Journal of Organometallic Chemistry, 65 (1974) 427—441
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THE MOLECULAR STRUCTURE OF BIS(TRIPHENYLPHOSPHINE)ALLENE-PALLADIUM

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(Received August 9th, 1973)

Summary

The molecular structure of $[(C_6H_5)_3P]_2Pd(C_3H_4)$ has been determined from three-dimensional X-ray diffraction data. The crystal belongs to the triclinic system, space group $P\bar{1}$, with two formula units in a cell of dimensions: $a = 19.475(2)$, $b = 10.204(2)$, $c = 18\ 341(2)$ Å, $\alpha = 108.46(2)$, $\beta = 85\ 46(1)$, and $\gamma = 118.80(1)°$

One of the olefinic bonds of allene is coordinated to the palladium atom. Pd—C(1) = 2 118(9) and Pd—C(2) = 2 067(8) Å The coordinated allene is no longer linear, the C(1)—C(2)—C(3) angle being 148.3(8)°. The C(1)—C(2) distance is 1.401(11) Å, whereas the uncoordinated bond remains unchanged [C(2)—C(3) = 1.304(12) Å]. The Pd, P(1), P(2), C(1) and C(2) atoms lie almost in the same plane.

Introduction

A number of allene complexes with transition metal ions were isolated in the course of the study of the polymerization of allene using various organometallic catalysts [1,2]. Some of these complexes show catalytic activity in the polymerization of allene, and others have no such activity. It was also found that the allene molecule adds reversibly to a transition metal ion in some complexes. There may be some relationship between the catalytic activities of allene complexes and the strength of the bonding of the allene and/or other ligands to the transition metal ions.

In this context, allene complexes of Ni, Pd and Pt are of most interest to us. The Ni complex shows catalytic activity in the polymerization of allene, and the remainder show no activity. Therefore, we have undertaken structural studies of this series of complexes by means of X-ray diffraction to elucidate the difference in chemical behavior. Preliminary results for the Pt complex have been reported elsewhere [3]. Here we describe the structure of the Pd complex.

This work also serves to elucidate the nature of the bonding of allenes to transition metals. A long-standing controversy exists as to whether complexes should be described as metallo-cyclopropane derivatives or as π-adducts to the metal atom. The molecular structures of some transition metal—allene complexes have been investigated by X-ray crystal analysis [4 - 6]. They can be classified into two groups on the basis of the manner in which allene coordinates to the central metal atom. In the first group the allene ligand lies in the coordination plane, while in the second it is perpendicular to the coordination plane.

Generally one observes distortions of the coordinated allene from its free state but there exists little precise structural information about coordinated allene (in particular unsubstituted allene). allenepalladium, as the first example of a palladium—allene complex, was studied in order to obtain data on this type of compound.

Experimental

The crystals of $Pd(PPh_3)_2(C_3H_4)$ used in this study were kindly supplied by Professor S Otsuka and his coworkers of Osaka University. They are pale yellow, hexagonal plates, and are stable in the air. Oscillation and Weissenberg photographs taken with Cu-$K\alpha$ radiation showed that the crystal is triclinic Cell dimensions were determined by the least-squares method using 2θ values of 35 strong reflections measured on a G.E. single crystal orienter equipped with a Rigaku SG-2 goniometer. The density was measured by flotation in an aqueous solution of potassium tartrate at room temperature

Crystal data: $C_{39}H_{34}P_2Pd$, formula wt. 671.0, triclinic, space group $P\bar{1}$, a = 19.475(2), b = 10.204(2), c = 18.341(2) Å, α = 108 46(2), β = 85.46(1), and γ = 118.80(1)°, V = 1623.0(3) Å^3, D_m = 1 37 g/cm^3, Z = 2, D_c = 1.37 g/cm^3 (Mo-$K\alpha$, λ = 0.71069 Å, μ = 7.48 cm^{-1}).

Intensity measurements were made on a Rigaku automated, four circle, single-crystal diffractometer, using zirconium-filtered Mo-K_α radiation. The setting angles of each reflection were computed by the Busing—Levy method [7] on a computer attached to the diffractometer The method requires precise values of the centering angles, 2θ, ω, χ and ϕ, of three linearly-independent reflections of known indices, in order to determine the orientation of the crystal on a goniometer and also the dimensions of the unit cell Although this method is theoretically sound, in our experience an inaccurate centering of three reflections tends to introduce appreciable errors in the setting angles of higher-order reflections. That arises, perhaps, because the measured values of the centering angles of three reflections may be affected by systematic errors arising from imperfections in the diffractometer, from alignment errors, and from crystal-centering errors. Therefore, the alignment of the diffractometer and the crystal-centering were carried out with great care. The centering angles, 2θ, ω, χ and ϕ, of several reflections were measured on the diffractometer. Any three linearly-independent reflections from them were combined, and the orientational parameters of the crystal and the unit cell constants were calculated by use of the centering angles. Those reflections which gave the best agreement of the cell constants with previously determined values, within 0.05% error, were finally chosen. Their indices were $\bar{5}00$, 050 and $00\overline{11}$.

A 2θ—ω scan technique was employed for data collection. The integrated intensity of each reflection was determined by scanning over the peak at a rate of 4° /min, and subtracting the background obtained by averaging the two values measured for 5 sec at both ends of a scan. The 2θ scan width was determined to be $(2.0 + 0.7 \tan \theta_c)^\circ$, where θ_c denotes the calculated Bragg angle for Mo-K_{α_1}. The pulse height analyzer was set to admit 95% of the Mo-K_α peak. Nickel attenuators were automatically inserted during the scan, when the peak intensity exceeded 8000 counts/sec.

Two crystals with similar dimensions (0.16 × 0.18 × 0.16 mm) were used for intensity measurement. After 2260 reflections with lower Bragg angles were measured with use of the first crystal, machine trouble forced us to interrupt the measurements. The remaining 2044 reflections were observed with the second crystal. The relative scaling between two sets of data was carried out by comparison of the intensities of standard reflections in two sets. In such a way, a total of 4304 independent reflections having $\sin \theta/\lambda$ values less than 0.5508 were obtained.

The intensities of three standard reflections 500, 050 and $00\overline{11}$ were measured periodically. No intensity decrease of these reflections was observed during the experiment, the crystal being stable under irradiation by X-rays. Lorentz and polarization corrections were made in an usual manner, while no absorption correction was applied to the intensity data.

Computations were carried out on a NEAC 2200—700 computer at Osaka University and on a FACOM 230—60 at Kyoto University. Figures 1 and 8 were drawn on a NUMERICON 7000 system at Osaka University with a local version of ORTEP [24].

Structure solution and refinement

For the structure solution and through the early stages of the refinement the first set of data (2260 reflections which gave relatively lower diffraction angles) were used. The structure was solved by the conventional heavy-atom method. From a three-dimensional Patterson function, approximate coordinates for the palladium and two phosphorus atoms were easily determined. The Fourier map based on these atomic locations revealed the positions of all the remaining non-hydrogen atoms.

Structure refinement was then carried out by the method of block-diagonal least-squares, the function minimized being $\Sigma(|F_o| - k\cdot|F_c|)^2$. The atomic scattering factors used in all the calculations were those of Hanson et al. [8]. The HBLS program written by Dr. T. Ashida was used [9]. After several cycles of isotropic refinement, the conventional R factor converged to 0.08 for non-zero reflections. No abnormal thermal parameters were observed. A few successive cycles of anisotropic refinement reduced R to 0.053. Then all the phenyl hydrogen atom positions were located from stereochemical consideration assuming the C—H bond length to be 1.08 Å. The hydrogen atoms were assigned the same thermal parameters as those of carbon atoms to which they were bonded. A few more cycles of refinement including phenyl hydrogen atoms reduced R to 0.040 for 2260 non-zero reflections, positional and thermal parameters of the phenyl hydrogen atoms being fixed during the refinement.

TABLE 1

FRACTIONAL COORDINATES OF REFINED ATOMS ESD's ARE LISTED IN PARENTHESES WITH RESPECT TO THE LEAST SIGNIFICANT DIGIT OF ANY PARAMETER

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Pd	0 41280	(6)	0 10780	(6)	0 22236	(3)
P(1)	0.4307	(2)	0 0391	(2)	0 3284	(1)
P(2)	0 2321	(2)	−0 1106	(2)	0 1317	(1)
C(1)	0 5017	(9)	0 2972	(2)	0 1764	(4)
C(2)	0 5829	(8)	0 3358	(7)	0 2444	(4)
C(3)	0 6967	(9)	0 4373	(8)	0 2938	(5)
C(11)	0 6210	(7)	0 1356	(7)	0 3685	(4)
C(12)	0 6661	(8)	0 2182	(8)	0 4462	(4)
C(13)	0 8137	(9)	0 2922	(9)	0 4711	(5)
C(14)	0 9141	(9)	0 2827	(10)	0 4203	(6)
C(15)	0 8701	(8)	0 2006	(10)	0 3426	(5)
C(16)	0.7242	(8)	0.1278	(9)	0 3161	(5)
C(21)	0 3407	(7)	0 1139	(8)	0 4083	(4)
C(22)	0 2655	(10)	0 0336	(10)	0 4590	(5)
C(23)	0 2005	(10)	0 0969	(11)	0 5176	(5)
C(24)	0 2135	(10)	0 2429	(11)	0 5269	(5)
C(25)	0 2902	(10)	0 3242	(10)	0 4765	(6)
C(26)	0 3540	(9)	0 2604	(9)	0 4171	(5)
C(31)	0 3630	(8)	−0 1656	(8)	0 3264	(4)
C(32)	0 2170	(9)	−0 2722	(8)	0 3052	(5)
C(33)	0 1612	(10)	−0 4287	(9)	0 3007	(5)
C(34)	0 2536	(11)	−0 4810	(9)	0 3142	(5)
C(35)	0 4000	(11)	−0 3766	(10)	0 3348	(6)
C(36)	0 4540	(9)	−0 2180	(9)	0 3417	(5)
C(41)	0 0425	(7)	−0 1857	(7)	0 1562	(4)
C(42)	−0 0739	(7)	−0 3115	(8)	0 1041	(4)
C(43)	−0 2165	(8)	−0 3641	(9)	0 1257	(5)
C(44)	−0 2431	(8)	−0 2922	(10)	0 1968	(5)
C(45)	−0.1290	(9)	−0 1664	(9)	0 2489	(5)
C(46)	0 0140	(8)	−0 1134	(8)	0 2285	(4)
C(51)	0 2128	(6)	−0 0939	(7)	0.0364	(4)
C(52)	0 2171	(8)	−0.1993	(8)	−0 0331	(4)
C(53)	0 1983	(9)	−0 1784	(10)	−0 1023	(4)
C(54)	0 1793	(8)	−0 0525	(10)	−0 1020	(4)
C(55)	0 1756	(8)	0 0506	(9)	−0 0334	(5)
C(56)	0 1948	(8)	0 0316	(8)	0 0358	(4)
C(61)	0 2585	(7)	−0 2759	(7)	0 1086	(4)
C(62)	0 4114	(8)	−0 2412	(9)	0 0920	(5)
C(63)	0 4558	(9)	−0 3527	(10)	0 0786	(5)
C(64)	0 3566	(10)	−0 5046	(10)	0 0821	(5)
C(65)	0 2159	(9)	−0 5388	(9)	0 0978	(5)
C(66)	0.1702	(8)	−0 4257	(8)	0 1114	(4)
H(1)	0 448	(7)	0 342	(7)	0 178	(4)
H(2)	0 540	(7)	0 271	(7)	0 121	(4)
H(3)	0 719	(8)	0 408	(8)	0 338	(4)
H(4)	0 752	(8)	0 522	(8)	0 283	(4)

At this stage the remaining 2044 reflections were added. The difference Fourier map calculated after a few cycles of refinement revealed peaks which could be assigned to the hydrogen atoms of the allene moiety. Several cycles of refinement of the allene carbon and hydrogen atoms were carried out, all other parameters except these being fixed. In the last cycle, the largest shifts of the positional and thermal parameters were about 0.10σ and 0.06σ, respectively. The final R factor is 0.051 for 4096 non-zero reflections. The final positional and thermal parameters along with their estimated standard deviations are listed in Tables 1 - 4*. Figure 1 shows the final difference Fourier maps, each of which

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* A list of observed and calculated structure factors can be obtained by application to the authors (N.K)

TABLE 2

THERMAL PARAMETERS OF REFINED ATOMS

Anisotropic temperature factors (X 10^4) are expressed in the form $\exp\{-(\beta_{11}h^2 + \beta_{22}\cdot k^2 + \beta_{33}\cdot l^2 + \beta_{12}\cdot h\cdot k + \beta_{13}\cdot h\cdot l + \beta_{23}\cdot k\cdot l)\}$ and isotropic temperature factors, $\exp(-B \sin^2\theta/\lambda^2)$

Atom	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	116 3(7)	95 5(7)	25.1(2)	75 0(11)	— 9 7(5)	32 5(6)
P(1)	118 (2)	91 (2)	23 (1)	88 (4)	— 2 (2)	31 (2)
P(2)	86 (2)	89 (2)	23 (1)	78 (4)	— 1 (2)	31 (2)
C(1)	188 (12)	109 (10)	42 (3)	52 (18)	—17 (9)	91 (9)
C(2)	132 (10)	91 (10)	45 (3)	32 (16)	— 8 (8)	58 (9)
C(3)	220 (14)	87 (10)	50 (3)	40 (19)	—53 (11)	54 (10)
C(11)	132 (9)	86 (9)	29 (2)	91 (15)	— 7 (7)	35 (8)
C(12)	142 (10)	134 (12)	34 (3)	95 (18)	—11 (8)	42 (9)
C(13)	169 (12)	155 (13)	46 (3)	70 (2)	—50 (10)	42 (11)
C(14)	133 (11)	167 (14)	68 (4)	97 (20)	—31 (11)	93 (13)
C(15)	106 (10)	166 (14)	66 (4)	79 (19)	18 (10)	83 (12)
C(16)	156 (11)	142 (12)	41 (3)	142 (19)	31 (9)	63 (10)
C(21)	120 (9)	126 (11)	26 (2)	104 (16)	0 (7)	3 (8)
C(22)	216 (14)	219 (16)	37 (3)	258 (25)	48 (10)	74 (11)
C(23)	201 (14)	233 (17)	44 (4)	192 (26)	58 (11)	60 (13)
C(24)	182 (14)	243 (18)	45 (4)	207 (26)	13 (11)	—14 (13)
C(25)	211 (15)	174 (15)	59 (4)	233 (25)	19 (12)	28 (13)
C(26)	168 (12)	147 (13)	38 (3)	168 (20)	19 (9)	40 (10)
C(31)	166 (11)	112 (10)	26 (2)	118 (17)	20 (8)	51 (8)
C(32)	174 (12)	126 (12)	35 (3)	74 (19)	—29 (9)	46 (9)
C(33)	227 (15)	129 (12)	42 (3)	96 (22)	—10 (11)	55 (10)
C(34)	275 (17)	107 (12)	46 (3)	116 (23)	52 (12)	72 (11)
C(35)	240 (16)	169 (15)	66 (4)	269 (26)	70 (13)	104 (13)
C(36)	168 (12)	137 (12)	52 (3)	169 (20)	45 (10)	76 (11)
C(41)	107 (8)	106 (10)	28 (2)	148 (15)	23 (7)	36 (8)
C(42)	98 (8)	131 (11)	33 (3)	91 (16)	— 9 (7)	44 (9)
C(43)	111 (9)	153 (12)	45 (3)	100 (18)	— 9 (9)	65 (10)
C(44)	123 (10)	207 (15)	49 (3)	164 (20)	31 (9)	116 (12)
C(45)	195 (13)	193 (14)	40 (3)	274 (23)	72 (10)	84 (11)
C(46)	142 (10)	138 (11)	34 (3)	192 (18)	25 (8)	41 (9)
C(51)	78 (8)	128 (10)	27 (2)	84 (14)	3 (7)	41 (8)
C(52)	140 (10)	157 (12)	30 (3)	163 (18)	26 (8)	41 (9)
C(53)	190 (13)	250 (17)	23 (3)	217 (25)	17 (9)	46 (10)
C(54)	136 (11)	267 (17)	31 (3)	135 (22)	13 (9)	111 (11)
C(55)	154 (11)	176 (13)	45 (3)	176 (20)	17 (9)	96 (11)
C(56)	148 (10)	146 (12)	31 (3)	168 (18)	2 (8)	47 (9)
C(61)	100 (8)	118 (10)	26 (2)	131 (15)	— 7 (7)	22 (8)
C(62)	106 (9)	147 (12)	46 (3)	127 (17)	— 8 (8)	42 (10)
C(63)	144 (11)	233 (16)	49 (3)	252 (23)	8 (10)	54 (12)
C(64)	241 (15)	235 (16)	35 (3)	365 (27)	— 2 (10)	48 (11)
C(65)	188 (12)	161 (13)	42 (3)	212 (21)	18 (10)	63 (10)
C(66)	149 (10)	122 (11)	36 (3)	159 (18)	20 (8)	53 (9)
H(1)	2 1(14)					
H(2)	2 0(14)					
H(3)	3 4(17)					
H(4)	3 1(16)					

is calculated on the planes through the CH_2 groups using the GPFR program written by Y. Matsu-ura.

Results and discussion

Figure 2 presents a stereoscopic projection of the molecule viewed along the normal to the Pd, C(1), C(2) plane. Figure 3 shows a drawing of the molecule and indicates the numbering scheme The coordination geometry around the

TABLE 3

CALCULATED COORDINATES AND ASSIGNED ISOTROPIC THERMAL PARAMETERS FOR PHENYL HYDROGEN ATOMS

Atom	x	y	z	B
H(12)	0 585	0 224	0 487	4 6
H(13)	0 850	0 359	0 533	5 8
H(14)	1 030	0 341	0 441	6 1
H(15)	0 951	0 192	0 302	5 4
H(16)	0 688	0 065	0 254	4 9
H(22)	0 257	−0 082	0 452	5 4
H(23)	0 137	0 032	0 557	6 2
H(24)	0 162	0 293	0 573	6 0
H(25)	0 302	0 441	0 484	6 4
H(26)	0 417	0 325	0 377	4 8
H(32)	0 143	−0 230	0 291	4 4
H(33)	0 042	−0 513	0 286	5 6
H(34)	0 208	−0 606	0 308	5 8
H(35)	0 472	−0 420	0 346	6 1
H(36)	0 570	−0 131	0 360	4 6
H(42)	−0 052	−0 368	0 047	3 6
H(43)	−0 308	−0 462	0 084	4 6
H(44)	−0 356	−0 336	0 215	5 2
H(45)	−0.151	−0 106	0 306	5 1
H(46)	0 106	−0 013	0 270	4 2
H(52)	0 237	−0 298	−0 032	3 9
H(53)	0 203	−0 259	−0 157	5 0
H(54)	0 159	−0 041	−0 157	5 0
H(55)	0 159	0 149	−0 033	5 3
H(56)	0 198	0 117	0 092	4 0
H(62)	0 492	−0 121	0 091	4 4
H(63)	0 568	−0 325	0.064	5 3
H(64)	0 394	−0 592	0 071	5 5
H(65)	0 140	−0 658	0 101	5 2
H(66)	0 057	−0 455	0 124	4 2

palladium atom is shown in Fig. 4, and can be compared with that in bis(triphenylphosphine)alleneplatinum [3] (Pt complex) (Fig 9). Figures 4 and 9 clearly show that the present Pd complex is isostructural with the Pt complex. The remarkable feature commonly found in these two complexes is that the allene lies on the coordination plane. The equation of the coordination plane in the present complex is $-0.888\,x + 0\ 167\,y + 0.428\,z + 2\ 098 = 0$. Deviations from this plane (in Å) are. Pd, 0.037; P(1), 0.014, P(2), −0.030; C(1), 0.083; C(2), −0.096, whereas that of the uncoordinated carbon atom, C(3), is −0.305 Å.

The two olefinic bond lengths of the allene ligand show a significant difference. The coordinated one [C(1)—C(2) = 1.401(11) Å] shows a lengthening, which suggests a decrease of bond order resulting from a ligand-to-metal charge transfer as well as an electron transfer from the metal to antibonding orbitals of the ligand. This bond length is approximately equal to those in bis(triphenylphosphine)ethyleneplatinum [10] and bis(triphenylphosphine)ethylenenickel [11] [1.434(13) Å and 1.431(15) Å, respectively]. The uncoordinated bond length [C(2)—C(3) = 1.304(12) Å] remains unchanged from that in the free molecule (1.308 Å) [12]. The coordinated allene is no longer linear, the

(continued p 435)

TABLE 4

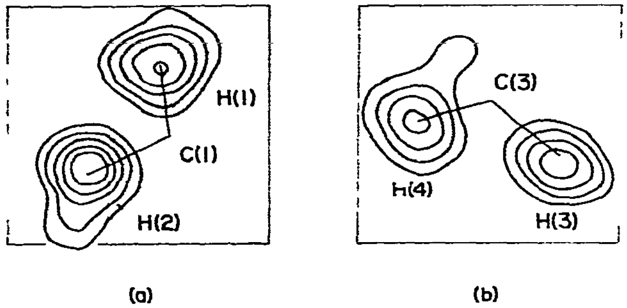
BOND LENGTHS (Å) AND BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS

(a) Concerning coordinating atoms

Pd –P(1)	2 314(2)	P(1) –Pd –P(2)	109 3(1)
Pd –P(2)	2 324(2)	P(1) –Pd –C(1)	143 2(3)
Pd –C(1)	2 118(9)	P(1) –Pd –C(2)	104 3(3)
Pd –C(2)	2 067(8)	P(2) –Pd –C(1)	107.5(3)
C(1) –C(2)	1 401(11)	P(2) –Pd –C(2)	145 9(3)
C(2) –C(3)	1 304(12)	C(1) –Pd –C(2)	39 1(3)
C(1) –H(1)	0 87 (7)	Pd –C(1) –C(2)	68 5(5)
C(1) –H(2)	1 06 (7)	Pd –C(2) –C(1)	72 4(5)
C(3) –H(3)	1 02 (8)	Pd –C(2) –C(3)	139 2(7)
C(3) –H(4)	0 86 (8)	C(1) –C(2) –C(3)	148 3(8)
		Pd –C(1) –H(1)	116 (5)
		Pd –C(1) –H(2)	114 (4)
		C(2) –C(1) –H(1)	118 (5)
		H(1) –C(1) –H(2)	111 (6)
		Pd –P(1) –C(11)	111 8(3)
		Pd –P(1) –C(21)	110 4(3)
		Pd –P(1) –C(31)	123 9(3)
		Pd –P(2) –C(41)	118 0(3)
		Pd –P(2) –C(51)	117.7(3)
		Pd –P(2) –C(61)	109 9(3)

(b) Concerning triphenylphosphine groups

P(1) –C(11)	1.834(8)	C(11)–P(1) –C(21)	103 6(4)
P(1) –C(21)	1 840(8)	C(21)–P(1) –C(31)	103 1(4)
P(1) –C(31)	1 843(8)	C(31)–P(1) –C(11)	102 0(4)
C(11)–C(12)	1 389(11)	C(11)–C(12)–C(13)	119 3(8)
C(12)–C(13)	1 391(13)	C(12)–C(13)–C(14)	121 0(9)
C(13)–C(14)	1 368(14)	C(13)–C(14)–C(15)	120 1(9)
C(14)–C(15)	1 385(14)	C(14)–C(15)–C(16)	120 2(9)
C(15)–C(16)	1 385(13)	C(15)–C(16)–C(11)	119 6(8)
C(16)–C(11)	1 403(11)	C(16)–C(11)–C(12)	119 8(7)
C(21)–C(22)	1 378(13)	C(21)–C(22)–C(23)	120.1(9)
C(22)–C(23)	1 381(15)	C(22)–C(23)–C(24)	120 2(10)
C(23)–C(24)	1 383(16)	C(23)–C(24)–C(25)	119 7(10)
C(24)–C(25)	1 384(15)	C(24)–C(25)–C(26)	120 3(10)
C(25)–C(26)	1 383(14)	C(25)–C(26)–C(21)	119 6(8)
C(26)–C(21)	1 390(12)	C(26)–C(21)–C(22)	120 1(8)
C(31)–C(32)	1 377(12)	C(31)–C(32)–C(33)	121 0(8)
C(32)–C(33)	1 386(13)	C(32)–C(33)–C(34)	119 9(9)
C(33)–C(34)	1 380(15)	C(33)–C(34)–C(35)	119 9(9)
C(34)–C(35)	1 376(15)	C(34)–C(35)–C(36)	119 6(10)
C(35)–C(36)	1 399(14)	C(35)–C(36)–C(31)	120 8(8)
C(36)–C(31)	1 379(12)	C(36)–C(31)–C(32)	118 7(8)
P(2) –C(41)	1 828(7)	C(41)– P(2)–C(51)	100 4(4)
P(2) –C(51)	1 844(8)	C(51)– P(2)–C(61)	103 4(4)
P(2) –C(61)	1 820(8)	C(61)– P(2)–C(41)	105 9(4)
C(41)–C(42)	1 396(11)	C(41)–C(42)–C(43)	119 8(7)
C(42)–C(43)	1 394(12)	C(42)–C(43)–C(44)	120 4(8)
C(43)–C(44)	1 360(13)	C(43)–C(44)–C(45)	120 5(9)
C(44)–C(45)	1 383(13)	C(44)–C(45)–C(46)	119 8(9)
C(45)–C(46)	1 392(12)	C(45)–C(46)–C(41)	120 3(8)
C(46)–C(41)	1 386(11)	C(46)–C(41)–C(42)	119 3(7)
C(51)–C(52)	1 398(11)	C(51)–C(52)–C(53)	118 9(8)
C(52)–C(53)	1 396(13)	C(52)–C(53)–C(54)	120 5(9)
C(53)–C(54)	1 390(15)	C(53)–C(54)–C(55)	120 1(9)
C(54)–C(55)	1 373(14)	C(54)–C(55)–C(56)	120.0(9)
C(55)–C(56)	1 386(12)	C(55)–C(56)–C(51)	120 5(8)
C(56)–C(51)	1 385(11)	C(56)–C(51)–C(52)	119 9(7)
C(61)–C(62)	1 394(11)	C(61)–C(62)–C(63)	121 0(8)
C(62)–C(63)	1 373(13)	C(62)–C(63)–C(64)	120 0(9)
C(63)–C(64)	1 409(15)	C(63)–C(64)–C(65)	118 9(9)
C(64)–C(65)	1 370(14)	C(64)–C(65)–C(66)	121.3(9)
C(65)–C(66)	1 398(12)	C(65)–C(66)–C(61)	119 6(7)
C(66)–C(61)	1 387(11)	C(66)–C(61)–C(62)	119 2(7)



(a) (b)

Fig 1. The difference Fourier map showing the allene hydrogen atoms calculated on the planes through (a) H(1)—C(1)—H(2) and (b) H(3)—C(3)—H(4)

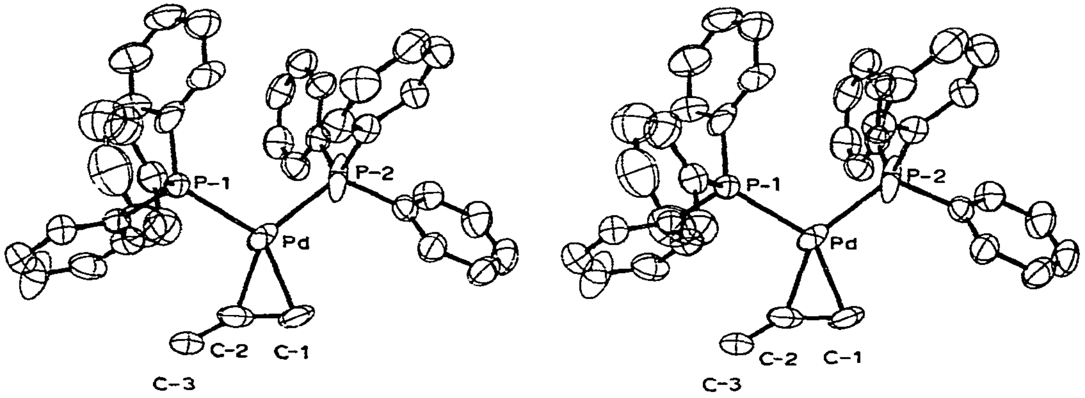


Fig 2 The stereodrawing of the $(Ph_3)_2Pd(C_3H_4)$ molecule The thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity

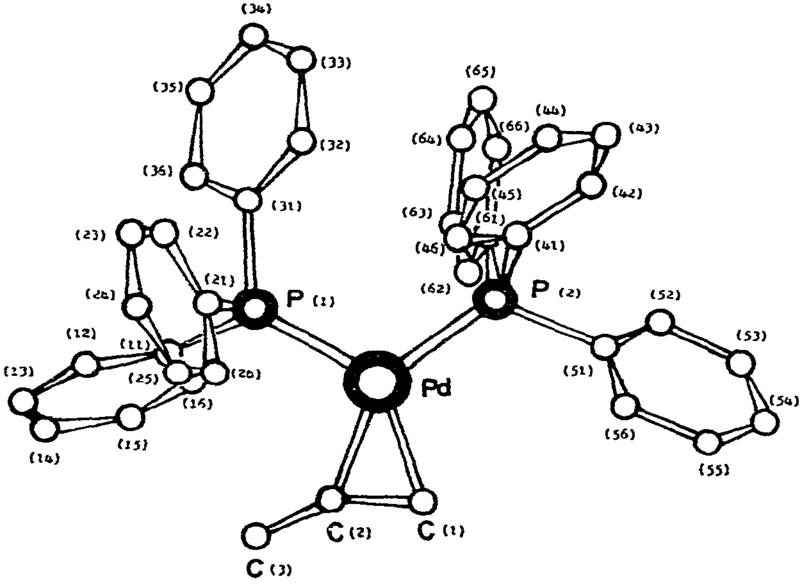


Fig 3 The molecular structure of $(Ph_3P)_2Pd(C_3H_4)$ projected on the coordination plane, and the numbering system of atoms

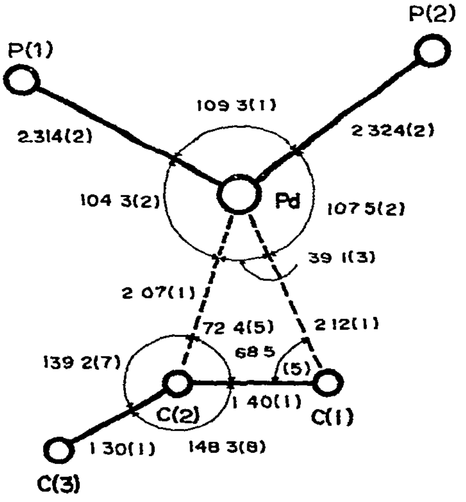


Fig 4 The coordination geometry around the palladium atoms.

C(2)—C(3) bond bends away from the palladium atom and the C(1)—C(2)—C(3) angle is 148.3(8)°.

The hydrogen atoms, H(1) and H(2), attached to C(1) bend back slightly from the metal as shown in Fig. 5. The C(1)—C(2) vector makes an angle of 26° with the plane defined by C(1), H(1) and H(2). The H(1)—C(1)—H(2) angle is 112(6)°, which can be compared with corresponding angles of 112.6(5)° and 112.4(6)° of tetramethylallene ligands in acetylacetonatobis(tetramethylallene)-rhodium(I) [6]. Both H(1)—C(1)—C(2) and H(2)—C(1)—C(2) angles are nearly 120° These facts show that the hybridization of the carbon atom C(1), though nearly sp^2, tends slightly towards sp^3. The H(1)—H(2) vector is approximately

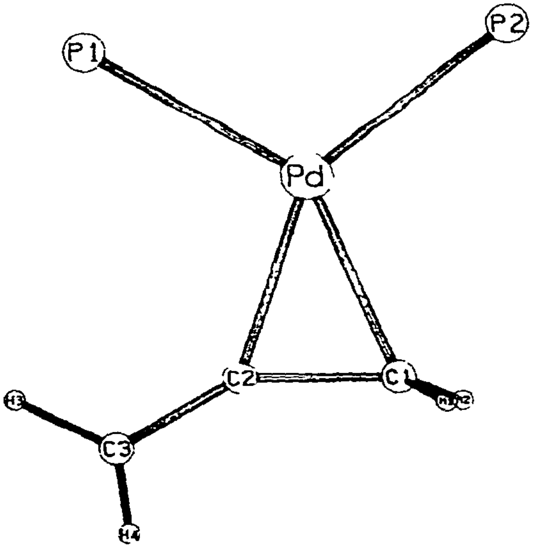


Fig. 5. A drawing showing the hydrogen atoms of allene.

TABLE 5

STRUCTURAL PARAMETERS OF THE COORDINATED ALLENE (BOND DISTANCES IN Å AND ANGLES IN DEGREES)

Compound	Angle (°)[a]	C(1)—C(2)	C(2)—C(3)	C—C—C	M—C(1)	M—C(2)	M C(1)—C(2)[b]	Coordination number of M	Reference
$RhI(PPh_3)_2(C_3H_4)$		1 35	1 34	158	2 17	2.04		4	4
$[PtCl_2(C_3Me_4)]_2 \cdot 2CCl_4$	95 4	1 37	1 36	151	2 25	2 07	2 05	4	6
$Rh(Acac)(C_3Me_4)_2$	97 8	1 373	1 325	147 2	2,177	2 027	1 99	4	5
	97 9	1,377	1 321	148 9	2 176	2 033	1 99		
$Rh_2(CO)_2(Acac)_2(C_3H_4)$	85 6	1,37		144 5	2,12	2 05		4	6
	95 5	1,41			2 14	2 06		4	
$Rh(Acac)(C_3H_2Me_2)_2$	102,5	1 40	1 30	153 3	2 13	2 07		4	5
	103,2	1 41	1 29	152 6	2,13	2 06			
$Pd(PPh_3)_2(C_3H_4)$	8 6	1 40	1 30	148 3	2,118	2 068	1 97	3	This work
$Pt(PPh_3)_2(C_3H_3Me)$		1 44	1 32	146	2,12	2 05		3	25
$Pt(PPh_3)_2(C_3H_4)$	9	1 48	1 31	142	2 13	2 03	1 95	3	3

[a] Dihedral angle between the ML_2 plane and the M, C(1), C(2) plane. [b] The distance from M to the centre of the C(1)—C(2) bond

perpendicular to the coordination plane, and it makes an angle of 85° with the Pd, C(1), C(2) plane. Four atoms, C(2), C(3), H(3) and H(4), are coplanar. As a whole, the geometry of the coordinated allene in this complex resembles that of tetramethylallene in $(C_5H_7O_2)Rh(C_7H_{12})_2$, and the allene molecule can be considered as a monodentate ligand in this case, similar to the case of $(C_5H_7O_2)Rh(C_7H_{12})_2$.

Table 5 presents a list of structural parameters of allene and substituted allene ligands in several transition metal—allene complexes. It is generally observed that the C(1)—C(2)—C(3) angle of the allene moiety is bent from linearity in proportion to the lengthening of the coordinated double bond. The allene ligand in the present complex also shows such a tendency. It should be pointed out that the distortion of the coordinated allene from its free state is larger in three-coordinated zero-valent complexes than in four-coordinated divalent complexes, and that the stronger the coordination of the ligand, the larger its distortion. Therefore, it can be concluded that the coordination of allene to the metal is stronger in the former than in the latter complexes. The variation of the metal—allene distances in Table 5 also supports this conclusion.

The nature of the bonding of the allene moiety to the transition metal atom can be easily described in complexes in which the allene is perpendicular to the coordination plane. It is clear that the allene molecule functions as a monodentate ligand in this case. However, for the nature of the bonding in $Pt(PPh_3)_2(C_3H_4)$ and in the present complex, in which the allene lies on the coordination plane, two types of bonding can be considered (Fig. 6). One is a doubly σ-bonded metallo-cyclopropane type (A) and the other a dative bond involving π-electrons on the allene (B). In the former the central metal is regarded as four-coordinated and divalent, while in the latter it is three-coordinated and zerovalent.

In the scheme (A), the C(2) atom of the allene possesses sp^2 character instead of sp character in the free allene, and this causes the coordinated allene to be bent away. Considered from the point of view of the structure of the allene moiety and the coordination geometry around the central metal, however, it would not seem reasonable to apply this scheme to the present complex In particular such an extremely distorted square planar configuration is not favourable, the C(1)—Pd—C(2) angle being 39.1(3)°. ESCA studies indicate that $Pt(PPh_3)_2(C_2H_4)$ is better described as a platinum (0) complex than as a derivative of platinum(II) [13]. This interpretation could be applied to the present complex.

In the scheme (B), the bonding is thought to be formed by an electron donation from the filled (C=C)π orbital to the vacant dp^2 hybrid ($d_{xy} + p_x + p_y$) on

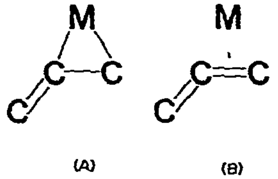


Fig 6 Two types of bonding for olefin—metal complexes

the palladium, supported by a back donation from a filled *d* orbital of the palladium to the unoccupied (C=C)π^* orbital [14]. For this back bonding interaction ($d_{x^2-y^2} - \pi^*_{xy}$), the planar coordination of P(1), P(2), C(1) and C(2) to Pd is calculated to be the most stable configuration. The observed bending of the allene molecule can be explained in the following manner. Upon coordination to a transition metal, the allene molecule is activated by an electron transfer, through the central atom, from the highest π orbital to the lowest unoccupied π^* orbital. Therefore, the electronic state of the coordinated allene resembles that of the lowest excited state of the free allene molecule, which appears to be bent like carbon disulfide [16]. In the transition metal—carbon disulfide or —acetylene complexes, successful explanations have been offered to relate the distortions of the ligand to the geometry of its excited state [17 - 20]. Furthermore, correlation has been attempted between the charge transferred to the ligand and its expected geometry [13]. Since no structural parameters of allene in its lowest excited state are available, it is impossible to compare quantitatively the structure of the coordinated allene with that of the excited allene, and to estimate the charge transferred (the strength of the back-donation)

The dihedral angle between the two planes defined by P(1), Pd, and P(2) and C(1), Pd, and C(2) is 8 6° (Fig. 7), and the angle between planes containing P(1), Pd, and P(2), and C(1), C(2) and C(3) is 11.0°. The C(2)—C(3) vector makes an angle of 9.2° with the coordination plane. Similar dihedral angles are observed in most trigonal complexes Distortions from perfect planarity can be rationalized on the basis of both electronic and steric effects. Twisting of the C(1)—C(2) vector from the P(1), Pd, P(2) plane allows the metal—ligand back donation to involve d_{xz} and d_{yz} electrons in addition to $d_{x^2-y^2}$ electrons, which makes the metal—ligand bonding stronger Such distortions could also arise from the requirement for minimization of non-bonded interaction.

The palladium atom is not equidistant from the two atoms C(1) and C(2) of the coordinated allene. The Pd—C(2) distance [2.067(8) Å] is significantly shorter than Pd—C(1) [2.118(9) Å]. This difference can be explained by the proposal of Hewitt and De Boer [6]. That is. in addition to the overlap between the filled $d_{x^2-y^2}$ orbital of the palladium atom and π^*_{xy} orbital of the central carbon atom, C(2) (ordinary back-donation), the d_{yz} orbital can also overlap with the π^*_{yz} orbital orthogonal to the π^*_{xy} However, the terminal carbon atom, C(1) has no corresponding π^*_{yz} orbital, and the additional overlap does not occur. This can cause the difference in the Pd—C distances. It is noteworthy

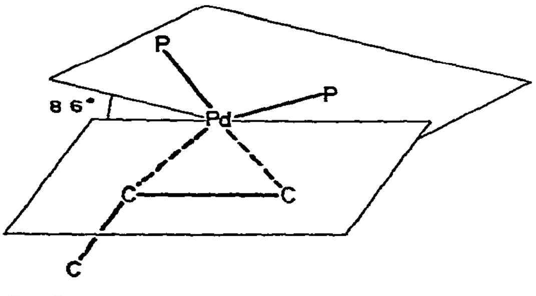


Fig. 7. The relative orientation of two planes, one containing the allene C—C and Pd atom, and the other the P ligand atoms and Pd atom

that the Pd—C(1) distance [but not the Pd—C(2)] is comparable with the Pt—C distances [2.116(9) and 2.106(9) Å] in Pt(PPh$_3$)$_2$(C$_2$H$_4$) [10] in spite of the difference in metallic radii. The distance from the palladium atom to the mid-point of the C(1)—C(2) bond is 1.97 Å. The uncoordinated carbon atom, C(3), is located far away from the palladium atom [3 171(9) Å].

The Pd—P(2) bond length of 2.324(2) Å [*trans* to C(2)] is only slightly longer than the Pd—P(1) bond length of 2.314(2) Å, implying that the back-donating power of Pd → P(2) is slightly weaker than that of Pd → P(1). The geometry around the phosphorus atoms is a distorted tetrahedral arrangement, average values of C—P—C and Pd—P—C angles being 103.0° and 115.3° respectively. The phenyl rings are normal: the average values of C—C bond lengths and C—C—C angles are 1.39 Å and 120.0° respectively.

The crystal structure is given in Fig. 8 All intermolecular contacts are normal, the shortest contact between non-hydrogen atoms being 3 54 Å [C(55)(x, y, z) —C(55)($\bar{x}$, $\bar{y}$, $\bar{z}$)].

It is interesting to compare the strengths of ligand bonding in the series of transition metals Pt, Pd and Ni. For the bonding of metal to triphenylphosphine ligand, the platinum seems to bond more strongly than palladium and nickel In view of the difference in the metallic radii, it can be said that M—P bonds are stronger in Pt(PPh$_3$)$_2$(C$_2$H$_4$) [10] than in Ni(PPh$_3$)$_2$(C$_2$H$_4$) [11]. M—P bond lengths in Pt(PPh$_3$)$_2$(CS$_2$) [17] are shorter than those in Pd(PPh$_3$)$_2$(CS$_2$) [21]. A similar relation to that described above has been found to hold for allene complexes· thus the average Pt—P distance of 2 282 Å is shorter than the average Pd—P distance of 2.319 Å. In the case of the metal-to-double bond distances, the ethylene complexes of Pt and Ni do not show significant differences in M—C distances. Owing to large values of estimated standard deviations, it is not easy to compare M—C and M—S (coordinated) distances in Pt(PPh$_3$)$_2$(CS$_2$) and Pd(PPh$_3$)$_2$(CS$_2$). However, the lengthening of the C—S (coordinated) distance and the change in the S—C—S angle in the Pt complex are far larger than those in the Pd complex. In the case of allene complexes, it is clear that the

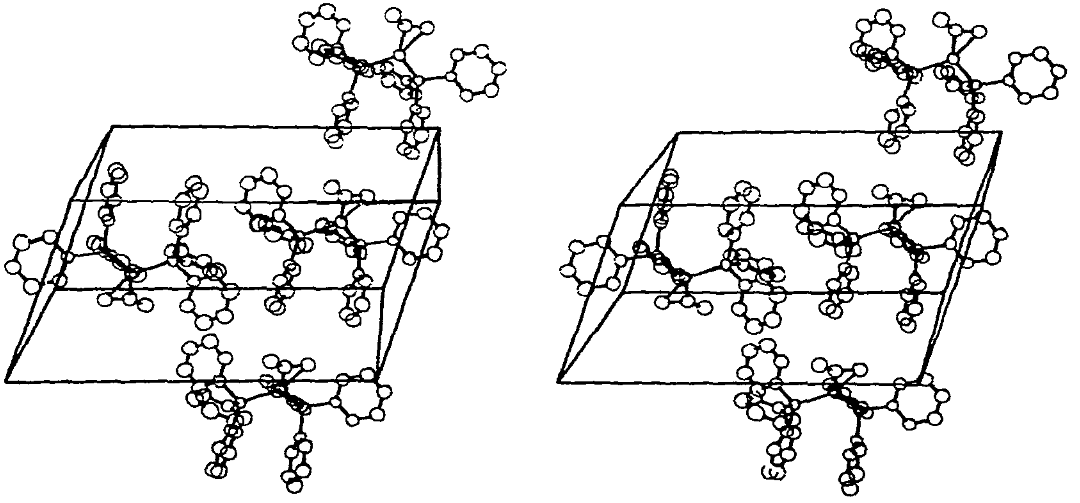


Fig 8 Stereoscopic view of the crystal structure of (Ph$_3$P)$_2$Pd(C$_3$H$_4$).

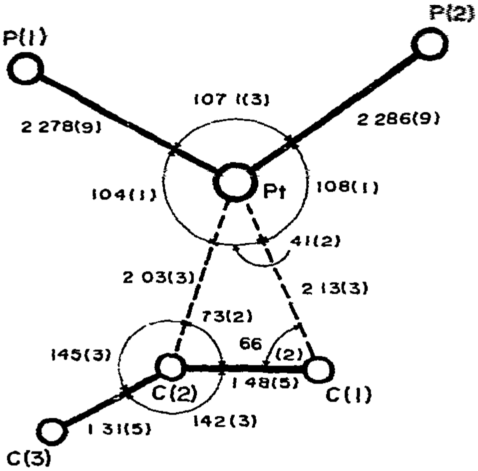


Fig 9 The coordination geometry around the platinum atom in $(Ph_3P)_2Pt(C_3H_4)$ (Kadonaga et al , 1971)

bonding of Pt to allene is stronger than that of Pd. Although the metallic radius of Pd (1.283 Å) is shorter than that of Pt (1.295 Å) [22], both M—C(1) and M—C(2) distances in the Pd complex are 0.01 and 0.04 Å respectively, longer than those in the Pt complex*. Moreover the C(1)—C(2) distance in the Pd complex is 0.06 Å shorter and C(1)—C(2)—C(3) angle is 6° larger than those in the Pt complex. As mentioned above, the distortion of the ligand from its free state is in proportion to the bonding strength of metal-to-ligand. This difference between the bonding of Pd and Pt to allene can explain the chemical behavior of the allene molecule in bonding reversibly to Pd, but irreversibly to Pt. Coordination bonds of metal—allene and metal—triphenylphosphine are both stronger in the Pt complex than in the Pd complex, making the former more stable than the latter. This is consistent with the results of NMR studies [23]. From the standpoint of allene polymerization, however, the coordination of both allene and triphenylphosphine ligands to the metal is strong enough to stabilize these two complexes. It is probably this which makes these complexes catalytically inactive for the polymerization of allene.

Acknowledgements

The authors express their sincere thanks to Professor Sei Otsuka and his coworkers for supplying crystals, and to Dr. Donald J Mullen who read the manuscript and improved its English.

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* The introduction of allene hydrogen atoms into the refinement results in considerable variation of the positions of the allene carbons, especially towards the palladium Structure refinement of $Pt(PPh_3)_2(C_3H_4)$ was carried out excluding all hydrogen atoms For this reason, structural parameters of the Pd complex used in the comparison with the Pt analogue are not those in the final refinement, but those in the refinement excluding all allene hydrogen atoms.

References

1 S. Otsuka and A Nakamura, J Polym Sci., Part B, Polym. Lett., 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 T Kashiwagi, N. Yasuoka, N Kasai and M Kakudo, Chem Commun., (1969) 317
5 P Racanelli, G Pantini, A Immirzi, G Allegra and L. Porri, Chem Commun., (1969) 361
6 T G Hewitt, K. Anzenhofer and J J. De Boer, J. Organometal Chem , 18 (1969) 91, Chem. Commun , (1969) 312, T G. Hewitt and J J De Boer, J Chem Soc. A, (1971) 817
7 W R Busing and H A Levy, Acta Crystallogr , 22 (1967) 457
8 H P Hanson, F Herman, J D Lea and S Skillman, Acta Crystallogr , 17 (1964) 1040
9 T. Ashida, in T Sakurai (Ed.), The Universal Crystallographic Computing System, Japanese Crystallographic Association, 1967
10 P.T Cheng and S C Nyburg, Can J Chem , 50 (1972) 912
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 A.G Maki and R A. Toth, J Mol. Spectrosc , 17 (1965) 136
13 C D Cook, K Y. Wan, U Gelius, K. Hamrin, H. Johansson, E. Olsson, H Siegbahn, C Nordling and K. Siegbahn, J Amer. Chem Soc , 93 (1971) 1904
14 J H Nelson, K S Wheelock, L C Cusachs and H B Jonassen, J Amer Chem. Soc 91 (1969) 7005. Chem Commun , (1969) 1019
15 K S Wheelock, J H. Nelson L C Cusachs and H B Jonassen, J Amer Chem. Soc , 92 (1970) 5110
16 A.D Walsh, J Chem Soc., (1953) 2260
17 R Mason and A I M Rae, J Chem Soc A, (1970) 1767
18 M Baird, G Hartwell, R Mason, A I M Rae and G Wilkinson, Chem Commun., (1967) 92
19 A C Blizzard and D P Santry, J Amer. Chem Soc , 90 (1968) 5749
20 R Mason, Nature, 217 (1968) 543
21 T Kashiwagi, N Yasuoka, T. Ueki, N Kasai and M Kakudo, Bull Chem Soc Japan, 40 (1967) 1998 T Kashiwagi, N Yasuoka, T Ueki, N Kasai, M Kakudo, S Takahashi and N Hagihara, Bull. Chem. Soc Japan, 41 (1968) 296
22 L Pauling, The Nature of the Chemical Bond 3rd Edn Cornell University Press, Ithaca, 1960
23 S Otsuka, K Tani and A. Nakamura Presented at the 24th Annual Meeting of the Chemical Society of Japan, April 1971
24 C K Johnson, ORTEP Report ORNL-3794 Oak Ridge National Laboratory, Tennessee, 1965
25 K Okamoto, unpublished work.