Acta Cryst. (1972). **B28**, 899

The Crystal and Molecular Structures of a Novel μ-Allyl Palladium Complex, μ-Allyl-μ-iodo-bis(triphenylphosphine palladium) Benzene Solvate

BY YOSHIKO KOBAYASHI AND YOICHI IITAKA
Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo, Japan

AND HIROSHI YAMAZAKI
Institute of Physical and Chemical Research, Wako-shi, Saitama, Japan

(*Received* 14 *June* 1971)

A new μ-allyl metal complex, $C_3H_5Pd_2(PPh_3)_2I$ has been synthesized and its crystal and molecular structures are investigated by X-ray diffraction methods. The complex, crystallized from benzene solutions, contains an equivalent molecule of benzene as solvent of crystallization. The cell dimensions are: $a=18{\cdot}95$, $b=14{\cdot}49$, $c=17{\cdot}97$ Å; $\beta=124{\cdot}7°$; space group $C2/c$; $Z=4$. Intensity data were collected by the photographic method using Cu $K\alpha$ radiation. The atomic coordinates and anisotropic thermal parameters were refined by the block-matrix least-squares method. The final R value for 1628 observed structure factors was 0·13. The structure of the complex was found to be that described as μ-allyl-μ-iodo-bis(triphenylphosphine palladium). The two triphenylphosphine palladium moieties are bound together through a Pd–Pd bond and the palladium atoms are bridged by iodine atom to form a triangular Pd_2I group. The allyl group lies parallel to the Pd–Pd bond and binds to the palladium atoms through σ-bonds formed by its terminal carbon atoms. The allyl groups are disordered over two sites in the crystal.

Introduction

It is well-known that the reaction of a bridged halogen-π-allyl palladium complex with an equimolar quantity of triphenylphosphine in chloroform or in other relatively non-polar solvents gives a complex of the type $[Pd.X.all.(PPh_3)]$, in which the allyl group is bonded asymmetrically through a σ- and an ethylenenic π-bond, while the reaction with two moles of triphenylphosphine gives a σ-allyl complex. The latter compound has not yet been isolated, but its existence in solution is suggested by n.m.r. studies. A similar reaction in aqueous acetone yields a π-allyl cation $[Pd.all.(PPh_3)]^+$ which is isolated as the tetraphenylborate.

In the course of a detailed study of these reactions, we have isolated a novel μ-allyl palladium complex from bis(halo-π-allyl-palladium) by treatment of excess tertiary phosphine in benzene solutions. In the present report, we describe the preparation and X-ray structure determination of this μ-allyl palladium complex, μ-$C_3H_5Pd_2(PPh_3)_2I$.

Experimental

The mixture of bis(iodo-π-allylpalladium) (0·17 g, 0·3 M) and triphenylphosphine (0·24 g, 0·9 M) in benzene (20 ml) was allowed to stand overnight under nitrogen atmosphere at room temperature. Insoluble colourless crystals of triphenylallylphosphonium iodide were formed but they were filtered off. The orange solution was concentrated to the half of its original volume and addition of hexane (5 ml) gave red brown crystals of bis(triphenylphosphine)palladium diiodide (0·04 g). After separation of the crystals, the solution was chromatographed on alumina with benzene as the eluent. The yellow eluate was concentrated and hexane was added to give yellow crystals of μ-$C_3H_5Pd_2(PPh_3)_2I.C_6H_6$ (0·18 g). The crystals decomposed without melting at about 150°C.

Found: C, 55·13; H, 4·26; I, 12·84%. Calculated for $C_{45}H_{41}IP_2Pd_2$: C, 54·96; H, 4·20; I, 12·90%.

The crystals lost the benzene molecule on recrystallization from methylene chloride and hexane.

Found: C, 51·49; H, 3·97; I, 14·65%. Calculated for $C_{39}H_{35}IP_2Pd_2$: C, 51·74; H, 3·90; I, 14·02%.

The n.m.r. spectrum in deutero-chloroform was recorded immediately after the preparation of the sample solution because the complex decomposes fairly rapidly in chloroform.

N.m.r.: $2{\cdot}2\sim 2{\cdot}8\tau$ (aromatic protons); $6{\cdot}75\tau$ (1:3:3:1 quartet, $J_{HH}=J_{HP}=6{\cdot}5$ Hz, *syn* protons of allyl); $7{\cdot}2\tau$ (broad, central proton of allyl); $8{\cdot}45\tau$ (doublet, $J_{HH}=13$ Hz, *anti* protons of allyl).

Fresh crystals of μ-$C_3H_5Pd_2(PPh_3)_2I.C_6H_6$ were chosen for the X-ray diffraction study. They were prisms elongated along the c axis and transparent yellow in colour at first, but when exposed to air they gradually decomposed becoming opaque and brown. The specimen was therefore enclosed in an evacuated thin-walled glass capillary for the experiment. The lattice constants and space group were determined from the b and c axis equatorial precession photographs taken with Cu $K\alpha$ radiation. Systematic absence of the reflexions indicated that the space group is either $C2/c$ or Cc. A test for piezoelectricity by the vibrating-electrode method (Iitaka, 1953) suggested the centric space group $C2/c$.

Crystal data

μ-Allyl-μ-iodo-bis(triphenylphosphine palladium) benzene solvate $C_3H_5Pd_2(PPh_3)_2I.C_6H_6$. M.W. 982·7. Monoclinic, space group $C2/c$, $Z=4$. $a=18·95\pm0·06$, $b=14·49\pm0·03$, $c=17·97\pm0·06$ Å; $\beta=124·7\pm0·3°$; $D_m=1·58$, $D_x=1·61$ g.cm^{-3}; $U=4055·8$ Å^3. Linear absorption coefficient for Cu $K\alpha$ radiation: $\mu=144·0$ cm^{-1}.

Three-dimensional intensity data were collected from multiple-film equi-inclination Weissenberg photographs. The layer lines from zero to the twelfth about the c axis and from zero to the fourth about the b axis were recorded using nickel-filtered Cu $K\alpha$ radiation. The intensities were measured by a Narumi microphotometer and corrected for Lorentz and polarization factors, but not for absorption factors since the size of the single crystal used for the intensity measurement was only about 0·13 × 0·13 mm in cross section which gives the μR value of 0·93. The structure factors obtained for the two axes were correlated and scaled to a common base, and a total of 1628 independent structure factors was finally derived.

Determination of the crystal structure

Since there are four molecules in the unit cell of space group $C2/c$ which has eightfold general positions, the iodine atom was supposed to be on a diad axis. Assuming that the molecule has a diad axis coinciding with that of the crystal, the coordinates of the iodine and palladium atoms were derived from the three-dimensional Patterson function. A three-dimensional Fourier map was then calculated on the basis of the contribution of these two atoms which gave the R value 0·37. Atomic positions of the iodine, palladium

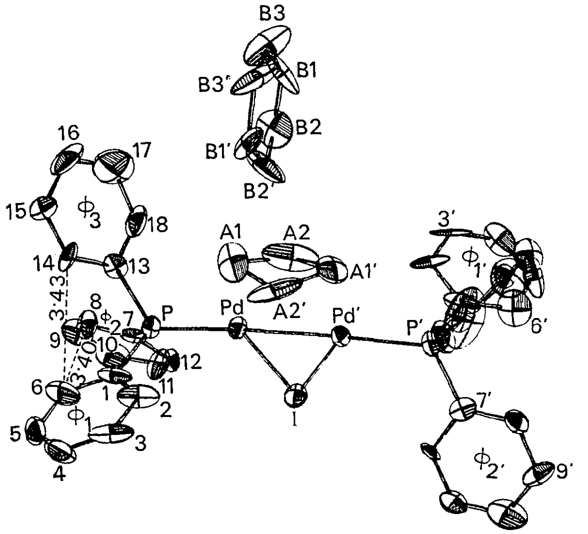

Fig. 1. Stereoscopic drawing of the structure. Each thermal ellipsoid encloses 50% of the probability of finding the centre of the atom in it. Shortest intramolecular interatomic distances between the phenyl groups are shown. Allyl molecules are disordered over the two sites $A1$–$A2$–$A1'$ and $A1$–$A2'$–$A1'$. The multiplicity factors for $A2$ and $A2'$ were taken to be 0·5.

Table 1. *Final parameters* (× 10^4)

Temperature factors are expressed as

$$T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}.$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I*	0 (0)	−1269 (2)	2500 (0)	33 (2)	20 (2)	56 (3)	0 (0)	27 (2)	0 (0)
Pd	788 (2)	308 (2)	2669 (2)	23 (1)	26 (1)	31 (2)	−1 (1)	17 (1)	2 (1)
P	2093 (7)	229 (8)	2885 (8)	25 (4)	33 (6)	37 (7)	−4 (4)	20 (5)	−3 (5)
C(1)	1979 (28)	139 (23)	1822 (27)	74 (25)	25 (19)	24 (22)	−8 (16)	32 (23)	−6 (16)
C(2)	1150 (30)	413 (26)	1015 (25)	60 (28)	30 (21)	11 (20)	14 (19)	1 (19)	11 (15)
C(3)	1052 (33)	387 (25)	226 (27)	77 (31)	13 (17)	9 (23)	0 (18)	7 (23)	8 (15)
C(4)	1700 (38)	92 (38)	160 (37)	82 (35)	57 (32)	58 (34)	−15 (27)	57 (31)	−23 (28)
C(5)	2522 (32)	−170 (46)	903 (36)	40 (24)	128 (50)	41 (32)	−35 (30)	32 (26)	−34 (34)
C(6)	2652 (30)	−137 (34)	1733 (32)	67 (26)	83 (32)	40 (29)	−8 (23)	32 (26)	−24 (26)
C(7)	2863 (24)	−652 (25)	3621 (26)	35 (18)	23 (16)	25 (23)	2 (14)	15 (19)	−9 (17)
C(8)	3739 (28)	−650 (29)	3973 (33)	39 (22)	30 (19)	60 (32)	−1 (18)	34 (24)	12 (22)
C(9)	4306 (33)	−1362 (32)	4545 (34)	43 (27)	42 (26)	46 (29)	25 (22)	19 (24)	9 (23)
C(10)	3980 (42)	−2169 (32)	4714 (40)	95 (42)	26 (24)	79 (39)	−3 (24)	57 (35)	−2 (24)
C(11)	3108 (30)	−2154 (29)	4395 (35)	43 (25)	30 (23)	72 (35)	−7 (19)	34 (26)	19 (23)
C(12)	2509 (25)	−1486 (24)	3797 (29)	33 (19)	22 (18)	36 (25)	−2 (14)	28 (20)	10 (16)
C(13)	2769 (25)	1235 (33)	3381 (25)	13 (16)	67 (28)	5 (19)	5 (18)	−4 (15)	−2 (20)
C(14)	3132 (22)	1805 (30)	3031 (26)	8 (15)	52 (25)	20 (22)	−10 (15)	−0 (16)	5 (19)
C(15)	3606 (31)	2573 (31)	3427 (34)	43 (25)	36 (23)	60 (32)	−14 (19)	31 (25)	−15 (22)
C(16)	3772 (36)	2900 (33)	4286 (45)	52 (30)	31 (25)	115 (48)	−22 (22)	42 (33)	−9 (28)
C(17)	3400 (36)	2420 (52)	4620 (42)	46 (32)	160 (64)	80 (44)	−14 (35)	11 (31)	−60 (46)
C(18)	2890 (32)	1579 (31)	4130 (39)	43 (25)	36 (23)	90 (41)	−10 (20)	47 (29)	3 (25)
C(*B*1)	275 (34)	5070 (39)	3370 (32)	60 (28)	96 (39)	30 (27)	59 (29)	34 (24)	28 (28)
C(*B*2)	201 (46)	4289 (38)	2966 (43)	118 (50)	42 (28)	110 (53)	−17 (32)	96 (51)	10 (30)
C(*B*3)	159 (37)	5908 (32)	2923 (41)	29 (32)	25 (22)	114 (58)	8 (20)	−2 (37)	19 (24)
C(*A*1)	728 (32)	1814 (21)	2653 (36)	84 (30)	29 (13)	119 (40)	10 (14)	78 (31)	25 (18)
C(*A*2)*	115 (53)	1642 (45)	2901 (54)	110 (45)	55 (28)	19 (52)	43 (34)	2 (48)	9 (39)

* Multiplicity factor = 0·5

Table 2. *Observed and calculated structure factors*

H	K	L	|F(OBS)|	|F(CAL)|
14	0	0	101.40	98.46
12	0	0	96.07	91.02
10	0	0	123.78	109.51
6	0	0	80.29	-66.31
4	0	0	74.54	73.20
2	0	0	55.74	65.37
15	1	0	51.69	52.80
13	1	0	66.12	84.86
11	1	0	101.17	99.49
7	1	0	87.47	-84.48
5	1	0	84.56	-78.73
3	1	0	16.46	2.78
18	2	0	32.50	-29.28
14	2	0	53.73	57.01
12	2	0	45.48	45.90
10	2	0	48.57	41.53
8	2	0	75.19	-61.51
6	2	0	141.37	-140.02
4	2	0	44.30	28.88
2	2	0	38.07	35.49
0	2	0	240.76	256.27
17	3	0	45.96	-42.77
9	3	0	36.01	-45.22
7	3	0	210.63	-204.18
5	3	0	85.53	-94.90
3	3	0	154.36	-170.24
1	3	0	95.95	76.88
18	4	0	32.62	-45.77
10	4	0	23.30	-18.11
8	4	0	99.68	-111.93
6	4	0	114.39	-137.75
4	4	0	144.63	-156.08
2	4	0	92.59	-91.74
0	4	0	177.90	129.84
17	5	0	36.53	-32.15
7	5	0	116.05	-116.18
5	5	0	84.44	-84.69
3	5	0	75.98	-67.09
1	13	0	89.42	-91.75
6	14	0	46.67	53.55
0	14	0	42.40	-42.24
5	15	0	44.18	61.27
8	16	0	31.75	43.61
6	16	0	44.42	65.60
4	16	0	40.44	42.64
1	5	0	84.50	68.60
8	6	0	53.84	-46.74
6	6	0	77.09	-63.98
4	6	0	35.94	29.87
0	6	0	136.63	114.89
11	7	0	48.27	47.88
9	7	0	43.88	45.05
5	7	0	79.15	68.37
3	7	0	26.63	31.94
1	7	0	104.84	99.93
10	8	0	36.88	29.90
8	8	0	56.51	44.78
6	8	0	54.14	50.09
4	8	0	93.52	82.29
2	8	0	41.93	34.97
0	8	0	102.35	76.84
9	9	0	36.94	35.78
7	9	0	41.51	38.07
5	9	0	73.35	65.73
6	10	0	35.70	31.02
2	10	0	56.65	-21.25
0	10	0	59.77	-44.17
7	11	0	77.45	-20.88
3	11	0	59.42	-49.70
1	11	0	88.00	-80.01
2	12	0	56.11	-69.28
0	12	0	65.33	-95.11
-3	1	1	33.80	46.18
1	1	1	40.50	37.86
3	1	1	25.62	14.11
5	1	1	53.55	66.62
7	1	1	87.29	90.61
9	1	1	53.73	50.07
-8	2	1	115.69	116.12
-6	2	1	118.18	120.98
-4	2	1	55.49	63.86
-2	2	1	42.04	34.54
0	2	1	21.47	-5.35
2	2	1	58.73	81.95
4	2	1	81.63	116.29
6	2	1	97.31	98.74
8	2	1	112.31	102.35
16	2	1	37.66	31.55
-17	3	1	27.93	32.88
-9	3	1	74.42	64.50
-7	3	1	105.02	104.87
-5	3	1	72.88	74.27
-3	3	1	145.05	144.53
-1	3	1	18.44	-11.34
1	3	1	81.12	-80.44
3	3	1	54.44	64.97
5	3	1	136.81	130.45
7	3	1	100.69	109.26
-14	4	1	38.43	-40.74
-12	4	1	55.50	-37.54
-8	4	1	54.56	47.96
-6	4	1	52.68	54.25
-4	4	1	67.07	60.14
-2	4	1	22.10	-19.45
0	4	1	81.30	-97.09
2	4	1	69.38	-71.90
4	4	1	31.19	26.59
6	4	1	182.89	101.02
8	4	1	51.12	37.23
12	4	1	47.80	-48.00
14	4	1	38.13	-37.87
-13	5	1	80.47	-78.71
-11	5	1	44.30	-43.39
-9	5	1	64.40	-55.29
-7	5	1	93.98	76.92
-5	5	1	54.62	-46.95
-3	5	1	18.15	-18.50
-1	5	1	167.82	-168.29
1	5	1	189.82	-186.32
3	5	1	22.08	-21.78
7	5	1	88.94	78.55
9	5	1	46.85	-48.80
11	5	1	92.57	-88.60
13	5	1	52.72	-59.39
15	5	1	35.09	-31.49
-12	6	1	83.28	-98.85
-10	6	1	55.15	-79.22
-8	6	1	54.38	46.53
-6	6	1	38.19	34.19
-4	6	1	24.25	-12.46
-2	6	1	168.82	-151.94
0	6	1	211.35	-207.77
2	6	1	125.42	-111.84
4	6	1	55.68	-34.80
8	12	3	67.78	64.04
6	12	3	32.14	-39.93
-13	13	3	30.68	37.84
-11	13	3	35.52	35.72
-1	13	3	75.84	96.35
6	6	1	58.85	52.90
10	6	1	64.10	-64.88
12	6	1	70.57	-78.40
14	6	1	67.36	-65.58
-9	7	1	89.44	-23.94
-7	7	1	45.25	64.95
-5	7	1	14.94	-5.59
-3	7	1	25.62	-26.67
-1	7	1	174.88	-183.72
1	7	1	101.36	-192.11
3	7	1	52.48	-45.45
5	7	1	67.84	44.73
7	7	1	82.07	73.89
9	7	1	51.41	-47.47
11	7	1	54.56	-59.78
13	7	1	68.79	-79.29
15	7	1	42.54	-31.10
-14	8	1	42.70	-56.13
-10	8	1	32.14	-21.50
-8	8	1	86.93	83.24
-6	8	1	82.07	77.37
-4	8	1	31.67	35.66
0	8	1	155.54	-150.45
2	8	1	85.93	-98.55
4	8	1	89.88	70.64
6	8	1	89.96	98.15
8	8	1	77.35	79.51
10	8	1	37.18	-44.37
12	8	1	45.07	-40.85
-9	9	1	74.60	42.69
-7	9	1	124.29	128.75
-5	9	1	87.88	81.68
-3	9	1	86.18	86.48
-1	9	1	88.08	-48.57
1	9	1	33.58	-35.92
3	9	1	51.77	39.90
5	9	1	92.15	81.29
7	9	1	121.03	123.70
-8	10	1	92.09	98.15
-6	10	1	94.58	111.50
-4	10	1	58.35	64.78
-2	10	1	36.65	26.48
0	10	1	54.44	-41.66
2	10	1	52.54	43.49
4	10	1	81.18	78.67
6	10	1	122.69	124.26
8	10	1	108.99	79.50
-9	11	1	31.55	27.98
-7	11	1	95.12	115.45
-5	11	1	46.73	53.24
-3	11	1	53.61	55.36
-1	11	1	33.50	-32.18
3	11	1	41.57	43.60
5	11	1	75.25	69.01
7	11	1	92.51	78.79
-14	12	1	30.18	-33.06
-8	12	1	31.37	35.88
-6	12	1	31.55	37.28
0	12	1	100.81	-109.32
6	12	1	41.15	49.35
10	12	1	22.12	-24.41
-13	13	1	29.65	-39.75
-7	13	1	24.02	27.97
-3	13	1	31.55	-32.14
-1	13	1	80.41	-86.51
1	13	1	45.72	-50.52
-10	14	1	40.09	-44.62
-4	14	1	44.77	-45.70
-2	14	1	45.25	-47.99
0	14	1	85.63	-82.19
2	14	1	45.01	-44.97
4	14	1	19.27	-32.43
-1	15	1	29.83	-24.62
-14	0	2	155.37	-143.28
-12	0	2	124.00	-105.09
-10	0	2	92.69	-86.94
-8	0	2	18.38	20.67
-6	0	2	12.87	-5.81
-4	0	2	220.48	-271.84
-2	0	2	97.67	-90.08
0	0	2	201.74	-301.51
2	0	2	237.26	-261.18
4	0	2	41.57	-43.66
6	0	2	74.78	63.40
8	0	2	36.88	26.90
10	0	2	114.63	-104.54
12	0	2	82.25	-79.77
14	0	2	77.21	-68.21
-15	1	2	96.78	-93.06
-13	1	2	85.15	-78.63
-11	1	2	83.55	-87.44
-9	1	2	43.05	30.58
-7	1	2	118.13	135.72
-5	1	2	39.26	27.22
-3	1	2	54.97	-42.87
-1	1	2	26.09	-231.02
1	1	2	127.91	-142.63
3	1	2	45.96	-45.77
5	1	2	51.29	47.81
7	1	2	75.25	92.52
9	1	2	50.35	-57.66
11	1	2	60.19	-72.48
13	1	2	83.14	-96.12
-18	2	2	31.19	32.71
-14	2	2	86.52	-79.69
-12	2	2	45.10	-43.14
-10	2	2	41.87	-41.04
-8	2	2	102.47	98.96
-6	2	2	78.51	80.42
-4	2	2	24.61	2.79
-2	2	2	100.34	-100.94
0	2	2	180.63	-221.82
2	2	2	21.70	11.89
4	2	2	25.68	16.91
6	2	2	111.66	126.44
8	2	2	60.78	62.70
10	2	2	43.53	-45.64
12	2	2	48.15	-46.57
14	2	2	46.73	-47.05
-19	3	2	36.59	40.47
-17	3	2	54.79	49.39
-15	3	2	41.44	-29.92
-9	3	2	81.60	76.45
-7	3	2	171.08	169.82
-5	3	2	136.86	146.11
-3	3	2	24.79	24.66
-1	3	2	94.11	85.27
1	3	2	69.44	-61.15
3	3	2	119.31	126.66
5	3	2	76.07	67.15
7	3	2	138.35	142.41
-18	4	2	49.48	51.95
-16	4	2	34.63	27.18
1	5	5	84.74	-73.45
5	5	5	39.43	38.08
-16	6	5	51.41	-47.82
-14	6	5	126.19	-127.77
-12	6	5	87.23	-82.15
-10	6	5	41.09	-34.31
-8	6	5	79.88	64.17
-6	6	5	23.78	19.18
-4	6	5	110.36	-95.05
-2	6	5	167.82	-151.58
0	6	5	172.03	-163.94
2	6	5	74.84	-57.99
6	6	5	57.88	47.42
-15	7	5	71.34	-76.21
-13	7	5	70.86	-80.35
-11	7	5	90.20	-76.66
-9	7	5	44.48	49.39
-7	7	5	66.36	61.70
-3	7	5	120.26	-103.08
-1	7	5	181.64	-172.41
1	7	5	83.08	-75.50
5	7	5	63.04	58.92
-18	8	5	35.22	36.07
-16	8	5	41.57	-36.96
-14	8	5	46.65	-46.47
-12	8	5	35.58	-32.82
-8	8	5	103.95	107.71
-6	8	5	84.86	65.32
-2	8	5	101.52	-80.39
0	8	5	112.08	-105.95
2	8	5	27.04	23.47
4	8	5	53.84	48.15
6	8	5	89.48	86.27
-19	9	5	34.28	41.43
-15	9	5	40.15	-35.05
-13	9	5	33.15	-21.59
-9	9	5	87.59	76.95
-7	9	5	138.35	135.19
-5	9	5	67.13	67.03
-1	9	5	82.25	-70.64
3	9	5	64.81	54.14
5	9	5	99.86	101.26
7	9	5	74.12	63.41
-18	10	5	40.21	48.26
-10	10	5	51.89	48.36
-8	10	5	116.47	115.29
-6	10	5	87.11	85.16
-4	10	5	67.25	53.23
-2	10	5	30.07	-25.40
2	10	5	52.66	51.03
4	10	5	71.52	78.77
6	10	5	87.65	85.91
-9	11	5	68.14	79.02
-7	11	5	100.16	103.48
-5	11	5	31.96	28.02
-1	11	5	54.38	-43.54
3	11	5	26.63	38.02
5	11	5	60.90	63.31
7	11	5	53.37	60.63
-14	12	5	36.63	-40.65
-8	12	5	59.77	55.35
-6	12	5	33.03	29.38
-2	12	5	67.78	-64.25
0	12	5	57.22	-50.18
6	12	5	42.93	46.00
-15	13	5	23.78	-44.42
-13	13	5	44.83	-39.62
-3	13	5	56.39	-46.36
-1	13	5	74.01	-73.77
1	13	5	34.45	-42.64
-14	14	5	32.38	-41.90
-12	14	5	29.69	-37.51
-10	14	5	28.94	-37.41
-2	14	5	42.70	-53.78
0	14	5	57.68	-59.12
-22	0	6	24.19	29.20
-16	0	6	117.59	-116.15
-14	0	6	138.29	-131.26
-12	0	6	92.33	-90.81
-10	0	6	92.33	-88.18
-8	0	6	91.50	75.88
-6	0	6	24.73	6.95
-4	0	6	70.80	-78.54
-2	0	6	199.54	-204.32
0	0	6	139.59	-149.81
2	0	6	66.71	-68.25
4	0	6	50.11	37.66
6	0	6	63.98	66.86
8	0	6	40.62	-46.28
10	0	6	37.48	-40.51
12	0	6	78.51	-68.29
-17	1	6	32.56	-22.39
-15	1	6	102.89	-95.97
-13	1	6	102.59	-102.17
-11	1	6	37.48	-40.48
-9	1	6	63.98	64.28
-7	1	6	78.57	78.60
-5	1	6	37.06	-35.16
-3	1	6	168.60	-168.99
-1	1	6	193.56	-200.22
1	1	6	87.76	-98.88
5	1	6	47.22	54.32
9	1	6	48.15	-68.66
-22	2	6	23.30	29.59
-18	2	6	40.21	38.53
-16	2	6	59.06	-53.95
-14	2	6	71.87	-68.29
-12	2	6	57.58	-58.71
-10	2	6	38.78	30.44
-8	2	6	120.79	117.36
-6	2	6	64.93	62.85
-4	2	6	54.91	48.61
-2	2	6	162.19	-166.29
0	2	6	66.48	-64.66
2	2	6	63.93	40.37
4	2	6	54.76	65.03
6	2	6	76.08	96.06
-21	3	6	45.90	39.16
-19	3	6	59.42	52.86
-17	3	6	65.11	37.09
-15	3	6	42.70	-34.99
-11	3	6	48.42	33.17
-9	3	6	106.42	84.68
-7	3	6	106.50	103.89
-5	3	6	48.27	42.70
-3	3	6	13.22	8.35
-1	3	6	58.88	-58.10
1	3	6	22.47	16.04
3	3	6	39.26	37.52
5	3	6	117.24	115.87
7	3	6	56.72	52.87
-22	4	6	29.23	36.93
-20	4	6	50.88	47.34
-18	4	6	55.98	48.15
-12	4	6	44.65	27.35
-10	4	6	77.08	79.84
-8	4	4	149.73	-181.69
-6	4	4	142.97	-145.61
-4	4	4	107.57	-112.25
-2	4	4	16.47	-16.94
0	4	4	44.36	34.14
2	4	4	116.18	-122.62
4	4	4	87.53	-86.06
6	4	4	125.72	-134.79
8	4	4	43.70	-50.37
-9	5	4	96.18	-80.91
-7	5	4	150.27	-123.75
-5	5	4	41.02	-60.95
-3	5	4	21.59	18.69
-1	5	4	74.78	52.42
3	5	4	75.91	-59.94
5	5	4	101.82	-77.00
7	5	4	94.05	-74.82
-14	6	4	63.69	50.63
-8	6	4	98.44	-78.91
-4	6	4	33.45	-32.06
-2	6	4	53.13	42.12
0	6	4	91.86	67.16
4	6	4	59.74	-42.65
6	6	4	62.27	-37.44
-13	7	4	56.78	49.62
-11	7	4	57.05	51.65
-9	7	4	45.90	39.56
-7	7	4	42.46	37.79
-5	7	4	61.79	49.47
-3	7	4	62.80	50.84
-1	7	4	140.42	99.38
1	7	4	94.76	70.84
3	7	4	50.76	40.94
5	7	4	43.64	36.81
-14	8	4	40.50	42.27
-10	8	4	53.55	45.60
-8	8	4	48.27	45.04
-6	8	4	99.56	86.30
-4	8	4	55.56	37.82
-2	8	4	62.21	43.81
0	8	4	73.86	60.78
2	8	4	62.92	49.64
4	8	4	56.16	46.41
6	8	4	46.67	27.52
8	8	4	59.66	29.91
-9	9	4	54.20	40.70
-7	9	4	45.84	40.21
-5	9	4	71.93	52.70
3	9	4	67.66	45.78
5	9	4	55.33	43.87
7	9	4	47.97	42.74
-8	10	4	44.18	30.84
-2	10	4	61.26	-46.82
-15	11	4	29.95	-44.11
-13	11	4	45.96	-43.88
-11	11	4	45.72	-49.95
-3	11	4	71.93	-60.16
-1	11	4	88.18	-66.16
1	11	4	60.43	-54.21
-14	12	4	29.71	-40.04
-12	12	4	51.77	-51.26
-4	12	4	35.94	-39.19
-2	12	4	110.00	-93.14
0	12	4	94.70	-87.82
-15	13	4	35.40	-41.25
-13	13	4	45.72	-48.44
-11	13	4	52.01	-43.11
-3	13	4	48.80	-55.63
-1	13	4	109.11	-97.76
1	13	4	42.93	-36.16
-8	14	4	41.45	57.85
-6	14	4	50.82	51.49
0	14	4	69.56	-53.03
4	14	4	30.48	33.74
6	14	4	56.34	53.02
-9	15	4	51.35	53.68
-7	15	4	84.09	73.51
-5	15	4	53.90	42.69
-1	15	4	44.30	-28.18
3	15	4	26.80	36.88
5	15	4	57.46	62.15
-8	16	4	62.27	68.02
-6	16	4	55.33	49.06
-4	16	4	43.47	41.79
4	16	4	35.46	43.20
-11	1	5	40.21	39.54
-9	1	5	62.21	67.29
-7	1	5	90.14	91.16
-5	1	5	94.46	80.82
-3	1	5	76.79	66.79
-1	1	5	43.70	-34.89
1	1	5	45.60	40.56
3	1	5	41.09	44.05
5	1	5	37.42	59.11
7	1	5	47.68	59.92
-18	2	5	51.83	48.32
-12	2	5	38.37	31.00
-10	2	5	73.59	71.35
-8	2	5	112.91	122.87
-6	2	5	105.14	104.92
-4	2	5	44.71	44.66
-2	2	5	63.93	52.69
0	2	5	28.58	30.27
2	2	5	85.87	62.52
4	2	5	75.90	92.84
6	2	5	60.25	83.43
8	2	5	25.80	34.99
-21	3	5	38.19	36.30
-19	3	5	31.43	31.14
-17	3	5	39.97	21.93
-9	3	5	87.41	87.73
-7	3	5	138.82	146.02
-5	3	5	91.32	84.12
-3	3	5	16.01	-7.14
-1	3	5	55.27	-50.31
1	3	5	31.31	30.77
3	3	5	62.92	59.46
5	3	5	100.22	90.95
7	3	5	36.17	47.76
-20	4	5	29.83	32.04
-14	4	5	49.10	-52.12
-12	4	5	32.98	-34.35
-8	4	5	73.77	74.86
-6	4	5	53.01	50.16
-4	4	5	30.90	25.90
-2	4	5	77.80	-66.05
0	4	5	98.38	-108.27
4	4	5	48.74	39.64
6	4	5	69.20	64.53
-15	5	5	87.35	-92.96
-13	5	5	68.49	-47.68
-11	5	5	94.17	-83.76
-9	5	5	28.64	22.31
-7	5	5	32.73	21.26
-3	5	5	112.43	-102.54
-1	5	5	196.52	-166.69
-3	5	3	101.88	107.93
-1	5	3	177.31	163.21
1	5	3	114.15	106.52
3	5	3	48.21	32.61
5	5	3	38.31	-22.86
-16	6	3	34.45	44.66
-14	6	3	121.51	103.79
-12	6	3	68.67	59.79
-10	6	3	82.17	76.15
-8	6	3	60.37	-55.01
-4	6	3	63.98	53.65
-2	6	3	151.99	144.84
0	6	3	236.25	-215.75
2	6	3	45.78	41.41
6	6	3	61.20	-41.80
-15	7	3	82.25	74.46
-13	7	3	123.46	100.17
-11	7	3	68.79	67.71
-9	7	3	28.17	-24.03
-7	7	3	94.76	-82.19
-5	7	3	15.00	15.61
-3	7	3	108.52	92.58
-1	7	3	185.67	181.88
1	7	3	116.23	110.15
3	7	3	35.70	27.98
5	7	3	29.00	-30.33
7	7	3	71.34	-61.92
9	7	3	42.70	43.44
-14	8	3	58.73	54.46
-12	8	3	56.10	61.14
-8	8	3	105.95	-110.25
-6	8	3	96.60	-92.25
-4	8	3	15.89	15.47
-2	8	3	80.29	79.59
0	8	3	107.69	89.06
4	8	3	34.45	-40.12
6	8	3	96.36	-97.23
-17	9	3	44.30	-41.69
-9	9	3	69.52	-63.13
-7	9	3	147.12	-147.87
-5	9	3	62.09	-54.23
-3	9	3	46.61	-33.36
-1	9	3	81.17	86.37
3	9	3	78.39	-71.06
5	9	3	84.27	-74.00
7	9	3	96.60	-85.65
-10	10	3	36.35	-35.86
-8	10	3	97.79	-107.84
-6	10	3	117.59	-114.71
-4	10	3	63.69	-57.57
0	10	3	35.64	35.52
2	10	3	51.95	-52.12
4	10	3	75.55	-70.32
6	10	3	95.41	-104.10
8	10	3	61.73	-66.65
-15	11	3	19.92	21.59
-9	11	3	47.26	-54.06
-7	11	3	95.59	-108.32
-5	11	3	43.11	-53.59
-3	11	3	40.68	-40.16
-1	11	3	63.27	62.35
3	11	3	42.16	-37.01
5	11	3	70.92	-80.11
7	11	3	58.47	-59.67
-14	12	3	33.86	46.40
-8	12	3	47.76	-53.03
-6	12	3	29.95	-28.98
-2	12	3	51.65	48.48
1	13	3	54.62	56.16
-10	14	3	24.85	44.29
-4	14	3	28.64	39.59
-2	14	3	53.84	56.36
0	14	3	69.86	69.44
4	14	3	23.60	29.11
-3	17	3	30.84	-34.61
-16	0	4	74.12	62.14
-14	0	4	128.33	131.84
-12	0	4	123.40	142.70
-10	0	4	118.24	105.20
-8	0	4	147.83	-124.49
-6	0	4	27.10	26.85
-4	0	4	90.14	84.35
-2	0	4	211.70	403.55
0	0	4	222.79	221.31
2	0	4	55.80	67.49
4	0	4	51.83	-55.00
6	0	4	44.53	-42.69
10	0	4	77.51	78.32
12	0	4	89.54	81.01
14	0	4	52.07	45.74
-21	1	4	28.35	-26.04
-19	1	4	20.34	-21.78
-15	1	4	100.10	90.80
-13	1	4	99.51	101.82
-11	1	4	65.88	60.20
-9	1	4	31.90	-26.20
-7	1	4	156.37	-151.23
-5	1	4	21.05	16.96
-3	1	4	52.18	48.63
-1	1	4	238.92	277.40
1	1	4	157.03	135.59
5	1	4	27.93	-30.30
7	1	4	29.77	-46.08
9	1	4	50.64	70.91
11	1	4	48.27	59.01
13	1	4	54.14	70.04
-18	2	4	34.51	-35.95
-14	2	4	88.06	83.33
-12	2	4	51.47	49.07
-10	2	4	26.57	23.71
-8	2	4	127.55	-125.81
-6	2	4	60.60	-59.67
-2	2	4	109.35	112.31
0	2	4	101.78	111.52
2	2	4	33.03	-7.23
4	2	4	78.22	-73.14
6	2	4	62.27	-98.54
8	2	4	31.73	-23.84
12	2	4	47.38	44.44
-21	3	4	41.69	-51.01
-19	3	4	43.76	-51.93
-17	3	4	52.24	-41.97
-15	3	4	33.15	32.77
-9	3	4	121.80	-128.88
-7	3	4	173.10	-180.46
-5	3	4	96.54	-90.82
-3	3	4	60.60	-48.48
-1	3	4	134.97	107.78
1	3	4	18.80	10.72
3	3	4	112.25	-101.95
5	3	4	127.44	-121.25
7	3	4	79.37	-85.52
-20	4	4	38.72	-48.25
-18	4	4	51.29	-46.59
-16	4	4	31.49	-32.81
-10	4	4	39.73	-48.46
-14	4	2	50.52	-36.25
-12	4	2	24.31	31.41
-10	4	2	29.06	27.36
-8	4	2	150.92	179.51
-6	4	2	108.40	130.41
-4	4	2	69.32	68.58
-2	4	2	64.87	63.71
0	4	2	11.62	-5.74
2	4	2	47.26	48.84
4	4	2	83.91	92.85
6	4	2	176.83	143.62
8	4	2	76.44	80.44
-17	5	2	54.88	56.44
-9	5	2	76.16	80.48
-7	5	2	121.62	114.11
-5	5	2	100.81	72.32
-3	5	2	32.30	26.66
-1	5	2	35.05	-17.24
1	5	2	87.65	-57.71
3	5	2	79.17	61.72
5	5	2	77.62	66.28
7	5	2	132.30	122.28
-14	6	2	40.38	-28.95
-10	6	2	40.92	-38.60
-8	6	2	56.63	50.04
-6	6	2	65.05	57.00
-4	6	2	17.85	7.25
-2	6	2	54.91	-38.61
0	6	2	112.20	-81.99
2	6	2	37.00	18.62
4	6	2	25.74	16.26
6	6	2	45.17	32.44
8	6	2	32.02	27.83
-15	7	2	48.33	-44.57
-13	7	2	40.38	-38.34
-11	7	2	41.57	-34.12
-9	7	2	52.30	-54.19
-5	7	2	76.67	-62.34
-3	7	2	92.51	-79.55
-1	7	2	111.84	-90.29
1	7	2	93.40	-84.20
3	7	2	75.84	-57.38
5	7	2	40.98	-33.81
7	7	2	20.10	-15.37
9	7	2	44.85	-41.21
-10	8	2	63.59	-66.58
-8	8	2	58.94	-58.19
-6	8	2	57.58	-51.46
-4	8	2	63.10	-52.94
-2	8	2	67.36	-52.08
0	8	2	74.84	-62.34
2	8	2	45.96	-35.74
4	8	2	64.16	-62.71
6	8	2	49.04	-43.81
8	8	2	57.40	-58.91
1	9	2	44.95	-46.30
5	9	2	54.38	-50.87
7	9	2	45.48	-32.70
0	10	2	35.58	24.64
-13	11	2	45.07	46.59
-11	11	2	34.69	44.54
-5	11	2	45.07	42.22
-3	11	2	33.33	38.48
-1	11	2	107.81	93.84
3	11	2	48.39	43.75
-14	12	2	38.72	49.22
-12	12	2	31.55	45.81
-4	12	2	34.99	30.68
-2	12	2	53.19	57.72
0	12	2	64.99	65.72
2	12	2	53.73	51.61
-3	13	2	46.91	48.67
-1	13	2	66.30	66.96
1	13	2	66.30	71.04
-8	14	2	42.87	-65.23
-6	14	2	34.04	-46.12
-2	14	2	31.31	33.27
0	14	2	65.53	63.04
6	14	2	42.22	-59.19
-9	15	2	33.74	-38.83
-7	15	2	52.84	-64.31
-5	15	2	32.26	-41.52
5	15	2	39.73	-52.14
7	15	2	46.37	-61.69
-8	16	2	51.53	-56.60
-6	16	2	52.01	-51.48
6	16	2	48.15	-56.34
-9	17	2	26.15	-24.18
-11	1	3	42.64	-37.14
-9	1	3	69.74	-74.27
-7	1	3	70.86	-74.26
-5	1	3	73.06	-78.06
-3	1	3	28.23	-28.58
1	1	3	65.05	-75.29
3	1	3	76.73	-74.64
5	1	3	68.73	-68.57
7	1	3	35.70	-52.99
-20	2	3	36.71	-27.68
-18	2	3	54.50	-48.33
-10	2	3	51.59	-56.87
-8	2	3	106.98	-106.78
-6	2	3	145.29	-156.35
-4	2	3	90.14	-85.87
-2	2	3	52.72	-57.26
0	2	3	47.38	42.42
2	2	3	56.22	-64.48
4	2	3	75.15	-98.76
6	2	3	95.00	-95.30
8	2	3	65.76	-70.30
10	2	3	38.49	-27.37
-21	3	3	27.10	-22.86
-19	3	3	24.61	-27.70
-17	3	3	40.44	-42.27
-9	3	3	92.51	-89.63
-7	3	3	154.12	-147.60
-5	3	3	38.49	-34.50
-3	3	3	30.18	-27.16
-1	3	3	18.98	-16.99
1	3	3	34.33	-29.59
3	3	3	52.48	-45.67
5	3	3	76.56	-82.15
7	3	3	103.42	-95.69
-14	4	3	51.41	56.57
-12	4	3	42.16	48.70
-8	4	3	101.88	-94.68
-6	4	3	52.66	-53.57
-2	4	3	82.13	87.72
0	4	3	74.18	68.48
2	4	3	38.90	-33.60
4	4	3	15.42	-8.17
6	4	3	78.92	-77.56
-15	5	3	57.46	63.96
-13	5	3	96.87	94.42
-11	5	3	73.35	71.20
-7	5	3	74.11	-72.08
-5	5	3	21.79	15.84

Table 2 (*cont.*)

-8	4	6	132.24	169.44
-6	4	6	129.16	130.40
-4	4	6	58.83	49.54
-2	4	6	25.74	-0.12
0	4	6	25.50	23.23
2	4	6	60.07	66.25
4	4	6	86.76	96.64
6	4	6	100.51	112.71
-19	5	6	43.53	44.97
-15	5	6	26.63	-23.04
-9	5	6	107.21	93.79
-7	5	6	100.22	87.21
-5	5	6	97.43	75.58
-1	5	6	94.35	-75.21
1	5	6	49.46	53.53
3	5	6	50.35	42.64
5	5	6	103.54	92.17
7	5	6	49.57	47.79
-14	6	6	59.89	-49.19
-8	6	6	74.78	53.38
-6	6	6	59.48	46.63
-2	6	6	50.82	-38.40
0	6	6	52.01	-36.01
4	6	6	29.23	21.05
6	6	6	40.38	37.92
-15	7	6	55.33	-48.86
-13	7	6	43.64	-32.54
-11	7	6	72.41	-54.10
-9	7	6	34.16	-32.51
-7	7	6	48.27	-37.32
-5	7	6	66.53	-51.87
-3	7	6	101.17	-83.44
-1	7	6	82.96	-64.88
1	7	6	52.95	-45.33
3	7	6	42.99	-33.13
-14	8	6	27.93	-23.59
-12	8	6	58.59	-55.66
-10	8	6	68.79	-55.86
-8	8	6	47.08	-34.09
-6	8	6	59.30	-50.62
-4	8	6	58.17	-50.93
-2	8	6	63.21	-45.83
0	8	6	45.13	-26.27
2	8	6	64.99	-54.70
4	8	6	57.34	-52.03
-9	9	6	70.80	-61.87
-7	9	6	60.31	-38.10
-5	9	6	37.66	-35.67
-1	9	6	35.94	-31.76
1	9	6	39.91	-14.98
3	9	6	39.38	-40.25
5	9	6	33.27	-25.22
-2	10	6	43.11	34.02
0	10	6	38.72	36.34
-15	11	6	48.09	44.24
-13	11	6	48.69	42.99
-5	11	6	39.67	27.35
-3	11	6	67.36	64.08
-1	11	6	79.82	65.58
1	11	6	44.42	41.34
-16	12	6	37.42	41.66
-14	12	6	51.53	49.82
-12	12	6	40.56	43.41
-4	12	6	33.21	33.56
-2	12	6	82.84	70.87
0	12	6	88.30	73.47
-15	13	6	39.43	50.05
-13	13	6	39.14	40.51
-11	13	6	28.29	22.87
-3	13	6	50.46	33.95
-1	13	6	98.85	85.52
1	13	6	32.67	27.51
-8	14	6	64.64	-65.19
-6	14	6	46.73	-40.43
-2	14	6	66.48	49.24
0	14	6	31.43	29.49
-9	15	6	50.70	-60.64
-7	15	6	63.87	-61.59
-5	15	6	42.04	-40.09
-1	15	6	38.72	30.30
-10	16	6	23.13	-29.32
-8	16	6	62.56	-62.35
-6	16	6	40.68	-36.92
-11	1	7	35.28	-42.30
-9	1	7	90.85	-81.67
-7	1	7	78.16	-62.25
-5	1	7	28.46	-32.46
-3	1	7	65.41	-55.61
1	1	7	55.45	-45.34
3	1	7	57.58	-57.30
-20	2	7	47.86	-35.77
-18	2	7	33.80	-30.75
-12	2	7	44.18	-39.04
-10	2	7	70.57	-77.14
-8	2	7	125.24	-138.77
-6	2	7	113.20	-109.23
-4	2	7	80.07	-80.40
-2	2	7	45.07	23.99
0	2	7	47.74	-39.54
2	2	7	57.64	-45.73
4	2	7	71.75	-88.01
6	2	7	54.85	-63.41
-21	3	7	24.55	-34.69
-19	3	7	39.43	-47.80
-11	3	7	38.78	-31.37
-9	3	7	95.83	-78.69
-7	3	7	104.40	-87.27
-5	3	7	52.07	-65.10
-3	3	7	41.87	-19.01
-1	3	7	50.76	45.98
1	3	7	48.85	-41.57
3	3	7	74.42	-48.29
5	3	7	91.92	-73.22
7	3	7	48.58	-42.09
-16	4	7	45.48	48.52
-14	4	7	57.78	42.41
-12	4	7	54.58	47.88
-10	4	7	44.71	-44.08
-8	4	7	99.56	-88.65
-6	4	7	32.97	-24.57
-4	4	7	34.16	31.73
-2	4	7	87.01	79.42
0	4	7	44.53	41.80
4	4	7	46.91	-34.78
6	4	7	51.12	-41.35
-15	5	7	111.19	105.91
-13	5	7	82.04	73.22
-11	5	7	58.11	48.88
-9	5	7	68.37	-49.94
-7	5	7	29.80	-16.90
-5	5	7	45.00	35.23
-3	5	7	124.95	95.23
-1	5	7	163.02	152.00
1	5	7	74.72	52.63
5	5	7	64.03	-55.30
-16	6	7	90.08	75.61
-14	6	7	96.18	90.28
-12	6	7	104.96	96.11
-8	6	7	41.63	-29.42
-4	6	7	87.29	77.71
-2	6	7	180.39	165.40
0	6	7	131.88	118.31
6	6	7	41.75	-24.91
-17	7	7	40.09	35.37
-15	7	7	114.03	95.66
-13	7	7	73.83	61.94
-11	7	7	65.29	-50.53
-9	7	7	81.12	-70.59
-7	7	7	47.44	-45.38
-5	7	7	19.75	14.25
-3	7	7	118.07	101.46
-1	7	7	168.35	165.16
5	7	7	74.24	-64.34
-20	8	7	30.95	-34.58
-18	8	7	22.71	-24.31
-16	8	7	35.52	41.70
-14	8	7	69.80	76.70
-12	8	7	33.03	23.42
1	11	7	74.78	67.42
-10	8	7	40.34	-37.39
-8	8	7	128.68	-107.42
-6	8	7	50.70	-48.60
-2	8	7	96.42	95.47
0	8	7	57.17	50.60
4	8	7	68.79	-60.59
6	8	7	69.80	-57.97
-19	9	7	35.22	-49.62
-11	9	7	25.80	-25.34
-9	9	7	124.41	-111.78
-7	9	7	101.70	-86.62
-5	9	7	58.05	-49.25
-1	9	7	66.24	52.93
1	9	7	36.71	-26.15
3	9	7	59.00	-49.41
5	9	7	91.38	-88.25
7	9	7	41.51	-38.14
-18	10	7	32.14	-41.51
-10	10	7	80.66	-56.27
-8	10	7	107.21	-122.71
-6	10	7	65.35	-59.28
-4	10	7	71.16	-66.14
-2	10	7	64.34	49.00
2	10	7	65.47	-56.81
4	10	7	63.63	-60.84
6	10	7	89.78	-77.49
-9	11	7	83.26	-77.18
-7	11	7	78.45	-83.37
-5	11	7	87.70	-43.97
-3	11	7	69.44	39.17
-1	11	7	33.68	32.65
3	11	7	38.60	-39.38
5	11	7	58.11	-56.12
-16	12	7	32.67	38.48
-14	12	7	36.17	39.12
-12	12	7	28.94	22.34
-14	12	7	36.17	39.12
-12	12	7	28.94	22.34
-8	12	7	56.45	-46.60
-2	12	7	65.53	58.44
0	12	7	37.24	31.03
-15	13	7	39.91	42.51
-13	13	7	37.71	42.45
-11	13	7	38.37	35.48
-3	13	7	55.45	48.19
-1	13	7	96.07	78.29
-14	14	7	29.53	41.19
-12	14	7	35.58	41.59
-2	14	7	53.67	53.84
0	14	7	41.15	39.32
-16	0	8	111.60	109.35
-14	0	8	139.30	133.15
-12	0	8	105.02	99.01
-10	0	8	47.56	-38.09
-8	0	8	90.79	-60.94
-6	0	8	26.86	12.43
-4	0	8	44.18	60.01
-2	0	8	248.88	235.17
0	0	8	81.00	90.59
4	0	8	33.62	-35.89
6	0	8	53.96	-60.84
8	0	8	60.72	58.23
10	0	8	34.08	42.63
12	0	8	56.93	57.13
-19	1	8	47.60	-32.86
-17	1	8	68.37	52.90
-15	1	8	99.68	96.62
-13	1	8	90.25	96.12
-11	1	8	76.14	63.80
-9	1	8	102.35	-95.63
-7	1	8	34.51	-18.46
-5	1	8	24.97	17.47
-3	1	8	137.16	147.56
-1	1	8	172.92	188.03
1	1	8	54.26	47.52
5	1	8	45.48	-55.15
-22	2	8	38.29	-32.50
-20	2	8	42.76	-33.60
-18	2	8	67.36	67.48
-14	2	8	49.28	54.63
-12	2	8	38.59	42.27
-10	2	8	47.56	-54.46
-8	2	8	152.70	-151.00
-6	2	8	26.09	15.50
-4	2	8	41.51	-42.11
-2	2	8	100.34	102.19
0	2	8	58.94	67.49
2	2	8	25.85	-17.27
6	2	8	64.10	-67.84
-21	3	8	49.07	-50.15
-19	3	8	60.98	-48.28
-15	3	8	27.46	24.10
-11	3	8	42.58	-33.28
-9	3	8	145.05	-135.46
-7	3	8	84.15	-70.90
-5	3	8	92.00	-79.20
-3	3	8	54.56	50.84
-1	3	8	81.72	72.63
1	3	8	58.41	-43.50
3	3	8	55.02	-63.11
5	3	8	81.00	-100.13
-22	4	8	37.38	-39.29
-20	4	8	52.72	-52.32
-18	4	8	82.58	-58.86
-10	4	8	98.85	-108.59
-8	4	8	142.58	-157.15
-6	4	8	92.88	-90.53
-4	4	8	94.64	-94.00
-2	4	8	83.02	76.02
0	4	8	17.55	-24.52
2	4	8	60.06	-54.35
4	4	8	75.49	-75.25
6	4	8	43.49	-65.55
-21	5	8	[illegible]	-29.65
-19	5	8	41.21	-40.23
-17	5	8	28.88	-10.32
-15	5	8	31.73	31.61
-9	5	8	127.85	-121.15
-7	5	8	85.90	-86.28
-5	5	8	23.19	-20.26
-3	5	8	30.36	-15.40
-1	5	8	82.82	90.05
1	5	8	57.76	-44.42
3	5	8	54.50	-45.68
5	5	8	85.81	-75.93
-12	6	8	49.10	42.18
-10	6	8	54.56	-52.08
-8	6	8	60.37	-44.90
-6	6	8	25.56	-18.60
-2	6	8	81.89	60.28
4	6	8	37.95	-26.47
-15	7	8	44.57	44.44
-13	7	8	55.92	59.05
-11	7	8	55.80	50.00
-7	7	8	40.80	41.93
-5	7	8	35.70	25.43
-3	7	8	48.74	35.01
-1	7	8	92.45	83.26
3	7	8	30.90	24.50
-16	8	8	33.98	36.88
-12	8	8	42.64	45.54
-10	8	8	59.42	46.35
-8	8	8	54.56	52.48
-6	8	8	78.99	51.67
-4	8	8	34.33	24.51
-2	8	8	78.28	72.06
0	8	8	34.75	26.61
2	8	8	34.75	27.86
4	8	8	36.77	40.27
-11	9	8	41.27	28.74
-9	9	8	34.10	42.37
-7	9	8	62.62	51.90
-5	9	8	37.95	35.61
3	9	8	42.76	41.27
0	10	8	35.70	-36.22
-15	11	8	37.60	-43.95
-13	11	8	38.37	-44.07
-3	11	8	71.69	-54.41
-1	11	8	64.22	-46.29
1	11	8	43.41	-38.33
-16	12	8	36.71	-35.83
-14	12	8	52.64	-52.65
-12	12	8	60.25	-41.67
-4	12	8	61.85	-51.91
-2	12	8	91.74	-77.42
0	12	8	55.45	-53.41
-15	13	8	43.94	-50.02
-13	13	8	35.40	-42.51
-3	13	8	61.02	-53.32
-1	13	8	66.18	-57.34
-8	14	8	60.31	59.29
-2	14	8	52.54	-52.01
4	14	8	34.33	40.10
-9	15	8	65.23	62.67
-7	15	8	59.69	55.58
-10	16	8	31.67	42.03
-8	16	8	57.28	54.43
-6	16	8	46.55	46.65
-13	1	9	33.92	28.09
-11	1	9	40.98	30.03
-9	1	9	81.95	67.90
-7	1	9	58.00	61.41
-5	1	9	38.78	36.02
-3	1	9	17.85	21.85
-1	1	9	33.03	21.56
3	1	9	42.87	44.58
-22	2	9	29.53	33.13
-20	2	9	42.18	41.05
-12	2	9	49.75	39.42
-10	2	9	76.45	81.61
-8	2	9	91.20	99.93
-6	2	9	51.95	63.75
-4	2	9	64.04	61.30
0	2	9	47.26	41.97
2	2	9	48.39	39.47
4	2	9	63.63	58.42
-21	3	9	25.02	35.71
-19	3	9	34.33	35.48
-11	3	9	44.95	46.30
-9	3	9	103.30	106.96
-7	3	9	71.52	67.24
-5	3	9	31.96	31.49
1	3	9	26.74	20.99
3	3	9	51.24	53.50
5	3	9	52.95	52.14
-16	4	9	84.16	-58.99
-14	4	9	25.38	-20.49
-12	4	9	31.55	-33.82
-10	4	9	39.61	35.94
-8	4	9	64.58	64.17
-6	4	9	24.31	17.07
-4	4	9	20.87	-13.83
-2	4	9	91.50	-89.76
0	4	9	46.19	-45.18
4	4	9	37.24	30.76
-17	5	9	42.10	-41.20
-15	5	9	82.72	-76.23
-13	5	9	75.43	-76.29
-11	5	9	39.67	-33.88
-9	5	9	55.56	43.90
-5	5	9	62.15	-51.19
-3	5	9	89.66	-77.53
-1	5	9	104.61	-93.75
5	5	9	56.34	52.07
-16	6	9	102.77	-103.49
-14	6	9	85.51	-82.04
-12	6	9	82.37	-73.51
-10	6	9	37.24	34.76
-8	6	9	42.34	35.38
-6	6	9	40.28	-29.91
-4	6	9	88.48	-86.63
-2	6	9	142.50	-133.68
0	6	9	87.53	-83.81
4	6	9	43.23	52.74
-17	7	9	37.00	-40.74
-15	7	9	91.56	-98.39
-13	7	9	62.60	-56.19
-11	7	9	28.05	-28.60
-9	7	9	78.57	79.26
-5	7	9	34.07	-31.95
-1	7	9	116.08	-118.30
-3	7	9	75.25	-73.58
5	7	9	91.20	40.57
-20	8	9	27.10	35.33
-16	8	9	56.93	-53.44
-14	8	9	43.78	-42.62
-12	8	9	50.20	-33.78
-10	8	9	67.13	58.04
-8	8	9	95.68	81.33
-6	8	9	76.09	50.18
-2	8	9	119.61	-96.40
4	8	9	45.42	41.82
-19	9	9	[illegible]	41.01
-15	9	9	30.42	[illegible]
-9	9	9	[illegible]	[illegible]
-7	9	9	[illegible]	64.16
-5	9	9	[illegible]	47.28
-3	9	9	44.36	-41.76
-1	9	9	29.83	-28.11
3	9	9	34.63	42.18
5	9	9	71.58	81.98
-18	10	9	24.10	33.42
-10	10	9	81.49	[illegible]
-8	10	9	[illegible]	[illegible]
-6	10	9	34.10	37.45
-4	10	9	23.30	20.43
2	10	9	19.51	42.43
4	10	9	49.10	49.21
6	10	9	51.41	52.61
-9	11	9	78.09	88.45
-7	11	9	43.84	29.42
-5	11	9	34.45	43.52
-3	11	9	30.95	-24.68
-1	11	9	50.46	-44.85
5	11	9	[illegible]	55.74
-16	12	9	28.55	-33.71
-8	12	9	45.19	47.22
-6	12	9	49.40	12.67
-15	13	9	35.28	-39.42
-11	13	9	32.18	-35.55
-3	13	9	48.45	-50.11
-1	13	9	65.81	-51.08
-12	14	9	26.98	-38.90
-2	14	9	50.94	-47.69
-16	0	10	112.61	-123.00
-14	0	10	92.86	-95.11
-12	0	10	83.47	-81.63
-10	0	10	59.48	48.40
-8	0	10	100.57	81.93
-6	0	10	50.35	-39.97
-4	0	10	76.91	-74.62
-2	0	10	167.17	-161.82
0	0	10	64.10	-55.78
-23	1	10	25.14	26.04
-19	1	10	28.88	34.85
-17	1	10	78.57	-79.58
-15	1	10	103.48	-105.27
-13	1	10	74.56	-72.17
-11	1	10	28.46	-25.50
-9	1	10	83.85	80.87
-7	1	10	8.42	3.96
-5	1	10	57.70	-64.42
-3	1	10	121.03	-113.67
-1	1	10	114.86	-120.33
5	1	10	48.33	56.89
-22	2	10	37.42	31.40
-16	2	10	78.22	-69.78
-14	2	10	57.82	-43.01
-12	2	10	34.81	-33.49
-10	2	10	79.05	83.09
-8	2	10	103.42	115.47
-6	2	10	30.54	21.48
-4	2	10	53.73	-60.25
-2	2	10	86.99	-99.16
4	2	10	55.56	42.25
-23	3	10	35.68	36.83
-21	3	10	42.28	43.80
-19	3	10	56.99	57.21
-15	3	10	48.33	-42.96
-11	3	10	30.30	22.64
-9	3	10	147.78	142.38
-7	3	10	70.63	63.51
-5	3	10	32.14	27.64
-3	3	10	34.35	-26.27
-1	3	10	46.73	-38.19
1	3	10	56.34	51.54
3	3	10	29.71	26.91
5	3	10	79.64	83.25
-22	4	10	38.55	40.41
-20	4	10	47.44	50.92
-18	4	10	50.82	47.52
-16	4	10	31.25	-31.15
-14	4	10	26.69	33.19
-12	4	10	25.80	19.52
-10	4	10	107.10	118.58
-8	4	10	110.48	116.13
-6	4	10	42.58	41.85
-4	4	10	30.12	29.93
-2	4	10	45.78	-37.60
0	4	10	31.13	23.57
2	4	10	36.05	39.57
4	4	10	81.77	67.06
6	4	10	41.69	34.49
-21	5	10	30.84	27.13
-19	5	10	41.39	39.93
-15	5	10	30.84	-23.05
-13	5	10	43.23	-8.06
-11	5	10	111.42	34.33
-9	5	10	110.65	94.72
-7	5	10	36.35	82.02
-3	5	10	28.46	-9.67
-1	5	10	50.52	-24.35
1	5	10	42.34	50.99
3	5	10	67.60	40.66
-16	6	10	45.96	-45.10
-10	6	10	30.48	31.33
-8	6	10	45.90	44.75
-2	6	10	81.06	-76.29
-17	7	10	35.40	-42.98
-15	7	10	31.67	-29.53
-13	7	10	51.71	-47.61
-11	7	10	47.02	-38.73
-7	7	10	22.71	-17.78
-5	7	10	38.90	-47.31
-3	7	10	43.15	-29.82
-1	7	10	41.87	-33.75
-16	8	10	38.19	-42.11
-14	8	10	24.55	-19.34
-12	8	10	40.21	-46.50
-10	8	10	49.04	-43.53
-8	8	10	39.52	-37.04
-6	8	10	52.24	-52.88
-2	8	10	49.93	-51.16
0	8	10	40.80	-45.92
2	8	10	31.47	-31.33
4	8	10	40.08	-19.89
6	8	10	36.71	-19.18
8	8	10	31.19	-24.99
-8	10	10	24.19	-20.41
-15	11	10	34.09	36.94
-13	11	10	45.31	47.46
-5	11	10	29.23	31.09
-3	11	10	65.41	52.00
-1	11	10	52.06	34.04
-10	12	10	29.68	45.94
-14	12	10	33.88	[illegible]
-12	12	10	23.11	23.14
-4	12	10	[illegible]	[illegible]
-2	12	10	[illegible]	50.43
0	12	10	[illegible]	[illegible]
-15	13	10	[illegible]	45.11
-13	13	10	24.14	[illegible]
-9	13	10	[illegible]	[illegible]
-3	13	10	[illegible]	[illegible]
-1	13	10	32.38	28.02
-10	14	10	39.18	-47.37
-8	14	10	40.52	-43.80
-2	14	10	39.08	39.58
-9	15	10	56.83	-62.15
-10	16	10	[illegible]	-40.54
-8	16	10	48.74	-51.27
-13	1	11	33.84	-24.18
-11	1	11	34.75	-29.44
-9	1	11	73.18	-73.31
-7	1	11	39.20	-51.99
-5	1	11	32.79	-29.67
-1	1	11	[illegible]	[illegible]
-22	2	11	36.59	-36.90
-20	2	11	39.73	-35.11
-18	2	11	29.59	-29.21
-14	2	11	22.89	-16.06
-12	2	11	52.30	-42.49
-10	2	11	83.06	-92.21
-8	2	11	78.45	-89.54
-6	2	11	46.37	-45.72
-4	2	11	16.37	-13.67
0	2	11	25.91	-26.12
2	2	11	68.61	-61.19
-23	3	11	31.31	-27.81
-21	3	11	35.82	-35.10
-19	3	11	35.58	-34.62
-11	3	11	38.13	-34.64
-9	3	11	100.99	-97.37
-7	3	11	49.34	-50.60
-5	3	11	43.59	-44.70
-3	3	11	47.56	39.38
1	3	11	32.44	-31.18
3	3	11	46.19	-39.52
-16	4	11	65.05	55.63
-14	4	11	49.34	40.86
-10	4	11	49.34	-42.10
-8	4	11	67.19	-66.77
-6	4	11	28.64	25.85
-4	4	11	37.60	35.15
-2	4	11	70.74	65.02
-17	5	11	71.87	62.81
-15	5	11	77.45	71.33
-13	5	11	74.18	63.23
-11	5	11	28.11	9.53
-9	5	11	67.84	-58.56
-5	5	11	57.28	48.65
-3	5	11	125.24	113.56
-1	5	11	82.11	68.58
-18	6	11	33.30	27.34
-16	6	11	101.46	87.94
-14	6	11	86.10	77.80
-12	6	11	77.03	60.02
-10	6	11	29.35	-29.45
-8	6	11	53.17	-43.50
-6	6	11	45.36	43.21
-4	6	11	69.26	69.66
-2	6	11	157.38	139.65
-17	7	11	68.97	59.42
-15	7	11	96.17	81.18
-13	7	11	58.15	51.75
-9	7	11	90.40	-82.74
-5	7	11	34.75	37.90
-3	7	11	112.37	103.24
-1	7	11	77.13	60.33
3	7	11	29.47	-35.07
-20	8	11	32.38	-29.07
-16	8	11	64.40	65.98
-14	8	11	41.87	38.85
-10	8	11	78.81	-78.11
-8	8	11	97.31	-84.38
-4	8	11	40.92	37.63
-2	8	11	93.08	78.31
2	8	11	36.11	-39.16
4	8	11	41.93	-39.48
-19	9	11	40.44	-44.98
-15	9	11	29.06	28.55
-11	9	11	27.04	-23.48
-9	9	11	115.81	-114.51
-7	9	11	47.20	-38.29
-5	9	11	41.93	-38.04
-3	9	11	82.38	45.45
-1	9	11	29.53	26.21
1	9	11	43.84	-44.37
3	9	11	34.28	-42.24
-20	10	11	29.69	-47.48
-10	10	11	93.52	-80.64
-8	10	11	101.88	-89.47
-6	10	11	52.95	-43.91
-2	10	11	51.29	43.17
2	10	11	36.71	-43.84
-19	11	11	33.39	-36.81
-15	11	11	24.25	36.68
-9	11	11	93.34	-88.57
-18	12	11	31.43	9.96
-10	12	11	34.81	-38.73
-8	12	11	32.26	-44.38
-2	12	11	69.14	55.78
-3	13	11	50.17	47.40
-1	13	11	48.51	50.90
-16	14	11	11.86	32.69
-14	14	11	[illegible]	25.87
-2	14	11	44.89	44.58
-18	0	12	[illegible]	36.19
-16	0	12	108.46	109.31
-14	0	12	64.52	71.12
-12	0	12	82.72	69.28
-10	0	12	82.25	-73.60
-8	0	12	21.41	-25.32
-6	0	12	13.46	9.62
-4	0	12	102.11	97.52
-2	0	12	110.06	137.94
0	0	12	31.37	35.61
-23	1	12	32.38	-25.40
-17	1	12	72.11	70.39
-15	1	12	93.81	106.55
-13	1	12	56.09	54.95
-11	1	12	30.72	21.42
-9	1	12	104.98	-105.09
-5	1	12	47.08	39.98
-3	1	12	106.58	103.67
-1	1	12	79.22	97.33
-24	2	12	30.78	-24.44
-22	2	12	49.10	-35.48
-20	2	12	43.17	-35.66
-16	2	12	100.50	83.15
-12	2	12	56.79	46.93
-10	2	12	79.76	[illegible]
-8	2	12	54.67	-56.38
-6	2	12	[illegible]	-25.98
-4	2	12	49.63	52.15
-2	2	12	88.53	98.42
0	2	12	16.50	[illegible]
-23	3	12	44.83	-37.94
-21	3	12	41.80	-42.14
-19	3	12	55.19	-55.46
-17	3	12	24.73	[illegible]
-15	3	12	33.27	[illegible]
-11	3	12	47.50	-42.78
-9	3	12	126.78	[illegible]
-7	3	12	81.91	-56.72
-5	3	12	26.21	-20.76
-3	3	12	54.14	38.58
-1	3	12	44.24	38.15
1	3	12	86.73	-60.19
-22	4	12	42.67	-45.98
-20	4	12	41.69	-42.62
-18	4	12	48.75	-45.24
-16	4	12	51.00	38.79
-14	4	12	29.32	-25.02
-10	4	12	99.21	-122.38
-8	4	12	87.29	-83.15
-6	4	12	52.48	-45.91
-2	4	12	63.93	46.24
2	4	12	58.65	-44.03
-23	5	12	36.05	-33.24
-19	5	12	41.21	-37.72
-11	5	12	48.86	-32.85
-9	5	12	124.06	-98.57
-7	5	12	51.12	-41.54
-5	5	12	40.74	-30.22
-3	5	12	22.71	8.34
1	5	12	27.54	-32.79
3	5	12	48.57	-43.82
-16	6	12	38.19	26.70
-12	6	12	22.71	16.72
-10	6	12	44.06	-35.31
-8	6	12	32.08	-23.42
-6	6	12	22.24	16.28
-4	6	12	18.09	9.17
-2	6	12	59.83	45.70
-17	7	12	42.28	38.46
-15	7	12	50.46	35.04
-13	7	12	26.27	31.23
-11	7	12	48.69	36.96
-9	7	12	20.93	16.07
-7	7	12	30.66	25.92
-3	7	12	57.54	45.61
-1	7	12	43.94	29.92
-20	8	12	20.34	22.15
-16	8	12	32.44	31.78
-14	8	12	33.09	27.25
-12	8	12	47.14	43.26
-10	8	12	42.10	40.34
-8	8	12	47.66	40.01
-6	8	12	63.15	48.94
-4	8	12	36.77	28.67
-11	9	12	36.53	32.52
-9	9	12	24.49	20.99
-7	9	12	52.90	47.33
-2	10	12	28.05	-23.37
-17	11	12	35.52	-34.68
-15	11	12	37.48	-32.95
-13	11	12	37.83	-37.84
-5	11	12	32.73	-28.62
-3	11	12	61.91	-48.26
-1	11	12	42.64	-35.86
-16	12	12	43.05	-42.48
-14	12	12	42.52	-42.11
-12	12	12	24.55	-21.80
-4	12	12	65.82	-56.78
-2	12	12	62.98	-50.64
0	12	12	24.85	-25.95
-15	13	12	33.98	-40.35
-13	13	12	25.97	-24.59
-3	13	12	62.15	-57.72
-1	13	12	35.94	-37.18
-10	14	12	44.59	44.14
-8	14	12	42.81	40.26
-2	14	12	40.09	-36.46
-11	15	12	31.67	32.10
-9	15	12	53.84	52.36
-7	15	12	36.83	41.72
-3	15	12	27.81	-22.29
-9	1	13	35.34	40.18
-7	1	13	43.76	45.08
-10	2	13	51.71	70.28
-21	3	13	35.76	21.24
-11	3	13	45.84	47.17
-9	3	13	79.94	80.73
-8	4	13	35.88	45.03
-16	0	14	89.96	-114.60
-14	0	14	41.45	-45.51
-10	0	14	73.35	74.97
-4	0	14	67.84	-70.04
-2	0	14	79.22	-74.66
-17	1	14	48.00	-64.00
-15	1	14	72.41	-94.17
-9	1	14	51.24	65.79
-3	1	14	79.22	-79.16
-10	2	14	44.30	61.63
-21	3	14	35.11	40.43
-11	3	14	51.83	54.48
-9	3	14	85.81	96.85
-22	4	14	26.33	36.02
-20	4	14	32.97	44.87
-10	4	14	56.87	69.39
-8	4	14	42.04	61.98
-12	1	15	45.19	-48.75
-10	2	15	39.91	-67.79
-11	3	15	39.85	-50.45
-9	3	15	45.19	-64.27
-10	4	15	53.07	-49.91
-16	0	16	65.29	80.34
-14	0	16	46.85	57.90
-10	0	16	46.79	-51.07
-4	0	16	61.73	73.36
-2	0	16	45.13	47.40
-10	2	16	40.50	-62.98
-11	3	16	40.26	-60.23
-9	3	16	63.21	-76.22
-10	4	16	52.30	-56.20
-11	3	17	39.85	42.95
-9	3	17	16.72	36.58
-18	0	18	65.29	-73.41
-16	0	18	43.35	-46.95
-4	0	18	53.37	-56.72
-11	3	18	39.73	52.65
-10	4	18	41.63	48.37

and phosphorus atoms were then refined by the block-matrix least-squares method. Successive use of difference Fourier syntheses and block-matrix least-squares calculations yielded the positions of all the lighter atoms. Refinement of the atomic parameters was carried out by five cycles of the block-matrix least-squares method (program by Okaya & Ashida, 1967) in which the anisotropic temperature factors were allowed for. The final *R* value was 0·13. The weighting system was chosen as:

$$\begin{aligned}\sqrt{w}&=48/F_o && \text{when } F_o>48,\\ \sqrt{w}&=1 && \text{when } 12\le F_o\le 48,\\ \sqrt{w}&=0 && \text{when } F_o<12.\end{aligned}$$

The refined atomic parameters are given in Table 1 along with their standard deviations. A list of observed and calculated structure factors is presented in Table 2.

Description and discussion of the structure

Several examples of μ-allyl metal complexes have been reported, which are characterized by the two metal atoms bridged by two allyl groups (McDonald, Mann, Raper, Shaw & Shaw, 1969; Aoki, Furusaki, Tomiie, Ono & Tanaka, 1969; Raper & McDonald, 1970; Mason, Robertson & Whimp, 1970). However, the structure of the complex found in the present study is quite unique in the respect that the two palladium atoms are bonded to each other and they are furthermore bridged from both sides of the Pd–Pd bond; one side by an iodine atom and the other side by an allyl group. The structure of the molecule is illustrated in Fig. 1 by a stereoscopic drawing which is calculated by the plotter program *ORTEP* (Johnson, 1965). As may be seen in Figs. 3 and 4, the complex molecule has itself a diad axis passing through the iodine atom. Two triphenylphosphine palladium groups are situated around the diad axis, and the palladium atoms are linked together forming a triangular Pd_2I group. The allyl and benzene molecules, the latter being enclosed as solvent of crystallization, are also arranged about the diad axis.

Bond lengths and angles are listed in Tables 3 and 4, and the *b* and *c* axis projections of the crystal structure are shown in Figs. 3 and 4.

Table 3. *Bond lengths*

I——Pd	2·650 (4) Å	P——C(13)	1·80 (5) Å
Pd——Pd′	2·686 (7)	C(13)–C(14)	1·43 (8)
Pd——P	2·278 (15)	C(14)–C(15)	1·35 (6)
		C(15)–C(16)	1·47 (10)
P——C(1)	1·80 (6)	C(16)–C(17)	1·35 (12)
C(1)—C(2)	1·46 (5)	C(17)–C(18)	1·49 (8)
C(2)—C(3)	1·32 (8)		
C(3)—C(4)	1·37 (11)	Pd——C(*A*1)	2.19 (3)
C(4)—C(5)	1·41 (7)	Pd——C(*A*2)	2·48 (9)
C(5)—C(6)	1·37 (9)	Pd——C(*A*2′)	2·39 (7)
P——C(7)	1·82 (4)	C(*A*1)–C(*A*2)	1·48 (14)
C(7)—C(8)	1·40 (7)	C(*A*1)–C(*A*2′)	1·34 (9)
C(8)—C(9)	1·42 (6)		
C(9)—C(10)	1·43 (9)	C(*B*1)–C(*B*2)	1·31 (9)
C(10)–C(11)	1·41 (10)	C(*B*1)–C(*B*3)	1·40 (8)
C(11)–C(12)	1·41 (5)	C(*B*2)–C(*B*2′)	1·39 (14)
		C(*B*3)–C(*B*3′)	1·28 (14)

From the space group requirement, the allyl group was considered to be on the diad axis laying the central carbon on it. However, the result of the X-ray analysis showed that this is not the case. As shown in Fig. 2 the three-dimensional difference Fourier synthesis phased by all the atoms except those of allyl and benzene molecules gave the four peaks of two kinds [C(*A*1) and C(*A*2)] around the diad axis at the positions expected for the allyl group. From the fact that the ratio of the peak heights of C(*A*1) and C(*A*2) was about 2:1 and that the angles C(*A*1)–C(*A*2)–C(*A*1′) and C(*A*2)–C(*A*1)–C(*A*2′) were 123° and 52° respectively, it was concluded that the allyl group lies nearly parallel to

Table 4. *Bond angles*

Pd–I——Pd′	60·9 (0·1)°	P——C(7)—C(8)	126 (3·5)°
I—Pd——Pd′	59·6 (0·1)	P——C(7)–C(12)	117 (3·1)
P—Pd——I	117·6 (0·4)	C(7)—C(8)—C(9)	123 (4·7)
Pd′-Pd——C(*A*1)	87 (1·4)	C(8)—C(9)—C(10)	120 (5·2)
P—Pd——C(*A*1)	95 (1·5)	C(9)–C(10)—C(11)	117 (5·6)
Pd–C(*A*1)–C(*A*2)	82 (4·6)	C(10)–C(11)–C(12)	125 (5·2)
Pd–C(*A*1)–C(*A*2′)	83 (4·2)	C(11)–C(12)–C(7)	117 (4·1)
Pd–P——C(1)	111 (1·6)	C(12)–C(7)—C(8)	118 (4·0)
Pd–P——C(7)	120 (1·5)		
Pd–P——C(13)	116 (1·6)	P——C(13)–C(14)	129 (3·5)
		P——C(13)–C(18)	118 (4·0)
C(1)–P——C(7)	106 (2·1)	C(13)–C(14)–C(15)	126 (4·4)
C(1)–P——C(13)	102 (2·2)	C(14)–C(15)–C(16)	120 (5·1)
C(7)–P——C(13)	99 (2·1)	C(15)–C(16)–C(17)	117 (6·0)
		C(16)–C(17)–C(18)	119 (6·3)
P——C(1)–C(2)	116 (3·4)	C(17)–C(18)–C(13)	125 (5·5)
P——C(1)–C(6)	124 (3·7)	C(18)–C(13)–C(14)	112 (4·5)
C(1)–C(2)–C(3)	118 (4·4)		
C(2)–C(3)–C(4)	121 (5·1)	C(*A*1)–C(*A*2)–C(*A*1′)	123 (7·1)
C(3)–C(4)–C(5)	124 (5·8)	C(*A*2)–C(*A*1)–C(*A*2′)	52 (5·5)
C(4)–C(5)–C(6)	116 (5·7)		
C(5)–C(6)–C(1)	121 (5·1)		
C(6)–C(1)–C(2)	119 (4·3)		

the Pd–Pd bond and occupies two sites C(*A*1)C(*A*2)-C(*A*1′) and C(*A*1)C(*A*2′)C(*A*1′) at random.

Table 5. *Least-squares planes through various groups of atoms and the deviations of the atoms from the plane*

Equation of the plane is the form of $AX+BY+CZ=D$, where X, Y, Z and D are measured in Å units along the axes $X \parallel a^*$, $Y \parallel b$ and $Z \parallel c$. Atoms marked by * are not included in the least-squares calculation.

Coordination around Pd			
	$0{\cdot}4254X+0{\cdot}0039Y+0{\cdot}9050Z=4{\cdot}0566$		
I	0·00 Å	C(*A*1)*	0·04 Å
Pd	0·04	C(*A*2)*	0·63
Pd′	−0·02		
P	−0·02		
Phenyl group 1			
	$0{\cdot}317X+0{\cdot}946Y-0{\cdot}074Z=1{\cdot}091$		
C(1)	−0·01 Å	C(4)	−0·01 Å
C(2)	0·00	C(5)	0·00
C(3)	0·01	C(6)	0·01
Phenyl group 2			
	$0{\cdot}176X+0{\cdot}465Y+0{\cdot}868Z=3{\cdot}292$		
C(7)	0·02 Å	C(10)	−0·04 Å
C(8)	−0·01	C(11)	0·05
C(9)	0·02	C(12)	−0·04
Phenyl group 3			
	$0{\cdot}831X-0{\cdot}554Y+0{\cdot}059Z=2{\cdot}744$		
C(13)	0·03 Å	C(16)	0·02 Å
C(14)	−0·02	C(17)	−0·01
C(15)	−0·01	C(18)	−0·02
Allyl group			
	$0{\cdot}154X+0{\cdot}927Y+0{\cdot}342Z=3{\cdot}972$		
	Dihedral angle to (010) = 22·0°		

Although the coordinates of the allyl carbon atoms could not be determined exactly owing to the disordering of the allyl group, and we must be cautious in deciding whether two terminal carbon atoms of an allyl group [for example, C(*A*1) and C(*A*1′) of allyl molecule C(*A*1)–C(*A*2)–C(*A*1′)] are exactly at the equivalent positions, the difference in the two bond lengths C(*A*1)–C(*A*2) and C(*A*2)–C(*A*1′) of 0·14 Å may be taken as indicating that the two bonds have different degrees of double bond character. The distances between the palladium and the carbon atoms of the allyl group Pd–C(*A*1), Pd–C(*A*2) and Pd′–C(*A*2) are 2·19, 2·48 and 2·39 Å respectively; the distance from the

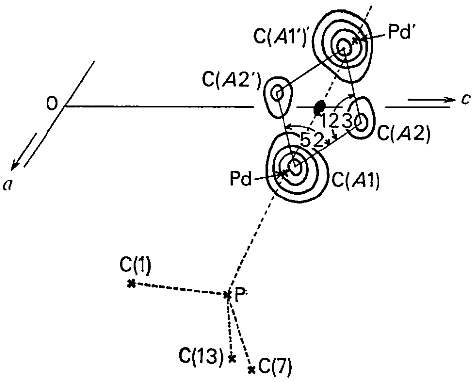

Fig. 2. Three-dimensional difference electron density map showing the disorder of allyl molecules. Contours are drawn at intervals of 1 e.Å^{-3} starting at 2 e.Å^{-3}. Skeleton of triphenylphosphine palladium group is shown by broken lines.

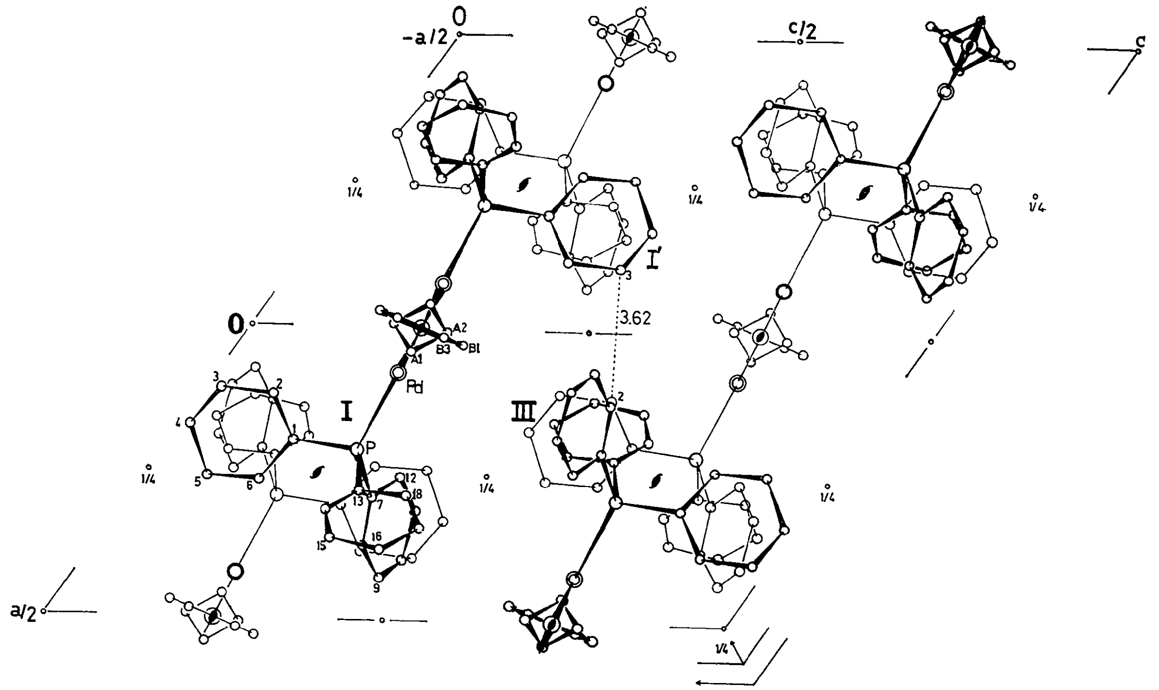

Fig. 3. Projection of the crystal structure along the *b* axis.

allyl plane C(*A*1)C(*A*2)C(*A*1′) to Pd is 2·02 Å and that to Pd′ is 2·03 Å. The bond length of Pd–C(*A*1) (2·19 Å) does not differ significantly from those reported for Pd–C σ-bonds (2·05∼2·14 Å; Oberhanli & Dahl, 1965; Lippard & Morehouse, 1964; Mason & Russell, 1966) and this bond seems to have considerable σ-bond character.

The central carbon atom of the allyl group, C(*A*2) is situated at longer distances from Pd. However, as shown in Table 5, the plane of the allyl group is inclined from the (010) plane by 22·0° in such a direction that C(*A*2) comes closer to Pd.

The distances, 2·39 Å and 2·48 Å for Pd···C(*A*2) and Pd′···C(*A*2) respectively, indicate that there might be a weak π-metal interaction between allyl and palladium atoms. In spite of the apparent difference in the C–C bond lengths in allyl group [C(*A*1)–C(*A*2) and C(*A*2)–C(*A*1′) or C(*A*1)–C(*A*2′) and C(*A*2′)–C(*A*1′)], the n.m.r. spectrum of the allyl protons was very simple, suggesting that, in solution the allyl group is rotating in its own plane or flipping over between the two sites on the two palladium atoms so that the protons at the two terminal carbon atoms become equivalent.

Each palladium atom has a square-planar coordination geometry using its *dsp*^{2} hybrid orbitals which form four bonds to iodine, palladium, phosphorus and to the terminal carbon atom of the allyl group. However, the angle P–Pd–I is considerably distorted from 90° because the iodine atom is situated at the bridge head. Deviations of the atoms from the least-squares plane through I, Pd, Pd′, P are shown in Table 5. The length of the Pd–Pd′ bond (2·69 Å) is short enough to conclude that the palladium atoms form a metal–metal bond (Allegra, Casagrande, Immirzi, Porri & Vitulli, 1970).

The Pd–P bond distance of 2·28 Å agrees well with the Pd–P bond length in PdCl(2-methylallyl)PPh$_3$ (Mason & Russell, 1966). The bonding around the phosphorus atom does not form a perfect tetrahedron and the bond angles are much distorted from the tetrahedral angle. Those formed by the bonds between the phosphorus atom and the carbon atoms of the phenyl groups; C(1)–P–C(7), C(1)–P–C(13) and C(7)–P–C(13)

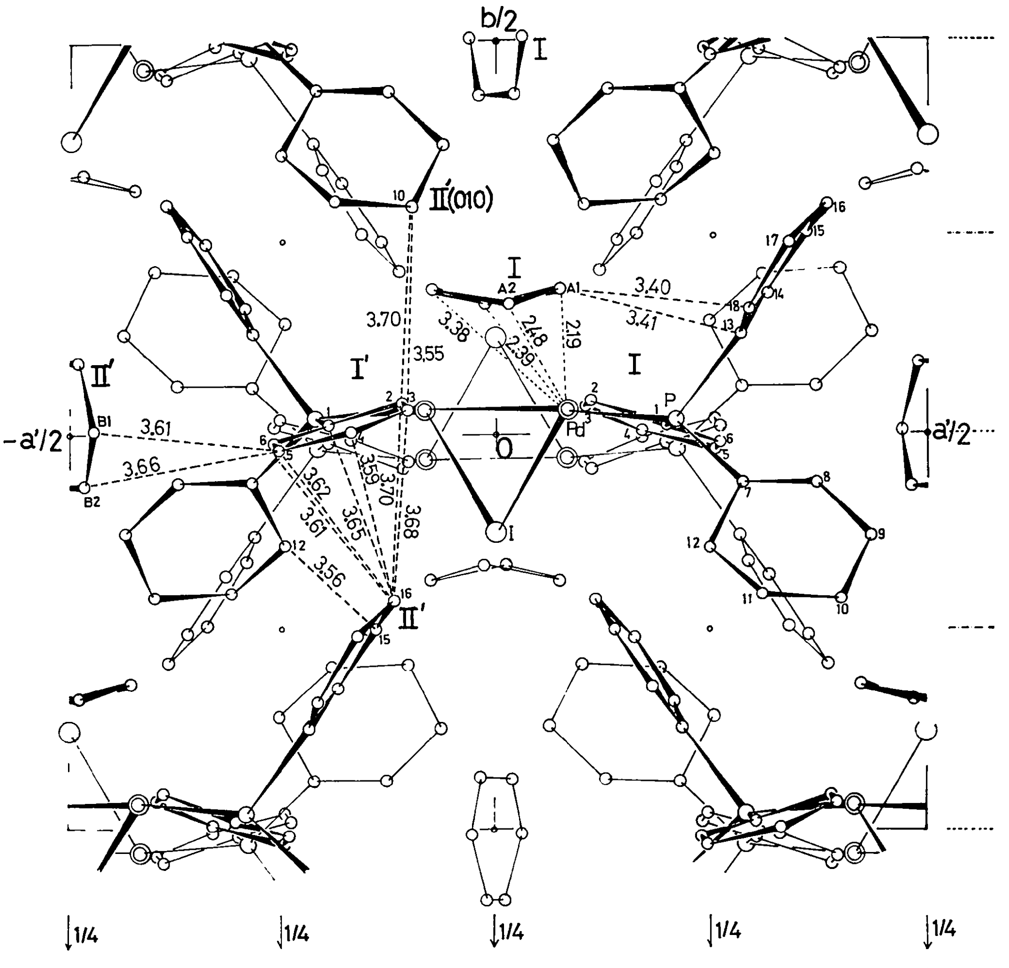

Fig. 4. Projection of the crystal structure along the *c* axis. Shortest intermolecular contacts less than 3·70 Å are shown by broken lines.

(99°, 102° and 106° respectively) are smaller than the usual tetrahedral angle while the angles Pd–P–C(1), Pd–P–C(7) and Pd–P–C(13) (111°, 116° and 120° respectively) are much larger. A similar tendency is generally observed in triphenylphosphine transition metal complexes (Churchill & O'Breien, 1968; Mason & Towl, 1970) or even in triphenylphosphine itself (Daly, 1964).

The arrangement of the three phenyl groups around the Pd–P bond is such that the plane formed by Pd–P–C(1) is nearly perpendicular to that of the Pd_2I group, while Pd–P–C(7) and Pd–P–C(13) intersect to the Pd_2I plane with roughly the same inclination angles. The internal rotation angles about the Pd–P bond; I–Pd–P–C(1), I–Pd–P–C(7) and I–Pd–P–C(13) are 85, −40 and −159° respectively. A similar arrangement is often observed for the angles about the bond connecting a tetrahedral and a planar groups.

As shown in Fig. 1, the plane of each phenyl group is twisted out of the plane of the corresponding Pd–P–C group; the dihedral angle between the plane formed by the phenyl group $\varphi_1[C(1)\sim C(6)]$ and that formed by Pd–P–C(1) is 17°, the corresponding angles for the groups $\varphi_2[C(7)\sim C(12)]$ and $\varphi_3[C(13)\sim C(18)]$ are 18° and 54°, respectively. These twistings are all in the same direction so that the three phenyl groups are arranged around the Pd–P bond like the blades of a propeller. The angle of twist of the third phenyl group φ_3 is about 36° greater than the other two. The reason for this may be a steric hindrance between the phenyl carbon C(18) and allyl carbon C(*A*1). As is clear from Fig. 4, C(18) would be situated much closer to C(*A*1) if the twist angle became smaller.

The packing of the molecules is shown in Figs. 3 and 4. The molecules are designated by the Roman numerals denoting the equivalent positions such as,

I	at	x	y	z
I′	at	$\bar{x}$	y	$\bar{z}$
II′	at	$x-\frac{1}{2}$	$y-\frac{1}{2}$	$z-\frac{1}{2}$
III	at	x	$\bar{y}$	$z+\frac{1}{2}$

where x, y and z are the coordinates of the atoms given in Table 1. The subscripts in parentheses indicate the translations along the three edges of the unit cell. Also in Figs. 3 and 4, the shortest intermolecular interatomic distances less than 3·70 Å are shown. It may be seen that several short contacts between the phenyl groups; φ_1[I′] to φ_3[II′], φ_1[I′] to φ_2[II′(010)], φ_2[I′] to φ_3[II′], pack the molecules rather closely along the b axis, the shortest carbon–carbon distance being 3·55 Å. The molecules of benzene are enclosed in the structure just above the allyl groups. These solvation molecules are fixed in their position through the interactions with the phenyl groups, φ_1s', in both **a** and $\bar{\mathbf{a}}$ directions and with allyl groups in **c** and $\bar{\mathbf{c}}$. However, the distance between C(*B*2′) and C(*A*1) is as much as 3·85 Å, and the interactions with the allyl groups may not be so strong as those with the phenyl groups.

The authors wish to express their thanks to C. Itoh Electronic Computing Service Co. Ltd for use of a CDC 3600 and 6600 computers.

References

ALLEGRA, G., CASAGRANDE, G. T., IMMIRZI, A., PORRI, L. & VITULLI, G. (1970). *J. Amer. Chem. Soc.* **92**, 289.

AOKI, T., FURUSAKI, A., TOMIIE, Y., ONO, K. & TANAKA, K. (1969). *Bull. Chem. Soc. Japan*, **42**, 545.

CHURCHILL, M. R. & O'BRIEN, T. A (1968). *J. Chem. Soc.* (*A*), p. 2970.

DALY, J. J. (1964). *J. Chem. Soc.* p. 3799.

IITAKA, Y. (1953). *Acta Cryst.* **6**, 663.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

LIPPARD, S. J. & MOREHOUSE, S. M. (1964). *J. Amer. Chem. Soc.* **91**, 2504.

MASON, R., ROBERTSON, G. B. & WHIMP, P. O. (1970). *J. Chem. Soc.* (*A*), p. 535.

MASON, R. & RUSSELL, D. R. (1966). *Chem. Commun.* p. 26.

MASON, R. & TOWL, A. D. C. (1970). *J. Chem. Soc.* (*A*), p. 1601.

MCDONALD, W. S., MANN, B. E., RAPER, G., SHAW, B. L. & SHAW, G. (1969). *Chem. Commun.* p. 1254.

OBERHANLI, W. E. & DAHL, L. F. (1965). *J. Organometal. Chem.* **3**, 43.

OKAYA, Y. & ASHIDA, T. (1967). *HBLS IV, The Universal Crystallographic Comptuing System* (I), p. 65. The Japanese Crystallographic Association.

POWELL, J. & SHAW, B. L. (1968). *J. Chem. Soc.* (*A*), p. 774.

RAPER, G. & MCDONALD, W. S. (1970). *Chem. Commun.* p. 655.