The Structure of a Hydridonaphthylruthenium(II) Complex

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Summary The compound, [Ru pp$_2$ (naphthalene)] [pp = 1,2-bis(dimethylphosphino)ethane], whose chemical reactions are consistent with its formulation as an ruthenium(0)–naphthalene complex, has been shown by an *X*-ray analysis to be, in the solid state, a hydridonaphthylruthenium(II) complex.

A NUMBER of reactions have been described in which an aryl or alkyl hydrogen becomes labile in the presence of certain transition metals. In some cases the hydrogen is lost entirely;[1] in others it becomes irreversibly attached to the central metal atom;[2] while in several cases[3,4] a tautomeric equilibrium is set up between the low-valent structure, and the higher-valent hydridic structure. One such equilibrium system is [Ru pp$_2$ (naphthalene)] [pp = 1,2-bis(dimethylphosphino)ethane],[4] which appears to behave chemically as a ruthenium(0)–naphthalene complex. For example, it readily pyrolyses to Ru pp$_2$. However, its physical properties suggest that in the solid state it is a hydridonaphthylruthenium(II) complex, which exists in solution in equilibrium with a small amount of the very reactive Ru^0 complex.

$$cis\text{-Ru}^{II}\text{H}(\text{C}_{10}\text{H}_7)(\text{Me}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PMe}_2)_2 \qquad \text{(Ia)}$$

$$\rightleftharpoons \text{Ru}^0(\text{C}_{10}\text{H}_8)(\text{Me}_2\cdot\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PMe}_2)_2 \qquad \text{(Ib)}$$

The preparation has been repeated and the crystal structure of [Ru pp$_2$(naphthalene)] determined confirming that, in the solid state, the compound has the hydridonaphthyl structure (Ia). Crystal data: monoclinic, a = 15·23, b = 10·14, c = 18·73 Å, β = 114°, space group $P2_1/c$, D_m = 1·30, Z = 4, D_c = 1·30, Picker diffractometer single-crystal data, Mo-K_α radiation (Nb filtered), μ = 8·2 cm.$^{-1}$ (no corrections were made for absorption). The structure was solved by standard techniques and refined by the method of least-squares (with calculation of anisotropic temperature factors for the ruthenium and phosphorus atoms) to R 0·080 for 3513 reflections.

The individual atom temperature factors suggest that some atoms have an excessive thermal motion or that there is possibly slight disorder within the crystal. As a consequence, the accurate determination of the positions of hydrogen atoms in the molecule is made difficult.

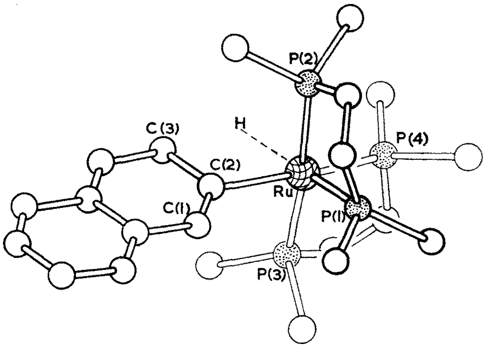

FIGURE 1.

The structure of the molecule is illustrated in Figure 1 and some bond distances and angles are given in Figure 2. The phosphine ligands and the naphthyl group form a square-pyramidal co-ordination arrangement around the metal atom. There is a peak of electron density, 0·4 eÅ^{-3} (background 0·15 eÅ^{-3}), 1·7 Å from the ruthenium atom in a position almost exactly *trans* to P(1). A hydrogen atom in such a position would complete an almost regular octahedral co-ordination arrangement around the ruthenium atom. The possible Ru–H bond-length, 1·7 Å, is the same distance as observed in $RuHCl(PPh_3)_3$,[5] and is comparable with Rh–H, 1·6 Å, in $RhHCO(PPh_3)_3$.[6]

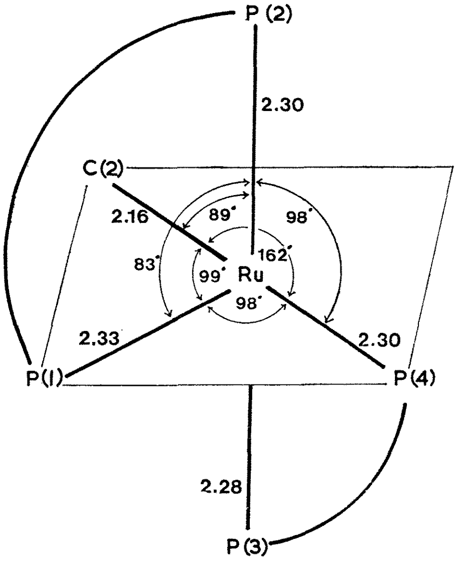

FIGURE 2. *Estimated standard deviations are for bond lengths,* Ru–P 0·005 Å, Ru–C 0·01 Å, *and for bond angles,* P–Ru–P 0·2°, P–Ru–C 0·3°.

Further evidence for the presence of an atom in the suggested position comes from the orientation of the plane of the naphthyl group. This group is inclined at 20° to the plane defined by the atoms, Ru, P(4), P(1), and C(2); in this orientation the contact distance between the hydrogen on C(3) and the hydrogen bound to ruthenium is 2·3 Å, approximately twice the van der Waals radius of 1·2 Å for hydrogen.[7] If the naphthyl group were to be rotated to be coplanar with the ruthenium equatorial plane, this contact would be reduced to an improbable 2·0 Å. The observed orientation of the naphthyl group seems to be determined by steric interaction with the hydridic hydrogen atom.

The crystal structure confirms that (Ia) is the 2-naphthyl isomer, as was shown originally using deuterium.[4] The ruthenium–carbon bond, 2·16 Å, is slightly longer than similar metal–carbon bonds, *e.g.* Rh–C, 2·08 Å in $[RhI_2(Me)(PPh_3)_2(C_6H_6)]$,[8] and in $[Rh_2I_2(Me)_4(SMe_2)_3]$,[9] and Pd–C, 2·0 Å in $[Pd(PEt_3)_2Cl(C_6H_4{\cdot}N{:}NPh)]$.[10]

The hydride migration in the interconversion (Ia) $\rightleftharpoons$ (Ib) is probably intramolecular as the aromatic nucleus apparently does not become detached from the complex during the migration.[4] The movement of the hydridic hydrogen is probably accompanied by a small rotation of the entire naphthyl group about an axis parallel to the Ru–P(2) bond. However the nature of the co-ordination of the naphthalene to the ruthenium atom in (Ib) remains uncertain.

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