Preparation of New Triple-bridged Dimers of Ruthenium(II) by Protonation of Basic Ruthenium Hydrides with the Weak Acids HX (X = OH, SH, SMe, or F); *X*-Ray Crystal and Molecular Structure of $[Ru_2(OH)_3(PMe_2Ph)_6][BPh_4]$

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Summary Solutions containing $[RuH(cod)L_3]^+$ [L = PMe_2Ph, $PMePh_2$, or $P(OMe)Ph_2$; cod = cyclo-octadiene] in refluxing acetone–methanol produce $[Ru_2X_3L_6]^+$ with HX (X = OH, SH, SMe, I, or F); the *X*-ray structure of $[Ru_2(OH)_3(PMe_2Ph)_6][BPh_4]$ has been determined and further reactions of some of the dimers are discussed.

ALTHOUGH the dimeric triple halogen-bridged cations $[L_3RuX_3RuL_3]^+$ (X = Cl or Br; L = tertiary phosphine) are known,[1] no general synthetic route to similar ruthenium(II) cations containing other anionic bridging groups has yet been devised. The recent reports[2] on the compounds $[(\eta^6\text{-}C_6H_6)Ru(OH)_3Ru(\eta^6\text{-}C_6H_6)]Cl\cdot 3H_2O$ and $[\{(\eta^6\text{-}C_6H_6)Ru(OH)\}_4][(SO_4)_2]\cdot 12H_2O$ have now prompted us to report our preliminary results on the interaction of weak acids with ruthenium(II) cations containing a basic hydride ligand. This has provided a route to high yields of novel ruthenium(II) dimeric salts and, by protonation of the conjugate base ligands in some of these compounds, to labile ruthenium(II) cations in solution.

We have recently[3] synthesised the salts $[RuH(cod)L_3][PF_6]$ [I; L = PMe_2Ph, $PMePh_2$, or $P(OMe)Ph_2$; cod = cyclo-octadiene] from $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ in degassed methanol. We now find that if the reaction is performed in refluxing acetone–methanol mixtures, deep red solutions initially form which, in the presence of H_2O, H_2S, HSMe, or HF, give the dimeric cations $[L_3RuX_3RuL_3]^+$ [II; X = OH, L = PMe_2Ph, $PMePh_2$, or P $(OMe)Ph_2$; X = F, SH, or SMe, L = PMe_2Ph] which were characterised as the PF_6^- or BPh_4^- salts. The presence of bridging OH and SH groups were inferred from bands ν(OH) at 3600 and ν(SH) at 2540 cm^{-1}, anomalously high but apparently[4] characteristic high field ^{1}H n.m.r. resonances between τ 12·5—13·5, and, in the case of one of the complexes, by a three-dimensional *X*-ray diffraction study. SMe resonances were observed as a singlet at τ 9·60.

Crystal data: $[Ru_2(OH)_3(PMe_2Ph)_6][BPh_4]$, M 1401·4, pale-yellow needles, space group $P2_12_12_1$, $a = 16{\cdot}26$, $b = 26{\cdot}73$, $c = 16{\cdot}21$ ($\pm 0{\cdot}02$)Å, $Z = 4$, $D_m = 1{\cdot}30$, $D_c = 1{\cdot}32$ g cm^{-3}. Intensity data were collected on a Philips automatic four-circle diffractometer† with graphite-monochromatized Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). The structure was solved by Patterson and Fourier methods using the 3406 observed reflections [$I > 2\sigma(I)$] and was refined by full-matrix least-squares, with isotropic temperature factors for all atoms, to $R = 0{\cdot}063$. Anisotropic refinement is still continuing.‡

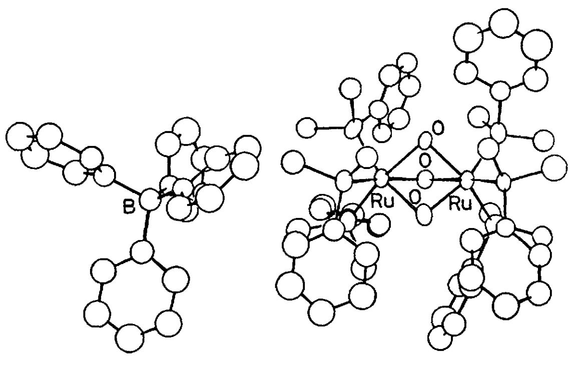

FIGURE. The structure of $[Ru_2(OH)_3(PMe_2Ph)_6][BPh_4]$.

The structure is illustrated in the Figure. The two ruthenium atoms have a distorted octahedral co-ordination and are linked by three bridging oxygen atoms. The remaining two sets of facial co-ordination sites are occupied by PMe_2Ph ligands. The Ru–O bonds range in length from 2·15 to 2·21 Å and the mean Ru–P distance is 2·28 Å. Repulsions between the substituents of the phosphine ligands, as shown by the mean P–Ru–P angle of 95°, and the small O–Ru–O angles (mean 75°), cause the observed distortion from ideal octahedral co-ordination. The Ru . . . Ru separation of 3·08 Å is significantly less than the separation found[5] in $[Ru_2Cl_3(PMe_2Ph)_6]^+$ (3·39 Å) and is simply the consequence of the Ru–O distances and Ru–O–Ru angles (mean 90°) which draw the two metal atoms close to each other. This feature is also demonstrated[6] in the anion $[W_2(OH)_3(CO)_6]^{3-}$ with no W–W bond, in which the W . . . W distance at 3·23 Å is similar to that found in the W–W bonded dimer $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$. However in the novel tetrameric complex $[\{(\eta^6\text{-}C_6H_6)Ru(OH)\}_4]^{4+}$ the larger Ru–O–Ru angle of 102° produces a Ru . . . Ru separation of 3·29 Å.[2b]

These products presumably form by the interaction of a basic ruthenium hydrido-species with the weak acid with concomitant loss of H_2, followed by a final step involving the deprotonation of, for example, a ruthenium-aquo species as shown in the Scheme. When (I; L = PMe_2Ph or $PMePh_2$) was heated to reflux in dry methanol containing either CHX_3 or HX, the complexes (II; X = Cl,[1] Br, or I; L = PMe_2Ph or $PMePh_2$) were obtained. A complex, analysing for (II; X = H, L = PMe_2Ph), was obtained by refluxing the complex $[Ru(O_2CH)(PMe_2Ph)_4][PF_6]$[7] in

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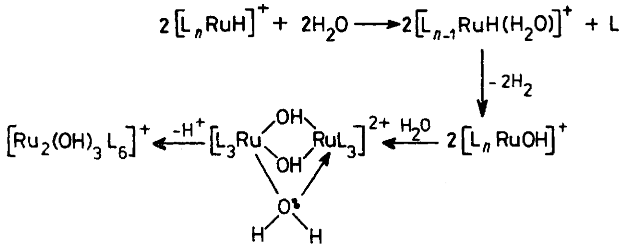
† The measurements were carried out at N.P.R.L., C.S.I.R.

‡ 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.

methanol in air but we have been unable to obtain confirmatory i.r. or ^{1}H n.m.r. data for the bridging hydride ligands and to date have not obtained crystals suitable for an *X*-ray analysis.



SCHEME

Attempts at forming labile ruthenium(II) cations by protonating the bridging groups are underway. For example, treatment of (II; X = OH or H, L = PMe_2Ph) with HPF_6 in MeCN gave initially *fac*-[$Ru(MeCN)_3(PMe_2Ph)_3$][$(PF_6)_2$] which readily isomerised to the *mer*-isomer on recrystallisation. Similar reactions in acetone solution gave effectively the solvolysed cation $[Ru(acetone)_3(PMe_2Ph)_3]^{2+}$ which appears to react with PhC≡CPh, PPh_3, and BPh_4^- to give π-arene products and with a range of donor molecules to give dicationic ruthenium(II) products.

Reactions of (II; X = OH or H; L = PMe_2Ph or $PMePh_2$) with HNO_3 and CF_3CO_2H gave the neutral compounds $[RuY_2L_3]$ (Y = ONO_2 or O_2CCF_3) which were also interconvertible on addition of the respective acid. Corresponding additions of these acids with the cation $[RuH(PMe_2Ph)_5]^+$ [8] produced $[Ru(Y)(PMe_2Ph)_4]^+$ (Y = ONO_2 or O_2CCF_3) and both the neutral products and the latter cations react with HPF_6 in acetone to give solvolysed 'unsaturated' species in solution with three and two free co-ordination sites, respectively.

We are at present extending our investigations into the formation of other ruthenium(II) bridged systems. For instance we find that refluxing the compounds $[RuX_2(cod)(NCR)_2]$ (III; X = Cl or Br, R = Me or Ph) in methanol produces [(cod)XRuX$_3$Ru(NCR)(cod)] whilst interaction of $SnMe_4$ with (III; X = Cl or Br) gives $[RuX(Me)(cod)(NCR)]_2$.

(*Received*, 23*rd August* 1977; *Com.* 897.

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