whereas the *cis* isomer (*11*) gives a coupling constants of 193 Hz.

2-*cis*-4-*trans*-6-Trimethyl-1,3-dioxane (*9*) exists mainly in the conformation with the methyl substituent at C-2 equatorial, as shown by Eliel and Knoeber from proton NMR spectra,[4] and we have in accordance herewith found that $^1J(^{13}C\text{-H2})$ is 159 Hz. In this compound the coupling constants to H-4 and H-6 are 138 Hz and 150 Hz, respectively. The assignment of these coupling constants is based on the value of $^1J(^{13}C\text{-H4}) = 138$ Hz in (*5*) and (*7*), where H-4 must be axially oriented. We here see that the lone pairs from only one oxygen atom can have a large influence on ^{13}CH coupling constants. This effect has also been found in methyl-pento-pyranosides.[2]

We conclude from these results that the difference in directly bonded ^{13}CH coupling constants to axial and equatorial protons is due to the effect of lone pairs on neighbouring oxygen atoms.

1. Bock, K., Lundt, I. and Pedersen, C. *Tetrahedron Letters* **1973** 1037.
2. Bock, K. and Pedersen, C. *To be published.*
3. Freeman, R. and Hill, H. D. W. *J. Magn. Res.* **5** (1971) 278.
4. Eliel, E. L. and Knoeber, S. M. C. *J. Am. Chem. Soc.* **90** (1968) 3444.
5. Jennings, W. B., Boyd, D. R., Watson, C. G., Becker, E. D., Bradley, R. B. and Jerina, D. M. *J. Am. Chem. Soc.* **94** (1972) 8501.
6. Gil, V. M. S. and Teixeira-Dias, J. J. C. *Mol. Phys.* **15** (1968) 47.
7. Yonezawa, T., Morishima, I., Fukuta, K. and Ohmori, Y. *J. Mol. Spectry.* **31** (1969) 341.
8. Albrand, J. P., Cogne, A., Gagnaire, D. and Robert, J. B. *Tetrahedron* **27** (1971) 2453.
9. Jones, A. J., Eliel, E. L., Grant, D. M., Knoeber, M. C. and Bailey, W. F. *J. Am. Chem. Soc.* **93** (1971) 4772.
10. Kellie, G. M. and Riddell, F. G. *J. Chem. Soc. Perkin Trans. 2* **1971** 1030.
11. Nader, F. W. and Eliel, E. L. *J. Am. Chem. Soc.* **92** (1970) 3050.

Received September 14, 1973.

Structure of Bis-(1-ethynylcyclohexanol)-bis-(triphenylphosphine)platinum

R. A. MARIEZCURRENA* and
S. E. RASMUSSEN

Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

Crystals of $Pt(P(C_6H_5)_3)_2(C_8H_{12}O)_2$ were kindly supplied by Dr. H. B. Jonassen of Tulane University, New Orleans. The complex has been subject to IR and NMR spectroscopic investigations by Roundhill and Jonassen.[1] Two kinds of crystals were found in the sample: a triclinic modification not yet extensively investigated and the monoclinic form reported here. The monoclinic crystals appear to be the more numerous.

Experimental. A plate-shaped crystal $0.3 \times 0.22 \times 0.51$ mm was mounted along c. Cell dimensions and systematic absences were obtained from Weissenberg and precession photographs and were confirmed by diffractometer measurements. The conditions limiting possible reflections were: $0k0$: $k = 2n$, $h0l$: $h + l = 2n$. hkl: no conditions. The crystals are monoclinic, space group $P2_1/n$, $Z = 2$, F.W. = 966.0, $a = 8.992$, $b = 23.012$, $c = 11.585$ Å, $\beta = 105.35°$, $V = 2311$ Å^3, $D_m = 1.43$, $D_c = 1.39$ g cm^{-3}, $\lambda(MoK\alpha) = 0.7107$ Å, $\mu(MoK\alpha) = 33.0$ cm^{-1}.

The density was measured by flotation in a mixture of heptane and carbon tetrachloride. Intensities were measured on an Arndt-Phillips linear diffractometer. MoKα radiation was selected by a graphite monochromator. The counting chain included a scintillation counter and a pulse height analyzer. 6288 reflections with $l = 0$ to 14 were measured to a $\sin \theta / \lambda$ limit of 0.64 Å^{-1}. Symmetry related reflections were averaged. 2898 independent reflections had intensities above two standard deviations as derived by counting statistics and were employed in subsequent computations. Lorentz and polarization factors were applied, assuming the graphite monochromator to behave as an ideal mosaic crystal. An absorption correction was applied, the correction factors ranging from 1.60 to 2.70.

* Now returned to Facultad de Quimica, Montevideo, Uruguay.

Table 1. Parameters from least squares analysis. Atomic coordinates are in fractions of cell edges. Where only one thermal parameter is given as $B11$, it is the conventional B-value: $B = 8\pi^2 u^2$ where u^2 is the mean square vibration amplitude in $Å^2$. Where six parameters are given, the temperature factor is calculated as exp $-$ $-2\pi^2[a^{*2}h^2B11 + b^{*2}k^2B22 + c^{*2}l^2B33 + 2a^*b^*hkB12 + 2a^*c^*hlB13 + 2b^*c^*klB23]$ where the B_{ij} values are in $Å^2$.

Atom	x	y	z	$B11$	$B22$	$B33$	$B12$	$B13$	$B23$
C 1	.136016	.051529	.289122	2.68					
C 2	.209959	.040924	.412879	4.12					
C 3	.304188	.084035	.480158	4.40					
C 4	.323127	.137135	.422720	4.83					
C 5	.250531	.148355	.299925	5.06					
C 6	.156302	.105244	.232645	3.94					
C 7	−.180392	.010465	.222885	2.75					
C 8	−.308706	−.017504	.141909	3.99					
C 9	−.456262	−.010958	.158887	4.47					
C 10	−.473395	.023463	.256600	4.61					
C 11	−.347188	.051525	.337819	4.40					
C 12	−.199633	.044979	.320840	4.00					
C 13	.071904	−.068618	.283905	2.68					
C 14	.223037	−.090325	.289709	4.20					
C 15	.276804	−.139614	.359054	5.14					
C 16	.178670	−.166492	.421605	5.07					
C 17	.028305	−.145490	.416792	6.11					
C 18	−.025462	−.096201	.347447	4.26					
C 19	−.225490	.184791	−.015024	6.81					
O	−.162564	.216910	−.092584	7.42					
C 20	−.153873	.215639	.110858	8.98					
C 21	−.458344	.158097	.055605	10.93					
C 22	−.220675	.189462	.210805	12.55					
C 23	−.405000	.187983	−.044000	13.22					
C 24	−.394305	.188636	.167141	14.39					
C 25	−.165129	.121518	−.009427	.008540	.000998	.004181	−.000274	.002625	−.000256
C 26	−.110476	.076124	−.007809	.009251	.000941	.004976	−.000323	.003072	.000467
P	.007912	−.003362	.200547	.022177	.001163	.010503	.000058	.004901	.001942
Pt	.000000	.000000	.000000	.014859	.000981	.006730	.000175	.003322	.001023

Structure determination. The platinum atom is located at the origin. The position of the phosphorus atom was found from a Patterson function. As y_p is close to zero (0.003), the phosphorus atom, like the platinum atom, does not contribute to reflections with $h + k + l = 2n + 1$. An electron density map phased on the platinum and the phosphorus positions therefore shows a false mirror plane perpendicular to y. The light atoms were poorly defined in this first map but approximate positions of the three phenyl rings were derived. As their geometry is known to an accuracy better than we could expect from our diffraction data, refinement by least squares was carried out with each phenyl group constrained to be planar with $2m$ symmetry. The Euler angles and the centers of gravity of the phenyl rings were

refined. Convergence was obtained at $R = 12\%$ when isotropic thermal movement was assumed for all atoms. When temperature factor parameters describing anisotropic vibration were assigned to the platinum and phosphorus atoms, R dropped to 9 %. A difference map still showed the effect of the pseudo mirror plane. It was, however, possible to find a group of atoms which corresponded to a 1-ethynylcyclohexanol molecule. Anisotropic thermal movement was assumed for the acetylene group and isotropic for the cyclohexanol group. The B-values of the atoms in the cyclohexanol group were large (9 − 14 $Å^2$) indicating a certain degree of disorder. The final R is 5.2 %.

The final parameters are given in Table 1. A table of calculated and observed structure factors can be obtained from

S.E. Rasmussen at request.

Atomic scattering factors were taken from Ref. 2, $\Delta f'$ for $Pt = -1.9$.

The following computer programs were used: Data reduction: G4.[3] Absorption correction: Wells.[4] Fourier synthesis: Fordap (A. Zalkin, modified by Lundgren and Liminga), unpublished. Least squares constrained refinement: Pawley.[5] Plot program and distance calculations: ORTEP, Johnson.[6]

Discussion. This study was undertaken as a preliminary to a neutron diffraction investigation of the positions of the hydrogen atoms. According to Roundhill and Jonassen[1] an octahedral configuration round the platinum is expected with hydrogen atoms completing the octahedron. This investigation has so far confirmed that the triphenylphosphine and the hydroxyacetylene molecules are coordinated to platinum, but our data are not accurate enough to yield positions of the hydrogen atoms. In the sample crystals of the size of several mm^3 occurred. These were intended for neutron investigation but proved to belong to the triclinic modification which is now being investigated by X-ray diffraction.

The molecule is depicted in Fig. 1. Interatomic distances are given in Table 2. The distances between the light atoms agree well with standard values in similar compounds. The distances found in the cyclohexanol group reflect the low accuracy
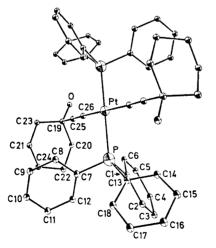

Fig. 1. Projection of a molecule of bis(1-ethynylcyclohexanol) bis (triphenylphosphine) platinum.

Table 2. Bond lengths (Å).

Triphenylphosphine group		
C	$-$ C(as inserted)	(1.41)
P	$-$ C(1)	1.808
P	$-$ C(7)	1.796
P	$-$ C(13)	1.830
Ethynylcyclohexanol group		
C(25) $-$ C(26)		1.15
C(25) $-$ C(19)		1.55
C(19) $-$ C(23)		1.57
C(23) $-$ C(21)		1.81
C(21) $-$ C(24)		1.44
C(24) $-$ C(22)		1.51
C(22) $-$ C(20)		1.56
C(20) $-$ C(19)		1.60
C(19) $-$ O		1.39
Pt $-$ P		2.307
Pt $-$ C(26)		2.004

of the determination of that part of the structure. The $Pt-P$ distance of 2.307 Å compares well with an average of 2.293 Å in ten structures of platinum phosphine complexes (2.240 to 2.345 Å). The Pt-C distance is normal. It is not possible to draw conclusions about the valence state of the platinum atom.

1. Roundhill, D. H. and Jonassen, H. B. *Chem. Commun.* **1968** 1233.
2. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
3. Grønbæk Hazell, R. ALGOL program, Department of Inorganic Chemistry, Aarhus University, Aarhus 1964.
4. Wells, M. *Acta Cryst.* **13** (1960) 722.
5. Pawley, G. S. Least Squares Constrained Program, Department of Physics, Edinburg University, Edinburg 1971.
6. Johnson, C. K. ORTEP, ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Received August 20, 1973.