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The Molecular Structure of the Dimer of Bis(tetramethyldiphosphinoethane)-ruthenium that Results from Paired Oxidative Additions of C–H Bonds to Two Metal Atoms

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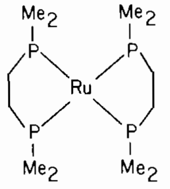
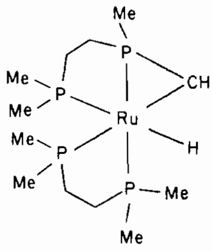
The compound of stoichiometry ($Me_2PCH_2CH_2PMe_2)_2Ru$ reported in 1965 and formulated as a mononuclear species containing an Ru–H bond and a three-membered Ru–P–C ring has been shown by x-ray crystallography to be a dinuclear species. This is formed by union of two $dmpe_2Ru$ molecules, where dmpe = $Me_2PCH_2CH_2PMe_2$, so that one C–H bond of a methyl group in one unit adds oxidatively to the Ru atom of the other unit. A central $\overline{Ru–P–C–Ru–P–C}$ ring with a chair configuration is formed and each metal atom is octahedrally coordinated by four P atoms, one C atom and one H atom. Crystal data: Space group, $P\bar{1}$; Z = 4($dmpe_2Ru$); a = 10.028(4) Å; b = 13.880(6) Å; c = 15.018(6) Å; α = 95.87(3)°; β = 101.27(3)°; γ = 112.02(3)°; V = 1865(1) Å^3. There are two crystallographically independent dinuclear molecules, each located on an inversion center (at 0,0,0 and 1/2,1/2,1/2). Anisotropic refinement of all non-hydrogen atoms gave residuals of R_1 = 0.052 and R_2 = 0.076. Using data for which $\lambda^{-1}\sin\Theta < 0.25$ Å^{-1} the ligate hydrogen atoms were then located; a mean Ru–H distance of 1.67(7) Å was obtained after refinement of the hydride positions.

Introduction

During the past decade the general importance of oxidative addition reactions has become increasingly evident.[1] A type that is of particular importance is the addition of C–H bonds to form C–M–H products. What appear to be the earliest examples of such reactions were reported by Chatt and Davidson[2] in 1965. An important compound in this work was a substance with the empirical formula $dmpe_2Ru$, where dmpe = $(CH_3)_2PCH_2CH_2P(CH_3)_2$. On the basis of ir data for the solid, it was suggested that instead of the conventional structure *a* the compound has a Ru–H bond and thus the structure *b*. In our view this structure appeared improbable.



a



b

Despite an earlier report[3] that the structure had resisted solution, with the difficulties being attributed to apparent disorder, we considered the problem of sufficient interest to warrant another attempt. We describe here the complete structure of the compound (which is neither *a* nor *b*), including the approximate location of the ligate hydrogen atom.

Experimental

Preparative Studies

Essentially all of the chemical operations reported by Chatt and Davidson were repeated and results essentially identical to theirs were obtained throughout. At the time we were attempting to grow crystals Dr. J. N. Davidson was consulted about how best to do this and he offered to supply crystals from his laboratory. Our work was then continued with crystals he supplied.

Collection of X-Ray Data

A white, well-formed crystal 0.40 × 0.30 × 0.20 mm was selected for the investigation and mounted in an argon-filled capillary in a random orientation. Preliminary examination of the crystal suggested $P\bar{1}$ as the space group. Crystal data are given in Table I.

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TABLE I. Crystal Data for $[Ru(dmpe)_2]_2$.

a	= 10.028(4)A	α	= 95.87(3)
b	= 13.880(6)A	β	= 101.27(3)
c	= 15.018(6)A	γ	= 112.02(3)
V	= 1865(1)Å^3	Z	= 2
μ	= 11.9 cm^{-1}	d_{calcd}	= 1.431

Data were collected at 21 ± 1 °C on a Syntex P$\bar{1}$ autodiffractometer using Mo Kα radiation as described previously,[4] in the range $0° < 2\Theta \leq 48°$. The $\Theta/2\Theta$ scan technique with a variable scan rate of 4.0–24.0 deg/min and a scan range of $2\Theta(K_{\alpha_1}) - 1.0°$ to $2\Theta(K_{\alpha_2}) + 0.7°$ was used. The orientation matrix and cell dimensions were obtained by least-squares refinement of the settings for 15 reflections chosen in the range $28° < 2\Theta < 30°$. A total of 5032 unique data were collected of which 3877 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement of the structure. The parameter p used in the calculation of standard deviations was set equal to 0.06. Three standard reflections were measured every 100 reflections to check on crystal and electronic stability. No trends in the standards were observed. An absorption correction was not made in view of the small linear absorption coefficient of 11.9 cm^{-1}.

Solution of the Structure[5]

Two ruthenium atoms were located from a three-dimensional Patterson map. Two cycles of least-squares refinement of these positions resulted in R_1 of 0.482 and R_2 of 0.582.[6] A difference Fourier map revealed the positions of four phosphorus atoms; isotropic refinement of the six atoms now located reduced R_1 to 0.177 and R_2 to 0.272. The remaining non-hydrogen atoms were then located in a difference Fourier. Two cycles of isotropic refinement yielded agreement indices of $R_1 = 0.079$ and $R_2 = 0.113$. One further cycle of refinement, in which the two ruthenium, eight phosphorus and two ruthenium bound carbon atoms were varied anisotropically and the remaining non-hydrogen atoms refined isotropically, produced an $R_1 = 0.058$ and $R_2 = 0.089$. It was at this stage that our preliminary report of the structure was published.[7]

Scattering factors for neutral ruthenium phosphorus carbon and hydrogen were obtained from Cromer.[8] Anomalous dispersion effects were included in the calculated structure factors for ruthenium and phosphorus using $\Delta f'$ and $\Delta f''$ values given by Cromer and Liberman.[9]

The further refinement of this structure was conducted using the PDP-11/45 computer and additional software of the Molecular Structure Corporation. Complete anisotropic refinement of all non-hydrogen atoms was carried out to convergence and resulted in agreement factors of 0.052 and 0.076. To locate the ligate hydrogen atoms a difference Fourier map was calculated using only data for which $\lambda^{-1}\sin\Theta < 0.30$Å^{-1}. The map showed no clearly defined peaks that could be assigned to the ligate hydrogen atoms, although there was evidence of diffuse residual electron density in the region of the vacant coordination site. However, from a difference Fourier map using only the 425 data for which $\lambda^{-1}\sin\Theta < 0.25$ Å^{-1}, the twelfth and seventeenth peaks could unambiguously be assigned to the hydride ligands on each metal. The latter peak had a height that was 68% of that belonging to the highest peak in the map. The coordinates of these two peaks were included in further least-squares refinement; isotropic thermal parameters of 5.0 Å^2 were assigned to each atom and were not refined. In addition the twenty hydrogen atoms whose positions were fixed by the remainder of the structure (*i.e.*, all except the methyl hydrogen atoms) were included in the structure factor (B = 5.0 Å^2) but were not refined. The final refinement results for 3870 observations ($I > 3\sigma(I)$) and 313 variable parameters are: $R_1 = 0.047$; $R_2 = 0.072$; error in an observation of unit weight = 1.56; largest parameter shift = 0.7 times its esd.

Results and Discussion

The fractional coordinates and thermal parameters for the anisotropically refined atoms are given in Table II, and the fractional coordinates of the hydrogen atoms in Table III. Tables IV and V present data on bond distances and bond angles. Table VI lists the final values of $|F_o|$ and $|F_c|$.* The coordination about the ruthenium atom is shown in Figure 1, which also

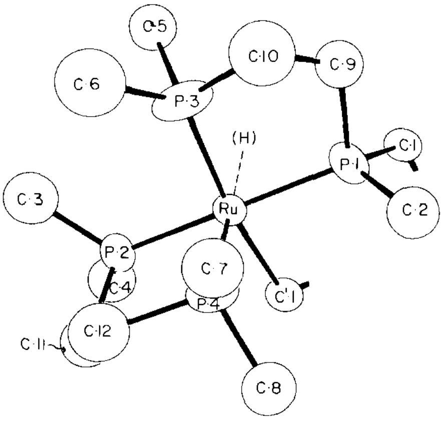

Figure 1. A drawing of the coordination about the ruthenium atoms, showing the basis of the numbering scheme. An additional number, 1 or 2, is added to distinguish between atoms in the two crystallographic, centrosymmetric molecules.

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* Table VI is available from the Editor upon request.

TABLE II. Positional and Thermal Parameters and Their Estimated Standard Deviations.[a]

Atom	x	y	z	β(1,1)	β(2,2)	β(3,3)	β(1,2)	β(1,3)	β(2,3)
Ru(1)	0.09915(6)	–0.34627(4)	0.43828(4)	0.00818(6)	0.00367(3)	0.00334(3)	0.00476(6)	0.00270(7)	0.00217(5)
Ru(2)	0.22096(6)	0.15337(4)	0.05431(4)	0.00834(6)	0.00468(3)	0.00385(3)	0.00521(7)	0.00223(8)	0.00106(6)
P(1,1)	–0.1060(2)	–0.4203(1)	0.4978(1)	0.0093(2)	0.00453(9)	0.0041(1)	0.0070(2)	0.0038(2)	0.0027(2)
P(1,2)	0.3157(2)	–0.2803(2)	0.3930(2)	0.0101(2)	0.00581(12)	0.0053(1)	0.0048(3)	0.0052(3)	0.0038(2)
P(1,3)	0.0902(2)	–0.1899(2)	0.4898(2)	0.0139(2)	0.00438(11)	0.0055(1)	0.0073(2)	0.0038(3)	0.0019(2)
P(1,4)	–0.0144(2)	–0.3656(2)	0.2841(2)	0.0140(3)	0.00650(12)	0.0040(1)	0.0083(3)	0.0020(3)	0.0028(2)
P(2,1)	0.0037(2)	0.0831(2)	0.1021(2)	0.0107(2)	0.00802(15)	0.0042(1)	0.0063(3)	0.0043(3)	–0.0014(2)
P(2,2)	0.4191(2)	0.2150(2)	–0.0083(2)	0.0097(2)	0.00747(14)	0.0073(1)	0.0062(3)	0.0059(3)	0.0060(2)
P(2,3)	0.2307(3)	0.3121(2)	0.1148(2)	0.0291(4)	0.00679(12)	0.0049(1)	0.0183(3)	0.0024(4)	0.0018(2)
P(2,4)	0.3853(3)	0.1370(2)	0.1766(2)	0.0163(3)	0.00708(13)	0.0059(2)	0.0112(3)	–0.0016(4)	0.0019(2)
C(1,1)	0.0942(7)	–0.5066(5)	0.4097(5)	0.0100(8)	0.0050(4)	0.0040(4)	0.0065(8)	0.0032(9)	0.0030(6)
C(1,2)	–0.2868(8)	–0.4992(7)	0.4142(7)	0.0075(8)	0.0083(6)	0.0059(5)	0.0034(11)	–0.0011(12)	0.0034(9)
C(1,3)	0.4601(9)	–0.3329(7)	0.4210(8)	0.0107(8)	0.0116(7)	0.0107(7)	0.0142(11)	0.0087(13)	0.0083(11)
C(1,4)	0.4380(11)	–0.1377(8)	0.4212(9)	0.0159(14)	0.0060(6)	0.0130(9)	–0.0004(16)	0.0081(19)	0.0045(12)
C(1,5)	0.1130(12)	–0.0797(6)	0.4256(8)	0.0290(16)	0.0058(5)	0.0108(7)	0.0147(13)	0.0144(18)	0.0096(9)
C(1,6)	0.2106(11)	–0.1128(7)	0.6061(7)	0.0213(14)	0.0071(6)	0.0058(6)	0.0076(15)	0.0016(16)	–0.0031(10)
C(1,7)	–0.1581(10)	–0.3156(7)	0.2420(7)	0.0236(12)	0.0095(5)	0.0070(6)	0.0200(11)	0.0016(15)	0.0064(9)
C(1,8)	–0.0964(11)	–0.4962(7)	0.2062(7)	0.0235(14)	0.0077(6)	0.0052(6)	0.0116(14)	0.0006(16)	–0.0008(10)
C(1,9)	–0.1438(8)	–0.3100(6)	0.5530(7)	0.0158(9)	0.0064(4)	0.0072(5)	0.0125(9)	0.0097(11)	0.0041(8)
C(1,10)	–0.0977(9)	–0.2165(6)	0.5089(8)	0.0172(10)	0.0064(5)	0.0100(7)	0.0141(10)	0.0083(14)	0.0040(10)
C(1,11)	0.2698(12)	–0.3030(10)	0.2656(7)	0.0234(14)	0.0168(10)	0.0061(6)	0.0154(20)	0.0145(14)	0.0086(12)
C(1,12)	0.1274(11)	–0.2930(9)	0.2282(7)	0.0160(13)	0.0146(9)	0.0049(5)	0.0093(18)	0.0023(15)	0.0071(11)
C(2,1)	0.1695(8)	–0.0090(6)	–0.0178(6)	0.0125(8)	0.0056(4)	0.0041(4)	0.0078(9)	0.0040(10)	–0.0004(7)
C(2,2)	0.0065(10)	0.0085(9)	0.1954(7)	0.0150(12)	0.0165(10)	0.0048(5)	0.0091(18)	0.0057(13)	0.0088(11)
C(2,3)	0.4060(11)	0.1651(10)	–0.1296(7)	0.0211(12)	0.0167(10)	0.0077(6)	0.0174(17)	0.0170(12)	0.0075(13)
C(2,4)	0.5086(13)	0.3582(8)	–0.0107(9)	0.0191(16)	0.0088(8)	0.0144(9)	–0.0008(20)	0.0112(20)	0.0112(13)
C(2,5)	0.1700(10)	0.3917(7)	0.0396(7)	0.0229(13)	0.0073(5)	0.0074(6)	0.0163(11)	0.0011(16)	0.0042(9)
C(2,6)	0.3883(18)	0.4211(9)	0.1960(11)	0.0582(29)	0.0081(8)	0.0158(12)	0.0242(22)	–0.0379(30)	–0.0109(16)
C(2,7)	0.4209(13)	0.1964(9)	0.2983(8)	0.0286(17)	0.0121(8)	0.0051(6)	0.0178(18)	–0.0062(18)	–0.0004(12)
C(2,8)	0.3870(12)	0.0054(7)	0.1902(8)	0.0310(16)	0.0081(5)	0.0083(7)	0.0204(13)	–0.0015(19)	0.0031(10)
C(2,9)	–0.0278(10)	0.1977(9)	0.1555(7)	0.0139(10)	0.0169(8)	0.0083(6)	0.0133(13)	0.0031(12)	–0.0146(10)
C(2,10)	0.1137(18)	0.2940(10)	0.1938(9)	0.0885(26)	0.0229(9)	0.0088(8)	0.0730(19)	0.0329(22)	0.0110(14)
C(2,11)	0.5722(10)	0.1867(10)	0.0545(9)	0.0149(11)	0.0173(9)	0.0127(9)	0.0190(15)	0.0117(16)	0.0122(15)
C(2,12)	0.5770(12)	0.2041(10)	0.1578(11)	0.0146(15)	0.0161(11)	0.0159(12)	0.0083(20)	–0.0019(23)	0.0135(17)

[a] The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

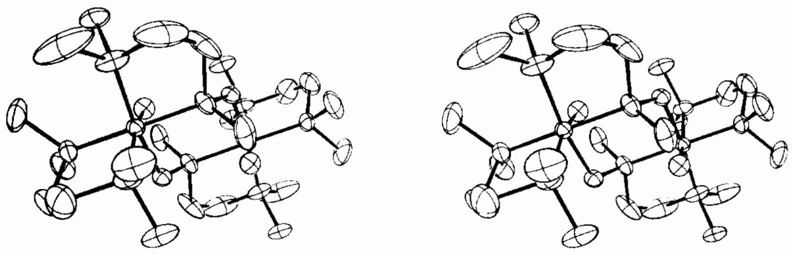


Figure 2. A stereo pair view of the molecular structure. The ligate hydrogen atoms are shown, but all others are omitted for clarity.

TABLE III. Positional and Thermal Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B
H(1)	0.167(8)	–0.336(6)	0.536(5)	5.0
H(2)	0.090(8)	0.130(6)	–0.058(5)	5.0
H(1,3)	0.1770	–0.4985	0.3813	5.0
H(1,4)	0.0049	–0.5471	0.3615	5.0
H(1,5)	–0.0914	–0.2903	0.6165	5.0
H(1,6)	–0.2477	–0.3349	0.5482	5.0
H(1,7)	–0.1686	–0.2300	0.4531	5.0
H(1,8)	–0.0945	–0.1579	0.5504	5.0
H(1,9)	0.2632	–0.3698	0.2421	5.0
H(1,10)	0.3472	–0.2493	0.2474	5.0
H(1,11)	0.1409	–0.2214	0.2385	5.0
H(1,12)	0.0928	–0.3223	0.1640	5.0
H(2,3)	0.1753	–0.0502	0.0307	5.0
H(2,4)	0.2484	–0.0043	–0.0461	5.0
H(2,5)	–0.0763	0.1797	0.2014	5.0
H(2,6)	–0.0894	0.2155	0.1067	5.0
H(2,7)	0.0895	0.3546	0.2026	5.0
H(2,8)	0.1616	0.2859	0.2506	5.0
H(2,9)	0.6644	0.2320	0.0456	5.0
H(2,10)	0.5559	0.1147	0.0345	5.0
H(2,11)	0.6404	0.1785	0.1918	5.0
H(2,12)	0.6105	0.2791	0.1811	5.0

illustrates the numbering scheme. A stereoview of the dimer is depicted in Figure 2.

In the unit cell there are two crystallographically independent binuclear molecules each lying at a crystallographic center of inversion. They do not differ in any chemically significant way.

The geometry about each ruthenium atom is octahedral with the four phosphorus atoms occupying adjacent facial sites. The ruthenium-bound carbon and the ligating hydrogen atom are *cis* to each other.

The dimeric structure is realized through a chair-shaped six-membered ring. The two carbon atoms in the ring are shared by ruthenium and phosphorus atoms, where the phosphorus is in a ligand on the adjacent ruthenium atom.

The geometry about the individual ruthenium atoms, as well as the distances and angles for the dimeric structure discussed herein, compare favorably with those of the parent complex (see later) RuH(naphthyl)(dmpe)$_2$.[3] The average Ru–H distance for the dimer is 1.65(7) Å compared to 1.7 Å for the naphthyl complex. The Ru–C bond lengths of 2.211(5) Å in the present case and 2.160(10) Å in the naphthyl complex agree very well when allowance is made for the fact that the covalent radius of an *sp*^{2} hybridized carbon

TABLE IV. Table of Bond Distances in Angstroms.[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ru(1)	P(1,1)	2.325(2)	P(1,1)	C(1,9)	1.863(7)	P(2,2)	C(2,4)	1.856(9)
Ru(1)	P(1,2)	2.286(2)	P(1,2)	C(1,3)	1.851(8)	P(2,2)	C(2,11)	1.833(10)
Ru(1)	P(1,3)	2.269(2)	P(1,2)	C(1,4)	1.846(8)	P(2,3)	C(2,5)	1.832(8)
Ru(1)	P(1,4)	2.312(2)	P(1,2)	C(1,11)	1.844(10)	P(2,3)	C(2,6)	1.830(11)
Ru(1)	C(1,1)	2.203(6)	P(1,3)	C(1,5)	1.857(8)	P(2,3)	C(2,10)	1.797(16)
Ru(1)	H(1)	1.47(7)	P(1,3)	C(1,6)	1.864(8)	P(2,4)	C(2,7)	1.834(10)
Ru(2)	P(2,1)	2.318(2)	P(1,3)	C(1,10)	1.866(8)	P(2,4)	C(2,8)	1.865(8)
Ru(2)	P(2,2)	2.277(2)	P(1,4)	C(1,7)	1.854(8)	P(2,4)	C(2,12)	1.888(12)
Ru(2)	P(2,3)	2.255(2)	P(1,4)	C(1,8)	1.845(8)	C(1,9)	C(1,10)	1.477(11)
Ru(2)	P(2,4)	2.307(2)	P(1,4)	C(1,12)	1.819(9)	C(1,11)	C(1,12)	1.492(13)
Ru(2)	C(2,1)	2.219(6)	P(2,1)	C(2,1)	1.792(7)	C(2,9)	C(2,10)	1.49(2)
Ru(2)	H(2)	1.83(7)	P(2,1)	C(2,2)	1.827(9)	C(2,11)	C(2,12)	1.535(17)
P(1,1)	C(1,1)	1.814(7)	P(2,1)	C(2,9)	1.867(10)			
P(1,1)	C(1,2)	1.845(7)	P(2,2)	C(2,3)	1.842(10)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

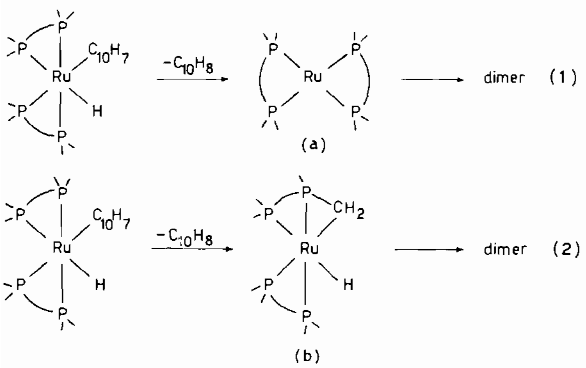
TABLE V. Table of Bond Angles in Degrees.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
P(1,1)	Ru(1)	P(1,2)	173.21(7)	C(2,1)	Ru(2)	H(2)	72.9(21)	C(2,1)	P(2,1)	C(2,9)	102.2(4)
P(1,1)	Ru(1)	P(1,3)	84.61(7)	Ru(1)	P(1,1)	C(1,1)	119.6(2)	C(2,2)	P(2,1)	C(2,9)	102.4(5)
P(1,1)	Ru(1)	P(1,4)	101.23(7)	Ru(1)	P(1,1)	C(1,2)	117.4(3)	Ru(2)	P(2,2)	C(2,3)	121.5(3)
P(1,1)	Ru(1)	C(1,1)	87.0(2)	Ru(1)	P(1,1)	C(1,9)	107.9(2)	Ru(2)	P(2,2)	C(2,4)	120.1(4)
P(1,1)	Ru(1)	H(1)	77.0(26)	C(1,1)	P(1,1)	C(1,2)	106.3(3)	Ru(2)	P(2,2)	C(2,11)	109.9(4)
P(1,2)	Ru(1)	P(1,3)	98.11(7)	C(1,1)	P(1,1)	C(1,9)	102.0(3)	C(2,3)	P(2,2)	C(2,4)	96.9(5)
P(1,2)	Ru(1)	P(1,4)	84.64(7)	C(1,2)	P(1,1)	C(1,9)	101.0(4)	C(2,3)	P(2,2)	C(2,11)	102.0(5)
P(1,2)	Ru(1)	C(1,1)	89.6(2)	Ru(1)	P(1,2)	C(1,3)	121.5(3)	C(2,4)	P(2,2)	C(2,11)	103.5(5)
P(1,2)	Ru(1)	H(1)	97.1(26)	Ru(1)	P(1,2)	C(1,4)	122.0(3)	Ru(2)	P(2,3)	C(2,5)	120.4(3)
P(1,3)	Ru(1)	P(1,4)	97.52(7)	Ru(1)	P(1,2)	C(1,11)	108.5(3)	Ru(2)	P(2,3)	C(2,6)	127.5(5)
P(1,3)	Ru(1)	C(1,1)	169.9(2)	C(1,3)	P(1,2)	C(1,4)	98.5(4)	Ru(2)	P(2,3)	C(2,10)	109.1(5)
P(1,3)	Ru(1)	H(1)	82.7(26)	C(1,3)	P(1,2)	C(1,11)	102.6(5)	C(2,5)	P(2,3)	C(2,6)	97.7(5)
P(1,4)	Ru(1)	C(1,1)	89.6(2)	C(1,4)	P(1,2)	C(1,11)	100.4(5)	C(2,5)	P(2,3)	C(2,10)	103.3(6)
P(1,4)	Ru(1)	H(1)	178.2(14)	Ru(1)	P(1,3)	C(1,5)	125.7(3)	C(2,6)	P(2,3)	C(2,10)	93.7(9)
C(1,1)	Ru(1)	H(1)	90.0(26)	Ru(1)	P(1,3)	C(1,6)	118.1(3)	Ru(2)	P(2,4)	C(2,7)	125.4(3)
P(2,1)	Ru(2)	P(2,2)	173.90(8)	Ru(1)	P(1,3)	C(1,10)	108.8(3)	Ru(2)	P(2,4)	C(2,8)	121.1(3)
P(2,1)	Ru(2)	P(2,3)	85.29(9)	C(1,5)	P(1,3)	C(1,6)	99.5(5)	Ru(2)	P(2,4)	C(2,12)	106.6(4)
P(2,1)	Ru(2)	P(2,4)	99.51(9)	C(1,5)	P(1,3)	C(1,10)	100.1(4)	C(2,7)	P(2,4)	C(2,8)	99.8(5)
P(2,1)	Ru(2)	C(2,1)	87.9(2)	C(1,6)	P(1,3)	C(1,10)	100.6(4)	C(2,7)	P(2,4)	C(2,12)	99.9(6)
P(2,1)	Ru(2)	H(2)	82.6(21)	Ru(1)	P(1,4)	C(1,7)	124.4(3)	C(2,8)	P(2,4)	C(2,12)	99.2(5)
P(2,2)	Ru(2)	P(2,3)	97.30(9)	Ru(1)	P(1,4)	C(1,8)	120.7(3)	Ru(1)	C(1,1)	P(1,1)	120.6(3)
P(2,2)	Ru(2)	P(2,4)	85.62(9)	Ru(1)	P(1,4)	C(1,12)	108.0(3)	P(1,1)	C(1,9)	C(1,10)	112.4(6)
P(2,2)	Ru(2)	C(2,1)	88.7(2)	C(1,7)	P(1,4)	C(1,8)	99.5(4)	P(1,3)	C(1,10)	C(1,9)	108.9(5)
P(2,2)	Ru(2)	H(2)	91.6(21)	C(1,7)	P(1,4)	C(1,12)	99.9(4)	P(1,2)	C(1,11)	C(1,12)	110.6(7)
P(2,3)	Ru(2)	P(2,4)	98.23(8)	C(1,8)	P(1,4)	C(1,12)	99.9(5)	P(1,4)	C(1,12)	C(1,11)	110.8(6)
P(2,3)	Ru(2)	C(2,1)	169.7(2)	Ru(2)	P(2,1)	C(2,1)	119.7(2)	P(2,1)	C(2,9)	C(2,10)	112.4(7)
P(2,3)	Ru(2)	H(2)	98.5(21)	Ru(2)	P(2,1)	C(2,2)	117.1(3)	P(2,3)	C(2,10)	C(2,9)	110.5(9)
P(2,4)	Ru(2)	C(2,1)	90.5(2)	Ru(2)	P(2,1)	C(2,9)	106.7(4)	P(2,2)	C(2,11)	C(2,12)	108.1(7)
P(2,4)	Ru(2)	H(2)	163.3(21)	C(2,1)	P(2,1)	C(2,2)	106.4(4)	P(2,4)	C(2,12)	C(2,11)	110.9(8)

atom is normally about 0.04 Å shorter than those for sp^3 hybridized carbon atoms.

The only other structurally characterized six-membered ring containing *para* transition metal atoms, with which this structure may be compared, is that recently reported[10] for $(OC)_4\overline{Cr(AsMe_2AsMe_2)_2Cr}(CO)_4$. The two structures have many similarities. In the present case the two possible chair conformations are not equivalent, and the one actually adopted is the one which places the ligand H rather than Me_2P in the most crowded position.

In conclusion, it should be noted that the compound studied here is not necessarily to be considered a product of oxidative addition of a C–H bond to Ru^0 in a direct sense, but perhaps only in an indirect sense. The compound is obtained by pyrolysis of $Ru(dmpe)_2(C_{10}H_7)H$. We do not know whether this reaction proceeds by mechanism (1), in which case the direct sense is appropriate, or by mechanism (2), in which case the indirect sense is appropriate. Still other mechanisms for this solid state reaction can be envisioned. Chatt and Davidson did, however, indicate that some of the reactions of the compound correspond better with structure *a* than with a structure having an Ru–H bond. Thus actual, direct interconversion of *a* and the dinuclear structure may actually occur in solution.



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6 We define $R_1 = \Sigma||F_o|-|F_c||/|F_o|$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$.
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