X-Ray Structure of the Dimer of Bis(tetramethyldiphosphinoethane)ruthenium: Intermolecular Oxidative Addition of a C–H Bond to a Metal Atom

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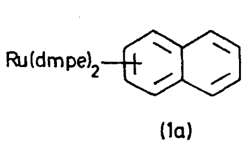
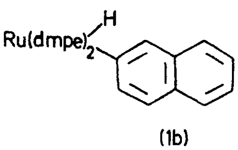
Summary The compound of stoicheiometry $(Me_2PCH_2CH_2PMe_2)_2Ru$, discovered a decade ago by Chatt and Davidson, is shown, by *X*-ray crystallography, to consist of centrosymmetric binuclear molecules resulting from oxidative addition of a methyl C–H bond originating on a ligand chelated to one Ru atom to the other Ru atom; the net result is a molecule with two octahedrally co-ordinated Ru atoms at the 1 and 4 positions of a $\overline{\mathrm{Ru{-}C{-}P{-}Ru{-}C{-}P}}$ ring, and a hydrogen atom ligand on each Ru atom at the most hindered position.

THE earliest examples of oxidative addition of a C–H bond to a transition-metal atom were two related compounds prepared by Chatt and Davidson[1] over a decade ago. $Ru(dmpe)_2C_{10}H_8$ (dmpe = $Me_2PCH_2CH_2PMe_2$; $C_{10}H_8$ = naphthalene) (**1**) was found to exist in solution in equilibrium between two tautomeric forms (**1a**) and (**1b**). In the solid state the substance consists of tautomer (**1b**) the structure of which has been reported in detail.[2] Pyrolysis of (**1**) gave (**2**), a rather insoluble solid of stoicheiometry $Ru(dmpe)_2$. I.r. data in particular indicated that in the solid state (**2**) contained an Ru–H bond. Hence, the tautomeric pair (**2a**) ⇌ (**2b**) were postulated, the solid being assumed to

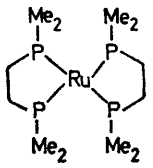


(1a)

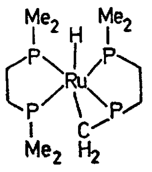


(1b)

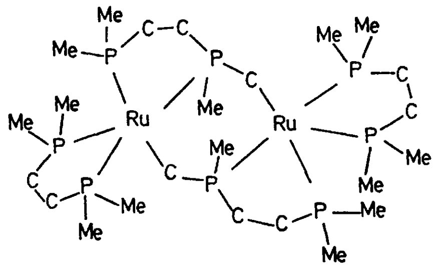
consist of (**2b**). An attempt[2] to confirm this foundered on a crystallographic error and we now report that the compound has the structure represented schematically in (**2c**) in the solid state. Chatt and Davidson were thus correct in their general conclusion that an oxidative addition of a PCH_2–H bond to Ru had occurred but incorrect in supposing it to have been an intramolecular process.



(2a)



(2b)



(2c)

We have confirmed as much of the reported chemistry of compounds (**1**) and (**2**) as we attempted to repeat, in attempts to obtain a crystalline sample of (**2**). However, just as we were isolating (**2**) we obtained from Dr. Davidson a crystalline sample. *Crystal data:* $C_{24}H_{64}P_8Ru_2$, space group $P\bar{1}$, $Z = 4$ [Ru(dmpe)$_2$ units], $a = 10{\cdot}028(4)$ $b = 13{\cdot}880(6)$, $c = 15{\cdot}018(6)$ Å, $\alpha = 95{\cdot}87(3)$, $\beta = 101{\cdot}27(3)$, $\gamma = 112{\cdot}02(3)^\circ$, $U = 1865(1)$ Å^3.† At the present stage of refinement, $R_1 = 0{\cdot}058$ and $R_2 = 0{\cdot}089$ for partly isotropic and partly anisotropic refinement. Complete anisotropic refinement will be carried out in the future.

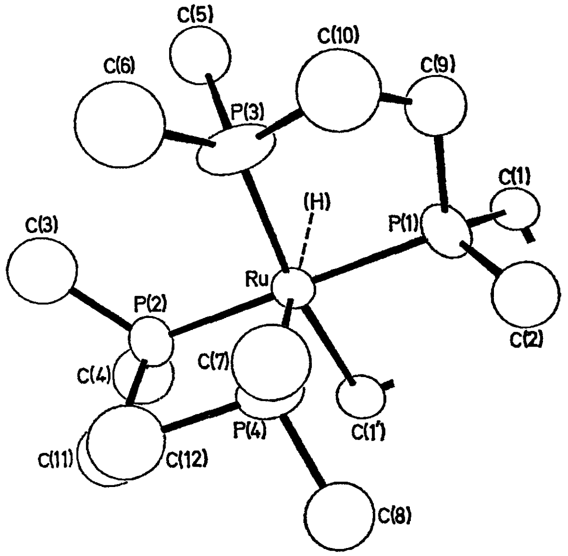


FIGURE. Co-ordination geometry of the ruthenium atom. Average bond distances (all with e.s.d.s of *ca* 0·01 Å) in Å: Ru–P(1), 2·32; Ru–P(2), 2·28; Ru–P(3), 2·26; Ru–P(4). 2·32; Ru–C(1'), 2·22; P–C, 1·85; C–C, 1·52.

There are two crystallographically independent binuclear molecules each lying at a crystallographic centre of inversion. They do not differ in any chemically significant way; the Figure shows the co-ordination sphere of a ruthenium atom with mean bond distances.

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† The previously reported unit cell had only half the correct volume, leading to an insoluble Patterson function.

[1] J. Chatt and J. N. Davidson, *J. Chem. Soc.*, 1965, 843.
[2] U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc.* (*A*), 1971, 1118.