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Preliminary communication

Synthesis and characterisation of a pyrazine bridged bis-allyl ruthenium(IV) complex. Crystal structure of $[\{(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2\}_2(\mu\text{-}C_4H_4N_2)] \cdot 2CHCl_3$

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Abstract

The reaction of pyrazine with the ruthenium(IV) bis-allyl dimer $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl(\mu\text{-}Cl)]_2$ gives the bridged binuclear complex $[\{(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2\}_2(\mu\text{-}C_4H_4N_2)]$ in high yield. The complex has been characterised by ^1H NMR spectroscopy and by a single-crystal X-ray diffraction study.

The organometallic chemistry of transition metals in high formal oxidation states is an area of growing interest [1,2]. An organometallic compound that has been known for many years yet has been little studied is the ruthenium(IV) dimer $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl(\mu\text{-}Cl)]_2$ [3], which is rather surprising given the profusion of studies on the related chloro-bridged ruthenium(II) dimers $[(\eta^6\text{-arene})RuCl(\mu\text{-}Cl)]_2$.

The crystal structure of $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl(\mu\text{-}Cl)]_2$ shows that the complex has C_i symmetry in the solid state, with the coordination about each metal atom best described as trigonal bipyramidal [4]. Nevertheless ^1H NMR studies clearly establish that in solution two diastereoisomers are present [5]. While one isomer is assumed to have the C_i symmetry observed in the solid state it is proposed that the second isomer has C_2 symmetry. In coordinating solvents the dimer is observed to be cleaved and exist as both equatorially and axially solvated monomers [5]. Reactions with neutral monodentate ligands also result in bridge cleavage and the formation of the simple adducts $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2L]$ ($L = CO, PR_3, C_5H_5N$, ^tBuNC) [6,7,8]. In this report we present our preliminary results on the synthesis of polynuclear compounds containing the "$[(\eta^3:\eta^3\text{-}C_{10}H_{16}Ru]^{2+}$" unit.

The reaction of $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl(\mu\text{-}Cl)]_2$ with between 1 and 10 molar equivalents of pyrazine in chloroform proceeds smoothly to give a compound with the stoichiometry $[\{(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2\}_2(\mu\text{-}C_4H_4N_2)]$ as the sole product (C,H,N,Cl analysis). The formation of appreciable quantities of the monomeric compound $[\{(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2(C_4H_4N_2)]$ was only observed when > 15 molar equivalents of the ligand were used. The ^1H NMR spectrum of the dinuclear compound recorded in $CDCl_3$ exhibited twice as many resonances as was expected

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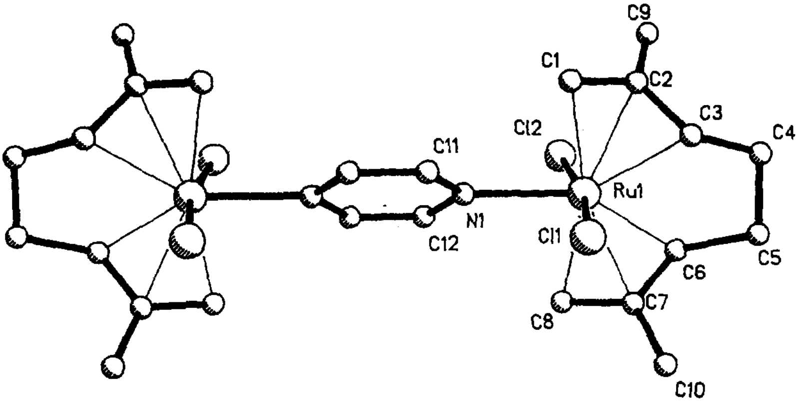

Fig. 1. Molecular structure of $[\{(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl_2\}_2(\mu\text{-}C_4H_4N_2)]$ showing the atom numbering scheme adopted. Selected bond lengths (Å): Ru(1)–N(1) 2.191(10), Ru(1)–Cl(1) 2.406(3), Ru(1)–Cl(2) 2.425(3), Ru(1)–C(1) 2.226(13), Ru(1)–C(2) 2.303(12), Ru(1)–C(3) 2.256(15), Ru(1)–C(6) 2.240(16), Ru(1)–C(7) 2.264(14), Ru(1)–C(8) 2.235 (12). Selected interbond angles (°): Cl(1)–Ru(1)–Cl(2) 170.2(1), Cl(1)–Ru(1)–N(1) 85.4(2), Cl(2)–Ru(1)–N(1) 84.8(2), Cl(1)–Ru(1)–C(2) 101.7(3), Cl(1)–Ru(1)–C(7) 83.3(4), Cl(2)–Ru(1)–C(2) 82.4(3), Cl(2)–Ru(1)–C(7) 100.8(4), C(2)–Ru(1)–C(7) 131.2(5), N(1)–Ru(1)–C(2) 114.7(4), N(1)–Ru(1)–C(7) 114.2(5).

for this formulation (e.g. four terminal allyl signals at δ 4.65, 4.62, 4.39, and 4.34 ppm). However, since both pyrazine resonances appeared as singlets (at δ 9.32 and 9.23 ppm) we were confident that the products were binuclear pyrazine-bridged species. It is likely that the doubling of the number of signals can be attributed to the presence of diastereoisomers similar to those observed in solutions of $[(\eta^3:\eta^3\text{-}C_{10}H_{16})RuCl(\mu\text{-}Cl)]_2$ [5]. To establish conclusively the structure of the product formed in this reaction we carried out a single crystal structural analysis *.

The X-ray study shows (Fig. 1) that in the crystalline material only one of the isomers is present. That isomer has overall C_i symmetry, while the organic ligands have local C_2 symmetry. This arrangement is similar to that observed for the parent chloro-bridged dimer in the solid state [3,4]. The geometry about the crystallographically unique metal ion is that of a distorted trigonal bipyramid with the chloride ligands occupying the axial positions, Cl(1)–Ru(1)–Cl(2) bond angle 170.2(1)°, and the organic moiety and neutral pyrazine ligand occupying the

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* *Crystal data for* $C_{26}H_{38}N_2Cl_{10}Ru_2$: $M = 935.27$, a 7.297(2), b 9.889(2), c 13.411(4) Å, α 70.77, β 83.29, γ 89.70°, V 906.9 Å^3, $Z = 1$, d_{calc} 1.71 g/cm^3, $F(000)$ 466, μ(Mo-K_α) 15.8 cm^{-1}, triclinic space group $P\bar{1}$ (the asymmetric unit contains one half of the centrosymmetric molecule and one molecule of chloroform of crystallisation).

Structure determination: A crystal of dimensions 0.10 × 0.17 × 0.30 mm was used to collect 3122 unique data in the range $5° \leqslant 2\theta \leqslant 50°$ on a Nicolet R3m/V diffractometer equipped with graphite-monochromated Mo-K_α radiation. The data were corrected for Lorentz and polarisation effects, and for crystal decay (ca. 40%). The structure was solved by conventional Patterson and difference-Fourier techniques. Non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08$ Å^2). Full-matrix least-squares refinement gave $R = 0.064$ and $R_w = 0.066$ ($w^{-1} = \sigma^2(F) + 0.0008F^2$) for the 1864 unique data with $I \geqslant 3\sigma(I)$. All calculation were performed on a MicroVax II computer using SHELXTL PLUS software. A table of atom coordinates and a list of bond lengths and angles has been deposited at the Cambridge Crystallographic Data Centre.

equatorial sites. Equatorial coordination of a neutral ligand was also observed in the X-ray crystal structure of [(η^3 : η^3-$C_{10}H_{16}$)$RuCl_2(PF_3)$] [8]. The Ru–$N_{(pyrazine)}$ distance is 2.19(1) Å, which is considerably greater than that observed in several well defined $[(NH_3)_5Ru(\mu\text{-pyz})Ru(NH_3)_5]^{n+}$ ($n = 4$, 3, 6) ions, 1.99–2.11 Å [9]. It is however similar to that observed in the organometallic ruthenium(II) cation [(η^6-p-$MeC_6H_4CHMe_2$)$Ru(pyz)_2Cl]^+$, 2.17 Å [10], although of course the pyrazine ligands in that complex are only coordinated to a single metal. The pyrazine ligand is inclined at an angle of 38.0° to the plane of the metal ion and halide ligands. The most likely structure for the second isomer, observed in solution, would have overall C_2 symmetry. Since the isomer ratio is independent of the precise conditions used in the synthesis we intend to study and report the kinetics of isomerism reaction at a later date.

Finally, using analogous synthetic procedures to those described above we examined the reaction of [(η^3 : η^3-$C_{10}H_{16}$)$RuCl(\mu\text{-}Cl)]_2$ with 1,3,5-triazine. In contrast to the results described above, these reaction lead to mixtures of products, viz. [(η^3 : η^3-$C_{10}H_{16}$)$RuCl_2(C_3H_3N_3)$], [{(η^3 : η^3-$C_{10}H_{16}$)$RuCl_2\}_2(\mu\text{-}C_3H_3N_3)$], and [{($\eta^3$: η^3-$C_{10}H_{16}$)$RuCl_2\}_3(\mu\text{-}C_3H_3N_3)$].

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