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The Crystal Structure of Norbornadiene-dichloropalladium II

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The structure of norbornadiene-dichloropalladium II ($C_7H_8PdCl_2$) has been determined. The unit cell is orthorhombic with cell dimensions:

$$a = 9{\cdot}424 \pm 0{\cdot}004,\ b = 7{\cdot}219 \pm 0{\cdot}003,\ c = 11{\cdot}712 \pm 0{\cdot}003\ \text{Å}\ .$$

The space group is *Pnma* with four molecules per unit cell. The norbornadiene molecule is chelated to the palladium atom through both double bonds. The plane made by the carbon atoms of both double bonds is perpendicular to the plane made by the palladium and chlorine atoms.

Introduction

The chemical study of olefin metal complexes has been quite extensive in recent years. Crystal structure studies of two complexes with palladium chloride have been carried out in this laboratory (Baenziger & Dempsey, 1955; Baenziger & Holden, 1955). Crystal studies of related compounds with platinum and silver have been carried out in other laboratories (Nyberg & Hilton, 1959; Rundle & Goring, 1950; Rundle & Smith, 1958; Wunderlich & Mellor, 1954, 1955; Bokii & Kukina, 1957; Lipscomb & Mathews, 1958, 1959; Aldeman, Owston & Rowe, 1960). In most of these olefin–metal complexes the metal atom is attached to only one double bond which is perpendicular to the direction of the metal hybrid orbital. Nyburg & Hilton (1959) found in cyclooctatetraene dimers complexed with the silver ion that the silver was closely associated with two double bonds of different dimer molecules. A similar situation exists in the silver perchlorate–benzene complex structure.

Norbornadiene complexes readily with Ag, Pd, and Pt metal ions (Alexander, Baenziger, Carpenter & Doyle, 1960), and chemical evidence suggests that norbornadiene chelates with palladium and platinum ions through both unsaturated bonds in the norbornadiene.

Experimental

Norbornadiene-dichloropalladium II ($C_7H_8PdCl_2$) can be prepared by two different methods. The action of norbornadiene on a benzene solution of bis-benzonitrile-dichloropalladium II gives a yellow solid which upon recrystallization from acetone yields yellow needle-shaped crystals of norbornadiene-dichloro-palladium (II). The crystals may also be obtained by the reaction of norbornadiene with an absolute methanol solution of sodium tetrachloropalladate II (Alexander, Baenziger, Carpenter & Doyle, 1960).

The crystals used in this study were prepared by the first method and carefully recrystallized. Untwinned specimens were selected under polarized light. The crystals used were very small with two axes approximately equal and the needle axis (b) about three times the dimensions of the short axis. The unit cell is orthorhombic with dimensions

$$a = 9{\cdot}424 \pm 0{\cdot}004,\ b = 7{\cdot}219 \pm 0{\cdot}003,\ c = 11{\cdot}712 \pm 0{\cdot}003\ \text{Å}$$
$$(\lambda \text{ of } \mathrm{Cu}\,K\alpha = 1{\cdot}54180\ \text{Å},\ \lambda \text{ of } \mathrm{Mo}\,K\alpha = 0{\cdot}71069\ \text{Å})\ .$$

The a and c cell dimensions were obtained from back reflection Weissenberg data by a least-squares analytical extrapolation method. The b cell dimension was obtained from precession camera films calibrated by the a and c cell dimensions. With four molecules per unit cell $D_x = 2{\cdot}31$ g.cm.$^{-3}$, which is comparable with ethylene palladium chloride, $D_x = 2{\cdot}68$ g.cm.$^{-3}$ (Baenziger & Dempsey, 1955) and styrene palladium chloride, $D_x = 2{\cdot}04$ g.cm.$^{-3}$ (Baenziger & Holden, 1955). The density of this compound measured by the pycnometer method is $2{\cdot}30$ g.cm.$^{-3}$.

Film data were obtained of $hk0$ and $0kl$ through $4kl$ by the precession camera and $h0l$ through $h4l$ from the Weissenberg camera. All films were visually estimated twice, the estimation covering all spots on the precession films and all the spots in the top half of the Weissenberg films. The only observed systematic extinctions in these films are $0kl$ with $k+l = 2n+1$ and $hk0$ with $h = 2n+1$. These indicated the space group to be either the centrosymmetric *Pnma* or the non-centrosymmetric $Pn2_1a$. Lorentz and polarization corrections were computed for all reflections without correcting for absorption errors. Small crystals kept this error to a minimum.

Determination of the structure

x and z parameters

The plane groups perpendicular to the b axis of both space groups are equivalent. Using the intensities of the $h0l$ reflections a Patterson projection was computed. Two parameters of the palladium atom and the position of one of the chlorine atoms were indicated from this projection. Using this position of the palladium atom to determine the signs of 98 out of 99 present reflections from the $h0l$ data an electron density map on the (010) plane was evaluated. This projection with the aid of two (F_o-F_c) syntheses indicated the positions of the seven carbon atoms and one chlorine atom.

The location of the carbon atoms indicated that the axes of the carbon–carbon double bonds were approximately perpendicular to the (010) plane. The location of the palladium and the chlorine atoms to the double bonds were such that if the palladium atoms were to have a dsp^2 configuration the other chlorine atom must have x and z parameters similar to those of the palladium atom.

A centrosymmetric structure would be one in which the plane made by the palladium and chlorine atoms would be parallel to the (010) plane and bisect the axis of both double bonds in the norbornadiene molecule. In the projection of such a structure the carbon atoms making up each of the double bonds would have identical x and z parameters. This would also be true of the bridgehead carbons. Such a structure would have only four parameters indicated for the carbon positions in the projection.

Although seven positions for the carbon atoms had been indicated, the positions for three pairs of carbon atoms were close to identical. If the seven positions were real and not due to incorrect signs given to the F_o data, then the molecule would tilt slightly out of the plane and the structure would be non-centrosymmetric. Since the electron density projections at this point in the refinement are not completely reliable, it was also possible the structure might be centrosymmetric.

To clarify this situation the $h0l$ data were refined by use of a least-squares procedure. Starting with the indicated x and z parameters and using separate overall temperature factors for each kind of atom the refinement on coordinates only was carried out until the change in the R value (0·18) was negligible. The x and z parameters on the carbon atom pairs in question had moved closer to identical values but still indicated a tilt of the molecule to the (010) plane.

The y parameter

As the next step, three dimensional least-squares refinement was carried out starting from the x and z parameters. Appropriate starting y parameters were calculated for the molecule from assumed bond distances. The plane of the molecule was given a tilt of 7° to the (010) plane as indicated by the carbon positions. The structure factors were computed using Vand, Eiland & Pepinsky's (1957) analytical scattering factors. All 684 present reflections were given unit weight. The 393 absent reflections were given zero weight unless $F_c > F_o(\text{min.})$, in which case they were given unit weight. (At the end of the refinements an evaluation of $\Sigma\Delta F/\Sigma F_o$ for the F_o data in the ranges $F_o(\text{max.})$ to $\frac{3}{4}F_o(\text{max.})$, $\frac{3}{4}F_o(\text{max.})$ to $\frac{1}{2}F_o(\text{max.})$, $\frac{1}{2}F_o(\text{max.})$ to $\frac{1}{4}F_o(\text{max.})$, and $\frac{1}{4}F_o(\text{max.})$ to $F_o(\text{min.})$ gave 0·075, 0·082, 0·097, and 0·151. A scheme that would have reduced the weights of data in the range $\frac{1}{4}F_o(\text{max.})$ to $F_o(\text{min.})$ could have led to a better overall reliability.) The least-squares refinement determined individual isotropic temperature factors for each atom. Changes in scale factor (K in $KF_o=F_c$) were calculated at the end of each series of data using $-\Delta K/K=\Sigma\Delta FF_c/\Sigma F_c^2$, summed over present reflections only. At the end of all the data, changes in atom parameters and temperature factors were calculated using only the diagonal terms of the least-squares matrix. After each cycle all interatomic distances were calculated to determine whether the norbornadiene portion of the molecule was chemically reasonable.

Several least-squares cycles were computed allowing all atom parameters to change by computation and without making any attempt to place atoms in positions that would give a more reasonable structure. The chlorine atoms during this period of refinement changed only in the y parameter decreasing the tilt to the (010) plane. Also, the x and z parameters of the carbon atoms changed only slightly while the y parameters changed considerably.

Leaving the chlorine and palladium atoms alone the carbon atoms were placed back in reasonable locations by altering the y parameters. Several more least-squares cycles were computed, each time placing the carbon atoms back in reasonable positions whenever the norbornadiene structure deviated too far from one with reasonable bond distances. Refinement was continued until an overall R value of 0·128 was obtained.

At this point the changes in all but the y parameters of the carbon atoms were less than a standard deviation. The chlorine atoms had moved very close to the (010) plane. The three pairs of carbon atoms that indicated a tilt of the molecule to the (010) plane now had x and z parameters that differed from each other by 0·002 to 0·007 (standard deviations 0·002 to 0·003).

The positions of the atoms indicated that the difference between non-centrosymmetric structure ($Pn2_1a$) and the centrosymmetric structure ($Pnma$) might be within two and one-half standard deviations of one another. Starting parameters for refinement of the centrosymmetric structure were achieved by using the x and z parameters from the $Pn2_1a$ results except that averages were used for the carbon atoms having similar parameters. The y parameters were chosen to give acceptable bond distances and to orient the molecule so that the mirror plane parallel to (010) bisected both double bonds.

On refinement of the centrosymmetric structure the carbon atoms moved in the y direction so as to lengthen all carbon–carbon bonds. After a few refinement cycles an R value of 0·127 was reached. At this point all position parameter changes were less than one-half of a standard deviation and in a random fashion. The

Table 1. *Final parameters, temperature factors and standard deviations*

(*Space group Pnma*)

	Pnma	*x*	*y*	*z*	*B* (Å^2)
Pd	4*c*	0·6005 ± 0·0002	0·2500	0·4774 ± 0·0001	− 1·99 ± 0·04
Cl_1	4*c*	0·5348 ± 0·0009	0·2500	0·2870 ± 0·0007	− 2·98 ± 0·07
Cl_2	4*c*	0·3708 ± 0·0008	0·2500	0·5452 ± 0·0006	− 2·90 ± 0·07
$C_1(C_4)$	8*d*	0·848 ± 0·002	0·419 ± 0·003	0·583 ± 0·002	− 2·9 ± 0·2
$C_2(C_3)$	8*d*	0·699 ± 0·002	0·356 ± 0·003	0·637 ± 0·002	− 2·4 ± 0·2
$C_5(C_6)$	8*d*	0·818 ± 0·002	0·145 ± 0·003	0·452 ± 0·002	− 3·3 ± 0·2
C_7	4*c*	0·945 ± 0·004	0·250	0·624 ± 0·003	− 3·5 ± 0·3

temperature factors were changing by a standard deviation or less.

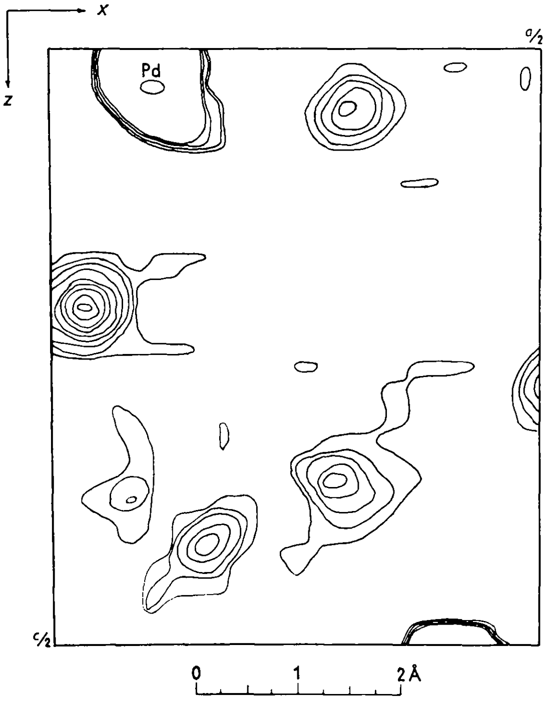

Fig. 1. Electron density projection on the (010) plane. Only the outer four contours are shown for the Pd atom.

The carbon–carbon distances were long but not unreasonable whereas in the last stages of the non-centrosymmetric refinement, the *y* parameters of the carbon atoms continued to change in a direction giving longer carbon–carbon distances. This persistent change in the *y* parameters in the non-centrosymmetric structure is probably due to the attempt of the carbon atoms to compensate for the tilt of the Pd–Cl plane from the (010) plane. As the refinement proceeded and the tilt became less, the rate of movement of carbon atoms decreased. It is for this reason that the centrosymmetric structure is probably the correct structure. The final parameters from the non-centrosymmetric structure do not differ significantly from those of the centrosymmetric structure. Another factor supporting a centrosymmetric structure is that the agreement in the individual groups of data is more uniform.

Fig. 1 is the electron density projected on the (010) plane. The signs of F_o were determined from the signs of F_c on the final least-squares refinement of the *Pnma* structure. The original electron density projection had only the palladium atom and one chlorine atom well defined. The positions of carbon atoms in the structure were not well defined, and led to the trial of the non-centrosymmetric structure.

Table 2. *Interatomic distances and standard deviations*

	Distance	σ
Pd–Cl_1	2·305 Å	0·012 Å
Pd–Cl_2	2·305	0·009
Pd–C_2 Pd–C_3	2·21	0·028
Pd–C_5 Pd–C_6	2·22	0·032
C_2=C_3	1·53	0·034
C_5=C_6	1·51	0·036
C_1–C_2 C_4–C_3	1·60	0·038
C_1–C_6 C_4–C_5	1·63	0·036
C_1–C_7 C_4–C_7	1·60	0·038

Table 3. *Bond angles and standard deviations*

	Angle	σ
Cl–Pd–Cl	95·0°	0·5°
C_2–C_1–C_6 C_3–C_4–C_5	98·3	1·5
C_1–C_7–C_4	99·4	1·7
C_7–C_1–C_2 C_7–C_4–C_3	99·7	1·8
C_7–C_1–C_6 C_7–C_4–C_5	99·0	1·7
C_1–C_2–C_3 C_4–C_3–C_2	106·5	1·6
C_1–C_6–C_5 C_4–C_5–C_6	106·7	1·6

C_2, C_3, Pd plane with C_5, C_6, Pd plane = 71·8°
C_2, C_3, C_1, C_4 plane with Pd, C_2, C_3 plane = 92·2
C_5, C_6, C_1, C_4 plane with Pd, C_5, C_6 plane = 92·0

Accuracy

The standard deviations of all atom positions and temperature factors have been computed and also those of all important bond lengths and angles. They are listed in Tables 1, 2, and 3. The final R value for centrosymmetric structure is 0·127 using all reflections, and 0·113 using only the present reflections. The standard deviation of all carbon–carbon bond lengths is approximately 0·04 Å while the standard deviation of the angles is approximately 1·5°. Both of these deviations agree with other structures reporting a similar R value.

Discussion of results

The packing of the molecules is shown in the isometric drawing of the cell (Fig. 2). The b axis of the cell is approximately two molecules thick. The stacking of the metal atoms is such that every metal atom has a non-bonded chlorine atom approximately above and below it. The closest non-bonded chlorine distance to a palladium atom is 3·63 Å. The other chlorine atom is so arranged as to be opposite the chlorine atom in the lower molecule. The palladium–chlorine distance is 2·305 Å for both chlorine atoms. In other olefin–palladium complexes this distance varies from 2·2 to 2·4 Å (Baenziger & Holden, 1955; Baenziger & Dempsey, 1955). In these instances where only one double bond was involved, the palladium atom has one chlorine atom *trans* to an olefin–metal linkage and the other chlorine atoms are at right angles to it. In norbornadiene–palladium chloride both chlorine atoms are opposite an olefin–metal linkage and therefore both Pd–Cl bonds should be about equal in length. The Cl–Pd–Cl angle is 95·0°, in agreement with similar angles in other olefin–palladium chloride structures. The angle formed by the centers of both double bonds with the palladium atom as the vertex is 71·8°. This is much less than 90° and may be partly responsible for the Cl–Pd–Cl angle being greater than 90°.

The distances from the palladium atom to the unsaturated carbon atoms—2·21 Å, 2·21 Å, 2·22 Å, 2·22 Å—and the distances to the centers of the double bonds—2·08 Å and 2·09 Å—are consistent with what has been found previously. Comparison with the palladium-carbon single bond distance (1·32 + 0·77 = 2·09) (Pauling, 1960) indicates that the bonds are electron deficient. The angles formed by lines from the palladium atom to the center of the double bonds and the planes formed by the bridgehead carbon atoms and unsaturated carbon atoms are 92·0° and 92·2°. These angles should be 90° for best overlap of the π orbital of the olefin with the dsp^2 hybrid orbital of Pd.

Since the palladium and chlorine atoms account for a large percentage of the scattering of X-rays, the uncertainty in the positions of the carbon atoms is large. The observed C–C bond distances are on the

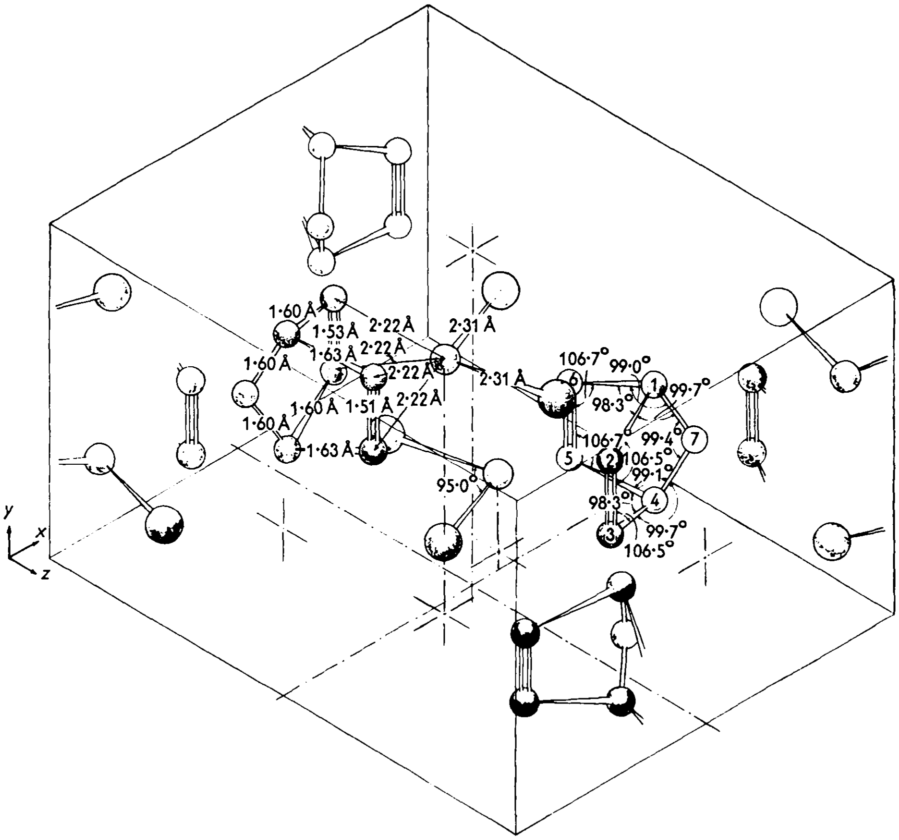

Fig. 2. Isometric view of unit cell contents. Smallest spheres are C atoms, largest spheres are Cl atoms.

Table 4. *Calculated and observed structure factors*

h	k	l	Obs.	Cal.
0	0	2	540	529
0	0	4	317	298
0	0	6	124	125
0	0	8	<46	42
0	0	10	<51	-13
0	0	12	123	-98
0	0	14	<45	-23
0	0	16	<32	-57
0	1	3	114	86
0	1	5	258	-257
0	1	7	205	-201
0	1	9	125	-123
0	1	11	167	-180
0	1	13	111	-107
0	1	15	103	-96
0	2	0	659	-682
0	2	2	317	-338
0	2	4	331	-338
0	2	6	161	-170
0	2	8	<45	-59
0	2	10	<48	-0
0	2	12	<48	96
0	2	14	<44	34
0	3	1	134	132
0	3	3	<39	20
0	3	5	133	122
0	3	7	120	109
0	3	9	103	95
0	3	11	126	148
0	3	13	90	97
0	3	15	103	108
0	4	0	344	344
0	4	2	211	213
0	4	4	266	272
0	4	6	112	123
0	4	8	<50	43
0	4	10	<50	34
0	4	12	<47	-54
0	4	14	<40	-34
0	5	1	89	-67
0	5	3	<48	31
0	5	5	<50	-45
0	5	7	105	-89
0	5	9	114	-109
0	5	11	120	-126
0	5	13	96	-68
0	6	0	296	-280
0	6	2	153	-171
0	6	4	154	-172
0	6	6	103	-65
0	6	8	<51	-23
0	6	10	<48	-28
0	6	12	<40	29
0	7	1	<53	36
0	7	3	<54	-8
0	7	5	<54	64
0	7	7	105	77
0	7	9	87	69
0	7	11	87	86
0	8	0	162	189
0	8	2	123	112
0	8	4	110	109
0	8	6	62	65
0	8	8	50	27
0	9	1	<53	-21
0	9	3	<51	-14
0	9	5	<48	-64
0	9	7	75	-53
0	10	0	138	-114
0	10	2	72	-68
1	0	3	233	245
1	0	4	242	-193
1	0	5	354	325
1	0	6	295	-286
1	0	7	<46	51
1	0	8	171	-162
1	0	9	102	62
1	0	10	122	-115
1	0	11	<52	-48
1	0	12	<53	-77
1	1	1	318	-315
1	1	2	151	-126
1	1	3	98	-100
1	1	4	<55	-2
1	1	5	106	-104
1	1	6	177	-161
1	1	7	93	-90
1	1	8	<50	-54
1	1	9	<53	-65
1	1	10	146	-159
1	1	11	<59	-1
1	1	12	123	-109
1	2	1	358	-396
1	2	2	134	122
1	2	3	231	-242
1	2	4	198	178
1	2	5	258	-255
1	2	6	213	201
1	2	7	<48	-9
1	2	8	127	119
1	2	9	50	-63
1	2	10	110	97
1	2	11	53	32
1	3	1	<58	51
1	3	2	97	85
1	3	3	95	103
1	3	4	<43	-6
1	3	5	131	144
1	3	6	129	140
1	3	7	94	89
1	3	8	<54	82
1	3	9	<56	73
1	3	10	140	160
1	3	11	<52	21
1	4	1	279	276
1	4	2	105	-99
1	4	3	171	198
1	4	4	101	-80
1	4	5	170	200
1	4	6	105	-100
1	4	7	<54	-2
1	4	8	109	-98
1	4	9	<59	32
1	4	10	117	-93
1	5	1	<50	-57
1	5	2	<51	-90
1	5	3	99	-81
1	5	4	<53	-26
1	5	5	77	-82
1	5	6	112	-108
1	5	7	<57	-39
1	5	8	<59	-57
1	5	9	61	-61
1	5	10	126	-116
1	6	1	139	-169
1	6	2	72	39
1	6	3	130	-134
1	6	4	57	42
1	6	5	131	-152
1	6	6	<58	79
1	6	7	<58	-17
2	0	4	196	158
2	0	5	333	-288
2	0	6	<50	47
2	0	7	202	-210
2	0	8	<60	25
2	0	9	145	-149
2	0	10	<69	61
2	0	11	153	-155
2	0	12	<77	-23
2	0	13	104	-98
2	1	3	47	39
2	1	4	251	-233
2	1	5	<45	-54
2	1	6	188	-203
2	1	7	<56	-53
2	1	8	140	-138
2	1	9	<60	-36
2	1	10	<65	-79
2	1	11	<65	-67
2	1	12	<67	-4
2	1	13	<67	-9
2	2	1	147	108
2	2	2	<50	-11
2	2	3	144	135
2	2	4	108	-102
2	2	5	238	231
2	2	6	<54	-31
2	2	7	217	228
2	2	8	<63	-21
2	2	9	165	189
2	2	10	<71	-43
2	2	11	167	156
2	2	12	<78	26
2	2	13	125	74
2	3	0	266	272
2	3	1	73	57
2	3	2	200	200
2	3	3	<48	-43
2	3	4	190	203
2	3	5	110	98
2	3	6	122	108
2	3	7	<61	78
2	3	8	<63	71
2	3	9	<65	27
2	3	10	<67	74
2	3	11	<67	62
2	3	12	<67	17
2	4	0	191	209
2	4	1	110	-106
2	4	2	<54	30
2	4	3	129	-142
2	4	4	<58	57
2	4	5	172	-187
2	4	6	<64	33
2	4	7	178	-195
2	4	8	<70	23
2	4	9	169	-175
2	4	10	<76	12
2	4	11	137	-127
2	5	0	140	-147
2	5	1	<61	-41
2	5	2	138	-133
2	5	3	<63	9
2	5	4	167	-180
2	5	5	<67	-96
2	5	6	106	-111
2	5	7	<69	-62
2	5	8	<70	-57
2	5	9	<70	-9
2	5	10	<71	-45
2	6	0	123	-115
2	6	1	<68	80
2	6	2	<68	-15
2	6	3	133	121
2	6	4	<71	-50
2	6	5	139	144
2	6	6	<74	-32
2	6	7	125	130
2	7	0	<95	104
2	7	1	<75	33
2	7	2	<75	84
2	7	3	<75	-6
2	7	4	<75	108
2	7	5	<75	43
3	0	6	249	-250
3	0	7	130	-143
3	0	8	159	-181
3	0	9	<62	18
3	0	10	155	-183
3	0	11	<72	28
3	0	12	131	-101
3	1	5	222	-218
3	1	6	<45	-42
3	1	7	85	-89
3	1	8	<57	31
3	1	9	131	-111
3	1	10	<67	-8
3	1	11	93	-22
3	1	12	<65	65
3	2	4	156	146
3	2	5	<43	-10
3	2	6	271	249
3	2	7	<55	64
3	2	8	144	158
3	2	9	<65	-33
3	2	10	155	159
3	2	11	<73	-6
3	2	12	100	99
3	3	1	264	236
3	3	2	73	57
3	3	3	168	145
3	3	4	<46	-13
3	3	5	186	186
3	3	6	<55	28
3	3	7	103	101
3	3	8	<64	-86
3	3	9	118	92
3	3	10	<64	-31
3	3	11	<66	-1
3	4	1	128	-139
3	4	2	90	-76
3	4	3	147	-156
3	4	4	123	-128
3	4	5	<57	-10
3	4	6	187	-220
3	4	7	<64	-20
3	4	8	137	-126
3	4	9	<72	44
3	4	10	137	-125
3	5	1	145	-190
3	5	2	<59	18
3	5	3	120	-107
3	5	4	<62	52
3	5	5	139	-130
3	5	6	<67	-17
3	5	7	114	-77
3	5	8	<68	55
3	5	9	<69	-68
3	5	10	<70	15
3	6	1	85	67
3	6	2	<66	50
3	6	3	110	100
3	6	4	<69	83
3	6	5	<70	29
3	6	6	133	153
3	6	7	<71	36
3	7	0	<73	0
3	7	1	<73	119
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5	4	4	49	67
5	4	5	87	-108
5	4	6	<36	-20
5	4	7	98	-112
5	4	8	<37	38
5	4	9	<36	-20
5	4	10	<34	-7
5	4	11	<31	10
6	4	0	136	-161
6	4	1	<34	-43
6	4	2	130	-154
6	4	3	62	78
6	4	4	63	-91
6	4	5	45	95
6	4	6	52	-72
6	4	7	97	100
6	4	8	<36	-44
6	4	9	84	75
6	4	10	<32	-4
7	4	1	45	8
7	4	2	<37	37
7	4	3	37	-36
7	4	4	104	136
7	4	5	<37	-39
7	4	6	103	96
7	4	7	<36	-20
7	4	8	134	134
7	4	9	<32	-19
7	4	10	90	76
8	4	0	90	92
8	4	1	<37	-8
8	4	2	64	84
8	4	3	45	75
8	4	4	<36	45
8	4	5	<36	30
8	4	6	<34	26
8	4	7	37	72
8	4	8	<31	-2
8	4	9	83	86
9	4	1	83	100
9	4	2	<34	-0
9	4	3	34	95
9	4	4	<34	17
9	4	5	32	39
9	4	6	<31	-12
9	4	7	37	30
10	4	0	36	67

borderline of being significantly different from normal C–C bond distances. However, a reasonable explanation can be given for the somewhat longer than normal hydrocarbon distances which are observed. The C–C single bonds average about 1·61 Å and the C–C double bond length averages 1·52 Å. The norbornadiene molecule itself is a very strained molecule. Bond angles throughout must be made less than normal tetrahedral angles and trigonal coplanar angles in order to form the structure. It seems not at all unlikely that the change caused by the compression of these angles may have some effect on the length of the bonds.

The $C_2=C_3$ and $C_5=C_6$ bond lengths of approximately 1·52 Å are very close to a single bond length. From infra-red data the normal C=C double bond stretching mode is found somewhere near 1650 cm.$^{-1}$ (West, 1956). In norbornadiene the band tentatively assigned to the C=C double bond stretching mode has a frequency of 1550 cm.$^{-1}$ (Cristol & Snell, 1958) which would indicate a lengthening of the double bond even in the unchelated molecule. The infrared absorption spectra have been measured on several metal complexes made with norbornadiene and in every case studied this 1550 cm.$^{-1}$ band disappeared and a new band appears at 1410 cm.$^{-1}$ (Alexander, Baenziger, Carpenter & Doyle, 1960). This new band is believed to be the stretching mode for the chelated carbon atoms, and its frequency is approaching the range where the normal C–C single bond stretching mode is found ($\sim$ 1000 cm.$^{-1}$). Thus the infrared data also are consistent with a greater length of the double bond in the complex. Aldeman, Owston & Rowe (1960) found the ethylene complex *trans* —$Pt(C_2H_4)(NH(CH_3)_2)Cl_2$— to have carbon–carbon double bond length of 1·47 Å and Baenziger (unpublished refinement) has found the carbon–carbon double bond in the styrene–palladium chloride to be 1·44 Å (Baenziger & Holden, 1955).

The angles in the norbornadiene structure must all be less than tetrahedral. Norbornadiene can be considered to be two fused cyclopentene rings having two sides and three carbons in common. Cyclopentane is almost a planar structure since the normal angle of an equilateral pentagon (108°) is close to the tetrahedral angle. In cyclopentene where one side of this structure is shortened and two angles approach the trigonal coplanar angle of 120°, the sum of the other three angles must decrease. In norbornadiene with two cyclopentenes fused together a warp is placed in by geometry. This warp, which is on a line running through the bridgehead carbons in each of the two fused rings, decreases the total sum of the angles in each ring still further. If the decrease is now distributed throughout the angles, they will all be less than normal. All angles in norbornadiene in the complex not adjacent to a double bond are approximately equal and average about 99°, which is about 10° less than the tetrahedral angle. The angles adjacent to the double bond average about 106·6°, which is about 3° less than the tetrahedral angle and about 14° less than the normal trigonal coplanar angle. The lengthening of these bonds has already been pointed out. However, since these angles are still about 8° larger than the other angles, some double bond character is indicated.

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