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Preliminary communication

The synthesis of new paracyclophane complexes of ruthenium(II): Crystal structure of $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(C_5H_5N)_2][PF_6]$

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Abstract

The dimer $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2]_2$ reacts with ligands L (L = PMe_2Ph, PPh_3, C_5H_5N) to give both neutral monomeric $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2L]$ and cationic monomeric $[Ru(\eta^6\text{-}C_{16}H_{16})ClL_2]^+$ products. One example, $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(C_5H_5N)_2]$-$[PF_6]$, has been characterised by X-ray crystallography. Reaction with the bidentate ligand 2,2′-bipyridyl gives the mononuclear cation $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(bipy)]^+$, isolated as its $[BPh_4]^-$ salt, whereas reaction with OMe^- or OEt^- gives dinuclear products $[Ru_2(\eta^6\text{-}C_{16}H_{16})_2(OR)_3]^+$.

During synthetic studies on a number of bis(η^6-[2n]cyclophane)ruthenium(II) and related oligomeric compounds, Boekelheide et al. made the dinuclear molecules $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2]_2$ [1,2]. These species were of interest to us as they are clearly closely related to the $[Ru(\eta^6\text{-arene})Cl_2]_2$ compounds whose chemistry we have extensively studied [3–10]. We now report the results of our preliminary investigations into the reactions of the paracyclophane complex, bis(η^6-[2_2](1,4)cyclophane)-dichlorobis(η-chloro)diruthenium(II), with a range of ligands.

We have prepared a range of orange red adducts $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2L]$ (L = PMe_2Ph, PPh_3, C_5H_5N) * by reaction of an excess of the appropriate ligand with a toluene suspension of the metal complex. All the complexes are monomeric in chloroform and are non-electrolytes in acetonitrile and nitromethane. The ^1H NMR spectrum of each complex typically shows three sets of resonances for the cyclophane ligand. The coordinated ring gives rise to a singlet (L = C_5H_5N) or doublet (L = PPh_3, PMe_2Ph; $^3J(P-H)$ ca. 1.5 Hz) resonance in the range δ 4.7–4.9 ppm, the uncoordinated ring appears as a singlet at ca. δ 6.7 ppm, and the methylene protons appear as an AA′BB′ pattern at ca. δ 2.8 ppm. Integration of the complete ^1H NMR spectra confirms that the products are 1/1 adducts.

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* Satisfactory elemental analyses have been obtained.

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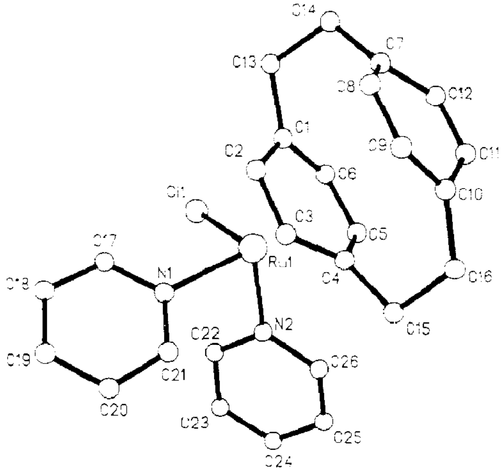

Fig. 1. View of the structure of one of the $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(C_5H_5N)_2]^+$ cations showing the atom labelling scheme. Important parameters: Ru(1)–Cl(1) 2.404(6), Ru(1)–N(1) 2.166(16), Ru(1)–N(2) 2.133(20), Ru(1)–C(1) 2.365(21), Ru(1)–C(2) 2.248(22), Ru(1)–C(3) 2.161(21), Ru(1)–C(4) 2.312(20), Ru(1)–C(5) 2.164(17), Ru(1)–C(6) 2.175(17) Å, Cl(1)–Ru(1)–N(1) 90.1(5), Cl(1)–Ru(1)–N92) 86.4(6), N(1)–Ru(1)–N(2) 84.8(6)°.

In contrast, if the reactions are carried out in methanolic solution and $[NH_4]PF_6$ is added to the reaction mixture then the compounds $[Ru(\eta^6\text{-}C_{16}H_{16})ClL_2][PF_6]$ * can be obtained. Integration of the ^1H NMR spectra was consistent with formation of the cationic 2/1 adducts. The monomeric nature of the products has been confirmed by X-ray structural analysis of a representative compound, $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(C_5H_5N)_2][PF_6]$ (see Fig. 1) *.

The geometry about the ruthenium ion is that of a distorted tetrahedron, with the paracyclophane and the other ligands adopting a "piano stool" configuration. The complex has a similar arrangement of ligands to that in several $[Ru(\eta^6\text{-arene})Cl_2L]$ and $[Ru(\eta\text{-arene})ClL_2]^+$ molecules [7,13]. The coordination of the chloride and heterocyclic nitrogen donor ligands closely resembles that observed in the cation $[Ru(\eta\text{-}p\text{-cymene})Cl(C_4H_4N_2)_2]^+$ [7]. The most marked contrast between the structures of (η^6-arene)ruthenium(II) compounds and the paracyclophane compound discussed here is the significant variation in the metal–carbon distances observed in the latter. In the case of (η^6-arene)ruthenium(II) compounds the metal–carbon distances typically fall in a narrow range about 2.14–2.21 Å [4,6–10,13], while the compound reported here has close distances in the range 2.16–2.36 Å. However this large variation in metal carbon distances has been observed previously [1,14], and is

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* *Crystal data for $C_{26}H_{26}ClF_6N_2PRu$:* $M = 647.99$, a 7.814(1), b 20.251(3), c 32.785(5) Å, V 5186(1) Å^3, $Z = 8$, d_{calc} 1.66 g/cm^3, $F(000)$ 2608, $\mu(\text{Mo-}K_\alpha)$ 7.74 cm^{-1}, orthorhombic space group $P2_12_12_1$ (the asymmetric unit contains two cations and two $[PF_6]^-$ anions).

Structure determination: A crystal of dimensions 0.15×0.10×0.40 mm was used to collect 6648 unique data up to θ 25° on a Nicolet R3m/V diffractometer. The positions of the ruthenium atoms were derived by direct methods and the remaining non-hydrogen atoms found by iterative application of least-squares refinement and difference-fourier synthesis [11]. The $[PF_6]^-$ anions are extensively disordered and this led to less than ideal refinement [12*]. The current R value is 0.075 from the 3399 reflections with $I > 2.5\sigma(I)$. The weighting scheme was $w = 1.0/(\sigma^2(F) + 0.000024\ F^2)$. The structure of one of the cations (the other is essentially identical) is presented in Fig. 1.

attributed to the presence of the two ethylenic bridges between the aromatic rings. Indeed it is a feature of the free ligand, as well as of its metal complexes, that the aromatic rings are non-planar [15].

When a solution of $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2]_2$ in methanol is stirred with an excess of 2,2′-bipyridyl for less than ca. 1 h a red solution is formed, and a brown solid separates on addition of $Na[BPh_4]$. Analytical and spectroscopic data are consistent with the formulation of this solid as $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(bipy)][BPh_4]$. Prolonged interaction between the dimer and 2,2′-bipyridyl results in the formation of the well-known cation $[Ru(bipy)_3]^{2+}$.

Finally reaction of $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2]_2$ with solutions of Na[OR] in ROH (R = Me, Et) gives yellow solutions from which solids can be precipitated by addition of $K[PF_6]$ or $Na[BPh_4]$. These solids have been identified as the dinuclear species $[(\eta^6\text{-}C_{16}H_{16})Ru(OR)_3Ru(\eta^6\text{-}C_{16}H_{16})]X$, ($X = PF_6^-$ or BPh_4^-) in which the cation has confacial bioctahedral geometry [16*].

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16 Preliminary X-ray examination has confirmed this geometry for the compound $[Ru_2(\eta^6\text{-}C_{16}H_{16})_2(OEt)_3]PF_6$.

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* Reference numbers with asterisks indicate notes in the list of references.