represent a true minimum N· · ·N separation. The average N· · ·N separation of 2.96 Å in the molybdenum dimer greatly exceeds this minimum distance, indicating repulsions between PPh_3 moieties probably dictate the equilibrium Mo-N-Mo angle and $Mo_1 \cdots Mo_2$ distance; the threefold symmetric arrangement of the PN bonds is also determined by $PPh_3 \cdots PPh_3$ repulsions. This is clearly shown in Figure 3. We summarize our position as follows: a metal-metal bond produces short metal-metal separations, but a short metal-metal separation does not necessarily imply the existence of a metal-metal bond. We therefore conclude the $Mo_2(CO)_6(\mu\text{-}Ph_3PNH)_3$, $Mn_2(CO)_6(N_3)_3^-$, and $W_2(CO)_6(OH)_3^{3-}$ all lack bonding metal-metal interactions.

The erroneous formulation of this complex as $Mo_2(CO)_6(Ph_3PNH)_4$ is solely the result of low molybdenum analyses. This also accounts for the CO:Mo ratio of 7:2 determined in the course of this work. When our CO evolution data (4.78 mmol of CO/g of complex) are recalculated using the actual molecular weight (1191), one finds 5.7 mmol of CO/mmol of dimer. Colorimetric assay by the original workers[2] and on our samples yielded 12.46, 12.47, 12.65% Mo. An atomic absorption determination on a sample prepared here yielded 14.87% Mo. When the structure determination was complete and the true molybdenum content known, a gravimetric (lead molybdate) procedure yielded 15.16% Mo. It is curious that the content of massive ligand was in error, while the normally difficult CO assay was correct as originally formulated. Structure I suggested earlier was, of course, based on the erroneous molybdenum analyses. The problem was compounded because this is not a simple hexacarbonyl substitution product; the phosphonium-amide functionality is without precedent, making it impossible to determine the molecular formula by analogy to known compounds. Hindsight shows that vapor pressure osmometric molecular weight determinations carried out in this study were accurate for $Mo_2(CO)_6(\mu\text{-}Ph_3PNH)_3$, but these were discounted as being "low" due to ligand dissociation and/or decomposition. Attempts to obtain a mass spectrum yielded only fragments of Ph_3PNH.

The complex as now formulated, $Mo_2(CO)_6(\mu\text{-}Ph_3PNH)_3$, is in agreement with the inert gas formalism without invoking a metal-metal bond. Each bridging phosphinimine donates four electrons and each CO two for a total of 24 electrons per dimer. This example serves to reinforce Tolman's comment[34] that the burden of proof lies with anyone who claims a violation of the 18-electron rule by more than two electrons.

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Registry No. $Mo_2(CO)_6(Ph_3PNH)_4$, 14897-20-2; $Mo_2(CO)_6(Ph_3PNH)_3$, 51263-57-1; $Mo_2(CO)_6[(C_6H_5)_3PNH]_3 \cdot {}^1/_2 C_4H_8O$, 51269-19-3.

Supplementary Material Available. Table IV, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1632.

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Crystal and Molecular Structures of Di-μ-chloro-dichlorobis(cyclopentene)diplatinum(II) and Di-μ-chloro-dichlorobis(cycloheptene)diplatinum(II)

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The crystal and molecular structures of di-μ-chloro-dichlorobis(cyclopentene)diplatinum(II) and the corresponding cycloheptene complex have been determined. Three-dimensional data were collected with Mo Kα radiation on a Syntex $P\bar{1}$ diffractometer to a maximum 2θ of 60° employing a θ–2θ scan technique. The compound $[PtCl_2(C_5H_8)]_2$ crystallizes in the orthorhombic space group *Ibam* with $a = 9.537$ (4) Å, $b = 18.703$ (7) Å, $c = 8.290$ (5) Å, and $Z = 4$. The molecular point group is C_{2h}. The compound $[PtCl_2(C_7H_{12})]_2$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 6.035$ (2) Å, $b = 8.030$ (3) Å, $c = 19.355$ (8) Å, $\beta = 91.03°$, and $Z = 2$. The molecular point group is C_i. All the coordinates and the anisotropic temperature factors of the nonhydrogen atoms were refined in a full-matrix least-squares manner. The final R indices were 0.081 for $[PtCl_2(C_5H_8)]_2$ and 0.093 for $[PtCl_2(C_7H_{12})]_2$. The structures of the cyclic olefin ligands were found to be almost identical with the calculated structures of the free olefins except for slight elongations of the double bonds.

Introduction

The nature of the platinum-olefin bond has been the object of extensive investigation. The presently accepted bonding scheme[1] consists of two parts: a σ bond involving donation of electrons from the filled σ and π molecular orbitals of the olefin to an empty dsp^2 hybrid orbital on the platinum and a π bond formed by the back-donation of electrons from a platinum dp hybrid orbital into the empty π* antibonding orbital of the olefin. The relative contribution of the σ and π bonds in the metal-olefin bonding scheme is, however, still the subject of considerable controversy.

X-Ray studies of Zeise's salt, $KPtCl_3(C_2H_4) \cdot H_2O$, have

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Table I. Physical Data and Data Collection Parameters

Molecular formula	$(PtCl_2\cdot C_5H_8)_2$	$(PtCl_2\cdot C_7H_{12})_2$
Mol wt	668.2	724.3
Crystal size, nm	0.044 × 0.070 × 0.090	0.030 × 0.065 × 0.065
Cell dimensions		
a, Å	9.537 (4)	6.035 (2)
b, Å	18.703 (7)	8.030 (3)
c, Å	8.290 (5)	19.355 (8)
β, deg		91.03 (3)
V, Å^3	1479 (1)	937.9 (6)
Space group	*Ibam*	$P2_1/c$
Molecules/unit cell	4	2
d_{calcd}, g/cm^3	3.00 ($Z = 4$)	2.56 ($Z = 2$)
d_{obsd},[a] g/cm^3	2.97	2.52
Scan technique	θ–2θ	
Scan speed	1°/min in 2θ	
Scan width	1.2° below Kα_1 to 1.2° above Kα_2	
Background count time	One-half scan time on each side of peak	
No. of reflections	1155	2754
No. of nonzero reflections[b]	819	1982

[a] Density was measured by the flotation technique using a mixture of $CHBr_2CHBr_2$ and CCl_4. [b] All intensities with values less than 2× standard deviation were set equal to zero with zero weight.

yielded carbon–carbon bond lengths in the ethylene moiety from ~1.5[2,3] to 1.44 (4)[4] to 1.37 (3) Å.[5] A number of X-ray structures on π complexes of platinum(II) and unsaturated ligands have been summarized in tabular form by Spagna and Zambonelli.[6] The conclusion is that the olefinic carbon–carbon distance is about 1.4 Å and that the olefin is almost perpendicular to the platinum dsp^2 plane. As of yet, however, no crystal structure of a Zeise's type dimer, $(PtX_2\cdot olefin)_2$, has been determined.

On the basis of infrared studies, many workers[1,7-9] have concluded that the ethylene moiety in Zeise's salt and Zeise's dimer changes very little upon complexation and thus there must be little π effect in the bonding. Others,[10,11] however, have assigned the vibrational spectrum of Zeise's salt on the basis of two Pt–C bonds; *i.e.*, the π interaction is considered to be so strong that the ethylene moiety is thought to be similar in structure to ethylene oxide.

We have recently initiated an investigation of cyclic olefins complexed to Pt(II) and Pd(II) in the hopes that the vibrational spectra and structure of the complexed rings would be more sensitive to the nature of the olefinic linkage. The vibrational spectra of di-μ-chloro-dichlorobis(cyclopentene)-diplatinum(II) and the corresponding dipalladium(II) complex were investigated and were found to be consistent with two Pt–C bonds and only one Pd–C bond.[12] Similar conclusions have been reached for the cyclohexene and cycloheptene complexes.[13]

Thus, owing to the fact that no crystal structure of a Zeise's type dimer has been reported and because of the nature of their vibrational spectra, we initiated an X-ray investigation of Zeise's type dimers of cyclic olefins. We report, herein, the structures of $[PtCl_2(C_5H_8)]_2$ and $[PtCl_2(C_7H_{12})]_2$.

Experimental Section

The X-ray analyses of both the cyclopentene and cycloheptene complex were quite similar and will be presented together. Orange, needle-shaped crystals suitable for an X-ray analysis were grown by the slow evaporation of a chloroform solution and cut to a suitable size. The crystal surveys, unit cell dimension determinations, and data collections were accomplished on a Syntex $P\bar{1}$ diffractometer using molybdenum radiation (λ 0.71069 Å) at 25°. The diffractometer was equipped with a graphite incident-beam monochromator mounted in the perpendicular mode. Final unit cell dimensions were obtained by a least-squares fit of 15 high-angle reflections ($2\theta > 25°$). Systematic absences indicated that the cyclopentene complex crystal belonged to the orthorhombic space group *Iba*2 or *Ibam* (hkl, $h + k + l = 2n + 1$; $0kl$, $k = 2n + 1$; $h0l$, $h = 2n + 1$). Subsequent refinement of the trial structure confirmed the center of symmetry and therefore space group *Ibam*. Systematic absences indicated that the cycloheptene complex crystal belonged to the monoclinic space group $P2_1/c$ ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). Systematic absences were ignored during both data collections in order to confirm these extinctions for the entire data set. Intensity data sets were collected to a resolution of 0.7 Å (maximum $(\sin\theta)/\lambda = 0.7$). A single check reflection was monitored every 30 reflections and revealed no systematic variation in intensity due to radiation damage or other causes. Details of the crystal surveys and data collection parameters are summarized in Table I.

The diffractometer output and all subsequent crystallographic calculations were processed using subprograms of the CRYM crystallographic computer system.[14] The data processing included corrections for background, Lorentz, and polarization effects. Polarization due to the monochromator was corrected for by a method suggested by Azaroff.[15] Processing also included the calculation of F^2 and its standard deviation for each of the reflections. The standard deviations were assigned on the basis of the equation

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2$$

where S is the number of counts collected during the scan, B_1 and B_2 are the background counts, d is an empirical constant set at 0.02, and α is the scan time to total background time ratio. Since the absorption of the crystals was significant ($\mu_{(C_5H_8\cdot PtCl_2)_2} = 206\ cm^{-1}$, $\mu_{(C_7H_{12}\cdot PtCl_2)_2} = 162\ cm^{-1}$), efforts were made to minimize and correct for absorption. Data were collected on extremely small crystals to minimize absorption effects. This practice of course limited the resolution of the data set and further manifested itself through the large number of zero intensities. Absorption corrections were made by the method of gaussian quadrature.[16] The crystals

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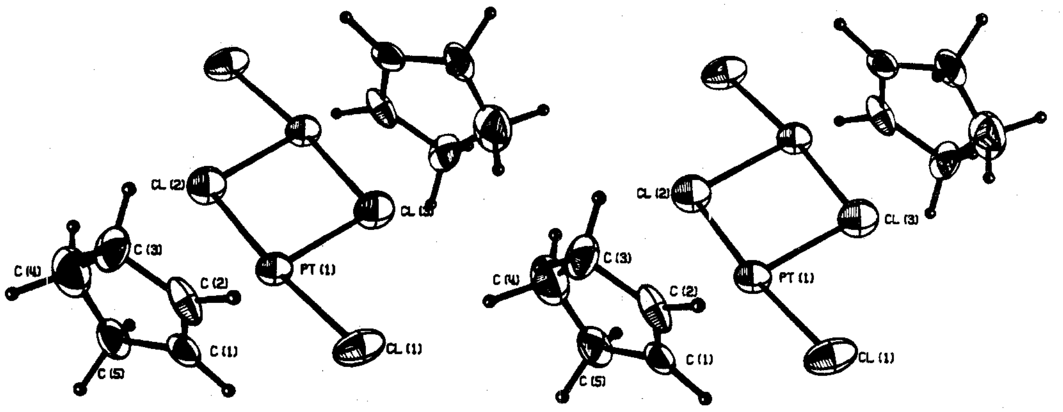

Figure 1. Stereoview of $(PtCl_2 \cdot C_5H_8)_2$.

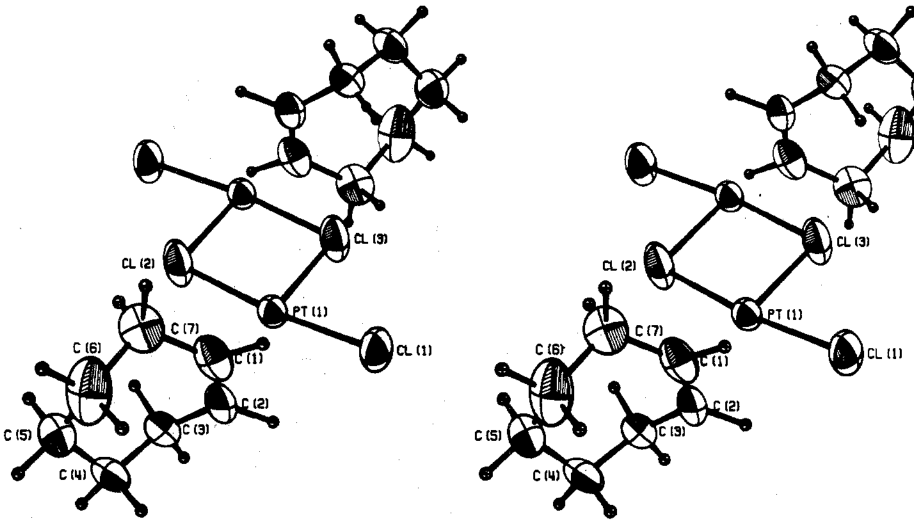

Figure 2. Stereoview of $(PtCl_2 \cdot C_7H_{12})_2$.

used in data collection were mounted in a general orientation to minimize secondary extinction; therefore no corrections were made for this effect.

Finally, the data sets were placed on an approximately absolute scale by Wilson statistics.[17] Atomic scattering factors for C and Cl were taken from the "International Tables for X-ray Crystallography,"[18] for Pt from Cromer and Mann,[19] and for H from Stewart, Davidson, and Simpson.[20] The scattering factors for Pt and Cl were corrected for both anomalous scattering components.[18b]

Determination and Refinement of Structures

The cyclopentene complex contained only four molecules in the unit cell. Therefore, the molecule must use either a twofold symmetry element (for space group *Iba*2) or a $2/m$ symmetry element (for space group *Ibam*). A trial structure was obtained using conventional Patterson and Fourier techniques. Refinement was begun in the acentric space group (*Iba*2), but it quickly became obvious that the $2/m$ symmetry element was present in the molecule and refinement was switched to the centric space group (*Ibam*). Refinement proceeded smoothly to an acceptable R index.

The cycloheptene complex contained only two molecules in the unit cell. Therefore, the molecule must use the $\bar{1}$ symmetry element in space group $P2_1/c$. A trial structure was obtained using conventional Patterson and Fourier techniques. The trial structure refined smoothly to an acceptable R index.

Both refinements were concluded using full-matrix least-squares techniques. The quantity minimized by the least-squares procedure was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Hydrogen positions were calculated but not refined. During the final cycles of refinement the nonhydrogen positions, anisotropic temperature factors, and scale factor were located in one matrix. Refinement of both structures was terminated when the shifts calculated for the parameters in the least-squares cycle were all less than one-sixth of the corresponding standard deviation. Final difference Fouriers revealed no missing or misplaced electron density. The data-fit criteria of the cyclopentene complex are $R = 0.081$, $R' = 0.008$, and GOF = 1.4. The data-fit criteria of the cycloheptene complex are $R = 0.093$, $R' = 0.017$, and GOF = 2.0. The definitions of the above data-fit criteria are $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma w(F_o^2 - F_c^2)^2/\Sigma F_o^4$, and GOF = $w(F_o^2 - F_c^2)^2/(m - s)$, where m is the number of observations and s is the number of parameters fitted. All criteria used for the data fit were based on nonzero reflections.

Discussion

The refined coordinates were plotted using the ORTEP computer program of Johnson[21] (Figures 1 and 2). The final coordinates and anisotropic temperature factors with their standard deviations are given in Tables II and III. Examination of both packing diagrams revealed no close contacts. In the cyclopentene complex, the closest intermolecular approach of platinum atoms was 4.193 (1) Å; that of chlorine atoms, 4.177 (8) Å. In the cycloheptene complex, the closest intermolecular approach of platinum atoms was 4.322 (1) Å; that of chlorine atoms, 4.236 (8) Å. The calculated and observed structure factors and the packing diagrams for both complexes have been deposited.

Tables IV and V give the relevant structural parameters of $[PtCl_2(C_5H_8)]_2$, the cyclopentene complex, and of $[PtCl_2(C_7H_{12})]_2$, the cycloheptene complex, respectively. The

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Table II. Atomic Parameters and Their Standard Deviations for $(PtCl_2 \cdot C_5H_8)_2$[a]

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Pt(1)	5330 (1)	4077 (0)	0 (0)	76 (1)	13 (0)	121 (1)	−2 (1)	0 (0)	0 (0)
Cl(1)	3873 (6)	3122 (2)	0 (0)	150 (9)	19 (1)	144 (13)	−34 (6)	0 (0)	0 (0)
Cl(2)	6592 (6)	5137 (2)	0 (0)	81 (8)	16 (1)	261 (15)	0 (5)	0 (0)	0 (0)
C(1)	7002 (14)	3356 (7)	842 (18)	71 (19)	30 (4)	107 (30)	53 (16)	55 (39)	43 (19)
C(4)	9093 (16)	3965 (12)	0 (0)	101 (34)	33 (8)	315 (75)	32 (29)	0 (0)	0 (0)
C(5)	8276 (26)	3700 (7)	1491 (21)	74 (21)	36 (5)	119 (34)	7 (17)	−88 (46)	9 (21)

[a] The values have been multiplied by 10^4. The temperature factor is in the form $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

Table III. Atomic Parameters and Their Standard Deviations for $(PtCl_2 \cdot C_7H_{12})_2$[a]

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Pt(1)	7046 (1)	6,509 (1)	4900 (0)	244 (2)	119 (1)	19 (0)	−89 (4)	−27 (0)	19 (1)
Cl(1)	9706 (11)	7,410 (9)	5645 (3)	729 (31)	228 (13)	35 (1)	−479 (35)	−186 (12)	59 (8)
Cl(3)	5788 (9)	4,681 (8)	5765 (2)	488 (23)	259 (14)	24 (1)	−364 (29)	−90 (8)	76 (7)
C(1)	8772 (31)	7,603 (30)	4058 (9)	220 (63)	220 (47)	25 (5)	−68 (86)	20 (29)	61 (28)
C(2)	7247 (47)	8,710 (29)	4318 (9)	802 (79)	176 (51)	15 (4)	98 (91)	−47 (40)	13 (27)
C(3)	5248 (40)	9,393 (28)	3938 (9)	605 (93)	137 (42)	26 (6)	33 (93)	−50 (40)	20 (28)
C(4)	5888 (41)	10,417 (29)	3325 (11)	651 (91)	138 (43)	37 (7)	−143 (96)	−120 (46)	63 (32)
C(5)	6620 (44)	9,413 (32)	2707 (10)	606 (89)	195 (52)	25 (6)	−101 (95)	−39 (42)	28 (31)
C(6)	8702 (38)	8,333 (42)	2816 (10)	366 (85)	473 (90)	28 (6)	−243 (92)	46 (36)	13 (45)
C(7)	8503 (30)	6,902 (29)	3358 (9)	211 (62)	248 (59)	31 (6)	137 (89)	53 (30)	3 (30)

[a] The values have been multiplied by 10^4. The temperature factor is in the form $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

Table IV. Bond Lengths and Angles of $(PtCl_2 \cdot C_5H_8)_2$ with Estimated Standard Deviations in Parentheses

	(a) Distances, Å		
Pt–Cl(1)	2.264 (6)	C(1)–C(2)	1.40 (2)
Pt–Cl(2)	2.320 (5)	C(2)–C(3)	1.48 (2)
Pt–Cl(3)	2.349 (5)	C(3)–C(4)	1.54 (2)
Pt–C(1)	2.20 (2)	C(4)–C(5)	1.54 (2)
Pt–C(2)	2.20 (2)	C(5)–C(1)	1.48 (2)
	(b) Angles, Deg		
Cl(1)–Pt–Cl(2)	173.4 (2)	C(1)–C(2)–C(3)	111 (1)
Cl(1)–Pt–Cl(3)	90.8 (2)	C(2)–C(3)–C(4)	105 (1)
Cl(1)–Pt–X[a]	87.7	C(3)–C(4)–C(5)	107 (1)
Cl(2)–Pt–X	99.0	C(4)–C(5)–C(1)	105 (1)
Cl(3)–Pt–X	181.5	C(5)–C(1)–C(2)	111 (1)

[a] X is the midpoint of the olefin double bond.

Table V. Bond Lengths and Angles of $(PtCl_2 \cdot C_7H_{12})_2$ with Estimated Standard Deviations in Parentheses

	(a) Distances, Å		
Pt–Cl(1)	2.257 (6)	C(2)–C(3)	1.51 (3)
Pt–Cl(2)	2.328 (6)	C(3)–C(4)	1.50 (3)
Pt–Cl(3)	2.362 (6)	C(4)–C(5)	1.52 (3)
Pt–C(1)	2.14 (2)	C(5)–C(6)	1.54 (4)
Pt–C(2)	2.10 (2)	C(6)–C(7)	1.56 (4)
C(1)–C(2)	1.38 (3)	C(7)–C(1)	1.47 (3)
	(b) Angles, Deg		
Cl(1)–Pt–Cl(2)	172.8 (2)	C(2)–C(3)–C(4)	112 (2)
Cl(1)–Pt–Cl(3)	88.9 (2)	C(3)–C(4)–C(5)	115 (2)
Cl(1)–Pt–X	90.8	C(4)–C(5)–C(6)	116 (2)
Cl(2)–Pt–X	96.4	C(5)–C(6)–C(7)	116 (2)
Cl(3)–Pt–X	180.3	C(6)–C(7)–C(1)	109 (2)
C(1)–C(2)–C(3)	126 (2)	C(7)–C(1)–C(2)	121 (2)

[a] X is that point where the olefin double bond intersects the Pt_2Cl_4 plane.

platinum atoms are four-coordinate with a square-planar configuration. The platinum-chlorine distances are in the range of distances reported previously. The longest Pt-Cl distance in each molecule (2.349 (5) and 2.362 (6) Å for the C_5H_8 and C_7H_{12} complexes, respectively) is the one trans to the olefin which is consistent with the strong trans influence associated with olefin ligands. The length of the trans Pt-Cl bond is 3σ greater than the other bridging Pt-Cl bond (2.320 (5) and 2.328 (6) Å for the C_5H_8 and C_7H_{12} complexes, respectively), and the elongation would appear greater in the cycloheptene complex which would be consistent with more back π bonding in the case of C_7H_{12} than in the C_5H_8 complex.

In the cycloheptene complex there is no plane of symmetry, but the two Pt-C distances, 2.10 (2) and 2.14 (2) Å, differ by only 1σ. The cyclopentene complex, on the other hand, does have a plane of symmetry and thus the olefin must be perpendicular to the Pt_2Cl_4 plane, and the two Pt-C distances are identical by symmetry, 2.20 (1) Å. The Pt-C distance in $[PtCl_2(C_5H_8)]_2$ is 0.08 Å (3σ) longer than the average of the two Pt-C distances in the $[PtCl_2(C_7H_{12})]_2$ complex. It is felt that this difference may be significant in light of vibrational studies[12,13] of these molecules in which two ν(Pt-C) modes were assigned for both complexes but the frequencies were some 80 cm^{-1} higher in the $[PtCl_2(C_7H_{12})]_2$ molecule.

The olefinic bond of the cyclopentene ring is bisected by the Pt_2Cl_4 plane and the midpoint of the bond is 2.09 Å from the platinum atom. The midpoint of the olefinic bond of the cycloheptene ring is 0.11 Å out of the Pt_2Cl_4 plane and is 2.00 Å from the Pt; the double bond intersects the Pt_2Cl_4 plane 2.01 Å from the Pt. For maximum overlap of the olefin π^* orbitals with the dp orbitals of platinum, the dihedral angle formed by the intersection of the PtC_2 plane with the sp^2 plane of the ring should be 90°. In the cycloheptene complex this dihedral angle is 113° and in the cyclopentene complex it is 110°. These deviations from 90°, however, can be accounted for on the basis of steric effects. The homoallylic carbon, C(5) in Figure 1, of the C_5H_8 ring lies in the Pt_2Cl_4 plane and is 3.24 (2) Å from the cis, bridging chlorine. A normal 90° orientation of the ring would place this carbon only 2.36 Å from the chlorine which is well within the sum of the van der Waals radii (3.50 Å). The cycloheptene ring is oriented in such a way that the allylic carbons (C(3) and C(7) in Figure 2) are each 3.38 (2) Å from the chlorines and, due to the twisted conformation of the ring, all of the other nonolefinic carbon atoms are over 4.5 Å from the chlorine. The largest interaction would be that of the hydrogens on C(7) with Cl(2) (Figure 2) where the Cl-H distance is only 2.16 Å as compared with a sum of the van der Waals radii of at least 2.9 Å. It is interesting to note, at this point, that in the infrared spectrum of $[PtCl_2$-

$(C_7H_{12})]_2$, one of the CH_2 rocking modes is some 34 cm^{-1} higher in frequency than in the pure C_7H_{12} whereas other CH_2 modes are essentially unchanged or shift to slightly lower frequency upon complexation of the ring.

It was hoped that changes in the structure of the rings would lead to a better understanding of the nature of the bonding. The structure of free cyclopentene has been studied by microwave spectroscopy[22] and gas-phase electron diffraction.[23] In addition, recent force field calculations[24,25] have yielded calculated structural parameters for both rings. Figure 3 compares the structures of the free and complexed cyclopentene and cycloheptene rings. The olefin bonds elongate to 1.40 (2) Å in cyclopentene and 1.38 (3) Å in cycloheptene. These bond lengths represent elongation of 3σ and 2σ for C_5H_8 and C_7H_{12}, respectively. Thus, the olefinic bond lengths do not appear to elongate significantly upon complexation. However, the epoxide C-C bond length in cyclopentene oxide has been assumed to be only 1.47 Å[26] to fit microwave data so that the complexed C_5H_8 olefinic bond length is only $(1/2)\sigma$ from the average of the corresponding bond lengths of cyclopentene and cyclopentene oxide. In free cyclopentene, the ring is puckered by $22.5 \pm 1°$.[22,24,25,27] Thus, the homoallylic carbon is 0.37 ± 0.02 Å out of the plane of the other four carbons. In the structure reported herein, the ring is perfectly planar. The barrier to inversion of free cyclopentene, however, is only 0.66 kcal/mol;[27] therefore we feel that the planarity of the ring is probably due to crystal packing forces rather than bonding changes due to complexation. An examination of Table V shows that the cycloheptene ring is not symmetrical, but all of the bond lengths and angles which would be equivalent if the ligand had C_2 symmetry differ by only 1σ or less. It is not inappropriate, therefore, to consider that the ring may well be in a symmetrical chair conformation which may be slightly distorted by steric interactions with the cis, bridging chlorine (*vide supra*). If one considers the complexed C_7H_{12} ring to be an "averaged" symmetric chair, *i.e.*, the ring has C_2 symmetry and all bond angles and lengths are averages of the "equivalent" pairs (see Figure 3), it will be noticed that all bond lengths and angles, except for the olefinic carbon-carbon bond length, are within 2σ of the calculated lengths and angles. The torsional angles do appear to differ slightly but are still in excellent agreement with the calculated values. Thus, aside from a slight elongation of the olefinic bonds and the planarity of the cyclopentene ring, it would appear that the structures of the rings are essentially unchanged with complexation.

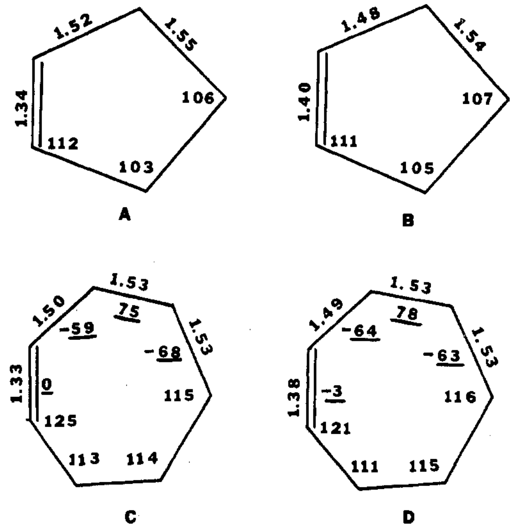

Figure 3. (A) Structure of cyclopentene calculated in ref 25. (B) Structure of cyclopentene complexed to platinum(II). (C) Structure of cycloheptene calculated in ref 25. (D) Structure of cycloheptene complexed to platinum(II). The standard deviations of the torsional angles (underlined in figure) on the complexed cycloheptene ring are 3°; all other standard deviations are given in Tables IV and V.

Registry No. $[PtCl_2(C_5H_8)]_2$, 43145-24-0; $[PtCl_2(C_7H_{12})]_2$, 51269-31-9.

Supplementary Material Available. A listing of structure factors and crystal packing diagrams will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1639.

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