

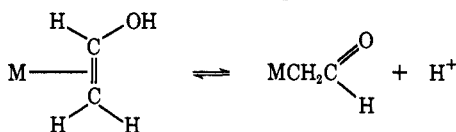
The Structure of a *Dihapto*(vinyl alcohol) Complex of Platinum(II)

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Abstract: The crystal and molecular structure of acetylacetonatochloro(1,2-*dihapto*(vinyl alcohol))platinum(II), PtCl(acac)(H₂CCHOH), has been determined from X-ray counter data. The molecular structure contains a metal to vinyl alcohol linkage which is intermediate between a conventional *dihapto* olefin (π -olefin) complex and a σ -bonded aldehyde complex. The principal coordination plane of the platinum atom does not bisect the olefin bond, as usually found in Pt(II) π -olefin structures. Instead the β carbon lies 0.09 Å below the plane, and the midpoint of the olefin bond is 0.59 Å above this plane. The Pt-C bond lengths are significantly different (2.098 (8) Å to β carbon and 2.222 (8) Å to α carbon) although both carbon atoms are within bonding distance of the metal. The trans influence of the vinyl alcohol is intermediate between those of a π -bonded olefin and a σ -bonded carbon atom. This is reflected in the Pt-O bond lengths of 1.994 (5) and 2.044 (5) Å. This is the first X-ray structural study of a vinyl alcohol complex. Crystallographic data are space group $P2_1/c$; $a = 8.556$ (7), $b = 10.826$ (5), $c = 10.727$ (4) Å; $\beta = 75.72$ (4)°; and $Z = 4$. The final conventional and weighted R values are 0.030 and 0.035.

Although vinyl alcohol is unstable with respect to its tautomer, acetaldehyde, it can be isolated as a ligand with metals which form olefin complexes. Three such complexes have been isolated: [PtCl₂(H₂CCHOH)]₂,¹ Fe(C₆H₅)(CO)₂(H₂CCHOH),² and PtCl(acac)(H₂CCHOH),³ where acac⁻ is the acetylacetonate anion. Two of us have previously reported³ nmr evidence for a very rapid ($k > 50 \text{ sec}^{-1}$) equilibrium in solution between vinyl alcohol and β -oxoethyl forms of the latter two complexes.



In view of the amount of atomic motion implied in the drawing and because the dissociation is very rapid, one might expect the structure of a vinyl alcohol complex to be considerably distorted toward the ionized β -oxoethyl complex. Since no structural work on vinyl alcohol complexes has been reported, we felt a single-crystal X-ray diffraction study of acetylacetonatochloro(π -vinyl alcohol)platinum(II) would be desirable. We were further prompted to investigate this complex because the structural effects of substituting electron donating or withdrawing atoms on ethylene can help to illuminate the finer details of olefin-transition metal bonding. Such data on Pt(II) complexes are rare, although a variety of Pt(0) olefin complexes have been studied.⁴⁻⁶ Therefore we have carried out a single-crystal X-ray study of PtCl(acac)(H₂CCHOH) and report the results here.

Experimental Section

X-Ray Data Collection. Air-stable yellow crystals of the compound, prepared as previously described,³ were grown from

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methylene chloride-heptane solution by slow evaporation at ambient conditions. A blade-shaped crystal of approximate dimensions 0.028 × 0.11 × 0.34 mm was examined on a Syntex P1 diffractometer equipped with a graphite-crystal, incident-beam monochromator. The operation of the diffractometer has been described previously.⁷ The following data were obtained; monoclinic space group $P2_1/c$, $a = 8.556$ (7) Å, $b = 10.826$ (5) Å, $c = 10.727$ (4) Å, $\beta = 75.72$ (4)°, $V = 963.0$ (9) Å³, $\rho_{\text{calcd}} = 2.58 \text{ g cm}^{-3}$ for $Z = 4$ and mol wt = 363.70, $\rho_{\text{obsd}} = 2.70$ (3) g cm⁻³ as measured by flotation in a methylene iodide-carbon tetrachloride mixture.

From ω scans of several strong reflections a width at half-height of 0.30° was measured. Data were collected at 24° using Mo K α radiation and the θ - 2θ scan technique. Scan rates from 2.0 to 24.0°/min were used with a symmetric scan range from 0.8° below the K α_1 peak to 0.8° above the K α_2 peak.

As a check on crystal stability, the intensities of four reflections were measured periodically. Two of these dropped in intensity by 5% during the first several hundred reflections, but thereafter no evidence of crystal decomposition or electronic instability was observed.

Of the 2037 unique reflections collected in the range 0° < 2θ (Mo K α) ≤ 40°, 1517 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ is the standard deviation of the observed intensity and the parameter p used in its calculation is set to 0.05.⁷ Lorentz and polarization corrections were applied to the data.⁸ An absorption correction was calculated by the numerical integration technique.⁸ Crystal faces were identified as 100, $\bar{1}00$, 010, 0 $\bar{1}0$, 011, and 0 $\bar{1}1$. The shape of a rounded end of the crystal was approximated by faces 0 $\bar{1}1$, 00 $\bar{1}$, and 0 $\bar{1}1$. Crystal dimensions were carefully measured under a microscope with a micrometer eyepiece. For a linear absorption coefficient of the material equal to 159 cm⁻¹, the transmission coefficients ranged from 0.20 to 0.64. A secondary extinction correction was applied to the data; the final value of the coefficient was 6.2(18) × 10⁻⁶.

Solution and Refinement of the Structure. The position of the platinum atom was readily located using a three-dimensional Patterson function⁹ based on the 539 reflections with $2\theta < 30^\circ$. Following a cycle of least-squares refinement⁸ of the Pt coordinates, a difference Fourier synthesis revealed all of the nonhydrogen atoms. These atoms were included in one least-squares cycle with isotropic thermal parameters and yielded an agreement factor $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.133$. The absorption corrections were then applied

(7) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *ibid.*, in press.

(8) Computer programs used in the solution and refinement of the crystal structure are as follows: DATARED by Frenz for data reduction; JIMDAP by Ibers, which is a version of Zalkin's FORDAP Fourier program; NUCLS by Doedens and Ibers, a least-squares refinement program based on Busing and Levy's ORFLS program; SADIAN by Baur and ORFFE by Busing, Martin, and Levy for bond distances and angles; AGNOST by Cahen for absorption corrections as originally written in Coppens's DATAPP program; ORTEP by Johnson for illustrations; RSCAN by Doedens for structure factor analysis, and LIST by Snyder for listing the structure factors.

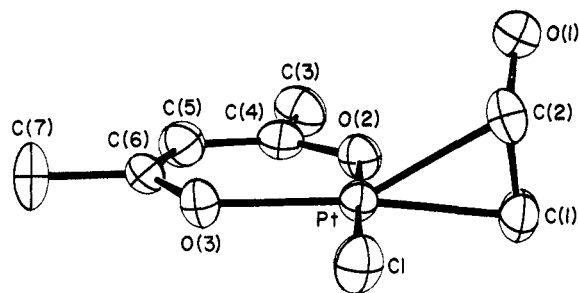


Figure 1. A view of the molecular structure of PtCl(acac)(H₂CCHOH) showing the 50% probability ellipsoids and the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

and two cycles of refinement with anisotropic temperature factors gave $R_1 = 0.033$ and $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2} = 0.042$. A difference Fourier synthesis then yielded the locations of all but one hydrogen atom, which was placed in a geometrically reasonable position by hand. Two additional cycles of refinement including positional and isotropic thermal parameters for the H atoms as variables resulted in final R values of 0.030 and 0.035. In the final cycle no parameter shifted by more than half of its standard deviation. A final difference Fourier map revealed a number of moderate ($1-2 \text{ e}/\text{\AA}^3$) peaks symmetrically disposed around the Pt atom at distances of less than 1.5 \AA . Aside from these peaks, which were not considered to be chemically significant, the largest residual electron density was $0.63 \text{ e}/\text{\AA}^3$, compared to the average hydrogen atom peak height of $0.75 \text{ e}/\text{\AA}^3$.

The function minimized in least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where the weight w is $1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$. A comparison of this function vs. $\lambda^{-1} \sin \theta$, $|F_o|$, and various classes of Miller indices revealed no unusual trends, thus suggesting that the weighting scheme was satisfactory. In the final least-squares cycle the error in an observation of unit weight was 1.06. Atomic scattering factors for Pt, Cl, C, and O were obtained from Cromer's calculations;⁹ those for H were from Stewart, Davidson, and Simpson.¹⁰ Anomalous dispersion effects for platinum were included using the values tabulated by Cromer and Liberman.¹¹

A tabulation of structure amplitudes in the form $10|F_o|$ and $10|F_c|$ (in electrons) is available.¹² The final positional parameters for nonhydrogen atoms are given in Table I; anisotropic temperature

Table I. Final Positional Parameters and Their Standard Deviations for the Nonhydrogen Atoms^a

Atom	x	y	z
Pt	0.20975 (3)	0.09905 (2)	0.30426 (3)
Cl	0.4349 (2)	0.1972 (2)	0.3334 (2)
O(1)	0.2151 (9)	0.0784 (6)	0.0243 (6)
O(2)	0.0165 (7)	0.0055 (5)	0.2846 (5)
O(3)	0.0812 (6)	0.2015 (5)	0.4549 (5)
C(1)	0.3454 (14)	-0.0207 (8)	0.1651 (8)
C(2)	0.3186 (12)	0.0809 (8)	0.0945 (8)
C(3)	-0.2522 (14)	-0.0568 (10)	0.3225 (12)
C(4)	-0.1274 (10)	0.0243 (7)	0.3533 (7)
C(5)	-0.1722 (11)	0.1129 (7)	0.4497 (8)
C(6)	-0.0735 (9)	0.1939 (7)	0.4948 (7)
C(7)	-0.1453 (12)	0.2828 (9)	0.6005 (10)

^a x, y, z are in fractional coordinates. Numbers in parentheses in this and other tables are estimated standard deviations in the least significant digits.

(9) "International Tables for X-Ray Crystallography," Vol. IV, in preparation.

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(12) This table will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-2483. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

parameters are given in the microfilm edition.¹² Parameters for hydrogen atoms are listed in Table II.

Table II. Atomic Positions and Isotropic Temperature Parameters for Hydrogen Atoms

Atom ^a	x	y	z	$B, \text{\AA}^2$
H on O	0.209 (15)	0.132 (9)	-0.010 (11)	5 (3)
H(1,1)	0.268 (12)	-0.104 (8)	0.159 (9)	4 (2)
H(1,2)	0.416 (10)	-0.041 (7)	0.188 (7)	3 (2)
H(2,1)	0.413 (11)	0.148 (8)	0.082 (8)	3 (2)
H(3,1)	-0.243 (14)	-0.035 (12)	0.233 (13)	7 (3)
H(3,2)	-0.323 (17)	-0.047 (12)	0.365 (13)	6 (4)
H(3,3)	-0.196 (17)	-0.131 (12)	0.286 (12)	8 (3)
H(5,1)	-0.290 (9)	0.123 (5)	0.486 (6)	1 (1)
H(7,1)	-0.105 (13)	0.256 (8)	0.679 (9)	4 (2)
H(7,2)	-0.286 (14)	0.264 (10)	0.652 (10)	7 (3)
H(7,3)	-0.098 (20)	0.365 (14)	0.612 (15)	10 (4)

^a The first number in parentheses specifies the carbon atom to which the hydrogen atom is attached.

Results and Discussion

A perspective view of the molecular structure of PtCl(acac)(H₂CCHOH) is given in Figure 1; the 50% probability thermal ellipsoids are shown, and the atomic numbering scheme is given.

The molecules are well separated in the unit cell. All intermolecular contacts between H atoms and O, C, or Cl atoms are greater than 2.7 \AA , except for the contact between the H on O(1) and the symmetry equivalent ($x, 1/2 - y, 1/2 + z$) of O(3) which is $2.19 (11) \text{ \AA}$. The O(1)··O(3) intermolecular distance is $2.823 (9) \text{ \AA}$; this is essentially the same as the sum of the van der Waals radii.

As in other Pt(II) olefin complexes,¹³ the molecular geometry is square-planar four coordinate with the olefin occupying one of the coordination positions. The vinyl C-C axis is roughly perpendicular (79°)

Table III. Selected Interatomic Distances (\AA)

Atoms	Distance	Atoms	Distance
Pt-Cl	2.288 (3)	C(3)-C(4)	1.482 (12)
Pt-O(2)	1.994 (5)	C(4)-C(5)	1.393 (11)
Pt-O(3)	2.044 (5)	C(5)-C(6)	1.385 (11)
Pt-C(1)	2.098 (8)	C(6)-C(7)	1.499 (11)
Pt-C(2)	2.222 (8)	C(6)-O(3)	1.290 (9)
C(1)-C(2)	1.387 (12)	C(4)-O(2)	1.286 (9)
C(2)-O(1)	1.297 (12)		

Table IV. Selected Bond Angles (Deg)

Atoms	Angle	Atoms	Angle
Cl-Pt-O(2)	176.7 (2)	Pt-C(2)-O(1)	114.5 (6)
Cl-Pt-O(3)	86.9 (2)	C(1)-C(2)-O(1)	121.9 (9)
Cl-Pt-C(1)	92.7 (3)	Pt-O(2)-C(4)	124.1 (5)
Cl-Pt-C(2)	91.3 (3)	O(2)-C(4)-C(3)	114.8 (8)
O(2)-Pt-O(3)	93.5 (2)	O(2)-C(4)-C(5)	125.7 (8)
O(2)-Pt-C(1)	86.5 (4)	C(3)-C(4)-C(5)	119.5 (9)
O(2)-Pt-C(2)	90.0 (3)	C(4)-C(5)-C(6)	128.0 (8)
O(3)-Pt-C(1)	173.5 (3)	C(5)-C(6)-C(7)	120.0 (8)
O(3)-Pt-C(2)	149.2 (3)	C(5)-C(6)-O(3)	126.1 (7)
C(1)-Pt-C(2)	37.3 (3)	C(7)-C(6)-O(3)	113.9 (7)
Pt-C(1)-C(2)	76.2 (5)	C(6)-O(3)-Pt	122.4 (5)
Pt-C(2)-C(1)	66.5 (5)		

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Table V. Comparison of Structural Data of Platinum(II) π Complexes^a

Compound ^b	Distance, Å			Midpoint plane ^c
	<i>cis</i> Pt-Cl	<i>trans</i> Pt-Cl	Pt-C (olefin)	
PtCl ₂ (NHMe ₂)(H ₂ C=CH ₂) ^d	2.30 (4)		2.21 (15)	0.00 ^e
PtCl ₃ (<i>cis</i> -HOCH ₂ CH=CHCH ₂ OH) ^f	2.33 (4)			
	2.291 (9)	2.296 (9)	2.10 (2)	0.01
[PtCl(C ₁₂ H ₁₇) ₂] ^g	2.301 (8)		2.18 (3)	
		2.308 (7)	2.17 (2)	0.02
			2.18 (2)	
			2.31 (2)	0.07
<i>trans</i> -[PtCl ₂ (MeC ₆ H ₄ NH ₂)(<i>t</i> -BuC≡C- <i>t</i> -Bu)] ^h	2.300 (2)		2.36 (2)	
			2.138 (13)	0.10
PtCl ₃ (<i>cis</i> -MeCH=CHCH ₂ NH ₃) ⁱ	2.293 (6)	2.320 (6)	2.180 (13)	
	2.301 (6)		2.15 (2)	0.12
[PtCl ₃ (H ₂ C=CH ₂)] ⁻ X-ray ^j	2.296 (7)	2.327 (5)	2.18 (2)	0.20
	2.314 (7)		2.12 (2)	
Neutron ^k	2.30	2.36	2.13 (2)	0.21
	2.34		2.14	
PtCl ₃ (<i>trans</i> -MeCH=CHCH ₂ NH ₃) ^l	2.288 (7)	2.339 (7)	2.12 (3)	0.21
	2.307 (6)		2.16 (3)	
PtCl ₂ (C ₁₀ H ₁₆) ^m	2.316 (8)		2.24 (3)	0.24
	2.343 (13)		2.25 (4)	
			2.11 (4)	0.37
			2.18 (2)	
<i>cis</i> -[PtCl ₂ (NC ₆ H ₅)(<i>trans</i> -MeCH=CHMe)] ⁿ	2.29 (2)	2.35 (2)	2.16 (5)	0.36
			2.17 (5)	
PtCl ₂ (C ₁₀ H ₁₄ O ₃) ^o		2.302 (7)	2.13 (2)	0.37
		2.310 (7)	2.33 (2)	
			2.04 (2)	0.38
			2.32 (2)	
PtCl ₃ (<i>trans</i> -H ₃ NCH ₂ CH=CHCH ₂ NH ₃) ^p	2.293 (2)	2.342 (2)	2.111 (8)	0.38
	2.311 (2)		2.148 (7)	
PtCl(acac)(H ₂ C=CHOH) ^q	2.288 (3)		2.098 (8)	0.59
			2.222 (8)	

^a Unreported distances have been calculated when possible. ^b The following abbreviations are used: Me = methyl, *t*-Bu = *tert*-butyl. ^c Distance from the midpoint of the olefin bond to the principal coordination plane. ^d Reference 14. ^e Crystallographic symmetry is imposed on the ethylene ligand. ^f Reference 15. ^g Reference 16. ^h Reference 17. ⁱ Reference 18. ^j Reference 19. ^k Reference 20. ^l Reference 21. ^m Reference 22. ⁿ Reference 23. ^o Reference 24. ^p Reference 13. ^q This work.

to the plane of the Pt atom and the other ligands. The dihedral angle between the principal coordination plane and the plane containing the Pt atom and the olefin carbon atoms is 86.1°.

Bond distances and angles are given in Tables III and IV, respectively. The average C-H and O-H bond distance is 1.0 (2) Å. The Pt-Cl bond length of 2.288 (3) Å is shorter than most reported Pt(II)-Cl bonds. It is shorter than the Pt-Cl bonds of the 11 complexes listed in Table V,¹³⁻²⁴ as well as the 2.308 (2) Å bond in K₂PtCl₄.²⁵ Two compounds of the type

trans-[Pt₂Cl₄X₂]₂ have shorter bonds: X = As(CH₃)₃, 2.268 (6) Å;²⁶ and X = P(C₂H₅)₃, 2.279 (9) Å.²⁷

The Pt-O bonds of the acetylacetonato group show a significant trans bond lengthening effect of the vinyl alcohol. The bond *trans* to the olefin is 0.050 (7) Å longer than the *cis* Pt-O bond of 1.994 (5) Å. A larger difference of 0.10 (2) Å has been observed for Pt-O bonds in K[PtCl(acac)].²⁸ Here the bond *trans* to the Cl atom is 1.968 (14) Å, while the bond *trans* to the σ -bonded C atom of the unidentate acac group is 2.072 (14) Å. In π complexes, such as those listed in Table V, the bond *trans* to the π ligand generally appears to be longer than the *cis* bond, although these differences are usually not significant in terms of the esd's. A π -bonded olefin has been compared¹⁶ in *trans* influence to a coordinated chlorine atom. Thus the *trans* influence of the vinyl alcohol ligand is intermediate between that of a σ -bonded carbon atom, which is fairly large, and that of a π -bonded olefin group.

The most striking feature of the molecular structure of PtCl(acac)(H₂CCHOH) is the position of the vinyl alcohol relative to the principal coordination plane of the metal atom. In previous structural determinations, as tabulated in Table V, the principal coordina-

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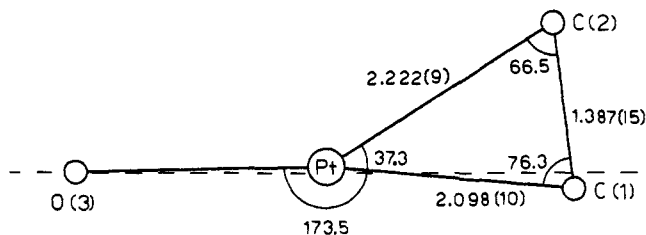


Figure 2. A scaled drawing of $\text{PtCl}(\text{acac})(\text{H}_2\text{CCHOH})$ as viewed along the $\text{Cl}-\text{O}(2)$ axis. The dashed line represents the $\text{Cl}-\text{O}(2)-\text{O}(3)$ plane.

tion plane approximately bisects the olefin bond. There are cases in which the midpoint of the olefin $\text{C}-\text{C}$ bond deviates by as much as 0.38 \AA from the plane. However, these deviations can usually be attributed to constraints imposed by a ring system in the case of diolefins, to crystal packing forces, or to uncertainties in the data. In the present case, however, the structure is determined with considerable precision, and the deviation is dramatically greater. The midpoint of the $\text{C}=\text{C}$ bond lies 0.59 \AA from the principal coordination plane; $\text{C}(1)$ is only 0.09 \AA below the plane as depicted in Figure 2. Parameters associated with the least-squares plane are given in the microfilm edition.¹²

The vinyl alcohol $\text{C}(1)-\text{C}(2)$ bond length of $1.387(15) \text{ \AA}$ is typical of ethylene- $\text{Pt}(\text{II})$ complexes in being nearer to the length in free ethylene (1.338 \AA)²⁹ than to the length of a $\text{C}-\text{C}$ single bond ($\sim 1.47 \text{ \AA}$ for two sp^2 carbon atoms). The $\text{Pt}-\text{C}(1)$ bond distance of $2.098(10) \text{ \AA}$ is the shortest bond listed in Table V. On the other hand, the $\text{Pt}-\text{C}(2)$ bond is long at $2.222(9) \text{ \AA}$ and is the longest of the monoolefin bonds given in the table.

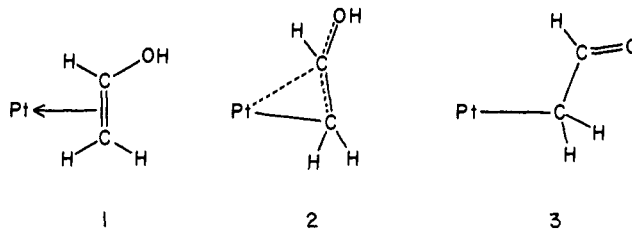
The $\text{C}(2)-\text{O}(1)$ bond of the vinyl alcohol is $1.297(12) \text{ \AA}$ in length. This can be compared to the following bond distances found in the X-ray study³⁰ of glycolic acid, HOCH_2COOH : $1.203(3) \text{ \AA}$ for $\text{C}=\text{O}$ (acid), $1.311(2) \text{ \AA}$ for $\text{C}-\text{OH}$ (acid), and $1.412(2) \text{ \AA}$ for $\text{C}-\text{OH}$ (alcohol). These values are entirely repre-

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sentative for each type of bond as observed in a variety of other compounds.³¹ Thus the present $\text{C}-\text{O}$ bond is intermediate between a double bond and a single bond and most closely resembles the $\text{C}-\text{OH}$ bond of a carboxylic acid.

All of the structural features of $\text{PtCl}(\text{acac})(\text{H}_2\text{CCHOH})$ can be interpreted in terms of a bonding model that is intermediate between a conventional π -olefin complex 1, and a σ -bonded aldehyde complex, 3. Such an intermediate structure is depicted sche-



matically as 2 and may be described as follows. First, the principal coordination plane of the Pt atom neither bisects the $\text{C}-\text{C}$ bond nor does it include the methylene carbon atom. Second, the $\text{Pt}-\text{C}$ bond lengths are significantly different, but both carbon atoms are within bonding distance of the metal atom. Third, the $\text{C}-\text{C}$ bond length implies that the bond order is intermediate between a single and a double bond. Fourth, the $\text{C}-\text{O}$ bond is intermediate between a single and a double bond. Fifth, the entire ligand exerts a trans influence that is intermediate between a π -bonded olefin species and a σ -bonded carbon atom. Thus this structure is in good agreement with the chemical evidence that the Pt -vinyl alcohol complex is a moderately strong acid ($\text{p}K_a = 3.5$) losing a proton to form the β -oxoethyl complex, with a rate of dissociation of at least 50 sec^{-1} based on nmr evidence.

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(31) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc. Spec. Publ., Suppl.*, No. 18 (1965).