Reaction of Low-valent Metal Complexes with Fluorocarbons. Part 30.[1] Bis(cyclo-octa-1,5-diene)platinum with Hexafluoroacetone, 1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene and *N*-Methylhexafluoroisopropylideneamine; Crystal and Molecular Structures of $[Pt_2\{(CF_3)_2CO\}(1,5\text{-}C_8H_{12})_2]$ and $[\overline{\mathrm{Pt\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2O}}\cdot(1,5\text{-}C_8H_{12})]$

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Reaction of $[Pt(1,5\text{-}C_8H_{12})_2]$ with hexafluoroacetone affords, depending on reaction conditions, the complexes $[Pt_2\{(CF_3)_2CO\}(1,5\text{-}C_8H_{12})_2]$, $[\overline{\mathrm{Pt\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}}(1,5\text{-}C_8H_{12})]$, $[\overline{\mathrm{Pt\cdot O\cdot C(CF_3)_2\cdot \underline{CH(CH_2)_2CH{:}CH(CH_2)_2CH}}}\text{-}(1,5\text{-}C_8H_{12})]$, and $[\overline{\mathrm{Pt\cdot C(CF_3)_2\cdot O}}(1,5\text{-}C_8H_{12})]$. The structural identities of the first two complexes have been established by the analysis of single-crystal *X*-ray data. The dinuclear complex is monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 9.917(3)$, $b = 14.957(6)$, $c = 13.358(3)$ Å; $\beta = 102.18(2)°$. The structure has been solved by conventional heavy-atom methods from 2 083 diffracted intensities and refined to R 0.038 (R' 0.044). The molecule contains an approximate mirror plane formed by the two platinum atoms [Pt–Pt 2.585(1) Å] and the carbon and oxygen atoms of the hexafluoroacetone molecule, with the cyclo-octa-1,5-diene molecules symmetrically bonded to each platinum atom in the tub configuration.

Crystals of the second complex are triclinic, space group $P\bar{1}$ with two molecules in a unit cell of dimensions $a = 8.212(3)$, $b = 9.329(2)$, $c = 12.610(3)$ Å; $\alpha = 91.87(2)$, $\beta = 102.10(2)$, $\gamma = 111.25(3)°$. The structure has been solved from 2 659 diffracted intensities to R 0.029 (R' 0.035) by conventional methods. The platinum atom forms part of a five-membered condensed (head-to-tail) ring $\overline{\mathrm{Pt\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}}$, and is co-ordinated by a cyclo-octa-1,5-diene molecule in a tub configuration. In both compounds the platinum atoms show essentially square-planar co-ordination.

In a third complex the hexafluoroacetone forms part of a five-membered ring, in which it links the platinum and an olefin carbon atom of cyclo-octa-1,5-diene. A similar complex, $[\overline{\mathrm{Pt\cdot C(CN)_2\cdot C(CF_3)_2\cdot \underline{CH\cdot C_6H_{10}\cdot CH}}}(1,5\text{-}C_8H_{12})]$, is a minor product from the reaction of $[Pt(1,5\text{-}C_8H_{12})_2]$ with 1,1-dicyano-2,2-bis(trifluroromethyl)ethylene. *N*-Methylhexafluoroisopropylideneamine and $[Pt(1,5\text{-}C_8H_{12})_2]$ afford $[\overline{\mathrm{Pt\cdot C(CF_3)_2\cdot N}}\mathrm{Me}(1,5\text{-}C_8H_{12})]$.

THE development[2] of a practical synthesis of bis(cyclo-octa-1,5-diene)platinum $[Pt(cod)_2]$ provided an opportunity for a study of the reaction of this molecule with electrophiles. We chose hexafluoroacetone (hfa) and the related molecules 1,1-dicyano-2,2-bis(trifluoromethyl)-ethylene and *N*-methylhexafluoroisopropylideneamine for an initial investigation because their reactions with a variety of phosphine-, phosphite-, and isocyanide-stabilised Ni^0, Pd^0, and Pt^0 complexes were already well understood.[3] In particular, the reaction of hfa and $[Ni(1,5\text{-}C_8H_{12})_2]$ was known[4] to give only the one product, $[\overline{\mathrm{Ni\cdot C(CF_3)_2\cdot O}}(1,5\text{-}C_8H_{12})]$. An additional impetus for this study was the possible analogy between hfa and carbon dioxide, the co-ordination chemistry of which is of growing importance in the context of CO_2 fixation.

Reaction (room temperature) of one molar equivalent of hfa with bis(cyclo-octa-1,5-diene)platinum in diethyl ether gave three products, (1), (2), and (3). The major product (1), which separated from the reaction mixture as yellow crystals, had an analysis which allowed its formulation as $[Pt_2\{(CF_3)_2CO\}(1,5\text{-}C_8H_{12})_2]$. In view of the unusual nature of this product (1) a single crystal *X*-ray diffraction study was undertaken, the results of which have been mentioned[5] in a preliminary communication.

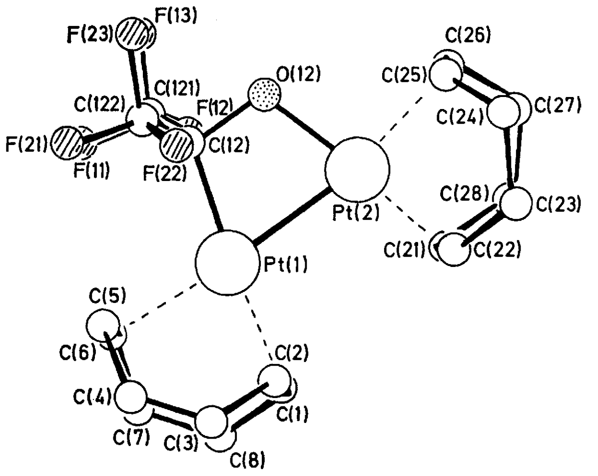

FIGURE 1 Projection of a molecule of $[Pt_2\{(CF_3)_2CO\}(1,5\text{-}C_8H_{12})_2]$ (1) onto the plane of the $\overline{\mathrm{Pt\cdot Pt\cdot C\cdot O}}$ ring showing the crystallographic numbering system

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This established that (1) contains an essentially planar four-membered ring formed by the two platinum atoms with the carbon and oxygen of the hfa molecule (Figure 1). Internuclear distances (uncorrected for thermal effects) and bond angles are listed in Table 1. The Pt–Pt interatomic distance [2.585(1) Å] is less than the predicted sum of the covalent radii (2.62 Å), and is one of the shortest Pt–Pt bond lengths reported; *cf.* 2.628(1) Å in $[Pt(SPEt_2)P(OPh)_3]_2$;[6] 2.633(1) Å in $[FePt_2(CO)_5\{P(OPh)_3\}_3]$;[7] 2.647(2) Å in $[(Ph_3P)_2Pt{\cdot}S{\cdot}Pt(CO)(PPh_3)]$,[8] and 2.604 Å in $[Pt_2(PPh_3)_2(PPh_2)_2]$.[9] It is, however, similar to that found in $[Pt_2(C_5H_5)_4]$[10] where the Pt–Pt bond, 2.581 Å, is bridged by a cyclopentadienyl moiety, and also to that found[11] in the anion $[Pt_2Cl_4(CO)_2]^{2-}$, which contains an unbridged Pt–Pt bond, of length 2.584(2) Å. Other examples are given in references 12—17.

TABLE 1

Internuclear distances (Å) and bond angles (°) (with estimated standard deviations in parentheses) for $[Pt_2\{(CF_3)_2CO\}(1,5\text{-}C_8H_{12})_2]$, (1)

Bonds			
Pt(1)–Pt(2)	2.585(1)	Pt(2)–O(12)	1.954(11)
Pt(1)–C(12)	2.080(16)	C(12)–O(12)	1.406(18)
Pt(1)–C(1,2) *	2.14(2)	Pt(2)–C(21,22)	2.11(2)
Pt(1)–C(5,6)	2.18(2)	Pt(2)–C(25,26)	2.21(2)
Cyclo-octa-1,5-diene ligands			
Pt(1)–C(1)	2.24(2)	Pt(2)–C(21)	2.15(2)
Pt(1)–C(2)	2.26(2)	Pt(2)–C(22)	2.13(2)
Pt(1)–C(5)	2.27(2)	Pt(2)–C(25)	2.29(2)
Pt(1)–C(6)	2.31(2)	Pt(2)–C(26)	2.33(2)
C(1)–C(2)	1.35(3)	C(21)–C(22)	1.41(3)
C(2)–C(3)	1.54(3)	C(22)–C(23)	1.49(3)
C(3)–C(4)	1.43(3)	C(23)–C(24)	1.52(3)
C(4)–C(5)	1.52(4)	C(24)–C(25)	1.49(3)
C(5)–C(6)	1.39(4)	C(25)–C(26)	1.33(3)
C(6)–C(7)	1.48(5)	C(26)–C(27)	1.55(3)
C(7)–C(8)	1.40(4)	C(27)–C(28)	1.45(4)
C(8)–C(1)	1.49(1)	C(28)–C(21)	1.56(3)
Trifluoromethyl groups			
C(12)–C(121)	1.53(3)	C(121)–F(13)	1.37(2)
C(12)–C(122)	1.54(3)	C(122)–F(21)	1.34(2)
C(121)–F(11)	1.34(2)	C(122)–F(22)	1.28(3)
C(121)–F(12)	1.31(3)	C(122)–F(23)	1.36(2)
Angles			
Pt(1)–Pt(2)–O(12)	75.7(3)	C(12)–O(12)–Pt(2)	106.9(9)
Pt(2)–Pt(1)–C(12)	70.4(4)	O(12)–C(12)–Pt(1)	106.9(9)
Cyclo-octa-1,5-diene ligands			
C(1)–Pt(1)–C(2)	35.0(8)	C(21)–Pt(2)–C(22)	38.6(8)
C(5)–Pt(1)–C(6)	35.3(9)	C(25)–Pt(2)–C(26)	33.5(8)
C(8)–C(1)–C(2)	125(2)	C(28)–C(21)–C(22)	120(2)
C(1)–C(2)–C(3)	127(2)	C(21)–C(22)–C(23)	125(2)
C(2)–C(3)–C(4)	117(2)	C(22)–C(23)–C(24)	118(2)
C(3)–C(4)–C(5)	121(2)	C(23)–C(24)–C(25)	114(2)
C(4)–C(5)–C(6)	124(2)	C(24)–C(25)–C(26)	130(2)
C(5)–C(6)–C(7)	123(2)	C(25)–C(26)–C(27)	120(2)
C(6)–C(7)–C(8)	121(3)	C(26)–C(27)–C(28)	118(2)
C(7)–C(8)–C(1)	120(2)	C(27)–C(28)–C(21)	118(2)
Trifluoromethyl groups			
Pt(1)–C(12)–C(121)	113(1)	Pt(1)–C(12)–C(122)	111(1)
C(121)–C(12)–C(122)	112(1)	C(122)–C(12)–O(12)	106(1)
C(121)–C(12)–O(12)	107(1)	F(21)–C(122)–F(22)	109(2)
F(11)–C(121)–F(12)	108(2)	F(22)–C(122)–F(23)	107(2)
F(11)–C(121)–F(13)	103(2)	F(21)–C(122)–F(23)	102(1)
F(12)–C(121)–F(13)	104(2)		

* C(*n*,*m*) indicates the mid-point of the line joining atoms C(*n*) and C(*m*).

The Pt(1)–C(12) distance [2.080(2) Å] compares well with other known carbon–platinum σ-bond lengths,[18-20] whereas the Pt(2)–O(12) distance [1.954(1) Å] is somewhat shorter than Pt–O bond lengths recorded for other similar ring systems,[18,21-23] except in the case of $[Pt(acac)_2Cl]^-$ where the oxygen atom lies *trans* to chlorine [Pt–O = 1.97(1) Å].[18] This is in agreement with the suggestion[19] than an η^2-bonded olefin has the same *trans*-influence as a chlorine atom.

The C(12)–O(12) distance [1.41(2)] Å is slightly shorter than that predicted for a carbon–oxygen single bond (1.44 Å), but is significantly longer than similar C–O bonds when the O atom is directly bonded to the metal atom (range 1.26–1.37 Å).[21,24,25] However, these compounds,[20-25] with the exception of those where the C–O bond concerned is external to the $Pt{\cdot}O{\cdot}Pt{\cdot}O$ ring, contain less strained ring systems than that present in complex (1). The C(12)–O(12) bond length is more nearly equivalent to those of the C–O bonds in $[Pt{\cdot}O{\cdot}C(CF_3)_2{\cdot}O{\cdot}C(CF_3){\cdot}O(PPh_3)_2]$[21] and in complex (3) (see later) where neither carbon nor oxygen is attached to the metal.

The four-membered ring forms an approximate and non-crystallographic mirror plane for the molecule as a whole, about which the CF_3 groups and the two cyclo-octa-1,5-diene ligands are symmetrically disposed. The trifluoromethyl groups lie in an eclipsed configuration with the angles around C(12), C(121), and C(122) all approximately tetrahedral, and the overall geometry of the $C(CF_3)_2$ group is as expected. The plane (Table 2, plane 8) defined by the two carbon–carbon bonds of the group lies perpendicular to the central plane of the ring (plane 1).

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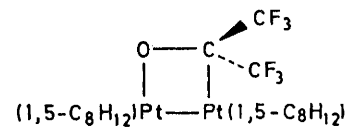
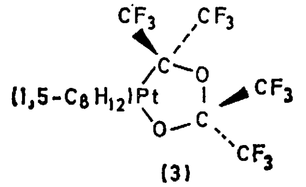
The C=C bond lengths in the two cyclo-octa-1,5-diene (cod) ligands are not equivalent, with the most significant variation being the C=C bond *trans* to the oxygen atom [C(21)–C(22) 1.41 Å]. This is coupled with the shorter Pt–C distance [Pt–C mean 2.14 Å]. The remaining C–C distances in both cod ligands have approximately the expected values for single C–C bonds. The skew character seen in other co-ordinated cod molecules,[26-29] and in the free ligand itself,[30] is also seen in (1) (Table 3). The cod ligands in the tub configuration can be regarded as comprising three planar sections, namely, planes 2, 3, and 4 of Table 2, hinged at C(6)–C(1) and C(2)–C(5). The dihedral angles between these planes are 132 and 130° for the ligand attached to Pt(1), and 133 and 126° for the corresponding planes of the ligand attached to Pt(2). The planes containing the two co-ordinated double bonds in both cod ligands lie almost perpendicular (92 and 91°, respectively) to the central plane of the four-membered ring.



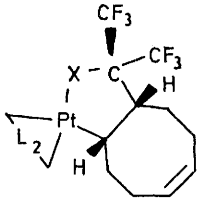
(1)



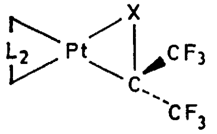
(3)

The deviation from exact square-planar co-ordination can be seen from Table 4, where the angles around each Pt atom give some indication of the distortions involved in the four-membered ring. The deviations from the least-squares plane of the atoms in the co-ordination plane of the two platinum atoms are given in Table 2.

It is interesting that the stoicheiometry of complex (1) is similar to that assigned to the product $[Ni_2(CO_2)(Pcy_3)_4]$ (cy = cyclohexyl) obtained[31] by allowing carbon dioxide to react with the dinitrogen complex $[N_2\{Ni(Pcy_3)_2\}_2]$. It seems possible that in the carbon dioxide complex a CO_2 unit bridges the two nickel atoms in a



(2) L_2=1,5-C_8H_{12}, X=O
(4) L_2=1,2-$C_6H_4(AsMe_2)_2$, X=O
(5) L_2=2PPh_3, X=O
(8) L_2=1,5-C_8H_{12}, X=$C(CN)_2$
(9) L_2=1,2-$C_6H_4(AsMe_2)_2$, X=$C(CN)_2$



(6) L_2=1,5-C_8H_{12}, X=O
(10) L_2=1,5-C_8H_{12}, X=NMe
(11) L_2=1,2-$C_6H_4(AsMe_2)_2$, X=NMe

TABLE 2

Molecular planes for compound (1)

(A) Coefficients. Each plane is represented in non-orthogonalised space by $px + qy + rz = s$, (Å), where x, y, and z are the atomic fractional co-ordinates. All atoms have unit weight

Plane	Description	p	q	r	s
1	Pt(1), Pt(2), C(12), O(12)	−6.342	−0.123	11.840	2.228
2	C(1,2,5,6)	3.342	13.631	2.135	2.891
3	C(2,3,4,5)	−2.823	9.872	9.880	4.024
4	C(6,7,8,1)	7.349	8.092	−7.281	0.774
5	C(21,22,25,26)	7.694	−7.512	6.026	8.011
6	C(22,23,24,25)	9.788	1.482	−4.438	3.910
7	C(21,26,27,28)	−0.475	−2.680	12.966	5.319
8	C(12,121,122)	3.849	12.738	3.505	6.482
9	Pt(1), Pt(2), C(1,2), C(5,6), C(12)	−6.583	0.450	11.628	2.210
10	Pt(1), Pt(2), O(12), C(21,22), C(25,26)	−6.190	−0.994	11.923	2.081

(B) Individual deviations (Å)

Plane	Deviation
1	Pt(1), 0.009; Pt(2), −0.010; C(12), −0.018; O(12), 0.018; C(1,2), 0.160; C(5,6), −0.070; C(21,22), −0.200; C(25,26), 0.110
2	C(1), −0.0001; C(2), 0.0001; C(5), −0.0001; C(6), 0.0001
3	C(2), −0.020; C(3), 0.042; C(4), −0.043; C(5), 0.021
4	C(6), −0.006; C(7), 0.012; C(8), −0.011; C(1), 0.005
5	C(21), −0.037; C(22), 0.038; C(25), −0.040; C(26), 0.039
6	C(22), −0.068; C(23), 0.130; C(24), −0.127; C(25), 0.065
7	C(21), 0.055; C(26), −0.056; C(27), 0.115; C(28), −0.115
9	Pt(1), −0.006; Pt(2), −0.048; C(1,2), 0.046; C(5,6), −0.049; C(12), 0.057
10	Pt(1), 0.059; Pt(2), 0.002; O(12), −0.074; C(21,22), −0.055; C(25,26), 0.068

(C) Dihedral angles (°)

2	4	5	8	Plane
92.4		90.7	90.9	1
132.1	130.5			3
		133.0		6
		126.2		7

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TABLE 3

Some distances (Å) and angles (°) showing distortion in the cyclo-octa-1,5-diene ligands

Compound (1)							
Pt(1)		Pt(2)		Compound (3)		Free ligand[a]	
C(1)–C(5)[b]	3.18(2)	C(21)–C(25)	3.30(3)	C(3)–C(7)[b]	3.27(2)	C(1)–C(5)	3.30
C(2)–C(6)	3.27(3)	C(22)–C(26)	3.16(3)	C(10)–C(6)	3.17(1)	C(2)–C(6)	3.32
C(1)–C(6)	2.91(3)	C(21)–C(26)	2.96(3)	C(3)–C(6)	2.88(2)	C(1)–C(6)	3.05
C(3)–C(7)	3.48(4)	C(23)–C(27)	3.09(4)	C(5)–C(9)	3.31(2)	C(3)–C(7)	3.13
C(4)–C(8)	3.32(4)	C(24)–C(28)	3.67(4)	C(4)–C(8)	3.69(2)	C(4)–C(8)	3.81
C(4)–C(7)	3.06(5)	C(24)–C(27)	3.07(4)	C(8)–C(5)	3.22(2)	C(4)–C(7)	3.19
C(1)–C(2)–C(3) C(4)–C(5)–C(6)	126.5	C(21)–C(22)–C(23) C(24)–C(25)–C(26)	127.5	C(3)–C(10)–C(9) C(6)–C(7)–C(8)	125.6	C(1)–C(2)–C(3) C(4)–C(5)–C(6)	127.8
C(2)–C(3)–C(4) C(3)–C(4)–C(5)	118.5	C(22)–C(23)–C(24) C(23)–C(24)–C(25)	116.0	C(10)–C(9)–C(8) C(9)–C(8)–C(7)	116.8	C(2)–C(3)–C(4) C(3)–C(4)–C(5)	116.8

[a] Data from ref. 30.

[b]

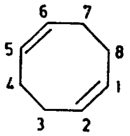

TABLE 4

Bond lengths (Å) and angles (°) in the co-ordination plane of the Pt atoms

Compound (1)					
Pt(1)		Pt(2)		Compound (3)	
C(1,2)–Pt(1)	2.14(2)	C(21,22)–Pt(2)	2.02(2)	C(6,7)–Pt	2.05(1)
C(5,6)–Pt(1)	2.18(2)	C(25,26)–Pt(2)	2.21(2)	C(3,10)–Pt	2.15(1)
C(1,2)–Pt(1)–C(5,6)	84.8(7)	C(21,22)–Pt(2)–C(25,26)	87.3(8)	C(6,7)–Pt–C(3,10)	86.7(4)
C(1,2)–Pt(1)–C(12)	172.6(6)	C(21,22)–Pt(2)–O(12)	175.9(8)	C(6,7)–Pt–O(1)	176.1(5)
C(5,6)–Pt(1)–C(12)	102.0(7)	C(25,26)–Pt(2)–O(12)	91.5(6)	C(3,10)–Pt–C(1)	170.7(3)
C(1,2)–Pt(1)–Pt(2)	103.0(5)	C(21,22)–Pt(2)–Pt(1)	105.7(6)	C(6,7)–Pt–C(1)	102.5(4)
C(5,6)–Pt(1)–Pt(2)	172.0(6)	C(25,26)–Pt(2)–Pt(1)	166.7(5)	C(3,10)–Pt–O(1)	90.2(3)
C(12)–Pt(1)–Pt(2)	70.4(4)	Pt(1)–Pt(2)–O(12)	75.7(3)	C(1)–Pt–O(1)	80.6(3)

similar manner to the $(CF_3)_2CO$ ligand bridging the platinum atoms in (1).

When the reaction between hfa and $[Pt(cod)_2]$ was repeated using an excess of hfa, or on changing the solvent from diethyl ether to benzene, the platinum–platinum bonded complex (1) was not obtained. The products of these reactions were the complexes (2) and (3), which were also obtained as minor products in the reaction in which (1) is actually formed, *i.e.* 1 : 1 molar ratio of reactants in diethyl ether as solvent.

Examination of the i.r. and n.m.r. spectra showed that complex (3) was identical with the product of the reaction of $[Pt(Pr^i)_2(1,5\text{-}C_8H_{12})]$ with hfa, and which had previously[3] been assigned the five-membered ring structure $[Pt{\cdot}C(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}O(1,5\text{-}C_8H_{12})]$ on the basis of ^{19}F n.m.r. studies. In order to confirm this structure, and secondly to enable a comparison to be made with the four-membered ring system (1), a single-crystal *X*-ray diffraction study of (3) was undertaken.

The platinum atom is part of a five-membered ring formed by the head-to-tail linkage of two hfa molecules (Figure 2) Internuclear distances (uncorrected for thermal effects) and bond angles are given in Table 5. The deviation from planarity can be seen from the equations listed in Table 6. The distortions of the bond angles around the platinum atom away from a regular square-planar configuration are given in Table 4. The Pt–O [1.99(1) Å] and Pt–C [2.10(1) Å] bond distances are similar to those of complex (1). The C–O distances within the ring show a similar variation to the related palladium complex[32] and other comparable hetero-atom ring systems.[21,24,25] The relative shortness of the

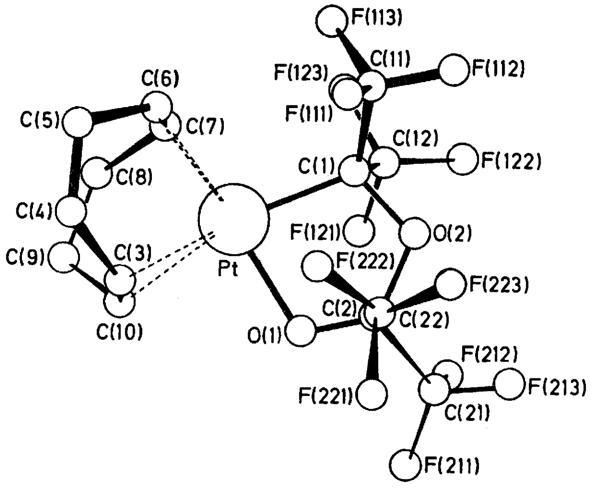

FIGURE 2 Projection of a molecule $[Pt{\cdot}C(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}O(1,5\text{-}C_8H_{12})]$ on to the *ab* face showing the crystallographic numbering system

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

C–O bond [C(2)–O(1) = 1.35(1) Å] succeeding the metal–oxygen bond has been ascribed [21,32] to donation into the antibonding orbitals of the $C(CF_3)_2$ moiety of the oxygen lone-pair electrons. This results from the raising of the energy of the lone-pair orbitals on oxygen due to its proximity to the electropositive metal atom. The C–O bond succeeding the metal-to-carbon bond does not show the same shortening effect [C(1)–O(2) = 1.42(1) Å].

TABLE 5

Internuclear distances (Å) and bond angles (°) in $[\overline{\text{Pt}\cdot\text{C}(\text{CF}_3)_2\cdot\text{O}\cdot\text{C}(\text{CF}_3)_2\cdot\text{O}}(1,5\text{-C}_8\text{H}_{12})]$ (3)

Bonds			
Pt–C(1)	2.102(9)	C(2)–O(1)	1.347(11)
C(1)–O(2)	1.450(9)	O(1)–Pt	1.992(5)
O(2)–C(2)	1.417(12)		
Cyclo-octa-1,5-diene ligand			
C(3)–C(4)	1.52(2)	C(9)–C(10)	1.52(2)
C(4)–C(5)	1.45(2)	C(10)–C(3)	1.40(2)
C(5)–C(6)	1.52(2)	Pt–C(3)	2.27(1)
C(6)–C(7)	1.46(1)	Pt–C(10)	2.26(1)
C(7)–C(8)	1.51(2)	Pt–C(6)	2.18(1)
C(8)–C(9)	1.49(2)	Pt–C(7)	2.17(1)
Trifluoromethyl groups			
C(1)–C(11)	1.52(1)	C(2)–C(21)	1.55(1)
C(11)–F(111)	1.34(1)	C(21)–F(211)	1.32(1)
C(11)–F(112)	1.34(1)	C(21)–F(212)	1.32(1)
C(11)–F(113)	1.32(1)	C(21)–F(213)	1.32(1)
C(1)–C(12)	1.55(1)	C(2)–C(22)	1.54(2)
C(12)–F(121)	1.33(1)	C(22)–F(221)	1.33(1)
C(12)–F(122)	1.33(1)	C(22)–F(222)	1.34(1)
C(12)–F(123)	1.33(1)	C(22)–F(223)	1.32(2)
Angles			
C(1)–Pt–O(1)	80.5(3)	C(2)–O(2)–C(1)	117.3(6)
Pt–O(1)–C(2)	114.2(5)	O(2)–C(1)–Pt	107.2(6)
O(1)–C(2)–O(2)	113.9(7)		
Cyclo-octa-1,5-diene ligand			
C(10)–C(3)–C(4)	126.2(10)	Pt–C(6)–C(5)	111.7(7)
C(3)–C(4)–C(5)	117.2(13)	Pt–C(6)–C(7)	70.0(4)
C(4)–C(5)–C(6)	117.7(9)	Pt–C(7)–C(6)	70.9(5)
C(5)–C(6)–C(7)	124.9(9)	Pt–C(7)–C(8)	109.1(7)
C(6)–C(7)–C(8)	126.4(10)	Pt–C(3)–C(4)	107.8(9)
C(7)–C(8)–C(9)	117.6(11)	Pt–C(3)–C(10)	71.7(7)
C(8)–C(9)–C(10)	116.0(13)	Pt–C(10)–C(3)	72.3(7)
C(9)–C(10)–C(3)	124.8(8)	Pt–C(10)–C(9)	109.1(9)
Trifluoromethyl groups			
Pt–C(1)–C(11)	116.5(6)	O(1)–C(2)–C(21)	107.8(7)
O(2)–C(1)–C(11)	104.7(6)	O(2)–C(2)–C(21)	105.2(8)
C(12)–C(1)–C(11)	110.9(8)	C(22)–C(2)–C(21)	111.3(7)
C(1)–C(11)–F(111)	110.6(8)	C(2)–C(21)–F(211)	110.9(9)
C(1)–C(11)–F(112)	112.0(6)	C(2)–C(21)–F(212)	111.0(8)
C(1)–C(11)–F(113)	113.0(8)	C(2)–C(21)–F(213)	111.8(8)
F(111)–C(11)–F(112)	106.1(8)	F(211)–C(21)–F(212)	108.4(9)
F(112)–C(11)–F(113)	107.8(8)	F(212)–C(21)–F(213)	106.6(9)
F(113)–C(11)–F(111)	107.0(7)	F(213)–C(21)–F(211)	108.0(8)
Pt–C(1)–C(12)	111.4(6)	O(1)–C(2)–C(22)	111.5(9)
O(2)–C(1)–C(12)	105.0(6)	O(2)–C(2)–C(22)	107.1(7)
C(1)–C(12)–F(121)	111.7(9)	C(2)–C(22)–F(221)	111.2(8)
C(1)–C(12)–F(122)	112.2(8)	C(2)–C(22)–F(222)	110.5(8)
C(1)–C(12)–F(123)	111.6(6)	C(2)–C(22)–F(223)	113.9(10)
F(121)–C(12)–F(122)	107.9(7)	F(221)–C(22)–F(222)	107.1(10)
F(122)–C(12)–F(123)	106.7(10)	F(222)–C(22)–F(223)	107.5(8)
F(123)–C(12)–F(121)	106.4(8)	F(223)–C(22)–F(221)	106.3(9)

The trifluoromethyl groups show the expected geometry with the angles around each CF_3 carbon and ring carbon atoms approximately tetrahedral. The planes defined by the two C–C bonds of the $C(CF_3)_2$ groups are almost perpendicular (Table 6) to the mean plane of the five-membered ring.

The cod ligand is co-ordinated to the platinum atom in the tub configuration and shows the same inequivalence of the C=C bond lengths as in complex (1), dependent on their position being *trans* to oxygen or to carbon [1.46(1) and 1.40(1) respectively]. Similarly there is a corresponding variation of Pt–C distances. The geometry of the ring itself can be seen in Tables 4—6, which illustrate the distortions seen in other co-ordinated cyclo-octa-1,5-diene ligands. The dihedral angles between the three planar sections (Table 6) are 127.6 and 123.9° [compared with mean values for compound (1) of 132.5 and 128°].

The two structures presented here provide six independent sets of measurements of the parameters associated with the co-ordination of an olefin, cyclo-octa-1,5-diene, to a platinum atom, and should give an insight into the structural implications of the *trans*-influence. Many previous studies of the platinum–olefin bond have failed to provide reliable and accurate data because of the overwhelming diffracting power of the heavy atom, and, although both the refinements reported here were comparatively good, estimated standard deviations are large relative to the changes in bond lengths. This is particularly true of the C=C bond length. Nevertheless, there is a linear relationship between the C=C and Pt–C mean bond lengths indicating a correlation between these parameters; the order of increasing *trans*-influence being O < C < Pt. The high *trans*-influence of σ-bonded platinum has previously been observed in relation to Pt–Cl stretching frequencies [33] and the Pt–Cl bond length [11] in the complex anion $[Pt_2Cl_4(CO)_2]^{2-}$.

TABLE 6

Molecular planes for compound (3)

(A) Coefficients. Each plane is represented in non-orthogonal space by $px + qy + rz = s$ (Å) where x, y, and z are the atomic fractional co-ordinates. All atoms have unit weight

Plane	Description	p	q	r	s
1	Pt, C(1), C(2), O(1), O(2)	0.137	1.138	11.877	−2.737
2	C(4), C(5), C(8), C(9)	−1.119	9.074	−1.169	2.104
3	C(5), C(6), C(7), C(8)	5.766	3.813	−3.216	2.771
4	C(3), C(4), C(9), C(10)	7.373	−6.859	−2.024	−0.833
5	C(1), C(11), C(12)	0.121	8.580	−2.977	−2.001
6	C(2), C(21), C(22)	7.214	−7.004	−0.237	2.453
7	Pt, C(1), O(1)	−0.073	−0.251	12.305	2.884
8	Pt, C(1), O(1), C(3,10), C(6,7) [a]	−0.085	−0.198	12.239	2.896

(B) Individual deviations (Å)

Plane	Deviation
1	Pt, 0.121; O(1), −0.181; O(2), 0.015; C(1), −0.095; C(2), 0.140; C(6,7), 0.357; C(3,10), 0.317
2	C(4), −0.092; C(5), 0.091; C(8), −0.089; C(9), 0.090
3	C(5), 0.005; C(6), −0.011; C(7), 0.012; C(8), −0.005
4	C(3), −0.009; C(4), 0.004; C(9), −0.004; C(10), 0.009
7	C(2), 0.501; O(2), 0.344; C(6,7), −0.085; C(3,10), 0.024
8	Pt, 0.014; C(1), 0.021; O(1), −0.031; C(3,10), 0.022; C(6,7), −0.026

(C) Dihedral angles (°)

6	5	2	Plane
93.7	91.0	97.4	1
		127.6	3
		123.9	4

[a] C(*n*,*m*) indicates the mid-point of the line joining atoms C(*n*) and C(*m*).

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[33] P. L. Goggin and R. J. Goodfellow, *J.C.S. Dalton*, 1973, 2355.

Complex (2) analysed as a 1 : 1 adduct of $[\mathrm{Pt(cod)_2}]$ and hfa. Reaction with 1,2-bisdimethylarsinobenzene (diars) or with triphenylphosphine led to the displacement of only one cod affording, respectively, the crystalline complexes (4) and (5). This suggested, in conjunction with the ^{1}H, ^{13}C, and ^{19}F n.m.r. spectra of (2), (4), and (5), that in the formation of the adduct (2) one of the hfa molecules had linked to an olefinic carbon atom of a co-ordinated cod forming a platinafuran derivative with the illustrated structure. The direction of addition of the hfa molecule was indicated by the appearance in the ^{19}F n.m.r. spectrum of two resonances at 71.0 and 76.7 p.p.m., in which only the high-field signal showed a small (11.0 Hz) ^{19}F–^{195}Pt coupling compared with a coupling of 78.1 Hz in the complex (6) (see below).

It has been previously observed [34] that hfa reacts with 1,3-diene(η^5-cyclopentadienyl)rhodium complexes to form η^3-allylic rhodium(III) adducts, in which hfa links the rhodium and the diene. A recent *X*-ray diffraction study has confirmed this structural feature.[35] We suggest that the formation of (2) is related to these reactions, and that the mechanisms proposed [34] for the formation of the rhodium adducts may be extended to include the production of (2) in the reaction of $[\mathrm{Pt(cod)_2}]$ with hfa.

Although hfa did not react with tris(bicyclo[2.2.1]-heptene)platinum,[2] the corresponding reaction with tris(ethylene)platinum [2] in the presence of cod gave the mononuclear complex (6) $[\overline{\mathrm{Pt{\cdot}C(CF_3)_2{\cdot}O}}(1,5\text{-}\mathrm{C_8H_{12}})]$, the platinum analogue of the product [4] of the reaction of hfa with $[\mathrm{Ni(cod)_2}]$. Clearly the complex (6) was a possible precursor of (1); however, treatment of (6) with $[\mathrm{Pt}(1,5\text{-}\mathrm{C_8H_{12}})_2]$ did not afford the dinuclear complex. This suggests that the formation of (1) involves the capture of an intermediate ionic species $\mathrm{(cod)Pt^+{-}C(CF_3)_2O^-}$ by $[\mathrm{Pt(cod)_2}]$ followed by ring closure to give (1).

Reaction of $[\mathrm{Pt(cod)_2}]$ with an equivalent proportion of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in diethyl ether as solvents gave as the major product a material which on the basis of elemental analysis is assigned the empirical formula $[\mathrm{Pt\{(CF_3)_2C{:}C(CN)_2\}}(1,5\text{-}\mathrm{C_8H_{12}})]$ (7). However, the properties of this compound show that it is not the previously described [3] monomeric complex $[\overline{\mathrm{Pt{\cdot}C(CF_3)_2{\cdot}C}}\mathrm{(CN)_2}(1,5\text{-}\mathrm{C_8H_{12}})]$.

On the basis of analysis a minor product was formulated as a 1 : 1 adduct of $[\mathrm{Pt(cod)_2}]$ and the olefin. The ^{1}H, ^{19}F, and ^{13}C spectra of the complex suggested a structure analogous to (2), in which the electronegatively substituted olefin links the platinum and one of the olefinic carbon atoms of one of the cod molecules. The absence of ^{195}Pt–^{19}F coupling suggests that the $\mathrm{C(CN)_2}$ group is adjacent to the platinum atom. This rules out a mechanism involving intramolecular collapse of an ionic species $\mathrm{(cod)_2Pt^+C(CF_3)_2C^-(CN)_2}$ *via* carbanion attack on co-ordinated cod, and suggests structure (8). Treatment of (8) with diars gave (9) *via* displacement of cod. It is interesting that reaction of (7) with the chelating arsine also gives (9). This is a somewhat surprising result; however, a reasonable explanation is that reaction of (7) with the arsine leads to displacement of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene from platinum, which then re-reacts at an olefinic carbon atom to form (9).

Reaction of *N*-methylhexafluoroisopropylideneamine with $[\mathrm{Pt(cod)_2}]$ in toluene gave only the one product (10), an analogue of (6), and treatment with diars gave (11).

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 MHz with $\mathrm{Me_4Si}$ (τ 10.00) as internal reference. ^{19}F, ^{31}P, and ^{13}C n.m.r. spectra were measured on a JEOL PFT-100 spectrometer at 94.1, 40.48, and 25.15 MHz respectively; chemical shifts are relative to $\mathrm{CFCl_3}$, $\mathrm{H_3PO_4}$, and $\mathrm{Me_4Si}$, respectively, as external references. I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer using Nujol mulls. Molecular weights were determined mass spectrometrically on an AEI MS902 spectrometer operating at 70 eV.* Reactions, except those in sealed tubes, were conducted in a dry oxygen-free nitrogen atmosphere.

*Reaction of Bis(cyclo-octa-*1,5*-diene)platinum with Hexafluoroacetone*.—(*a*) A suspension of $[\mathrm{Pt}(1,5\text{-}\mathrm{C_8H_{12}})_2]$ (0.4 g, 1 mmol) in diethyl ether (30 cm^3) was introduced into a Carius tube and after hexafluoroacetone (0.15 g, 0.9 mmol) was condensed (−196 °C) into the tube, it was sealed *in vacuo*. The tube was warmed to room temperature and shaken until solid material had dissolved. After 16 h yellow crystals formed. The volume of the solvent was reduced (10 cm^3) *in vacuo* to give yellow *crystals* of (1) (0.27 g, 70%), m.p. 180 °C (decomp.) (Found: C, 29.9; H, 3.1%; *M*, 772. $\mathrm{C_{19}H_{24}F_6OPt_2}$ requires C, 29.5; H, 3.1%; *M*, 772), $\nu_{\max.}$ 1 550w, 1 530w, 1 485m, 1 438m, 1 345w, 1 322w, 1 282s, 1 255s, 1 245s, 1 232s, 1 188s, 1 142s,br, 1 112m, 1 100m, 1 088s, 992m, 968w, 939s, 918s, 905m, 872m, 835w, 828w, 792w, 780w, 768w, 755w, 732w, 708w, 680w, 588w, 580w, 552w, and 488w cm^{-1}. The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$) showed resonances at τ 4.48 (m, 8 H, CH=CH) and 7.78 (m, 16 H, $\mathrm{CH_2CH_2}$). The ^{19}F n.m.r. spectrum ($\mathrm{CDCl_3}$) showed a resonance at 67.9 p.p.m. [s, with two pairs of ^{195}Pt satellites, $J_{\mathrm{Pt(1)F}}$ 115.9, and $J_{\mathrm{Pt(2)F}}$ 11.5 Hz]; ^{19}F-{^{195}Pt} INDOR gives two ^{195}Pt chemical shifts at 190 and 824 p.p.m., and a value for $J_{\mathrm{Pt(1)Pt(2)}}$ of 5 355 Hz.

Evaporation of the mother liquors gave a white solid. Recrystallisation from diethyl ether–light petroleum gave white crystals (30%), characterised by ^{19}F n.m.r. spectroscopy as a mixture of (2) (20%) and (3) (10%).

(*b*) In a similar manner, reaction of $\mathrm{(CF_3)_2CO}$ (3.32 g, 20 mmol) with $[\mathrm{Pt}(1,5\text{-}\mathrm{C_8H_{12}})_2]$ (0.4 g, 1 mmol) in diethyl ether (100 cm^3) gave (24 h) a clear solution. The volatile material was removed *in vacuo* and the residue chromatographed. Elution with diethyl ether–light petroleum (1 : 1) gave white *crystals* of (2) (0.33 g, 80%), m.p. 102 °C (Found: C, 39.8; H, 4.3%, *M*, 578. $\mathrm{C_{19}H_{24}F_6OPt}$ requires C, 39.5; H, 4.2%; *M*, 577). The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$) showed resonances at τ 4.43 (m, 6 H, CH=CH, J_{HPt} 56 Hz), 6.18 [m, 1 H, C*H*$\mathrm{C(CF_3)_2}$] and 7.71 (m, 16 H, $\mathrm{CH_2CH_2}$); the signal due to PtC*H* was not detected. The

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* 1 eV ≈ 1.60×10^{-19} J.

[34] M. Green and B. Lewis, *J.C.S. Dalton*, 1975, 1137.

[35] P. Caddy, M. Green, J. A. K. Howard, J. M. Squire, and P. Woodward, unpublished observations.

^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 71.0 p.p.m. (q, 3 F, CF_3, J_{FF} 8.5 Hz) and 76.7 (q, 3 F, CF_3, J_{FF} 8.5, J_{PtF} 11.0 Hz). The ^{13}C n.m.r. spectrum ($CDCl_3$, ^{1}H decoupled) showed resonances at 130.1 p.p.m. (no ^{195}Pt satellites, *C*H=CH), 129.2 (no ^{195}Pt satellites, *C*H=CH), 112.9 (*C*H=CH *trans* to C, J_{PtC} 24.4 Hz), 112.7 (*C*H=CH *trans* to C, J_{PtC} 27.5 Hz), 79.8 (*C*H=CH *trans* to O, J_{PtC} 224.3 Hz), 79.4 (*C*H=CH *trans* to O, J_{PtC} 228.9 Hz), 51.9 [no ^{195}Pt satellites, *C*H–$C(CF_3)_2$], 48.4 (*C*HPt, J_{PtC} 709.5 Hz), 35.3 ($J_{PtC} < 10$ Hz), 32.5 (J_{PtC} 20 Hz), 30.6 (J_{PtC} 20 Hz), 27.8 (*C*H_2), 27.3 (*C*H_2), 26.5 (*C*H_2), and 25.5 (*C*H_2); ^{13}C n.m.r. resonances ($CDCl_3$, ^{19}F decoupled), 125.2 and 124.3 p.p.m.

Further elution gave white crystals of (3) (0.13 g, 20%), m.p. 181 °C (lit.,[3] 183—184 °C) (Found: C, 26.5; H, 2.1. Calc. for $C_{14}H_{12}F_{12}O_2Pt$: C, 26.5; H, 1.9%). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 67.0 (m, 6 F, CF_3, J_{FF} 3.1, J_{PtF} 66.6 Hz) and 80.4 p.p.m. (m, 6 F, CF_3, J_{FF} 3.1 Hz) in agreement with the literature.[3] The ^{13}C n.m.r. spectrum ($CDCl_3$, ^{1}H decoupled) showed resonances at 113.2 [*C*H=CH *trans* to $C(CF_3)_2$, J_{PtC} 70.8 Hz], 87.0 (*C*H=CH *trans* to O, J_{PtC} 178.2 Hz), 32.2 (J_{PtC} 14.7 Hz), and 27.13 p.p.m. (J_{PtC} 12.2 Hz).

(*c*) Similarly, $(CF_3)_2CO$ (0.25 g, 1.5 mmol) and [Pt(1,5-$C_8H_{12})_2$] (0.4 g, 1 mmol) reacted in benzene (100 cm^3) as solvent to give crystals of (2) (0.5 g, 95%). The ^{19}F n.m.r. spectrum ($CDCl_3$) of the product showed a characteristic band of (6) as an impurity (*ca.* 8%) at 67.0 p.p.m. [J_{PtF} 78.1 Hz].

*Reaction of Hexafluoroacetone with Tris(ethylene)platinum in the Presence of Cyclo-octa-*1,5*-diene.*—Bis(cyclo-octa-1,5-diene)platinum (0.4 g, 1 mmol) was dissolved in light petroleum (20 cm^3) and the solution saturated (−20 °C) with ethylene. Hexafluoroacetone (0.24 g, 1.5 mmol) was condensed (−196 °C) into the solution contained in a Schlenk tube. The tube and contents were allowed to slowly (2 h) warm to room temperature under a nitrogen atmosphere. The solution slowly deposited yellow crystals of (1) (0.32 g, 83%). The mother liquor was reduced in volume (5 cm^3) and cooled to −50 °C to give white *crystals* of (6) (0.05 g, 10%), m.p. 92 °C (Found: C, 28.6; H, 2.7. $C_{11}H_{12}F_6OPt$ requires C, 28.2; H, 2.6%). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed a resonance at 67.0 p.p.m. (J_{PtF} 78.1 Hz).

Reaction of Hexafluoroacetone with Tris(bicyclo[2.2.1]*heptene)platinum.*—Hexafluoroacetone (1.66 g, 10 mmol) was condensed into a Carius tube containing [Pt($C_7H_{10})_3$] (0.47 g, 1 mmol) dissolved in diethyl ether (100 cm^3). After 31 days at room temperature the volatile material was removed *in vacuo* to give white crystals of unreacted [Pt($C_7H_{10})_3$] (0.47 g).

A similar reaction in benzene (40 cm^3) carried out at 60 °C gave platinum metal.

Reactions of (1).—(*a*) *With triphenylphosphine.* A solution of triphenylphosphine (0.26 g, 1 mmol) in diethyl ether (10 cm^3) was added dropwise with stirring to a solution of (1) (0.2 g, 0.25 mmol) in diethyl ether (50 cm^3). After 2 h at room temperature the solvent was reduced (10 cm^3) in volume and the solution cooled (−50 °C) to give white crystals of $[\overline{\mathrm{Pt{\cdot}C(CF_3)_2{\cdot}O}}(PPh_3)_2]$ (70 mg, 32%), m.p. 216 °C (lit.: 216 °C) identical (i.r. and n.m.r.) with an authentic sample.[36]

The ^{31}P n.m.r. spectrum of a solution in benzene (1.5 cm^3) of (1) (0.05 mmol) and PPh_3 (0.2 mmol) measured at room temperature showed resonances at −50.4 (J_{PtP} 4 461.6 Hz) assigned to $Pt(PPh_3)_3$, and at −20.5 [d of septets, ^{31}P *trans* to $C(CF_3)_2$, J_{PtP} 3 222.6, J_{PP} 10.9, and J_{PF} 10.9 Hz] and −18.4 p.p.m. (d, ^{31}P *trans* to O, J_{PtP} 5 084.2, J_{PP} 10.9 Hz) assigned to $[\overline{\mathrm{Pt{\cdot}C(CF_3)_2{\cdot}O}}(PPh_3)_2]$.

(*b*) *With hexafluoroacetone* A solution of (1) (0.3 g, 0.39 mmol) and hexafluoroacetone (0.99 g, 6 mmol) in toluene (60 cm^3) was heated (70 °C,10 d) in a Carius tube. The volatile material was removed *in vacuo* and the residue recrystallised from diethyl ether–light petroleum to give white crystals of (3) (0.41 g, 83%).

Reactions of (2).—(*a*) *With* 1,2*-bisdimethylarsinobenzene.* A solution of diars (0.2 cm^3, 1 mmol) in diethyl ether was added dropwise with stirring to a stirred solution of (2) (0.3 g, 0.5 mmol) in diethyl ether (30 cm^3). After 1.5 h at room temperature the volume of the solvent was reduced (to 10 cm^3) *in vacuo*. Addition of light petroleum gave white crystals of (4) (0.32 g, 85%), m.p. 174 °C (Found: C, 33.2; H, 3.8%; *M*, 755. $C_{21}H_{28}As_2F_6OPt$ requires C, 33.4; H, 3.7%, *M*, 755.4). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2.40 (m, 4 H, C_6H_4), 4.33 (m, 2 H, CH, no ^{195}Pt satellites), 7.44 [m, 1 H, $CH(CF_3)_2$], 7.92 (m, 8 H, CH_2), and 8.38 (m, 12 H, CH_3). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 70.96 (q, 3 F, CF_3, J_{FF} 10.0 Hz) and 76.94 p.p.m. (q, 3 F, CF_3, J_{FF} 10.0, J_{PtF} 8.0 Hz).

(*b*) *With triphenylphosphine.* Similarly, reaction of PPh_3 (0.26 g, 1.0 mmol) in diethyl ether (10 cm^3) with (2) (0.30 g, 0.5 mmol) in Et_2O (30 cm^3) gave (18 h, room temperature) white *crystals* of (5) (0.45 g, 90%), m.p. 255 °C (Found: C, 56.9; H, 4.5. $C_{47}H_{42}F_6OP_2Pt$ requires C, 56.8; H, 4.3%). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2.40 (m, 6 H, C_6H_5), 2.84 (m, 24 H, C_6H_5), 4.81 (m, 2 H, CH, no ^{195}Pt satellites), 7.50 [m, 1 H, $CHC(CF_3)_2$], 8.24 (m, 8 H, CH_2). The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 69.5 (q, 3 F, CF_3, J_{FF} 8.3 Hz) and 77.3 p.p.m. (q, 3 F, CF_3, J_{FF} 8.3 Hz). The ^{31}P n.m.r. spectrum ($CDCl_3$) showed resonances at −22.83 (d, 1 P, ^{31}P *trans* to CH, J_{PP} 10.7, J_{PtP} 1 537.5 Hz) and −14.95 p.p.m. (d, 1 P, ^{31}P *trans* to O, J_{PP} 10.7, J_{PtP} 4 315.7 Hz).

*Reaction of Bis(cyclo-octa-*1,5*-diene)platinum with* 1,1*-Dicyano-*2,2*-bis(trifluoromethyl)ethylene.*—A solution of $(CN)_2C{:}C(CF_3)_2$ (0.2 g, 1.0 mmol) in diethyl ether (5 cm^3) was added to a stirred solution (−20 °C) of [Pt(cod)$_2$] (0.4 g, 1.0 mmol) in Et_2O (30 cm^3). A white precipitate was immediately formed. After 2 h the solid was separated by filtration and washed with Et_2O (3 × 10 cm^3) to give white *crystals* of (7) (0.35 g, 68%), m.p. 300 °C (decomp.) (Found: C, 32.5; H, 2.4; N, 5.0. $C_{14}H_{12}F_6N_2Pt$ requires C, 32.5; H, 2.3; N, 5.4%).

The ethereal solution was evaporated to dryness and the solid residue recrystallised from diethyl ether–light petroleum to give white crystals of (8) (0.13 g, 21%), m.p. 125 °C (decomp.) (Found: C, 42.3; H, 4.1; N, 3.9. $C_{22}H_{24}F_6N_2Pt$ requires C, 42.2; H, 3.9; N, 4.4%). The ^{19}F n.m.r. spectrum (C_6D_6) showed resonances at 58.4 (q, 3 F, CF_3, J_{FF} 8.0 Hz) and 64.5 p.p.m. (q, 3 F, CF_3, J_{FF} 8.0 Hz). The ^{13}C n.m.r. spectrum (C_6D_6, ^{1}H decoupled) showed resonances at 130.8 (CH not bonded to Pt), 129.2 (CH not bonded to Pt), 112.8 (CH= *trans* to C, J_{PtC} 39.7 Hz), 110.1 (CH= *trans* to C, J_{PtC} 35.3 Hz), 101.0 [CH= *trans* to $C(CN)_2$, J_{PtC} 137.3 Hz], 98.9 [CH= *trans* to $C(CN)_2$, J_{PtC} 134.3 Hz],

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[36] B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 167.

48.5 [$CHC(CF_3)_2$], 42.7 (CHPt, J_{PtC} 677.5 Hz), 35.3 (CH_2, J_{PtC} 22.9 Hz), 32.6 (CH_2, J_{PtC} 19.3 Hz), and 31.1, 30.0, 27.4 (2 C), and 25.3 p.p.m. (2 C) (CH_2).

Reaction of (7) *with* 1,2-*Bisdimethylarsinobenzene*.—A suspension of (7) (0.30 g, 0.58 mmol) in diethyl ether (60 cm^3) was treated with diars (0.2 cm^3, 1.0 mmol). After being stirred at room temperature for 10 h the solution was filtered and the solvent removed *in vacuo*. The residue was recrystallised from diethyl ether to give white *crystals* of (9) (0.44 g, 70%), m.p. 226 °C (Found: C, 35.7; H, 3.7; N, 3.5. $C_{24}H_{28}As_2F_6N_2Pt$ requires C, 35.9; H, 3.5; N, 3.5%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2.34 (m, 4 H, C_6H_4), 4.31 (m, 2 H, CH=CH, no ^{195}Pt satellites), 7.22 [m, 1 H, $CHC(CF_3)_2$], 7.80 (m, 8 H, CH_2), and 8.33 (m, 12 H, CH_3).

The ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 58.4 (q, 3 F, CF_3, J_{FF} 8.0 Hz) and 65.0 p.p.m. (q, 3 F, CF_3, J_{FF} 8.0 Hz).

Reaction of (8) *with* 1,2-*Bisdimethylarsinobenzene*.—Diars (0.1 cm^3, 0.51 mmol) was added to a stirred solution of (8) (0.20 g, 0.32 mmol) in diethyl ether (60 cm^3). The solution was filtered, the solvent removed *in vacuo*, and the residue recrystallised from diethyl ether–light petroleum to give white crystals of (9), identical (analysis, i.r. and n.m.r. spectra) to the material obtained above.

Reaction of Bis(*cyclo-octa*-1,5-*diene*)*platinum with* N-*Methylhexafluoroisopropylideneamine*.—An excess of $(CF_3)_2C$:NMe (0.7 g, 4.0 mmol) was condensed (−196 °C) into a tube containing a solution of [$Pt(cod)_2$] (0.4 g, 1.0 mmol) in toluene (40 cm^3). After 14 h at room temperature, the volatile material was removed *in vacuo*. The residue was recrystallised from light petroleum to give white *crystals* of (10) (0.38 g, 80%), m.p. 92 °C (Found: C, 30.7; H, 3.3; N, 2.5%, *M*, 482. $C_{12}H_{15}F_6NPt$ requires C, 29.9; H, 3.1; N, 2.9%, *M*, 482). The ^1H n.m.r. spectrum (C_6D_6) showed resonances at τ 5.04 (m, 4 H, CH=CH, J_{PtH} 62.0 Hz), 6.60 (s, 3 H, NMe, J_{PtH} 31.0 Hz), and 8.44 (m, 8 H, CH_2, J_{PtH} 24.0 Hz). The ^{19}F n.m.r. spectrum (C_6D_6) showed a resonance at 60.3 p.p.m. (s, 6 F, J_{PtF} 105.9 Hz).

Reaction of (10) *with* 1,2-*Bisdimethylarsinobenzene*.—Diars (0.2 cm^3, 1.0 mmol) was added to a stirred solution of (10) (0.24 g, 0.5 mmol) in diethyl ether (30 cm^3). After 2 h at room temperature volatile material was removed *in vacuo*. The residue was recrystallised from diethyl ether–light petroleum to give white *crystals* of (11) (0.30 g, 92%), m.p. 125 °C (decomp.) (Found: C, 25.7; H, 3.0; N, 2.0. $C_{14}H_{19}As_2F_6NPt$ requires C, 25.5; H, 2.9; N, 2.1%). The ^1H n.m.r. spectrum (C_6D_6) showed resonances at τ 2.84 (m, 4 H, C_6H_4), 6.26 (s, 3 H, NMe, J_{PtH} 36.0 Hz), 8.74 (s, 6 H, $AsMe_2$, J_{PtH} 23.0 Hz), and 8.91 (s, 6 H, $AsMe_2$, J_{PtH} 20.0 Hz). The ^{19}F n.m.r. spectrum ($CDCl_3$) showed a resonance at 59.6 p.p.m. (s, 6 F, CF_3, J_{PtF} 96.7 Hz).

Crystal Structure Determinations of Complexes (1) *and* (3).—Crystals of (1) grow as flat yellow plates from diethyl ether, and that used for data collection was of dimensions 0.14 × 0.025 × 0.36 mm (faces 100, $\bar{1}00$, 010, $0\bar{1}0$, $00\bar{1}$, 001). The data crystal of compound (3), which grows as colourless prisms, was of dimensions 0.10 × 0.10 × 0.25 mm. Diffracted intensities for both compounds were recorded on a Syntex $P2_1$ four-circle diffractometer for $2.9 < 2\theta < 50°$, according to methods described earlier.[32] Of a total of 3 267 (1) and 2 989 (3) independent intensities, 2 083 (1) and 2 659 (3) were deemed 'observable' according to the criterion $I \geqslant 2.5\sigma(I)$ [σ is the estimated standard deviation of the measured intensity based on counting statistics]. The observed reflections only, corrected in both cases for absorption, were used to solve and refine the structures.

Crystal data for (1).—$C_{19}H_{24}F_6OPt_2$, $M = 772.58$, Monoclinic, space group $P2_1/c$, $a = 9.917(3)$, $b = 14.957(6)$, $c = 13.358(3)$ Å, $\beta = 102.18(2)°$, $U = 1\,936.8$ Å^3, $D_m = 2.55$ g cm^{-3} (flotation), $Z = 4$, $D_c = 2.66$ g cm^{-3}, $F(000) = 1\,388$, Mo-K_α *X*-radiation, graphite monochromator ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 152.57 cm^{-1}.

Crystal data for (3).—$C_{14}H_{12}F_{12}O_2Pt$, $M = 635.32$, Triclinic, space group $P\bar{1}$, $a = 8.212(3)$, $b = 9.329(2)$, $c = 12.610(3)$ Å, $\alpha = 91.87(2)$, $\beta = 102.10(2)$, $\gamma = 111.25(3)°$, $U = 874.0$ Å^3, $D_m = 2.32$ g cm^{-3} (flotation), $Z = 2$, $D_c = 2.41$ g cm^{-3}, $F(000) = 596$, Mo-K_α *X*-radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 90.21 cm^{-1}.

Structure Solution and Refinement.—Both structures were solved by conventional heavy-atom methods and refined in the final stages by blocked-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms. Weights were applied according to the scheme $w = x.y$, where w is the reciprocal of that used in the least squares refinement, and $x = 1$ if $\sin\theta > b$; but $x = \sin\theta/b$ if $\sin\theta \leqslant b$, and $y = 1$ if $|F_o| < c$; with $y = c(|F_o|)^{-1}$ if $|F_o| \geqslant c$; and $b = 0.15$, $c = 200$ for (1) and $b = 0.24$, $c = 64.0$ for (3). These values of b and c were chosen from an analysis

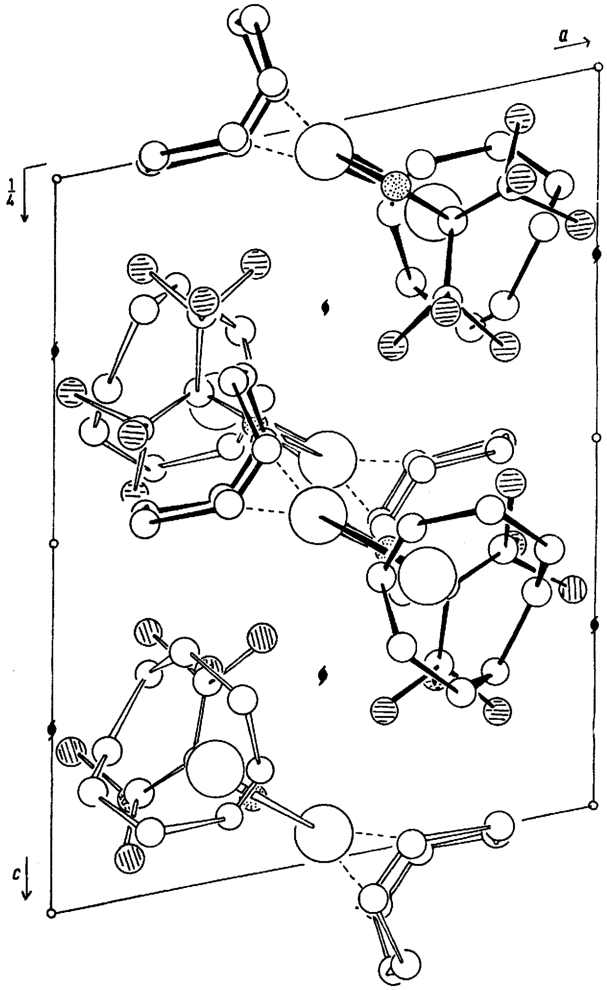

FIGURE 3 Contents of the unit cell of compound (1), viewed down the *b* axis towards the origin

TABLE 7

Final positional (fractional co-ordinate) and anisotropic temperature * (Å^3 × 10^2) factors for the non-hydrogen atoms in complex (1), with estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	0.304 65(6)	0.199 05(4)	0.354 28(5)	2.6(1)	3.2(1)	3.4(1)	−0.03(3)	0.0(4)	−0.13(3)
Pt(2)	0.508 56(6)	0.287 06(4)	0.462 72(5)	2.1(1)	3.1(1)	3.3(1)	−0.15(3)	−0.04(4)	0.29(3)
C(12)	0.269 0(16)	0.335 6(11)	0.334 2(12)	3.0(9)	3.0(9)	2.9(9)	0.4(7)	0.2(7)	0.4(7)
O(12)	0.380 6(11)	0.379 6(7)	0.397 6(9)	3.4(6)	3.1(7)	5.2(8)	−0.4(5)	−0.9(5)	1.4(6)
Trifluoromethyl groups									
C(121)	0.266 6(22)	0.366 3(12)	0.224 9(16)	6.4(13)	2.8(11)	5.7(13)	−1.2(9)	0.9(10)	1.6(9)
F(11)	0.153 2(17)	0.343 5(11)	0.155 6(11)	11.7(12)	11.1(12)	6.1(9)	−2.3(9)	−2.8(8)	1.0(8)
F(12)	0.374 4(17)	0.339 1(11)	0.191 4(12)	12.1(13)	11.7(13)	8.7(11)	4.2(10)	6.4(10)	3.6(9)
F(13)	0.269 2(15)	0.457 3(9)	0.216 3(10)	10.8(11)	6.4(9)	7.8(9)	−1.3(7)	−0.3(8)	3.7(7)
C(122)	0.138 7(20)	0.364 6(15)	0.371 9(18)	4.0(10)	5.6(14)	6.5(15)	0.5(9)	1.1(10)	−2.1(11)
F(21)	0.0199 (10)	0.344 3(7)	0.307 4(11)	2.8(6)	4.8(7)	13.4(12)	1.3(5)	−0.5(6)	−1.5(7)
F(22)	0.136 6(15)	0.332 8(10)	0.460 2(12)	9.8(11)	9.7(11)	9.0(11)	2.6(9)	5.7(9)	0.7(9)
F(23)	0.130 9(12)	0.455 2(7)	0.378 2(11)	6.1(8)	3.2(7)	12.9(12)	0.8(5)	1.9(7)	−2.6(7)
Cyclo-octa-1,5-diene ligands									
C(1)	0.390 9(21)	0.060 6(13)	0.354 8(17)	5.9(13)	3.0(11)	5.7(13)	0.3(9)	−0.1(10)	0.4(9)
C(2)	0.324 0(22)	0.064 8(13)	0.433 2(16)	6.4(13)	3.8(12)	4.8(13)	−0.1(10)	0.1(10)	−0.6(9)
C(3)	0.178 2(22)	0.029 2(17)	0.433 2(17)	4.8(13)	8.2(17)	6.2(15)	−3.4(12)	0.0(11)	1.7(12)
C(4)	0.067 6(24)	0.065 1(21)	0.357 3(30)	3.8(14)	10.7(24)	19.3(36)	−1.2(14)	1.2(17)	8.0(24)
C(5)	0.090 0(21)	0.144 4(13)	0.290 9(22)	4.1(11)	3.1(12)	10.5(20)	−0.6(9)	−1.4(12)	2.1(12)
C(6)	0.159 8(24)	0.139 8(15)	0.211 1(17)	6.4(14)	5.4(14)	5.0(14)	−0.5(11)	−2.9(11)	−1.7(11)
C(7)	0.226 9(4)	0.057 4(27)	0.184 9(26)	12.5(27)	17.6(36)	11.4(26)	7.9(26)	−4.8(21)	−11.8(26)
C(8)	0.336 0(28)	0.017 6(15)	0.253 9(19)	9.0(19)	5.0(14)	7.2(17)	2.6(13)	1.6(14)	−1.2(12)
C(21)	0.679 6(18)	0.195 7(15)	0.480 0(17)	2.6(9)	6.4(14)	7.2(15)	1.9(9)	−1.6(9)	−3.0(22)
C(22)	0.620 6(18)	0.192 8(13)	0.567 4(15)	3.1(10)	4.8(12)	4.4(12)	0.7(8)	−1.4(8)	0.1(9)
C(23)	0.680 0(22)	0.234 9(17)	0.668 0(14)	6.1(13)	8.6(17)	2.5(11)	−1.1(12)	−1.6(9)	1.9(10)
C(24)	0.646 1(29)	0.332 2(17)	0.683 5(17)	10.1(21)	7.6(17)	4.5(14)	1.0(14)	−1.0(13)	−2.5(12)
C(25)	0.613 9(19)	0.385 0(13)	0.586 9(15)	3.6(10)	4.1(11)	4.5(12)	0.4(8)	−1.4(9)	0.0(9)
C(26)	0.683 6(19)	0.391 7(12)	0.512 0(17)	4.2(10)	2.7(10)	7.0(15)	−0.1(8)	0.1(10)	1.1(9)
C(27)	0.821 4(20)	0.340 5(19)	0.519 7(21)	2.0(10)	8.8(19)	11.2(21)	0.7(11)	1.1(11)	1.1(16)
C(28)	0.815 2(22)	0.249 1(18)	0.482 8(20)	3.3(12)	9.3(19)	8.1(17)	1.3(12)	1.7(11)	0.3(14)

* Anisotropic thermal parameters in the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

TABLE 8

Final positional (fractional co-ordinate) and anisotropic temperature * (Å^2 × 10^2) factors for the non-hydrogen atoms in complex (3), with estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.253 70(4)	0.015 67(3)	0.236 21(3)	2.98(4)	2.32(5)	4.56(6)	1.04(2)	1.27(2)	0.79(1)
C(1)	0.360 8(10)	−0.157 4(9)	0.233 3(7)	3.2(4)	2.8(4)	4.2(5)	1.0(3)	0.9(3)	0.6(3)
C(2)	0.064 6(11)	−0.292 9(9)	0.269 5(7)	4.0(5)	2.7(4)	6.1(6)	1.3(4)	2.2(4)	1.7(4)
O(1)	0.032 6(7)	−0.170 2(6)	0.231 1(6)	2.7(3)	3.3(3)	9.6(5)	0.8(2)	1.6(3)	1.9(3)
O(2)	0.230 4(7)	−0.297 8(6)	0.257 6(4)	3.3(3)	2.7(3)	5.0(3)	1.2(2)	1.5(2)	1.3(2)
Trifluoromethyl groups									
C(11)	0.533 8(11)	−0.130 5(10)	0.317 9(8)	3.9(5)	3.8(5)	6.3(6)	2.3(4)	0.9(4)	0.9(4)
F(111)	0.516 9(8)	−0.097 3(7)	0.418 1(4)	6.9(4)	8.5(4)	5.1(3)	3.2(3)	−0.5(3)	−0.3(3)
F(112)	0.575 3(8)	−0.256 5(7)	0.321 3(5)	6.4(4)	6.1(4)	10.5(5)	4.1(3)	−0.0(3)	0.5(3)
F(113)	0.672 9(7)	−0.014 9(7)	0.301 3(5)	3.8(3)	6.8(4)	10.4(5)	1.2(3)	2.2(3)	1.4(3)
C(12)	0.378 4(13)	−0.198 0(10)	0.116 9(8)	6.3(6)	3.4(5)	5.4(6)	1.8(4)	3.0(5)	0.7(4)
F(121)	0.237 7(9)	−0.202 3(8)	0.040 6(5)	9.3(5)	10.1(5)	4.6(3)	4.0(4)	0.7(3)	0.2(3)
F(122)	0.394 6(10)	−0.333 7(6)	0.105 5(5)	13.2(6)	4.3(3)	8.0(4)	4.2(3)	5.8(4)	0.9(3)
F(123)	0.522 2(8)	−0.093 3(6)	0.093 7(5)	8.8(4)	5.6(3)	8.8(4)	2.3(3)	6.1(4)	1.9(3)
C(21)	−0.082 1(13)	−0.441 6(11)	0.200 1(9)	4.8(6)	3.8(5)	6.7(7)	0.2(4)	0.9(5)	1.1(5)
F(211)	−0.244 1(8)	−0.441 0(8)	0.193 8(7)	3.5(3)	7.2(4)	16.4(7)	0.6(3)	0.9(4)	0.0(4)
F(212)	−0.059 4(10)	−0.453 4(7)	0.100 5(5)	9.0(5)	7.2(4)	7.3(4)	0.2(4)	−0.2(4)	−1.1(3)
F(213)	−0.076 4(9)	−0.568 4(6)	0.241 9(6)	7.8(4)	3.6(3)	13.3(6)	1.3(3)	2.5(4)	2.1(3)
C(22)	0.065 6(13)	−0.296 0(12)	0.391 5(9)	4.5(5)	6.5(6)	6.6(7)	2.0(5)	2.9(5)	1.6(5)
F(221)	−0.099 5(9)	−0.333 4(9)	0.406 9(6)	6.9(4)	12.7(6)	10.5(5)	3.9(4)	5.5(4)	3.8(5)
F(222)	0.166 1(10)	−0.155 8(8)	0.447 3(5)	10.5(6)	8.9(5)	7.2(4)	2.2(4)	2.6(4)	−1.4(4)
F(223)	0.128 2(10)	−0.396 6(8)	0.438 0(5)	11.1(6)	11.0(5)	7.4(4)	6.5(5)	4.2(4)	5.1(4)
Cyclo-octa-1,5-diene									
C(3)	0.124 8(15)	0.169 3(12)	0.297 4(10)	6.5(7)	6.4(7)	8.4(8)	4.8(6)	3.1(6)	1.1(6)
C(4)	0.272 7(19)	0.303 6(16)	0.374 4(13)	8.4(10)	9.1(10)	12.5(12)	3.8(8)	1.6(9)	−4.6(9)
C(5)	0.454 7(16)	0.344 4(12)	0.360 4(10)	6.4(7)	5.1(6)	9.2(9)	1.1(5)	1.1(6)	−3.3(6)
C(6)	0.492 8(12)	0.226 4(9)	0.294 0(8)	4.7(5)	2.5(4)	6.6(6)	0.0(4)	2.3(5)	−0.8(4)
C(7)	0.448 1(11)	0.199 9(9)	0.175 2(8)	4.1(5)	2.8(4)	6.4(6)	0.6(4)	2.3(4)	1.2(4)
C(8)	0.350 4(17)	0.277 9(14)	0.097 8(10)	8.3(8)	7.7(8)	9.3(9)	4.4(7)	4.4(7)	5.2(7)
C(9)	0.177 6(18)	0.278 8(16)	0.116 4(12)	8.4(9)	10.6(10)	13.2(12)	5.8(8)	5.0(8)	8.7(10)
C(10)	0.083 9(12)	0.156 3(11)	0.183 2(9)	4.4(5)	4.7(5)	9.2(8)	2.9(4)	2.3(5)	2.8(5)

* Anisotropic thermal parameters in the form: $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$.

of the variation of $w\Delta^2$ [where $\Delta = |F_o - F_c|$] with F_o and $\sin\theta$, for intervals of approximately equal numbers of reflections. This scheme gave a satisfactory weight analysis after both final refinements.

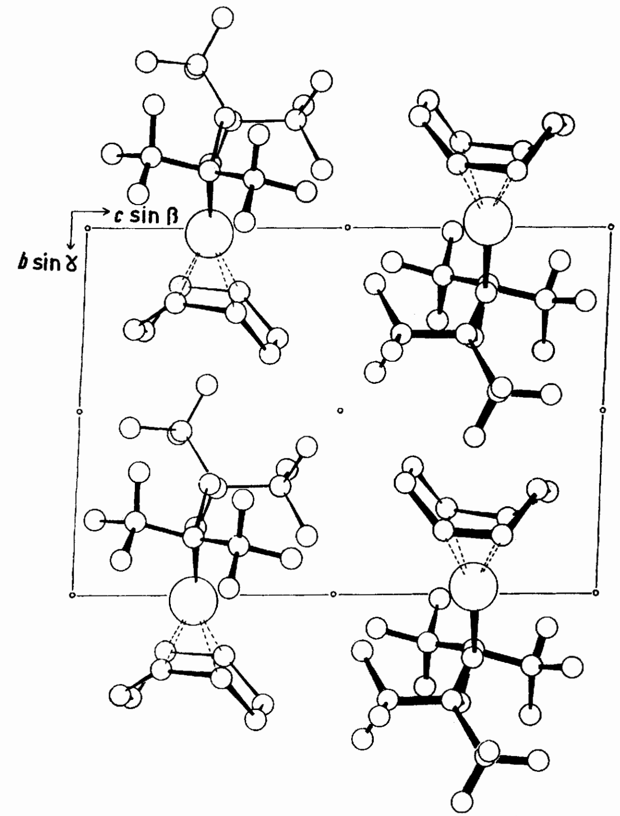

FIGURE 4 Contents of the unit cell of compound (3), viewed down the *a* axis towards the origin

The atomic scattering factors used are those of refs. 37 (C and O), 38 (Pt and F), and 39 (H). Those for Pt were corrected for the effects of anomalous dispersion ($\Delta f' = -2.352$, $\Delta f'' = 8.388$). The hydrogen atoms were included at positions estimated from the electron density maps (1), and at calculated positions (C–H 0.95 Å) for (3), but neither their positional nor thermal parameters were refined [U_H 0.06 Å^2]. The hydrogen-atom parameters are deposited with the structure factor Tables.

Refinement converged at R 0.038 (R' 0.044) for the 2 083 independent intensities of (1), and at R 0.029 (R' 0.035) for the 2 659 independent intensities of (3), with a mean shift-error for the last four cycles of 0.1 for both (1) and (3). Molecular packing diagrams for compounds (1) and (3) are shown in Figures 3 and 4, respectively.

The residual electron density synthesis showed no peaks >1.2 or < -1.2 eÅ^{-3} for (1), nor >0.9 or < -1.0 eÅ^{-3} for (3). All computational work was carried out at the University of London Computing Centre using the '*X*-ray System' of programmes.

Positional and thermal parameters are given in Tables 7 (1) and 8 (3), interatomic distances and angles in Tables 1 (1) and 5 (3), and some least squares planes in Tables 2 (1) and 6 (3). Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21868 (16 pp., 1 microfiche).*

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

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