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THE REACTIONS OF $[Ru(\eta^6\text{-arene})Cl_2]_2$ COMPOUNDS WITH A SERIES OF AMINOPYRIDINE LIGANDS: X-RAY CRYSTAL STRUCTURES OF $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ AND $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$

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Abstract—The reactions of the dimers $[Ru(\eta^6\text{-arene})Cl_2]_2$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$, [2.2](1,4)$C_{16}H_{16}$) with a range of aminopyridine ligands have been investigated. These ligands can potentially coordinate to a single metal centre in a monodentate fashion through either pyridyl or amino nitrogen atoms, can chelate a single metal centre, or can bridge across two metal ions. Spectroscopic data collected on 12 compounds is exclusively consistent with monodentate coordination via the pyridyl nitrogen atoms. This mode of coordination has been conclusively established by X-ray structure determinations of the compounds $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ and $Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$.

Recently we reported the results of our investigations into the reactions of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ and $[Ru(\eta^6\text{-}C_6H_6)Cl(O_2CCF_3)]$ with α-pyridone and related ligands.[1] Coordination of this series of ligands was almost exclusively of the bidentate type to a single metal centre. In only one instance was monodentate coordination, via the pyridone oxygen atom, observed. Other workers[2] have observed bidentate coordination of the hydroxypyridinate anion in the compound $[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl(NC_5H_4O)]$. In an extension to that earlier work we have examined the reactions of 2-aminopyridine and several variously substituted derivatives with several $[Ru(\eta^6\text{-arene})Cl_2]_2$ compounds, including the paracyclophane compound $[Ru(\eta^6\text{-}[2_2](1,4)C_{16}H_{16})Cl_2]_2$, whose chemistry we are currently studying intensively.[3–5]

EXPERIMENTAL

Microanalyses were carried out by the Chemistry Department of University College London. NMR spectra were obtained on Varian XL-200 and VXR-400 spectrometers (chemical shifts quoted in ppm with positive values to high frequency of $SiMe_4$). IR spectra were recorded in the range 4000–200 cm^{-1} on a Perkin–Elmer 983 spectrophotometer using Nujol mulls on CsI plates.

Materials

The compounds $[Ru(\eta^6\text{-arene})Cl_2]_2$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$, [2.2](1,4)$C_{16}H_{16}$) were prepared by published literature methods.[6–8] All other reagents were obtained from normal commercial suppliers. All reactions were carried out in degassed solvents under a nitrogen atmosphere.

$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_4NH_2)]$

A solution of 2-aminopyridine (0.11 g, 2.2 mmol) in toluene (5 cm^3) was added to a suspension of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (0.1 g, 0.2 mmol) in toluene (15 cm^3) and the mixture stirred for 12 h at room temperature. The red–orange product was filtered off, washed with diethyl ether and methanol, and then dried *in vacuo* for 4 h. Yield 36%. IR spectrum ν(N—H) 3287, 3179 cm^{-1}, ν(Ru—Cl) 278 cm^{-1}.

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Each of the following compounds were prepared in an analogous manner.

$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_3CH_3NH_2)]$

Yield 50%. IR spectrum ν(N—H) 3295, 3183 cm^{-1}, ν(Ru—Cl) 291 cm^{-1}.

$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_4NHC_6H_5)]$

Yield 26%. IR spectrum ν(N—H) 3234 cm^{-1}, ν(Ru—Cl) 282 cm^{-1}.

$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_4NHCH_2C_6H_5)]$

Yield 66%. IR spectrum ν(N—H) 3298 cm^{-1}, ν(Ru—Cl) 278 cm^{-1}.

$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$

Yield 46%. IR spectrum ν(N—H) 3278, 3174 cm^{-1}, ν(Ru—Cl) 282 cm^{-1}.

$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_3CH_3NH_2)]$

Yield 47%. IR spectrum ν(N—H) 3302, 3235 cm^{-1}, ν(Ru—Cl) 287 cm^{-1}.

$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NHC_6H_5)]$

Yield 69%. IR spectrum ν(N—H) 3229 cm^{-1}, ν(Ru—Cl) 281 cm^{-1}.

$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NHCH_2C_6H_5)]$

Yield 76%. IR spectrum ν(N—H) 3243 cm^{-1}, ν(Ru—Cl) 283 cm^{-1}.

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$

Yield 70%. IR spectrum ν(N—H) 3281, 3160 cm^{-1}, ν(Ru—Cl) 297 cm^{-1}.

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_3CH_3NH_2)]$

Yield 94%. IR spectrum ν(N—H) 3306, 3192 cm^{-1}, ν(Ru—Cl) 300 cm^{-1}.

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NHC_6H_5)]$

Yield 65%. IR spectrum ν(N—H) 3195 cm^{-1}, ν(Ru—Cl) 297 cm^{-1}.

$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NHCH_2C_6H_5)]$

Yield 44%. IR spectrum ν(N—H) 3290 cm^{-1}, ν(Ru—Cl) 288 cm^{-1}.

Tables 1 and 2 contain microanalytical and ^1H NMR data for the 12 new compounds.

X-ray studies

The structures of $[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ and $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$ were determined using general procedures which have been described previously.[9,10] The structures were solved routinely by direct methods and refined, with all non-hydrogen atoms anisotropic, by full-matrix least-squares. Hydrogen atoms were not included in the refinement. In the latter cycles of the refinement of the structure of $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$, a methanol of crystallization was located on the four-fold axis at $\frac{1}{4}, \frac{1}{4}, y$ and subsequently included in the refinement. Pertinent crystallographic data are

Table 1. Microanalytical data for some ruthenium(II) compounds

Compound	Analyses [Found(calc.)(%)] C	H	N	Cl
$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_4NH_2)]$	37.4(38.4)	3.4(3.5)	7.9(8.1)	20.9(20.6)
$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_3CH_3NH_2)]$	40.1(40.2)	3.6(3.9)	7.4(7.8)	19.6(19.8)
$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_4NHC_6H_5)]$	47.8(48.3)	3.4(3.8)	6.7(7.0)	17.3(16.8)
$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_4NHCH_2C_6H_5)]$	49.6(49.8)	3.9(4.1)	5.9(6.4)	16.7(16.3)
$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$	44.7(45.0)	4.7(5.0)	7.4(7.0)	17.1(17.6)
$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_3CH_3NH_2)]$	46.3(46.2)	5.1(5.3)	6.9(6.9)	16.8(17.1)
$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NHC_6H_5)]$	53.3(53.8)	5.2(5.6)	5.6(5.7)	15.2(14.9)
$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NHCH_2C_6H_5)]$	53.0(53.7)	5.2(5.6)	5.5(5.7)	14.7(14.4)
$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$	52.3(53.1)	4.5(4.7)	5.4(5.9)	
$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_3CH_3NH_2)]$	53.6(54.1)	4.9(4.9)	5.7(5.7)	
$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NHC_6H_5)]$	58.1(58.9)	4.6(4.7)	4.6(5.1)	
$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NHCH_2C_6H_5)]$	58.8(59.6)	4.9(5.0)	4.4(5.0)	

Table 2. ^1H NMR data for some ruthenium(II) compounds at 298 K in $CDCl_3$

Compound	δ (ppm) η-Arene	Aminopyridine
$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_4NH_2)]$	5.68(s)	8.55(d), 7.34(t), 6.65(t), 6.50(d), 6.06(s, NH_2)
$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_3CH_3NH_2)]$	5.67(s)	8.68(d), 7.23(d), 6.78(t), 6.08(s, NH_2), 2.15(s)
$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_4NHC_6H_5)]$	5.75(s)	8.84(d), 7.22(m, br), 6.75(t), 9.78(s, NH)
$[Ru(\eta^6\text{-}C_6H_6)Cl_2(NC_5H_4NHCH_2C_6H_5)]$	5.65(s)	8.74(d), 8.11(t, NH), 7.43(t), 7.36(m), 6.59(t), 6.43(d), 4.41(d)
$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$	5.48, 5.33(AB), 2.94(sp), 1.26(d), 1.61(s)	8.57(d), 7.36(t), 6.58(t), 6.50(d), 6.06(s, NH_2)
$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_3CH_3NH_2)]$	5.43, 5.30(AB), 2.96(sp), 1.62(s), 1.26(d)	8.86(d), 7.23(t), 6.78(d), 6.08(s, NH_2), 2.19(s)
$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NHC_6H_5)]$	5.42, 5.30(AB), 2.96(sp), 1.63(s), 1.28(d)	9.78(s, NH), 8.81(d), 7.21(m), 6.73(t)
$[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NHCH_2C_6H_5)]$	5.40, 5.28(AB), 2.96(sp), 1.61(s), 1.26(d)	8.73(d), 8.10(t, NH), 7.35(m), 6.57(t), 6.41(d), 1.50(d)
$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$	6.85(s), 4.97(s), 3.19, 2.74(AA'XX')	8.32(d), 7.45(t), 6.61(d), 6.51(t), 6.13(s, NH_2)
$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_3CH_3NH_2)]$	6.85(s), 4.96(s), 3.19, 2.72(AA'XX')	8.23(d), 7.33(t), 6.46(d), 6.12(s, NH_2)
$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NHC_6H_5)]$	6.83(s), 5.44(s), 3.16, 2.70(AA'XX')	8.54(d), 7.58(t), 7.35(m), 7.05(d), 6.70(t), 9.51(s, NH)
$[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NHCH_2C_6H_5)]$	6.70(s), 4.84(s), 3.07, 2.64(AA'XX')	8.52(d), 7.30(m), 6.45(t), 6.29(d), 7.76(t, NH)

included in Table 3. Tables 4 and 5 contain selected bond lengths and bond angles for $[Ru(\eta^6\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ and $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$, respectively. Crystallographic calculations used the SHELXTL PLUS program package.[11]

Final atomic coordinates, full listings of bond lengths and angles, thermal parameters and structure factor tables have been deposited with the Editor, and with the Cambridge Crystallographic Data Centre, as supplementary material.

RESULTS AND DISCUSSION

Orange or red, microcrystalline compounds of general formula $[Ru(\eta^6\text{-arene})Cl_2(Hap)]$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$, $C_{16}H_{16}$; Hap = 2-aminopyridine, 2-amino-3-picoline, 2-benzylaminopyridine, 2-anilinopyridine) have been prepared by the reaction of the dinuclear compounds $[Ru(\eta^6\text{-arene})Cl_2]_2$ with an excess of the appropriate ligand in toluene. Non-polar solvents have frequently been employed in the past to give a wide range of $[Ru(\eta^6\text{-arene})Cl_2L]$ (L = pyridine, tertiary phosphines, etc.) compounds.[12,13] However, when polar solvents have been employed, cationic products, $[Ru(\eta^6\text{-arene})ClL_2]^+$, have usually been formed. Alternatively, if the incoming ligand can be deprotonated, e.g. a carboxylic acid, then a neutral compound such as $[Ru(\eta^6\text{-}C_6H_6)Cl(O_2CCF_3)]$[14] is often formed. Surprisingly the products which were isolated when we reacted $[Ru(\eta^6\text{-arene})Cl_2]_2$ compounds with this series of Hap ligands in methanol were almost invariably identical to those obtained from the non-polar solvent, although admittedly the isolated yield was often smaller. This was particularly surprising given that previously we have been able to prepare a range of neutral compounds of the type $[Ru(\eta^6\text{-arene})Cl(hp)]$[1,15] (Hhp = 2-hydroxypyridine, 6-methyl-2-hydroxypidine, 6-chloro-2-hydroxypyridine) by using precisely these reaction conditions. The differences in reactivity can most likely be explained by invoking the appreciably lower acidity of the amino protons in these ligands, when compared with the hydroxyl protons on the

Table 3. Crystallographic data for $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ (**1**) and $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]CH_3OH$ (**2**)

	1	**2**
Formula	$C_{15}H_{20}N_2Cl_2Ru$	$C_{22}H_{26}N_2OCl_2Ru$
Formula weight	400.34	506.47
Space-group	$P2_12_12_1$	$P4/n$
a (Å)	9.527(2)	21.116(3)
b (Å)	12.265(2)	21.116(3)
c (Å)	14.210(2)	9.128(1)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	1660	4069
Z	4	8
$F(000)$	808	2064
d_{calc} (g cm^{-3})	1.60	1.65
Crystal size (mm)	$0.20\times0.26\times0.45$	$0.06\times0.15\times0.55$
μ(Mo-K_α) (cm^{-1})	12.4	10.4
Data collection instrument	Nicolet R3mV	
Radiation	Mo-K_α (λ = 0.71073 Å)	
Orientation reflections: number, range (2θ)	30, $16 \leqslant 2\theta \leqslant 29°$	30, $16 \leqslant 2\theta \leqslant 26°$
Temperature (K)	292	
Unique data measured	1613	3524
Number of unique with $I \geqslant 3.0\sigma(I)$	1534	1949
Number of parameters	181	241
R^a	0.0303	0.0506
$R_w{}^b$	0.0329	0.0620
Weighting scheme	$w^{-1} = \sigma^2(F)+0.00039F^2$	$w^{-1} = \sigma^2(F)+0.00611F^2$
Largest shift/ESD, final cycle	0.01	0.01
Largest peak (e/Å^3)	0.42	0.90

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$.
[b] $R_w = \Sigma w^{1/2}[|F_o| - |F_c|]/\Sigma w^{1/2}|F_o|$.

various hydroxypyridine ligands used in our earlier study. Given that each of the aminopyridine ligands employed in this study only coordinates unidentately to a ruthenium(II) centre, then there are two potential ligand donor atoms, namely the amino and pyridyl nitrogen atoms. Although it is known[16,17] that ammonia will bind to a "Ru(η^6-arene)" fragment, there are few examples of other coordinated amines in this area of chemistry. In contrast, there are numerous examples of co-ordinated pyridines or pyridyl ligands. Comparison of the H NMR signals from free and coordinated Hap ligands strongly suggested that coordination to the metal was via the pyridyl nitrogen atoms.

Table 4. Selected bond lengths (Å) and bond angles (°) for $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$

Bond lengths			
Ru(1)—Cl(1)	2.409(2)	Ru(1)—Cl(2)	2.421(2)
Ru(1)—N(1)	2.160(6)	Ru(1)—C(1)	2.198(7)
Ru(1)—C(2)	2.177(7)	Ru(1)—C(3)	2.160(6)
Ru(1)—C(4)	2.220(7)	Ru(1)—C(5)	2.181(6)
Ru(1)—C(6)	2.178(6)	N(1)—C(11)	1.391(9)
N(1)—C(15)	1.357(9)	N(2)—C(15)	1.377(10)
Bond angles			
Cl(1)—Ru(1)—Cl(2)	85.6(1)	Cl(1)—Ru(1)—N(1)	87.3(1)
Cl(2)—Ru(1)—N(1)	88.6(1)	Ru(1)—N(1)—C(15)	125.4(5)
N(1)—C(15)—N(2)	117.9(6)		

Table 5. Selected bond lengths (Å) and bond angles (°) for $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$

	Bond lengths		
Ru(1)—Cl(1)	2.405(3)	Ru(1)—Cl(2)	2.402(3)
Ru(1)—C(1)	2.337(9)	Ru(1)—C(2)	2.226(9)
Ru(1)—C(3)	2.146(9)	Ru(1)—C(4)	2.260(8)
Ru(1)—C(5)	2.131(9)	Ru(1)—C(6)	2.159(10)
Ru(1)—N(1)	2.121(7)	N(1)—C(17)	1.374(13)
N(1)—C(21)	1.344(13)	N(2)—C(21)	1.377(17)
	Bond angles		
Cl(1)—Ru(1)—Cl(2)	85.7(1)	Cl(1)—Ru(1)—N(1)	85.7(2)
Cl(2)—Ru(1)—N(1)	92.5(2)	Ru(1)—N(1)—C(21)	125.5(7)
N(1)—C(21)—N(2)	117.3(10)		

This was conclusively established by single crystal X-ray diffraction experiments on $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ and $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$.

X-ray crystal structures of $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ *and* $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$

The molecular structures of $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ and $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$ are shown in Figs 1 and 2, respectively. Important bond lengths and bond angles are presented in Tables 4 and 5. The geometry about each ruthenium ion is that of a distorted octahedron with the η-arene ring and the other ligands adopting a "piano stool" configuration. Both the complexes have an overall geometry similar to that of several $[Ru(\eta^6\text{-arene})Cl_2L]$ and $[Ru(\eta^6\text{-arene})ClL_2]^+$ species[1-3,17,18] described previously. The two Ru—N distances are closely similar, however there are significant variations in the Ru—Cl distances. In particular, the two Ru—Cl distances, 2.409(2) and 2.421(2) Å, in the compound $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ are statistically different. Both chloride ligands are involved in hydrogen bonding to amino nitrogen atoms. The ligand Cl(1) is involved in an intermolecular hydrogen bond of 3.23 Å, while Cl(2) forms an intramolecular hydrogen bond, of 3.24 Å, to N(2). In contrast, only Cl(2) is involved in intramolecular hydrogen bonding, to N(2), 3.16 Å, in $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$, and the two Ru—Cl bond distances in this molecule are indistinguishable.

In $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ the Ru—C distances lie in the range 2.16–2.22 Å, and the ring centroid is 1.67 Å from the ruthenium ion. Similar distances are observed in the ruthenium(II) *p*-cymene complexes $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(hp)]^2$, $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(pyz)_2][PF_6]$[14] and $[Ru_2(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(\mu\text{-}Cl)_3][BPh_4]$.[19] The C—C bond length alternation which has been observed in several other studies on η^6-arenes coordinated to transition metal ions[18,20] is not readily apparent in this

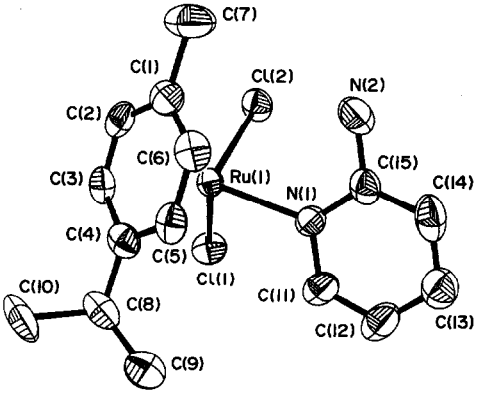

Fig. 1. Thermal ellipsoid plot of the $[Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NC_5H_4NH_2)]$ molecule. Atoms are represented by thermal vibration ellipsoids at the 50% confidence level, and the atom-labelling scheme is defined.

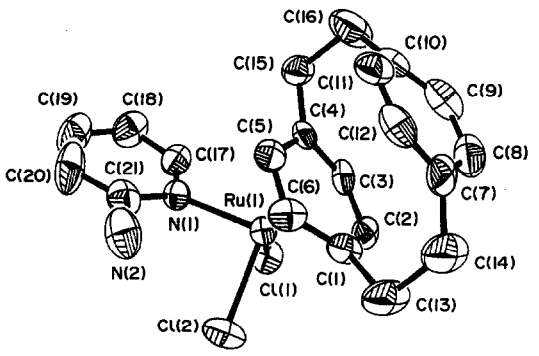

Fig. 2. Thermal ellipsoid plot of the $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(NC_5H_4NH_2)]$ molecule. Atoms are represented by thermal vibration ellipsoids at the 50% confidence level, and the atom-labelling scheme is defined.

study. The methyl and isopropyl groups are bent towards the ruthenium ion by 2.3 and 3.4°, respectively. The isopropyl group is not symmetrically placed with respect to the C_6 ring but forms a torsion angle, C(5)—C(4)—C(8)—C(9) = 14.7°, with the mean plane.

In [Ru(η^6-$C_{16}H_{16}$)Cl_2($NC_5H_4NH_2$)] the Ru—C distances fall into two sets; there are four short bonds, to C(2), C(3), C(5) and C(6), 2.13–2.22 Å, and two long bonds to the bridgehead carbons C(1) and C(4), 2.337(9) and 2.260(8) Å, respectively. This variation in metal–carbon bond length is attributed to the presence of the two ethylenic bridges between the aromatic decks of the cyclophane and has been commented on in several previous reports.[3–5,21,22] Indeed, it is a feature of the free ligand, as well as its metal complexes, that the aromatic rings are non-planar. The two bridgehead carbon atoms of the coordinated deck lie, on average, 0.18 Å above the mean plane of the other four coordinated carbon atoms, while the two bridgehead carbons of the non-coordinated deck lie *ca* 0.15 Å below the plane defined by the remaining four carbon atoms of the second deck. It is also noteworthy that the two Ru—C bonds *trans* to the pyridyl nitrogen atom are significantly lengthened with respect to the remaining four Ru—C bonds. Similar observations have been made on the Ru—C bonds *trans* to the tertiary phosphine ligands in the compounds [Ru(η^6-arene)Cl_2(PMe_2Ph)].[18] The two decks are not precisely eclipsed with respect to each other. There is an average torsion angle in the ethylenic bridges of 4.4°. This compares with an estimated value of *ca* 3.2° in the disordered structure of the free ligand.[23] The shallow boat conformation of the free ligand has been ascribed to electronic interactions between the stacked decks. On coordination to a metal ion these unfavourable interactions are reduced and the separation between decks is decreased from 3.09 Å, in the non-coordinated ligand, to 2.99 Å for this compound.

The molecular parameters of the coordinated 2-aminopyridine ligands in the two structures are not significantly different from each other.

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