Metallation and Rearrangement Reactions in Ruthenium–Triphenyl Phosphite Complexes: Crystal Structure of $HRu_2(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]$

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Summary The structure of a binuclear complex hydride obtained by controlled pyrolysis of $Ru_3(CO)_9[P(OPh)_3]_3$ has been determined; unusual features include the bridging of the two metal atoms by both an $OP(OPh)_2$ group and the phenyl ring of one of the two *ortho*-metallated phosphite ligands.

Chromatography of the deep yellow solution obtained by heating $Ru_3(CO)_9[P(OPh)_3]_3$ in decalin affords two isomers of $Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$ (I), $H_4Ru_4(CO)_9[P(OPh)_3]_3$ (II), and the binuclear complex $HRu_2(CO)_3[P(OC_6H_4)(OPh)_2]_2$-$[OP(OPh)_2]$ (III). The formation of *ortho*-metallated complexes of type (I) by similar treatment of $RuCl_2(CO)_2$-$[P(OPh)_3]_2$ has been reported previously;[1] our complexes were characterised by the same methods. The polynuclear hydride (II) was characterised by analysis and mass spectrometry; the ^1H n.m.r. spectrum contained a broad resonance at τ 27·31.

Consistent analyses and molecular weight determinations (including mass spectrometry) on (III) indicated the presence of only eight phenyl groups. A strong band in the i.r. spectrum at 1075 cm^{-1} is assigned to ν(PO). Both observations are consistent with a $OP(OPh)_2$ group σ-bonded to a metal atom, as described previously for some π-cyclopentadienyl–molybdenum and –iron complexes.[2] In the latter, however, ν(PO) occurs in the region 1160–1180 cm^{-1}, so that this group may also be co-ordinated to ruthenium by the oxygen atom in complex (III).

The ν(CO) spectrum of (III) contains three strong terminal CO bands, and the fingerprint region of the i.r. spectrum contained absorptions in regions previously associated with *ortho*-metallated ligands. The ^1H n.m.r. spectrum confirmed the presence of metallated aryl groups, and also contained an eight-line multiplet at τ 20·8, indicating the presence of a metal-bonded proton, coupled to three different phosphorus nuclei.

A single-crystal *X*-ray study of complex (III) confirms the presence of both *ortho*-metallated phosphite ligands, and the three CO groups. In addition, however, the bridging of both ruthenium atoms by the $OP(OPh)_2$ group, and by one of the metallated aryl groups, deserves comment.

Crystal data:—$C_{51}H_{39}O_{12}P_3Ru_2$, M = 1138·9; white monoclinic crystals, a = 22·06, b = 11·11, c = 20·06 Å, β = 91·75°; space group $P2_1/c$; D_m = 1·52, D_c = 1·54 for Z = 4. At the present stage of refinement R = 0·12 for the 2234 independent reflexions having $I/\sigma(I) \geqslant 2{\cdot}5$.

The structure of complex (III) is shown in the Figure. The two ruthenium atoms are separated by 2·889(6) Å, and are bonded to one [Ru(1)] and to two [Ru(2)] terminal CO groups, respectively (mean Ru–C, 1·84; mean C–O, 1·22 Å). An *ortho*-metallated $P(OC_6H_4)(OPh)_2$ group is attached to Ru(1); this is analogous to those found in $IrCl[P(OC_6H_4)$-

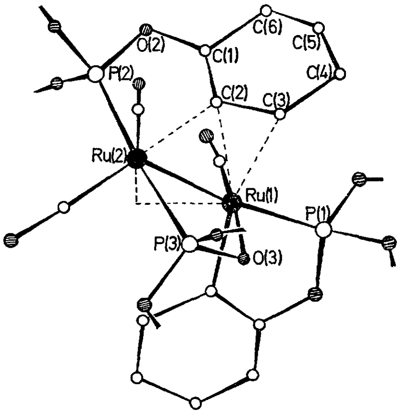

Figure. *Molecular structure of* $HRu_2(CO)_3[P(OC_6H_4)(OPh)_2]_2$-$[OP(OPh)_2]$ (*six phenyl groups have been omitted for clarity*). *Intersection of dotted lines from* Ru(1) *and* Ru(2) *indicates probable position of the hydrogen atom* [Ru(2)–H = 1·7 Å].

$(OPh)_2]_2[P(OPh)_3]$.[3] A point of interest is the Ru(1)–P(1) distance of 2·134(4) Å, one of the shortest yet found in ruthenium–phosphine complexes.

The two metal atoms are bridged by a diphenylphosphonate group to give a four-membered ring which is substantially planar. The Ru(1)–O(3) distance [2·29(3) Å] is longer by some 0·1 Å than the sum of the covalent radii, while the P(3)–O(3) distance [1·49(3) Å] reflects its multiple bond character.

The second *ortho*-metallated phosphite ligand is bonded to both metal atoms. The Ru(2)–C(2) bond length is 2·12(4) Å and both C(2) and C(3) are found to be within bonding distance of Ru(1) [2·33(4) and 2·59(4) Å, respectively]. This interaction is best described in terms of a four-centre three-electron contribution from the bridging aryl group to the two metal atoms, both C(1) and C(4) being too distant from Ru(1) to be involved in any more extensively delocalised π-type interaction. The Ru(2)–C(2) distance is similar to that found in the *ortho*-metallated phosphite chelated to Ru(1) [2·17(4) Å], and to the Ru–C σ-bond lengths reported for $Ru_2(CO)_6(C_8H_8)$ [2·14(2) Å][4] and $RuH(C_{10}H_7)(dmpe)_2$ [2·16(1) Å].[5] The bridging phenyl ring is coplanar with atoms Ru(2), P(2), and O(2), and the constraints imposed by this planarity of the fused five- and six-membered ring system may explain the asymmetric interaction between Ru(1) and the phenyl ring. There is some similarity between this bridging aryl group and the complexed benzyne group found in $Os_3(CO)_7(PPh_2)_2(C_6H_4)$.[6]

A reasonable location for the metal-bonded hydrogen atom is in an asymmetric bridging position, nearer to Ru(2). There is a vacant octahedral site, *trans* to a CO group, on this atom, and such a position is consistent with both the chemical shift (lying between values found for terminal and bridging hydrogens), and with the interaction with all three phosphorus atoms. A formal electron count reveals that both metal atoms attain the conventional 18-electron total.

Complex (III) is probably an intermediate in the production of the mononuclear *ortho*-metallated complexes (I); there is an interesting resemblance of the co-ordination of the bridging aryl group in complex (III) to Parshall's proposed intermediate in the palladation reaction.[7] This complex also provides another example of the growing class of polynuclear complexes which can be envisaged as being formed by an oxidative-addition reaction across a metal–metal bond, many of which are formed in the reactions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$.

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