

Contribution from the Department of Chemistry,  
Michigan State University, East Lansing, Michigan 48823**Crystal Structure of Bis(triphenylphosphine)tetramethyleneplatinum(II)**

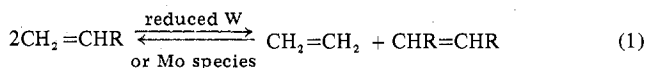
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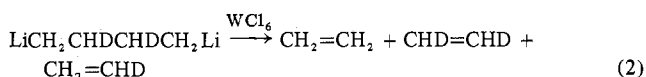
The crystal structure of bis(triphenylphosphine)tetramethyleneplatinum(II), Pt[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>C<sub>4</sub>H<sub>8</sub>, has been determined from room temperature diffractometer data. The structure is triclinic, space group  $P\bar{1}$ , with  $a = 9.78$  (1),  $b = 17.75$  (2), and  $c = 9.66$  (1) Å;  $\alpha = 94.06$  (4),  $\beta = 102.74$  (7), and  $\gamma = 98.54$  (6)°; with  $Z = 2$ . The structure was solved by conventional Patterson and Fourier techniques, using 3504 independent reflections; it was refined to a discrepancy index, based on  $F$ , of 7.4%. The phosphine ligands and the terminal carbon atoms of the tetramethylene ring comprise a distorted square-planar configuration about the Pt atom in which the coordinated C atoms are 2.12 (2) and 2.05 (2) Å from the metal. The angle between the tetramethylene ring and the plane defined by Pt, P(1), and P(2) is 175 (1)°. Stereochemical implications with respect to the possible mode of rearrangement of the metalocycle in olefin metathesis reactions are examined.

**Introduction**

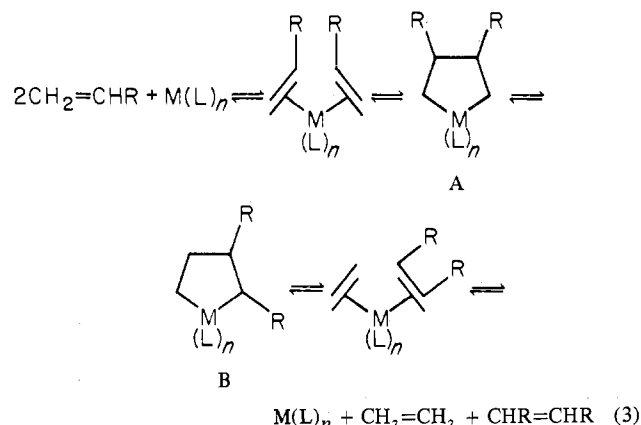
A tetramethylenemetalocyclic species was recently suggested<sup>1</sup> as an intermediate in the olefin metathesis reaction 1. Evidence to support such an intermediate was pro-



vided by the reaction of labeled 1,4-dilithiobutane with tungsten hexachloride, which produced ethylenes with scrambled labels (2). The intermediate needed to effect



reactions 1 and 2 should be similar since analogous products are obtained. The probable role of the intermediate is shown in eq 3, where intermediate A rearranges to inter-



mediate B and thus produces the characteristic scrambling of groups in the products. Due to the instability of the tungsten metalocycle, its existence could not be proven; however, reaction of 1,4-dilithiobutane with group VIII metal halides yielded stable compounds. Consequently, the structure of bis(triphenylphosphine)tetramethyleneplatinum(II) was determined both to demonstrate the formation of metalocyclic species in these reactions<sup>2</sup> and to determine if conformational features of the molecule which could indicate mechanisms for general reactions of such compounds exist.

(1) R. Grubbs and T. K. Brunck, *J. Amer. Chem. Soc.*, **94**, 2538 (1972).

(2) A communication by A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, **95**, 597 (1973), which appeared after this paper had been written, has given preliminary results on a structure of an iridium metalocycle and supports this contention.

**Experimental Section**

Treatment of *cis*-bis(triphenylphosphine)dichloroplatinum(II) with 1 equiv of 1,4-dilithiobutane produced a stable compound.<sup>3</sup> Recrystallization of the purified product from a mixture of hexane and benzene produced crystals suitable for a complete single-crystal X-ray analysis. Crystals of bis(triphenylphosphine)tetramethyleneplatinum(II) [bis(triphenylphosphine)tetrahydroplatinole], Pt[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>C<sub>4</sub>H<sub>8</sub>, were found to be triclinic, space group  $P\bar{1}$ , with cell dimensions  $a = 9.78$  (1),  $b = 17.75$  (2),  $c = 9.66$  (1) Å;  $\alpha = 94.06$  (4),  $\beta = 102.74$  (7),  $\gamma = 98.54$  (6)°. These parameters were obtained from the least-squares refinement<sup>4</sup> of 12 reflections which had been hand centered on a computer-controlled, four-circle, Picker goniometer. The data were measured with Mo  $K\alpha$  radiation and a graphite monochromator ( $\lambda = 0.7093$  Å) at  $t = 23$  (2)°. The density calculated for  $Z = 2$  is 1.60 g/cm<sup>3</sup>; the density measured by flotation is 1.57 (1) g/cm<sup>3</sup>.

The crystal used in this investigation was clear, golden in color, and roughly triangular (0.44 × 0.36 × 0.44 mm and *ca.* 0.15 mm at its thickest point). The crystal was mounted parallel to a triangular face such that the (0,14,5) reflection was coincident with the diffractometer  $\phi$  axis. Four octants (*hkl*, *hkl*, *hkl*, *hkl*) of data were collected in two sets, an inner sphere for which  $3.5^\circ < 2\theta < 20^\circ$  and an outer sphere for which  $20^\circ < 2\theta < 50^\circ$ , by using the  $\omega$ -scan technique with a scan range of  $1^\circ$ , scan rate of  $0.5^\circ/\text{min}$ , and a  $K\alpha_1$ - $K\alpha_2$  dispersion factor of 0.692. The counting system employed a scintillation counter with pulse height discrimination. Individual background measurements were made at the end points of the scan range for 10 sec each. Neither filters nor attenuators were used, and three standard reflections, the (050), (023), and (144), were checked every 200 reflections. About one-third of the way through the data collection, the standard counts began to decrease markedly. Upon investigation the monochromator was found to have slipped. Readjustment brought the standard counts to 7% above the initial rate. A correction factor was applied in the program INCOR<sup>5</sup> to bring all data to a similar scale. After correction the variation in standard counts was approximately 3%. A total of 476 and 6000 reflections were collected in the inner and outer sets, respectively, excluding standard reflections.

The data were corrected for background and considered to be observed by the criterion  $I > 2\sigma(I)$  where  $I = P - C[10(B + 1)]$  and  $\sigma^2(I) = P + C(B) + [D(P - B)]^2$ , in which  $P$  is the integrated count,  $B$  is the measured background,  $C$  is the ratio of total peak count time to total background count time, and  $D$  is a 2% instrumental drift factor. An absorption correction was not attempted (linear absorption coefficient for Mo  $K\alpha$  radiation =  $47.1 \text{ cm}^{-1}$ ) because the irregular shape of the crystal with possible reentrant angles made definition of the boundary planes virtually impossible. Furthermore, examination of 33 Friedel pairs in the inner-sphere data revealed only five whose intensities were not within one standard deviation of each other. The data were corrected for Lorentz and polarization effects by the program INCOR<sup>5</sup> which was altered to include a perpendicular monochromator correction.

**Structure Determination.** The solution and refinement of the structure were accomplished in four main steps. Least-squares,

(3) T. K. Brunck, D. Carr, and R. Grubbs, unpublished work.

(4) W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, Report ORNL-4143, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1968.

(5) Written by A. Zalkin and converted for use on a CDC 6500.

Table I. Positional and Thermal Parameters for Pt[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>C<sub>4</sub>H<sub>8</sub><sup>a,c</sup>

Atom	x	y	z	Anisotropic atoms <sup>b</sup>					
				B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
Pt	0.3682 (1)	0.26012 (5)	0.36429 (9)	3.57 (4)	2.12 (3)	1.87 (3)	0.36 (2)	0.96 (2)	0.45 (2)
P(1)	0.2455 (6)	0.1567 (3)	0.2103 (5)	3.20 (27)	2.61 (25)	2.16 (23)	0.28 (20)	0.75 (20)	0.46 (19)
P(2)	0.2097 (6)	0.3424 (3)	0.3130 (5)	3.59 (28)	2.82 (25)	2.27 (23)	0.76 (21)	1.10 (20)	0.66 (19)
Isotropic atoms									
Atom	x	y	z	B	Atom	x	y	z	B
C(1)	0.309 (2)	0.065 (1)	0.228 (2)	3.02 (38)	H(2) <sup>c</sup>	0.467	0.092	0.123	7.00
C(2)	0.244 (3)	0.007 (2)	0.297 (3)	6.36 (62)	H(3)	0.558	-0.025	0.144	7.00
C(3)	0.302 (3)	-0.060 (2)	0.307 (3)	8.28 (79)	H(4)	0.457	-0.121	0.264	7.00
C(4)	0.418 (3)	-0.072 (1)	0.254 (3)	5.27 (54)	H(5)	0.259	-0.101	0.356	7.00
C(5)	0.476 (2)	-0.016 (1)	0.185 (2)	3.74 (42)	H(6)	0.161	0.016	0.338	7.00
C(6)	0.424 (2)	0.052 (1)	0.172 (2)	3.62 (42)	H(8)	-0.046	0.109	0.025	7.00
C(7)	0.067 (2)	0.131 (1)	0.232 (2)	3.08 (39)	H(9)	-0.274	0.080	0.082	7.00
C(8)	-0.054 (2)	0.111 (1)	0.125 (2)	3.44 (41)	H(10)	-0.290	0.084	0.322	7.00
C(9)	-0.187 (2)	0.095 (1)	0.159 (2)	4.13 (45)	H(11)	-0.085	0.119	0.504	7.00
C(10)	-0.196 (3)	0.096 (1)	0.298 (3)	5.16 (53)	H(12)	0.145	0.150	0.450	7.00
C(11)	-0.077 (2)	0.117 (1)	0.404 (2)	4.88 (51)	H(14)	0.374	0.270	1.068	7.00
C(12)	0.058 (2)	0.136 (1)	0.373 (2)	3.69 (42)	H(15)	0.409	0.285	0.833	7.00
C(13)	0.246 (2)	0.167 (1)	1.024 (2)	2.86 (37)	H(16)	0.302	0.192	0.658	7.00
C(14)	0.329 (2)	0.230 (1)	0.991 (2)	2.99 (37)	H(17)	0.157	0.078	0.699	7.00
C(15)	0.349 (2)	0.239 (1)	0.855 (2)	4.71 (51)	H(18)	0.121	0.064	0.938	7.00
C(16)	0.287 (2)	0.185 (1)	0.755 (2)	4.90 (52)	H(20)	0.902	0.697	0.978	7.00
C(17)	0.202 (2)	0.118 (1)	0.776 (3)	5.09 (52)	H(21)	1.125	0.737	1.140	7.00
C(18)	0.181 (2)	0.110 (1)	0.916 (2)	4.11 (45)	H(22)	1.341	0.745	1.052	7.00
C(19)	0.971 (2)	0.686 (1)	0.800 (2)	2.49 (35)	H(23)	1.303	0.718	0.802	7.00
C(20)	0.985 (2)	0.701 (1)	0.941 (2)	4.36 (51)	H(24)	1.081	0.685	0.647	7.00
C(21)	1.116 (2)	0.726 (1)	1.037 (2)	3.96 (45)	H(26)	0.476	0.407	0.260	7.00
C(22)	1.243 (2)	0.730 (1)	0.986 (2)	4.84 (51)	H(27)	0.556	0.520	0.155	7.00
C(23)	1.219 (3)	0.713 (1)	0.839 (3)	5.39 (55)	H(28)	0.388	0.594	0.060	7.00
C(24)	1.090 (2)	0.696 (1)	0.749 (2)	2.73 (36)	H(29)	0.156	0.571	0.067	7.00
C(25)	0.270 (2)	0.427 (1)	0.228 (2)	2.80 (37)	H(30)	0.073	0.456	0.172	7.00
C(26)	0.409 (2)	0.441 (1)	0.220 (2)	3.98 (44)	H(32)	0.120	0.275	0.539	7.00
C(27)	0.455 (3)	0.506 (1)	0.158 (2)	5.33 (55)	H(33)	0.083	0.328	0.767	7.00
C(28)	0.357 (3)	0.550 (1)	0.104 (3)	5.63 (57)	H(34)	0.119	0.459	0.827	7.00
C(29)	0.223 (2)	0.537 (1)	0.107 (2)	4.32 (47)	H(35)	0.180	0.545	0.676	7.00
C(30)	0.174 (2)	0.469 (1)	0.168 (2)	3.73 (44)	H(36)	0.217	0.497	0.449	7.00
C(31)	0.174 (2)	0.384 (1)	0.477 (2)	3.44 (1)	H(37a)	0.456	0.343	0.625	7.00
C(32)	0.133 (3)	0.332 (2)	0.567 (3)	6.46 (64)	H(37b)	0.481	0.404	0.490	7.00
C(33)	0.111 (3)	0.363 (2)	0.700 (3)	6.84 (66)	H(38a)	0.716	0.364	0.641	7.00
C(34)	0.134 (3)	0.439 (2)	0.735 (3)	5.90 (59)	H(38b)	0.689	0.348	0.451	7.00
C(35)	0.167 (3)	0.489 (2)	0.647 (3)	6.97 (68)	H(39a)	0.635	0.236	0.658	7.00
C(36)	0.189 (2)	0.462 (1)	0.515 (2)	4.79 (51)	H(39b)	0.758	0.240	0.543	7.00
C(37)	0.490 (2)	0.347 (1)	0.524 (2)	3.85 (45)	H(40a)	0.500	0.153	0.476	7.00
C(38)	0.647 (3)	0.332 (1)	0.543 (3)	5.10 (55)	H(40b)	0.587	0.194	0.347	7.00
C(39)	0.653 (2)	0.251 (1)	0.554 (2)	3.90 (45)					
C(40)	0.539 (2)	0.207 (1)	0.437 (2)	3.82 (45)					

<sup>a</sup> Standard deviations of the least significant digits are given in parentheses. <sup>b</sup> The anisotropic thermal ellipsoid is of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ , where  $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$ . <sup>c</sup> The hydrogen atom parameters were not refined.

Fourier, and Patterson calculations were performed on a CDC 6500 computer with programs provided by A. Zalkin. A Patterson synthesis with the inner-sphere data revealed the position of the platinum atom. After two cycles of least-squares refinement, the reliability factor,  $R$ , was 37.7%, where  $R = [\sum w(\Delta F)^2/w(F_O)^2]$ ,  $w = 1/\sigma^2 F$ , and  $\sigma_F = F/2I\sigma(I)$ . A difference Fourier then revealed the positions of the phosphorus atoms. Refinement with these atoms included gave  $R = 31.9\%$ . After Lorentz and polarization factors had been calculated and all Friedel pairs averaged, 3505 unique reflections remained<sup>6</sup> which provided approximately 17 reflections per parameter.

A set of the 1684 strongest reflections was selected from the data. From a series of difference Fourier maps calculated with this small data set, all 40 carbon atoms were located. Refinement was done by full-matrix calculation and in three sections with platinum and phosphorus atoms included in each: (1) four carbon atoms which composed the butylene ring, (2) all the carbon atoms in one phosphine group, and (3) all the carbon atoms of the other phosphine. With only the platinum and phosphorus atoms treated anisotropically,  $R$  reduced to 6.4% and  $R_w$  to 6.5%. When all 3505 reflections were used with the same parameters,  $R = 7.7\%$ . Examination of  $F$ 's at this point revealed one reflection (1014) for which the initial intensity

had been mispunched; it was deleted. The planarity of the phenyl rings was checked with the program LSQPLN<sup>7</sup> and the greatest deviation from planarity was found to be 5%.

The final step was the location of the hydrogen atoms. Examination of a difference Fourier indicated large peaks and valleys, of the order 4–5 e/Å<sup>3</sup>, surrounding the platinum atom position and apparently due to series termination effects in the Fourier summation. We therefore determined the hydrogen atom positions by geometrical considerations. The phenyl hydrogen positions were calculated from the equation  $r_H = r_{C_B} + (1.0/2.8)(r_{C_B} - r_{C_A})$ ,<sup>8</sup> where  $r_H$ ,  $r_{C_B}$ , and  $r_{C_A}$  represent a hydrogen atom, the carbon atom to which it is bonded, and the carbon atom para to  $C_B$ , respectively. The hydrogen atom positions on the butylene carbon atoms were calculated from tetrahedral geometry and a carbon-hydrogen bond length of 1.10 Å. Refinement of the hydrogen atom positions was effected by recalculation of their parameters after each of four cycles of least-squares analysis on the corresponding carbon atoms. The final unweighted and weighted  $R$  values were 7.4 and 6.8%, respectively. Final shifts in all parameters were less than 1% of their standard deviations; negative and positive residual peaks of the order of 1.7 e/Å<sup>3</sup> were symmetrically arranged around the platinum in the final

(6) 772 reflections with  $h$ ,  $k$ , and  $l$  all even were deleted due to problems with alignment of the monochromator. These data could not be recollected separately due to a major change in the configuration of the monochromator which would prevent proper merging of the two sets of data.

(7) J. Guildys, Program B-125 (3600F), "Least Squares Plane and Line Fitter," Argonne National Laboratory, Argonne, Ill.

(8) K. Anzenhofer and J. J. DeBoer, *Z. Kristallogr.*, 131, 103 (1970).

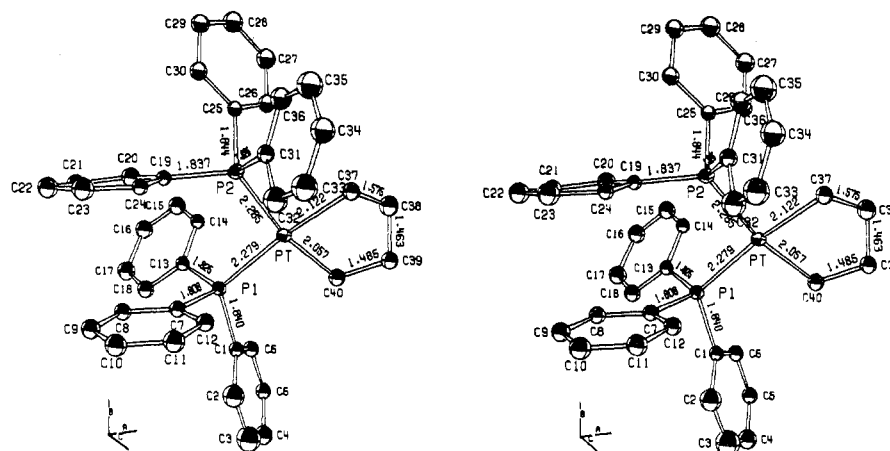


Figure 1. ORTEP stereoscopic drawing of a single molecule of  $\text{Pt}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{C}_4\text{H}_8$  with all hydrogen atoms omitted, 20% probability ellipsoids.

Table II. Interatomic Distances (with Esd's) within the  $\text{Pt}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{C}_4\text{H}_8$  Molecule

Atoms	Dist, Å	Atoms	Dist, Å
(A) Distances from Central Platinum Atom			
Pt-P(1)	2.279 (5)	Pt-C(37)	2.12 (2)
Pt-P(2)	2.285 (6)	Pt-C(40)	2.05 (2)
(B) Phosphorus-Phenyl Distances			
P(1)-C(1)	1.83 (2)	P(2)-C(19)	1.83 (2)
P(1)-C(7)	1.80 (2)	P(2)-C(25)	1.84 (2)
P(1)-C(13)	1.82 (2)	P(2)-C(31)	1.82 (2)
		Mean P-C (phenyl) <sup>a</sup>	1.82 (1)
(C) Carbon-Carbon Distances within $\text{C}_4\text{H}_8$ Ligand			
C(37)-C(38)	1.57 (3)	C(39)-C(40)	1.48 (3)
C(38)-C(39)	1.45 (3)	Mean C-C <sup>a</sup>	1.50 (6)
(D) Carbon-Carbon Distances within the Phenyl Rings			
C(1)-C(2)	1.41 (3)	C(19)-C(20)	1.35 (3)
C(2)-C(3)	1.41 (4)	C(20)-C(21)	1.39 (3)
C(3)-C(4)	1.38 (5)	C(21)-C(22)	1.43 (3)
C(4)-C(5)	1.36 (3)	C(22)-C(23)	1.39 (3)
C(5)-C(6)	1.39 (3)	C(23)-C(24)	1.34 (3)
C(6)-C(1)	1.39 (3)	C(24)-C(19)	1.35 (3)
C(7)-C(8)	1.37 (2)	C(25)-C(26)	1.37 (3)
C(8)-C(9)	1.40 (3)	C(26)-C(27)	1.40 (3)
C(9)-C(10)	1.37 (3)	C(27)-C(28)	1.36 (4)
C(10)-C(11)	1.35 (3)	C(28)-C(29)	1.31 (4)
C(11)-C(12)	1.41 (3)	C(29)-C(30)	1.43 (3)
C(12)-C(7)	1.39 (3)	C(30)-C(25)	1.35 (3)
C(13)-C(14)	1.39 (3)	C(31)-C(32)	1.39 (4)
C(14)-C(15)	1.38 (3)	C(32)-C(33)	1.44 (4)
C(15)-C(16)	1.28 (3)	C(33)-C(34)	1.34 (4)
C(16)-C(17)	1.40 (3)	C(34)-C(35)	1.32 (4)
C(17)-C(18)	1.43 (3)	C(35)-C(36)	1.40 (4)
C(18)-C(13)	1.37 (2)	C(36)-C(31)	1.39 (3)
		Mean C-C	1.38 (4)

<sup>a</sup> Esd's for mean bond distances are calculated from the equation  $\sigma = \{[\sum_{i=1}^{i=N} (X_i - \bar{X})^2] / (N - 1)\}^{1/2}$ , where  $X_i$  is the  $i$ th bond length and  $\bar{X}$  is the mean of the  $N$  equivalent bond lengths.

difference Fourier and were attributed to series termination effects in the Fourier summations.

Cromer and Waber's<sup>9</sup> scattering factors for neutral atoms were used for Pt, P, and C, while that for hydrogen was taken from the International Tables.<sup>10</sup> The real and imaginary parts of the anomalous scattering of platinum and phosphorus<sup>11</sup> were included in the calculated structure factors. A correction for secondary extinction did not seem necessary and so was not included.

The final positional and thermal parameters are given in Table I, each with its calculated standard deviation. The observed and calculated structure factors ( $\times 1.53$ ) are available.<sup>12</sup> Selected bond dis-

Table III. Interatomic Angles (deg) within the  $\text{Pt}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{C}_4\text{H}_8$  Molecule

Atoms	Angles	Atoms	Angles
(A) Angles around Platinum Atom			
P(1)-Pt-P(2)	98.8 (2)	P(2)-Pt-C(37)	86.5 (6)
P(1)-Pt-C(37)	173.4 (6)	P(2)-Pt-C(40)	167.2 (5)
P(1)-Pt-C(40)	93.9 (5)	C(37)-Pt-C(40)	80.9 (8)
(B) Angles around Phosphorus Atoms			
Pt-P(1)-C(1)	118.3 (6)	Pt-P(2)-C(19)	124.0 (6)
Pt-P(1)-C(7)	111.8 (6)	Pt-P(2)-C(25)	115.6 (7)
Pt-P(1)-C(13)	113.8 (6)	Pt-P(2)-C(31)	110.1 (7)
C(1)-P(1)-C(7)	100.8 (9)	C(19)-P(2)-C(25)	99.4 (8)
C(7)-P(1)-C(13)	111.1 (8)	C(25)-P(2)-C(31)	103.8 (9)
C(1)-P(1)-C(13)	99.9 (9)	C(19)-P(2)-C(31)	101.6 (9)
(C) Angles within the $\text{C}_4\text{H}_8$ Ligand			
Pt-C(37)-C(38)	104.5 (14)	C(38)-C(39)-C(40)	107.3 (18)
Pt-C(40)-C(39)	116.1 (15)	C(37)-C(38)-C(39)	110.6 (18)
(D) Angles within the Phenyl Rings			
C(1)-C(2)-C(3)	116.6 (26)	C(19)-C(20)-C(21)	123.7 (23)
C(2)-C(3)-C(4)	123.5 (29)	C(20)-C(21)-C(22)	118.6 (21)
C(3)-C(4)-C(5)	118.3 (24)	C(21)-C(22)-C(23)	114.1 (19)
C(4)-C(5)-C(6)	121.3 (22)	C(22)-C(23)-C(24)	124.5 (24)
C(5)-C(6)-C(1)	120.4 (19)	C(23)-C(24)-C(19)	121.1 (19)
C(6)-C(1)-C(7)	119.9 (20)	C(24)-C(19)-C(20)	117.4 (17)
C(7)-C(8)-C(9)	119.8 (19)	C(25)-C(26)-C(27)	118.4 (20)
C(8)-C(9)-C(10)	120.4 (18)	C(26)-C(27)-C(28)	118.1 (23)
C(9)-C(10)-C(11)	119.8 (23)	C(27)-C(28)-C(29)	124.8 (24)
C(10)-C(11)-C(12)	121.3 (23)	C(28)-C(29)-C(30)	117.8 (22)
C(11)-C(12)-C(7)	118.5 (17)	C(29)-C(30)-C(25)	118.5 (19)
C(12)-C(7)-C(8)	120.3 (19)	C(30)-C(25)-C(26)	122.1 (19)
C(13)-C(14)-C(15)	123.3 (16)	C(31)-C(32)-C(33)	116.9 (23)
C(14)-C(15)-C(16)	118.5 (21)	C(32)-C(33)-C(34)	120.4 (27)
C(15)-C(16)-C(17)	123.4 (24)	C(33)-C(34)-C(35)	123.2 (28)
C(16)-C(17)-C(18)	118.1 (19)	C(34)-C(35)-C(36)	118.9 (26)
C(17)-C(18)-C(13)	118.9 (19)	C(35)-C(36)-C(31)	120.3 (23)
C(18)-C(13)-C(14)	117.8 (18)	C(36)-C(31)-C(32)	120.1 (22)
		Mean	120.0 (24) <sup>a</sup>

<sup>a</sup> See footnote *a* to Table II.

tances and bond angles, presented in Tables II and III, were calculated with program ORFFE.<sup>13</sup> The hydrogen atom numbers match those of the carbon atom to which the hydrogen is bonded. A stereoscopic view (produced by the program ORTEP<sup>14</sup>) of a single

(12) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2166.

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(10) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1965.

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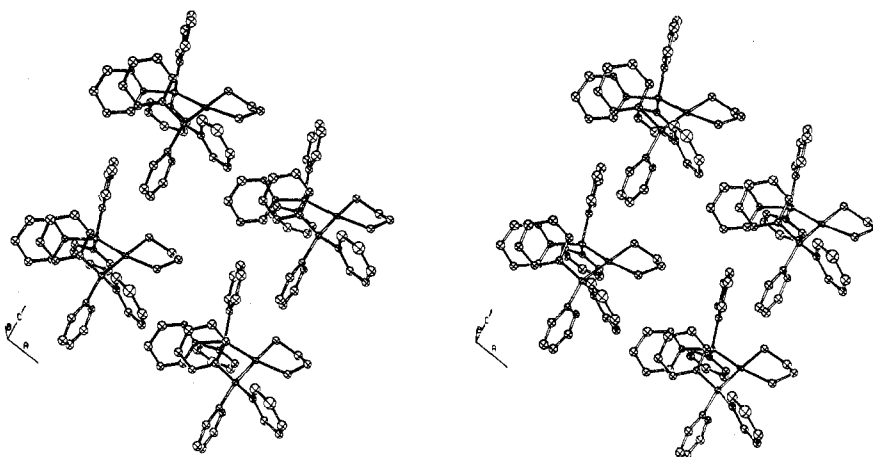


Figure 2. ORTEP stereoscopic drawing of the packing of four molecules of  $\text{Pt}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{C}_4\text{H}_8$  in front half of four unit cells. Crystallographic axes appear in the lower left-hand corner.

molecule is presented in Figure 1 and that of the packing of four molecules in the front half of four unit cells in Figure 2.

### Discussion

The crystal structure consists of the packing of discrete molecules (Figure 2). The molecular configuration is essentially a square plane, consisting of the platinum atom bonded to two phosphorus atoms and two carbon atoms which are, in turn, connected by a two-carbon bridge. The Pt-P bond distances of 2.279 (5) and 2.285 (6) Å may be compared with values of 2.29 (1) and 2.30 (1) Å in  $\text{Pt}[(\text{C}_6\text{H}_5)_3\text{P}]_2(\text{C}_2(\text{CN})_4)$ ,<sup>15</sup> 2.25 (1)–2.28 (1) Å in  $\text{Pt}[(\text{C}_6\text{H}_5)_3\text{P}]_3$ ,<sup>16</sup> and 2.24 (1) and 2.35 (1) Å in  $\text{Pt}[(\text{C}_6\text{H}_5)_3\text{P}]_2(\text{CS}_2)$ .<sup>17</sup> This bond length is shorter than what would be predicted from the usual sum rules for a normal covalent bond and probably reflects slight  $\pi$  interactions. The Pt-C distances of 2.05 (2) and 2.12 (2) Å may be compared to values of 2.10 (3) and 2.11 (3) Å in  $\text{Pt}[(\text{C}_6\text{H}_5)_3\text{P}]_2(\text{C}_2(\text{CN})_4)$ ,<sup>15</sup> and 2.105 (17) Å in  $[\text{Pt}(\text{acac})_2\text{Cl}]^-$ <sup>18</sup> and 2.04 (3) Å in  $\text{PtCl}(\text{OMe})(1,5\text{-C}_8\text{H}_{12})\text{-}(\text{py})$ .<sup>19</sup> It is interesting to compare these distances to those of some Pt-C bonds in  $\sigma$ -allyl complexes: 1.97 (5) and 2.00 (5) Å in  $[\text{Pt}_2(\text{acac})_2(\text{allyl})_2]$ <sup>20</sup> and 1.95 (8) Å in  $\text{PtBr}_3\text{OEt}(\text{oA})_2$ <sup>21</sup> where oA is *o*-allylphenyldimethylarsine. The P-C<sub>6</sub>H<sub>5</sub> bond lengths average 1.82 (1) Å which is comparable to the sum of the covalent radii, 1.87 Å,<sup>22</sup> and to values reported elsewhere, for example, 1.835 (13)–1.850 (14) Å in  $(\text{C}_3\text{H}_5)_2\text{Ru}[(\text{C}_6\text{H}_5)_3\text{P}]_2$ <sup>23</sup> and a mean P-C<sub>6</sub>H<sub>5</sub> distance of 1.83 (1) Å in  $\text{Rh}(\text{CO})[(\text{C}_6\text{H}_5)_3\text{P}]_3$ .<sup>24</sup> The average C-C bond length in the phenyl rings of 1.38 (4) Å compares well with the average C-C bond distance of 1.395 (3) Å<sup>25</sup> in benzene. The C-C bonds in the butylene ring range from

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Table IV. Deviation from Planarity of the Phenyl Rings

Ring <sup>a</sup>	Av dev  ( $\times 10^3$ ), Å	Ring <sup>a</sup>	Av dev  ( $\times 10^3$ ), Å
1	9 (28)	4	28 (20)
2	11 (19)	5	17 (26)
3	4 (21)	6	14 (26)

<sup>a</sup> Ring 1 consists of C(1)–C(6) with the corresponding hydrogen atoms. Ring 2 consists of C(7)–C(12) with the corresponding hydrogen atoms, etc.

1.45 (3) to 1.57 (3) Å compared to a single C–C bond length of 1.541 (3) Å.<sup>25</sup> In view of the standard errors in these bond lengths, the difference in the three C–C single bond lengths is probably insignificant.

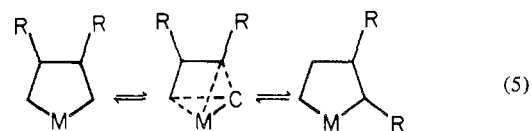
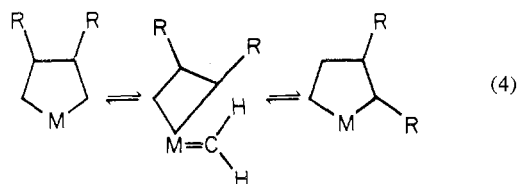
The square-planar geometry around the platinum atom is distorted. The degree of distortion, which can be expressed quantitatively by the angle between the planes through the atoms [Pt, P(1), P(2)] and [Pt, C(40), C(37)], is 175 (1)°. However, compared to an angle of 116 (1)° (between the cyclopropene ring and the plane defined by the Pt and 2P atoms) in the related compound  $\text{Pt}[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{C}_5\text{H}_{10}$ ,<sup>26</sup> the degree of distortion is small. A second way to visualize the distortion from square-planar geometry is to examine the placement of the remaining atoms around the platinum with respect to these two planes. The relationship of the four carbon atoms in the butylene group to the platinum-phosphorus plane is that C(37) and C(39) are above the plane [0.15 (2) and 0.02 (2) Å, respectively] and C(40) and C(38) are below it [0.05 (2) and 0.49 (2) Å, respectively]. In turn, the relationship of the phosphorus atoms and the remaining two carbon atoms of the butyl group to the platinum-carbon plane is that P(1) is 0.16 (55) Å above the plane while P(2), C(38), and C(39) are below it by 0.098 (5), 0.62 (2), and 0.002 (16) Å, respectively. A third measure of the distortion from square-planar geometry are the angles around the platinum. The P(1)–Pt–P(2) and C(37)–Pt–C(40) angles are 98.8 (2) and 80.9 (8)°, respectively, as would be expected. However, one would expect the P(1)–Pt–C(40) and P(2)–Pt–C(37) angles to be almost identical since they involve the same types of atoms, but they were found to be 93.9 (5) and 86.5 (6)°, respectively. The 7.4° difference is well outside the standard deviation (12σ). Finally, the angles P(1)–Pt–C(37) and P(2)–Pt–C(40) are 173.4 (6) and 167.2 (5)°, respectively, well outside the 180° angle expected for square-planar geometry.

The geometry around the phosphorus atom is, as expected,

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tetrahedrally distorted; the angles around P(1) range from 99.9 (9) to 118.3 (6)° and those around P(2) from 99.4 (8) to 124.0 (6)°. The deviation from planarity of the phenyl rings is given in Table IV.

One of the most interesting features of the structure is the puckering of the tetrahydroplatinole ring. One might expect to find C(40) and C(37) placed symmetrically above and below a plane through the Pt, C(38), and C(39); however, C(37) is 0.76 (2) Å above this plane while C(40) is only 0.40 (2) Å below it. When only the carbon atoms of the ring are considered, C(40) is significantly [1.04 (2) Å] below the plane formed by the other three atoms. A close examination of the packing of molecular units (Figure 2) indicates that puckering does not result from packing requirements. The geometry of the tetrahydroplatinole ring provides an indication of the mechanism whereby rearrangement of metallocycle intermediates in the olefin metathesis reactions occurs. Two analogous mechanisms which are reasonable and which fit the requirements of the observed geometry are



In metals with readily accessible, higher coordination numbers,<sup>27,28</sup> the above mechanisms could provide a mode for facile rearrangement. The preparation of similar complexes and characteristic reactions of both these and Pt[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>-C<sub>4</sub>H<sub>8</sub> will be reported.

**Registry No.** *cis*-Bis(triphenylphosphine)dichloroplatinum(II), 15604-36-1; 1,4-dithiobutane, 2123-72-0; [bis(triphenylphosphine)tetrahydroplatinole], 40548-16-1.

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Contribution No. 4609 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109

## Crystal Structure of $\mu$ -Peroxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(III)] Perchlorate

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The crystal and molecular structure of  $\mu$ -peroxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(III)] perchlorate, [(en)(dien)Co(O<sub>2</sub>)Co(en)(dien)](ClO<sub>4</sub>)<sub>4</sub>, Co<sub>2</sub>C<sub>12</sub>N<sub>10</sub>O<sub>18</sub>H<sub>42</sub>Cl<sub>4</sub>, has been determined by three-dimensional X-ray crystallographic analysis. The compound crystallizes in the monoclinic space group *P2<sub>1</sub>/n* with cell constants *a* = 9.062 (2) Å, *b* = 15.981 (8) Å, *c* = 11.153 (4) Å, and  $\beta$  = 92.53 (3)°. The calculated density, 1.790 (2) g cm<sup>-3</sup>, with *Z* = 2, agrees well with the 1.80 (2) g cm<sup>-3</sup> measured by flotation. Intensity data were collected with a Datex-automated General Electric diffractometer using iron-filtered cobalt K $\alpha$  radiation. The structure was solved by the heavy-atom Patterson method and refined by conventional Fourier and least-squares techniques to a final *R* index of 0.053 for 2130 independent reflections. The O<sub>2</sub> bridge is a peroxide group with the O-O distance 1.488 (6) Å. The Co-O-O-Co linkage is planar, the halves of the cation being related by a center of symmetry centered on the O-O bond. Comparison with other peroxide-bridged compounds suggests that the planarity of the Co-O-O-Co linkage is a consequence of Coulomb repulsion between the two highly charged cobalt centers. The Co-O distance is 1.896 (4) Å and the Co-O-O angle is 110.0 (3)°. The coordination about the cobalt atom is slightly distorted octahedral. The trans effect of the peroxide oxygen atom is apparent in the significant lengthening of the trans Co-N bond relative to the cis Co-N bonds. The terminal nitrogen atoms of the dien ligand are trans to one another.

### Introduction

There has been a renewed interest lately in the chemistry and structure of peroxo-bridged dicobalt complexes, although Werner first elucidated their constitution at the turn of the century.<sup>1</sup> In particular, these compounds are of interest because of the ability of some of them to decompose quantitatively to their starting materials, a cobalt(II) species and

molecular oxygen. In order to understand the structural basis of the ability of certain of these complexes to function as reversible oxygen carriers it is necessary to have structural data for some of the irreversible oxygen adducts for comparison. As part of our studies on reversible oxygen carriers we have therefore determined the structure of the irreversibly formed complex  $\mu$ -peroxo-bis[(ethylenediamine)(diethylenetriamine)Co(III)] perchlorate.

In addition to accumulating basic structural information on these compounds we also were intrigued by several particular features of this complex. First, as no structures of  $\mu$ -peroxo-

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