(20) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Am. Chem. Soc.*, **90**, 7135 (1968).

(21) S. W. Kirtley, Ph.D. Dissertation, University of California at Los Angeles, 1972.

(22) H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *J. Am. Chem. Soc.*, **91**, 1021 (1969).

(23) M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, **11**, 1818 (1972).

(24) (a) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Commun.*, 458 (1970); (b) M. R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, **93**, 5670 (1971).

(25) G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. A*, 797 (1969).

(26) R. Mason, lecture presented at the 23rd International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971; *Pure Appl. Chem.*, **6**, 31 (1971).

(27) J. A. de Beer and R. J. Haines, *J. Organomet. Chem.*, **24**, 757 (1970).

(28) J. A. de Beer, R. J. Haines, R. Greatrex, and J. A. van Wyk, *J. Chem. Soc., Dalton Trans.*, 2341 (1973).

(29) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967). The expression used was $\sigma(I) = [(\text{peak count}) + (\text{background count}) + 0.04(\text{net intensity})^2]^{1/2}$.

(30) All the major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. R. E. Marsh's group at the California Institute of Technology.

(31) $R = (\sum\|F_o| - |F_c\|)/(\sum|F_o|)$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(32) K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 2339 (1969).

(33) R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, **3**, 101 (1964).

(34) W. S. McDonald, J. R. Moss, G. Raper, B. L. Shaw, R. Greatrex, and N. N. Greenwood, *Chem. Commun.*, 1295 (1969).

(35) R. Greatrex, N. N. Greenwood, I. Rhee, M. Ryang, and S. Tsutsumi, *Chem. Commun.*, 1193 (1970).

(36) Supplementary material.

(37) M. B. Smith and R. Bau, *J. Am. Chem. Soc.*, **95**, 2388 (1973).

(38) L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orio, and H. B. Gray, *J. Am. Chem. Soc.*, **94**, 1135 (1972).

(39) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

(40) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).

(41) J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, **6**, 1236 (1967).

(42) L. Marko, G. Bor, E. Klumpp, B. Marko, and G. Almasy, *Chem. Ber.*, **96**, 955 (1963).

(43) P. Dapporto, G. Fallani, S. Midollini, and L. Sacconi, *J. Am. Chem. Soc.*, **95**, 2021 (1973).

Contribution from the Sterling Chemistry Laboratory,
Yale University, New Haven, Connecticut 06520

Structure and Bonding in $\Delta^{1,4}$-Bicyclo[2.2.0]hexenebis(triphenylphosphine)platinum, $Pt[C_6H_8][P(C_6H_5)_3]_2$

MARK E. JASON and JOHN A. McGINNETY*

Received May 1, 1975 AIC50300J

$\Delta^{1,4}$-Bicyclo[2.2.0]hexene displaces ethylene from the complex $Pt[C_2H_4][P(C_6H_5)_3]_2$. The crystal and molecular structure of the resulting bicyclic olefin complex, $Pt[C_6H_8][P(C_6H_5)_3]_2$, has been determined from three-dimensional X-ray diffraction data. $Pt[C_6H_8][P(C_6H_5)_3]_2$ crystallizes in space group $P2_12_12_1$ of the orthorhombic system with four molecules in a unit cell of dimensions $a = 17.726$ (3), $b = 9.748$ (2), $c = 19.724$ (3) Å. The structural parameters were refined by least-squares techniques and the absolute configuration was deduced by comparison of the R factors, after refinement of the two possible configurations. The final R factor on F was 4.0% for the 3510 independent reflections (measured using a four-circle diffractometer) classed as observed and for which $2\theta \leq 55°$. No symmetry is crystallographically imposed upon the molecules. The six carbon atoms in the coordinated olefin form two squares having a common edge with a dihedral angle of 56 (1)° between the two four-membered rings. The olefinic carbon atoms form the common edge and are separated by 1.52 (2) Å, a greater separation than observed in several analogous complexes formed by acyclic olefins. The other six C–C bond lengths within the olefin moiety are, as expected, not significantly different from that typical of carbon atoms linked by a single σ bond. Coordination around platinum is not quite planar, the dihedral angle between the PtP_2 and PtC_2 planes being 3.2 (5)°. The olefinic carbon atoms are not exactly equidistant from platinum with Pt–C distances of 2.067 (14) and 2.138 (16) Å. This asymmetry may be due to minimization of intramolecular contacts since, even with this structure, there appear to be several short contacts between hydrogen atoms in one of the triphenylphosphine ligands and hydrogen atoms on the olefin. The Pt–P bond lengths are 2.289 (3) and 2.278 (3) Å, the slight difference possibly due to a trans effect since the longer Pt–P separation is trans to the shorter Pt–C separation. The binding energy of the Pt $4f_{7/2}$ electrons in $Pt[C_6H_8][P(C_6H_5)_3]_2$ is closer to that in Pt(0) compounds than in Pt(II) compounds. Thus transfer of electrons from the metal to the olefin is not the major component in the olefin–metal bonding, and redistribution of the olefin electrons through the intermediacy of the metal must be important. That the redistribution of the olefin electrons is considerable is shown by the large deviation from coplanarity of the two four-membered rings in the olefin and the relatively large separation of the olefinic carbon atoms.

Introduction

The compounds of general formula $PtL[P(C_6H_5)_3]_2$, where L is an olefin, have been chosen for a systematic investigation of the way in which different olefins are affected by interaction with a given metal system. Earlier reports from this laboratory[1,2] described studies of the complexes where L is 4,4'-dinitro-*trans*-stilbene and octafluoro-*trans*-but-2-ene. Surprising, perhaps, was the observation that the separation of the olefinic carbon atoms was the same (1.42 Å) in both of these complexes in spite of the widely differing electronic characteristics of the olefin substituents. One of the objectives of this investigation was to see if the olefinic C–C separation can be increased to an unusual degree by interaction with a metal system, since unusual reactivities might be induced thereby. This objective has not been achieved with the acyclic olefins examined so far and alternative approaches were sought.

Ring strain increases the coordinative ability of an olefin: 1,2-dimethylcyclopropene displaces ethylene from $Pt[C_2H_4][P(C_6H_5)_3]_2$.[3] The structure of the resulting complex has been reported[4] and the separation of the olefinic carbon atoms is 1.50 (2) Å, significantly longer than in the acyclic olefin complexes discussed above. Work by Wiberg et al.[5] resulted in the synthesis of $\Delta^{1,4}$-bicyclo[2.2.0]hexene as a mixture with 1,2-dimethylenecyclobutane. This paper reports the structure and properties of the platinum complex formed by $\Delta^{1,4}$-bicyclo[2.2.0]hexene; a preliminary communication of this work has appeared.[6]

Preparation of $Pt[C_6H_8][P(C_6H_5)_3]_2$

All solvents were distilled from EDTA and dried prior to use. All reactions were performed under vacuum or dry nitrogen. The synthesis of $\Delta^{1,4}$-bicyclo[2.2.0]hexene has been reported earlier.[5] Freshly

---

* To whom correspondence should be addressed at the Natural Environment Research Council, Alhambra House, London WC2H OAX, England.

powdered sodium methoxide, 0.36 g, was added to spiro[2.3]hexan-4-one tosylhydrazone,[7] 1.5 g in diglyme, 30 ml. After 2 hr of stirring, the mixture was pumped to dryness. The salt was pyrolyzed using a microburner until nitrogen no longer evolved. Toluene, 30 ml, was distilled into the trap containing the pyrolysate at −196°. The temperature was raised to −78°, and ethylenebis(triphenylphosphine)platinum,[8] 2.16 g, was added. The mixture was stirred at −78° for 30 min and then warmed slowly to −20°C. Ether, 60 ml, was added and the mixture was cooled to −78°. A fine white precipitate formed and was filtered off and rejected. The filtrate was allowed to stand at room temperature overnight whereupon light yellow crystals, 0.5 g, of the desired product formed. The complex had a decomposition point of 150° (under vacuum). Ir spectrum (CH_2Cl_2, 0.1-mm path): 3130 (m), 2990 (s), 2908 (m), 1560 (s), 1500 (m), 1168 (s), 1136 (m), 1100 (m) cm^{-1}. NMR spectrum (C_6D_6): δ 6.76 (12 H, multiplet), δ 6.22 (18 H, multiplet), and two broad multiplets centered at δ 2.7 (4 H) and δ 2.3 (4 H). Anal. Calcd for $PtP_2C_{42}H_{38}$: C, 62.07; H, 4.79; P, 7.75; Pt, 24.39. Found: C, 62.88; H, 4.88; P, 7.80, Pt, 24.46.

A Hewlett-Packard 5950A instrument was used to record the ESCA data as described previously.[2] Using a standard value of 285.0 eV for the carbon 1s binding energy (only one peak observed), the Pt $4f_{7/2}$ binding energy was 72.2 eV for $Pt[C_6H_8][P(C_6H_5)_3]_2$. The reproducibility of the spectrum was good, and the standard deviation in the binding energy was <0.2 eV.

Collection and Reduction of X-Ray Diffraction Data

Optical examination and preliminary X-ray photography indicated that the crystal belonged to the orthorhombic system. The space group was shown to be $P2_12_12_1$ by the systematic absences (observed on Weissenberg and precision photographs and during data collection): $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. The cell constants, obtained by least-squares refinement using the setting angles of 12 reflections centered on a Picker four-circle automatic diffractometer with Mo Kα X-radiation (λ 0.7107 Å), are (at 20°) $a = 17.726$ (3), $b = 9.748$ (2), $c = 19.724$ (3) Å. For four formula weights of the molecule in the unit cell, the calculated density is 1.59 g cm^{-3}; the density observed by flotation is 1.54 g cm^{-3}.

The crystal used in data collection was bounded by the faces 010, 001, $00\bar{1}$, 100, $\bar{1}00$, $1\bar{1}0$, and $\bar{1}\bar{1}0$; the lengths of the normals from the faces to a convenient origin were 0.30, 0.085, 0.085, 0.17, 0.17, 0.03, 0.03 mm, respectively. The crystal was initially aligned about the b axis of the cell and was misset before data collection. The diffraction intensity data were collected using a Picker four-circle automatic diffractometer in the ω–2θ scan mode with crystal-monochromated Mo Kα X-radiation. A symmetric scan of 2.0° in 2θ was used with a scan rate of 1° min^{-1}. Stationary-crystal, stationary-counter background counts of 10 sec were measured at each end of the scan. The intensities of the hkl reflections were recorded out to a 2θ value of 55° and those of the $hk\bar{l}$ reflections out to a 2θ value of 45°. Three standard reflections were measured at intervals throughout data collection: these intensities varied erratically and, at the conclusion of the experiment, the losses averaged about 15% of the original intensity.

The data were corrected for background and the changes in the standard reflections. The linear absorption coefficient is 40.2 cm^{-1} and corrections were applied,[9] the transmission coefficients ranging between 0.48 and 0.70. The hkl and $hk\bar{l}$ reflections were processed separately since Friedel pairs are not equivalent in this space group. The independent reflections were corrected for Lorentz–polarization effects and individual standard deviations, $\sigma(F^2)$, of the corrected intensities were calculated from counting statistics. A total of 5545 reflections were measured and processed. There were 4866 independent reflections of which 3510 were classed as observed.[1]

During the initial stages of refinement (prior to determination of the absolute configuration), a truncated data set was used; this consisted of the 1512 reflections obtained by averaging the hkl and $hk\bar{l}$ reflections and rejecting those classed as unobserved.

Solution and Refinement of the Structure

Initial values of the atomic coordinates of the platinum atom were obtained from a three-dimensional Patterson function.[9] Succeeding applications of least-squares refinement and difference Fourier calculations yielded the coordinates of all nonhydrogen atoms, the carbon atoms of the phenyl rings being refined as groups. The scattering factors were calculated using analytical approximations for neutral atoms[10] and the effects of anomalous dispersion[11] were included in F_c. The function minimized in refinement was $\sum w\|F_o| - |F_c\|^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Isotropic thermal parameters were used for all atoms, with only one overall thermal parameter for each group, and the R factor (on F) converged to 8.3% for the averaged and truncated data set of 1512 reflections. The platinum and phosphorus atoms were refined with anisotropic thermal parameters. Contributions from all hydrogen atoms were included by assuming an idealized geometry (those in phenyl rings as groups and those in the olefin moiety with a C–C–H angle of 114.0°) with a C–H bond length of 0.95 Å and thermal parameters 0.3 $Å^2$ higher than the carbon atoms to which they were bound. Individual thermal parameters were refined for the carbon atoms in the groups and after two cycles a systematic variation was observed, as in other cases.[1,2] An overall thermal parameter for each group was defined (and subsequently refined); the differences from this overall parameter for each of the positions around a ring (not subsequently varied) were averaged for all of the rings. The mean differences are as follows: C(1), −1.33 $Å^2$; C(2) and C(6), −0.36 Å; C(3) and C(5), 0.8 $Å^2$; C(4), 0.6 $Å^2$. The R factor converged to 3.6% after one additional cycle.

The absolute configuration of the molecules was determined by refinement of the two choices using the 3510 observed reflections (consisting of hkl and $hk\bar{l}$ reflections, which are not symmetry equivalent and which would be equivalent only if Friedel's law were applicable).[12] After one cycle of refinement, the initial configuration (based on that chosen arbitrarily for platinum from the Patterson function) gave an R factor of 5.6% and the alternative configuration gave an R factor of 4.0%. This clear indication that the alternative configuration was the correct choice was confirmed by examination of those Friedel pairs for which the calculated difference between the pair was of high statistical significance and, in general, significantly better agreement between the observed and calculated structure factors was obtained with the alternative configuration; e.g., for the 12,2,7 and 12,2,$\bar{7}$ reflections, F_o was 99.9 (6) and 101.6 (7) and F_c (initial configuration) was 101.1 and 97.3, whereas F_c (alternative configuration) was 98.2 and 101.2, respectively. Subsequent calculations were performed using this alternative and presumably correct configuration only.

One further cycle of refinement was performed and the final values of the R factor and weighted R factor, $R_w = [\sum w(F_o - F_c)^2/wF_o^2]^{1/2}$, were 4.0% and 4.3%. The error in an observation of unit weight was 0.98. A final difference Fourier showed no peaks higher than 0.3 e $Å^{-3}$. The final values of the positional and thermal parameters for the nongroup atoms and their standard deviations, calculated from the inverse matrix, are given in Table I.[13] The phenyl ring atoms were refined as groups and the parameters are given in Table II. Table III lists the fractional coordinates (derived from the group parameters) and the thermal parameters for the carbon atoms in the groups. Table IV gives the root-mean-square amplitudes of vibration for those atoms refined with anisotropic thermal parameters.

Description of the Structure

The crystal structure consists of the packing of the monomeric molecular units $Pt[C_6H_8][P(C_6H_5)_3]_2$; there are no exceptionally short intermolecular contacts. An overall view of the molecule is given in Figure 1; Figures 2 and 3 show the coordination sphere around platinum and details of the coordinated olefin moiety from viewpoints important with respect to the molecular structure. The olefin moiety can be considered as two square, four-membered rings with a common edge: it has mm symmetry within experimental error and some parameters describing its structure are given in Table V. The listed torsion angles show that the vectors describing the sides of each of the four-membered rings can be classed into the following pairs, each pair being mutually parallel to a good approximation: C(1)–C(2), C(4)–C(3); C(1)–C(6), C(4)–C(5); C(1)–C(4), C(2)–C(3); C(1)–C(4), C(6)–C(5). The planarity of each ring is emphasized in Figure 3 and the dihedral angle between the rings is 56 (1)°; this planarity can be compared to the analogous situation in cyclobutene and contrasted to the nonplanar array of carbon atoms in cyclobutane and bicyclo[2.2.0]hexane.[14] The separation of the olefinic carbon atoms C(1)–C(4), 1.52 (2) Å, is significantly greater than the separation (1.42 Å) observed in related complexes formed by acyclic olefins[1,2] and is close to the

Table I. Positional and Thermal Parameters for Nongroup Atoms in $Pt[C_6H_8][P(C_6H_5)_3]_2$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.80849 (3)	0.47391 (5)	0.13485 (3)	0.00258	0.00821 (5)	0.00207 (1)	0.00053 (3)	0.00012 (2)	−0.00023 (3)
P(1)	0.8101 (2)	0.3465 (3)	0.0374 (2)	0.0028	0.0087 (4)	0.0022 (1)	0.0000 (2)	0.0004 (1)	−0.0003 (1)
P(2)	0.7079 (2)	0.6187 (3)	0.1274 (2)	0.0026 (1)	0.0083 (4)	0.0019 (1)	0.0003 (2)	0.0001 (1)	−0.0003 (2)

Atom	x	y	z	B_{iso}, Å^2	Atom	x	y	z	B_{iso}, Å^2
C(1)	0.8612 (8)	0.5209 (16)	0.2254 (7)	5.4 (3)	H22[b]	0.9521	0.6426	0.2631	8.0
C(2)	0.9304 (11)	0.6198 (18)	0.2205 (10)	7.7 (5)	H31[b]	0.9846	0.5238	0.1363	7.4
C(3)	0.9726 (9)	0.5023 (17)	0.1820 (8)	7.1 (4)	H32[b]	1.0167	0.4705	0.2044	7.4
C(4)	0.9067 (9)	0.4110 (15)	0.1896 (8)	5.6 (4)	H51[b]	0.9351	0.2947	0.2763	7.0
C(5)	0.8911 (10)	0.3207 (17)	0.2524 (9)	6.7 (4)	H52[b]	0.8629	0.2401	0.2423	7.0
C(6)	0.8453 (9)	0.4337 (15)	0.2862 (8)	6.3 (4)	H61[b]	0.8671	0.4673	0.3270	6.7
H21[b]	0.9215	0.6993	0.1938	8.0	H62[b]	0.7935	0.4120	0.2921	6.7

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] None of the parameters for this atom were varied in the refinement.

Table II. Group[a] Parameters[b] in $Pt[C_6H_8][P(C_6H_5)_3]_2$

Group	x_c	y_c	z_c	ϕ	θ	ρ
1A	0.8969 (3)	0.4947 (5)	−0.0863 (3)	−0.790 (8)	−2.391 (6)	−1.546 (8)
1B	0.8917 (3)	0.0514 (6)	0.0536 (3)	−2.861 (7)	−2.511 (6)	1.283 (7)
1C	0.6476 (4)	0.2538 (6)	−0.0213 (3)	−3.025 (6)	−2,701 (6)	−0.356 (6)
2A	0.5473 (3)	0.4821 (6)	0.1664 (2)	−2.751 (5)	2.852 (6)	0.237 (5)
2B	0.6838 (4)	0.75.7 (5)	−0.0209 (3)	1.794 (5)	−3.139 (5)	−1.141 (5)
2C	0.7146 (3)	0.8932 (6)	0.2209 (3)	0.744 (7)	2.361 (5)	0.936 (7)

[a] Each set of six parameters applies to the carbon and hydrogen atoms of a phenyl ring. [b] The parameters have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

Table III. Thermal Parameters and Derived Fractional Coordinates of Phenyl Group Carbon Atoms in $Pt[C_6H_8][P(C_6H_5)_3]_2$

Ring	Atom	B_{iso}, Å^2	x	y	z
1A	C(1)	4.1	0.8573	0.4284	−0.0344
	C(2)	5.1	0.9122	0.5247	−0.0195
	C(3)	6.3	0.9513	0.5902	−0.0711
	C(4)	6.1	0.9361	0.5602	−0.1375
	C(5)	6.3	0.8819	0.4651	−0.1530
	C(6)	5.1	0.8424	0.3990	−0.1018
1B	C(1)	4.1	0.8543	0.1813	0.0452
	C(2)	5.1	0.8583	0.1170	0.1077
	C(3)	6.2	0.8905	−0.0118	0.1158
	C(4)	6.0	0.9237	−0.0768	0.0619
	C(5)	6.2	0.9250	−0.0142	−0.0003
	C(6)	5.1	0.8930	0.1146	−0.0089
1C	C(1)	3.6	0.7198	0.2906	0.0011
	C(2)	4.6	0.6905	0.2906	0.0156
	C(3)	5.7	0.6189	0.1263	−0.0067
	C(4)	5.5	0.5764	0.2175	−0.0433
	C(5)	5.7	0.6048	0.3447	−0.0580
	C(6)	4.6	0.6764	0.3817	−0.0359
2A	C(1)	2.8	0.6163	0.5442	0.1505
	C(2)	3.8	0.6060	0.4047	0.1413
	C(3)	5.0	0.5375	0.3436	0.1572
	C(4)	4.8	0.4793	0.4209	0.1822
	C(5)	5.0	0.4888	0.5590	0.1915
	C(6)	3.8	0.5570	0.6210	0.1757
2B	C(1)	3.0	0.6913	0.6930	0.0436
	C(2)	4.0	0.6221	0.6957	0.0112
	C(3)	5.1	0.6149	0.7536	−0.0528
	C(4)	4.9	0.6764	0.8091	−0.0846
	C(5)	5.1	0.7453	0.8075	−0.0531
	C(6)	4.0	0.7530	0.7499	0.0109
2C	C(1)	3.1	0.7105	0.7757	0.1802
	C(2)	4.1	0.6802	0.8988	0.1583
	C(3)	5.2	0.6845	1.0151	0.1988
	C(4)	5.0	0.7187	1.0092	0.2610
	C(5)	5.2	0.7488	0.8879	0.2833
	C(6)	4.1	0.7449	0.7712	0.2432

Table IV. Root-Mean-Square Amplitudes of Principal Axes of Vibration for $Pt[C_6H_8][P(C_6H_5)_3]_2$

Pt	0.185 (1)	0.206 (1)	0.212 (1)
P(1)	0.188 (6)	0.206 (5)	0.227 (6)
P(2)	0.183 (6)	0.204 (6)	0.208 (5)

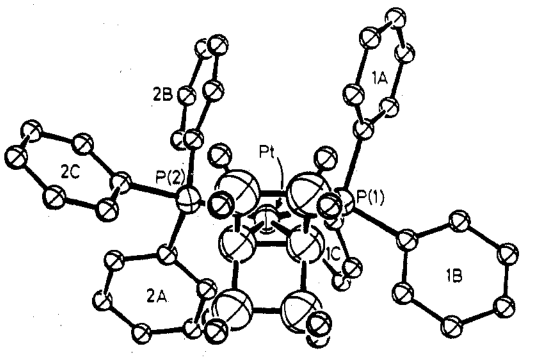

Figure 1. General view of a molecule of $Pt[C_6H_8][P(C_6H_5)_3]_2$. The platinum and phosphorus atoms are represented by 50% probability ellipsoids and all other atoms have been assigned artificial thermal parameters for the purpose of clarity. The hydrogen atoms of the triphenylphosphine ligands are omitted. The ring nomenclature is specified in this figure.

Table V. Stereochemistry of the Coordinated $\Delta^{1,4}$-Bicyclo[2.2.0]hexene Moiety in $Pt[C_6H_8][P(C_6H_5)_3]_2$

(i) Bond Lengths, Å

C(1)–C(4)	1.52 (2)		
C(1)–C(2)	1.56 (2)	C(4)–C(3)	1.48 (2)
C(1)–C(6)	1.50 (2)	C(4)–C(5)	1.54 (2)
C(2)–C(3)	1.56 (2)	C(5)–C(6)	1.53 (2)

(ii) Bond Angles, Deg

C(1)–C(4)–C(3)	92 (1)	C(4)–C(1)–C(2)	89 (1)
C(1)–C(4)–C(5)	86 (1)	C(4)–C(1)–C(6)	94 (1)
C(4)–C(3)–C(2)	91 (1)	C(1)–C(2)–C(3)	87 (1)
C(4)–C(5)–C(6)	92 (1)	C(1)–C(6)–C(5)	88 (1)
C(2)–C(1)–C(6)	123 (1)	C(3)–C(4)–C(5)	125 (1)

(iii) Torsion Angles, Deg

C(1)–C(2)–C(3)–C(4)	−1.6 (13)	C(1)–C(6)–C(5)–C(4)	0.3 (12)
C(1)–C(4)–C(3)–C(2)	1.6 (14)	C(1)–C(4)–C(5)–C(6)	0.3 (12)

separation (1.50 Å) observed in the 1,2-dimethylcyclopropene complex.[4] The other six carbon–carbon bond lengths range from 1.48 (2) to 1.56 (2) Å (mean 1.53 Å); none of these bond lengths can be considered significantly different from the mean value which is typical for carbon atoms linked by a single σ bond. The angles C(2)–C(1)–C(6) and C(3)–C(4)–C(5) are

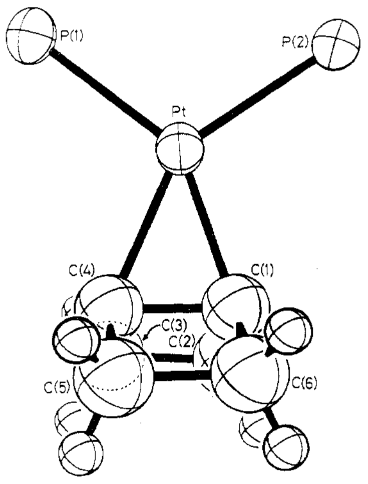

Figure 2. $Pt[C_6H_8][P(C_6H_5)_3]_2$ from a viewpoint normal to the PtC_2 plane and above the centroid of the Pt, C(1), C(4) triangle. The carbon and hydrogen atoms of the triphenylphosphine ligands have been omitted. Atom C(3) is almost completely obscured and is indicated by a noncontinuous outline; this is not done for other obscurations. The atom nomenclature is specified in this figure.

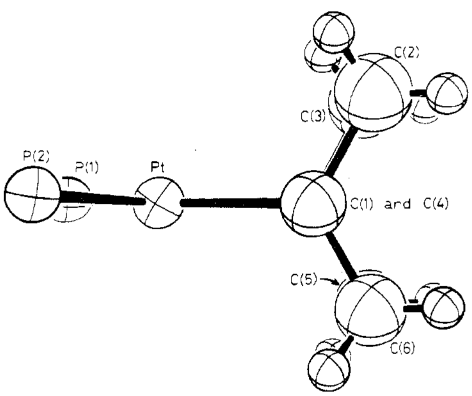

Figure 3. $Pt[C_6H_8][P(C_6H_5)_3]_2$ viewed along the C(1), C(4) vector and including the same atoms as Figure 2.

an expression of the dihedral angle between the two four-membered rings, the mean value being 124°; none of the other angles given in Table V are significantly different from their mean value, 90°. The positions of the hydrogen atoms were not determined in this experiment.

In complexes formed by acyclic olefins, $R_2C{=}CR_2$, it is customary to report the angles between the C–C vector and each of the CR_2 planes, these angles indicating how great are the changes in olefin geometry that occur upon coordination to a metal. These angles are not significant in the title compound since they will be close to 0°, no matter how great are the deviations from planarity of the olefin. An appropriate alternative is provided by the dihedral angles between the Pt, C(1), C(4) plane and the C(4), C(1), C(2), C(3) and C(4), C(1), C(6), C(5) planes; the mean of these two angles is 62° and this can be compared with the mean value of 63° observed[2] in $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$, a compound in which the olefin distortions are relatively large for acyclic olefin complexes. If the coordinated olefin were unchanged from its free geometry (and therefore planar), the angle would be 90°.

The title compound is a heterotricyclo$[2.2.1.0^{1,4}]$heptane and the bridgehead carbon atoms, C(1) and C(4), have inverted geometry (see Figure 2). One measure of this inversion is the distance along the C(1), C(4) vector of each bridgehead carbon from the plane defined by the three nonbridgehead atoms to which it is bound. In a number of tricyclic [3.2.1.0] molecules, these distances are in the range 0.07–0.09 Å.[7] In $Pt[C_6H_8][P(C_6H_5)_3]_2$, the distances are 0.15 and 0.24 Å for C(1) and C(4), respectively. Since the magnitude of these distances is a function of the atom separations, a more appropriate measure of this angular distortion is the angle between the vector from the bridgehead atom to the atom in the smallest ring and the normal to the plane through the bridgehead atom and the two other nonbridgehead atoms to which it is bound; the plane is to be defined such that the angle is <90° for an inverted bridgehead carbon atom. In the tricyclic [3.2.1.0] molecules referred to above, this angle lies in the range 75–86°. In the title compound, a [2.2.1.0] molecule, these angles are smaller, 68 and 65° for C(1) and C(4), respectively.

Table VI. Stereochemistry of the Coordination Sphere around Platinum in $Pt[C_6H_8][P(C_6H_5)_3]_2$

Parameter 1		Parameter 2		Difference,[a] parameter 1 – parameter 2
(i) Bond Lengths, Å				
Pt-P(1)	2.289 (3)	Pt-P(2)	2.278 (3)	0.010 (4)
Pt-C(4)	2.138 (16)	Pt-C(1)	2.067 (14)	0.071 (22)
(ii) Bond Angles, Deg				
C(1)-Pt-C(4)	42.2 (5)			
P(1)-Pt-P(2)	107.0 (1)			
P(1)-Pt-C(4)	105.0 (4)	P(2)-Pt-C(1)	105.8 (4)	−0.8 (6)
Pt-C(4)-C(1)	66.4 (8)	Pt-C(1)-C(4)	71.4 (8)	−5.0 (11)
Pt-C(4)-C(3)	114.9 (11)	Pt-C(1)-C(2)	116.0 (11)	−1.1 (16)
Pt-C(4)-C(5)	114.9 (11)	Pt-C(1)-C(6)	118.8 (10)	−3.9 (15)
(iii) Torsion Angles, Deg				
P(1)-Pt-C(4)-C(3)	98.1 (11)	P(1)-Pt-C(4)-C(5)	106.9 (11)	−8.8 (16)
P(2)-Pt-C(1)-C(2)	97.2 (12)	P(2)-Pt-C(1)-C(6)	98.5 (11)	−1.3 (17)
(iv) Dihedral Angles, Deg				
[Pt, C(1), C(4)]-[C(6), C(1), C(2)]				93 (1)
[Pt, C(1), C(4)]-[C(5), C(4), C(3)]				93 (1)
[Pt, C(1), C(4)]-[Pt, P(1), P(2)]				3.2 (5)
[Pt, C(1), C(4)]-[C(1), C(4), C(3), C(2)]				63 (1)
[Pt, C(1), C(4)]-[C(1), C(4), C(5), C(6)]				61 (1)

[a] Given for the parameters which would be related if there were a mirror plane normal to the Pt, C(1), C(4) plane and passing through Pt and a point midway between C(1) and C(4). Since some of the differences listed in this column are statistically significant, the molecule does not have this symmetry element.

The coordination sphere of platinum does not have the *mm* symmetry of the olefin moiety. The metal–olefin fragment does have one plane of symmetry, since the dihedral angles between the Pt, C(1), C(4) plane and the planes C(1), C(4), C(3), C(2) and C(1), C(4), C(5), C(6) do not differ significantly; these angles are 63 (1) and 61 (1)°, respectively. This local *m* symmetry does not extend to the phosphorus ligand atoms and coordination around platinum is not precisely planar, with a dihedral angle of 3.2 (5)° between the Pt, C(1), C(4) and Pt, P(1), P(2) planes. Atoms P(1) and P(2) are displaced by 0.03 (3) and 0.11 (3) Å from the Pt, C(1), C(4) plane, with both displacements having the same sense. Figure 2 shows that the platinum atom lies much closer to the C(6), C(1), C(2) plane than to the C(5), C(4), C(3) plane, the displacements being 0.53 (7) and 0.91 (7) Å, respectively. Related aspects of this asymmetry can be found in Table VI, which lists and compares some parameters describing the stereochemistry around platinum. The Pt–C(1) separation is shorter than the Pt–C(4) separation and the customary trans effect[1,2] is observed, Pt–P(1) being longer than Pt–P(2); these bond length differences are only marginally statistically significant. There are no intermolecular contacts short enough to cause this asymmetry, but there are three relatively short (<2.5 Å) intramolecular contacts between the hydrogen atoms of phenyl rings 1A, 1B, 1C and the hydrogen atoms on the olefin. While the magnitudes of these separations were not determined in this experiment, one of these contacts is apparently particularly short: the distance between H(2) of ring 1B and one of the hydrogen atoms on C(5) is 2.1 Å, calculated using the assumed fractional coordinates of these atoms. The asymmetry in the olefin–metal interaction may be a result of minimization of intramolecular contacts.

The directions of the principal axes of vibration of the platinum and two phosphorus atoms are indicated in Figures 1–3. None of these atoms vibrate with great anisotropy and corrections for thermal motion (calculated using the riding model) to the Pt–P bond lengths are negligibly small, <0.001 Å. The triphenylphosphine ligands are of normal geometry: the P–C bond lengths range from 1.83 (1) to 1.85 (1) Å, mean 1.84 Å, the Pt–P–C angles range from 114 (1) to 119 (1)°, mean 116°, and the C–P–C angles range from 101 (1) to 104 (1)°, mean 102°.

Bonding in $Pt[C_6H_8][P(C_6H_5)_3]_2$

The bonding interaction between an olefin and a metal may have two components, redistribution of the bonding electrons of the olefin through the intermediacy of the metal and a net transfer of electrons from the metal to the olefin. The ESCA technique can be used to determine whether the latter component is important in a specific complex because the binding energy of the Pt $4f_{7/2}$ electrons varies considerably with the formal oxidation state of platinum and the nature of the ligands around platinum.[15] For the series of compounds under consideration, $PtL[P(C_6H_5)_3]_2$, where L is an olefin, useful reference compounds are $Pt[P(C_6H_5)_3]_4$ and $PtCl_2[P(C_6H_5)_3]_2$ for which the Pt $4f_{7/2}$ electron binding energies are 71.7 and 73.3 eV, respectively. In $Pt[C_6H_8][P(C_6H_5)_3]_2$ there is only moderate net transfer of electron density from the metal olefin, because the Pt $4f_{7/2}$ electron binding energy is 72.2 eV, relatively close to that in the platinum(0) compound, $Pt[P(C_6H_5)_3]_4$; similar binding energies are observed in the analogous ethylene[15] and 4,4'-dinitro-*trans*-stilbene[2] complexes, and it can be assumed that the major component of the bonding in all three of these olefin complexes is redistribution of the olefin bonding electrons. By way of contrast, the analogous octafluoro-*trans*-but-2-ene complex has a more significant charge-transfer component in the bonding interaction,[2] the observed Pt $4f_{7/2}$ binding energy being 73.0 eV.

Since $\Delta^{1,4}$-bicyclo[2.2.0]hexene and cyclopropene displace ethylene from $Pt[C_2H_4][P(C_6H_5)_3]_2$, there is presumably a greater degree of electron redistribution in the strained ring complex and thus the structures should differ slightly. It has been postulated[1] that the length of a Pt–P bond is a function of the electron density in the region trans to that bond. The mean Pt–P bond length in $Pt[C_6H_8][P(C_6H_5)_3]_2$ is 2.284 Å, the same as in the 1,2-dimethylcyclopropene complex and somewhat longer than the mean length of 2.268 Å observed in the ethylene complex. The difference between these mean values, 0.016 Å, is statistically significant since the largest esd in any of these lengths is 0.003 Å. This indicates that the electron density in the region trans to phosphorus is somewhat lower in the ethylene complex than in the strained ring complexes, as expected if there is less electron redistribution in the ethylene complex. However, the mean Pt–C separation is the same in all three complexes. Since the greater electron redistribution in the strained ring complexes does not result in shorter Pt–C separations, it can be assumed that the geometrical constraints imposed by the rings result in this electron density being in orbitals not optimally shaped for short Pt–C separations.

The separation of the olefinic carbon atoms in these platinum complexes is greater by about 0.1 Å for a strained ring olefin than for an acyclic olefin. Ring strain is unlikely to be the major direct cause of this lengthening since, in the many strained-ring hydrocarbons of known structures,[14,16] there is no evidence that ring strain can cause lengthenings of this magnitude. The lengthening provides the strongest evidence that, in the strained ring complexes, there is a greater redistribution of the olefin bonding electrons (with concomitant lowering of the olefinic carbon–carbon bond order); this greater redistribution presumably occurs because there is a relatively small gap between the π and π^* energy levels in the parent olefins. The ring strain in $\Delta^{1,4}$-bicyclo[2.2.0]hexene has not been greatly relieved by coordination to platinum, and the proximity of platinum to the ring system could make available reaction pathways whereby relief of ring strain is achieved. Facile addition of ethanol to $Pt[C_6H_8][P(C_6H_5)_3]_2$ has been observed:[6] the C(1)–C(4) bond is cleaved to form $Pt[C_6H_9OC_2H_5][P(C_6H_5)_3]_2$ in which there is a cyclohexane ring constrained to the boat conformation by σ bonds from Pt to C(1) and C(4).

While this experiment provides no direct information about the structure of the parent olefin, two features can be deduced. Since each of the four-membered rings is planar in the complex, it is unlikely that they are nonplanar in the parent olefin. Although the coordinated olefin is distinctly nonplanar, its deviation from overall planarity is about the same as occurs in complexes of some acyclic olefins (which are presumably planar when free) and thus all six carbon atoms in the parent olefin could be coplanar.

Acknowledgment. The authors are indebted to the National Science Foundation for support of this work under Grant GH-39294 and by a National Science Foundation graduate fellowship.

Registry No. $Pt[C_6H_8][P(C_6H_5)_3]_2$, 54071-60-2; $Pt[C_2H_4][P(C_6H_5)_3]_2$, 12120-15-9.

Supplementary Material Available. 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 Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50300J-12-75.

References and Notes

(1) J. M. Baraban and J. A. McGinnety, *Inorg. Chem.*, **13**, 2864 (1974).
(2) J. M. Baraban and J. A. McGinnety, *J. Am. Chem. Soc.*, **97**, 4232 (1975).
(3) J. P. Visser, A. J. Schipperijn, and J. Lukas, *J. Organomet. Chem.*, **47**, 433 (1973).
(4) J. P. Visser, A. J. Schipperijn, J. Lukas, D. Bright, and J. J. DeBoer, *Chem. Commun.*, 1266 (1971).
(5) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *J. Am. Chem. Soc.*, **93**, 246 (1971).
(6) M. E. Jason, J. A. McGinnety, and K. B. Wiberg, *J. Am. Chem. Soc.*, **96**, 6531 (1974).
(7) G. J. Burgmaier, Ph.D. Dissertation, Yale University, 1970.
(8) C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, **90**, 1464 (1968).
(9) Calculations were performed on an IBM 370/158 computer and the programs used included modified version of Zalkin's FORDAP, Busing, Martin, and Levy's ORFLS (with the Doedens and Ibers subroutines for group refinements) and ORFFE, Johnson's ORTEP, and Coppens and Hamilton's DATTAP.
(10) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(11) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(12) J. A. Ibers, *Acta Crystallogr.*, **22**, 604 (1967).
(13) Supplementary material.
(14) (a) B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Anderson, and G. O. Sorensen, *J. Mol. Struct.*, **3**, 369 (1969); (b) L. Wolloe, Ph.D. Dissertation, University of Oslo, 1965; (c) B. Andersen and R. Srinivasan, *Acta Chem. Scand.*, **26**, 3468 (1972).
(15) (a) C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Am. Chem. Soc.*, **93**, 1904 (1971); (b) W. M. Riggs, *Anal. Chem.*, **44**, 830 (1972).
(16) (a) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969); (b) R. D. Suenram and M. D. Harmony, *ibid.*, **56**, 3837 (1972).