^4) = 2.26^b$
		2.360 (CH)	5.940 (BB′)	6.357 (H^4)	$^3J(H^4H^5) = 2.67^b$
		$J = 6.91$	$J_{AB} = 6.10$	7.630 (H^5)	$^4J(H^3H^5) = 0.71^b$
				12.48 (NH^1)	
^{13}C	17.89	22.06 (Me)	101.17 (CMe)	142.99 (C^3)	$^1J(C^3H^3) = 192.3^c$
		30.92 (CH)	82.92 (C_A)	107.27 (C^4)	$^1J(C^4H^4) = 181.1^c$
			85.57 (C_B)	132.40 (C^5)	$^1J(C^5H^5) = 190.7^c$
			104.55 (CPr^i)		
(20) ^1H	1.756	1.055 (Me)	5.762 (AA′)	7.849 (H^3)	$^3J(H^3H^4) = 2.2$, $^3J(H^3H^5) = 0.4$ (Me)
		2.327 (CH)	5.850 (BB′)	6.028 (H^4)	$^4J(H^4H^5) = 0.8$ (Me)
		$J = 6.91$	$J_{AB} = 6.20$	2.283 (Me)	
				12.01 (NH^1)	$^4J(H^1H^3) = 2.0$, $^4J(H^1H^4) = 2.0$
^{13}C	17.81	21.96 (Me)	101.19 (CMe)	143.60 (C^3)	$^1J(C^3H^3) = 190.7$
		30.78 (CH)	82.33 (C_A)		$^2J(C^3H^4) = {}^3J(C^3H^1) = 7.0$
			85.49 (C_B)	106.77 (C4)	$^1J(C^4H^4) = 179.1$, $^2J(C^4H^3) = 9.2$
			104.00 (CPr^i)		$^3J(C^4Me) = {}^3J(C^4H^1) = 3.6$
				143.37 (C^5)	$^2J(C^5H^4) = {}^3J(C^5H^3) = {}^2J(C^5Me) = {}^2J(C^5H^1) = 6.6$
				10.72 (Me)	$^1J = 129.7$
(21) ^1H	1.74	1.14 (Me)	5.86 (AA′)	2.18 (Me^3)	
		2.78 (CH)	6.13 (BB′)	5.88 (H^4)	
		$J = 6.9$	$J_{AB} = 6.2$	2.20 (Me^5)	
(22) ^1H	1.794	1.082 (Me)	5.98 (AA′)	8.739 (H^3)	$^5J(H^3H^7) = 0.97$, $^3J(H^4H^5) = 8.31$
		2.401 (CH)	6.09 (BB′)	7.680 (H^4)	$^4J(H^4H^6) = 1.02$, $^5J(H^4H^7) = 0.99$
		$J = 6.90$	$J_{AB} = 6.05$	7.114 (H^5)	$^3J(H^5H^6) = 6.92$, $^4J(H^5H^7) = 0.86$
				7.338 (H^6)	$^3J(H^6H^7) = 8.63$
				7.521 (H^7)	
				12.08 (NH^1)	$^4J(H^1H^3) = 1.79$, $^5J(H^1H^4) = 0.68$
^{13}C	17.99	22.04 (Me)	102.18 (CMe)	139.49 (C^3)	$^1J(C^3H^3) = 195.1$, $^3J(C^3H^4) = 1.9$
		30.95 (CH)	83.02 (C_A)	122.74 (C^{3a})	$^3J(C^3H^1) = 5.4$
			86.71 (C_B)	120.73 (C^4)	$^1J(C^4H^4) = 164.3$, $^3J(C^4H^6) = 8.0$
			104.74 (CPr^i)	122.37 (C^5)	$^1J(C^5H^5) = 161.8$, $^3J(C^5H^7) = 7.4$
				129.00 (C^6)	$^1J(C^6H^6) = 161.8$, $^3J(C^6H^4) = 8.1$
				110.29 (C^7)	$^1J(C^7H^7) = 168.4$, $^3J(C^7H^5) = 7.8$

[a] Vertical lines correspond to two-dimensional (^1H–^{13}C) correlations (COSY experiments). [b] Couplings determined after NH irradiation. [c] Complex multiplets due to couplings with NH.

$Na(acac){\cdot}H_2O$ (0.59 g, 4.25 mmol) in acetone (100 cm^3) was stirred for 40 min while the colour changed from red to orange. The solvent was vacuum-evaporated until dryness and the residue was extracted with dichloromethane (4 × 20 cm^3). The solvent was then removed *in vacuo* and the residue dissolved in acetone. The resulting solution was partially concentrated under reduced pressure and an orange solid precipitated (600 mg). It was filtered off, washed with diethyl ether, and air-dried. A second fraction (250 mg) was obtained from the resulting filtrate by addition of diethyl ether or by cooling in a refrigerator for 24 h.

$[Ru(MeC_6H_4Pr^i\text{-}p)I(acac)]$ (**4**). A suspension of complex (**2**) (0.17 g, 0.46 mmol) and $NaI{\cdot}2H_2O$ (0.89 g, 4.70 mmol) in acetone (30 cm^3) was stirred for 7 h while the colour changed from orange to dark red. The solvent was vacuum-evaporated until dryness and the residue extracted with dichloromethane (3 × 10 dm^3). The product crystallized from this solution as a dark red solid (0.18 g) on addition of n-hexane. The analogous complexes (**3**) and (**5**) were obtained by the same method.

$[Ru(MeC_6H_4Pr^i\text{-}p)(idz)(acac)]$ (**9**) To a solution of complex (**2**) (100.0 mg, 0.27 mmol) in acetone (25 cm^3) were added Hidz (31.9 mg, 0.27 mmol) and KOH (3.14 cm^3, 0.086 mol dm^{-3}, 0.27 mmol) in methanol. The resulting suspension was stirred for 30 min and vacuum-evaporated until dryness. The residue was extracted with dichloromethane (3 × 10 cm^3). The solution was concentrated under reduced pressure and the slow addition of n-hexane gave complex (**9**) (77 mg) which was filtered off, washed with n-hexane, and air-dried. Proton n.m.r. measurements revealed that complex (**9**) was obtained as a mixture of isomers (**9a**) and (**9b**) in variable relative proportions (see above). Complexes (**6**)—(**8**) were obtained by the same method.

$[Ru(MeC_6H_4Pr^i\text{-}p)(acac)(PPh_3)]BF_4$ (**11**). *Method A*. To a solution of complex (**2**) (100.0 mg, 0.27 mmol) in acetone (20 cm^3) was added $AgBF_4$ (52.6 mg, 0.27 mmol). The resulting suspension was stirred for 15 min and then filtered to remove the AgCl formed. To the yellow filtrate was added PPh_3 (70.9 mg, 0.27 mmol). The solution obtained was stirred for 20 min and then concentrated to *ca.* 2 cm^3. Addition of diethyl ether gave a yellow solid (132 mg) which was filtered off, washed with diethyl ether, and air-dried. The analogous complexes (**10**) and (**12**)—**17**) were obtained by the same method.

Method B. To a solution of complex (**2**) (100.0 mg, 0.27 mmol) in acetone (25 cm^3) were added PPh_3 (106.0 mg, 0.40 mmol) and $NaBF_4$ (38.6 mg, 0.35 mmol). The resulting suspension was stirred for 1 h, then the solvent was vacuum-evaporated until dryness and the residue extracted with dichloromethane

Table 8. N.m.r. chemical shifts (relative to $SiMe_4$) and coupling constants (Hz) of the complexes $[Ru(MeC_6H_4Pr^i\text{-}p)(pz)_2(Hpz)]$ (**25**), $[Ru(MeC_6H_4Pr^i\text{-}p)(pz)(Hpz)_2]BF_4$ (**24**), and $[Ru(MeC_6H_4Pr^i\text{-}p)(Hpz)_3][BF_4]_2$ (**23**) (solvent $CDCl_3$)*

Compound and nucleus	*p*-Cymene			Azole	
	Me	Pr^i	Aromatic		
(**25**) ^1H	1.908	1.089 (Me) 2.519 (CH) $J = 6.92$	5.430 (AA′) 5.538 (BB′) $J_{AB} = 6.13$	6.768 (H^3) 6.101 (H^4) 7.618 (H^5) 12.93 (NH^1)	$^3J(H^3H^4) = 1.93$ $^3J(H^4H^5) = 2.03$ $^4J(H^3H^5) = 0.62$
^{13}C	17.82	22.23 (Me) 30.49 (CH)	100.12 (CMe) 85.55 (C_A) 86.03 (C_B) 105.24 (CPr^i)	140.82 (C^3) 104.63 (C^4) 135.51 (C^5)	$^1J(C^3H^3) = 184.0$ $^2J(C^3H^4) = 5.6$, $^3J(C^3H^5) = 8.1$ $^1J(C^4H^4) = 177.4$ $^2J(C^4H^3) = {}^2J(C^4H^5) = 10.1$ $^1J(C^5H^5) = 182.6$ $^2J(C^5H^4) = {}^3J(C^5H^3) = 6.8$
(**24**) ^1H	1.865	1.041 (Me) 2.378 (CH) $J = 6.90$	5.816 (AA′) 5.881 (BB′) $J_{AB} = 6.09$	7.391 (H^3) 6.314 (H^4) 7.653 (H^5) 10.61 (NH^1)	$^3J(H^3H^4) = 2.12$ $^3J(H^4H^5) = 2.37$ $^4J(H^3H^5) = 0.64$
^{13}C	18.02	22.16 (Me) 31.06 (CH)	102.24 (CMe) 84.50 (C_A) 87.76 (C_B) 104.72 (CPr^i)	142.78 (C^3) 107.16 (C^4) 133.91 (C^5)	$^1J(C^3H^3) = 186.8$ $^2J(C^3H^4) = 6.4$, $^3J(C^3H^5) = 7.7$ $^1J(C^4H^4) = 178.9$ $^2J(C^4H^3) = {}^2J(C^4H^5) = 9.2$ $^1J(C^5H^5) = 188.4$ $^2J(C^5H^4) = {}^3J(C^5H^3) = 6.7$
(**23**) ^1H	1.732	1.071 (Me) 2.049 (CH) $J = 6.88$	6.371 (AA′) 6.213 (BB′) $J_{AB} = 6.09$	6.808 (H^3) 6.477 (H^4) 8.021 (H^5) 12.37 (NH^1)	$^3J(H^3H^4) = 2.51$ $^3J(H^4H^5) = 2.73$ $^4J(H^3H^5) = 0.66$
^{13}C	17.77	21.80 (Me) 30.75 (CH)	105.44 (CMe) 83.74 (C_A) 86.61 (C_B) 108.16 (CPr^i)	144.57 (C^3) 108.31 (C^4) 135.50 (C^5)	$^1J(C^3H^3) = 191.5$ $^2J(C^3H^4) = {}^3J(C^3H^5) = 7.0$ $^1J(C^4H^4) = 183.4$ $^2J(C^4H^3) = {}^2J(C^4H^5) = 8.2$ $^1J(C^5H^5) = 194.3$ $^2J(C^5H^4) = {}^3J(C^5H^3) = 6.7$

* Vertical lines correspond to two-dimensional (^1H–^{13}C) correlations (COSY experiments).

(3×10 cm^3). The solvent was removed *in vacuo* and the residue dissolved in acetone (3 cm^3). Slow addition of n-hexane gave a yellow solid (160 mg) which was filtered off, washed with n-hexane, and air-dried.

$[Ru(MeC_6H_4Pr^i\text{-}p)(acac)(Hpz)]Cl$ (**18**). To a solution of complex (**2**) (125.0 mg, 0.34 mmol) in acetone (30 cm^3) was added Hpz (46.0 mg, 0.68 mmol). The resulting solution was stirred for 4 h while the colour changed from orange to yellow. The solvent was partially concentrated under reduced pressure. Slow addition of diethyl ether gave a yellow solid (69 mg) which was filtered off, washed with diethyl ether, and air-dried. Proton n.m.r. spectrum (200 MHz, $CDCl_3$, standard $SiMe_4$, room temperature): δ 1.18 (6 H, d, $CHMe_2$, J 6.7), 1.92 (6 H, s, acac), 2.05 (3 H, s, Me), 2.70 (1 H, spt, $CHMe_2$), 5.07 (1 H, s, acac), 5.80, 5.86 (4 H, AB system, J 6.9 Hz), 6.17 [1 H, br s, H^4(pz)], 6.69 [1 H, br s, H^3(pz)], and 7.84 [1 H, br s, H^5 (pz)].

$[Ru(MeC_6H_4Pr^i\text{-}p)Cl(Hpz)_2]BF_4$ (**19**). *Method A*. To a suspension of $[\{Ru(MeC_6H_4Pr^i\text{-}p)Cl\}_2(\mu\text{-}Cl)_2]$ (**1**) (100.0 mg, 0.16 mmol) in methanol (20 cm^3) were added Hpz (56.0 mg, 0.82 mmol) and $NaBF_4$ (54.3 mg, 0.49 mmol). The resulting suspension was stirred for 30 min, while the colour changed from red to orange, and vacuum-evaporated until dryness. The residue was extracted with dichloromethane (3×10 cm^3). The solution was concentrated under reduced pressure and the addition of diethyl ether gave a yellow solid (113 mg) which was filtered off, washed with diethyl ether, and air-dried. The analogous complexes (**20**—(**22**) were obtained by the same method.

Method B. To a solution of complex (**2**) (125.0 mg, 0.34 mmol) in methanol (30 cm^3) an aqueous solution of HBF_4 (67.3 μl, 35% w/w, 0.34 mmol) and Hpz (46.2 mg, 0.68 mmol) were added. The resulting solution was stirred for 45 min and then partially concentrated under reduced pressure to *ca*. 3 cm^3. Slow addition of diethyl ether gave complex (**19**).

Method C. To a solution of $[Ru(MeC_6H_4Pr^i\text{-}p)Cl_2(Hpz)]$ (100.0 mg, 0.27 mmol) in acetone (20 cm^3) was added $AgBF_4$ (52.0 mg, 0.27 mmol). The resulting suspension was stirred for 15 min and then filtered to remove the AgCl formed. To the yellow filtrate was added Hpz (18.2 mg, 0.27 mmol). The solution obtained was stirred for 20 min and then concentrated under reduced pressure until dryness. Complex (**19**) was obtained by stirring in diethyl ether for 4 h.

$[Ru(MeC_6H_4Pr^i\text{-}p)(Hpz)_3][BF_4]_2$ (**23**). To a suspension of complex (**1**) (200.0 mg, 0.33 mmol) in acetone (40 cm^3) was added $AgBF_4$ (254.0 mg, 1.31 mmol). The suspension was stirred for 15 min and then filtered to remove the AgCl formed. To the orange filtrate was added Hpz (133.0 mg, 1.96 mmol) and the solution obtained was stirred for 20 min. The solvent was removed *in vacuo* and complex (**23**) obtained from the residue by crystallization from dichloromethane–diethyl ether as a yellow powder (338 mg).

$[Ru(MeC_6H_4Pr^i\text{-}p)(pz)(Hpz)_2]BF_4$ (**24**). To a solution of complex (**23**) (273.0 mg, 0.44 mmol) in acetone (40 cm^3) was added KOH (2.68 cm^3, 0.164 mol dm^{-3}, 0.44 mmol) in methanol. The resulting suspension was stirred for 30 min and vacuum-evaporated until dryness. The residue was extracted

Table 9. Crystal data and data collection parameters

Crystal data	
Formula	$C_{19}H_{25}BF_4N_6Ru$
Crystal habit	Rectangular prism
Crystal size (mm)	0.30 × 0.10 × 0.07
Symmetry, space group	Monoclinic, $P2_1/c$
Unit-cell determination	Least-squares fit from 90 reflections ($3 < \theta < 45°$)
Unit-cell dimensions	9.882 6(2), 13.966 3(3), 31.690 2(15) Å β = 94.650(3)°
Packing: U/Å^3, Z	4 359.6(2), 8
D_c/g cm^{-3}, M, F(000)	1.601, 525.3, 2 128
μ/cm^{-1}	64.25
Experimental data	
Technique	Philips diffractometer PW 1100 Bisecting geometry Graphite-oriented monochromator: Cu-K_α ω—2θ scans, scan width 1.4° Detector apertures 1.0 × 1.0°
Total measurements	Up to 65°
Speed	1 reflection min^{-1}
Number of reflections	
Measured	7 425
Independent	7 425
Observed	5 503 [$I > 3\sigma(I)$]
Standard reflections	2 every 90 min Variation: none
Max., min. transmission factors	1.116, 0.779[a]
R values before and after absorption correction	0.089, 0.078
Solution and refinement	
Solution	Patterson functions and DIRDIF[b] system
Refinement	Least squares on $F_{obs.}$ with four blocks
Parameters	
Number of variables	786
Degrees of freedom	4 717
Ratio of freedom	7.0
H atoms	Difference synthesis
Final shift/error ratio	0.47
Final ΔF peak	0.54 e Å^{-3} near Ru atom
Final R, R'	0.045, 0.036
Computer and programs	VAX 11/750 *X*-RAY System[c] DIRDIF[b]
Scattering factors	*d*

[a] N. Walker and D. Stuart, DIFABS, *Acta Crystallogr., Sect. A*, 1983, **39**, 158. [b] P. T. Beurskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, Th. E. M. Van den Hack, P. A. J. Prick, J. H. Noordick, G. Beurkens, V. Parthasarathi, H. J. Bruins Slot, and R. C. Haltiwanger, DIRDIF System, Crystallography Laboratory, Toernooivel, Nijmegen, 1983. [c] J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck, and H. Flack, The *X*-RAY System, Technical report TR-446, Computer Science Center, University of Maryland, 1976. [d] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

with dichloromethane (3 × 10 cm^3). The solution was concentrated under reduced pressure and the addition of n-hexane led to the precipitation of a yellow solid (190 mg) which was filtered off, washed with n-hexane, and air-dried.

[Ru(MeC$_6$H$_4$Pr^i-*p*)(pz)$_2$(Hpz)] (**25**). To a solution of complex (**24**) (120.0 mg, 0.23 mmol) in acetone (25 cm^3) was added KOH (1.40 cm^3, 0.163 mol dm^{-3}, 0.23 mmol) in methanol. The resulting suspension was stirred for 20 min and vacuum-evaporated until dryness. The residue was extracted with dichloromethane (3 × 10 cm^3) and the solution was concentrated under reduced pressure. Slow addition of n-hexane gave complex (**25**) as a yellow solid (66 mg) which was filtered off, washed with n-hexane, and air-dried.

Crystallography.—Crystallographic data and data collection parameters are given in Table 9. The stability and orientation of the sample was checked by measuring two standard reflections every 90 min. No significant variations were detected. In the final cycles of the refinement weighting schemes were applied so as to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle F_o\rangle$ and $(\sin\theta)/\lambda$ with $w = k/\sigma_1^2\sigma_2^2$ where $k = 1$, $\sigma_1 = f(F_o)$, and $\sigma_2 = g(\sin\theta/\lambda)$. The values of ΔF were first least-squares linearly adjusted to $|F_o|$ and the function taken as σ_1. Then, σ_1^2 was fitted to $(\sin\theta)/\lambda$ and the function taken as σ_2^2. Final positional parameters are given in Table 10. Selected geometrical features are listed in Table 2.

One of the BF$_4$ groups is disordered in two positions, with one fluorine atom in common. The population parameters were set as 0.7 and 0.3 for the disordered fluorine atoms. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Characterization.—Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer (range 4 000—200 cm^{-1}) using Nujol mulls between polyethylene sheets. Conductivities were measured in acetone with a Philips 9509/01 conductimeter at concentrations of 10^{-4}—10^{-3} mol dm^{-3}. The C, H, and N analyses were carried out with a Perkin-Elmer 240C micro-analyser. Routine n.m.r. measurements [^{1}H of compounds (**3**)—(**5**), (**7**), (**8**), (**10**), (**11**), (**13**), (**16**), (**18**), and (**21**) and ^{31}P-{^{1}H} of (**11**) and (**13**)] were recorded for CDCl$_3$ and CDCl$_3$–CHCl$_3$ (1:1) solutions at room temperature on a Varian XL 200 spectrometer [80.9 (^{31}P) and 200 MHz (^{1}H)] using SiMe$_4$ and 85% H$_3$PO$_4$ as external standards, respectively. The study of compounds (**6**), (**9**), (**14**), (**15**), (**17**), (**19**), (**20**), (**22**), (**24**), and (**25**) was carried out on a Bruker AM-200 operating at 200.15 and 50.32 MHz for ^{1}H and ^{13}C, respectively (Madrid).

Proton n.m.r. spectra were obtained using the following conditions: pulse angle, 27°; acquisition time, 6 s; sweep width, 2 800 Hz, and data size, 32 K. Homonuclear double-resonance experiments were carried out under the same conditions with a decoupler intensity of 20 Hz. For n.O.e. experiments a delay time of 2 s and an irradiating time of 1 s was applied. Homonuclear chemical shift correlations were established using the two-dimensional COSY. Typical conditions were: spectral width, 1 500 Hz and ±750 Hz; relaxation delay, 1.3 s; number of experiments, 128; and 512 × 512 points for the data table.

Decoupled ^{13}C n.m.r. spectra were obtained with WALTZ decoupling using the following conditions: pulse angle, 53°; acquisition time, 0.7 s; sweep width, 12 000 Hz; and data size, 32 K. Proton-coupled spectra were recorded using the heteronuclear gated decoupling sequence. Selective ^{13}C-{^{1}H} decoupled experiments were performed by irradiating the protons with single continuous-wave heteronuclear decoupling and using power gating for generation of n.O.e. Direct proton–carbon chemical shift correlations were established using the two-dimensional heteronuclear chemical shift correlations. Typical conditions were: ^1J(C–H) = 170 Hz; spectral width in ^{13}C dimension, 2 800 Hz, in ^{1}H dimension ± 350 Hz; number of experiments 256; and 512 × 1 024 points for the data table.

Computer-assisted analyses for four-, five-, and six-spin systems were performed with the iterative program PANIC 86 on a Bruker Aspect 2000 computer. The errors in the chemical shifts and coupling constants were estimated to be ±0.004 and

Table 10. Final atomic co-ordinates for complex (**24**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	0.210 06(4)	0.044 68(4)	0.401 61(1)
N(1)	0.142 9(5)	0.128 9(4)	0.349 2(2)
N(2)	0.011 6(5)	0.148 5(4)	0.336 0(2)
C(3)	0.003 8(7)	0.203 5(5)	0.301 0(2)
C(4)	0.131 9(8)	0.221 5(5)	0.291 0(2)
C(5)	0.216 0(7)	0.173 0(5)	0.321 1(2)
N(11)	0.205 7(5)	−0.067 1(3)	0.356 7(2)
N(12)	0.114 7(6)	−0.137 6(4)	0.355 2(2)
C(13)	0.142 1(8)	−0.202 6(5)	0.325 8(3)
C(14)	0.253 5(8)	−0.171 4(5)	0.307 1(2)
C(15)	0.291 8(7)	−0.086 2(5)	0.326 8(2)
N(21)	0.004 9(5)	0.020 1(4)	0.410 1(2)
N(22)	−0.052 0(6)	−0.068 5(4)	0.407 0(2)
C(23)	−0.176 7(7)	−0.059 6(6)	0.420 5(2)
C(24)	−0.201 0(6)	0.033 1(7)	0.432 5(2)
C(25)	−0.083 4(7)	0.081 1(5)	0.426 1(2)
C(30)	0.374 2(6)	0.147 0(5)	0.418 3(2)
C(31)	0.434 3(6)	0.057 3(5)	0.411 6(2)
C(32)	0.392 4(7)	−0.024 1(5)	0.433 9(2)
C(33)	0.290 7(7)	−0.015 6(5)	0.462 8(2)
C(34)	0.233 3(7)	0.076 1(5)	0.468 9(2)
C(35)	0.273 3(6)	0.159 1(5)	0.448 0(2)
C(36)	0.213 4(8)	0.255 9(6)	0.458 4(2)
C(37)	0.304 8(10)	0.301 4(7)	0.494 2(3)
C(38)	0.190 8(10)	0.321 6(6)	0.420 3(3)
C(39)	0.452 8(9)	−0.121 4(6)	0.426 1(3)
Ru(2)	0.270 04(4)	0.452 91(4)	0.655 46(1)
N(41)	0.426 6(5)	0.420 1(3)	0.616 4(2)
N(42)	0.440 6(5)	0.464 6(5)	0.579 2(2)
C(43)	0.557 7(8)	0.438 9(7)	0.563 0(3)
C(44)	0.621 8(8)	0.372 7(6)	0.590 0(3)
C(45)	0.537 1(8)	0.366 8(6)	0.623 2(3)
N(51)	0.138 8(5)	0.408 7(3)	0.603 6(2)
N(52)	0.092 9(5)	0.318 3(4)	0.597 3(2)
C(53)	0.005 2(7)	0.316 0(6)	0.563 0(2)
C(54)	−0.007 7(7)	0.405 5(6)	0.546 2(2)
C(55)	0.078 0(6)	0.462 5(5)	0.572 4(2)
N(61)	0.297 3(5)	0.311 3(3)	0.676 3(2)
N(62)	0.233 8(6)	0.234 5(4)	0.658 7(2)
C(63)	0.276 7(8)	0.155 0(5)	0.679 9(3)
C(64)	0.372 9(8)	0.180 0(5)	0.711 1(2)
C(65)	0.381 0(8)	0.278 5(5)	0.708 2(2)
C(70)	0.136 0(6)	0.575 0(4)	0.662 5(2)
C(71)	0.262 2(7)	0.610 3(4)	0.651 7(2)
C(72)	0.383 4(7)	0.584 1(5)	0.675 7(2)
C(73)	0.374 4(6)	0.523 9(4)	0.710 8(2)
C(74)	0.247 2(7)	0.489 5(4)	0.721 3(2)
C(75)	0.125 9(6)	0.514 3(4)	0.697 3(2)
C(76)	−0.006 3(6)	0.474 1(5)	0.710 8(2)
C(77)	−0.042 7(9)	0.524 6(6)	0.751 6(3)
C(78)	−0.123 1(8)	0.477 4(7)	0.676 2(3)
C(79)	0.519 4(8)	0.617 7(6)	0.662 8(3)
B(1)	−0.366 9(8)	0.123 9(6)	0.299 4(3)
F(1)	−0.262 8(5)	0.091 7(5)	0.326 4(2)
F(2)	−0.348 4(10)	0.213 8(5)	0.285 9(3)
F(3)	−0.357 0(9)	0.068 8(7)	0.261 7(3)
F(4)	−0.489 0(7)	0.109 5(9)	0.310 4(4)
F(21)	−0.430 7(22)	0.180 5(18)	0.330 5(12)
F(31)	−0.452 4(16)	0.056 8(13)	0.292 0(6)
F(41)	−0.325 9(17)	0.168 9(21)	0.267 8(6)
B(2)	0.279 8(8)	0.696 1(6)	0.535 3(3)
F(5)	0.375 0(6)	0.724 2(6)	0.565 0(2)
F(6)	0.155 1(5)	0.695 4(4)	0.552 2(2)
F(7)	0.304 4(5)	0.601 0(4)	0.524 4(2)
F(8)	0.273 9(7)	0.749 8(4)	0.499 8(2)

±0.008 Hz, respectively and the standard deviation between the observed and calculated line frequencies was 0.03 Hz.

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