Crystal Structure of (1-Ethynylcyclohexanol)bis(triphenylphosphine)-platinum(0)

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The crystal structure of the title compound was determined by single-crystal *X*-ray analysis from diffractometer data. Crystals are triclinic, space group $P\bar{1}$, with a = 17.72(2), b = 17.44(2), c = 12.78(1) Å, α = 97.8(1), β = 101.6(1), γ = 86.9(1)°, and Z = 4. The structure was solved by the heavy-atom method and refined by least-squares constrained refinement to R 0.053 for 7 205 observed reflections. The two independent molecules in the asymmetric unit are isomers in that the acetylene group is equatorially bonded to the cyclohexane ring in one molecule but axially bonded in the other. The acetylene group is symmetrically co-ordinated to platinum in both molecules [mean Pt–C 2.074(7) Å] and adopts the usual *cis*-bent configuration. The co-ordination about platinum is approximately planar, the dihedral angles between the P,Pt,P and C,Pt,C planes in the two molecules being 6.7(8) and 7.2(7)°.

THE reaction of 1-ethynylcyclohexanol with tetrakis(triphenylphosphine)platinum(0) yields a colourless crystalline compound originally formulated[1] as $[Pt(PPh_3)_2(C_8H_{12}O)_2]$. I.r. and n.m.r. spectroscopic data indicated [1] an octahedral platinum(IV) acetylide hydride with the 1-ethynylcyclohexanol ligands in ***trans***. In a subsequent *X*-ray single-crystal investigation,[2] the product was found to contain both monoclinic and triclinic crystals. The structure of the monoclinic form was determined, its formula and structure being found [2] to be consistent with that suggested by Roundhill and Jonassen.[1] The present investigation was undertaken in order to determine the nature of the triclinic modification.

EXPERIMENTAL

Crystal Data.—$C_{44}H_{42}OP_2Pt$, M = 843.82, Triclinic, a = 17.72(2), b = 17.44(2), c = 12.78(1) Å, α = 97.8(1), β = 101.6(1), γ = 86.9(1)° (diffractometer measurements), U = 3 831 Å^3, Z = 4, D_c = 1.46 g cm^{-3}. Mo-K_α radiation, λ = 0.7107 Å, μ(Mo-K_α) = 39.7 cm^{-1}. Space group $P1$ (No. 1) or $P\bar{1}$ (No. 2), shown to be the latter from structure analysis.

Collection and Reduction of Data.—A crystal was mounted along the c axis. Intensities were measured for $2\theta < 53°$ with a Picker four-circle diffractometer, by use of graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz-polarisation effects and for absorption, and symmetry-related reflections were averaged. Of 14 911 independent reflections measured, 7 205 having $F_o^2 > 3.0\ \sigma(F_o^2)$, according to counting statistics, were used in the subsequent calculations.

Determination and Refinement of the Structure.—The positions of the two platinum atoms in the asymmetric unit were determined from a three-dimensional Patterson function and the remaining ninety-four non-hydrogen atoms were located from successive electron-density calculations. All atoms occupy general positions. At the commencement of the investigation the complex was assumed to have the formula $[Pt(PPh_3)_2(C_8H_{12}O)_2]$, but it soon became apparent that there was only one 1-ethynylcyclohexanol ligand bonded to each platinum atom.

Preliminary least-squares refinement of the positional and

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[1] D. M. Roundhill and H. B. Jonassen, *Chem. Comm.*, 1968, 1233.

[2] R. A. Mariezcurrena and S. E. Rasmussen, *Acta Chem. Scand.*, 1973, **27**, 2678.

isotropic thermal parameters, in which the phenyl rings were constrained[3] to be planar with *mmm* symmetry, yielded R 0.086. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with unit weights. In the final refinement the mirror plane of the phenyl ring, relating the carbon atom bonded to phosphorus to that diametrically opposite, was removed, the phenyl rings thus being constrained to be planar with *2mm* symmetry. The hydrogen atoms of the phenyl rings were inserted as part of the constrained groups and ***T***, ***L***, and ***S*** tensors were refined for each of the four triphenylphosphine groups. Anisotropic thermal parameters were included for the platinum atoms, while the atoms of the 1-ethynylcyclohexanol ligands were assumed to have isotropic thermal motion. In the final cycles of refinement the F_o values were weighted according to $w = [\{\sigma(F_o^2) + 1.02\ F_o^2\}^{\frac{1}{2}} - |F_o|]^{-2}$. A final R value of 0.053 (R' 0.053) was obtained for 273 parameters. Scattering factors from ref. 4 were employed for platinum (with values of $\Delta f'$ and $\Delta f''$ from ref. 5), from ref. 6 for hydrogen, and from ref. 7 for remaining atoms. Apart from some ripples of the order of 1.0 $e\text{Å}^{-3}$ in the vicinity of the platinum atoms, a final difference-Fourier showed no peaks >0.5 $e\text{Å}^{-3}$.

The final co-ordinates of the non-hydrogen atoms and the thermal parameters for the platinum and phosphorus atoms and the atoms of the 1-ethynylcyclohexanol ligands are given in Table 1. Centres, Euler angles,[3] and ring co-ordinates for the twelve phenyl groups and ***T***, ***L*** and ***S*** for the four triphenylphosphine groups are listed with structure factors in the supplementary publication (No. SUP 21569, 32 pp., 1 microfiche).* The ring co-ordinates refer to orthogonal molecular axes defined with the origin at the centre of the ring, the z axis perpendicular to the plane of the ring, and the x axis joining the carbon atom bonded to phosphorus with that diametrically opposite. The positive direction of the x axis is towards the carbon atom bonded to phosphorus. The atom numbering system used in the analysis is shown in Figure 1.

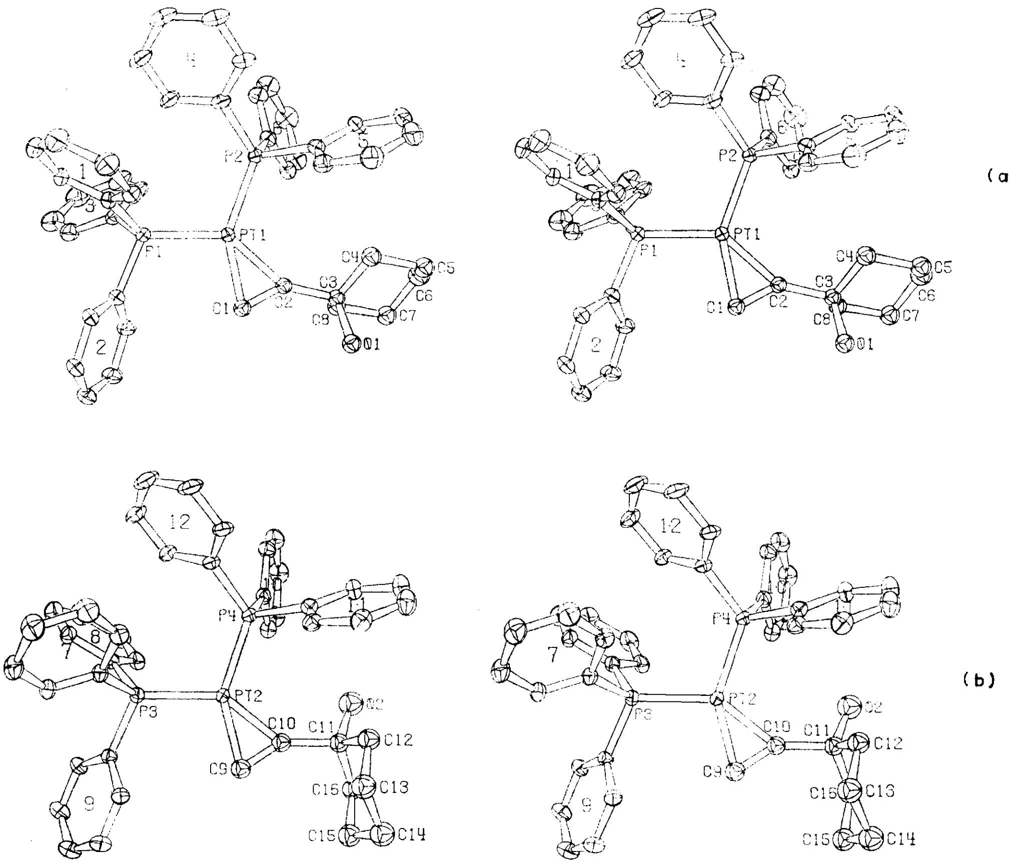

FIGURE 1 Stereoscopic projections, perpendicular to the P,Pt,P planes, of the two molecules in the asymmetric unit

Calculations.—Calculations were carried out on a CDC 6400 computer, with the following programs: data reduction and averaging, DATAPP, DSORTH, State University of New York at Buffalo; Patterson and Fourier syntheses, FORDAP and JIMDAP, A. Zalkin; constrained refinement, G. S. Pawley, modified by R. G. Hazell; distances and angles, ORFFE, W. R. Busing, K. O. Martin, and H. A. Levy; stereoscopic drawings, ORTEP, C. K. Johnson.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[3] G. S. Pawley, *Adv. Struct. Res. Diffraction Methods*, 1972, **4**, 1.

[4] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[5] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

TABLE 1

Atomic co-ordinates, expressed as fractions of the cell edges, for the non-hydrogen atoms, and thermal parameters * for the platinum and phosphorus atoms (Å^2 × 10^{-4}) and the atoms of the 1-ethynylcyclohexanol ligands (Å^2). Estimated standard deviations are in parentheses

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	0.035 65(3)	0.182 15(3)	0.482 47(4)	359(4)	370(4)	328(4)	42(3)	113(3)	69(3)
Pt(2)	0.573 86(3)	0.295 98(3)	0.862 29(4)	328(4)	328(4)	350(4)	−60(3)	54(3)	60(3)
P(1)	0.083 51(21)	0.222 55(20)	0.345 30(30)	426(23)	364(22)	386(23)	50(18)	143(19)	103(18)
P(2)	−0.065 77(21)	0.263 19(20)	0.518 21(29)	387(22)	376(22)	318(22)	43(17)	67(18)	70(18)
P(3)	0.537 18(20)	0.190 25(20)	0.926 06(29)	373(22)	321(21)	325(22)	−39(17)	89(18)	42(17)
P(4)	0.475 36(20)	0.329 84(20)	0.728 13(29)	318(21)	378(22)	351(23)	−54(17)	31(18)	66(18)

	x/a	y/b	z/c	B
O(1)	0.0685(5)	−0.0203(5)	0.6734(7)	4.14(20)
O(2)	0.6678(6)	0.4252(6)	0.7124(10)	7.28(30)
C(1)	0.1059(7)	0.0858(7)	0.5130(11)	3.63(28)
C(2)	0.0638(7)	0.0972(7)	0.5865(10)	3.35(27)
C(3)	0.0544(8)	0.0636(7)	0.6894(11)	3.39(28)
C(4)	−0.0276(8)	0.0821(8)	0.7114(12)	4.60(33)
C(5)	−0.0339(9)	0.0537(9)	0.8225(13)	5.16(36)
C(6)	0.0284(10)	0.0908(9)	0.9145(14)	6.14(41)
C(7)	0.1097(9)	0.0687(8)	0.8914(12)	5.18(36)
C(8)	0.1189(8)	0.0971(8)	0.7840(11)	4.13(31)
C(9)	0.6843(8)	0.3155(8)	0.9479(12)	4.47(33)
C(10)	0.6690(8)	0.3623(8)	0.8726(11)	4.20(31)
C(11)	0.6941(8)	0.4340(8)	0.8282(12)	4.48(31)
C(12)	0.6640(9)	0.5101(9)	0.8803(13)	5.19(36)
C(13)	0.6993(10)	0.5283(9)	0.9977(14)	6.21(41)
C(14)	0.7887(10)	0.5327(10)	1.0125(14)	6.55(43)
C(15)	0.8217(9)	0.4519(9)	0.9611(13)	5.71(39)
C(16)	0.7858(9)	0.4303(9)	0.8444(13)	5.21(36)

	x/a	y/b	z/c		x/a	y/b	z/c
Ring (1)				Ring (7)			
C(17)	−0.0467	0.1858	0.1869	C(53)	0.3992	0.2508	0.9834
C(18)	−0.1006	0.1917	0.0930	C(54)	0.3361	0.2521	1.0327
C(19)	−0.0917	0.2453	0.0270	C(55)	0.3327	0.1997	1.1028
C(20)	0.0167	0.2330	0.2167	C(56)	0.4598	0.1974	1.0030
C(21)	0.0241	0.2867	0.1485	C(57)	0.4547	0.1452	1.0742
C(22)	−0.0295	0.2929	0.0544	C(58)	0.3918	0.1461	1.1238
Ring (2)				Ring (8)			
C(23)	0.1508	0.1084	0.2064	C(59)	0.4534	0.0556	0.8204
C(24)	0.2070	0.0542	0.1824	C(60)	0.4354	−0.0045	0.7375
C(25)	0.2740	0.0463	0.2567	C(61)	0.4737	−0.0131	0.6529
C(26)	0.1602	0.1557	0.3045	C(62)	0.5096	0.1082	0.8206
C(27)	0.2284	0.1465	0.3779	C(63)	0.5473	0.0980	0.7341
C(28)	0.2849	0.0923	0.3545	C(64)	0.5297	0.0380	0.6508
Ring (3)				Ring (9)			
C(29)	0.1959	0.3282	0.3263	C(65)	0.6513	0.1921	1.1137
C(30)	0.2400	0.3938	0.3571	C(66)	0.7102	0.1627	1.1876
C(31)	0.2277	0.4458	0.4435	C(67)	0.7347	0.0867	1.1699
C(32)	0.1389	0.3133	0.3807	C(68)	0.6157	0.1465	1.0211
C(33)	0.1278	0.3668	0.4676	C(69)	0.6417	0.0700	1.0054
C(34)	0.1717	0.4325	0.4989	C(70)	0.7006	0.0401	1.0789
Ring (4)				Ring (10)			
C(35)	−0.0914	0.3558	0.3495	C(71)	0.4298	0.2922	0.5014
C(36)	−0.1342	0.3979	0.2723	C(72)	0.4418	0.2633	0.3993
C(37)	−0.2129	0.4055	0.2627	C(73)	0.5142	0.2376	0.3850
C(38)	−0.1261	0.3205	0.4183	C(74)	0.4895	0.2962	0.5908
C(39)	−0.2056	0.3291	0.4066	C(75)	0.5620	0.2699	0.5738
C(40)	−0.2488	0.3712	0.3296	C(76)	0.5745	0.2408	0.4719
Ring (5)				Ring (11)			
C(41)	−0.1736	0.2345	0.6473	C(77)	0.4691	0.4783	0.6525
C(42)	−0.2313	0.1929	0.6711	C(78)	0.4668	0.5587	0.6661
C(43)	−0.2578	0.1272	0.6044	C(79)	0.4597	0.5987	0.7642
C(44)	−0.1414	0.2115	0.5571	C(80)	0.4644	0.4366	0.7361
C(45)	−0.1694	0.1449	0.4913	C(81)	0.4573	0.4786	0.8342
C(46)	−0.2271	0.1030	0.5145	C(82)	0.4550	0.5589	0.8485
Ring (6)				Ring (12)			
C(47)	−0.0659	0.4133	0.6397	C(83)	0.3154	0.3517	0.7306
C(48)	−0.0435	0.4673	0.7294	C(84)	0.2414	0.3260	0.7220
C(49)	0.0084	0.4461	0.8168	C(85)	0.2271	0.2482	0.6984
C(50)	−0.0371	0.3375	0.6354	C(85)	0.3763	0.3005	0.7158
C(51)	0.0152	0.3178	0.7248	C(87)	0.3601	0.2222	0.6920
C(52)	0.0379	0.3714	0.8148	C(88)	0.2863	0.1961	0.6833

* The anisotropic temperature coefficient is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$, while the isotropic temperature coefficient is $\exp[-B(\sin^2\theta/\lambda^2)]$.

DISCUSSION

Description of the Structure.—Stereoscopic projections of the two molecules in the asymmetric unit are shown in Figure 1. These projections are normal to the P(1) Pt(1) P(2) and P(3) Pt(2) P(4) planes, respectively.

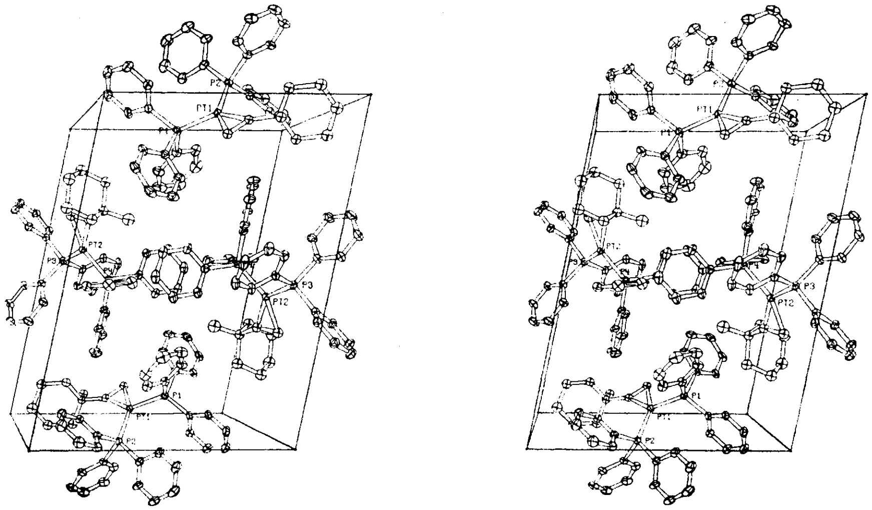

FIGURE 2 Stereoscopic projection, along the *b* axis, of the contents of one unit cell. The *c* axis is horizontal

Some bond distances and angles within the molecules are given in Tables 2 and 3 and some dihedral angles in Table 4. A stereoscopic projection, along the *b* axis, of the contents of one unit cell is shown in Figure 2. There are no exceptionally short intermolecular contacts.

TABLE 2

Bond lengths (Å) with standard deviations (× 10^3) in parentheses

Molecule (1)		Molecule (2)		Mean
Pt(1)–P(1)	2.298(4)	Pt(2)–P(3)	2.287(4)	2.298(2)
Pt(1)–P(2)	2.306(4)	Pt(2)–P(4)	2.301(4)	
Pt(1)–C(1)	2.069(13)	Pt(2)–C(9)	2.061(15)	2.074(7)
Pt(1)–C(2)	2.097(13)	Pt(2)–C(10)	2.067(14)	
C(1)–C(2)	1.302(16)	C(9)–C(10)	1.322(18)	1.312(12)
C(2)–C(3)	1.551(17)	C(10)–C(11)	1.560(18)	1.556(12)
C(3)–C(4)	1.544(17)	C(11)–C(12)	1.522(18)	1.553(5)
C(4)–C(5)	1.591(19)	C(12)–C(13)	1.502(20)	
C(5)–C(6)	1.542(20)	C(13)–C(14)	1.563(21)	
C(6)–C(7)	1.546(19)	C(14)–C(15)	1.604(20)	
C(7)–C(8)	1.561(18)	C(15)–C(16)	1.506(20)	
C(8)–C(3)	1.561(17)	C(16)–C(11)	1.595(18)	
C(3)–O(1)	1.465(14)	C(11)–O(2)	1.450(16)	1.458(10)
P(1)–C(20)	1.848	P(3)–C(56)	1.830	1.846
P(1)–C(26)	1.851	P(3)–C(62)	1.843	
P(1)–C(32)	1.861	P(3)–C(68)	1.857	
P(2)–C(38)	1.858	P(4)–C(74)	1.851	
P(2)–C(44)	1.839	P(4)–C(80)	1.836	
P(2)–C(50)	1.848	P(4)–C(86)	1.826	
C(17)–C(18)	1.387			1.384
C(18)–C(19)	1.376			
C(17)–C(20)	1.389			
C(17)–H(1)	0.924			0.887
C(18)–H(2)	0.902			
C(19)–H(3)	0.836			

The most striking difference between the two independent [$Pt(PPh_3)_2(C_8H_{12}O)$] molecules is that the acetylene group equatorially bonded to the cyclohexane ring in molecule (1) but axially bonded in molecule (2). Molecule (1) thus resembles bis(1-ethynylcyclohexanol)bis(triphenylphosphine)platinum.[2] As in the latter compound,[2] both cyclohexanol groups exhibit the chair configuration, the mean C–C bond length [1.553(5) Å] and the mean C–C–C bond angle [111.0(4)°] agreeing well with the values found for cyclohexane.[8]

TABLE 3

Bond angles (°) with standard deviations in parentheses, associated with the platinum co-ordination polyhedron in the molecules, and the difference (Δ) between the two values

Molecule (1)		Molecule (2)		Δ
P(1)–Pt(1)–P(2)	109.3(1)	P(3)–Pt(2)–P(4)	108.0(1)	−1.3(2)
P(1)–Pt(1)–C(1)	101.0(4)	P(3)–Pt(2)–C(9)	104.2(4)	3.2(6)
P(2)–Pt(1)–C(2)	113.5(4)	P(4)–Pt(2)–C(10)	110.4(4)	−3.1(5)
C(1)–Pt(1)–C(2)	36.4(4)	C(9)–Pt(2)–C(10)	37.4(5)	1.0(6)
C(1)–C(2)–C(3)	139.4(12)	C(9)–C(10)–C(11)	146.8(14)	7.4(19)
Pt(1)–C(1)–C(2)	73.0(8)	Pt(2)–C(9)–C(10)	71.6(9)	−1.4(12)
Pt(1)–C(2)–C(1)	70.6(8)	Pt(2)–C(10)–C(9)	71.1(9)	0.5(12)

TABLE 4

Dihedral angles (°) with standard deviations in parentheses

P(1)–Pt(1)–P(2)	C(2)–Pt(1)–C(1)	6.7(8)
P(3)–Pt(2)–P(4)	C(10)–Pt(2)–C(9)	7.2(7)
(1)–(2) *		94
(1)–(3)		68
(2)–(3)		68
(4)–(5)		78
(4)–(6)		85
(5)–(6)		90
(7)–(8)		96
(7)–(9)		90
(8)–(9)		85
(10)–(11)		102
(10)–(12)		69
(11)–(12)		74

* Ring.

The triphenylphosphine groups have the usual propeller-like arrangement, the orientation of the phenyl

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[8] M. Davis and O. Hassel, *Acta Chem. Scand.*, 1963, **17**, 1181.

rings differing somewhat in the two molecules (*cf.* Figure 1 and Table 4). There are some short intramolecular non-bonded contacts (3.1—3.4 Å) between phenyl rings. The mean Pt–P and P–C distances [2.298(2) and 1.85 Å] are consistent with distances in similar compounds.[2,9]

The configuration of ligands about platinum is typical for acetylene complexes of platinum(0).[10] The dihedral angles between the P(1), Pt(1), P(2) and C(2), Pt(1), C(1) planes and between the P(3), Pt(2), P(4) and C(10), Pt(2), C(9) planes [6.7(8) and 7.2(7)°] lie within the range (6—14°) quoted for such complexes.[10] A dihedral angle of 9.7(4)° has recently been reported [11] for [Pd(PPh$_3$)$_2${C$_2$(CO$_2$Me)$_2$}] while somewhat smaller values [*i.e.* 2.8(7) and 2.4(7)°] have been found [12] in [Ni(Ph$_2$C$_2$)(Me$_3$CNC)$_2$]. Molecular orbital calculations [13] indicate that the planar or nearly planar configuration ought to be the most stable for platinum(0) acetylene complexes, whereas the pseudotetrahedral form, in which the C⋮C linkage is approximately perpendicular to the co-ordination plane, ought to be favoured for platinum(II). In [PtClMe(AsMe$_3$)$_2$(C$_4$F$_6$)], in which platinum is trigonal bipyramidally co-ordinated and formally in oxidation state II, the platinum, the two arsenic, and the carbon atoms of the hexafluorobut-2-yne ligand are, however, co-planar.[14]

The mean C⋮C bond length is 1.312(12) Å as compared with 1.32(9) in [Pt(PPh$_3$)$_2$(Ph$_2$C$_2$)],[9] 1.32(4) in [PtClMe(AsMe$_3$)$_2$(C$_4$F$_6$)],[14] 1.279(11) in [Pd(PPh$_3$)$_2${C$_2$(CO$_2$Me)$_2$}],[11] and 1.284(16) Å in [Ni(Ph$_2$C$_2$)(Me$_3$CNC)$_2$].[12] A shorter C⋮C bond [1.24(2) Å] has been reported [15] for *trans*-dichloro(π-di-t-butylacetylene)-*p*-toluidineplatinum(II) in which the acetylene group is almost perpendicular to the co-ordination plane.

The acetylene group is symmetrically co-ordinated to platinum and the mean Pt–C distance [2.074(7) Å] is normal.[10] The acetylene group would appear to have the usual *cis*-bent configuration, there being, however, a significant difference [7.4(19)°] between the C(9)–C(10)–C(11) angle [146.8(14)°] in molecule (2) and the corresponding angle [139.4(12)°] in molecule (1). Both these angles lie well within the range observed previously.[9,11,12,14] Angles very close to that found for molecule (2) have been found, *i.e.* 146.4(7) and 144.9(7),[11] and 148.6(14)°.[12] The slightly smaller angle obtained for molecule (1) is probably a result of steric effects, there being some relatively short non-bonded contacts (3.48—3.66 Å) between the cyclohexanol group of molecule (1) and phenyl ring (5). The shortest comparable contact for molecule (2) [between C(12) and phenyl ring (11)] is 3.65 Å. The change in geometry of the ethynyl group on co-ordination, *i.e.* the lengthening of the C⋮C bond and the *cis*-bent configuration, has been accounted for by the original Dewar–Chatt–Duncanson model [16] and subsequent extensions.[13,17]

The P(2)–Pt(1)–C(2) angle [113.5(4)°] is significantly larger [12.5(6)°] than that for P(1)–Pt(1)–C(1) [101.0(4)°]. The same is true for molecule (2), the difference here being 6.2(6)°. Similar differences have been observed in unsymmetrically substituted olefin complexes,[18] and where the substituents differ in orientation with respect to the Pd,C,C plane.[11] There are also significant differences between corresponding P–Pt–C angles in the two molecules (Table 3). Again it would seem reasonable to attribute these to steric effects.

The reaction between 1-ethynylcyclohexanol and tetrakis(triphenylphosphine)platinum(0) thus yields a mixture consisting of [Pt(PPh$_3$)$_2$(C$_8$H$_{12}$O)$_2$], which is a typical acetylide,[2] presumably of platinum(IV),[1] and [Pt(PPh$_3$)$_2$(C$_8$H$_{12}$O)], which is a typical platinum(0) acetylene complex.

We thank Dr. H. B. Jonassen for supplying the crystals.

[5/1382 *Received*, 14*th July*, 1975]

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[9] J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometallic Chem.*, 1967, **7**, P9.

[10] J. H. Nelson and H. B. Jonassen, *Co-ordination Chem. Rev.*, 1971, **6**, 27.

[11] J. A. McGinnety, *J.C.S. Dalton*, 1974, 1038.

[12] R. S. Dickson and J. A. Ibers, *J. Organometallic Chem.*, 1972, **36**, 191.

[13] K. S. Wheelock, J. H. Nelson, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1970, **92**, 5110.

[14] B. W. Davies, R. J. Puddephatt, and N. C. Payne, *Canad. J. Chem.*, 1972, **50**, 2276.

[15] G. R. Davies, W. Hewertson, R. H. B. Mais, P. G. Owston, and C. G. Patel, *J. Chem. Soc.* (*A*), 1970, 1873.

[16] M. J. S. Dewar, *Bull. Soc. chim. France*, 1951, **18C**, 79; J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.

[17] R. Mason, *Nature*, 1968, **217**, 543; A. C. Blizzard and D. P. Santry, *J. Amer. Chem. Soc.*, 1968, **90**, 5749; E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 3879; R. M. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 1969, **47**, 20; J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1969, **91**, 7005.

[18] A. McAdam, J. N. Francis, and J. A. Ibers, *J. Organometallic Chem.*, 1971, **29**, 149.