Toluene-*p*-sulphonate as a Metal–Metal Bond Bridging Ligand; the Crystal Structure of $[\{Rh_2(6\text{-methylpyridin-2-olato})_3(p\text{-}MeC_6H_4SO_2O)\}_2]\cdot Et_2O$

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Toluene-*p*-sulphonic acid displaces one of the 6-methylpyridin-2-olato (mhp) ligands of $[Rh_2(mhp)_4]$; the product dimerises to form $[\{Rh_2(mhp)_3(p\text{-}MeC_6H_4SO_2O)\}_2]$, in which each toluene-*p*-sulphonate ligand bridges a Rh–Rh bond, as demonstrated by a crystal structure determination.

The anion of 6-methyl-2-hydroxypyridine (Hmhp) promotes the formation of dimeric metal complexes $[M_2(mhp)_4]$, with very short M–M separations.[1] The reactions of $[Rh_2(O_2CMe)_4]$ with Na(mhp) or Hmhp have been found to be complex, with a large number of products. From the reaction with Na(mhp), apart from the symmetric dimer $[Rh_2(mhp)_4]$ (**1**), two complexes $[Rh_2(mhp)_4(Hmhp)]$ (**2**) and $[\{Rh_2(mhp)_4\}_2]$ (**3**) were obtained,[2] each having a 3 : 1 rather than the 2 : 2 arrangement of bridging mhp ligands across the Rh–Rh single bond. This arrangement leaves the axial site of one of the Rh atoms open for attachment of a further ligand, as in (**2**), or for formation of the 'dimer of dimers' (**3**) through additional bonding of one of the ligand oxygen atoms. Complex (**1**) was also produced in the reaction with Hmhp, together with some complexes with the 3 : 1 ligand arrangement and various axial ligands depending on solvent and recrystallisation conditions, and some complexes with partial rather than complete replacement of acetate by mhp ligands.[3]

$[Rh_2(mhp)_4]$ (**1**)

$[Rh_2(mhp)_4(Hmhp)]$ (**2**)

$[\{Rh_2(mhp)_4\}_2]$ (**3**)

$[\{Rh_2(mhp)_3(OTs)\}_2]\cdot Et_2O$ (**4**)

In view of the richness of this Rh–mhp chemistry, we have investigated the reaction of the yellow-brown (**1**) with toluene-*p*-sulphonic acid (TsOH), in an attempt to achieve controlled cleavage of the mhp ligands from the dimetal centre. The reaction (1 : ≤5 molar ratio in toluene solution) typically gave a green microcrystalline product with a chemical analysis corresponding to approximately 3 mhp and 2 TsO groups per Rh_2 pair. Recrystallisation by diffusion of Et_2O into a CH_2Cl_2 solution produced fine green needles. *X*-Ray crystallography established the chemical nature of these as $[\{Rh_2(mhp)_3(OTs)\}_2]\cdot Et_2O$ (**4**).†

The molecular structure is shown in Figure 1. The crystal structure also contains Et_2O molecules. It seems likely from the chemical analysis that the product obtained initially from the synthesis contains co-crystallised TsOH. Thus, we suggest that in the reaction of (**1**) with TsOH one bridging TsO ligand is substituted for one mhp; one Rh atom is then open to axial attack, and dimerisation takes place, as in (**3**). We have found this 'dimer of dimers' arrangement to be particularly stable. In this particular case, it appears that no further substitution takes place, despite the presence of excess of TsOH. The molecular framework of (**4**) is very similar to that of (**3**), the Rh–Rh bonds being insignificantly longer [2.377(3) and 2.376(3) Å, *cf.* 2.369(1) Å in (**3**)]. The molecule has non-crystallographic two-fold rotation symmetry. The central Rh_2O_2 ring is slightly folded (6.0°) about the O···O line, and the two Rh–Rh bonds lie slightly (5.6 and 3.2°) out of the Rh_2O_2 mean plane. As in molecules containing a 3 : 1 arrangement of four mhp ligands bridging a Rh–Rh bond, there is a very considerable twisting distortion of the ligands about the Rh–Rh bonds: N–Rh–Rh–O or O–Rh–Rh–O torsion angles for the eight ligands are 19.5, 16.3, 18.6, 16.1, 22.6, 22.4, 18.8, and 21.1°, similar to values around 20° in various $[Rh_2(mhp)_4L]$ complexes.[2,3] All the mhp ligands and the toluene-*p*-substituents of TsO are essentially planar (r.m.s. deviations from respective mean planes are 0.02—0.06 Å).

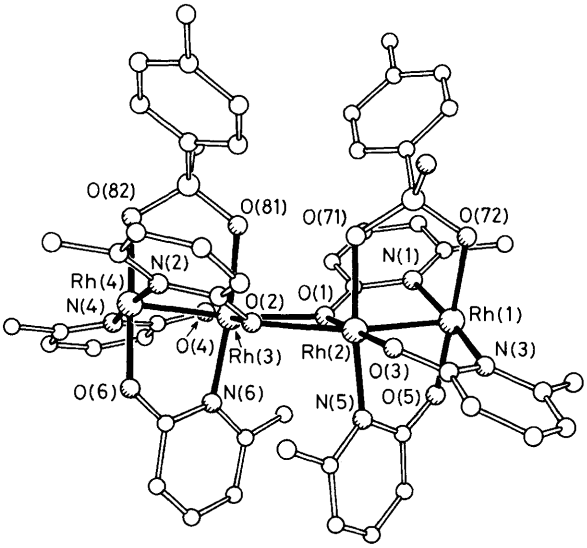

Figure 1. Molecular structure of (**4**). Crystals are monoclinic, a = 9.014(2), b = 23.488(4), c = 27.336(9) Å, β = 99.08(2)°, U = 5715.1 Å^3, Z = 4, D_c = 1.716 g cm^{-3}, space group $P2_1/c$; crystal size *ca.* 0.25 × 0.03 × 0.03 mm. Intensities were measured to $2\theta_{max}$ = 42° with Mo-K_α radiation (λ = 0.71069 Å) on a Stoe–Siemens AED diffractometer. For 3709 unique reflections with $F > 3\sigma(F)$, anisotropically refined atoms, and isotropic H atoms in calculated positions, R = 0.096. Selected bond lengths (Å): Rh(1)–Rh(2) 2.377(3), Rh(3)–Rh(4) 2.376(3), Rh(2)–O(1) 2.05(1), Rh(3)–O(2) 2.02(1), Rh(2)–O(3) 2.02(1), Rh(3)–O(4) 2.02(1), Rh(1)–O(5) 1.99(1), Rh(4)–O(6) 1.99(1), Rh(3)–O(1) 2.24(1), Rh(2)–O(2) 2.30(2), Rh(1)–N(1) 2.05(1), Rh(4)–N(2) 2.05(1), Rh(1)–N(3) 2.04(1), Rh(4)–N(4) 2.04(1), Rh(2)–N(5) 2.03(1), Rh(3)–N(6) 2.05(1), Rh(2)–O(71) 2.11(1), Rh(1)–O(72) 2.11(1), Rh(3)–O(81) 2.12(1), Rh(4)–O(82) 2.06(1).

The replacement of mhp by TsO as a bridging ligand is very interesting, especially in view of the general use of toluene-*p*-

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23843 (23 pp.) from the British Library Lending Division. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, issue 3, p. xvii.

sulphonate as a *leaving* group of low basicity. Although bridging OSO_2Me ligands have been introduced into dimolybdenum complexes,[4] OTs has previously functioned only as a weakly bound axial ligand or a non-bonded counter-ion in this field of chemistry.[5]

The substitution of mhp by OTs under mild conditions provides a method of partially replacing the bridging mhp ligands of $[Rh_2(mhp)_4]$, thus leading to the possibility of the controlled development of the chemistry of Rh_2^{4+}–mhp and related complexes.

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