Inorganica Chimica Acta, 16 (1976) 203–207

The Mechanism of Formation and Crystal Structure of *trans*-dichlorotetrakis-(dimethylphosphine)ruthenium(II), $RuCl_2[PH(CH_3)_2]_4$

F. A. COTTON, B. A. FRENZ and D. L. HUNTER
Department of Chemistry, Texas A & M University, College Station, Texas 77843, U.S.A.
Received June 30, 1975

The title compound has been prepared by the reaction of tetramethylbiphosphine and ruthenium trichloride hydrate. When ethanol is present in the reaction medium it is oxidized to acetaldehyde; however, in the absence of ethanol the water of hydration is the source of hydrogen, as shown by incorporation of deuterium, introduced as D_2O. The single crystal x-ray structural study demonstrates that the compound has a trans-octahedral configuration as anticipated from proton nmr. Crystal data: space group, Pbca; $a = 11.571(3)$ Å; $b = 12.133(2)$ Å; $c = 12.831(4)$ Å; $V = 1801.3(8)$ Å^3; $Z = 4$. The molecule lies on a crystallographic inversion center and has the following metal–ligand bond lengths: Ru–P, 2.323(1) Å, 2.331(1) Å, Ru–Cl, 2.440(1) Å. The P–C distances range from 1.837(7) Å to 1.841(7) Å, with a mean of 1.839 Å.

Introduction

Octahedral ruthenium phosphine complexes have been much studied in the past. Complexes with chelating phosphine ligands such as $RuX_2(R_2P(CH_2)_nPR_2)_2$ with n = 1,2 and R = Me, Et, Ph are well known,[1,2] but the case where n = 0, *i.e.,* with ligands of the type R_2PPR_2, had not been reported at the time we undertook this work in early 1972, with any metal whatever. A few complexes with the intact Me_2PPMe_2 molecule present as a ligand have since been reported.[3] The scarcity of such complexes is understandable considering the highly strained P–Ru–P ring that would be present. Following the preparative methods of Chatt and Hayter[1], we employed tetramethylbiphosphine (TMBP) to see if a complex containing the three-membered ring could be isolated or whether the ligand would undergo change in preference to forming the strained three-membered ring. The yellow product that was isolated from the reaction arises by reductive scission of the P–P bond during the reaction yielding a dimethylphosphine complex, $RuCl_2[PH(CH_3)_2]_4$.

To our knowledge only three metal complexes of dimethylphosphine have previously been reported.[4–6] $[Cr(NCS)_4(PHMe_2)_2]^-$ has been prepared by phosphine substitution of thiocyanate[4] and the diffuse-reflectance and solution spectra recorded in a study of the spectrochemical series of various phosphines. Also palladium complexes of dimethylphosphine starting with dimethylphosphine as a ligand have been reported by Hayter.[5]

The compound $(CH_3)_2HPBH_3$ has recently been described and its structure determined by microwave spectroscopy.[6]

A point of particular interest in our own study was the determination of the source of hydrogen atoms used to reduce the P–P bond and form dimethylphosphine. *Trans*-dichlortetrakis(dimethylphosphine)ruthenium(II), $RuCl_2[PH(CH_3)_2]_4$, has been fully characterized by ir, nmr and a single crystal x-ray study.

Experimental

Infrared spectra were recorded on a Perkin–Elmer Model 461 spectrophotometer and calibrated with polystyrene. A Varian Associates HA-100 spectrometer was used for the collection of proton nmr data.

Synthesis

(a) Ruthenium trichloride hydrate, 1.0 g, and TMBP,[7] 0.6 ml, were added under nitrogen to 100 ml of freeze–thaw degassed absolute ethanol. A dark solid was immediately formed. The reaction mixture was refluxed for about 20 hours during which the color of the solution changed from green to yellow–orange. The mixture was reduced in volume and placed on a Florisil (100–200 mesh) column (1.0 × 36.0 cm) in 3 to 5 ml of chloroform. The column was washed with 30 ml of hexane and the yellow compound was then eluted with chloroform. The complex was recrystallized from tetrachloroethylene and pentane. Yield, 0.3 g (19%). Mp 209–210° C; it sublimes in vacuum between 145° C and 175° C. A parent ion multiplet is observed in the mass spectrum with the principal peak at m/e = 421. The calculated mean molecular weight of 420.21 is obtained using the chemical atomic weight of ruthenium, 101.07. However, the predominant isotope (32%) is ^{102}Ru and this accounts for the main peak in the parent ion multiplet at 421.

(b) The preparation was repeated as above using dry tetrahydrofuran (distilled over a Na–K alloy with benzophenone present as an indicator) as a solvent. The yield of 1 was comparable to that obtained in (a). The mp, as well as the ir and nmr spectra were identical with those of the product prepared in ethanol.

(c) Deuterium oxide was added, 3 mol per mol of $RuCl_3 \cdot 3H_2O$, to a dry THF solution and the preparation by method (b) was repeated. The solution was refluxed for one hour with the $RuCl_3 \cdot xH_2O$ before the TMBP was added. The mp of the product was identical to that of the product obtained by procedures (a) and (b).

(d) The preparation was again repeated in dry THF with 1.5 mol of ethanol being added per mol of ruthenium. The product, characterized by mp, ir and nmr, was identical to that isolated previously. During the reaction and the solvent removal step of the reaction workup, the solvents were trapped. A phenylhydrazone derivative was prepared from that solution. This derivative, after recrystallization, had a melting point of 62°–63° C, compared with a literature[8] mp of 63° C for the phenylhydrazone derivative of acetaldehyde.

Collection of X-ray Data

A yellow cube-like crystal grown by vapor diffusion of n-pentane and tetrachloroethylene in two sample vials at 0° C was used. The crystal of approximate dimensions 0.5 × 0.5 × 0.5 mm, was fixed on the top of a glass fiber with epoxy glue. Data were collected at a temperature of 18° ± 2° C on a Syntex P$\bar{1}$ automated diffractometer using MoK_α radiation monochromatized with a graphite crystal in the incident beam. Least-squares refinement of fifteen centered reflections produced the orientation matrix for data collection and gave the following dimensions for the orthorhombic unit cell: a = 11.571(3)Å; b = 12.133(2)Å; c = 12.831(4)Å; V = 1801.3(8)Å^3. The space group was shown to be Pbca from the systematically absent reflections: 0kl, k = 2n + 1; h0l, l = 2n + 1; hk0, h = 2n + 1. The calculated density is 1.55 g cm^{-3} for four formula units of $RuC_8H_{28}Cl_2P_4$.

Intensity data were collected in the range $0° < 2\Theta \leqq 55.0°$. The Θ–2Θ scan technique with a variable scan rate from 4.0–24.0° C per min and a scan range from $2\Theta(MoK\alpha_1) - 0.7°$ C to $2\Theta(MoK\alpha_2) + 0.7°$ C was used. The intensities of three standard reflections, measured every 100 reflections, showed no significant variations.

The intensities of 2463 independent reflections were recorded; of these, 1478 had intensities three times greater than their estimated standard deviations, $\sigma(I)$. Here $\sigma(I)$ is calculated from the expression given previously[9] using values of 0.065 and 0.5 for p and R, respectively. No absorption correction (μ = 14.7 cm^{-1}) was made.

TABLE I. Positional and Thermal Parameters[a].

A. *Anisotropically Refined Atoms*[b]

Atom	X	Y	Z	β_{11}	β_{22}	β_{22}	β_{12}	β_{13}	β_{23}
Ru	0.0	0.0	0.0	0.00416(5)	0.00333(4)	0.00381(4)	–0.00003(3)	–0.00013(3)	0.00016(2)
Cl	0.0734(1)	–0.1459(1)	0.1129(1)	0.0078(1)	0.00487(8)	0.00575(8)	0.00059(8)	–0.00108(8)	0.00137(7)
P(1)	0.1928(1)	0.0321(1)	–0.0403(1)	0.00472(9)	0.00543(9)	0.0068(1)	–0.0037(9)	0.00070(9)	0.00010(9)
P(2)	0.0014(1)	0.1303(1)	0.1335(1)	0.0066(1)	0.00474(9)	0.00498(8)	0.00058(8)	–0.00044(8)	–0.00076(7)
C(1,1)	0.3013(6)	0.0505(6)	0.0632(6)	0.0058(4)	0.0103(6)	0.0010(6)	–0.0010(5)	–0.0022(4)	0.0003(5)
C(1,2)	0.2245(7)	0.1434(7)	–0.1330(6)	0.0092(6)	0.0122(7)	0.0119(7)	–0.0029(6)	0.0020(5)	0.0060(6)
C(2,1)	0.0630(7)	0.0943(6)	0.2609(5)	0.0142(8)	0.0095(5)	0.0049(3)	0.0020(6)	–0.0023(5)	–0.0014(4)
C(2,2)	0.0621(6)	0.2677(4)	0.1086(5)	0.0111(6)	0.0040(3)	0.0082(4)	–0.0011(4)	–0.0006(4)	–0.0013(3)

B. *Isotropically Refined Atoms*

Atom	X	Y	Z	B(Å^2)
H(1)	0.249(5)	–0.069(4)	–0.069(4)	4(1)
H(2)	–0.092(7)	0.144(6)	0.138(6)	9(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit. [b] Anisotropic temperature parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Structure Solution and Refinement[10]

A Patterson function was calculated and the ruthenium atom (in the special position 0,0,0) as well as one chlorine atom and two phosphorus atoms were located. Because the ruthenium is situated on an inversion center only one-half of the molecule needed to be accounted for in the usual combination of least-squares refinements and difference Fourier syntheses employed to solve the structure.

The atoms located in the Patterson map were refined to give $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.170$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.271$. A difference electron density map then showed the positions of the four carbon atoms. Two cycles of isotropic refinement, yielding $R_1 = 0.074$ and $R_2 = 0.120$, followed by two cycles of anisotropic refinement ($R_1 = 0.038$ and $R_2 = 0.076$) and then a difference map yielded the positions of the phosphine hydrogen atoms. A final two cycles of refinement in which the hydrogen atoms were treated isotropically and all other atoms anisotropically gave residuals of $R_1 = 0.037$ and $R_2 = 0.068$.

In all refinements the atomic scattering factors were taken from the tabulations of Cromer and Waber[11] and corrected for anomalous dispersion using $\Delta f'$ and $\Delta f''$ from Cromer and Liberman.[12]

A final difference map had no peak with a density exceeding 0.37 $eÅ^{-3}$ while the density of a phosphorus hydrogen atom was about 0.6 $eÅ^{-3}$ in a previous map. No shift in the last cycle of the least-squares refinement exceeded 0.33 times the esd of the parameters. Of the 1478 reflections used in the refinement, there were 62 for which $||F_o|-|F_c||$ exceeded $3\sigma(F_o)$. No dependence of the $\Sigma w(|F_o|-|F_c|)^2$ values on the indices, on $(\sin\Theta)/\lambda$ or on $|F_o|$ was noted. The error in an observation of unit weight is 1.66.

A listing of observed and calculated structure factor amplitudes for the data included in refinement is given in a Table which may be obtained from the Editor upon request.

The final positional and thermal parameters are listed in Table I, with root-mean-square amplitudes of vibration given in Table II.

TABLE II. Root Mean Square Amplitudes of Vibration (Å).

Atom	Min	Intermed	Max
Ru	0.157(1)	0.167(1)	0.180(1)
Cl	0.165(2)	0.224(2)	0.244(2)
P(1)	0.174(2)	0.203(2)	0.240(2)
P(2)	0.177(2)	0.200(2)	0.224(2)
C(1,1)	0.182(8)	0.276(8)	0.300(9)
C(1,2)	0.170(9)	0.284(9)	0.378(10)
C(2,1)	0.186(8)	0.254(8)	0.330(9)
C(2,2)	0.162(8)	0.264(7)	0.279(8)

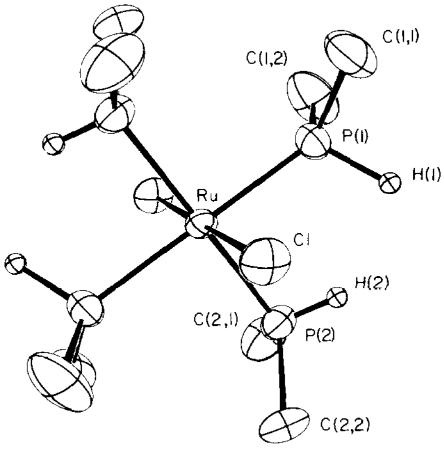

Figure 1. An ORTEP drawing of the molecule $RuCl_2[PH(CH_3)_2]_4$. Thermal ellipsoids enclose 50% of the electron density, except for H atoms which are of arbitrary size. The numbering scheme is shown; unnumbered atoms are related by an inversion center to those numbered.

TABLE III. Ineratomic Distances (Å).

Ru–Cl	2.440(1)		
Ru–P(1)	2.323(1)		
Ru–P(2)	2.331(1)		
P(1)–C(1,1)	1.841(7)	P(2)–C(2,1)	1.836(6)
P(1)–C(1,2)	1.837(7)	P(2)–C(2,2)	1.837(6)
P(1)–H(1)	1.44(5)	P(2)–H(2)	1.10(8)

Results and Discussion

Crystal Structure

The structure of *trans*-$RuCl_2(PHMe_2)_4$ is shown in Figure 1. The bond distances and bond angles are listed in Tables III and IV. The geometry around the ruthenium atom, which lies on a center of inversion, is that of an octahedron with the chlorine atoms occupying positions *trans* to each other. The coordination geometry around the phosphorus atoms is distorted tetrahedral.

The distances found in this structure are all reasonable when compared to those in other chlorophosphine ruthenium structures.[13–15] The novel portion of this structure is the $PH(CH_3)_2$ ligand. There are few published data on a complex of this ligand with which to make comparisons. For the $PH(CH_3)_2$ molecule Bartell[16] has reported the dimensions P–H = 1.45(2), P–C = 1.853(3) and ∠CPC = 99.2° C. It appears that the coordination of the phosphine causes a significant increase in the C–P–C angle, from 99.2 to 104.0° C. This might be explained by assuming that in the free $PH(CH_3)_2$ molecule the lone pair occupies an orbital of predominently *3s* character, but that in order to make these electrons more accessible for use in the P→Ru

TABLE IV. Interatomic Angles (deg).

Cl–Ru–P(1)	94.65(5)	Cl–Ru–P(1)′	85.35(5)
Cl–Ru–P(2)	93.10(5)	Cl–Ru–P(2)′	86.90(5)
P(1)–Ru–P(2)	92.52(5)	P(1)–Ru–P(2)′	87.48(5)
Ru–P(1)–C(1,1)	121.0(2)	Ru–P(2)–C(2,1)	119.8(2)
Ru–P(1)–C(1,2)	117.3(3)	Ru–P(2)–C(2,2)	119.4(2)
Ru–P(1)–H(1)	110(2)	Ru–P(2)–H(2)	98(4)
C(1,1)–P(1)–H(1)	89(2)	C(2,1)–P(2)–H(2)	112(4)
C(1,2)–P(1)–H(1)	112(2)	C(2,2)–P(2)–H(2)	104(4)
C(1,1)–P(1)–C(1,2)	104.0(3)	C(2,1)–P(2)–C(2,2)	102.8(3)

bond rehybridization occurs giving more 3*p* character in the orbital containing them and, correspondingly, more 3*s* character in the orbitals used in the P–C bonds. This same assumption could also account for the fact that there is a slight decrease in the P–C distances, from 1.853(3) to 1.839 ± 0.002Å, since increasing *s* character will decrease the covalent radius of the phosphorus atom. Similar effects were observed in $(CH_3)_2HPBH_3$,[6] where the C–P–C angle is 105.5° ± 1.0° C and the P–C distances are 1.81 ± 0.01Å.

One of the P–H distances has a realistic value, 1.43(5)Å, but the other, 1.10(8), is obviously spurious as a result of the poor reliability of hydrogen atom positions in x-ray structure determinations, especially in a case such as this where so many heavy atoms are in close proximity to the hydrogen atom.

Since the best electron density difference map did not give any indication of the positions of the methyl hydrogen atoms, they were omitted entirely in the refinement.

Nmr Spectra

The proton spectrum in C_6D_6 consists of a single multiplet centered at τ8.79. The structure of this multiplet is complex, with five major components and several shoulders. We have not attempted to account for the fine structure since several couplings of similar magnitude must be expected to contribute and the problem is complicated. Nor would an analysis serve any useful purpose. The spectrum does demonstrate that the configuration in solution is also *trans*, since for a *cis* configuration there would be two types of phosphine ligands and thus two multiplets in the spectrum.

The absence of a signal due to the phosphine hydrogen atoms is not as surprising as it might at first sight appear. The spectrum of the free dimethylphosphine has been reported.[17] From the reported data the phosphine hydrogen atom would be expected to give a doublet of complex multiplets centered around τ3.1 for a 100 MHz instrument with J_{P-H} of the order of 190 Hz. However, it is likely that the signal is split into so many components that it becomes indistinguishable from the noise. Dimethylphosphine itself has an A_6BX type spectrum, in which the P–H signal is a doublet of septuplets. In the complex, virtual coupling of *trans* phosphorus atoms would probably produce an A_6BX_2 pattern, *i.e.*, a triplet of septuplets. If, in addition there is significant coupling to the *cis* phosphorus atoms and their protons, it is easy to imagine that the signal would become too spread out to be observed.

Mechanism of Formation

The origin of the dimethylphosphine ligands is a point of interest. The generation of this species from tetramethyldiphosphine requires a reducing agent and a source of hydrogen, which might of course be one and the same reagent. The reaction was first carried out in ethanol, and it is an obvious possibility that the ethanol could supply the hydrogen and also serve as the reducing agent, thus being itself oxidized to acetaldehyde. This was verified by adding ethanol to the reaction carried out in THF and then preparing a phenylhydrazone derivative from the distillate of solvent. The melting point of the derivative demonstrated the presence of acetaldehyde. While this is one possibility, it is certainly not the only way in which the reaction can proceed.

The reaction has been carried out using scrupulously dried THF (dried over Na–K alloy with benzophenone indicator) distilled just prior to use into carefully dried apparatus. Thus the presence of ethanol is not required nor is any external source of water. The source of the hydrogen is therefore the water of hydration in the $RuCl_3 \cdot xH_2O$. However, under these conditions the identity of the reducing agent remains uncertain.

The incorporation of hydrogen from water, either added or present in the $RuCl_3 \cdot xH_2O$, in the $PH(CH_3)_2$ has been directly confirmed by introducing D_2O into the reaction carried out in THF and demonstrating its presence in the product by infrared spectroscopy. For dimethyl phosphine itself, the P–H stretching vibration occurs at 2305 cm^{-1} and is shifted to 1674 cm^{-1} in $PD(CH_3)_2$.[18] For *trans*-$RuCl_2(PHMe_2)_4$ there is a strong band in the infrared spectrum at 2300 cm^{-1} which can be assigned to ν(P–H). When the preparative reaction was carried out with added D_2O, the relative intensity of this band was reduced and a new band of similar intensity appeared at 1678 cm^{-1}.

Clearly, there are still many unanswered questions about the course of this reaction, such as the relative order of biphosphine splitting and coordination of phosphorus atoms to ruthenium, the possible intervention of Ru–H bonds, and, as already noted, the identity of the reducing agent when ethanol is not present. Unfortunately, it is not possible for us to continue our studies on this problem. The work is therefore being reported in its present, incomplete form with the hope that others may wish to pursue it further.

Acknowledgement

We are grateful to The Robert A. Welch Foundation for generous support through Grant No. A494.

References

1 J. Chatt and R.G. Hayter, *J. Chem. Soc.*, 896, 2605 (1961).
2 J. Chatt and J.M. Davidson, *J. Chem. Soc.*, 843 (1965).
3 M. Brockhaus, F. Staudacher and H. Vahrenkamp, *Ber.*, *105*, 3716 (1972).
4 G. Thomas, *Z. anorg. allg. Chem.*, *360*, 15, *362*, 191 (1968).
5 R.G. Hayter, *Inorg. Chem.*, *3*, 301 (1964).
6 J.R. Durig, B.A. Hudgens, Y.S. Lin and J.D. Odom. *J. Chem. Phys.*, *61*, 4890 (1974).
7 G. Kordosky, B.R. Cook, J. Cloyd, Jr. and D.W. Meek, *Inorg. Syn.*, *14*, 14 (1973).
8 R.L. Shriner, R.C. Fuson and D.Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, 5th Ed., 1964, pp. 147, 320.
9 F.A. Cotton, B.A. Frenz, C. Deganello and A. Shaver, *J. Organometal. Chem.*, *50*, 227 (1973).
10 The following computer programs written for the IBM 360 were used: DATARED, a data reduction program by Frenz; FOURIER, a Fourier summation program (based on Zalkin's FORDAP) by Dellaca and Robinson; NUCLS, a least-squares program by Ibers and Doedens which closely resembles Busing and Levy's ORFLS program, the quantity minimized is $\Sigma w(|F_o|-|F_c|)^2$; SADIAN, a program for calculating atomic distances and angles by Baur; PERFACT, a program for analysis of structure factors by Frenz; ORTEP, a plotting program by Johnson; ORFFE, a function and error program by Busing, Martin and Levy and modified by Brown, Johnson and Thiessen; and LIST, a data listing program by Snyder.
11 D.T. Cromer and J.T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England (1974); Table 2.3.1.
12 D.T. Cromer and D. Liberman, *J. Chem. Phys.*, *53*, 1891 (1970).
13 G. Chioccola and J.J. Daly, *J. Chem. Soc. (A)*, 1981 (1968).
14 S.J. LaPlaca and J.A. Ibers, *Inorg. Chem.*, *4*, 778 (1965).
15 I. Kawada, *Tetrahedron Letters*, 793 (1969).
16 L.S. Bartell, *J. Chem. Phys.*, *32*, 832 (1960).
17 S.L. Manatt, G.J. Juvinall, R.I. Wagner and D.D. Elleman, *J. Am. Chem. Soc.*, *88*, 2689 (1966).
18 J.A. Lannon and E.R. Nixon, *Spectrochim. Acta*, *23A*, 2713 (1967).