

Crystal Structures of Bis(acetylacetonato- μ -allyl-platinum), $[\text{Pt}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_7\text{O}_2)]_2$, and Bis-[di- μ -allyl-(di- μ -chloro-diplatinum)], $[\text{Pt}(\text{C}_3\text{H}_5)\text{Cl}]_4$

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The X-ray crystal structures of the title compounds have been determined from photographic data. The acetylacetonato-complex (I) is dimeric, with approximate C_2 symmetry, and crystallises in the monoclinic space-group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions: $a = 10.01 \pm 0.01$, $b = 10.00 \pm 0.01$, $c = 17.29 \pm 0.03$ Å, $\beta = 100.2^\circ \pm 0.2^\circ$. The chloro-complex (II) exists as a tetramer of approximate D_2 symmetry, and crystallises in the triclinic space-group $P\bar{1}$, with $Z = 4$ in a unit cell of dimensions: $a = 13.34 \pm 0.03$, $b = 16.16 \pm 0.03$, $c = 8.33 \pm 0.01$ Å, $\alpha = 90.2 \pm 0.2$, $\beta = 100.2 \pm 0.2$, $\gamma = 93.2^\circ \pm 0.2^\circ$. Both structures were solved by conventional Patterson and Fourier methods and refined by least-squares techniques to R 11.3% [(I); 1948 independent reflections] and 12.0% [(II); 2975 independent reflections].

In (I) each allyl group of the Pt...Pt bridge is σ -bonded to one platinum and π -bonded to the other. Similarly diallyl bridges occur in (II) where non-planar dichloro-bridges alternate with the diallyl bridges in the ring. The Pt-O bond lengths in (I) and Pt-Cl bond lengths in (II) reflect the differing *trans*-influences of the σ - and π -bonded allyl group.

REACTION of diallylplatinum with dry hydrogen chloride gives¹ chloro(allyl)platinum, $[\text{Pt}(\text{C}_3\text{H}_5)\text{Cl}]_x$, which with thallium(I) acetylacetonate gives² the dimeric acetylacetonato(allyl)platinum, $[\text{Pt}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_7\text{O}_2)]_2$. The dimeric formula of $[\text{Pt}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_7\text{O}_2)]_2$ suggested the presence of bridging allyl groups, whilst the very low solubility of $[\text{Pt}(\text{C}_3\text{H}_5)\text{Cl}]_x$ suggested a polymer which might have both chloro- and allyl-bridges. The only previous structure determination of a compound with bridging allyl groups is that of the hexamethyl Dewar benzene derivative, $[\text{Pt}(\text{C}_{12}\text{H}_{17})\text{Cl}]_2$.³ In this compound, however, the highly substituted and constrained allyl group cannot be considered typical, and it was of interest to determine the structure of a compound containing unsubstituted allyl bridges.

The insolubility of the chloro-complex (II) at first prevented the preparation of suitable crystals and we initially carried out a structure analysis on the acetylacetonato-complex (I), but satisfactory crystals of (II) were later obtained, and a structure determination on this also completed. Preliminary accounts of this work have been published.^{2,4}

EXPERIMENTAL

Acetylacetonato-complex (I)

Crystal Data.— $[\text{Pt}(\text{C}_3\text{H}_5)(\text{C}_5\text{H}_7\text{O}_2)]_2$, $\text{C}_{16}\text{H}_{24}\text{O}_4\text{Pt}_2$, $M = 670$, Monoclinic, $a = 10.01 \pm 0.01$, $b = 10.00 \pm 0.01$, $c =$

¹ G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmermann, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151.

17.29 ± 0.03 Å, $\beta = 100.2^\circ \pm 0.2^\circ$, $U = 1704$ Å³, $D_m = 2.59$, $Z = 4$, $D_c = 2.61$, $F(000) = 1232$. Space-group $P2_1/c$. Cu- K_α radiation, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K_\alpha) = 315$ cm⁻¹.

The cell dimensions were determined from zero-level precession photographs taken with Mo- K_α radiation ($\lambda = 0.7107$ Å). Intensities were recorded on equi-inclination Weissenberg photographs of layers 0—7*kl*, taken with Cu- K_α radiation, and visual estimation gave 1948 independent reflections. The crystal was a needle of radius *ca.* 0.003 cm, and no absorption corrections were applied.

The two independent platinum atoms were located from the Patterson synthesis, giving R 28%, and the oxygen and carbon positions were determined from two successive difference Fourier syntheses. Using the program of Smith and Cruickshank for the KDF 9, block-diagonal least-squares refinement of co-ordinates, isotropic temperature factors, and eight layer scales reduced R to 14.6%, and allowance for anisotropic vibrations for the platinum atoms gave a final R of 11.3%. The weighting scheme used in the final cycles was $w = 1/(25 + F_o + 0.0045 F_o^2 + 0.00005 F_o^3)$. The atomic scattering factors for platinum were taken from ref. 5 (with inclusion of the real part of anomalous scattering) and for carbon and oxygen from ref. 6.

The final co-ordinates and vibration parameters, with

² W. S. McDonald, B. E. Mann, G. Raper, B. L. Shaw, and G. Shaw, *Chem. Comm.*, 1969, 1254.

³ R. Mason, G. B. Robertson, and P. O. Whimp, *J. Chem. Soc. (A)*, 1970, 535.

⁴ G. Raper and W. S. McDonald, *Chem. Comm.*, 1970, 655.

⁵ D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

⁶ 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

their estimated standard deviations are given in Table 1. The observed and calculated structure factors for both compounds (I) and (II) are listed in Supplementary Publication No. SUP 20267 (18 pp., 1 microfiche).*

TABLE 1

Acetylacetonato-complex (I): atomic co-ordinates and isotropic temperature factors (\AA^2), with estimated standard deviations in parentheses

Atom	x	y	z	U_{iso}
Pt(1)	0.3837(2)	0.2186(1)	0.1478(1)	*
Pt(2)	0.2322(2)	-0.0974(1)	0.1341(1)	*
O(1)	0.261(3)	0.347(2)	0.187(1)	0.043(6)
O(2)	0.380(3)	0.332(3)	0.047(1)	0.046(6)
O(3)	0.030(2)	-0.110(2)	0.144(1)	0.035(5)
O(4)	0.182(3)	-0.146(3)	0.021(1)	0.049(6)
C(1)	0.388(4)	0.115(4)	0.245(2)	0.044(8)
C(2)	0.273(4)	0.023(3)	0.239(2)	0.038(7)
C(3)	0.290(5)	-0.114(4)	0.258(2)	0.053(10)
C(4)	0.430(4)	-0.079(3)	0.123(2)	0.041(7)
C(5)	0.454(4)	0.053(3)	0.089(2)	0.037(7)
C(6)	0.561(5)	0.132(5)	0.122(3)	0.071(13)
C(7)	0.111(6)	0.540(5)	0.191(3)	0.074(13)
C(8)	0.212(4)	0.457(4)	0.154(2)	0.045(8)
C(9)	0.229(5)	0.502(4)	0.083(2)	0.057(10)
C(10)	0.314(4)	0.436(3)	0.035(2)	0.039(8)
C(11)	0.318(5)	0.504(5)	-0.048(3)	0.067(12)
C(12)	-0.202(6)	-0.157(6)	0.116(3)	0.082(14)
C(13)	-0.058(4)	-0.142(4)	0.096(2)	0.041(8)
C(14)	-0.055(4)	-0.180(3)	0.014(2)	0.040(8)
C(15)	0.066(4)	-0.170(4)	-0.015(2)	0.052(9)
C(16)	0.061(5)	-0.213(4)	-0.099(2)	0.059(10)

* Anisotropic temperature factors (\AA^2):

Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Pt(1)	0.038(1)	0.024(1)	0.049(1)	-0.003(1)	0.020(1)	-0.001(1)
Pt(2)	0.037(1)	0.021(1)	0.049(1)	0.004(1)	0.020(1)	-0.002(1)

The temperature factors take the form: $\exp[-8\pi^2 U (\sin^2 \theta / \lambda)^2]$ for the isotropic case, and $\exp[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}hkb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$ for the anisotropic case.

Chloro-complex (II)

Crystal Data.— $[\text{Pt}(\text{C}_3\text{H}_5\text{Cl})_4]$, $\text{C}_{12}\text{H}_{20}\text{Cl}_4\text{Pt}_4$, $M = 1086$, Triclinic, $a = 13.34 \pm 0.03$, $b = 16.16 \pm 0.03$, $c = 8.33 \pm 0.01$ \AA , $\alpha = 90.2^\circ \pm 0.2^\circ$, $\beta = 100.2^\circ \pm 0.2^\circ$, $\gamma = 93.2^\circ \pm 0.2^\circ$, $U = 1765$ \AA^3 , D_m ca. 4, $Z = 4$, $D_c = 4.10$, $F(000) = 1888$. Space-group $P\bar{1}$, $\mu(\text{Cu}-K\alpha) = 650$.

The cell dimensions were determined from zero-level precession and Weissenberg photographs ($\text{Mo}-K\alpha$ radiation). Visual estimation of $\text{Cu}-K\alpha$ Weissenberg photographs of reciprocal lattice levels $hkl-7$ gave 2975 independent reflections. The irregularly shaped crystal had a maximum linear dimension of ca. 0.006 cm, and no absorption corrections were applied.

The three-dimensional Patterson synthesis showed all the major peaks close to the sections $x = 0$ and $x = \frac{1}{2}$. If the space-group is $P\bar{1}$ the asymmetric unit contains eight platinum atoms. The Patterson synthesis was interpreted in terms of two sets of four platinum atoms, the atoms in each set lying at the corners of a square of edge 3.2 \AA , and all eight having x co-ordinates close to $\frac{1}{4}$, with the crystallographic centre of symmetry relating these to two more groups of four at $x = \frac{3}{4}$. The presence of all 64 symmetry-independent $\text{Pt} \cdots \text{Pt}$ vectors in the Patterson map was verified.

A structure-factor calculation based on the eight platinum

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

atoms gave R 38%, reduced to 21% by least-squares refinement of platinum positions and isotropic temperature factors. The eight chlorine atoms were then located on a difference Fourier synthesis, and further least-squares refinement reduced R to 13.8%. A further difference synthesis revealed the 24 carbon atom positions. Finally block-diagonal least-squares refinement of the co-ordinates and isotropic temperature factors of all non-hydrogen atoms, together with 8 layer scale-factors, gave a final R value at convergence of 12.0%. Scattering factors were as for the previous determination.^{5,6} The weighting scheme in the final cycles was $w = 1/(40 + F_o + 0.002 F_o^2)$.

The final co-ordinates and vibration parameters, with their estimated standard deviations are given in Table 2.

TABLE 2

Chloro-complex (II): atomic co-ordinates and isotropic temperature factors (\AA^2), with estimated standard deviations in parentheses

Atom	Molecule (1)			
	x	y	z	U
Pt(1)	0.2167(2)	0.1643(2)	0.1408(4)	0.029(1)
Pt(2)	0.2484(2)	0.0487(2)	0.4659(4)	0.031(1)
Pt(3)	0.2415(3)	0.2096(2)	0.6926(4)	0.036(1)
Pt(4)	0.2587(2)	0.3274(2)	0.3771(4)	0.029(1)
Cl(1)	0.3550(15)	0.2637(11)	0.1881(25)	0.040(4)
Cl(2)	0.1190(15)	0.0875(11)	0.6061(25)	0.040(4)
Cl(3)	0.3692(15)	0.1142(12)	0.6977(26)	0.043(5)
Cl(4)	0.1125(14)	0.2836(11)	0.1816(23)	0.035(4)
C(1)	0.299(4)	0.069(3)	0.136(7)	0.010(11)
C(2)	0.359(6)	0.055(4)	0.292(9)	0.037(17)
C(3)	0.355(6)	-0.020(5)	0.382(10)	0.046(20)
C(4)	0.122(9)	0.009(7)	0.255(15)	0.088(35)
C(5)	0.097(6)	0.077(5)	0.189(10)	0.042(19)
C(6)	0.092(6)	0.091(4)	0.018(9)	0.035(17)
C(7)	0.313(6)	0.316(4)	0.719(9)	0.035(17)
C(8)	0.382(8)	0.321(7)	0.585(14)	0.074(29)
C(9)	0.387(7)	0.398(6)	0.519(12)	0.059(24)
C(10)	0.169(6)	0.367(4)	0.506(10)	0.037(17)
C(11)	0.132(6)	0.302(5)	0.610(10)	0.040(18)
C(12)	0.125(6)	0.287(4)	0.760(10)	0.037(17)

Molecule (2)

Atom	x	y	z	U_{iso}
Pt(5)	0.2790(2)	0.8285(2)	0.9926(4)	0.029(1)
Pt(6)	0.2610(3)	0.7144(2)	0.6639(4)	0.035(1)
Pt(7)	0.2599(2)	0.5515(2)	0.8876(4)	0.032(1)
Pt(8)	0.2310(2)	0.6658(2)	1.1978(4)	0.031(1)
Cl(5)	0.1318(13)	0.7861(10)	1.1002(22)	0.031(4)
Cl(6)	0.3862(16)	0.6159(12)	0.7315(26)	0.044(5)
Cl(7)	0.1352(15)	0.5942(12)	0.6665(25)	0.041(4)
Cl(8)	0.3725(15)	0.7605(11)	1.2365(25)	0.039(4)
C(13)	0.189(5)	0.870(4)	0.780(8)	0.028(15)
C(14)	0.144(5)	0.802(4)	0.688(9)	0.030(15)
C(15)	0.151(6)	0.786(5)	0.530(10)	0.040(18)
C(16)	0.366(5)	0.815(4)	0.693(9)	0.033(16)
C(17)	0.402(6)	0.823(4)	0.881(9)	0.036(17)
C(18)	0.407(6)	0.907(4)	0.945(9)	0.034(17)
C(19)	0.136(9)	0.509(7)	0.997(15)	0.086(34)
C(20)	0.114(7)	0.582(6)	1.093(12)	0.055(23)
C(21)	0.108(8)	0.593(6)	1.255(13)	0.065(26)
C(22)	0.324(6)	0.565(5)	1.256(10)	0.039(18)
C(23)	0.379(6)	0.553(5)	1.114(11)	0.048(21)
C(24)	0.374(7)	0.474(5)	1.029(11)	0.051(21)

DISCUSSION

The molecular structures of (I) and (II) are shown in Figures 1 and 2, which show the atom numbering; Figures 3 and 4 show their respective arrangements of molecules in the unit cells. The dimeric molecule of (I) has no crystallographic symmetry but closely approximates two-fold (C_2) symmetry. Neither of the two

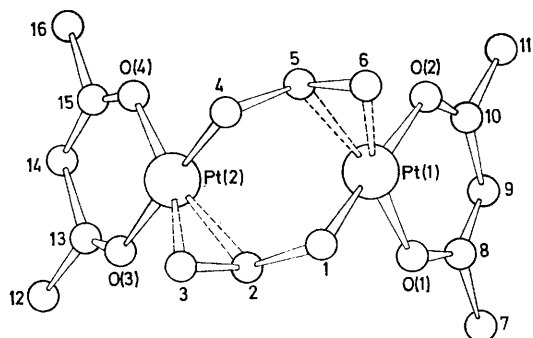


FIGURE 1 Acetylacetonato-complex (I): projection down the non-crystallographic two-fold axis

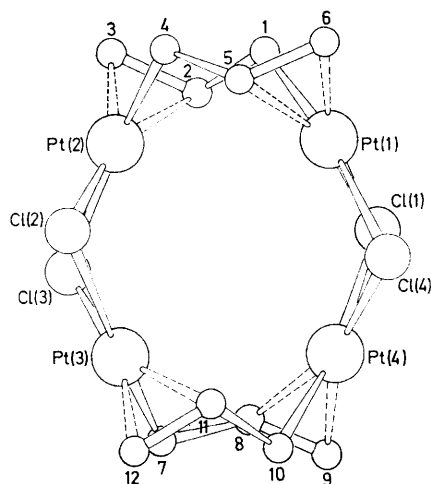


FIGURE 2 Chloro-complex (II): projection of molecule (1) down a non-crystallographic two-fold axis. The atom numbering of molecule (2) follows the same sequence

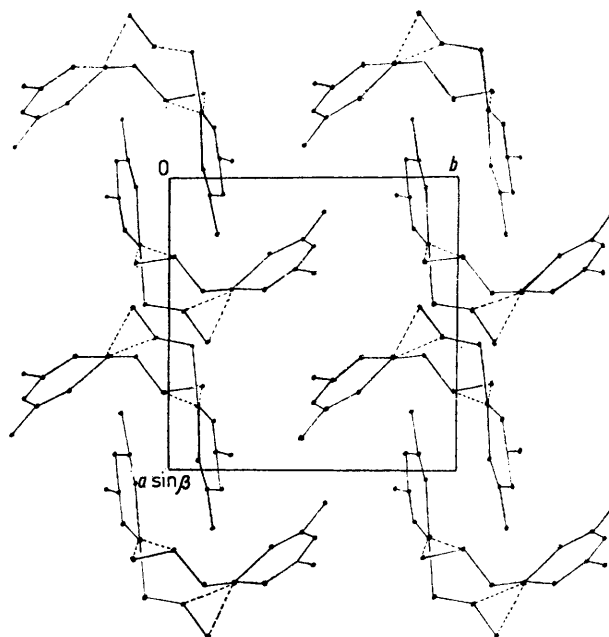


FIGURE 3 (I): Projection down the c axis

independent tetrameric molecules of (II) has crystallographic symmetry, but both approximate $222 (D_2)$ symmetry, and do not differ significantly in their dimensions. In the crystal of (II) molecules pack in layers at $x = \frac{1}{4}$ and $x = \frac{3}{4}$, each layer having approximate pgg symmetry, resulting in the angle α being very close to 90° , but the mutual orientation of different layers is such that the plane symmetry is not preserved in the three-dimensional structure.

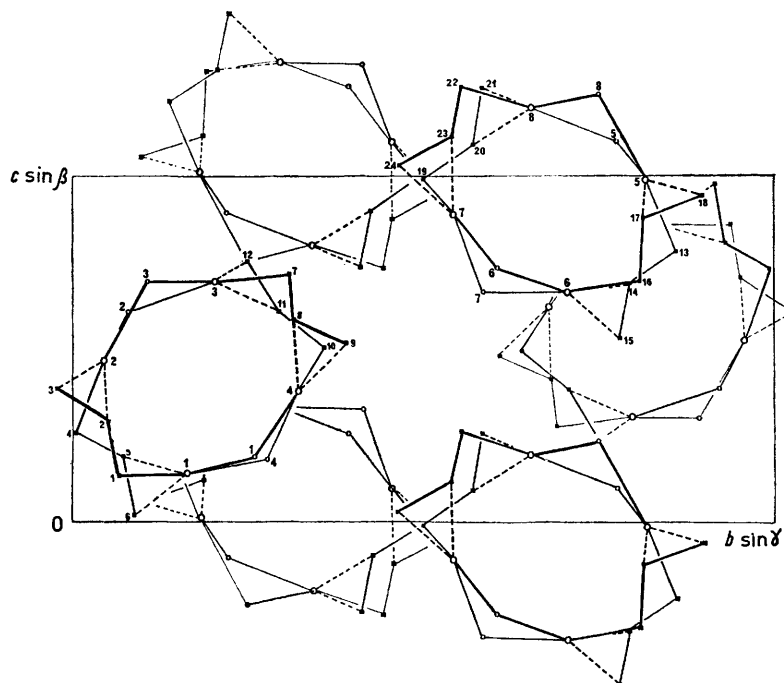


FIGURE 4 (II): Projection down the a axis

The bond lengths and angles for the two compounds are listed in Tables 3 and 4. For (II) the means of chemically equivalent dimensions are also given in Table 4. The equations of some mean planes and dihedral angles are in Table 5.

TABLE 3

Acetylacetonato-complex (I): bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses. Pairs of dimensions equivalent under the non-crystallographic two-fold symmetry are given on the same line

Pt(1)-O(1)	1.98(2)	Pt(2)-O(4)	1.99(2)
Pt(1)-O(2)	2.07(2)	Pt(2)-O(3)	2.07(2)
Pt(1)-C(1)	1.97(3)	Pt(2)-C(4)	2.02(4)
Pt(1)-C(5)	2.13(3)	Pt(2)-C(2)	2.15(3)
Pt(1)-C(6)	2.09(5)	Pt(2)-C(3)	2.12(4)
O(1)-C(8)	1.30(4)	O(4)-C(15)	1.24(5)
O(2)-C(10)	1.23(4)	O(3)-C(13)	1.14(4)
C(7)-C(8)	1.54(6)	C(15)-C(16)	1.51(6)
C(8)-C(9)	1.34(5)	C(14)-C(15)	1.39(6)
C(9)-C(10)	1.45(6)	C(13)-C(14)	1.49(5)
C(10)-C(11)	1.59(6)	C(12)-C(13)	1.54(7)
C(1)-C(2)	1.46(5)	C(4)-C(5)	1.49(5)
C(2)-C(3)	1.41(5)	C(5)-C(6)	1.37(6)
Pt(1) ... Pt(2)	3.495(2)		
O(1)-Pt(1)-O(2)	91(1)	O(3)-Pt(2)-O(4)	89(1)
O(1)-Pt(1)-C(1)	88(1)	O(4)-Pt(2)-C(4)	91(1)
O(2)-Pt(1)-C(1)	179(1)	O(3)-Pt(2)-C(4)	178(1)
Pt(1)-O(1)-C(8)	127(2)	Pt(2)-O(4)-C(15)	126(2)
Pt(1)-O(2)-C(10)	122(2)	Pt(2)-O(3)-C(13)	127(2)
Pt(1)-C(1)-C(2)	112(2)	Pt(2)-C(4)-C(5)	111(2)
Pt(1)-C(6)-C(5)	73(3)	Pt(2)-C(3)-C(2)	72(2)
Pt(1)-C(5)-C(6)	70(2)	Pt(2)-C(2)-C(3)	69(2)
O(1)-C(8)-C(7)	120(3)	O(4)-C(15)-C(16)	114(4)
O(1)-C(8)-C(9)	126(4)	O(4)-C(15)-C(14)	129(4)
O(2)-C(10)-C(11)	114(3)	O(3)-C(13)-C(12)	120(3)
O(2)-C(10)-C(9)	130(3)	O(3)-C(13)-C(14)	129(4)
C(1)-C(2)-C(3)	123(3)	C(4)-C(5)-C(6)	121(3)
C(7)-C(8)-C(9)	114(4)	C(14)-C(15)-C(16)	116(4)
C(8)-C(9)-C(10)	124(4)	C(13)-C(14)-C(15)	119(3)
C(9)-C(10)-C(11)	116(3)	C(12)-C(13)-C(14)	112(3)

TABLE 4

Chloro-complex: distances (Å) and angles (°) with estimated standard deviations in parentheses

Molecule (1)		Molecule (2)	
Pt(1) ... Pt(2)	3.273(4)	Pt(5) ... Pt(6)	3.262(4)
Pt(3) ... Pt(4)	3.283(4)	Pt(7) ... Pt(8)	3.262(4)
Mean Pt ... Pt(di- μ -C ₃ H ₅)	3.270(2)		
Pt(2) ... Pt(3)	3.225(4)	Pt(6) ... Pt(7)	3.230(4)
Pt(4) ... Pt(1)	3.248(4)	Pt(8) ... Pt(5)	3.236(4)
Mean Pt ... Pt(di- μ -Cl)	3.235(2)		
Pt(1)-Cl(1)	2.36(2)	Pt(5)-Cl(5)	2.37(2)
Pt(2)-Cl(2)	2.36(2)	Pt(6)-Cl(6)	2.37(2)
Pt(3)-Cl(3)	2.36(2)	Pt(7)-Cl(7)	2.38(2)
Pt(4)-Cl(4)	2.38(2)	Pt(8)-Cl(8)	2.34(2)
Mean Pt-Cl(<i>trans</i> to π -C ₃ H ₅)	2.37(1)		
Pt(1)-Cl(4)	2.50(2)	Pt(5)-Cl(8)	2.48(2)
Pt(2)-Cl(3)	2.48(2)	Pt(6)-Cl(7)	2.50(2)
Pt(3)-Cl(2)	2.51(2)	Pt(7)-Cl(6)	2.49(2)
Pt(4)-Cl(1)	2.46(2)	Pt(8)-Cl(5)	2.47(2)
Mean Pt-Cl(<i>trans</i> to σ -C ₃ H ₅)	2.49(1)		
Pt(1)-C(1)	1.95(5)	Pt(5)-C(13)	2.09(7)
Pt(2)-C(4)	2.27(12)	Pt(6)-C(16)	2.07(7)
Pt(3)-C(7)	1.91(7)	Pt(7)-C(19)	2.10(12)
Pt(4)-C(10)	1.87(8)	Pt(8)-C(22)	2.11(7)
Mean Pt-C(σ)	2.05(3)		

TABLE 4 (Continued)

Molecule (1)		Molecule (2)	
Pt(1)-C(5)	2.17(8)	Pt(5)-C(17)	2.03(8)
Pt(2)-C(2)	2.24(7)	Pt(6)-C(14)	2.20(7)
Pt(3)-C(11)	2.17(7)	Pt(7)-C(23)	2.24(8)
Pt(4)-C(8)	2.17(11)	Pt(8)-C(20)	2.08(9)
Mean Pt-C(π , central C)	2.16(3)		
Pt(1)-C(6)	2.09(7)	Pt(5)-C(18)	2.16(7)
Pt(2)-C(3)	2.07(8)	Pt(6)-C(15)	2.09(7)
Pt(3)-C(12)	2.19(7)	Pt(7)-C(24)	2.20(9)
Pt(4)-C(9)	2.16(9)	Pt(8)-C(21)	2.09(10)
Mean Pt-C(π , terminal C)	2.13(3)		
Cl(1)-Pt(1)-Cl(4)	84.4(6)	Cl(5)-Pt(5)-Cl(8)	84.5(6)
Cl(2)-Pt(2)-Cl(3)	85.7(7)	Cl(6)-Pt(6)-Cl(7)	85.2(7)
Cl(3)-Pt(3)-Cl(2)	85.1(7)	Cl(7)-Pt(7)-Cl(6)	85.0(7)
Cl(4)-Pt(4)-Cl(1)	84.7(6)	Cl(8)-Pt(8)-Cl(5)	85.3(6)
Mean Cl-Pt-Cl	85.0(2)		
Pt(1)-Cl(1)-Pt(4)	84.9(6)	Pt(5)-Cl(5)-Pt(8)	83.9(6)
Pt(2)-Cl(2)-Pt(3)	82.9(6)	Pt(6)-Cl(6)-Pt(7)	83.3(7)
Pt(3)-Cl(3)-Pt(2)	83.7(6)	Pt(7)-Cl(7)-Pt(6)	82.8(6)
Pt(4)-Cl(4)-Pt(1)	83.5(6)	Pt(8)-Cl(8)-Pt(5)	84.3(6)
Mean Pt-Cl-Pt	83.7(2)		
Pt(1)-C(1)-C(2)	111(4)	Pt(5)-C(13)-C(14)	109(5)
Pt(2)-C(4)-C(5)	103(8)	Pt(6)-C(16)-C(17)	104(4)
Pt(3)-C(7)-C(8)	106(5)	Pt(7)-C(19)-C(20)	105(7)
Pt(4)-C(10)-C(11)	113(5)	Pt(8)-C(22)-C(23)	107(5)
Mean Pt-C-C	107(2)		
C-C (' single bond')	1.26(14)-1.57(13), mean 1.46(4)		
C-C (' double bond')	1.29(11)-1.46(10), mean 1.40(4)		
C-C-C	113(8)-142(7) ^o , mean 125(3) ^o		

TABLE 5

Equations of mean planes and dihedral angles in the form $AX + BY + CZ = D$

(a) Acetylacetonato-complex (I): planes referred to unit (Å) axes parallel to \mathbf{a}^* , \mathbf{b} , and \mathbf{c} .

	A	B	C	D
Plane (1): Pt(1), O(1), O(2), C(7)-(11)	0.787	0.531	0.314	4.742
Plane (2): Pt(2), O(3), O(4), C(12)-(16)	-0.161	0.960	-0.230	-1.700

(b) Chloro-complex (II): planes referred to unit (Å) axes parallel to \mathbf{a}^* ($\mathbf{a}^* \times \mathbf{c}$) and \mathbf{c} .

	A	B	C	D
Plane (3): Pt(1)-(4)	0.997	-0.042	-0.065	2.844
Plane (4): Pt(1), Cl(1), Cl(4)	0.128	-0.194	0.972	0.512
Plane (5): Pt(2), Cl(2), Cl(3)	0.040	-0.877	0.478	1.179
Plane (6): Pt(3), Cl(2), Cl(3)	0.037	0.190	-0.981	-4.364
Plane (7): Pt(4), Cl(1), Cl(4)	0.058	0.869	-0.492	3.386
Plane (8): Pt(5)-(8)	0.995	-0.070	0.075	3.132
Plane (9): Pt(5), Cl(5), Cl(8)	0.072	0.860	0.506	15.418
Plane (10): Pt(6), Cl(6), Cl(7)	0.008	+0.167	0.986	6.728
Plane (11): Pt(7), Cl(6), Cl(7)	0.035	-0.876	-0.481	-10.762
Plane 12): Pt(8), C(5), Cl(8)	0.138	-0.192	-0.972	-10.742

(c) Dihedral (deg.).

(1)-(2)	71.9	(6)-(7)	49.5	(10)-(11)	129.8
(4)-(5)	50.1	(7)-(4)	129.8	(11)-(12)	50.2
(5)-(6)	129.4	(9)-(10)	50.0	(12)-(9)	130.3

The diallyl bridge between platinum atoms is common to both compounds. Each allyl group is σ -bonded to one platinum and π -bonded to the other, and each platinum forms one σ - and one π -bond to allyl groups. Although the Pt-C and C-C bond lengths show no significant differences between the two compounds, the non-bonded Pt \cdots Pt distances differ considerably; in the acetylacetonato-complex Pt \cdots Pt is 3.495(2) Å and in the chloro-complex it is 3.270(2) Å. The lower value for the latter probably results from a folding across the bridge in order to achieve the cyclic structure. The differing Pt \cdots Pt distances are reflected in the dihedral angles defined by the co-ordination planes of the metal atoms (Table 5). In the acetylacetonato-complex the angle between the planes of the two [Pt(acac)] rings is 72° while in the chloride the angle at the diallyl bridge, as defined by the two (Cl₂Pt) planes is 50°. The only other structure determination revealing³ a diallyl bridge is that of [Pt₂Cl₂(C₁₂H₁₇)₂] where the C₁₂H₁₇ ligand contains both an allyl group which bridges, as in our compounds, and an olefin group which also co-ordinates to the metal. In this compound the Pt \cdots Pt distance is 3.262(2) Å and the dihedral angle 57°.

The differing *trans* influences of σ - and π -bonded allyl may be seen in both compounds. In the acetylacetonato-complex the Pt-O distances *trans* to σ -bonded allyl are each 2.07(2) Å while those *trans* to π -bonded allyl

are 1.98(2) and 1.99(2) Å. Similarly in the chloro-complex the mean Pt-Cl distance *trans* to σ -bonded allyl is 2.49(1) Å and that *trans* to π -bonded allyl is 2.37(1) Å.

As is normally the case, each π -bonded olefin group is approximately perpendicular to the co-ordination plane of its attached platinum atom. Thus in the acetylacetonato-complex the angle between the C(5)-C(6) bond and the normal to the O(1), Pt, O(2) plane is 3.6°, *σ ca.* 2° and for the C(2)-C(3) bond the angle is 1.4°. The corresponding angles in the chloro-complex range between 1 and 10°, *σ ca.* 4°.

In addition to the previously mentioned folding of the diallyl bridge, the cyclic structure of (II) also requires that the dichloro-bridges shall depart greatly from planarity. The dihedral angles at the bridging chlorines (Table 5) are all close to 130° (*i.e.* 50° departure from planarity) whilst in most other di- μ -chloro-palladium and -platinum compounds the bridge is planar. Large departures from planarity have been found in some di- μ -chloro-rhodium compounds, notably the dihedral angle of 116° in [Rh₂Cl₂(CO)(C₆H₁₀)₂]₂ which resembles (II) in having a tetranuclear cyclic structure.⁷

The mean Pt-C distances to σ -bonded carbon, central carbon, and terminal π -bonded carbon are: 1.99(3), 2.14(2), and 2.10(3) Å for the acetylacetonato- and 2.05(3), 2.16(3), and 2.13(3) Å for the chloro-complex.

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⁷ L. R. Bateman, P. M. Maitlis, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1969, **91**, 7292.