Inorganica Chimica Acta Letters, 37 (1979) L521–L522
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

New Synthetic Route to Organophosphorus Ruthenium Dihydride Complexes. X-ray Crystal Structure of *Cis*-$H_2Ru(Ph_2PCH_2CH_2PPh_2)_2 \cdot C_6H_6$

P. PERTICI, G. VITULLI

Centro C.N.R. per le Macromolecole Stereoordinate ed Otticamente Attive, via Risorgimento 35, 56100 Pisa, Italy

W. PORZIO and M. ZOCCHI

Istituto di Chimica delle Macromolecole del C.N.R., via A. Corti 12, 20133 Milan, Italy and Istituto di Chimica Industriale del Politecnico, Sezione di Strutturistica, Piazza Leonardo da Vinci 32, 20133 Milan, Italy

Received July 2, 1979

Organophosphorus ruthenium dihydride complexes, H_2RuL_4, have attracted considerable interest during recent years, especially in connection with catalytic processes [1] and structure elucidation [2]. The synthesis of these complexes generally involves reactions of the appropriate phosphino-metal halide with hydrogen–hydrazine mixtures [3] or with sodium borohydride or lithium aluminum hydride [4].

We found a very simple general route to H_2RuL_4 complexes in the reaction of (η^4-cycloocta-1,5-diene)(η^6-cycloocta-1,3,5-triene)ruthenium(0) with hydrogen and a trivalent phosphorus compound, at room temperature. The cycloocta-1,5-diene and the cycloocta-1,3,5-triene are hydrogenated to a mixture of cyclooctene and cyclooctane and the vacant coordination positions on the ruthenium are filled by the phosphorus ligand and hydrogen atoms. This method has been used successfully for the preparation of the complexes $H_2Ru(PPh_3)_4$, $H_2Ru(PPh_2Me)_4$, $H_2Ru(PPhMe_2)_4$, $H_2Ru[P(OMe)_3]_4$, $H_2Ru(PPh_2CH_2CH_2PPh_2)_2$.

The molecular structure of the solvated complex $H_2Ru(Ph_2PCH_2CH_2PPh_2)_2 \cdot C_6H_6$, as determined by single crystal X-ray diffraction analysis, is shown in Fig. 1 and selected bond distances and angles are given in Table I. In the $H_2Ru(Ph_2PCH_2CH_2PPh_2)_2$ molecule, of non-crystallographic symmetry C_2, the coordination geometry around the ruthenium atom is that of a distorted octahedron with the hydridic hydrogens *cis* to each other and approximately in the plane defined by the metal atom and the phosphorus atoms P(2) and P(4). The distortion from a more regular octahedral geometry is a steric effect obviously associated with the small size of the hydrogen atoms. The molecular conformation is defined by the torsion angles reported in Table II.

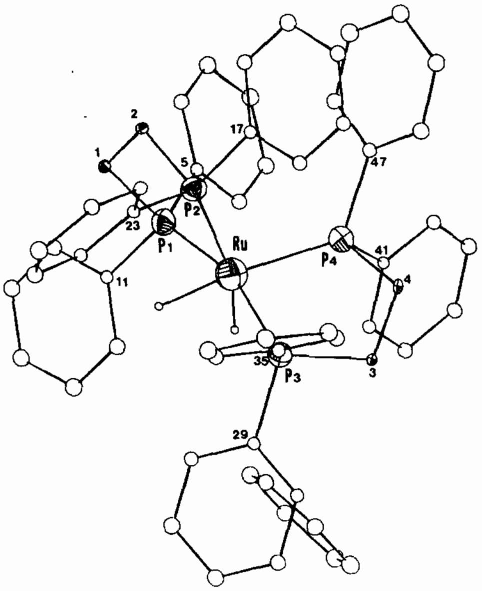

Fig. 1. The molecular structure of $H_2Ru(Ph_2PCH_2CH_2PPh_2)_2 \cdot C_6H_6$, as viewed along the *b* axis. For the sake of clarity the first carbon atom of each phenyl ring has been labelled with a number. The solvated benzene is shown in the lower part of the figure.

TABLE I. Relevant Bond Distances (Å) and Angles (deg), with e.s.d. s in Parentheses.

Ru–P(1)	2.288(3)	Ru–P(2)	2.322(3)
Ru–P(3)	2.278(3)	Ru–P(4)	2.317(3)
P(1)–C(1)	1.84(1)	P(1)–C(5)	1.84(1)
P(3)–C(3)	1.86(1)	P(3)–C(29)	1.85(1)
P(1)–C(11)	1.85(1)	P(2)–C(2)	1.85(1)
P(1)–C(35)	1.85(1)	P(4)–C(4)	1.85(1)
P(2)–C(17)	1.84(1)	P(2)–C(23)	1.87(1)
P(4)–C(41)	1.86(1)	P(4)–C(47)	1.86(1)
C(1)–C(2)	1.55(2)	Ru–H(1)	1.58(15)
C(3)–C(4)	1.54(2)	Ru–H(2)	1.58(15)
P(1)–Ru–P(2)	85.4(1)	P(2)–Ru–P(3)	106.0(1)
P(3)–Ru–P(4)	85.3(1)	P(1)–Ru–P(4)	106.9(1)
P(1)–Ru–P(3)	161.5(2)	P(2)–Ru–P(4)	101.8(1)
Ru–P(1)–C(1)	107.9(4)	Ru–P(1)–C(5)	123.5(3)
Ru–P(3)–C(3)	108.8(4)	Ru–P(3)–C(29)	119.5(3)
Ru–P(1)–C(11)	117.9(3)	Ru–P(2)–C(2)	108.3(4)
Ru–P(3)–C(35)	122.5(3)	Ru–P(4)–C(4)	107.6(4)
Ru–P(2)–C(17)	124.0(2)	Ru–P(2)–C(23)	119.1(2)
Ru–P(4)–C(41)	120.5(3)	Ru–P(4)–C(47)	122.9(3)
P(1)–C(1)–C(2)	109.9(7)	P(2)–C(2)–C(1)	109.6(7)
P(3)–C(3)–C(4)	107.7(7)	P(4)–C(4)–C(3)	110.1(7)

No interatomic non-bonding distance in the molecule is smaller than the sum of the relevant Van der Waals radii and the same is true for the intermolecular distances which define the crystal packing, also including the solvated benzene molecules. It may be interesting to note that the two phenyl rings C(17)–C(22) and C(47)–C(52), which are bonded

TABLE II. Relevant Torsion Angles (deg).[a]

Ru–P(1)–C(1)–C(2)	–42
Ru–P(3)–C(3)–C(4)	–41
Ru–P(2)–C(2)–C(1)	–33
Ru–P(4)–C(4)–C(3)	–37
P(1)–Ru–P(2)–C(2)	6
P(3)–Ru–P(4)–C(4)	9
P(2)–Ru–P(1)–C(1)	17
P(4)–Ru–P(3)–C(3)	15
P(3)–Ru–P(1)–C(1)	–113
P(1)–Ru–P(3)–C(3)	–118
P(3)–Ru–P(2)–C(2)	171
P(1)–Ru–P(4)–C(4)	175
P(4)–Ru–P(1)–C(1)	118
P(2)–Ru–P(3)–C(3)	115
P(4)–Ru–P(2)–C(2)	–100
P(2)–Ru–P(4)–C(4)	–96
P(1)–C(1)–C(2)–P(2)	47
P(3)–C(3)–C(4)–P(4)	49
P(3)–Ru–P(1)–C(5)	126
P(1)–Ru–P(3)–C(35)	122
P(3)–Ru–P(1)–C(11)	3
P(1)–Ru–P(3)–C(29)	–2
P(4)–Ru–P(2)–C(17)	19
P(2)–Ru–P(4)–C(47)	23
P(4)–Ru–P(2)–C(23)	146
P(2)–Ru–P(4)–C(41)	153

[a] The torsion angle is counted positive when, looking along the torsion axis, the far bond is rotated clockwise with respect to the near bond.

to P(2) and P(4) respectively, face each other in a graphite-like manner at an average distance of 3.68 Å.

The average Ru–H distance is 1.58(15) Å, in good agreement with the value of 1.67 Å [5] and 1.65 Å [6] found by others. The *trans*-effect induced by the hydridic hydrogens onto the diphosphino groups is shown by the difference between the average distance of the Ru–P bonds *trans* to the hydrogen atoms [2.320(4) Å] and that of the two other Ru–P bonds [2.293(3) Å]. This difference is very significant in view of the smallness of the corresponding standard deviation [0.005 Å].

Studies are now in progress to prepare analogous complexes, using optically active organophosphorus compounds as ligands.

Experimental

All manipulations were carried out under rigorously oxygen-free conditions.

Only the preparation of the complex $H_2Ru(Ph_2PCH_2CH_2PPh_2)_2$ is described in details, the experimental procedure being substantially the same for all other compounds of the same type. The yields of the purified products were in the range of 60–80%.

In a typical experiment a solution of 150 mg (0.47 mmol) of (η^4-cycloocta-1,5-diene)(η^6-cycloocta-1,3,5-triene)ruthenium and 468 mg (118 mmol) of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ in tetrahydrofuran (15 ml) was stirred for 3 hr at room temperature, under atmospheric pressure of hydrogen. Evaporation of the solvent and recrystallization of the residue from benzene–pentane yielded 340 mg of solvated product $H_2Ru(Ph_2PCH_2CH_2PPh_2)_2 \cdot C_6H_6$. νRu–H 1880 cm^{-1}. *Anal.* Calcd. for $C_{58}H_{56}P_4Ru$: C, 71.3; H, 5.73; P. 12.68. Found: C, 71.05; H, 5.80; P, 12.55.

The $H_2Ru(Ph_2PCH_2CH_2PPh_2)_2 \cdot C_6H_6$ crystal is monoclinic, space group $P2_1/c$ with a = 14.254(3), b = 12.401(2), c = 28.263(8) Å, β = 96.63(6)°, D_c = 1.31 g cm^{-3} for Z = 4. Three-dimensional intensity data were collected with MoKα radiation on a Philips PW1100 four-circle diffractometer by the ω-scan technique. Intensity data were corrected for Lorentz and polarization effects but not for adsorption, in view of the small crystal sizes and absorption coefficient (μ = 4.77 cm^{-1}). The intensities were considered observed when $I > 3.5\sigma$ (σ^2 = peak counts + total background counts). The crystal structure was solved by Patterson and Fourier methods and was refined by least squares in the block diagonal approximation. The phenyl rings were treated as rigid bodies. The contribution of the hydrogen atoms to the structure factors was taken into account in the last cycles of the least-squares refinement (final R value of 0.064). The hydride hydrogens were located in a Fourier difference map.

Acknowledgment

One of us (M.Z.) acknowledges financial support by the C.N.R., Rome, Italy.

References

1 C. A. Tolman in 'Transition Metal Hydrides', Vol. 1, E. L. Muetterties Ed., Marcel Dekker, New York, N.Y., Chapter 6 (1971).

2 J. P. Jesson, *ibid.*, Chapter 4.

3 K. C. Dewhirst, W. Keim and C. A. Reilly, *Inorg. Chem., 7,* 546 (1968).

4 D. H. Gerlach, W. G. Peet and E. L. Muetterties, *J. Am. Chem. Soc., 94,* 4545 (1972).

5 U. Gregory, S. D. Ibekwe and B. T. Kilbourn, *J. Chem. Soc. A,* 1118 (1971).

6 F. A. Cotton, D. L. Hunter and B. A. Frenz, *Inorg. Chem. Acta, 10,* 127 (1974).