Journal of Organometallic Chemistry, 90 (1975) 111—121
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE MOLECULAR STRUCTURE OF BIS(TRIPHENYLPHOSPHINE)-1,1-DIMETHYLALLENEPLATINUM

NORITAKE YASUOKA, MAMORU MORITA, YASUSHI KAI and NOBUTAMI KASAI

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565 (Japan)

(Received October 9th, 1974)

Summary

The molecular structure of $[(C_6H_5)_3P]_2Pt(C_5H_8)$ has been determined from three-dimensional X-ray diffraction data (R = 0.045 for 6033 reflections). The crystal belongs to the triclinic system, space group $P\bar{1}$, with two formula units in a cell of dimensions: a = 18.557(2), b = 10.216(2), c = 9.647(2) Å, α = 98.29 (3), β = 73.44(2), and γ = 88.34(2)°.

One of the olefinic bonds of dimethylallene, which has no adjacent methyl groups, is coordinated to the platinum atom: Pt—C(1) = 2.108(8), Pt—C(2) = 2.049(7) Å. The coordinated dimethylallene molecule is no longer linear, the C(1)—C(2)—C(3) angle being 140.8(8)°, which is significantly smaller than that found in $[(C_6H_5)_3P]_2Pd(C_3H_4)$. The C(1)—C(2) distance is 1.430(11) Å, whereas the uncoordinated bond distance is normal [C(2)—C(3) = 1.316(11) Å].

Introduction

Otsuka and his coworkers have synthesized a number of allene complexes with transition metals [1, 2]. A series of compounds $(Ph_3P)_2M(RR'C{=}C{=}CR''R''')$ (M = Ni, Pd or Pt, and R, R'... = H or CH_3) are particularly interesting from the point of view of their structural chemistry, because they enable us to study the differences due to the change in the metal atom as well as the effect of the substituents in the allene ligand.

In this context, we have already reported the molecular structure of $(Ph_3P)_2Pt(C_3H_4)$ [3] and $(Ph_3P)_2Pd(C_3H_4)$ [4], and have discussed the nature of the bonding and the structural differences arising from this change in central metal atom. We now report the result of a structural investigation of $(Ph_3P)_2Pt(C_5H_8)$. The electronic effects as well as the steric effects of the substituents on coordinated ethylene molecules already have been discussed by Ibers and his coworkers [5]. We will discuss the steric effect of the methyl groups of dimethylallene.

Experimental

The crystals of $(Ph_3P)_2Pt(C_5H_8)$ used in this study were kindly supplied by Professor S. Otsuka and his coworkers of Osaka University. They are pale yellow and fairly stable in the air. After preliminary photographic X-ray work, which showed the crystals belonged to the triclinic system, accurate cell dimensions were determined by a least-squares fit of 2θ values of 20 higher order reflections measured on a Rigaku automated four-circle, single crystal diffractometer.

Crystal data. $C_{41}H_{38}P_2Pt$, formula wt. 787.7, triclinic, space group $P\bar{1}$, a = 18.557(2), b = 10.216(2), c = 9.647(2) Å, α = 98.29(3), β = 73.44(2), γ = 88.34(2)°, U = 1730.0(4) Å^3, D_m = 1.56 g/cm^3, Z = 2, D_c = 1.51 g/cm^3. (Mo $K\alpha_1$, λ = 0.70926 Å, μ = 45.3 cm^{-1}).

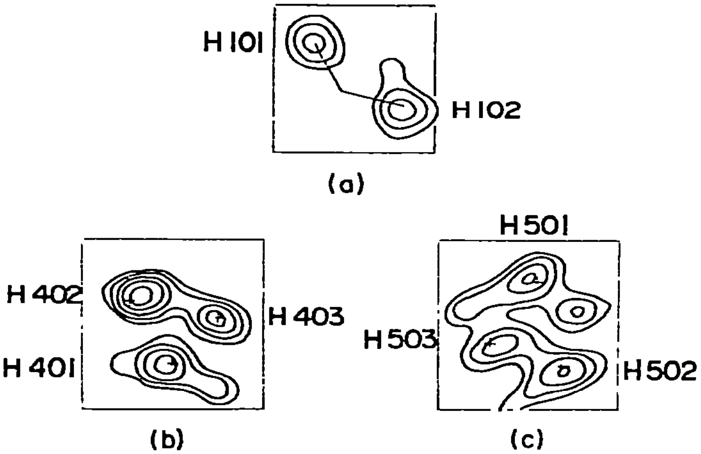
Intensity data were measured on a Rigaku diffractometer, using graphite-monochromatized Mo-$K\alpha$ radiation. The setting angles of each reflection were computed on-line with a FACOM R computer by the Busing—Levy method [6]. The setting parameters, which determine the UB orientation matrix, were determined by a least-squares method using the precise values of centering angles 2θ, ω, χ and ϕ of 20 higher order reflections.

The θ—2θ scan technique was employed for data collection. The integrated intensity was determined by scanning the peak at a rate of 4°/min, and subtracting the background obtained by averaging the two values measured for 7.5 sec at both ends of a scan. The scan range in 2θ was from —1.0° from the K_{α_1} peak to 1.0° from the K_{α_2} peak. A crystal used for intensity measurement had the dimensions of 0.15 × 0.20 × 0.20 mm. A total of 6033 unique reflections was measured out to a 2θ(Mo-K_{α_1}) value of 50°, and of these 503 reflections were less than $\sigma(F)$ and were recorded as zero. Three standard reflections were measured after every 50 reflections, and the intensities of these reflections remained constant throughout the data collection. Lorentz and polarization corrections were made, but no absorption correction was applied to the intensity data (μr = 0.9), which might limit the accuracy of the present structure determination.

Solution and refinement of the structure

The structure was solved by the conventional heavy-atom method. A three-dimensional Patterson function was computed and interpreted to give the coordinates of the platinum and phosphorus atoms. The remaining non-hydrogen atoms were easily located on the successive Fourier maps.

Structure refinement was carried out by the method of block-diagonal least-squares, the function minimized being $\Sigma w(|F_o|-|F_c|)^2$ with HBLS V program [7]. The atomic scattering factors used in all the calculations were those of Hanson et al. [8]. Anomalous dispersion for Pt and P was included in F_c [9]. A few cycles of isotropic refinement followed by anisotropic cycles, based on the inner 4155 non-zero reflections, converged the values of R_1 and R_2 to



(a)

(b)

(c)

Fig. 1. The difference Fourier map showing the hydrogen atoms in the 1,1-dimethylallene moiety calculated on the plane through (a) H(101) C(1) H(102); (b) H(401) H(402) H(403); (c) H(501) H(502) H(503). The framework or atomic positions indicated by crosses are also drawn.

0.034 and 0.044, respectively, where $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_2 = \{\Sigma(|F_o|-|F_c|)^2/\Sigma|F_o|^2\}^{1/2}$. All the phenyl hydrogen atom positions were located from stereochemical considerations assuming the C—H bond length to be 1.08 Å. However, the hydrogen atoms of the dimethylallene ligand were located from a difference Fourier synthesis. A few more cycles were carried out using all reflections, because it has been pointed out that the exclusion of weak reflections might possibly introduce some systematic error in the refined parameters [10]. Unit weights were used for each reflection throughout the refinement, because the average $w(\Delta F)^2$ for subsets of reflections, calculated as a function of both size of $|F_o|$ and $(\sin\theta/\lambda)$ did not deviate significantly from each other. The final least-squares cycles reduced the values of R_1 and R_2 to 0.045 and 0.043, respectively, for 6033 reflections (R_1 = 0.034 for 5530 non-zero reflections). During the last cycles, positional parameters of allene hydrogens were refined, but only the thermal parameters of methylene hydrogens were refined, those of methyl hydrogens being fixed to the same value as the isotropic temperature factors of the corresponding methyl carbon atoms. This procedure will be discussed later. The difference map calculated on the planes through the hydrogen atoms is shown in Fig. 1. The final positional and thermal parameters along with their estimated standard deviations are listed in Tables 1 and 2*.

Results and discussion

Figure 2 presents a stereo drawing of the $(Ph_3P)_2Pt(C_5H_8)$ molecule. Figure 3 indicates the numbering scheme. The coordination geometry around the

(continued on p 116)

---

[*] The table of structure factors has been deposited as NAPS Document No. 02528, with ASIS/NAPS, c/o Microfiche Publications, 440 Park Ave. So., New York, New York 10016. A copy may be secured by citing the document and remitting $ 1.50 for microfiche or $ 5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 1

ATOMIC PARAMETERS OF HEAVIER ATOMS IN $(Ph_3P)_2Pt(C_5H_8)$. POSITIONAL PARAMETERS IN FRACTION OF CELL EDGES AND THERMAL PARAMETERS IN THE FORM OF exp $\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$. STANDARD DEVIATIONS SHOWN IN PARENTHESES ARE APPLIED TO THE LEAST SIGNIFICANT DIGIT.

ATOM	X	Y	Z	B(11)
PT	.230152(13)	.37298(2)	.02227(3)	.001983(7)
P(1)	.32531(9)	.34304(16)	-.19195(17)	.00224(5)
P(2)	.13891(9)	.23013(16)	.00011(18)	.00197(5)
C(1)	.1855(4)	.4751(7)	.2378(8)	.0034(3)
C(2)	.2611(4)	.5058(7)	.1716(7)	.0035(3)
C(3)	.3153(4)	.5733(7)	.2029(7)	.0047(3)
C(4)	.3917(5)	.5755(9)	.1026(10)	.0046(4)
C(5)	.3006(6)	.6596(10)	.3525(10)	.0069(5)
C(11)	.3117(4)	.2616(7)	-.3647(7)	.0024(2)
C(12)	.2970(4)	.1293(7)	-.3750(8)	.0034(3)
C(13)	.2854(5)	.0639(9)	-.5028(10)	.0036(3)
C(14)	.2895(5)	.1314(11)	-.6179(10)	.0042(4)
C(15)	.3046(5)	.2626(11)	-.6103(9)	.0046(4)
C(16)	.3169(4)	.3285(9)	-.4822(8)	.0037(3)
C(21)	.3621(4)	.5006(6)	-.2425(7)	.0030(2)
C(22)	.3098(5)	.6055(8)	-.2207(9)	.0039(3)
C(23)	.3332(6)	.7275(9)	-.2571(10)	.0064(5)
C(24)	.4089(6)	.7450(9)	-.3105(11)	.0075(5)
C(25)	.4608(5)	.6418(10)	-.3299(10)	.0052(4)
C(26)	.4385(4)	.5178(8)	-.2984(9)	.0032(3)
C(31)	.4085(3)	.2420(6)	-.1884(7)	.00192(20)
C(32)	.4604(4)	.1786(8)	-.3160(9)	.0030(3)
C(33)	.5228(5)	.1047(8)	-.3101(10)	.0032(3)
C(34)	.5325(4)	.0942(8)	-.1759(11)	.0032(3)
C(35)	.4809(4)	.1565(8)	-.0470(10)	.0035(3)
C(36)	.4183(4)	.2292(7)	-.0524(8)	.0032(3)
C(41)	.1210(3)	.1773(7)	-.1751(7)	.0023(2)
C(42)	.1083(4)	.0468(7)	-.2259(8)	.0036(3)
C(43)	.0925(5)	.0176(9)	-.3588(9)	.0045(3)
C(44)	.0889(5)	.1145(10)	-.4421(9)	.0054(4)
C(45)	.1014(5)	.2423(9)	-.3945(9)	.0053(4)
C(46)	.1185(4)	.2731(8)	-.2635(9)	.0036(3)
C(51)	.0440(3)	.2871(6)	.1199(7)	.0021(2)
C(52)	-.0154(4)	.3086(10)	.0668(10)	.0028(3)
C(53)	-.0863(5)	.3523(11)	.1620(12)	.0025(3)
C(54)	-.0984(5)	.3730(10)	.3104(12)	.0036(3)
C(55)	-.0385(5)	.3546(9)	.3637(9)	.0043(3)
C(56)	.0319(4)	.3103(8)	.2694(8)	.0033(3)
C(61)	.1566(4)	.0745(6)	.0609(7)	.0027(2)
C(62)	.0993(5)	-.0015(8)	.1265(9)	.0045(3)
C(63)	.1150(6)	-.1184(8)	.1682(11)	.0077(5)
C(64)	.1882(6)	-.1649(8)	.1463(11)	.0079(5)
C(65)	.2472(5)	-.0918(8)	.0777(10)	.0049(4)
C(66)	.2310(4)	.0284(7)	.0378(8)	.0032(3)

B(22)	B(33)	B(12)	B(13)	B(23)
.00641(2)	.00743(3)	-.001505(19)	-.00119(2)	.00053(4)
.00731(16)	.00783(19)	-.00120 (15)	-.00125(16)	-.0001 (3)
.00745(17)	.0091 (2)	-.00160 (14)	-.00217(16)	.0019 (3)
.0107 (8)	.0101 (9)	-.0016 (7)	-.0003 (8)	-.0012 (14)
.0090 (7)	.0080 (8)	-.0039 (7)	-.0014 (7)	.0022 (12)
.0092 (8)	.0085 (8)	-.0046 (8)	-.0033 (8)	.0013 (13)
.0152 (12)	.0167 (13)	-.0077 (10)	-.0065 (11)	-.0006 (20)
.0161 (13)	.0155 (13)	-.0073 (13)	-.0085 (13)	-.008 (2)
.0106 (8)	.0078 (8)	-.0007 (7)	-.0003 (7)	-.0007 (12)
.0103 (9)	.0136 (11)	-.0005 (8)	-.0031 (9)	-.0065 (15)
.0141 (11)	.0185 (14)	.0011 (9)	-.0051 (11)	-.0120 (20)
.0232 (16)	.0132 (12)	.0023 (12)	-.0045 (11)	-.012 (2)
.0253 (17)	.0107 (11)	-.0000 (13)	-.0045 (10)	.004 (2)
.0160 (11)	.0088 (9)	.0002 (9)	-.0031 (8)	.0039 (16)
.0081 (7)	.0081 (8)	-.0013 (6)	-.0007 (7)	.0018 (12)
.0106 (9)	.0148 (12)	.0003 (8)	-.0010 (9)	.0040 (16)
.0107 (10)	.0157 (13)	-.0001 (10)	-.0001 (12)	.0066 (18)
.0104 (10)	.0181 (15)	-.0058 (12)	.0010 (14)	.0060 (19)
.0152 (12)	.0176 (14)	-.0074 (11)	-.0003 (12)	.010 (2)
.0135 (10)	.0144 (11)	-.0029 (8)	-.0006 (9)	.0062 (17)
.0080 (7)	.0119 (9)	-.0004 (6)	-.0022 (7)	.0036 (12)
.0111 (9)	.0161 (12)	.0015 (8)	-.0020 (9)	-.0014 (17)
.0121 (10)	.0195 (14)	.0014 (8)	-.0012 (10)	-.0015 (19)
.0100 (9)	.0247 (17)	-.0007 (8)	-.0052 (11)	.0045 (19)
.0132 (10)	.0216 (15)	-.0022 (9)	-.0098 (11)	.0131 (20)
.0099 (8)	.0125 (10)	-.0026 (7)	-.0043 (8)	.0043 (14)
.0098 (8)	.0098 (8)	-.0015 (6)	-.0026 (7)	.0012 (13)
.0105 (8)	.0100 (9)	-.0031 (7)	-.0035 (8)	.0028 (14)
.0156 (12)	.0146 (12)	-.0060 (10)	-.0072 (11)	-.0014 (19)
.0200 (14)	.0117 (11)	-.0067 (12)	-.0074 (11)	.0065 (20)
.0170 (12)	.0120 (11)	-.0030 (11)	-.0069 (11)	.0076 (19)
.0118 (9)	.0142 (11)	-.0027 (8)	-.0048 (9)	.0063 (16)
.0081 (7)	.0120 (9)	-.0023 (6)	-.0016 (7)	.0032 (13)
.0176 (13)	.0167 (13)	.0009 (9)	-.0029 (10)	-.004 (2)
.0234 (17)	.0263 (19)	.0033 (11)	-.0055 (12)	.001 (3)
.0147 (12)	.0234 (17)	-.0013 (10)	.0032 (12)	.001 (2)
.0152 (12)	.0137 (12)	-.0036 (10)	.0019 (10)	-.0001 (19)
.0132 (10)	.0120 (10)	-.0029 (8)	.0013 (8)	.0029 (16)
.0071 (7)	.0109 (9)	-.0006 (6)	-.0047 (7)	.0001 (12)
.0102 (9)	.0163 (12)	-.0056 (9)	-.0066 (10)	.0078 (17)
.0084 (9)	.0198 (15)	-.0053 (11)	-.0099 (14)	.0104 (18)
.0085 (9)	.0221 (16)	.0001 (11)	-.0151 (16)	.0027 (19)
.0119 (10)	.0168 (13)	.0028 (9)	-.0087 (11)	-.0009 (18)
.0093 (8)	.0123 (10)	.0002 (7)	-.0055 (8)	.0014 (14)

TABLE 2

ATOMIC PARAMETERS OF HYDROGEN ATOMS IN $(Ph_3P)_2Pt(C_5H_8)$. THERMAL PARAMETERS ARE IN THE FORM OF $\exp\{-B(\sin\theta/\lambda)^2\}$. STANDARD DEVIATIONS ARE SHOWN ONLY FOR REFINED PARAMETERS.

ATOM	X	Y	Z	B
H(101)	.143(5)	.548(9)	.244(10)	5.3(24)
H(102)	.188(5)	.392(9)	.320(10)	5.4(25)
H(401)	.426(5)	.545(9)	.154(10)	5.3
H(402)	.404(5)	.511(9)	.013(10)	5.3
H(403)	.402(5)	.659(9)	.085(10)	5.3
H(501)	.247(6)	.678(10)	.405(11)	6.1
H(502)	.339(6)	.622(10)	.401(11)	6.1
H(503)	.322(6)	.740(10)	.345(11)	6.1
H(12)	.295	.077	-.284	4.5
H(13)	.273	-.039	-.512	5.3
H(14)	.281	.080	-.717	6.0
H(15)	.307	.314	-.702	6.0
H(16)	.331	.431	-.475	4.4
H(22)	.251	.593	-.175	4.5
H(23)	.292	.809	-.244	6.0
H(24)	.427	.840	-.337	6.2
H(25)	.520	.656	-.370	6.7
H(26)	.480	.436	-.317	4.6
H(32)	.452	.187	-.421	4.8
H(33)	.563	.056	-.410	5.4
H(34)	.581	.036	-.171	5.7
H(35)	.490	.148	.057	5.2
H(36)	.377	.276	.048	3.9
H(42)	.111	-.031	-.162	4.1
H(43)	.083	-.083	-.397	5.2
H(44)	.076	.090	-.545	5.8
H(45)	.098	.319	-.459	5.8
H(46)	.130	.373	-.229	4.5
H(52)	-.007	.292	-.050	5.5
H(53)	-.133	.370	.118	6.6
H(54)	-.154	.403	.384	6.5
H(55)	-.046	.375	.480	5.6
H(56)	.078	.294	.313	4.8
H(62)	.041	.033	.145	4.8
H(63)	.069	-.175	.219	6.5
H(64)	.200	-.257	.181	5.8
H(65)	.305	-.129	.056	5.5
H(66)	.276	.087	-.011	3.8

platinum atom is shown in Fig. 4. The bond lengths and bond angles are listed in Table 3.

The best plane passing through the Pt, P(1), P(2), C(1) and C(2) atoms is represented by the equation: $0.531\,X - 0.785\,Y + 0.319\,Z + 0.522 = 0.0$. Deviations from this plane (in Å) are: Pt, 0.021; P(1), 0.032; P(2), −0.081; C(1), 0.071; C(2), −0.066; whereas that of the uncoordinated carbon atom, C(3), is −0.240 Å. The dihedral angle between the two planes defined by P(1), Pt and P(2), and C(1), Pt and C(2), is 7.8°. A similar angle has been reported for many olefin-platinum, -palladium and -nickel complexes [11-14].

The main purpose of the present work is to compare the coordination geometry of $(Ph_3P)_2Pt(C_5H_8)$ with $(Ph_3P)_2Pd(C_3H_4)$ and $(Ph_3P)_2Pt(C_3H_4)$. The

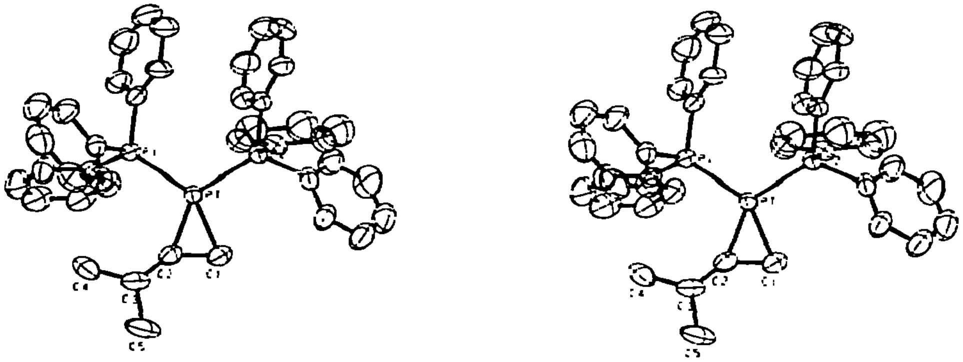


Fig. 2. The stereo drawing of the $(Ph_3P)_2Pt(C_5H_8)$ molecule. The thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity.

corresponding interatomic distances and angles found in these three compounds are summarized in Table 4. Although the first two structures have been determined accurately, it is unfortunate that the structural investigation of the last compound is of only limited accuracy. Nevertheless some conclusions on the structure can be drawn from these results.

We have already noted that the bonding of platinum to allene is stronger than that of palladium [4]. This is again confirmed in the present work. The C(1)—C(2)—C(3) angle is smaller and the C(1)—C(2) distance longer in Pt complexes than in Pd analogs, although the difference is not fully significant, i.e.,

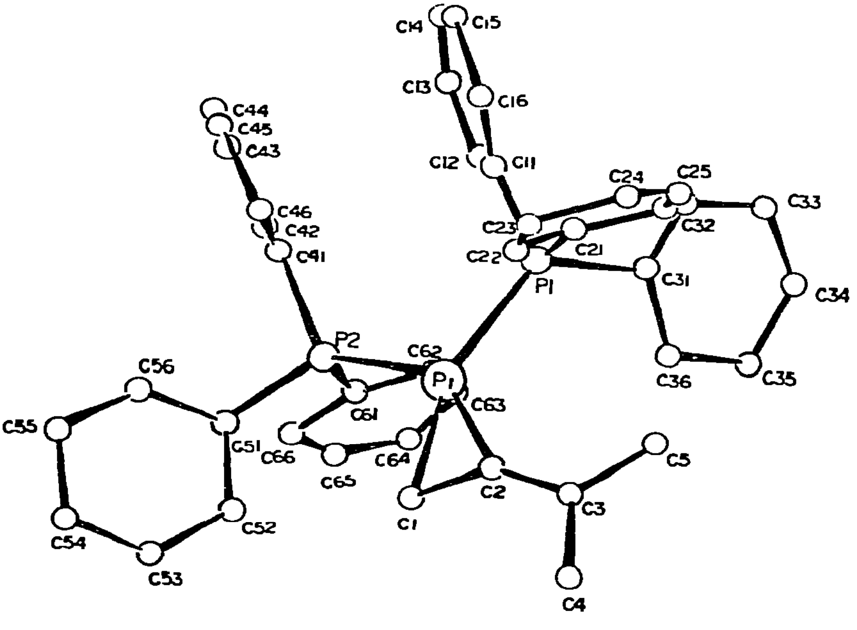


Fig. 3. The molecular structure of $(Ph_3P)_2Pt(C_5H_8)$, and the numbering system of atoms.

TABLE 3

BOND LENGTHS (Å) AND BOND ANGLES (°) WITH THEIR ESTIMATED STANDARD DEVIATIONS

Coordinating atoms			
Pt—P(1)	2.278(2)	P(1)—Pt—P(2)	109.1(1)
Pt—P(2)	2.303(2)	P(1)—Pt—C(1)	148.2(3)
Pt—C(1)	2.107(8)	P(1)—Pt—C(2)	108.2(3)
Pt—C(2)	2.049(7)	P(2)—Pt—C(1)	102.7(3)
C(1)—C(2)	1.430(11)	P(2)—Pt—C(2)	142.4(3)
C(2)—C(3)	1.316(11)	C(1)—Pt—C(2)	40.2(3)
C(3)—C(4)	1.475(13)	Pt—C(1)—C(2)	67.7(5)
C(3)—C(5)	1.526(14)	Pt—C(2)—C(1)	72.1(5)
C(1)—H(101)	1.05 (10)	Pt—C(2)—C(3)	147.0(7)
C(1)—H(102)	1.25(11)	C(1)—C(2)—C(3)	140.8(8)
C(4)—H(401)	0.98(10)	C(2)—C(3)—C(4)	125.2(8)
C(4)—H(402)	0.97(10)	C(2)—C(3)—C(5)	119.9(8)
C(4)—H(403)	0.91(10)	C(4)—C(3)—C(5)	115.0(8)
C(5)—H(501)	0.98(11)	Pt—C(1)—H(101)	111(6)
C(5)—H(502)	1.06(11)	Pt—C(1)—H(102)	106(5)
C(5)—H(503)	0.92(11)	C(2)—C(1)—H(101)	115(6)
		C(2)—C(1)—H(102)	108(5)
		H(101)—C(1)—H(102)	131(8)
		Pt—P(1)—C(11)	121.7(3)
		Pt—P(1)—C(21)	112.5(3)
		Pt—P(1)—C(31)	114.0(3)
		Pt—P(2)—C(41)	121.9(3)
		Pt—P(2)—C(51)	114.4(3)
		Pt—P(2)—C(61)	110.6(3)
Triphenylphosphine groups			
P(1)—C(11)	1.840(7)	C(11)—P(1)—C(21)	101.7(4)
P(1)—C(21)	1.843(7)	C(21)—P(1)—C(31)	104.7(4)
P(1)—C(31)	1.844(7)	C(31)—P(1)—C(11)	100.2(4)
C(11)—C(12)	1.382(11)	C(11)—C(12)—C(13)	119.6(8)
C(12)—C(13)	1.391(13)	C(12)—C(13)—C(14)	119.7(9)
C(13)—C(14)	1.375(15)	C(13)—C(14)—C(15)	121.7(11)
C(14)—C(15)	1.373(16)	C(14)—C(15)—C(16)	118.9(11)
C(15)—C(16)	1.402(15)	C(15)—C(16)—C(11)	119.7(9)
C(16)—C(11)	1.388(11)	C(16)—C(11)—C(12)	120.5(8)
C(21)—C(22)	1.376(11)	C(21)—C(22)—C(23)	120.1(9)
C(22)—C(23)	1.392(14)	C(22)—C(23)—C(24)	120.1(10)
C(23)—C(24)	1.379(16)	C(23)—C(24)—C(25)	119.8(11)
C(24)—C(25)	1.363(15)	C(24)—C(25)—C(26)	120.9(10)
C(25)—C(26)	1.392(13)	C(25)—C(26)—C(21)	119.3(8)
C(26)—C(21)	1.393(11)	C(26)—C(21)—C(22)	119.7(8)
C(31)—C(32)	1.385(11)	C(31)—C(32)—C(33)	120.5(8)
C(32)—C(33)	1.382(13)	C(32)—C(33)—C(34)	119.2(9)
C(33)—C(34)	1.376(14)	C(33)—C(34)—C(35)	121.0(10)
C(34)—C(35)	1.388(14)	C(34)—C(35)—C(36)	119.9(9)
C(35)—C(36)	1.378(12)	C(35)—C(36)—C(31)	119.5(8)
C(36)—C(31)	1.398(10)	C(36)—C(31)—C(32)	119.9(7)
P(2)—C(41)	1.824(7)	C(41)—P(2)—C(51)	101.9(4)
P(2)—C(51)	1.834(7)	C(51)—P(2)—C(61)	102.2(4)
P(2)—C(61)	1.825(7)	C(61)—P(2)—C(41)	103.7(4)
C(41)—C(42)	1.403(10)	C(41)—C(42)—C(43)	119.8(8)
C(42)—C(43)	1.388(12)	C(42)—C(43)—C(44)	121.2(9)
C(43)—C(44)	1.373(14)	C(43)—C(44)—C(45)	119.8(10)

(continued)

TABLE 3 (continued)

C(44)—C(45)	1.370(14)	C(44)—C(45)—C(46)	119.9(9)
C(45)—C(46)	1.384(13)	C(45)—C(46)—C(41)	121.5(8)
C(46)—C(41)	1.396(11)	C(46)—C(41)—C(42)	117.8(7)
C(51)—C(52)	1.366(12)	C(51)—C(52)—C(53)	120.5(10)
C(52)—C(53)	1.390(15)	C(52)—C(53)—C(54)	120.9(11)
C(53)—C(54)	1.368(16)	C(53)—C(54)—C(55)	118.7(11)
C(54)—C(55)	1.371(15)	C(54)—C(55)—C(56)	120.5(9)
C(55)—C(56)	1.381(13)	C(55)—C(56)—C(51)	121.0(8)
C(56)—C(51)	1.379(11)	C(56)—C(51)—C(52)	118.5(8)
C(61)—C(62)	1.391(11)	C(61)—C(62)—C(63)	121.3(9)
C(62)—C(63)	1.364(14)	C(62)—C(63)—C(64)	120.7(11)
C(63)—C(64)	1.373(16)	C(63)—C(64)—C(65)	119.2(11)
C(64)—C(65)	1.404(15)	C(64)—C(65)—C(66)	119.8(9)
C(65)—C(66)	1.389(12)	C(65)—C(66)—C(61)	120.3(8)
C(66)—C(61)	1.391(10)	C(66)—C(61)—C(62)	118.6(7)

the greater the bending of the C(1)—C(2)—C(3) angle, the longer the C(1)—C(2) bond length. A similar observation has been reported for tetracyanoethylene-metal complexes [5].

The steric influence of two methyl groups in $(Ph_3P)_2Pt(C_5H_8)$ is seen from Table 4. The P(1)—M—C(2) angle and the P(2)—M—C(1) angle in this compound are significantly larger and smaller, respectively, than the corresponding angles in allene complexes. The non-bonding repulsion between the C(4) methyl group

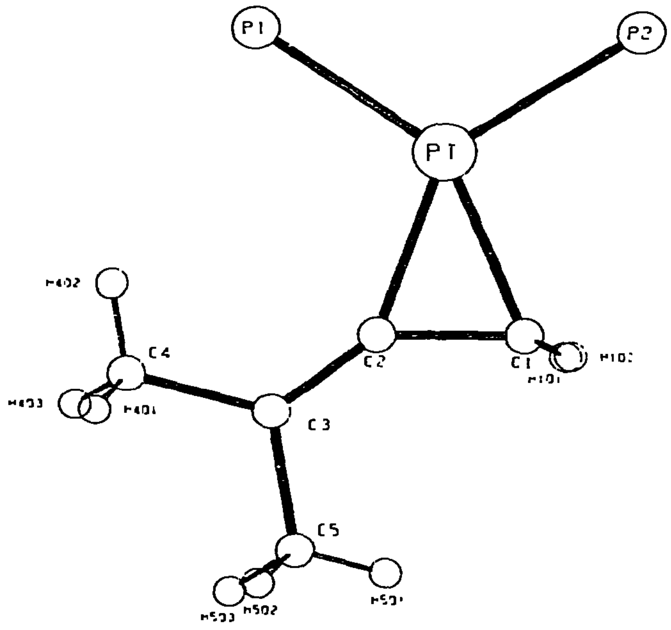


Fig. 4. Inner coordination geometry around the platinum atom. Hydrogen atoms are also shown.

TABLE 4

STRUCTURAL PARAMETERS OF THE COORDINATION AROUND THE METAL ATOM

	$(PPh_3)_2Pt(C_5H_8)$	$(PPh_3)_2Pd(C_3H_4)$	$(PPh_3)_2Pt(C_3H_4)$
M—P(1)	2.278(2)	2.314(2)	2.278(9)
M—P(2)	2.303(2)	2.324(2)	2.286(9)
M—C(1)	2.107(8)	2.118(9)	2.13(3)
M—C(2)	2.049(7)	2.067(8)	2.03(3)
C(1)—C(2)	1.430(11)	1.401(11)	1.48(5)
C(2)—C(3)	1.316(11)	1.304(12)	1.31(5)
C(1)—C(2)—C(3)	140.8(8)	148.3(8)	142(3)
P(1)—M—P(2)	109.1(1)	109.3(1)	107.1(3)
P(1)—M—C(2)	108.2(2)	104.3(3)	104(1)
P(2)—M—C(1)	102.7(2)	107.5(3)	108(1)
M—C(2)—C(3)	146.9(6)	139.2(7)	145(3)
Angle [a]	7.8	8.6	9
Reference	This work	4	3

[a] Dihedral angle between ML_2 plane and the M, C(1), C(2) plane.

and phenyl groups attached to the P(1) atom may have caused this. The non-bonded distances of C(4)...C(21), C(4)...C(26) and C(4)...C(36) are 3.507(12), 3.670(13) and 3.597(12) Å, respectively. The shortest distance between hydrogen atoms is H(402)...H(36) of 2.50 Å. These net repulsions might hinder the rotation of the C(4) methyl group. Figure 1 shows the difference maps in which the contributions of heavier atoms are subtracted, each being calculated on the plane where hydrogen atoms of dimethylallene ligand are expected to be. The C(4) methyl hydrogens (Fig. 1b) as well as methylene hydrogen atoms (Fig. 1a) are clearly identified on these maps, while the C(5) methyl hydrogens (Fig. 1c) are somewhat smeared out. This suggests that the C(4) methyl group packs in one conformation whereas the C(5) methyl group may assume several conformations in the crystal, the observed one being favored and occurring most often. Therefore the parameters of C(5) methyl hydrogen atoms only give one of the probable positions. The bond angles C(2)—C(3)—C(4) and C(4)—C(3)—C(5) are 125.2(8) and 114.1(8)°, respectively, and are significantly different from 120° which

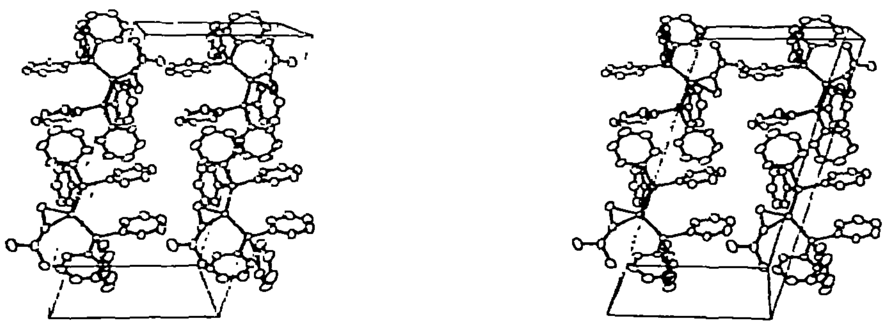


Fig. 5. Stereoscopic view of the crystal structure of $(Ph_3P)_2Pt(C_5H_8)$.

would be the bonding angle for an sp^2 hybridized carbon atom. On the other hand, the C(2)—C(3)—C(5) angle is 120.7(8)°. The C(4) atom is −0.421 Å away from the metal coordination plane. This means the C(4) methyl group is bent away from the bulky triphenylphosphine group. The non-bonded interaction described above might have caused this distortion. Five carbon atoms which consitute a dimethylallene moiety lie almost on a plane with a maximum deviation of 0.025 Å; the dihedral angle between this plane and the plane containing P(1), Pt and P(2) is 9.7°.

A packing diagram is drawn in Fig. 5. All intermolecular contacts are considered to be at the usual van der Waals distances, the shortest contact between non-hydrogen atoms being 3.552(20) Å [C(35) (x,y,z)...C(35) $(1-x,\bar{y},\bar{z})$].

All the computations throughout this work were carried out on a NEAC 2200-700 computer at Osaka University. Figures 2, 4 and 5 were drawn on a NUMERICON 7000 system at Osaka University with a local version of ORTEP [15]. Figure 1 is evaluated by the GPFR program [16].

Acknowledgements

The authors express their sincere thanks to Professor Sei Otsuka and his coworkers for supplying crystals, and to Dr. Colin H.L. Kennard who read the manuscript and improved its English.

References

1 S. Otsuka and A. Nakamura, J. Polym. Sci., Part B, 5 (1967) 973.
2 S. Otsuka, A. Nakamura and K. Tani, J. Organometal. Chem., 14 (1968) 30.
3 M. Kadonaga, N. Yasuoka and N. Kasai, Chem. Commun., (1971) 1597.
4 K. Okamoto, Y. Kai, N. Yasuoka and N. Kasai, J. Organometal. Chem., 65 (1974) 427.
5 J.K. Stalick and J.A. Ibers, J. Amer. Chem. Soc., 92 (1970) 5333; A. McAdam, J.N. Francis and J.A. Ibers, J. Organometal. Chem., 29 (1971) 131; J.N. Francis, A. McAdam and J.A. Ibers, ibid., 29 (1971) 149.
6 W.R. Busing and H.A. Levy, Acta Crystallogr., 22 (1967) 457.
7 T. Ashida, The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka University, 1973, p. 55.
8 H.P. Hanson, F. Herman, J.D. Lea and S. Skillman, Acta Crystallogr., 18 (1964) 1040.
9 J.A. Ibers and W.C. Hamilton, Acta Crystallogr., 18 (1965) 17.
10 F.L. Hirshfeld and D. Rabinovich, Acta Crystallogr. Part A, 29 (1973) 510.
11 P.T. Cheng, C.D. Cook, C.H. Koo, S.C. Nyburg and M.T. Shiomi, Acta Crystallogr., Part B, 27 (1971) 1904.
12 P.T. Cheng and S.C. Nyburg, Can. J. Chem., 50 (1972) 912.
13 C. Parattoni, R. Graziani, G. Bandoli, D.A. Clemente and U. Belluco, J. Chem. Soc. B, (1970) 371.
14 G. Bombieri, E. Forsellini, C. Panattoni, R. Graziani and G. Bandoli, J. Chem. Soc. A, (1970) 1313.
15 C.K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.
16 Y. Matsuura, The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka University, 1973, p. 51.