Synthesis of Ethylene, Cyclo-octa-1,5-diene, Bicyclo[2.2.1]heptene, and trans-Cyclo-octene Complexes of Palladium(o) and Platinum(o); Crystal and Molecular Structure of Tris(bicyclo[2.2.1]heptene)platinum

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Reaction of $[Pt(1,5-C_8H_{12})Cl_2]$ with $Li_2(C_8H_8)$ in diethyl ether in the presence of excess of $1,5-C_8H_{12}$ gives the white crystalline complex $[Pt(1,5-C_8H_{12})_2]$ in good yield. A similar reaction of $[Pd(1,5-C_8H_{12})Cl_2]$ in the presence of propene affords $[Pd(1,5-C_8H_{12})_2]$, stable below ambient temperatures. The reaction of $[M(1,5-C_8H_{12})Cl_2]$ (M = Pd or Pt) with $Li_2(C_8H_8)$ and excess of bicyclo[2.2.1]heptene gives, respectively, tris(bicyclo[2.2.1]heptene)-palladium and -platinum. These complexes are also obtained by displacement of cyclo-octa-1,5-diene from $[M(1,5-C_8H_{12})_2]$ (M = Pd or Pt) by bicyclo[2.2.1]heptene. Related displacement reactions with trans-cyclo-octene and ethylene afford, respectively, tris(trans-cyclo-octene)palladium, tris(trans-cyclo-octene)platinum, tris(ethylene)palladium, and tris(ethylene)platinum. The ethylene complexes are highly volatile, and can be isolated as crystalline species, although they readily deposit the metals. The structural identity of tris(bicyclo-[2.2.1]heptene)platinum has been established by analysis of single-crystal X-ray data recorded on a four-circle diffractometer both at room temperature and at 190 K. The complex is orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 5.717(1)$, $b = 10.735(4)$, $c = 28.749(12)$ Å, at 300 K; at 190 K $a = 5.598(6)$, $b = 10.775(16)$, $c = 28.562(40)$ Å. Full-matrix least-squares refinement, using 1 781 reflections, has converged to R 0.055 (R' 0.066) (190 K data). The molecule has a trigonal-planar structure in which the maximum deviation from planarity is 0.03 Å.

THE synthesis of the complexes bis(cyclo-octa-1,5-diene)nickel and trans,trans,trans-cyclododeca-1,5,9-trienenickel, [Ni(cdt)], together with the observed lability of the olefinic ligands, particularly cdt, led to the rapid development of organonickel chemistry.[1] Clearly, a similar important role for 'pure-olefin' complexes of palladium(o) [2,3] and platinum(o) [4] can be envisaged. However, at the outset of our investigation [5] the zero-valent chemistry of these two transition metals was concentrated [6] around phosphine and phosphite species, and, moreover, there was a suggestion [1] that nickel was possibly unique in the facility with which it forms stable 'pure-olefin' complexes.

Our attention was initially focussed on the report by Müller and Göser [7] that bis(cyclo-octa-1,5-diene)-

platinum was formed by reductive elimination on photolysis of (cyclo-octa-1,5-diene)di-isopropylplatinum in the presence of excess of cyclo-octa-1,5-diene. However, a reinvestigation of this reaction sequence led in our hands to inconsistent results in the synthesis of (1), and it

(1) M = Pt
(2) M = Pd

became clear that sufficient quantities of $[Pt(1,5-C_8H_{12})_2]$ for a synthetic study could not be obtained by this route,
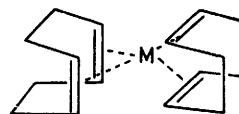
[1] P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1974, vol. 1; 1975, vol. 2.

[2] Y. Takahashi, T. Ito, S. Sakai, and Y. Ishii, Chem. Comm., 1970, 1065.

[3] K. Moseley and P. M. Maitlis, Chem. Comm., 1971, 982.

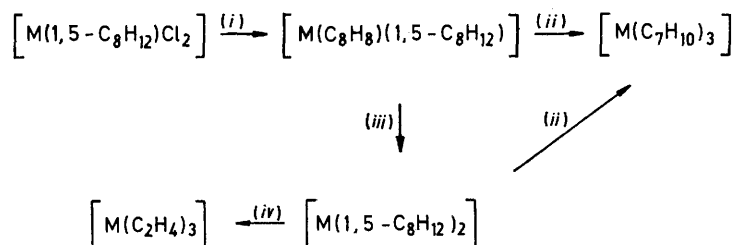[4] U. Belluco, 'Organometallic and Coordination Chemistry of Platinum,' Academic Press, New York, 1974.

[5] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, J.C.S. Chem. Comm., 1975, 449.

[6] L. Malatesta and S. Cenini, 'Zerovalent Compounds of Metals,' Academic Press, London, 1974.

[7] J. Müller and P. Göser, Angew. Chem. Internat. Edn., 1967, 6, 364.

and, therefore, an alternative approach to this complex and to other 'ligand-free' platinum(0) complexes was sought.

It has been observed [1] that strained olefins form more stable complexes with Ni^0. The origin of this effect is possibly a lowering in energy of the π^* orbital and an

$$\left[M(1,5-C_8H_{12})Cl_2\right] \xrightarrow{(i)} \left[M(C_8H_8)(1,5-C_8H_{12})\right] \xrightarrow{(ii)} \left[M(C_7H_{10})_3\right]$$

$$(iii)\downarrow \qquad (ii)\nearrow$$

$$\left[M(C_2H_4)_3\right] \xleftarrow{(iv)} \left[M(1,5-C_8H_{12})_2\right]$$

SCHEME 1 M = Pd or Pt. (i) $Li_2(C_8H_8)$–OEt_2, low temperature; (ii) excess of bicyclo[2.2.1]heptene; (iii) excess of cyclo-octa-1,5-diene; (iv) excess of ethylene

Reaction at low temperatures (−30 °C) of dichloro-(cyclo-octa-1,5-diene)platinum with a solution of the dilithium salt of the cyclo-octatetraene dianion [8] in diethyl ether in the presence of an excess of cyclo-octa-1,5-diene gave, in consistently good yields, bis(cyclo-octa-1,5-diene)platinum as a white crystalline complex (1). The complex is stable in air and can be handled without difficulty. It is assumed that the synthesis involves initial attack by $C_8H_8{}^{2-}$ on platinum with formation of (cyclo-octa-1,5-diene)(cyclo-octatetraene)-platinum as an intermediate, from which cyclo-octatetraene is displaced by cyclo-octa-1,5-diene (see Scheme 1). Although carbanions have been shown to react with $[Pt(1,5-C_8H_{12})Cl_2]$ at an olefinic carbon atom, there was no evidence in the reaction with $C_8H_8{}^{2-}$ for such a process. It is interesting to note that $[\{M(1,5-C_8H_{12})-Cl_2\}_x]$ (M = Ru or Os) have been shown [9] to react with $K_2(C_8H_8)$ to form $[M(C_8H_8)(1,5-C_8H_{12})]$. The platinum complex was characterised by elemental analysis, and by ^{13}C and ^1H n.m.r. spectroscopy, and is formulated as a tetrahedral species, isostructural with bis(cyclo-octa-1,5-diene)nickel.[10] The ^1H n.m.r. parameters observed agreed with those reported by Müller and Göser.[7]

An initial attempt to prepare the hitherto unknown bis(cyclo-octa-1,5-diene)palladium(II) by a straight adaptation of the procedure used for the platinum complex was unsuccessful. However, when the reaction of $[Pd(1,5-C_8H_{12})Cl_2]$ with $Li_2(C_8H_8)$ was conducted in the presence of propene then (2) could be isolated (30—40% yield) as a white crystalline complex, stable at −20 °C in the solid state. At ambient temperatures it rapidly decomposes, releasing cyclo-octa-1,5-diene and depositing palladium. The complex has also been prepared from palladium vapour.[11] It is suggested that the function of propene in the synthesis described herein is to stabilise Pd^0 in solution as a very soluble complex, and prevent extensive deposition of palladium metal. In the work-up procedure, the volatile propene is removed leaving cyclo-octa-1,5-diene to co-ordinate to the palladium.

increase in the energy of the π orbital leading to more favourable overlap with the metal d orbitals. With this in view the direct synthesis of tris(bicyclo[2.2.1]heptene)-platinum and -palladium, (3) and (4), was attempted.

(3) M = Pt
(4) M = Pd
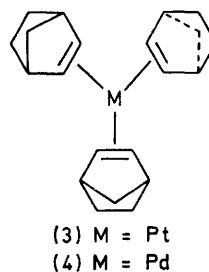
Reaction (−30°) of $[M(1,5-C_8H_{12})Cl_2]$ (M = Pt or Pd) with $Li_2(C_8H_8)$ in the presence of an excess of bicyclo[2.2.1]heptene gave a good yield of the required trisolefin complexes. The less stable palladium complex (4) tended to decompose in solution in the absence of free bicyclo[2.2.1]heptene. However, in the solid state both complexes exist as well defined white crystalline solids.

The tris(bicyclo[2.2.1]heptene) complexes could also be obtained respectively from (1) or (2) by direct displacement of cyclo-octa-1,5-diene with bicyclo[2.2.1]heptene (Scheme 1). An extension of the displacement reaction to that with trans-cyclo-octene afforded as crystalline

(5) M = Pt
(6) M = Pd

complexes tris(trans-cyclo-octene)-platinum (5) and -palladium (6). In contrast to the cyclo-octa-1,5-diene and bicyclo[2.2.1]heptene complexes, the nickel analogue of the tris(trans-cyclo-octene)-palladium and -platinum

[8] T. J. Katz, J. Amer. Chem. Soc., 1960, 82, 3784.

[9] R. R. Schrock and J. Lewis, J. Amer. Chem. Soc., 1973, 95, 4102.

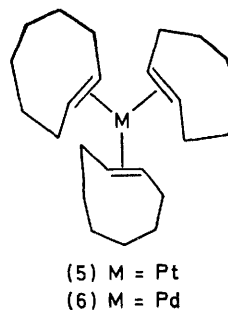[10] H. Dierks and H. Dietrich, Z. Krist., 1965, 122, 1; see also ref. 1, vol. 1, p. 258.

[11] R. M. Atkins, R. McKenzie, P. L. Timms, and T. W. Turney, J.C.S. Chem. Comm., 1975, 764.

complexes has not been described. The trisolefin complexes showed the expected ^{1}H and ^{13}C n.m.r. spectra, there being no evidence of rapid exchange in solution in the presence of excess of olefin.

Although tris(ethylene)nickel is formed [12] on reaction of ethylene with [Ni(cdt)], the corresponding reaction with [Ni(1,5-C$_8$H$_{12}$)$_2$] does not readily afford [Ni(C$_2$H$_4$)$_3$]. This is in interesting contrast with the platinum and palladium systems. The addition of solid [Pt(1,5-C$_8$H$_{12}$)$_2$] or [Pd(1,5-C$_8$H$_{12}$)$_2$] to a stirred (—10 and —25 °C, respectively) solution of ethylene in light petroleum followed by cooling to —100° afforded the white crystalline complexes tris(ethylene)-platinum (7) and -palladium (8). Both complexes are volatile, and the platinum complex could be further purified by slow sublimation at 20 °C on to a cold finger under an atmosphere of ethylene. In the absence of ethylene, both complexes deposit pure platinum or palladium metal films on to the walls of the containing vessel.

The ^{1}H and ^{13}C n.m.r. spectra of (7) and (8) showed chemical shifts and coupling constants (^{195}Pt^{-1}H, and ^{195}Pt^{-13}C) typical of a π-bonded ethylene complex. There are two possible structures for these complexes: a trigonal-' planar ' structure in which all the olefinic

(7) M = Pt
(8) M = Pd
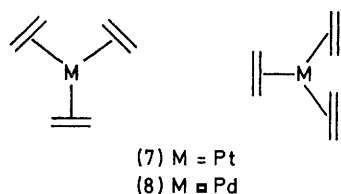
carbon atoms lie in the co-ordination plane; and a trigonal-' upright ' arrangement where the C=C double bonds are perpendicular to the co-ordination plane. Both structures have D_{3h} symmetry. A theoretical analysis [13] based on symmetry arguments supported by semi-empirical molecular-orbital calculations suggests that the illustrated ' planar ' structure is preferred. The analysis assumes that σ bonding is equally strong in both the ' planar ' and ' upright ' structures, but that back bonding is maximised for the planar structure.

Whereas an X-ray crystallographic study of tris-(bicyclo[2.2.1]heptene)nickel showed [14] an essentially planar structure, one of the olefin systems is twisted by 16° out of the trigonal plane. The availability of both complexes (3) and (4) provided an opportunity to re-examine this question. A single-crystal X-ray diffraction study of (3) established the overall molecular geometry shown in Figure 1, the hydrogen atoms being omitted for clarity. The C=C double bonds of the bicyclo[2.2.1]heptene ligands lie in the co-ordination plane of the platinum atom, with the carbon atoms at a mean distance of 2.18(2) Å from the central metal atom; the Pt–C(π) bond length corresponds to that found for other platinum π-olefin complexes.[15] The maximum

[12] K. Fischer, K. Jonas, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1973, **12**, 565.
[13] N. Rösch and R. Hoffmann, *Inorg. Chem.*, 1974, **13**, 2656.

deviation of any atom from the mean plane is 0.03 Å. As in the nickel system,[14] two of the bridged methylene groups are on one side of the co-ordination plane (2.17 and 2.27 Å) with the other on the opposite side (2.25 Å). The three bicyclo[2.2.1]heptene ligands all show the general shape A–C 110°, A–B 130°, and B–C 120° (angles between planes, as shown in Scheme 2), with
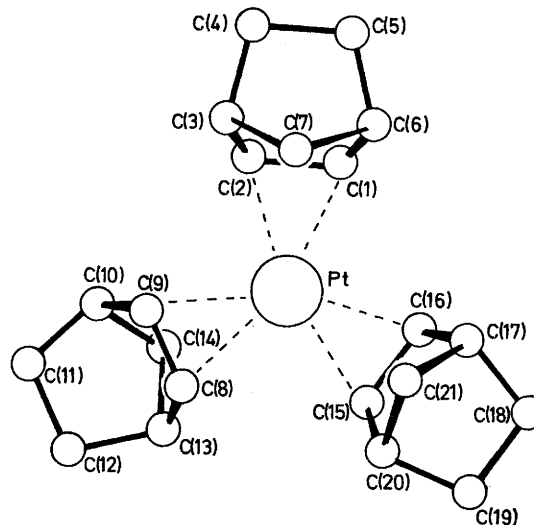

FIGURE 1   Molecular structure of tris(bicyclo[2.2.1]heptene)-platinum (hydrogen atoms omitted), showing the atom-numbering system

little distortion on co-ordination from the expected geometry, except of course for the lengthening of the C=C double bond to 1.39 Å (mean) and consequent bending back of the H atoms on these carbon atoms.

Crystals of the palladium complex (4) [space group $P2_12_12_1$, $a = 5.705(1)$, $b = 10.784(5)$, $c = 28.776(15)$ Å, at 300 K] are isomorphous with the platinum complex (3), and comparison of the intensities of the several X-ray
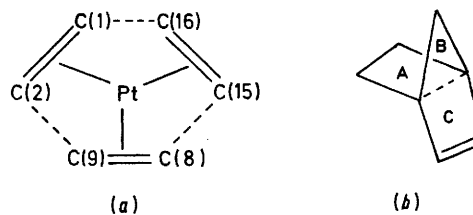
SCHEME 2   (a) Co-ordination around the platinum atom; (b) the bicyclo[2.2.1]heptene ligand

photographs taken strongly support the two complexes being isostructural. Thus, in three-co-ordinate trisolefin complexes a trigonal-' planar ' structure is preferred,

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra, unless otherwise specified, were recorded on a Varian Associates HA 100 spectrometer at 100 MHz. Carbon-13 n.m.r. spectra were measured on a JEOL JNM-PFT-100 spectrometer operating in the Fourier-transform mode, at 25.15 MHz. For ^{13}C shifts δ is

[14] C. Kruger and Y-H. Tsay, *Abs. 6th Internat. Conf. Organometallic Chem. (Amherst)*, 1973, 80; see also ref. 12.
[15] J. A. Ibers and S. D. Ittel, *Adv. Organometallic Chem.*, 1976, **14**, 33.

measured relative to SiMe$_4$, positive values to high frequency.* I.r. spectra were recorded on a Perkin-Elmer 457 grating spectrometer.

Unless otherwise stated, experiments were carried out under a dry oxygen-free nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. Alumina (B.D.H., Brockman Activity II) was used without modification. Cyclo-octa-1,5-diene was freshly distilled from sodium. Cyclo-octatetraene was filtered through alumina prior to use. Ethylene was CP grade and was used without further purification. *trans*-Cyclo-octene was prepared by the published method.[16]

Syntheses.—Bis(cyclo-octa-1,5-diene)platinum. A suspension of finely powdered [Pt(1,5-C$_8$H$_{12}$)Cl$_2$] (3.7 g, 10 mmol) in cyclo-octa-1,5-diene was treated dropwise with a diethyl ether solution of Li$_2$(C$_8$H$_8$) (*ca.* 40 cm^3 of a 0.24 mol dm^{-3} solution) at −30 °C. The mixture was stirred for a further 0.5 h as the temperature rose to −10 °C, and then the solvent was removed *in vacuo* until the residue was completely dry. Extraction with toluene (6 × 50 cm^3) gave a brown solution, which was filtered through a column of alumina (8 cm). The volume of solvent was reduced to *ca.* 15 cm^3, and the mother liquor decanted from the off-white product, which was washed with several small portions of cold toluene until the washings were almost colourless. Bis(cyclo-octa-1,5-diene)platinum, (1) (1.6—2.4 g, 40—60%), thus prepared was suitable for many purposes. Pure white *crystals* were obtained by dissolving the crude material in light petroleum (b.p. 40—60 °C) {*ca.* 80 cm^3 for each mmol of [Pt(1,5-C$_8$H$_{12}$)$_2$]}, filtering through alumina (6 cm), and cooling to −78 °C (Found: C, 47.7; H, 5.7. Calc. for C$_{16}$H$_{24}$Pt: C, 47.4; H, 5.9%); $\nu_{max.}$ at 3 020(sh), 3 000(sh), 2 930m, 2 910(sh), 2 865m, 2 825m, 1 475m, 1 465m, 1 433m, 1 327s, 1 306w, 1 238m, 1 212m, 1 178w, 1 158w, 1 090vw, 1 075w, 1 009w, 998m, 970(sh), 962w, 890vw, 865(sh), 855m, 829(sh), 823m, 810m, 788m, 769vw, 580vw, 510vw, and 465vw cm^{-1}. The ^{1}H n.m.r. spectrum (in C$_6$D$_6$) showed resonances at τ 5.80 [m, 8 H, CH=CH, *J*(PtH) 55 Hz] and 7.81 (m, 16 H, CH$_2$). The ^{13}C n.m.r. spectrum (in [^{2}H$_6$]benzene, ^{1}H decoupled) showed resonances at 73.3 [C=C, *J*(PtC) 143] and 33.2 p.p.m. [CH$_2$, *J*(PtC) 15 Hz].†

Bis(cyclo-octa-1,5-diene)palladium. Careful addition of Li$_2$(C$_8$H$_8$) (*ca.* 50 cm^3 of a 0.26 mol dm^{-3} solution) in diethyl ether to a slurry of finely divided [Pd(1,5-C$_8$H$_{12}$)Cl$_2$] (3.7 g, 13 mmol) at −50 °C in cyclo-octa-1,5-diene (20 cm^3) gave a khaki suspension. The nitrogen atmosphere was displaced with propene and the reaction mixture stirred vigorously at −35 °C for 1.5 h, during which time the suspension became almost black. This mixture was then poured rapidly, under an atmosphere of propene, on to a short column (5 cm) of alumina contained in a cold-jacketed (−35 °C) filtration apparatus, and washed off the column with cold diethyl ether (20 cm^3). The yellow filtrate was collected in a Schlenk tube immersed in a cold-bath at −40 °C, so that at no point was the solution in contact with glass at above −25 °C. After removal of the filtration unit, the tube containing the filtrate was carefully evacuated at −30 °C until a dirty grey solid precipitated. This was allowed to settle; the supernatant liquid was decanted under nitrogen, and the residue washed twice with cold

diethyl ether. The crude product was then taken up in liquid propene (35 cm^3) at −65 °C and filtered through alumina at −70 °C to give a colourless filtrate which, on evaporation of the propene, gave the pale cream solid bis(cyclo-octa-1,5-diene)palladium, (2) (1.3 g, 31%) (Found: C, 60.5; H, 7.7; Pd, 32.7. C$_{16}$H$_{24}$Pd requires C, 59.5, H, 7.5; Pd, 33.0%); $\nu_{max.}$ (in Nujol, low temperature) at 1 523m, 1 335s, 1 316w, 1 245m, 1 238m, 1 189m, 1 161w, 1 091w, 1 019m, 998m, 951m, 940w, 860s, 826s, 754m, 680m, and 544m cm^{-1}.

Tris(bicyclo[2.2.1]heptene)platinum. Finely powdered [Pt(1,5-C$_8$H$_{12}$)Cl$_2$] (3.7 g, 10 mmol) was slurried with diethyl ether (15 cm^3) and bicyclo[2.2.1]heptene (6.0 g, 64 mmol) at −30 °C. After the slow (20 min) addition of a diethyl ether solution of Li$_2$(C$_8$H$_8$) (40 cm^3 of a 0.24 mol dm^{-3} solution) the solvent was removed *in vacuo* (15 °C), and the residue extracted (15 °C) with light petroleum (6 × 50 cm^3). The extract was filtered through a column (8 cm) of alumina, and the filtrate evaporated *in vacuo* until a mass of fine needles began to precipitate. On cooling (−50°) a further crop of crystals separated, which were collected and recrystallised from light petroleum, to give colourless *needles* of tris(bicyclo[2.2.1]heptene)platinum, (3) (2.1 g, 45%) (Found: C, 53.1; H, 6.5. C$_{21}$H$_{30}$Pt requires C, 52.8; H, 6.3%); $\nu_{max.}$ at 3 020(sh), 3 010m, 1 315m, 1 296wm, 1 272s, 1 254w, 1 210vw, 1 170w, 1 128m, 1 070m, 1 003w, 993w, 966w, 955vw, 939w, 919(sh), 912m, 910(sh), 881vw, 850m, 809w, 770w, 555s, and 478m cm^{-1}. The ^{1}H n.m.r. spectrum (in [^{2}H$_6$]benzene) showed resonances at τ 6.64 [m, 6 H, CH=CH, *J*(PtH) 64.0 Hz], 7.04 (m, 6 H, CH), 8.44 (m, 12 H, CH$_2$), and 9.78 (AB, 6 H, CH$_2$ bridge). The ^{13}C n.m.r. spectrum (in [^{2}H$_6$]benzene, ^{1}H decoupled) showed resonances at 68.0 [C=C, *J*(PtC) 189], 42.8 [CH$_2$, *J*(PtC) 14.0], 39.5 [CH$_2$ bridging, *J*(PtC) 49.0], and 28.6 [CH bridgehead, *J*(PtC) 44.0 Hz].

Tris(bicyclo[2.2.1]heptene)palladium. A solution (80 cm^3 of a 0.24 mol dm^{-3} solution) of Li$_2$(C$_8$H$_8$) was added (40 min, −30°) to a stirred slurry of [Pd(1,5-C$_8$H$_{12}$)Cl$_2$] (5.7 g, 20 mmol) and bicyclo[2.2.1]heptene (10.0 g, 109 mmol) in diethyl ether (30 cm^3). Since prolonged pumping on [Pd(C$_7$H$_{10}$)$_3$] at temperatures above −30 °C caused decomposition to palladium metal, the volume of the solvent was only partially reduced (−30 °C). The reaction mixture was extracted with pentane (6 × 50 cm^3) and the resulting solution was filtered through alumina (8 cm) at 0 °C. Reduction of the volume of the solvent *in vacuo* and cooling (−50 °C) gave white crystals. These were collected and recrystallised (−50 °C) from pentane–bicyclo[2.2.1]heptene (20 : 1) to give colourless *needles* of tris(bicyclo[2.2.1]heptene)palladium, (4) (4.0 g, 52%) (Found: C, 65.9; H, 8.1. C$_{21}$H$_{30}$Pd requires C, 64.9; H, 7.8%); $\nu_{max.}$ at 3 030(sh), 3 015m, 1 324m, 1 297w, 1 276s, 1 255w, 1 210vw, 1 168vw, 1 125m, 1 080m, 982w, 968w, 953w, 940w, 912s, 883w, 848m, 822w, 805w, 770w, 718w, 685w, 555(sh), 525m, and 465s cm^{-1}. The ^{1}H n.m.r. spectrum (in [^{2}H$_8$]toluene, −40 °C) showed resonances at τ 5.90 (m, 6 H, CH=CH), 6.90 (m, 6 H, CH), 8.5 (m, 12 H, CH$_2$), and 9.46 (s, 6 H, bridging CH$_2$).

Displacement Reactions of Bis(cyclo-octa-1,5-diene)platinum. (*a*) *With* trans-*cyclo-octene.* A pentane solution (5 cm^3) of *trans*-cyclo-octene (2.5 mmol) was added (room temperature) to a toluene (5 cm^3) solution of [Pt(1,5-C$_8$H$_{12}$)$_2$] (0.20 g, 0.5 mmol). Almost immediately radial

* In ref. 5 ^{13}C shifts were given the reverse sign.

† The corresponding signals in the ^{13}C n.m.r. spectrum (in [^{2}H$_6$]benzene, ^{1}H decoupled) of [Ni(1,5-C$_8$H$_{12}$)$_2$] were at 89.6 (C=C) and 30.8 p.p.m. (CH$_2$). The ^{1}H n.m.r. spectrum of the nickel complex is given in refs. 1 (p. 290) and 7.

[16] E. Vedejs, K. A. J. Snoble, and P. L. Fuchs, *J. Org. Chem.*, 1973, **38**, 1178.

clusters of crystals began to form. Crystallisation was complete at −20 °C, the supernatant liquid decanted, and the residue washed with light petroleum to give colourless *crystals* of tris(*trans*-cyclo-octene)platinum, (5) (0.20 g, 76%) (Found: C, 55.0; H, 8.7. $C_{24}H_{42}Pt$ requires C, 54.9; H, 8.1%); $\nu_{max.}$ at 1 353w, 1 345w, 1 332w, 1 275s, 1 246s, 1 221w, 1 188w, 1 147w, 1 082m, 983m, 954w, 924m, 876w, 853m, 821w, 720w, 544s, and 510w cm⁻¹. The ¹H n.m.r. spectrum (in [²H₆]benzene) showed resonances at τ 6.94 [m with ¹⁹⁵Pt satellites, 6 H, CH=CH, *J*(PtH) 58 Hz], 7.14 (m, 6 H), 8.0 (m, 18 H), and 8.8 (m, 12 H). The ¹³C n.m.r. spectrum (in [²H₆]benzene, ¹H decoupled) showed resonances at 72.9 [C=C, *J*(PtC) 154.0], 37.1 [*J*(PtC) 60], 36.2 [*J*(PtC) 28 Hz], and 29.3 p.p.m.

(b) *With bicyclo[2.2.1]heptene.* In a similar reaction, treatment of [Pt(1,5-C₈H₁₂)₂] with bicyclo[2.2.1]heptene gave (3) in essentially quantitative yield.

(c) *With ethylene.* Light petroleum (25 cm³) was stirred (0 °C) under an atmosphere of ethylene, and solid [Pt-(1,5-C₈H₁₂)₂] was added portionwise (*ca.* 0.1 g) until no more dissolved (*ca.* 1.0 g, 2.5 mmol). Cooling the solution to −100 °C afforded a white precipitate from which the supernatant solution was decanted. The solid was redissolved in light petroleum at room temperature, and the solution was filtered and cooled (−78 °C) to give white crystals. The mother liquor was removed and the crystalline solid dried in a stream of ethylene (15°) to give white *crystals* of tris(ethylene)platinum (7) (0.40 g, 60%) (Found: C, 25.2; H, 4.5. C₆H₁₂Pt requires C, 25.8; H, 4.3%); $\nu_{max.}$ at 3 065w, 1 505w, 1 420w, 1 225s, 980m, 935m, 830m, and 820w cm⁻¹. The ¹H n.m.r. spectrum (in C₆H₆, 18 °C) showed a resonance at τ 6.94 [s, 12 H, CH₂=CH₂, *J*(PtH) 57 Hz]. The ¹³C n.m.r. spectrum (PhCH₂D, +20 to −70 °C) showed a resonance at 48.4 p.p.m. [CH₂=CH₂, *J*(PtC) 113.0 Hz]. Further purification of [Pt(C₂H₄)₃] could be achieved by slow sublimation (20 °C) on to a cold finger cooled with ice–water under an atmosphere of ethylene. Removal of the volatile material from the mother liquors gave starting material [Pt(1,5-C₈H₁₂)₂] (0.30 g, 0.75 mmol).

Displacement Reactions of Bis(cyclo-octa-1,5-diene)palladium.—(a) *With trans-cyclo-octene.* The reaction of [Pd(1,5-C₈H₁₂)₂] with excess of *trans*-cyclo-octene in toluene at −20 °C afforded white *crystals* of tris(*trans*-cyclo-octene)-palladium, (6) (Found: C, 66.8; H, 10.5. C₂₄H₄₂Pd requires C, 66.0; H, 9.7%); $\nu_{max.}$ at 1 525w, 1 354w, 1 346w, 1 333w, 1 306w, 1 278s, 1 255m, 1 247(sh), 1 220m, 1 190vw, 1 150w, 1 123vw, 1 083m, 1 029w, 984m, 950w, 925w, 892m, 878w, 850m, 820m, 720w, 537s, and 507m cm⁻¹. The ¹H n.m.r. spectrum (Jeol PFT-100, Fourier transform, 100 MHz, in [²H₆]benzene–[²H₈]toluene; −15 °C) showed resonances at τ 6.40 (m, 2 H, CH=CH), 7.02 (m, 2 H), 7.82 (m, 4 H), and 8.54 (m, 6 H).

(b) *With bicyclo[2.2.1]heptene.* Similarly, reaction of [Pd(1,5-C₈H₁₂)₂] suspended in diethyl ether at −20 °C with excess of bicyclo[2.2.1]heptene afforded white crystals of tris(bicyclo[2.2.1]heptene)palladium, (4).

(c) *With ethylene.* Bis(cyclo-octa-1,5-diene)palladium (2.2 g, 6.8 mmol) was added in portions (0.1 g) to cold (−35 °C) light petroleum (40 cm³) under an atmosphere of ethylene over a period of *ca.* 40 min. The solution was filtered through a small pad of alumina (degassed at 80 °C, 10⁻² mmHg for 15 min) * and the colourless filtrate was cooled to −100 °C for 1 h during which time a mass of feathery white crystals formed. The mother liquor was

* 1 mmHg ≈ 13.6 × 9.8 Pa.

decanted and the crude product recrystallised from liquid butane at −100 °C and dried (−65 °C, 10⁻² mmHg) for 5 h, giving pure white *crystals* of tris(ethylene)palladium, (8) (0.9 g, 70%) {Found: C₂H₄/Pd, 0.790. Calc. for [Pd-(C₂H₄)₃]: C₂H₄/Pd, 0.792}. In the analysis of the complex a sample was thermally decomposed in a vessel attached to a vacuum line and the liberated ethylene condensed into a tube and weighed. $\nu_{max.}$ (in Nujol–n-octane, low temperature) at 3 080w, 1 525m, 1 427m, 1 261s, 1 230w, 1 218w, 1 094m, 913s, 898m, 881m, 828m, 812m, 760m, and 626m cm⁻¹. The ¹H n.m.r. spectrum (in [²H₈]toluene, C₂H₄ atmosphere, −60 °C) showed sharp resonances at τ 4.72 (s, unco-ordinated C₂H₄) and 6.62 {s, [Pd(C₂H₄)₃]}. At −15 °C both signals broadened indicating exchange, but this was accompanied by extensive decomposition to palladium metal. On recooling the solution to −50 °C the resonances sharpened. The ¹³C n.m.r. spectrum (in [²H₈]toluene, −70 °C, ¹H decoupled) showed a resonance at 63.5 p.p.m. {[Pd(C₂H₄)₃]}.

Crystal-structure Determination of Tris(bicyclo[2.2.1]-heptene)platinum.—The complex crystallises as colourless rectangular prisms elongated along *a*. Intensity data were collected at two temperatures, 300 and 190 K, from the same crystal (0.24 × 0.11 × 0.12 mm) mounted in a Lindemann glass capillary on a Syntex *P*2₁ four-circle diffractometer, in the range 2.9 < 2θ < 50°, with Mo-*K*α *X*-radiation (graphite monochromator) according to methods described earlier.[17] The mode of data collection at low temperatures differed slightly from that described [17] previously for the Syntex *P*2₁ diffractometer at room temperature because of the restrictions imposed on the χ circle by the glass Dewar tubing. Any reflection falling within the ' forbidden ' region was measured as its equivalent in the alternative hemisphere (a full description of the low-temperature apparatus and its use will be given elsewhere).

The crystal was cooled by a stream of cold dry nitrogen gas, whose outer surface was heated (to prevent frosting) by a small coil at a point of exit of the gas from the Dewar tubing. Just below the crystal a heated deflector dispersed the cold stream to avoid icing of the crystal mount and goniometer. The direction of the gas stream was maintained parallel with φ axis, regardless of the circle movements, by the use of swivel joints in the transfer tubing, and the exit nozzle itself was attached directly to the χ circle. The flow rate and pressure of the cooling gas were kept constant throughout data collection, as were the temperature controls for the outer gas-stream heater and the deflector. A constant level of liquid nitrogen in the heat exchanges was maintained by automatic refilling from a larger reservoir. The temperature of the experiment was recorded using a calibrated copper–constantan thermocouple.

Using the criterion *I* > 2.5σ(*I*), 1 695 data were deemed ' observable ' at 300 K from the 2 410 recorded intensities, and 1 781 from 2 112 at 190 K, and only these data were used in the solution and refinement of the structure. The data were corrected for Lorentz and polarisation effects, and for *X*-ray absorption.

Crystal data. C₂₁H₃₀Pt, *M* = 478.37, Orthorhombic, space group *P*2₁2₁2₁, *F*(000) 936.0, *Z* = 4 at 300 K, *a* = 5.717(1), *b* = 10.735(4), *c* = 28.749(12) Å, *U* = 1 764.32 Å³; at 190 K, *a* = 5.598(6), *b* = 10.775(16), *c* = 28.562(40) Å, *U* = 1 722.82 Å³, *D*ₘ (300 K) 1.76 g cm⁻³, *D*c (300 K)

[17] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

1.81 g cm⁻³, D_c (190 K) 1.85 g cm⁻³, Mo-K_α radiation ($\lambda =$ 0.710 69 Å), μ(Mo-K_α) = 83.6 cm⁻¹.

Structure solution and refinement. The molecular structure, shown in Figure 1, was solved originally from the

TABLE 1

Final position (fractional co-ordinate) and anisotropic temperature [a] factors (Å² × 10²) in tris(bicyclo[2.2.1]-heptene)platinum with estimated standard deviations in parentheses

Atom	x	y	z	U_{iso} [b]
Pt [c]	0.296 18(14)	0.092 84(6)	0.136 25(2)	
C(1)	0.091 1(37)	0.119 3(16)	0.201 3(6)	2.5(4)
H(1)	−0.2	0.08	0.18	
C(2)	0.240 8(35)	0.016 6(15)	0.206 3(6)	2.4(4)
H(2)	0.21	−0.08	0.19	
C(3)	0.424 5(41)	0.055 4(18)	0.244 7(7)	3.3(5)
H(3)	0.56	−0.01	0.24	
C(4)	0.272 9(5)	0.054 0(20)	0.290 1(8)	4.2(5)
H(41)	0.36	0.08	0.31	
H(42)	0.20	−0.05	0.29	
C(5)	0.107 6(4)	0.165 5(21)	0.283 5(8)	3.8(5)
H(51)	0.14	0.24	0.305	
H(52)	−0.09	0.14	0.27	
C(6)	0.168 7(14)	0.217 3(2)	0.235 8(7)	3.0(4)
H(6)	0.12	0.295	0.245	
C(7)	0.446 0(44)	0.195 5(2)	0.237 2(8)	3.5(5)
H(71)	0.56	0.185	0.205	
H(72)	0.60	0.21	0.26	
C(8)	0.547 7(33)	0.002 6(15)	0.088 3(6)	1.9(3)
H(8)	0.65	0.07	0.07	
C(9)	0.547 2(31)	−0.064 2(14)	0.130 9(6)	1.9(3)
H(9)	0.70	−0.04	0.15	
C(10)	0.444 2(41)	−0.189 2(19)	0.120 4(7)	2.9(4)
H(10)	0.38	0.23	0.145	
C(11)	0.629 0(35)	−0.257 7(16)	0.091 2(6)	2.4(4)
H(111)	0.605	−0.35	0.095	
H(112)	0.76	−0.25	0.11	
C(12)	0.634 6(41)	−0.185 6(19)	0.44 1(7)	3.2(4)
H(121)	0.56	−0.26	0.025	
H(122)	0.76	−0.16	0.04	
C(13)	0.433 8(33)	−0.083 7(18)	0.053 2(6)	2.4(3)
H(13)	0.32	−0.05	0.03	
C(14)	0.260 3(35)	−0.158 8(16)	0.082 3(6)	2.6(4)
H(141)	0.105	−0.130	0.085	
H(142)	0.20	−0.25	0.065	
C(15)	0.243 5(34)	0.207 3(16)	0.075 3(6)	2.4(4)
H(15)	0.21	0.14	0.05	
C(16)	0.097 9(46)	0.251 1(20)	0.110 8(8)	3.5(5)
H(16)	−0.04	0.24	0.13	
C(17)	0.191 0(47)	0.381 7(18)	0.121 5(7)	3.4(4)
H(17)	0.13	0.41	0.15	
C(18)	0.114 9(47)	0.465 1(22)	0.078 7(8)	4.0(5)
H(181)	−0.04	0.41	0.055	
H(182)	0.13	0.55	0.08	
C(19)	0.265 2(40)	0.412 9(21)	0.038 6(7)	3.8(4)
H(191)	0.39	0.47	0.02	
H(192)	0.16	0.38	0.025	
C(20)	0.419 9(42)	0.307 6(19)	0.063 2(7)	3.1(4)
H(20)	0.49	0.25	0.05	
C(21)	0.450 0(22)	0.366 2(18)	0.109 8(7)	3.0(5)
H(211)	0.54	0.32	0.135	
H(212)	0.49	0.45	0.11	

[a] Defined as exp[−2π²($U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl$)]. [b] Fixed at 6.33 × 10⁻² Å² for the hydrogen atoms. [c] Anisotropic thermal parameters (Å² × 10²):

U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
2.23(4)	2.24(4)	2.25(4)	0.07(3)	−0.22(3)	−0.33(3)

room-temperature data set.[5] The overall molecular geometry shows little change between the two data sets, but the estimated errors are reduced using the low-temperature measurements. For example, mean Pt–C and C=C are 2.22(3) and 1.38(4) Å, respectively, at 300 K, compared with 2.18(2) and 1.39(3) Å at 190 K. The final R factors

TABLE 2

Bond lengths (Å) and angles (°) in tris(bicyclo[2.2.1]heptene)platinum

(a) Co-ordination around the Pt atom

(i) Distances		(ii) Angles	
Pt–C(1)	2.20(2)	C(1)–Pt–C(2)	37.1(7)
Pt–C(2)	2.18(2)	C(8)–Pt–C(9)	37.5(6)
Pt–C(8)	2.19(2)	C(15)–Pt–C(16)	37.4(8)
Pt–C(9)	2.20(2)		
Pt–C(15)	2.15(2)		
Pt–C(16)	2.16(2)		
Pt–C(1,2) [a]	2.08(2)	C(1,2)–Pt–C(8,9)	119.6(7)
Pt–C(8,9)	2.08(2)	C(8,9)–Pt–C(15,16)	118.2(7)
Pt–C(15,16)	2.04(2)	C(15,16)–Pt–C(1,2)	122.1(7)
C(2) ⋯ C(9)	2.89(2)		
C(1) ⋯ C(16)	2.95(3)		
C(8) ⋯ C(15)	2.81(2)		

(b) Bicyclo[2.2.1]heptene ligands

(i) Distances		(ii) Angles	
C(1)–C(2)	1.39(3)	C(6)–C(1)–C(2)	108(2)
C(2)–C(3)	1.56(3)	C(1)–C(2)–C(3)	105(1)
C(3)–C(4)	1.55(3)	C(2)–C(3)–C(4)	103(2)
C(4)–C(5)	1.53(3)	C(2)–C(3)–C(7)	102(2)
C(3)–C(7)	1.53(3)	C(4)–C(3)–C(7)	98(2)
C(5)–C(6)	1.51(3)	C(3)–C(4)–C(5)	103(2)
C(6)–C(7)	1.57(3)	C(4)–C(5)–C(6)	105(2)
C(6)–C(1)	1.51(3)	C(5)–C(6)–C(7)	98(2)
C(1)–H(1) [b]	0.97	C(5)–C(6)–C(1)	105(2)
C(2)–H(2)	1.15	C(7)–C(6)–C(1)	101(2)
C(3)–H(3)	1.04	C(6)–C(7)–C(3)	94(2)
C(4)–H(41)	0.80		
C(4)–H(42)	1.19		
C(5)–H(51)	1.03		
C(5)–H(52)	1.20		
C(6)–H(6)	0.92		
C(7)–H(71)	1.12		
C(7)–H(72)	1.09		
C(8)–C(9)	1.41(2)	C(13)–C(8)–C(9)	105(1)
C(9)–C(10)	1.50(2)	C(8)–C(9)–C(10)	107(1)
C(10)–C(11)	1.52(3)	C(9)–C(10)–C(11)	107(2)
C(12)–C(13)	1.59(3)	C(9)–C(10)–C(14)	102(2)
C(13)–C(14)	1.51(3)	C(11)–C(10)–C(14)	100(1)
C(14)–C(10)	1.53(3)	C(10)–C(11)–C(12)	104(2)
C(13)–C(8)	1.51(2)	C(11)–C(12)–C(13)	101(2)
C(8)–H(8)	0.95 [b]	C(12)–C(13)–C(8)	104(1)
C(9)–H(9)	1.05	C(12)–C(13)–C(14)	100(1)
C(10)–H(10)	0.90	C(14)–C(18)–C(8)	104(1)
C(11)–H(111)	1.01	C(13)–C(14)–C(10)	94(2)
C(11)–H(112)	0.91		
C(12)–H(121)	1.05		
C(12)–H(122)	0.76		
C(13)–H(13)	0.99		
C(14)–H(141)	0.93		
C(14)–H(142)	1.15		
C(15)–C(16)	1.38(5)	C(20)–C(15)–C(16)	108(2)
C(16)–C(17)	1.53(3)	C(15)–C(16)–C(17)	105(2)
C(17)–C(21)	1.50(3)	C(15)–C(20)–C(19)	105(2)
C(17)–C(18)	1.58(3)	C(20)–C(15)–C(16)	108(2)
C(18)–C(19)	1.53(3)	C(15)–C(16)–C(17)	105(2)
C(19)–C(20)	1.59(3)	C(15)–C(20)–C(19)	105(2)
C(20)–C(21)	1.48(3)	C(15)–C(20)–C(21)	100(2)
C(20)–C(15)	1.50(3)	C(21)–C(20)–C(19)	99(2)
C(15)–H(15)	1.04	C(20)–C(19)–C(18)	103(2)
C(16)–H(16)	0.95	C(19)–C(18)–C(17)	103(2)
C(20)–H(20)	0.83	C(18)–C(17)–C(16)	106(2)
C(17)–H(17)	0.93	C(18)–C(17)–C(21)	99(2)
C(19)–H(191)	1.07	C(16)–C(17)–C(21)	100(2)
C(19)–H(192)	0.96	C(17)–C(21)–C(22)	98(2)
C(18)–H(181)	1.25		
C(18)–H(182)	0.92		
C(21)–H(211)	1.00		
C(21)–H(212)	0.93		

[a] C(n,m) indicates the midpoint of the bond joining atom C(n) to C(m). [b] C–H bond lengths have no estimated standard deviations because the H atom co-ordinates were not refined.

of 0.103(300) and 0.055(190 K) reflect the improvement in the quality of the data and the number of intensities 'observed' increased from 70 to 84% on decreasing the temperature. Because of this improvement, only the results obtained at 190 K are given here.

full-matrix least squares, with only the platinum atom given anisotropic thermal parameters, and using the weighting scheme $1/w = xy$ (where $x = b/\sin\theta$ if $\sin\theta < b$, $x = 1$ if $\sin\theta > b$; $y = F/a$ if $F > a$, $y = 1$ if $F < a$; $a = 100.0$ and $b = 0.22$), which gave a satisfactory weight
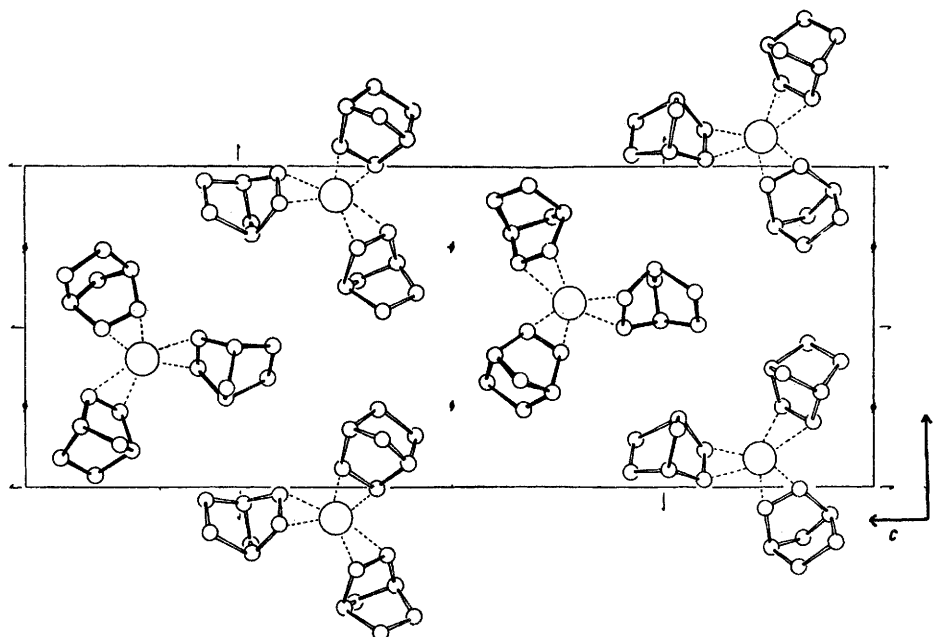

FIGURE 2 Molecular-packing diagram looking along the a axis towards the origin. Hydrogen atoms are omitted

TABLE 3

Equation of some least-squares planes in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates: distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): Co-ordination plane of the Pt atom: Pt, C(1), C(2), C(8), C(9), C(15), C(16)

$$4.061x + 6.468y + 9.614z = 3.079$$

[C(7), 2.28; C(14), −2.26; C(21), 2.17; Pt, 0.033; C(1), −0.002; C(2), −0.010; C(8), −0.011; C(9), −0.013; C(15), −0.025; C(16), 0.007]

Plane (2): Pt, C(1), C(2)

$$40.046x + 6.386y + 10.150z = 3.174$$

Plane (3): Pt, C(8), C(9)

$$4.125x + 6.260y + 9.867z = 3.147$$

Plane (4): Pt, C(15), C(16)

$$4.102x + 6.547y + 8.750z = 3.015$$

Angles between planes: (2)–(3) 1.20; (2)–(4) 2.98; and (3)–(4) 2.72°.

The platinum atom was located from a Patterson synthesis, and the remaining carbon skeleton from successive electron-density difference syntheses. Hydrogen atoms were included at positions estimated from the electron-density maps, but neither their positional nor thermal parameters were refined. The structure was refined by

analysis. The refinement converged at R 0.055 (R' 0.066) at 190 K, with a mean shift–error in the last cycle of refinement of 0.01. The final electron-density synthesis showed no peaks >0.9 e Å^{-3} or < -0.9 e Å^{-3}, except in the immediate vicinity of the platinum atom where $|\rho_{max.}| = 2$ e Å^{-3}.

The scattering factors used were those of ref. 18 for platinum, ref. 19 for carbon, and ref. 20 for hydrogen. Corrections for the effects of anomalous dispersion were applied for the platinum atom ($\Delta f' = -2.352$, $\Delta f'' = 8.388$). Refinement of the structure, reversing the signs of all the atomic co-ordinates, showed that the original choice of enantiomorph was correct. Computational work was carried out using the 'X-Ray' system of programs at the University of London Computing Centre. The atomic co-ordinates are given in Table 1, the molecular parameters in Table 2, and the equations of some least-squares planes in Table 3. The molecular packing diagram is shown in Figure 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21866 (11 pp., 1 microfiche).*

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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