Following several cycles of full-matrix least-squares refinement, in which positional and isotropic thermal parameters were varied for the nonhydrogen atoms, a difference map revealed the hydrogen positions. Additional least-squares refinement, in which the nonhydrogen atoms were allowed to vary in both positional and anisotropic thermal parameters, converged at $R_1 = 0.0551$[14] and $R_2 = 0.0831$.[15] Scattering factors used were those of Hanson et al.,[16] and the least-squares refinement was based on minimization of $\sum w_2(|F_o| - |F_c|)^2$, with weights w_i equal to $1/\sigma(F_o)^2$. Estimated standard deviations in bond lengths (Table I) and angles (Table II), positional parameters and isotropic thermal parameters (Table IV), and anisotropic thermal parameters (Table V) were calculated from a full variance-covariance matrix in the final cycle of least-squares refinement.

Acknowledgment. This work was supported in part by grants, including departmental instrument grants for X-ray and NMR facilities, from the National Science Foundation.

Registry No. [μ-(η^5-C_5H_5)Be]B_5H_8, 71163-79-6; [$\mu_{2,3}$-(η^5-C_5H_5)Be]($\mu_{3,4}$-CH_3Zn)B_5H_7, 77123-44-5; (μ-CH_3Zn)B_5H_8, 77123-45-6; $(CH_3)_2Zn$, 544-97-8; C_5H_5BeCl, 36346-97-1; KB_5H_8, 56009-95-1.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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(14) $R_1 = \sum(|F_o| - |F_c|)/|F_o|$.

(15) $R_2 = [\sum w_i(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$, where $w_i = 1/\sigma(F_o)^2$.

(16) Hanson, H. P.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1964**, *17*, 1040-1044.

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Variations in Platinum-Carbon (sp^3) Bond Lengths. Crystal and Molecular Structure of (1,5-Cyclooctadiene)(η^1-cyclopentadienyl)methylplatinum(II), Pt(1,5-C_8H_{12})(η^1-C_5H_5)(CH_3)

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The crystal and molecular structure of the title compound has been determined by X-ray diffraction methods. The complex crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and cell dimensions $a = 6.589$ (1) Å, $b = 12.187$ (2) Å, $c = 15.447$ (2) Å, and $\beta = 95.30$ (1)°. The observed and calculated densities were 2.049 and 2.062 g/cm^3, respectively. The structure has been refined to a final R factor on F of 0.037 for 15 anisotropic nonhydrogen atoms and 2606 absorption corrected ($\mu r = 2.09$) reflections having $I > 3\sigma(I)$. The structure consists of discrete molecules with a square-planar arrangement of the carbon ligands. The platinum-methyl bond distance (2.068 (8) Å) is significantly shorter than the platinum-Cp distance (2.151 (8) Å). The platinum-olefin distance trans to the Cp ligand is shorter than the one trans to the methyl group. These facts are consistent with the previous observation that the NMR trans influence of the Cp ligand is much smaller than that of the methyl group. The differences in the bonding of the two sp^3-hybridized carbons are discussed in terms of σ-π hyperconjugation of the Pt-Cp bond with the diene.

Introduction

Recently the title compound (**1**) was prepared and some of its reactions reported.[2] This complex undergoes a Diels-Alder addition of hexafluoro-2-butyne in which the acetylene adds to the Cp ring (Cp = C_5H_5) trans to the platinum atom substituent.[3] This was taken to imply that the metal does not take part in the mechanism of the addition other than possibly acting as a bulky steric hindrance to the approach on one side of the Cp ring. This is in contrast to "metal-assisted" cycloaddition reactions observed in some iron[4] and nickel[5] systems. It was of interest, therefore, to determine the structure of **1** to establish if there was any unusual steric feature that might prevent precoordination of an acetylene.

Also of interest was the comparison of the Pt-CH_3 and Pt-(η^1-Cp) bond distances. A priori, they would be predicted to be very similar since both are single bonds to sp^3 carbon atoms. However, the Mo-CH_3 bond distance in (η^5-Cp)$_2$Mo(NO)CH_3 is about 0.1 Å shorter than the Mo-(η^1-Cp) bond distance in $Cp_3Mo(NO)$.[6] The title complex is an ideal model to investigate the generality of such differences since both types of ligands, CH_3 and η^1-Cp, are in the same complex, and they are situated trans to identical olefin ligands.

There is spectroscopic evidence that a significant difference in the bonding of the methyl and Cp groups exists in **1**. NMR coupling constants are often used to estimate the relative trans influences of different groups in platinum complexes.[7] Comparison of the J(Pt-C) and J(Pt-H) values for the COD group (COD = 1,5-cyclooctadiene) trans to the methyl and Cp ligands indicated that the NMR trans influence of the latter was much less than that of the methyl group.[2] This seems inconsistent with both groups being bound to the platinum atom by identical metal-carbon (sp^3) bonds, particularly, since other NMR studies have shown there is little or no discrimination among sp^3-hybridized carbon ligands.[8]

Experimental Section

Large, well-shaped, yellow single crystals of **1** suitable for X-ray studies were grown from diethyl ether at -20 °C. Weissenberg and precession photographs were used to determine the probable space group and a preliminary set of lattice constants indicated monoclinic, $2/m$, symmetry. The systematically absent reflections were those uniquely required by the centrosymmetric space group, $P2_1/n$ (a special

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(2) H. C. Clark and A. Shaver, *Can. J. Chem.*, **54**, 2068 (1976).

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setting of $P2_1/c—C_{2h}^5$).[9] This choice was fully supported by the results of sensitive tests for piezoelectricity[10] and by all stages of the subsequent structure determination.

A nearly cube-shaped specimen, 0.40 mm on an edge, was cut from a larger single crystal and ground to a sphere having a diameter of 0.35 mm before being glued to the end of a thin-glass fiber having a tip diameter of 0.10 mm. This crystal was then accurately centered optically on a computer-controlled four-circle Syntex P$\bar{1}$ autodiffractometer, and a total of 15 high-angle ($2\theta_{\text{Mo K}\bar{\alpha}} > 25°$) reflections, chosen to give a good sampling of reciprocal space and diffractometer settings, were used to align the crystal and calculate angular settings for each reflection. A least-squares refinement of the diffraction geometry for these 15 reflections, recorded at the ambient laboratory temperature of 20 ± 1 °C with graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.710 69 Å) gave the lattice constants a = 6.589 (1) Å, b = 12.187 (2) Å, c = 15.447 (2) Å, and β = 95.30 (1)°. A unit cell content of four $Pt(\eta^1\text{-}C_5H_5)(CH_3)(1,5\text{-}C_8H_{12})$ molecules gives a calculated density of 2.062 g/cm^3, in good agreement with the observed density of 2.049 g/cm^3 measured by flotation in aqueous zinc bromide solution.

Intensity measurements utilized graphite-monochromated Mo K$\bar{\alpha}$ radiation and the θ–2θ scanning technique with a 4° takeoff angle and a normal-focus X-ray tube. A scanning rate of 1°/min. was employed for the scan between 2θ settings 1.0° above and below the calculated Kα doublet values ($\lambda_{K\alpha_1}$ = 0.709 26 Å and $\lambda_{K\alpha_2}$ = 0.713 54 Å) of each reflection. Background counts, each lasting for half the total scan time, were taken at both ends of the scan range. A total of 4260 independent reflections having $2\theta_{\text{Mo K}\bar{\alpha}} < 63.7°$ (1.5 times the number of data in the limiting Cu K$\bar{\alpha}$ sphere) were measured in concentric shells of increasing 2θ containing approximately 1420 reflections each. The six standard reflections, measured every 300 reflections as a monitor for possible disalignment and/or deterioration of the crystal, gave no indication of either.

The linear absorption coefficient of the crystal for Mo K$\bar{\alpha}$ radiation[11] is 11.91 mm^{-1}, yielding a μr of 2.09 for the spherical crystal used in data collection. The intensities of all reflections were corrected for absorption as a strict function of scattering angle[12] before reducing them to a set of relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 4260 reflections examined, 1654 were eventually rejected as objectively unobserved by applying the rejection criterion $I < 3\sigma(I)$, where $\sigma(I)$ is the standard deviation in the intensity computed from

$$(\sigma(I))^2 = C_t + k^2B$$

C_t being the total count from scanning, k the ratio of scanning time to total background time (in this case, k = 1), and B the total background count. The heavy-atom technique, difference Fourier syntheses, and full-matrix least-squares were used with the remaining 2606 observed intensities in the determination and refinement of the structure.

The atomic coordinates of the platinum atom were readily derived from the Patterson synthesis calculated with 1672 independent data having $2\theta_{\text{Mo K}\bar{\alpha}} < 43°$ and $I > \sigma(I)$. Two cycles of least-squares refinement of the structural parameters for the platinum atom resulted in a conventional unweighted residual, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, of 0.159 and a set of phases which were sufficiently accurate to allow the location of all remaining atoms (except hydrogens) of the totally general-position asymmetric unit from a single difference Fourier synthesis. Unit-weighted full-matrix least-squares refinement of the fractional atomic coordinates and isotropic thermal parameters of the 15 crystallographically independent nonhydrogen atoms resulted in R_1 = 0.058 and a conventional weighted residual, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0.059 for 1496 independent reflections having $2\theta_{\text{Mo K}\bar{\alpha}} < 43°$ and $I > \sigma(I)$.

Utilization of anisotropic thermal parameters for all nonhydrogen atoms in further cycles of least-squares refinement gave R_1 = 0.040 and R_2 = 0.042 for 1496 reflections. When a difference Fourier synthesis calculated at this point failed to give discernible peaks at chemically anticipated positions for the hydrogen atoms, atomic positions were calculated for all hydrogen atoms except those of the methyl ligand by assuming idealized sp^2 or sp^3 geometry and a C–H bond length of 0.95 Å. Hydrogen atoms with isotropic thermal parameters of 6 Å^2 at these idealized positions (recalculated after each cycle of least-squares refinement) were included in all subsequent structure factor calculations. Additional cycles of unit-weighted full-matrix least-squares minimization of the function $w(|F_o| - K|F_c|)^2$ (where K is the scale factor and w is the weight assigned each reflection), in which structural parameters for all anisotropic nonhydrogen atoms were varied but those for isotropic nonmethyl hydrogen atoms were not, converged to the following R_1 values for various values of the $I/\sigma(I)$ rejection criterion with the more complete ($2\theta_{\text{Mo K}\bar{\alpha}} <$ 63.7°) data set: R_1 = 0.053 for 3332 reflections having $I > \sigma(I)$; R_1 = 0.043 for 2886 reflections having $I > 2\sigma(I)$; R_1 = 0.037 for 2606 reflections having $I > 3\sigma(I)$. Differences in the structural parameters resulting from these various refinements were insignificant. These and all subsequent structure factor calculations employed the atomic form factors compiled by Cromer and Mann,[13] an anomalous dispersion correction to the scattering factor of the platinum atom,[14] and a least-squares refinable extinction correction[15] of the form $1/(1 + gI_c)^{1/2}$ (where the extinction coefficient, g, refined to a final value of 5.64 × 10^{-7}).

Empirical weights ($w = 1/\sigma^2$) were then calculated from

$$\sigma = \sum_0^3 a_n|F_o|^n = 2.48 - 4.49 \times 10^{-2}F_o + 4.30 \times 10^{-4}F_o^2 + 5.38 \times 10^{-7}F_o^3$$

the a_n being coefficients derived from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$$

where the F_c values were calculated from the fully refined model by using unit weighting and an $I > 3\sigma(I)$ rejection critierion. The final cycles of full-matrix least-squares refinement utilized these weights with 2606 reflections to vary the scale factor, extinction correction, and structural parameters of the anisotropic nonhydrogen atoms; final values of 0.035 and 0.039 for R_1 and R_2, respectively, were obtained. During the final cycle of refinement, no parameter shifted by more than $0.03\sigma_p$, where σ_p is the estimated standard deviation of the parameter.

The following programs were used on an IBM 360/65 computer for this work: MAGTAPE, SCALEUP, and SCTFT$_2$, data reduction programs written by V. W. Day; FORDAP, a highly modified version of Zalkin's original Fourier and Patterson synthesis program; ORFLSE, full-matrix least-squares structure refinement program, a highly modified version of Busing, Martin, and Levy's original ORFLS; ORFFE, bond lengths and angles with standard deviations by Busing, Martin, and Levy; ORTEP2, thermal ellipsoid plotting program by C. K. Johnson; MPLANE, least-squares mean plane calculation program from L. F. Dahl's group.

Description of Structure

The structure of **1** consists of discrete molecules with a square-planar arrangement of the carbon ligands (Figures 1 and 2). The atomic coordinates and temperature factors of **1** and the calculated hydrogen positions are given in Tables I–III while Tables IV–VIII give distances and angles. The coordination sphere about the platinum atom is quite unsymmetrical. The Pt–Cp$_1$ distance is 0.083 Å longer than the Pt–C$_m$ distance. Conversely the Pt–olefin distance trans to the Cp ligand is 0.100 Å shorter than the Pt–olefin distance trans to the methyl ligand. There is a noticeable distortion of the square-planar geometry. The polyhedral edge from Cp$_1$ to C$_1$C$_2$ is longer than edge directly across from it (Figure 2). The angle at the platinum atom between the Cp ligand and

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(9) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969, p 99.

(10) The results of tests for piezoelectricity, made with a Geibe–Schiebe detector, were kindly supplied by Professor J. L. Hoard of Cornell University.

(11) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, p 166.

(12) "International Tables for X-Ray Crystallography", Vol. II, Kynoch Press, Birmingham, England, 1967, p 302.

(13) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, *A24*, 321 (1968).

(14) D. T. Cromer, *Acta Crystallogr., Sect. A*, **A18**, 17 (1965).

(15) W. H. Zacharissen, *Acta Crystallogr., Sect. A*, **A23**, 558 (1967).

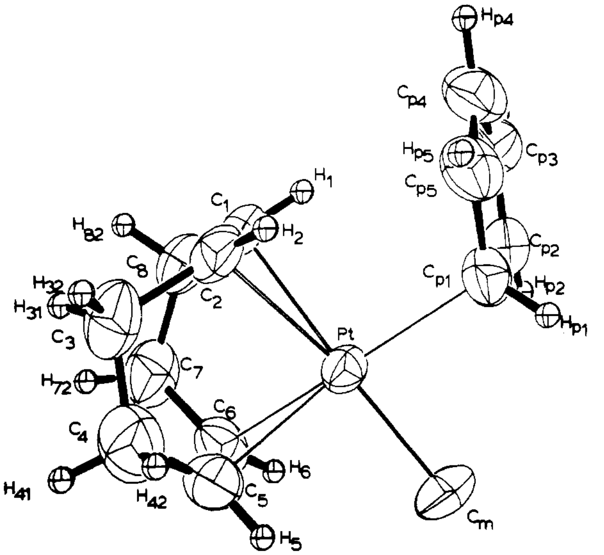


Figure 1. Perspective ORTEP drawing of the $Pt(\eta^1\text{-}C_5H_5)(CH_3)(1,5\text{-}C_8H_{12})$ molecule. All nonhydrogen atoms are represented by (50% probability) ellipsoids which reflect their refined anisotropic thermal parameters. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

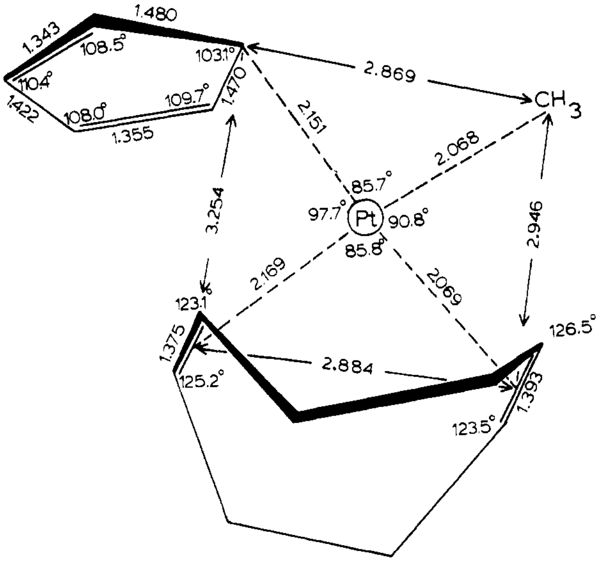


Figure 2. Diagram derived from Figure 1 showing bond lengths, angles, and polyhedral edge lengths in the $Pt(\eta^1\text{-}C_5H_5)(CH_3)(1,5\text{-}C_8H_{12})$ molecule as given in Tables IV–VII.

this olefin is 97.7°, whereas that between the methyl carbon and the C_5C_6 olefin is 90.8°.

The COD ligand in **1** is twisted; the olefin carbon atoms C_1, C_2, C_5, and C_6 are not planar. Figure 3 shows the atomic displacements from the mean plane of the eight carbon atoms of the COD ligand. As in the gas phase,[16] the twist is symmetrical with the diagonally related atoms displaced to the same extent. Thus C_1 and C_5 are closer to the platinum atom than C_2 and C_6. There are no short intermolecular contacts that might cause this effect. The final geometry of the COD ligand seems to be a compromise between the tendency for the olefins to be plane parallel in order to maximize the platinum olefin bonding and the tendency to twist the ring in order to minimize the eclipsing of the hydrogen atoms on neighboring methylene groups.

Table I. Atomic Coordinates in Crystalline $Pt(\eta^1\text{-}C_5H_5)(CH_3)(1,5\text{-}C_8H_{12})$[a]

	fractional coordinates		
atom type[b]	10^4x	10^4y	10^4z
C_m	2658 (15)	−237 (7)	689 (6)
C_{p1}	3119 (15)	1997 (8)	154 (5)
C_{p2}	1122 (13)	2364 (8)	396 (5)
C_{p3}	1130 (15)	3468 (8)	495 (6)
C_{p4}	3035 (16)	3871 (9)	268 (7)
C_{p5}	4215 (16)	3040 (9)	43 (6)
C_1	4874 (13)	2547 (7)	2148 (5)
C_2	6709 (14)	2247 (7)	1862 (6)
C_3	8322 (15)	1600 (11)	2418 (7)
C_4	8156 (18)	377 (11)	2295 (8)
C_5	6019 (17)	−62 (8)	2133 (6)
C_6	4339 (16)	260 (8)	2555 (5)
C_7	4459 (17)	1062 (10)	3294 (5)
C_8	4176 (16)	2263 (9)	3024 (6)
atom type	10^5x	10^5y	10^5z
Pt	42145 (4)	10714 (2)	12880 (2)

[a] Figures in parentheses are the estimated standard deviations.
[b] Each symbol for an atom of the cyclopentadienyl ring carries a literal subscript p to identify it as part of that ring and a numerical subscript that follows the numbering scheme used in Figures 1–3 to distinguish atoms of the same element. Numerical subscripts are used to distinguish atoms of the same element within the cyclooctadienyl ring in accordance with Figures 1–3. The methyl carbon is denoted by the symbol C_m.

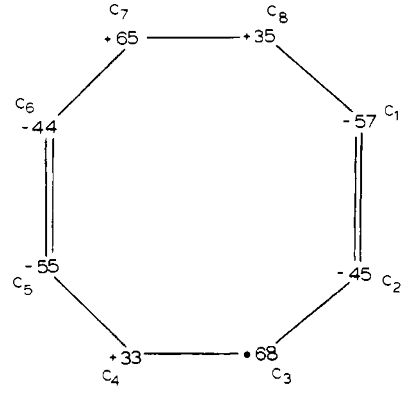
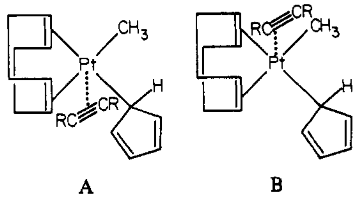


Figure 3. Diagram to illustrate the nonplanarity of the $1,5\text{-}C_8H_{12}$ ligand. Symbols for the atoms of the ligand are labeled in agreement with Figure 1. Numbers represent the atomic displacements, in units of 0.01 Å, from the mean plane of the eight carbon atoms of the cyclooctadiene ligand, described by the equation $-0.438X - 0.092Y - 0.894Z = -5.080$, where X, Y, and Z are the orthogonal coordinates measured in Å along a, b, and c, respectively, of the crystallographic coordinate system.

Discussion

The structure of **1** is fairly crowded about the platinum atom. Examination of the structure and of models of other rotamers of the Cp group that might be possible in solution suggests that the diene residue of the Cp ring is quite hindered on the side of the platinum atom. There does not appear to be enough room for prior coordination of an acetylene such that is could closely approach the diene as in A. This is



consistent with the observation that the cycloaddition of

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(16) O. Bastiansen, H. M. Seip, and J. E. Boggs, "Perspectives in Structural Chemistry", Vol. IV, J. D. Dunitz and J. A. Ibers, Eds., Wiley, New York, 1971, p 144.

Table II. Anisotropic Thermal Parameters in Pt(η^1-C_5H_5)(CH_3)(1,5-C_8H_{12})[a]

atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[b] Å^2
Pt	3.45 (1)	3.15 (1)	2.69 (1)	−0.27 (1)	0.27 (1)	−0.28 (1)	3.1
C_m	5.3 (4)	3.8 (4)	4.8 (4)	−1.5 (3)	0.6 (3)	−1.4 (3)	4.3
C_{p1}	6.1 (5)	4.6 (4)	2.8 (3)	0.5 (4)	−0.1 (3)	0.3 (3)	4.3
C_{p2}	4.0 (4)	5.0 (4)	3.7 (3)	0.1 (3)	−0.2 (3)	0.1 (3)	4.2
C_{p3}	5.0 (4)	4.7 (4)	4.3 (4)	0.3 (3)	0.4 (3)	0.4 (3)	4.6
C_{p4}	6.1 (5)	4.6 (4)	5.4 (4)	−0.3 (4)	0.3 (4)	1.7 (4)	5.1
C_{p5}	5.6 (5)	5.5 (5)	3.9 (4)	−0.5 (4)	1.2 (3)	1.5 (3)	4.6
C_1	4.3 (4)	3.9 (4)	3.7 (3)	−0.6 (3)	−0.6 (3)	−1.1 (3)	3.8
C_2	4.2 (4)	4.3 (4)	4.7 (4)	−1.6 (3)	−0.6 (3)	−0.3 (3)	4.1
C_3	3.4 (4)	7.6 (6)	6.5 (5)	−0.4 (4)	−0.9 (4)	−0.5 (5)	5.4
C_4	5.0 (5)	7.5 (7)	7.4 (7)	1.2 (5)	−0.8 (5)	−0.1 (6)	6.4
C_5	6.2 (5)	4.1 (4)	4.5 (4)	0.7 (4)	0.1 (4)	0.2 (3)	4.8
C_6	5.8 (5)	5.1 (4)	3.3 (3)	0.8 (4)	0.5 (3)	1.0 (3)	4.5
C_7	6.8 (5)	7.0 (6)	2.9 (3)	−0.4 (5)	0.5 (3)	−0.2 (4)	5.2
C_8	6.0 (5)	5.6 (5)	3.3 (3)	−0.3 (4)	0.1 (3)	−1.4 (3)	4.6

[a] The number in parentheses that follows each B value is the estimated standard deviation in the last significant figure. The B_{ij}'s in Å^2 are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a^*_i a^*_j$. [b] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Calculated Atomic Coordinates for Hydrogen in Crystalline Pt(η^1-C_5H_5)(CH_3)(1,5-C_8H_{12})

	fractional coordinates		
atom type[a]	10^4x	10^4y	10^4z
H_{p1}	2983	1586	−373
H_{p2}	−6	1897	470
H_{p3}	51	3899	683
H_{p4}	3419	4623	274
H_{p5}	5533	3110	−156
H_1	3972	2968	1763
H_2	6985	2451	1291
H_{31}	8192	1763	3011
H_{32}	9628	1828	2271
H_{41}	8783	37	2805
H_{42}	8879	185	1812
H_5	5791	−615	1700
H_6	3047	−45	2364
H_{71}	3428	880	3662
H_{72}	5759	990	3611
H_{81}	2766	2434	3011
H_{82}	4921	2704	3449

[a] The subscript p is used to distinguish the hydrogen atoms on the cyclopentadienyl ring. The first numerical subscript denotes the carbon atom to which the hydrogen atom is bonded; the second number, when given, is used to distinguish atoms of the same element.

Table IV. Bond Distances (Å) and Polyhedral Edge Lengths (Å) in the Coordination Group of Pt(η^1-C_5H_5)(CH_3)(1,5-C_8H_{12})[a]

type	length	type	length
Pt–C_m	2.068 (8)	$C_{p1}\cdots C_{1,2}$[b]	3.254
Pt–C_{p1}	2.151 (8)	$C_m\cdots C_{5,6}$[b]	2.946
Pt–C_1	2.254 (8)	$C_m\cdots C_5$	3.002 (15)
Pt–C_2	2.296 (8)	$C_m\cdots C_6$	3.052 (13)
Pt–C_5	2.177 (9)	$C_{p1}\cdots C_1$	3.259 (11)
Pt–C_6	2.188 (8)	$C_{p1}\cdots C_2$	3.391 (12)
Pt–$C_{1,2}$[b]	2.169	$C_1\cdots C_5$	3.269 (13)
Pt–$C_{5,6}$[b]	2.069	$C_2\cdots C_6$	3.124 (13)
$C_{1,2}\cdots C_{5,6}$[b]	2.884	$C_1\cdots C_6$	2.887 (13)
$C_m\cdots C_{p1}$	2.869 (13)	$C_2\cdots C_5$	2.887 (13)

[a] The figure in parentheses following each individual distance is the estimated standard deviation in the last significant figure. [b] $C_{1,2}$ and $C_{5,6}$ refer to midpoints of the C_1=C_2 and C_5=C_6 bonds of the COD ligand, respectively. Distances involving these positions are reported without estimated standard deviations.

hexafluoro-2-butyne occurred trans to the platinum atom. However, the reactions of **1** with small molecules such as CO and phosphites[2] indicate that coordination such as in B may be possible. This might still have an effect on the reaction since in B the acetylene should be even more electrophilic than when uncoordinated. Kinetic studies are needed to test this possibility, although we feel it is unlikely.

The most interesting feature of the structure is the difference in the metal–carbon (sp^3) bond distances. The values fall on either side of the sum of the atomic radii (Pt–C(sp^3) = 2.09 Å[17]) but within the extremes previously reported.[18] Comparisons with other structures may be misleading since the systems studied vary greatly in the number and type of substituent on the sp^3-carbon atom and in the type of ligand trans to it. However, the significantly longer Pt–CH_3 distance with respect to the Pt–Cp distance is consistent with the observations[6] on the Mo–CH_3/Mo–Cp system previously mentioned. In the case of **1**, there is the additional spectroscopic evidence that the NMR trans influence of the Cp ligand is much smaller than that of the CH_3 group.[2] Comparing the bond distances of the olefin ligands also indicates that the Cp ligand has a weaker structural trans influence since the metal–olefin distance trans to it is shorter than the one trans to the CH_3 ligand.

The trans influence of a ligand is thought to depend on the hybridization of the metal–ligand bond.[7] Differences in the trans influence of similar groups such as CH_3 and Cp in complexes such as **1** are due to differences in the relative contributions of the metal s, p, and d orbitals to the hybrid bonding orbital to each group. The low trans influence of the Cp group with respect to the CH_3 ligand, as observed in the NMR coupling constants and in the bond distances, is consistent with a greater relative contribution of the platinum p orbital (or conversely less s orbital) to the Pt–Cp bond than to the Pt–CH_3 bond.

The crowded nature of the coordination sphere in **1** raises the question that the differences observed might be due to steric effects. In situations such as this it is impossible to completely rule out steric effects, but fortunately examination of a related complex does seem to indicate their reduced importance here. The structue of the Diels–Alder reaction

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Table V. Bond Angles (Deg) Subtended at the Pt Atom in the Coordination Group of $Pt(\eta^1\text{-}C_5H_5)(CH_3)(1,5\text{-}C_8H_{12})$[a]

type	angle[b]		type	angle[b]	
C_mPtC_{p1}	85.7 (4)		C_1PtC_5	95.1 (3)	91.7 (4, 34, 34)
$C_{p1}PtC_{1,2}$[c]	97.7		C_2PtC_6	88.3 (4)	
$C_mPtC_{5,6}$[c]	90.8		$C_{p1}PtC_{5,6}$[c]	176.5	
$C_{1,2}PtC_{5,6}$[c]	85.8		$C_mPtC_{1,2}$[c]	175.9	
C_mPtC_5	90.0 (4)	90.8 (4, 8, 8)	$C_{p1}PtC_5$	160.8 (4)	161.1 (4, 3, 3)
C_mPtC_6	91.6 (4)		$C_{p1}PtC_6$	161.4 (4)	
$C_{p1}PtC_1$	95.4 (3)	97.4 (4, 20, 20)	C_mPtC_1	160.0 (4)	162.1 (4, 21, 21)
$C_{p1}PtC_2$	99.3 (4)		C_mPtC_2	164.1 (4)	
C_1PtC_6	81.0 (3)	80.7 (4, 4, 4)	C_1PtC_2	35.2 (3)	36.2 (4, 10, 10)
C_2PtC_5	80.3 (4)		C_5PtC_6	37.2 (4)	

[a] The figure in parentheses following each individual angle is the estimated standard deviation in the last significant figure. [b] Average values given throughout; the figures in parentheses following each averaged value are the root-mean-square value of the estimated standard deviation for an individual datum, the mean deviation, and maximum deviation from the average value. [c] Angles involving these positions are reported without estimated standard deviations.

Table VI. Bond Lengths (Å) for the Cyclopentadienyl and Cyclooctadiene Ligands of $Pt(\eta^1\text{-}C_5H_5)(CH_3)(1,5\text{-}C_8H_{12})$

type	length		type	length	
$C_{p1}\text{-}C_{p5}$	1.480 (13)	1.457 (13, 24, 35)[a]	$C_2\text{-}C_3$	1.522 (14)	1.512 (15, 9, 16)
$C_{p1}\text{-}C_{p2}$	1.470 (13)		$C_6\text{-}C_7$	1.500 (14)	
$C_{p3}\text{-}C_{p4}$	1.422 (14)		$C_3\text{-}C_4$	1.505 (17)	
$C_{p2}\text{-}C_{p3}$	1.355 (14)	1.349 (15, 6, 6)	$C_7\text{-}C_8$	1.528 (14)	
$C_{p4}\text{-}C_{p5}$	1.343 (15)		$C_4\text{-}C_5$	1.506 (16)	
$C_1\text{-}C_2$	1.375 (13)	1.384 (14, 9, 9)	$C_8\text{-}C_1$	1.509 (12)	
$C_5\text{-}C_6$	1.393 (14)				

[a] Average values given throughout. See footnote *b* in Table V.

Table VII. Bond Angles (Deg) for the Cyclopentadienyl and Cyclooctadienyl Rings in $Pt(\eta^1\text{-}C_5H_5)(CH_3)(1,5\text{-}C_8H_{12})$

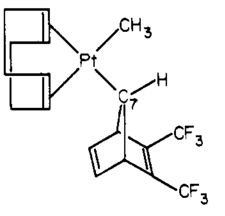
type	angle		type	angle	
$C_{p2}C_{p1}C_{p5}$	103.1 (8)		$C_8C_1C_2$	125.2 (9)	125.9 (10, 6, 7)
$C_{p1}C_{p2}C_{p3}$	109.7 (8)	109.2 (9, 9, 12)[a]	$C_4C_5C_6$	126.5 (10)	
$C_{p2}C_{p3}C_{p4}$	108.0 (9)		$C_1C_2C_3$	123.1 (8)	123.3 (9, 2, 2)
$C_{p3}C_{p4}C_{p5}$	110.4 (9)		$C_5C_6C_7$	123.5 (10)	
$C_{p4}C_{p5}C_{p1}$	108.5 (8)		$C_2C_3C_4$	113.8 (9)	114.4 (8, 6, 6)
			$C_6C_7C_8$	114.9 (7)	
			$C_3C_4C_5$	115.4 (9)	115.3 (8, 2, 2)
			$C_7C_8C_1$	115.1 (7)	

[a] Average values given throughout. See footnote *b* of Table V.

Table VIII. Short Intramolecular Nonbonded Contacts (Å) in $Pt(\eta^1\text{-}C_5H_5)(CH_3)(1,5\text{-}C_8H_{12})$

type	dist	type	dist
$C_{p1}\cdots H_1$	2.76	$C_{p5}\cdots H_2$	2.63
$C_{p2}\cdots H_1$	2.79	$C_{p4}\cdots H_{72}$	2.85
$C_{p3}\cdots H_1$	2.65	$C_m\cdots H_5$	2.51
$C_{p4}\cdots H_1$	2.58	$C_m\cdots H_6$	2.59
$C_{p5}\cdots H_1$	2.68	$C_m\cdots H_{p1}$	2.78

product between **1** and $CF_3C{\equiv}CCF_3$ has been determined and is shown below (**2**).[19] It might be argued that the crowding



2

between the diene residue of the Cp ligand and the COD olefin cis to it causes the bond distances to these ligands to be longer, thus explaining the differences. However, **2** is identical to **1** except for the addition of the acetylene to the Cp ring which causes the atoms Cp_3 and Cp_4 of the latter to bend even closer to the COD ligand. The bond distances in **2** do not follow the same trend as in **1**. There is no difference between the two sp^3-carbon ligands: $Pt\text{-}CH_3 = 2.054\ (14)$, $Pt\text{-}C_7 = 2.054\ (10)$, $Pt\text{-}C_1C_2$ (average) = 2.259 (13), and $Pt\text{-}C_5C_6$ (average) = 2.255 (12) Å. Moreover, while the resonances due to the vinyl protons of the two different COD olefins in **2** were resolved in the NMR, the $J(\text{Pt-H})$ values were identical, and no assignment with respect to being cis or trans to the CH_3 ligand could be made.[3] Thus the NMR trans influences of both sp^3-carbon ligands in **2** are also very similar. It is reasonable to conclude that the differences in the NMR trans influences observed for **1** are not due primarily to steric effects. While crowding in **1** may account for some of the differences between the two ligands, clearly an explanation based on simple steric effects is inadequate since complex **2** would be expected to be just as crowded.

The electronic and steric differences in the bonding of the Cp and CH_3 ligands raises the possibility that hyperconjugation of the electrons in the Pt–Cp bond with the diene residue of the Cp ring ($\sigma\text{-}\pi$) may be important. Similar $\sigma\text{-}\pi$ hyperconjugation has been postulated for cyclopentadiene,[20] silylcyclopentadienes,[21] and (pentachlorocyclopentadienyl)-mercurials.[22] Comparison of the energies of platinum 6s and

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6p orbitals[23] with the levels calculated for cyclopentadiene[20,24] suggests that hyperconjugation should favor a high contribution of the 6p orbital in the Pt–Cp bond. This means that it would have more 6p character (less 6s) than the Pt–CH_3 bond. Thus the presence of hyperconjugation in **1** would lead to the prediction that the Pt–Cp bond would be longer and have a weaker NMR and structural trans influence than the Pt–CH_3 bond, as was observed. Hyperconjugation is not possible for **2**, where the diene no longer exists; thus the close similarity of the NMR trans influences observed for the two sp^3-carbon ligands is expected.

Ultraviolet data for substituted cyclopentadienes have been analyzed and used as a criterion to predict the presence or absence of σ–π hyperconjugation.[22a] The value of the lowest band ($\pi_2 \rightarrow \pi_3{}^*$) is low (4.0 eV) for molecules such as $C_5Cl_4(OCH_3)_2$ where hyperconjugation is not expected due to the electronegativity of the substituent. The same band in the spectrum of **1** appears at 4.8 eV, very close to the values for C_5H_5 (4.8 eV) and $C_5H_5SiMe_3$ (5.1 eV) for which hyperconjugation is thought to be important. Thus the ultraviolet spectrum of **1** is also consistent with the postulate of hyperconjugation.

The spectroscopic and structural features of **1** are consistent with the postulate that steric and hyperconjugative effects cause the Pt–Cp bond to be quite different from Pt–CH_3 bond. The consistency of these features with hyperconjugation is particularly noteworthy. The latter phenomenon has been correlated[21] with the ease of fluxional[25] behavior and other ground-state parameters of group 4A cyclopentadienyl complexes. The Cp ring in **1** is nonrigid and exhibits a sharp line in its ^{1}H NMR spectrum even at −90 °C.[2] Thus, the barrier to rearrangement in transition-metal η^1-Cp complexes may also be directly related to the degree of σ–π hyperconjugation of the M–Cp bond.

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Supplementary Material Available: Listing of structure amplitudes (12 pages). Ordering information is given on any current masthead page.

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Structure of the Diels–Alder Product from Reaction of Hexafluoro-2-butyne with the η^1-C_5H_5 Ring in (1,5-Cyclooctadiene)(η^1-cyclopentadienyl)methylplatinum(II)

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A three-dimensional X-ray structure analysis has shown that the Diels–Alder ($2\pi + 4\pi$) addition of $CF_3C{\equiv}CCF_3$ to the η^1-C_5H_5 ring in Pt(COD)(η^1-C_5H_5)(CH_3) (**1**), where COD = 1,5-C_8H_{12}, occurs from the side opposite the platinum atom to give the norbornadiene derivative Pt(COD)(7-η-$C_9F_6H_5$)(CH_3) (**2**). Crystals are monoclinic, space group $P2_1/n$, with four molecules in a cell of dimensions a = 23.606 (5) Å, b = 8.361 (3) Å, c = 8.936 (2) Å, and β = 93.30 (1)°. Full-matrix least-squares refinement on F converged at R = 0.072. The molecule is a square-planar Pt(II) complex with equal Pt–C(sp^3) distances: Pt–CH_3, 2.054 (14) Å; Pt–C(7), 2.054 (10) Å. The Pt–olefin distances are very similar. This is consistent with the similarity of the NMR trans influences previously found for the two carbon sp^3 ligands in **2**.

Introduction

Cycloaddition reactions between electrophiles and transition-metal-coordinated polyolefins have been known for some time.[2-10] Of the many examples of this class of reaction, the recent applications to the synthesis of natural product derivatives[11] are among the most interesting. It is clear that these sophisticated schemes are based[12] upon a great many investigations of simpler systems. The metal can play any one or more of a number of crucial roles by: (a) lifting symmetry constraints thus permitting symmetry forbidden thermal cycloadditions, (b) producing a template effect via coordination

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