The Synthesis of New Binuclear Paracyclophane Complexes of Ruthenium(II): Crystal Structure of $[Ru_2(\eta^6\text{-}C_{16}H_{16})_2(OEt)_3][PF_6]$

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Recently we reported [1] that reaction of $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2]_2$ with a variety of donor ligands L (L = pyridine, PPh_3, PMe_2Ph) gave rise to a range of products of the types $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2L]$ and $[Ru(\eta^6\text{-}C_{16}H_{16})ClL_2]^+$. The mononuclear nature of these products was confirmed by crystal structure determinations of the representative compounds $[Ru(\eta^6\text{-}C_{16}H_{16})Cl(C_5H_5N)_2][PF_6]$ [1] and $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2(PPh_3)]$ [2]. In this report we describe the synthesis and characterisation of some new binuclear compounds containing the '$Ru(\eta^6\text{-}C_{16}H_{16})$' moiety.

Results and Discussion

In recent years it has been shown that hydroxo-bridged arene–ruthenium complexes such as $[Ru_4(\eta^6\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2\cdot 2Me_2CO$ and $[Ru_2(\eta^6\text{-}C_6Me_6)(OH)_3]Cl$ react with ROH (R = Me, Et) to form the binuclear cations $[Ru_2(\eta^6\text{-arene})_2(OR)_3]^+$ which have a confacial bioctahedral geometry with three alkoxo bridging ligands shared by the two metal ions [3, 4]. Alkoxide-bridged species of this type were also obtained when the dimers $[Ru(\eta^6\text{-arene})Cl_2]_2$ were treated with freshly prepared solutions of NaOR in ROH [3, 5]. We now report the results of our preliminary investigations into the reactions of the paracyclophane compound bis(η^6-$[2_2]$(1,4)cyclophane)dichlorobis(μ-chloro)diruthenium with solutions of NaOR (R = Me, Et).

The reaction between $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2]_2$ and NaOMe in methanol proceeds smoothly to give a yellow solution from which an orange solid can be precipitated by addition of $Na[BPh_4]$. The infrared spectrum of this product contains no bands attributable to ν(Ru–Cl) but exhibits a strong ν(C–O) vibration at *c.* 1050 cm^{-1}. The presence of a $[BPh_4]^-$ counterion is confirmed by the presence of strong bands at 708, 722 and 734 cm^{-1}. The ^1H NMR spectrum in CD_2Cl_2 reveals three signals due to the coordinated cyclophane ligand. The coordinated and non-coordinated rings give rise to singlet resonances at δ 4.55 and 6.62 ppm, respectively, while the methylene protons appear as an AA′BB′ signal centred at δ 2.87 ppm. The methoxide ligands appear as a singlet at δ4.22 ppm, while the protons of the $[BPh_4]^-$ anion give rise to multiplet signals at δ 6.91, 7.06 and 7.34 ppm. Integration of the spectrum is consistent with a $C_{16}H_{16}:[OMe]^-:[BPh_4]^-$ ratio of 2:3:1, suggesting the formulation $[Ru_2(\eta^6\text{-}C_{16}H_{16})_2(OMe)_3][BPh_4]$. Microanalytical data and conductivity measurements support this formulation. Similarly, the reaction of $[Ru(\eta^6\text{-}C_{16}H_{16})Cl_2]_2$ with NaOEt/K$[PF_6]$ in ethanol gives a product which is characterised by analytical and spectroscopic measurements as $[Ru_2(\eta^6\text{-}C_{16}H_{16})_2(OEt_3)][PF_6]$. The binuclear nature of the cationic products formed in these reactions has been confirmed by the X-ray structural analysis of the hexafluorophosphate salt.

Crystal data for $C_{38}H_{47}O_3F_6PRu_2$: $M = 934.9$, $a = 18.170(3)$, $b = 21.560(3)$, $c = 19.696(2)$ Å; $\beta = 105.54(1)°$, $V = 7431(2)$ Å^3, $Z = 8$; $D_{calc} = 1.61$ g cm^{-3}, $F(000) = 3648$, $\mu = 8.70$ cm^{-1}, monoclinic space group $C2/c$. Structure determination: a crystal of dimensions 0.52 × 0.25 × 0.06 mm was used to collect 6582 unique data in the range $5° < 2\theta < 50°$ on a Nicolet R3m/V diffractometer. The positions of the two ruthenium ions in the asymmetric unit were derived by direct methods and the remaining non-hydrogen atoms found by iterative application of least-squares refinement and difference-Fourier synthesis [6]. The final least-squares refinement included 454 parameters for 5054 ($I > 1.5\sigma(I)$) variables. The last cycle gave $R = 0.0641$, $R_w = 0.0693$ (weighting scheme $w^{-1} = \sigma^2(F) + 0.000596 F^2$). The structure of the cation is presented in Fig. 1.

The cation has a confacial-bioctahedral geometry (see Fig. 1 and Table 1 for selected intramolecular distances and angles) with a Ru···Ru distance of 3.015(1) Å, which is similar to that found for the related cation $[Ru_2(\eta^6\text{-}C_6H_6)_2(OMe)_3]^+$, 3.005(2) Å [5], as well as for other triply bridged arene–ruthenium(II) compounds (cf. 3.283 Å in $[Ru_2(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Cl_3]^+$ [7], and 2.989(3) Å in $[Ru_2(\eta^6\text{-}C_6Me_3H_3)_2(OH)_3]^+$ [4]). The Ru–O distances lie in the range 2.055 to 2.084 Å and have an average value of 2.068(5) Å, which is indistinguishable from that of 2.060(8) Å observed in the compound $[Ru_2(\eta^6\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ [5]. As with the other examples of paracyclophane complexes of ruthenium(II) which we have characterised, there is considerable variation in the Ru–C distances, with bonds to the carbon atoms attached to the ethylenic bridging functions being appreciably longer than those to the remaining arene carbon atoms (average values of 2.292(9) and 2.178(9) Å respectively). The resulting non-planarity of the aromatic rings is a well-

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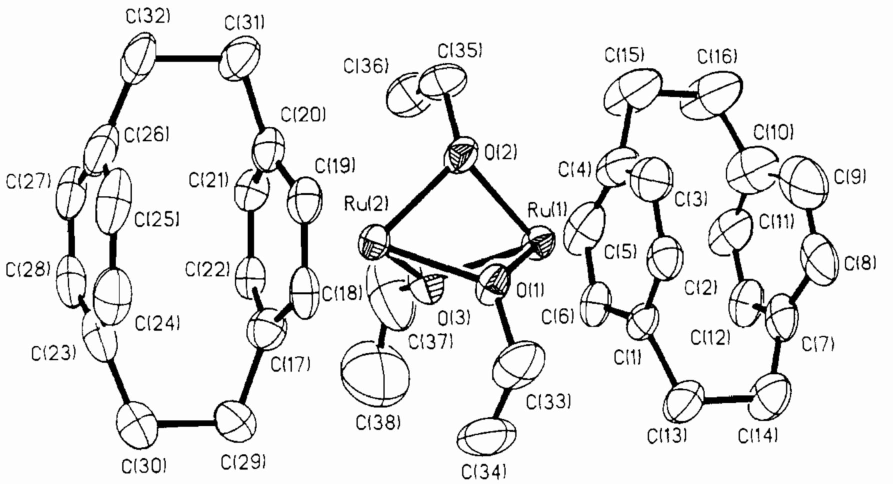

Fig. 1. Thermal ellipsoid plot of the $[Ru_2(\eta^6\text{-}C_{16}H_{16})_2(OEt)_3]^+$ cation. Atoms are represented by thermal vibration ellipsoids at the 50% level, and the atomic labelling scheme is defined.

TABLE 1. Selected bond lengths and angles for $[Ru_2(\eta^6\text{-}C_{16}H_{16})_2(OEt)_3][PF_6]$

Bond lengths (Å)			
Ru(1)–Ru(2)	3.015(1)	Ru(2)–O(1)	2.084(5)
Ru(1)–O(1)	2.058(5)	Ru(2)–O(2)	2.076(5)
Ru(1)–O(2)	2.081(5)	Ru(2)–O(3)	2.054(5)
Ru(1)–O(3)	2.055(5)	Ru(2)–C(17)	2.271(9)
Ru(1)–C(1)	2.269(7)	Ru(2)–C(18)	2.159(8)
Ru(1)–C(2)	2.155(9)	Ru(2)–C(19)	2.196(7)
Ru(1)–C(3)	2.175(10)	Ru(2)–C(20)	2.332(8)
Ru(1)–C(4)	2.298(9)	Ru(2)–C(21)	2.183(8)
Ru(1)–C(5)	2.177(9)	Ru(2)–C(22)	2.215(8)
Ru(1)–C(6)	2.167(8)		
Bond angles (°)			
Ru(1)–O(1)–Ru(2)	93.4(2)	O(1)–Ru(2)–O(2)	69.8(2)
Ru(1)–O(2)–Ru(2)	93.0(2)	O(1)–Ru(2)–O(3)	73.3(2)
Ru(1)–O(3)–Ru(2)	94.4(2)	O(2)–Ru(2)–O(3)	74.4(2)
O(1)–Ru(1)–O(2)	70.3(2)		
O(1)–Ru(1)–O(3)	73.8(2)		
O(2)–Ru(1)–O(3)	74.3(2)		

established feature in the chemistry of paracyclophane and its metal complexes [1, 2, 7–9]. The two coordinated cyclophane rings are staggered with respect to each other as might have been expected. However, one ring, C17–C18–C19–C20–C21–C22, is eclipsed with respect to the three oxygen sites. The ethoxide bridging ligands have not adopted the three-fold symmetry which might have been expected.

Further work on the synthesis and characterisation of other binuclear cyclophane–ruthenium(II) compounds is in progress [10]. These studies will be described in a future publication.

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