Synthesis and Spectroscopic Studies of Ruthenium Complexes with Poly(pyrazol-1-yl)methane Ligands. Crystal Structure of [RuCl(cod)(tpzm)]Cl·EtOH [cod = cycloocta-1,5-diene, tpzm = tris(pyrazol-1-yl)methane]†

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Neutral six-co-ordinate complexes of Ru^{II}, $[RuCl_2(bpzm)(cod)]$ **1** and $[RuCl_2(btpzm)(cod)]$ **2** with bis(pyrazol-1-yl)methane (bpzm) or bis(5-trimethylsilylpyrazol-1-yl)methane (btpzm) were synthesised from $[\{RuCl_2(cod)\}_n]$ (cod = cycloocta-1,5-diene) and the corresponding ligand. Complex **1** reacts with $LiBEt_3H$ to give the hydride $[RuH(Cl)(bpzm)(cod)]$ **3**. The reactivity of **2** allowed the synthesis of the new complex $[RuCl_2(btpzm)_2]\cdot 0.5thf$ **4** (thf = tetrahydrofuran) with two bidentate btpzm ligands. The reaction of $[\{RuCl_2(cod)\}_n]$ with the tris(pyrazol-1-yl)methane ligand (tpzm) yielded the six-co-ordinate cationic complex $[RuCl(cod)(tpzm)]Cl\cdot EtOH$ **5**. Finally, the reaction of $[RuCl_3(tpzm)]$ with both pyridine and triethylamine afforded $[RuCl_2(py)(tpzm)]$ **6**. Spectroscopic data are provided for all these compounds. The crystal structure of compound **5** has been determined by X-ray diffraction methods: monoclinic, space group $P2_1/c$, with $a = 9.330(2)$, $b = 15.579(4)$, $c = 15.667(4)$ Å, $\beta = 97.79(2)^\circ$ and $Z = 4$. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to $R = 0.0414$ for 3362 observed reflections. It consists of complex cations, chloride anions and ethanol molecules of solvation linked by strong hydrogen bonds. The ruthenium is approximately octahedrally co-ordinated to one tridentate tpzm ligand, one chloride ion and two η^2-C=C olefinic groups of the cod ligand.

In the last years a fairly large number of metal poly(pyrazol-1-yl)borato complexes have been prepared[1] because of the importance of pyrazole ligands in co-ordination chemistry and the apparent similarity in co-ordination and electronic structure with the cyclopentadienyl ligand. However, the co-ordination behaviour of the isosteric poly(pyrazol-1-yl)methane ligands has received little attention. Rhodium and iridium,[2] palladium and platinum,[3] molybdenum and tungsten[4] poly(pyrazol-1-yl)methane complexes have been widely studied. However, to date, few examples have been reported for ruthenium.[5] A. Llobet *et al.*[6] described the complex $[RuCl_3(tpzm)]$ [tpzm = tris(pyrazol-1-yl)methane]. In order to explore the behaviour of ruthenium complexes towards this type of ligand we decided to try new routes for the synthesis of poly(pyrazol-1-yl)methane ruthenium complexes. This paper will focus on the preparation and structural details of bis- and tris-(pyrazol-1-yl)methane ruthenium(II) compounds.

Results and Discussion

Synthesis and Characterization of the Complexes.—The complex $[\{RuCl_2(cod)\}_n]$ (cod = cycloocta-1,5-diene) reacts with bis(pyrazol-1-yl)methane [bpzm, $H_2C(pz)_2$] and bis(5-trimethylsilylpyrazol-1-yl)methane(btpzm) (molar ratio 1:1), in refluxing ethanol and tetrahydrofuran (thf) respectively, to give the complexes $[RuCl_2(bpzm)(cod)]$ **1** and $[RuCl_2(btpzm)(cod)]$ **2**. The complexes were isolated from the reaction mixtures, upon appropriate work-up, as air-stable crystalline materials. They have appropriate microanalysis and IR spectra consistent with the presence of both the nitrogen-donor ligand and cod. However, NMR spectroscopy proved more efficient for their characterization. The ^1H NMR spectra are in accord with the presence of a bis(pyrazol-1-yl)methane ligand and a cycloocta-1,5-diene ligand; two chloride ligands complete the co-ordination sphere for the ruthenium(II) centre in an octahedral environment.

The ^1H NMR spectra of the *N,N'* ligands have already been published.[7] In the spectrum of complex **1**, three sets of peaks at δ 7.62, 7.47 and 6.37 appear corresponding to the aromatic protons of the two equivalent co-ordinated pyrazol-1-yl groups (Scheme 1). It has been pointed out[2b,c] that complexation shifts all the ligand signals to lower field in a similar way to that noted for quaternization.[8] We have observed a similar behaviour for our complexes. The signal at δ 6.37 must be assigned to the more shielded H^4; however, it is more difficult to assign the signals at δ 7.62 and 7.47 corresponding to H^5 and H^3. Several procedures for H^3 and H^5, which lead to different assignments, have been

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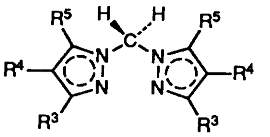
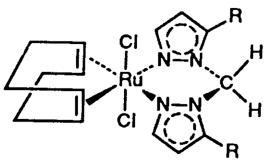
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 Molecular structure of the (pyrazol-1-yl)methane ligands. For bpzm $R^3 = R^4 = R^5 = H$; for btpzm $R^3 = R^4 = H, R^5 = SiMe_3$



Scheme 2 R = H or $SiMe_3$

described.[1,2b,c,9] We have applied the method of homonuclear NOE (nuclear Overhauser enhancement) difference spectroscopy[9b] for the assignment of the H^3 and H^5 resonances of complex **1**. The result agrees with those previously described for rhodium[2b,10] and ruthenium[9a] complexes. The ^1H NMR spectrum of complex **1** exhibits in addition resonances corresponding to three different kinds of protons, one olefinic at δ 4.66 and two aliphatic at δ 2.77 and 2.18 of the cycloocta-1,5-diene ligand. This situation is in accordance with a C_{2v} symmetry for the cod ligand.

The pyrazol-1-yl region in the ^1H NMR spectrum of complex **2** is much simpler due to the presence of a $SiMe_3$ group in the 5 position of the pyrazol-1-yl rings. The single protons at the 4 and 3 positions show signals at δ 6.50 and 7.47 respectively and the $SiMe_3$ resonance occurs at δ 0.43. In the region of the cycloocta-1,5-diene resonances, the ^1H NMR spectrum shows a similar pattern to that of **1**. We have also recorded the ^{13}C NMR spectra of **1** and **2**. In order to assign the resonances of C^3 and C^5 in the pyrazol-1-yl region, a two-dimensional heteronuclear chemical shift correlation experiment was carried out on complex **1**. The proton at δ 7.62 (H^5) is bonded to the carbon atom giving a peak at δ 134.2 and the proton at δ 7.47 (H^3) to the carbon atom having δ 143.5. With these results we can conclude that C^5 resonates at higher field than does C^3, in accordance with data reported for ruthenium and rhodium complexes.[2b,c,9a] In addition, the cod ligand shows in both spectra only two resonances, one corresponding to the four methylenic carbon atoms and the other to the four olefinic carbon atoms (see Experimental section).

With the assumption of octahedral geometry, the observed NMR data suggest that complexes **1** and **2** exhibit structures with the chloride ligands occupying two *trans* sites (Scheme 2).

We have explored the reactivity of complex **1** towards the formation of hydride species. It reacts with $LiBEt_3H$ (molar ratio 1 : 1) to give the hydride complex [RuH(Cl)(bpzm)(cod)] **3** which has been isolated as an air-stable white solid. Complex **3** shows in its IR spectrum a terminal hydride band at 2023 cm^{-1}.[11] The ^1H NMR spectrum of **3** displays at low field the three sets of signals for the aromatic protons of the pyrazol-1-yl groups and a singlet for the CH_2 group (see Experimental section). It is noteworthy that the cod ligand shows four signals for the aliphatic protons and two signals for the olefinic protons (see Experimental section), in accordance with a C_s symmetry. The ^{13}C NMR spectrum of **3** shows resonances for the carbon atoms of the pyrazolyl rings, the methylenic group and the cod ligand (see Experimental section).

To determine the stability of the bis(pyrazol-1-yl)methane ruthenium derivatives, we also initiated an investigation on the reactivity of complexes **1** and **2**. Several examples of bis(olefin)poly(pyrazol-1-yl)borato complexes of rhodium, where the olefin ligands are kinetically labile, have been described.[12] No reaction took place with ligands such as PPh_3, $P(OMe)_3$, pyridine or CO at room temperature. However in refluxing ethanol for several hours reaction does take place to give mixtures of products which have not so far yielded to characterization. Displacement of the cod ligand from complex **2** was observed if btpzm is the entering ligand. So, when a mixture of both complex **2** and btpzm was allowed to react in refluxing 1,2-dichloroethane, after appropriate work-up, the complex $[RuCl_2(btpzm)_2]\cdot0.5thf$ **4** was isolated as the main product. Under identical conditions, a similar experiment with complex **1** yielded no reaction and the starting materials were recovered. We do not have any conclusive explanation for this different surprising behaviour. Complex **4**, which has been isolated as an air-stable microcrystalline orange solid, has appropriate microanalysis in accordance with its formulation. Contrary to complex **2**, the ^1H NMR spectrum of **4** indicates that the two pyrazolyl groups of both ligands are not equivalent. The spectrum shows at low field four signals corresponding to the two non-equivalent H^3 and H^4 atoms respectively (see Experimental section). Also the two signals at δ 0.46 and 0.40 must be assigned to the two different $SiMe_3$ groups. The most interesting feature is that the resonances of the two protons of the central methylene group have been split into well resolved signals at δ 8.21 and 6.11 (J_{gem} = 12.8 Hz), because the protons are diastereotopic and appear as an AB system. Previously, several bis(pyrazol-1-yl)methane rhodium complexes which exhibit the CH_2 signal as a well resolved AB system have been described.[2b] In our complex it must be assumed that there is a conformationally rigid boat structure of the metallocycle $Ru(N\text{–}N)_2C$ unit.[13] In conclusion, the observed ^1H NMR data suggest for **4** a six-co-ordinate octahedral structure with two bis(5-trimethylsilylpyrazol-1-yl) groups occupying four sites and two chloride ligands in a *cis* situation.

Finally, we have undertaken studies on the reactivity of Ru^{II} with the tris(pyrazol-1-yl)methane ligand, tpzm. The starting complex, $[\{RuCl_2(cod)\}_n]$, reacts with tpzm (molar ratio 1 : 1) in refluxing ethanol giving an orange solution from which, upon appropriate work-up, an air-stable orange microcrystalline solid [RuCl(cod)(tpzm)]Cl·EtOH **5** was isolated. Also, when a mixture of $[RuCl_3(tpzm)]$, pyridine (py) and triethylamine was allowed to react in refluxing ethanol, upon appropriate work-up, the complex $[RuCl_2(py)(tpzm)]$ **6** was isolated as an air-stable yellowish solid. Both complexes have appropriate microanalysis and IR spectra consistent with the presence of the tris(pyrazol-1-yl)methane ligand. Once more NMR spectroscopy has been efficient for the characterization of **5** and **6**. The NMR spectra of tpzm have previously been described.[14] In our complexes the ^1H NMR spectra indicate that two pyrazol-1-yl rings are not equivalent to the third. Again irradiation of the singlet signal at δ 11.12 of the CH group in complex **5** and calculation of the NOE effect on the rest of the signals allowed us to assign the lowest-field signals to the H^5 protons. A similar situation has been assumed for complex **6** (see Experimental section). The ^1H NMR spectra of **5** and **6** also show the resonances of the pyridine ligand and the aliphatic (four signals) and olefinic (two signals) protons from the cod ligand, in accordance with its expected C_s symmetry (see Experimental section). The ^{13}C NMR spectrum of **5** also indicates that two pyrazolyl rings are equivalent. It shows two resonances for the C^3, C^4 and C^5 carbon atoms. The cod ligand exhibits two resonances for the olefinic and methylenic atoms respectively (see Experimental section).

In the cation of complex **5** there are also one cod and one chloride and in **6** two chlorides and one pyridine. In order to confirm the proposed structure we have carried out a crystal structure analysis of complex **5**.

Structure of [RuCl(cod)(tpzm)]Cl·EtOH **5**.—The structure consists of complex cations, chloride anions and ethanol molecules of solvation. A perspective view of the cation is shown in Fig. 1, and the bond lengths and angles are listed in Table 1. The geometry at ruthenium is approximately octahedral, the ligating atoms being the three nitrogen atoms of the pyrazole moieties, a chlorine atom and the carbon atoms of the two

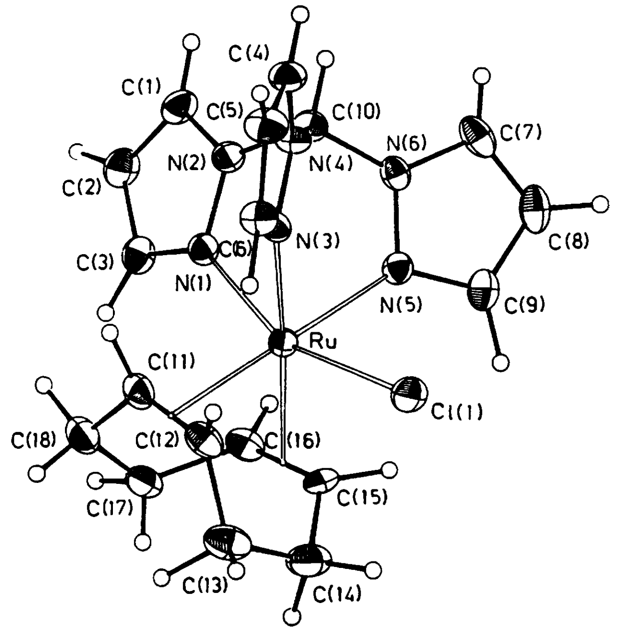


Fig. 1 Perspective view of the cationic $[RuCl(cod)(tpzm)]^+$ of complex **5**. The thermal ellipsoids are drawn at the 30% probability level

Table 1 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **5**

Ru–Cl(1)	2.424(2)	Ru–C(12)	2.216(6)
Ru–N(1)	2.147(5)	Ru–C(15)	2.235(6)
Ru–N(3)	2.130(5)	Ru–C(16)	2.256(6)
Ru–N(5)	2.125(4)	Ru–CE(1)	2.117(6)
Ru–C(11)	2.231(6)	Ru–CE(2)	2.139(6)
CE(1)–Ru–CE(2)	84.2(2)	N(1)–Ru–N(5)	79.9(2)
N(5)–Ru–CE(2)	97.1(2)	N(1)–Ru–N(3)	83.9(2)
N(5)–Ru–CE(1)	178.0(2)	Cl(1)–Ru–CE(2)	97.7(2)
N(3)–Ru–CE(2)	176.4(2)	Cl(1)–Ru–CE(1)	95.7(2)
N(3)–Ru–CE(1)	92.2(2)	Cl(1)–Ru–N(5)	82.6(1)
N(3)–Ru–N(5)	86.6(2)	Cl(1)–Ru–N(3)	82.6(1)
N(1)–Ru–CE(2)	96.8(2)	Cl(1)–Ru–N(1)	158.5(1)
N(1)–Ru–CE(1)	101.5(2)		

CE(1) and CE(2) are the midpoints of the C(11)–C(12) and C(15)–C(16) bonds respectively.

olefinic groups of the cod ligand. The Ru–N bond lengths are similar [2.147(5), 2.130(5) and 2.125(4) Å] but significantly longer than those found in $[Ru(H_2O)_3(tpzm)][p\text{-}MeC_6H_4SO_3]_2\cdot1.5H_2O$ [2.006(2), 2.008(2) and 2.028(2) Å].[5a] In the diruthenium complex $[(tpzm)Ru(\mu\text{-}O)\{\mu\text{-}O_2PO(OH)\}_2Ru(tpzm)]$[5b] the nitrogen atoms are bound in an asymmetric fashion [2.039(14), 2.058(15) and 2.139(25) Å] and this is due to the different natures of the oxygen atoms *trans* to them; nevertheless despite the different oxidation number of the ruthenium atom, one Ru–N bond length is comparable with those found in complex **5**. In this last compound the lengthening of the Ru–N bonds is in agreement with the comparable *trans* effect of the chloride and olefinic groups. The *trans* angle Cl(1)–Ru–N(1) 158.5(1)° deviates significantly from linearity due to the steric hindrance of the bulky cod ligand which moreover influences the dihedral angles between the pyrazole ring N(1)N(2)C(1)C(2)C(3) (A) and the other two. The dihedral angles between the rings A and N(3)N(4)C(4)C(5)C(6) (B) [126.8(2)°] and the rings A and N(5)N(6)C(7)C(8)C(9) (C) [112.7(3)°] deviate by *ca.* 7° from the theoretical value of 120° while the BC angle is 120.5(2)°. The $HC(pz)_3$ ligand consists of three nearly perfectly planar pyrazole groups bound to the central carbon atom C(10) which lies out of the mean plane of the three pyrazole rings A, B and C by 0.210(6), 0.045(6) and 0.005(6) Å respectively. Here again the maximum deviation is observed for ring A.

The chloride ion is involved in two strong hydrogen bonds, one with the CH group of the tpzm ligand, according to its acidic nature, the other with the hydroxyl group of the ethanol molecule of solvation [$C(10)\cdots Cl(2^I)$ 3.302(6), $H\cdots Cl(2^I)$ 2.38(7) Å, $C(10)\text{–}H\cdots Cl(2^I)$ 155(5)°, $O(1)\cdots Cl(2^{II})$ 3.055(7), $H\cdots Cl(2^{II})$ 1.99(7) Å, $O(1)\text{–}H\cdots Cl(2^{II})$ 177(5)°: Symmetry relations I $= x, \frac{3}{2} - y, \frac{1}{2} + z$; II $-x, 1 - y, -z$].

Experimental

All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. The poly(pyrazol-1-yl)methane ligands and the complexes $[RuCl_2(cod)]$ and $[RuCl_3(tpzm)]$ were prepared as reported previously.[6,15] Microanalyses were performed with a Perkin Elmer 2400 CHN analyser. Infrared spectra were obtained in the region 4000–200 cm^{-1} using a Perkin Elmer 883 spectrophotometer, ^1H and ^{13}C NMR spectra on a Unity Varian FT300 spectrometer and referenced to the residual deuteriated solvent. NOE Difference spectra were recorded at 40 °C on a Bruker AM-500 spectrometer (operating frequency 500.13 MHz) equipped with an Aspect 3000 computer. Acquisition parameters: 32 K data points; spectral width 5000 Hz; acquisition time 3.27 s; digital resolution 0.305 Hz per point; pulse width 5.50 μs (90°); relaxation delay 4 s; irradiation power 50–55 L; number of scans 88. The two-dimensional NMR spectrum was acquired on a Unity Varian 3000 spectrometer using standard Varian FT software, and processed using an IPC-Sun computer.

Preparations.—$[RuCl_2(bpzm)(cod)]$ **1**. The ligand bpzm (0.264 g, 1.78 mmol) was added to an ethanol suspension (40 cm^3) of $[RuCl_2(cod)]$ (0.500 g, 1.78 mmol) and the mixture was refluxed for 3 h. An orange solution was obtained which was filtered and evaporated to dryness. Complex **1** was obtained as a yellow microcrystalline solid by crystallization from dichloromethane–diethyl ether (1:1). Yield 0.610 g (80%) (Found: C, 42.15; H, 4.75; N, 13.30. $C_{15}H_{20}Cl_2N_4Ru$ requires C, 42.05; H, 4.60; N, 13.05%). NMR (reference $SiMe_4$): ^1H ([^2H]chloroform) δ 7.62 [d, 2 H, $^3J(H^4H^5) = 2.5$, H^5], 7.47 [d, 2 H, $^3J(H^3H^4) = 2.2$ Hz, H^3], 6.99 (s, 2 H, CH_2), 6.37 (qnt, 2 H, H^4), 4.66 (m, 4 H, olefin H of cod), 2.77–2.75 (m, 4 H, H^{exo} of cod) and 2.21–2.13 (m, 4 H, H^{endo} of cod); ^{13}C [$(CD_3)_2SO$], δ 143.47 ($^1J = 188.8$, C^3), 134.18 ($^1J = 192.7$, C^5), 106.96 ($^1J = 180.7$, C^4), 88.77 ($^1J = 159.0$, sp^2 C of cod), 61.88 ($^1J = 156.9$, CH_2) and 29.44 ($^1J = 126.8$, sp^3 C of cod).

$[RuCl_2(btpzm)(cod)]$ **2**. The ligand btpzm (0.420 g, 1.42 mmol) was added to a thf suspension (80 cm^3) of $[RuCl_2(cod)]$ (0.400 g, 1.42 mmol) and the mixture was refluxed for 24 h. The resulting orange-green solution was filtered and evaporated to dryness. The residue was washed with hexane and complex **2** was obtained as a green-yellow solid. Yield 0.270 g (33%) (Found: C, 43.95; H, 6.30; N, 9.80. $C_{21}H_{36}Cl_2N_4RuSi_2$ requires C, 44.00; H, 6.30; N, 9.70%). NMR ($CDCl_3$, reference $SiMe_4$): ^1H, δ 7.47 [d, 2 H, $^3J(H^3H^4) = 1.76$ Hz, H^3], 6.98 (s, 2 H, CH_2), 6.5 (d, 2 H, H^4), 4.64 (br s, 4 H, olefinic H of cod), 2.78–2.75 (br s, 4 H, H^{exo} of cod), 2.16–2.13 (m, 4 H, H^{endo} of cod) and 0.43 (s, 18 H, $SiMe_3$); ^{13}C, δ 155.96 (C^5), 142.46 ($^1J = 187.2$, C^3), 116.94 ($^1J = 178.5$, C^4), 91.51 ($^1J = 158.03$, sp^2 C of cod), 64.84 ($^1J = 154.2$, CH_2), 29.41 ($^1J = 128.1$, sp^3 C of cod) and 0.03 ($^1J = 119.6$ Hz, $SiMe_3$).

$[RuH(Cl)(bpzm)(cod)]$ **3**. A solution of $LiBEt_3H$, 1.0 mol dm^{-3} in thf (0.7 cm^3, 0.7 mmol), was added to a thf solution (30 cm^3) of complex **1** (0.300 g, 0.7 mmol) at −78 °C. The solution was stirred and allowed to warm to room temperature for 1 h. The white precipitate of complex **3** was filtered off and washed with diethyl ether. Yield 0.260 g (96%) (Found: C, 46.20; H, 5.60;

Table 2 Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms of complex **5**, with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	5322.2(4)	5529.7(3)	2671.9(2)
Cl(1)	6319(2)	6751(1)	1996(1)
Cl(2)	83(2)	8377(1)	−308(1)
O	−220(7)	3217(4)	1431(5)
N(1)	3823(5)	4799(3)	3304(3)
N(2)	2760(5)	5250(3)	3619(3)
N(3)	5151(4)	6436(3)	3671(3)
N(4)	3831(4)	6615(3)	3879(3)
N(5)	3335(5)	6038(3)	2054(3)
N(6)	2357(4)	6322(3)	2553(3)
C(1)	1809(6)	4718(4)	3945(4)
C(2)	2271(7)	3904(4)	3847(4)
C(3)	3507(7)	3981(4)	3441(4)
C(4)	3916(6)	7211(4)	4506(4)
C(5)	5333(7)	7410(4)	4688(4)
C(6)	6074(6)	6921(4)	4164(4)
C(7)	1250(6)	6744(4)	2082(4)
C(8)	1509(7)	6726(4)	1256(4)
C(9)	2819(7)	6297(4)	1268(4)
C(10)	2589(6)	6159(4)	3465(4)
C(11)	6985(6)	4793(4)	3533(4)
C(12)	7677(6)	5341(4)	3048(4)
C(13)	8429(7)	5037(4)	2301(5)
C(14)	7487(8)	5016(4)	1421(5)
C(15)	5892(6)	4911(4)	1476(4)
C(16)	5352(6)	4278(3)	1950(4)
C(17)	6313(6)	3602(4)	2445(4)
C(18)	6894(7)	3840(4)	3374(4)
C(19)	1121(9)	3646(6)	1467(6)
C(20)	1388(10)	4006(7)	633(7)

N, 13.75. $C_{15}H_{21}ClN_4Ru$ requires C, 45.70; H, 5.35; N, 14.20%). IR (KBr): 2023 cm^{-1} [ν(Ru–H)]. NMR (reference $SiMe_4$): ^1H ([$^2H_6$]acetone), δ 8.04 [d, 2 H, $^3J(H^4H^5) = 2.7$, H^5], 7.43 [d, 2 H, $^3J(H^3H^4) = 2.1$ Hz, H^3], 6.46 (br s, 2 H, CH_2), 6.37 (qnt, 2 H, H^4), 3.7 (br s, 2 H, olefinic H of cod), 3.4 (br s, 2 H, olefinic H of cod), 1.91 (br s, 2 H, H^{exo} of cod), 1.83 (br s, 2 H, H^{exo} of cod), 1.72 (br s, 2 H, H^{endo} of cod), 1.69 (br s, 2 H, H^{endo} of cod) and −5.31 (1 H, hydride); ^{13}C [$(CD_3)_2SO$], δ 149.1 ($^1J = 178.3$, C^3), 139.9 ($^1J = 195.0$, C^5), 115.36 ($^1J = 178.5$, C^4), 92.3 ($^1J = 156.0$, sp^2 C of cod), 92.2 ($^1J = 156.0$, sp^2 C of cod), 73.26 ($^1J = 153.7$, CH_2), 41.29 ($^1J = 130$, sp^3 C of cod) and 36.99 ($^1J = 130.4$ Hz, sp^3 C of cod).

[$RuCl_2(btpzm)_2$]·0.5thf **4**. The ligand btpzm (0.330 g, 1.14 mmol) was added to an 1,2-dichloroethane (20 cm^3) suspension of [$RuCl_2(cod)$] (0.160 g, 0.57 mmol). The mixture was refluxed in a sealed tube at 110 °C for 22 h. The orange solution was filtered and evaporated to dryness. Complex **4** was obtained as an orange solid by crystallization from thf–hexane (1 : 1). Yield 0.180 g (42%) (Found: C, 42.95; H, 6.40; N, 14.60. $C_{28}H_{52}Cl_2N_8O_{0.5}RuSi_4$ requires C, 42.35; H, 6.55; N, 14.10%). ^1H NMR ([^2H]chloroform, reference $SiMe_4$): δ 8.49 (s, 2 H, H^3), 7.16 (AB system: 8.21, A; 6.11, B; $J_{AB} = 12.8$ Hz), 6.61 (s, 2 H, $H^{3'}$), 6.18 (s, 2 H, H^4), 5.92 (s, 2 H, $H^{4'}$), 3.73 (m, 2 H, thf), 1.84 (m, 2 H, thf), 0.46 (s, 18 H, $SiMe_3$) and 0.40 (s, 18 H, $SiMe_3$).

[RuCl(cod)(tpzm)]Cl·EtOH **5**. The ligand tpzm (0.310 g, 1.43 mmol) was added to an ethanol (60 cm^3) suspension of [$RuCl_2(cod)$] (0.400 g, 1.43 mmol). The mixture was refluxed for 7 h and the resulting solution filtered and evaporated to dryness. Complex **5** was obtained as an orange solid by crystallization from ethanol–hexane (1 : 1). Yield 0.620 g (81%) (Found: C, 44.40; H, 5.30; N, 15.75. $C_{20}H_{28}Cl_2N_6ORu$ requires C, 44.35; H, 5.20; N, 15.55%). NMR (reference $SiMe_4$): ^1H [$(CD_3)_2SO$], δ 11.12 (s, 1 H, CH), 8.88 [d, 1 H, $^3J(H^4H^5) = 2.6$, H^5], 8.67 [d, 2 H, $^3J(H^4H^5) = 2.5$, $H^{5',5''}$), 8.55 [d, ^{1} H, $^3J(H^3H^4) = 2.1$, H^3], 8.03 [d, 2 H, $^3J(H^3H^4) = 2.1$ Hz, $H^{3',3''}$], 6.79 (qnt, 1 H, H^4), 6.64 (qnt, 2 H, $H^{4',4''}$), 5.01 (br s, 2 H, olefinic H of cod), 4.06 (br s, 2 H, olefinic H of cod), 2.73–2.69 (m, 4 H, H^{exo} of cod) and 2.37–2.27 (m, 4 H, H^{endo} of cod); ^{13}C ([^2H]chloroform), δ 147.65 ($^1J = 191$, C^3), 144.55 ($^1J = 192$, $C^{3',3''}$), 137.20 ($^1J = 206$, C^5), 133.78 ($^1J = 200$, $C^{5',5''}$), 108.9 ($^1J = 171$, C^4), 108.36 ($^1J = 178$, $C^{4',4''}$), 95.86 ($^1J = 155$, sp^2 C of cod), 73.40 ($^1J = 161.9$ Hz, CH_2), 29.52 (no resolved signal, sp^3 C of cod) and 29.26 (no resolved signal, sp^3 C of cod).

[$RuCl_2(py)(tpzm)$] **6**. Triethylamine (1 cm^3) and pyridine (75 μl, 0.48 mmol) were added to an ethanol (40 cm^3) solution of [$RuCl_3(tpzm)$]·EtOH (0.200 g, 0.42 mmol). After stirring at room temperature for 12 h the green solution was filtered and evaporated to dryness. Complex **6** was obtained as a yellowish solid by dissolution in dichloromethane and precipitation with diethyl ether. Yield 0.137 g (70%) (Found: C, 38.05; H, 3.55; N, 20.40. $C_{15}H_{15}Cl_2N_7Ru$ requires C, 38.70; H, 3.20; N, 21.05%). ^1H NMR [$(CD_3)_2SO$, reference $SiMe_4$]: δ 9.85 (s, 1 H, CH), 8.63–8.59 (mc, 5 H, $H^{5,5',5''}$ and H^2 of py), 8.15 (s, 1 H, H^3), 7.88 (t, 1 H, H^4 of py), 7.43–7.37 (m, 4 H, $H^{3',3''}$ and H^3 of py), 6.73 (qnt, 1 H, H^4) and 6.65 (qnt, 2 H, $H^{4',4''}$).

X-Ray Structural Determination.—Crystal data. $C_{18}H_{22}Cl_2N_6Ru{\cdot}C_2H_5OH$ **5**, $M = 540.46$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.330(2)$, $b = 15.579(4)$, $c = 15.667(4)$ Å, $\beta = 97.79(2)°$, $U = 2256(1)$ Å^3 [by least-squares refinement on diffractometer angles for 30 automatically centred reflections ($20 \leqslant \theta \leqslant 39°$), $\bar{\lambda} = 1.541\,838$ Å], $T = 295$ K, $Z = 4$, $D_c = 1.591$ g cm^{-3}, $F(000) = 1104$. Crystal dimensions 0.13 × 0.18 × 0.21 mm, μ(Cu-Kα) = 81.90 cm^{-1}.

Data collection and processing. Siemens AED diffractometer, θ–2θ scan mode, scan width 1.20 + 0.142 tanθ, scan speed 3–12° min^{-1}, nickel-filtered Cu-Kα radiation; 4432 reflections measured ($3 \leqslant \theta \leqslant 70°$, ±*hkl*), 4278 unique giving 3362 with $I \geqslant 2\sigma(I)$ [merging $R = 0.0253$ after absorption correction (maximum, minimum transmission factors 1.1901, 0.8381)[16]]. No decay during data collection.

Structure analysis and refinement. Direct methods (Ru and Cl atoms) followed by normal heavy-atom procedures. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, hydrogen atoms clearly located in difference map and refined isotropically. Unit weights were used in the last cycles of the refinement as a weighting scheme $w = k[\sigma(F_o) + gF_o^2]^{-1}$, with *k* and *g* values to be refined, did not give better results. Number of refined parameters: 383. The final Δ*F* synthesis showed no Δρ above 1.15 (near the Ru atom) or below −1.47 e Å^{-3}. Final *R* and *R′* values are 0.0414 and 0.0451. Final atomic coordinates for the non-hydrogen atoms are given in Table 2.

The calculations were carried out on the Gould POWERNODE 6040 and ENCORE 91 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma and the programs and sources of scattering factors are given in ref. 17.

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

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