Reactions of Low-valent Metal Complexes with Fluorocarbons. Part 33.[1] Bis(cyclo-octa-1,5-diene)platinum with Hexafluorobut-2-yne; Crystal and Molecular Structures of Bis(cyclo-octa-1,5-diene)tetrakis(hexafluorobut-2-yne)triplatinum and Bis(cyclo-octa-1,5-diene)bis(hexafluorobut-2-yne)diplatinum

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Reaction of $[\mathrm{Pt(cod)_2}]$ (cod = $1,5\text{-}\mathrm{C_8H_{12}}$) with hexafluorobut-2-yne (hfb) affords $[\mathrm{Pt\{C(CF_3){:}C(CF_3)\}(cod)}]$, which reacts with triphenylphosphine, carbon monoxide, or hexafluorobut-2-yne to afford $[\mathrm{Pt\{C(CF_3){:}C(CF_3)\}(PPh_3)_2}]$, $[\mathrm{Pt\{C(CF_3){:}C(CF_3){\cdot}Pt{\cdot}C(CF_3){:}C(CF_3)\}(CO)_2(cod)}]$, and $[\mathrm{Pt\{C(CF_3){:}C(CF_3){\cdot}Pt{\cdot}C(CF_3){:}C(CF_3){\cdot}Pt{\cdot}C(CF_3){:}C(CF_3){\cdot}C(CF_3){:}C(CF_3)\}(cod)_2}]$ containing three-, four-, six-, and eight-membered rings. The triplatinum species has been structurally identified by *X*-ray crystallography. The crystals are orthorhombic, space group *Pbca*, $Z = 8$ in a unit cell of dimensions $a = 16.513(10)$, $b = 28.536(30)$, and $c = 15.429(8)$ Å. This complex is also the major product in the reaction of $[\mathrm{Pt(C_2H_4)_3}]$ with hfb in the presence of cod. A minor product in this reaction, $[\mathrm{Pt\{C(CF_3){:}C(CF_3){\cdot}Pt{\cdot}C(CF_3){:}C(CF_3)\}(cod)_2}]$, is formed in high yield on treatment of $[\mathrm{Pt{\cdot}C(CF_3)_2{\cdot}O{\cdot}Pt(cod)_2}]$ with hfb. A crystal-structure determination has established the presence in this molecule of a six-membered ring containing two platinum atoms. Crystals are triclinic, space group $P\bar{1}$, $Z = 2$ in a unit cell of dimensions $a = 11.099(5)$, $b = 9.413(2)$, and $c = 14.317$ (4) Å, $\alpha = 110.72(2)$, $\beta = 93.50(3)$, and $\gamma = 113.08(3)°$.

ALTHOUGH considerable progress has been made in transition-metal–acetylene chemistry there are still many important aspects which have eluded our understanding. With this in mind, the reaction of bis(cyclo-octa-1,5-diene)platinum,[2] $[\mathrm{Pt(cod)_2}]$, with hexafluorobut-2-yne (hfb) was studied, there being comparative studies available of the corresponding reactions with bis(cyclo-octa-1,5-diene)nickel [3] and with *trans*-stilbenebis(triethylphosphine)platinum.[4]

RESULTS AND DISCUSSION

Treatment of hexafluorobut-2-yne with $[\mathrm{Pt(cod)_2}]$ in diethyl ether using a reactant ratio of 1.5 : 1 respectively afforded a single product, the white crystalline complex (1). Analysis and mass spectroscopy indicated that the molecule was $[\mathrm{Pt\{C(CF_3){:}C(CF_3)\}(cod)}]$, this being confirmed by the presence in the i.r. of a band at 1 790s cm^{-1}, corresponding to the ν(C=C) stretching frequency of π-bonded hexafluorobut-2-yne, and by the presence in the n.m.r. spectra of the expected resonances, in particular a single ^{19}F resonance with satellites due to ^{195}Pt–^{19}F coupling. Further confirmation was provided by the observation that treatment of (1) with 2 molar equivalents of triphenylphosphine led to the displacement of the co-ordinated cyclo-octa-1,5-diene, and formation of the

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[1] Part 32, J. Forniés, M. Green, A. Laguna, M. Murray, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1515.

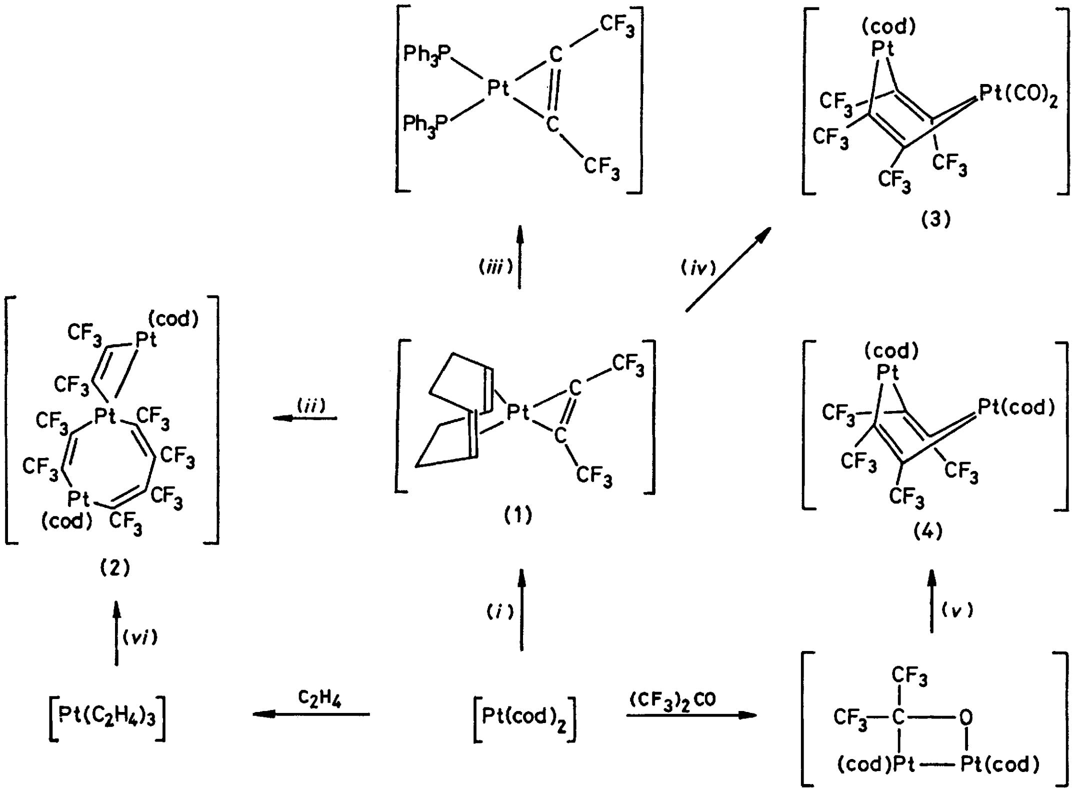
[2] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271.

[3] J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 448.

[4] J. Browning, M. Green, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 97.

known[5] (hexafluorobut-2-yne)bis(triphenylphosphine)-platinum complex.

When an excess of hfb was used in the reaction with $[Pt(cod)_2]$ a lower yield (75%) of (1) was obtained, and there was evidence for formation of an additional yellow product. In the belief that (1) was in fact the precursor of this new product, treatment of (1) with an excess of hfb was examined. Reaction at room temperature gave *ca.* 30% of the yellow crystalline complex (2). Analysis and molecular-weight measurements indicated the remarkable molecular formula $[Pt_3(hfb)_4(cod)_2]$. Since the i.r. and n.m.r. spectra * of (1) did not provide an insight into the molecular structure of this apparent trinuclear species, a single-crystal *X*-ray diffraction study of (2) was undertaken.



SCHEME 1 (*i*) $CF_3C_2CF_3$, 1 : 1.5; (*ii*) excess of $CF_3C_2CF_3$; (*iii*) PPh_3, Et_2O; (*iv*) CO, Et_2O; (*v*) $CF_3C_2CF_3$; (*vi*) $CF_3C_2CF_3$, cod

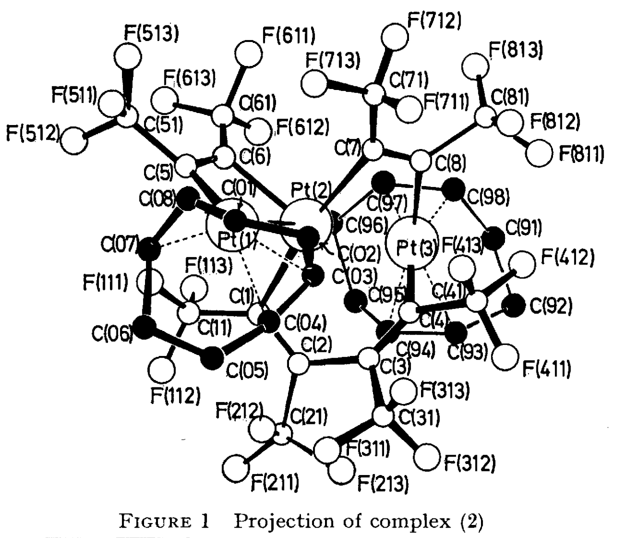


FIGURE 1 Projection of complex (2) $Pt\{C(CF_3){:}C(CF_3){\cdot}Pt{\cdot}C(CF_3){:}C(CF_3){\cdot}Pt{\cdot}C(CF_3){:}C(CF_3){\cdot}C(CF_3){:}C(CF_3)\}(cod)_2]$ on the *ac* face showing the crystallographic numbering system

The overall geometry of (2) is shown in Figure 1 and bond lengths and angles in Table 1. The molecule consists of three platinum atoms, which are not linear [160.98(5)°]; two of the metal atoms Pt(1) and Pt(2) are bridged by a hexafluorobut-2-yne molecule to form a four-membered ring with a Pt–Pt bond. Atoms Pt(2) and Pt(3) are bridged on one side by an hfb molecule, and on the other by two hfb molecules linked together, forming overall an eight-membered ring containing the two platinum atoms. The terminal metal atoms [Pt(1) and Pt(3)] are each co-ordinated by a cyclo-octa-1,5-diene molecule. These ligands are twisted (Table 1) as has been observed in other molecules containing co-

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* The ^{19}F n.m.r. spectrum was temperature dependent, but was still insufficiently resolved at −90 °C to provide useful structural data or to provide an insight into the dynamic behaviour.

[5] J. L. Boston, S. O. Grim, and G. Wilkinson, *J. Chem. Soc.*, 1963, 2468.

TABLE 1

Bond lengths (Å) and angles (°) for complex (2)

(*a*) Distances

Pt(1)–Pt(2)	2.630(3)	C(21)–F(211)	1.36(5)
Pt(1)–C(5)	2.01(3)	C(21)–F(212)	1.33(5)
C(5)–C(51)	1.44(5)	C(21)–F(213)	1.32(5)
C(51)–F(511)	1.25(4)	C(2)–C(3)	1.54(4)
C(51)–F(512)	1.28(5)	C(3)–C(31)	1.52(4)
C(51)–F(513)	1.38(5)	C(31)–F(311)	1.39(4)
Pt(2)–Pt(3)	2.841(2)	C(31)–F(312)	1.29(4)
Pt(2)–C(6)	2.05(3)	C(31)–F(313)	1.35(4)
Pt(2)–C(7)	1.99(3)	Pt(1)–C(07,08) *	2.05(3)
Pt(2)–C(1)	2.10(3)	Pt(1)–C(03,04)	2.14(3)
C(6)–C(61)	1.49(4)	Pt(3)–C(97,98)	2.15(3)
C(61)–F(611)	1.36(5)	Pt(3)–C(93,94)	2.20(3)
C(61)–F(612)	1.17(5)	C(3)–C(4)	1.33(4)
C(61)–F(613)	1.28(4)	C(4)–C(41)	1.55(4)
C(7)–C(71)	1.47(5)	C(41)–F(411)	1.33(4)
C(71)–F(711)	1.35(6)	C(41)–F(412)	1.34(4)
C(71)–F(712)	1.34(4)	C(41)–F(413)	1.33(4)
C(71)–F(713)	1.29(5)	Pt(3)–C(4)	2.13(3)
C(1)–C(11)	1.45(4)	Pt(3)–C(8)	2.08(3)
C(11)–F(111)	1.33(5)	C(8)–C(81)	1.52(5)
C(11)–F(112)	1.29(4)	C(81)–F(811)	1.38(4)
C(11)–F(113)	1.23(6)	C(81)–F(812)	1.34(5)
C(1)–C(2)	1.38(4)	C(81)–F(813)	1.30(4)
C(2)–C(21)	1.60(4)		

cod ligands

Pt(1)–C(03)	2.24(3)	Pt(3)–C(93)	2.31(3)
Pt(1)–C(04)	2.24(3)	Pt(3)–C(94)	2.29(4)
Pt(1)–C(07)	2.14(3)	Pt(3)–C(97)	2.26(3)
Pt(1)–C(08)	2.19(4)	Pt(3)–C(98)	2.25(3)
C(01)–C(02)	1.52(5)	C(91)–C(92)	1.54(5)
C(02)–C(03)	1.53(6)	C(92)–C(93)	1.49(5)
C(03)–C(04)	1.36(5)	C(93)–C(94)	1.31(6)
C(04)–C(05)	1.48(5)	C(94)–C(95)	1.58(6)
C(05)–C(06)	1.61(5)	C(95)–C(96)	1.57(5)
C(06)–C(07)	1.56(4)	C(96)–C(97)	1.54(5)
C(07)–C(08)	1.42(5)	C(97)–C(98)	1.40(5)
C(08)–C(01)	1.50(5)	C(98)–C(91)	1.50(5)

(*b*) Angles

Pt(1)–Pt(2)–Pt(3)	160.98(5)	Pt(2)–Pt(3)–C(8)	63.2(7)
Pt(2)–Pt(1)–C(5)	76.6(9)	Pt(2)–Pt(3)–C(4)	64.6(8)
Pt(1)–C(5)–C(6)	101(2)	C(7)–C(8)–C(81)	125(3)
C(51)–C(5)–C(6)	128(3)	Pt(3)–C(8)–C(81)	115(2)
C(51)–C(5)–Pt(1)	131(2)	Pt(3)–C(8)–C(7)	119(2)
C(5)–C(51)–F(511)	115(3)	C(8)–C(81)–F(811)	115(3)
C(5)–C(51)–F(512)	116(3)	C(8)–C(81)–F(812)	115(3)
C(5)–C(51)–F(513)	111(3)	C(8)–C(81)–F(813)	113(3)
F(511)–C(51)–F(512)	110(3)	F(811)–C(81)–F(812)	102(3)
F(512)–C(51)–F(513)	101(3)	F(812)–C(81)–F(813)	107(3)
F(511)–C(51)–F(513)	101(3)	F(811)–C(81–F)(813)	103(3)
Pt(1)–Pt(2)–C(6)	67.6(7)	Pt(2)–C(1)–C(11)	125(2)
Pt(1)–Pt(2)–C(7)	103.1(8)	Pt(2)–C(1)–C(2)	109(2)
Pt(1)–Pt(2)–C(1)	87.8(7)	C(11)–C(1)–C(2)	123(3)
C(1)–Pt(2)–Pt(3)	93.3(8)	C(1)–C(11)–F(111)	106(3)
C(1)–Pt(2)–C(6)	99.8(11)	C(1)–C(11)–F(112)	118(3)
Pt(1)–Pt(2)–C(7)	103.1(8)	C(1)–C(11)–F(113)	112(3)
C(6)–Pt(2)–C(7)	92.9(11)	F(111)–C(11)–F(112)	102(3)
C(7)–Pt(2)–Pt(3)	73.4(8)	F(112)–C(11)–F(113)	108(4)
Pt(3)–Pt(2)–C(1)	93.3(8)	F(111)–C(11)–F(113)	109(4)
C(7)–Pt(2)–C(1)	165.8(11)	C(1)–C(2)–C(3)	120(2)
C(6)–Pt(2)–Pt(3)	130.6(7)	C(1)–C(2)–C(21)	124(3)
Pt(2)–C(6)–C(5)	115(2)	C(21)–C(2)–C(3)	115(2)
Pt(2)–C(6)–C(61)	113(2)	C(2)–C(21)–F(211)	112(3)
C(61)–C(6)–C(5)	132(3)	C(2)–C(21)–F(212)	109(3)
C(61)–C(6)–F(611)	107(3)	C(2)–C(21)–F(213)	110(3)
C(6)–C(61)–F(612)	119(4)	F(211)–C(21)–F(212)	108(3)
C(6)–C(61)–F(613)	113(3)	F(212)–C(21)–F(213)	109(3)
F(611)–C(61)–F(612)	103(4)	F(211)–C(21)–F(213)	108(3)
F(612)–C(61)–F(613)	109(3)	C(2)–C(3)–C(31)	115(2)
F(611)–C(61)–F(613)	103(4)	C(2)–C(3)–C(4)	121(3)
Pt(2)–C(7)–C(71)	131(2)	C(31)–C(3)–C(4)	123(3)
Pt(2)–C(7)–C(8)	104(2)	C(3)–C(31)–F(311)	110(3)
C(71)–C(7)–C(8)	125(3)	C(3)–C(31)–F(312)	118(3)
C(7)–C(71)–F(711)	110(3)	C(3)–C(31)–F(313)	110(2)

TABLE 1 (*Continued*)

C(7)–C(71)–F(712)	118(4)	F(311)–C(31)–F(312)	107(2)
C(7)–C(71)–F(713)	115(3)	F(312)–C(31)–F(313)	107(3)
F(711)–C(71)–F(712)	101(3)	F(311)–C(31)–F(313)	103(3)
F(712)–C(71)–F(713)	106(3)	C(4)–Pt(3)–C(93)	88.6(11)
F(711)–C(71)–F(713)	104(4)	C(4)–Pt(3)–C(94)	93.4(13)
C(3)–C(4)–C(41)	122(3)	C(4)–Pt(3)–C(97)	163.7(12)
C(3)–C(4)–Pt(3)	129(2)	C(4)–Pt(3)–C(98)	158.9(11)
Pt(3)–C(4)–C(41)	108(2)	C(8)–Pt(3)–C(93)	155.6(11)
C(4)–C(41)–F(411)	112(2)	C(8)–Pt(3)–C(94)	170.1(14)
C(4)–C(41)–F(412)	112(3)	C(8)–Pt(3)–C(97)	92.9(10)
C(4)–C(41)–F(413)	110(3)	C(8)–Pt(3)–C(98)	93.2(11)
F(411)–C(41)–F(412)	106(2)	C(98)–C(91)–C(92)	113(3)
F(412)–C(41)–F(413)	110(2)	C(91)–C(92)–C(93)	112(3)
F(411)–C(41)–F(413)	108(3)	C(92)–C(93)–C(94)	130(3)
C(5)–Pt(1)–C(03)	159.8(12)	C(93)–C(94)–C(95)	127(4)
C(5)–Pt(1)–C(04)	163.0(11)	C(94)–C(95)–C(96)	115(3)
C(5)–Pt(1)–C(07)	97.3(12)	C(95)–C(96)–C(97)	110(3)
C(5)–Pt(1)–C(08)	101.3(13)	C(96)–C(97)–C(98)	129(3)
Pt(2)–Pt(1)–C(03)	95.9(9)	C(97)–C(98)–C(91)	124(3)
Pt(2)–Pt(1)–C(04)	98.2(8)	C(07,08)–Pt(1)–C(5)	99.8(9)
Pt(2)–Pt(1)–C(07)	157.3(8)	C(07,08)–Pt(1)–C(03,04)	86.3(10)
Pt(2)–Pt(1)–C(08)	163.8(10)	C(03,04)–Pt(1)–Pt(2)	97.4(11)
C(08)–C(01)–C(02)	111(3)	Pt(2)–Pt(1)–C(5)	76.6(9)
C(01)–C(02)–C(03)	117(3)	C(97,98)–Pt(3)–C(93,94)	83.6(9)
C(02)–C(03)–C(04)	126(3)	C(93,94)–Pt(3)–C(4)	91.0(8)
C(03)–C(04)–C(05)	122(3)	C(4)–Pt(3)–C(8)	91.9(11)
C(04)–C(05)–C(06	112(3)	C(8)–Pt(3)–C(97,98)	93.2(7)
C(05)–C(06)–C(07)	110(3)	Pt(2)–Pt(3)–C(97,98)	120.0(8)
C(06)–C(07)–C(08)	126(3)	Pt(2)–Pt(3)–C(93,94)	125.2(8)
C(07)–C(08)–C(01)	125(3)		

* C(*n*,*m*) indicates the midpoint of the line joining atoms C(*n*) and C(*m*).

ordinated cyclo-octa-1,5-diene [6-9] and in the free ligand.[10] The distance [2.630(3) Å] between Pt(1) and Pt(2) lies within the limits expected [11] for a Pt–Pt bond. Thus Pt(1) has a distorted square-planar configuration, and the mean deviation from the least-squares plane containing Pt(1) and its four bonds is 0.032 Å. The double bonds in this cyclo-octa-1,5-diene molecule are not equivalent, as that *trans* to Pt(2) has a shorter co-ordination distance to Pt(1) [2.05(3) Å] compared with the double bond lying *trans* to C(5) [2.14(3) Å]. This observation is in fact opposite to the trend observed previously [11] of the greater *trans* influence of platinum compared with carbon. For the cod molecule co-ordinated to Pt(3) there is no significant difference in the bond lengths between Pt(3) and the co-ordinated double bonds This is not surprising as here the double bonds both lie *trans* to carbon atoms C(4) and C(8). The co-ordination geometry around Pt(3) can be considered to be approximately square-planar (Table 1), with the mean deviation from the least-squares plane containing Pt(3) and its four bonds being 0.06 Å. The distance between Pt(2) and Pt(3) is 2.841(2) Å. This also lies within the

[6] H. Dierks and H. Dietrich, *Z. Krist.*, 1965, **122**, 1.

[7] J H. van den Hende and W. C. Baird, *J. Amer. Chem. Soc.*, 1963, **85**, 1009.

[8] J. A. Ibers and R. G. Snyder, *Acta Cryst.*, 1962, **15**, 923.

[9] M. D. Glick and L. F. Dahl, *J. Organometallic Chem.*, 1965, **3**, 200.

[10] L. Hedberg and K. Hedberg, *Abs. Nat. Meeting Amer. Cryst. Assoc.*, Montana, 1964.

[11] M. Green, J. A. K. Howard, A. C. Laguna, L. E. Smart, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 278 and refs. therein.

limits found for Pt–Pt bonding,[11] but this does not necessarily imply that a bond exists. The co-ordination around Pt(2) is highly irregular, and cannot conveniently be described in terms of either four or five co-ordination.

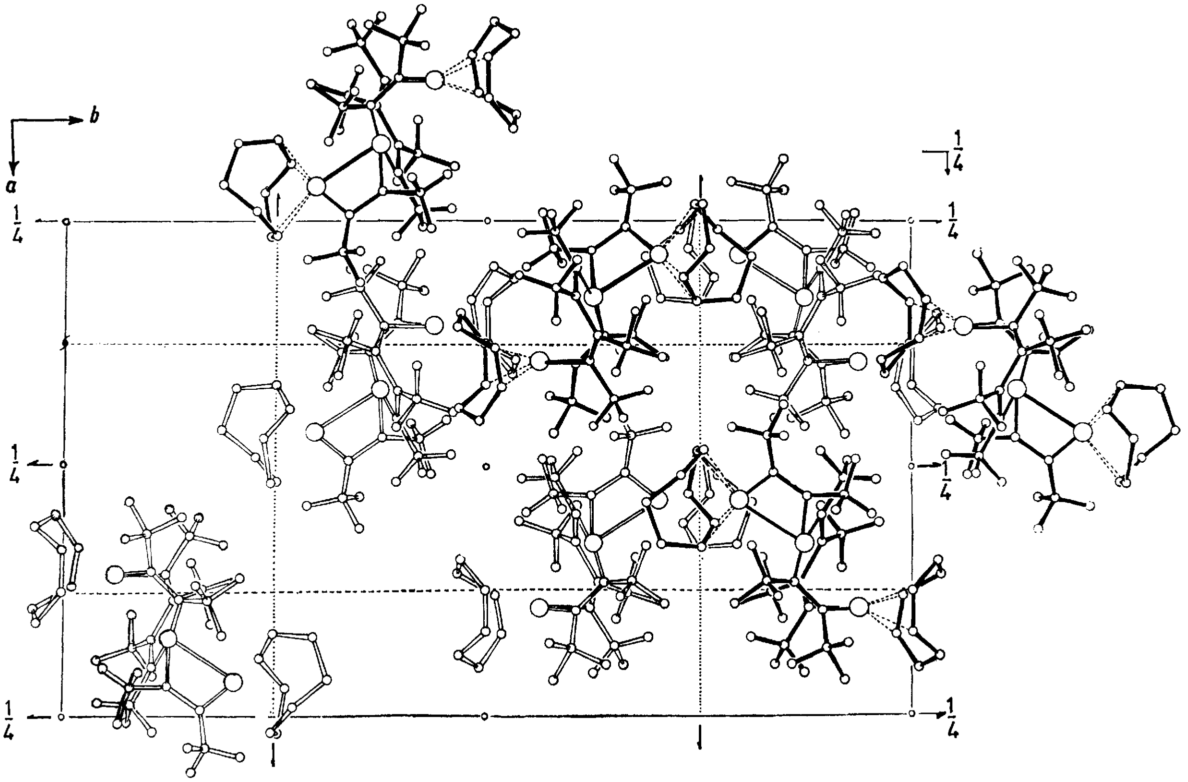

Figure 2 Contents of the unit cell of (2) viewed down the *c* axis towards the origin

In the hfb ligands the Pt–C distances are not significantly different, the average value [2.06(3) Å] comparing well with other known Pt–C σ-bond lengths.[12-14] In the two hfb moieties linked together in the eight-membered ring the C(2)–C(3) single bond distance is 1.54(4) Å, and the C–C double bond distances are C(1)–C(2) 1.38(4) and C(3)–C(4) 1.33(4) Å. Since the Pt(2)–C(2) and the Pt(3)–C(3) distances are 2.87(3) and 3.14(3) Å respectively, any interaction by these double bonds with the Pt atoms is precluded. The geometry of the trifluoromethyl groups is approximately tetrahedral and the bond lengths are unexceptional (Table 1).

Table 2

Molecular planes for complex (2) represented by $px + qy + rz = s$, where x, y, and z are the atomic fractional co-ordinates in direct space, and deviations (Å) from the planes (in square brackets)

Plane (1): Pt(1), Pt(2), C(5), C(03,04),* C(07,08)

$9.089x + 11.449y - 11.297z = 2.535$

[Pt(1) 0.014, Pt(2) −0.037, C(5) 0.036, C(03,04) 0.031, C(07,08) −0.044]

Plane (2): Pt(3), C(4), C(8), C(93,94), C(97,98)

$16.499x + 1.147y - 0.138z = 4.864$

[Pt(3) −0.075, C(4) −0.035, C(8) 0.075, C(93,94) 0.074, C(97,98) −0.039]

Plane (3): Pt(2), Pt(3), C(7), C(8)

$8.079x + 19.244y + 8.533z = 3.965$

[Pt(2) −0.021, Pt(3) 0.022, C(7) 0.045, C(8) −0.046]

Plane (4): Pt(1), Pt(2), C(5), C(6)

$-9.426x - 11.141y + 11.145z = -2.516$

[Pt(1) 0.0008, Pt(2) −0.0009, C(5) −0.0016, C(6) 0.0017]

Dihedral angles (°)

Plane	(2)	(4)
(1)	55.1	
(3)		81.8

* C(*n,m*) indicates the midpoint of the line joining C(*n*) to C(*m*).

A packing diagram of (2) is shown in Figure 2, and some least-squares planes in Table 2. There are no significantly short intermolecular contacts.

Complex (2) was also the major product in the reaction of hexafluorobut-2-yne with tris(ethylene)platinum in the presence of cyclo-octa-1,5-diene. In addition, however, complex (1) and a binuclear species (4) were produced. Elemental analyses and mass spectroscopy indicated that (4) had the formula $[\mathrm{Pt_2(hfb)_2(cod)_2}]$. In order to study in more detail this latter complex a higher-yield synthesis of (4) was sought. This was achieved by treating the binuclear complex $[\overline{\mathrm{Pt{\cdot}C(CF_3)_2{\cdot}O{\cdot}Pt}}\mathrm{(cod)_2}]$ [11] with hfb. The i.r. spectrum of (4) showed no bands assignable to

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[12] R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc.* (*A*), 1969, 485.

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

[14] M. R. Truter and R. C. Watling, *J. Chem. Soc.* (*A*), 1967, 1955.

co-ordinated hfb, and the ^{19}F n.m.r. spectrum showed a single resonance with inequivalent coupling to two platinum nuclei. The co-ordinated cod molecules in (4) were readily displaced by Bu^{t}NC forming (6), a complex which showed similar (i.r. and n.m.r.) spectroscopic characteristics to the parent molecule. In view of the unusual nature of these molecules a single-crystal *X*-ray study of (4) was undertaken.

As can be seen (Figure 3), (4) consists of two platinum atoms bridged by two hfb molecules giving a six-membered ring in a boat conformation. Bond distances and bond lengths are given in Table 3. Each platinum atom is co-ordinated by a cod molecule. The C–C double bond lengths in both cod molecules do not vary significantly [mean 1.38(2) Å]. The average Pt–C distance to the double bonds is 2.27 Å. The geometry about each platinum atom is approximately square planar, and the average deviation from the least-squares planes containing a platinum atom and its four co-ordinated bonds is 0.04 Å for both Pt(1) and Pt(2). The Pt(1)–Pt(2) distance [3.129(2) Å] is too long for any appreciable metal–metal interaction to occur. It is important, however, in that it indicates that the Pt(2)–Pt(3) distance [2.84(2) Å] in complex (2) is not the result of the spatial requirement of the bridging hfb ligands. The average Pt–C distance for the co-ordinated hfb molecules is 2.06(2) Å. The angle between the two planes containing Pt(1), Pt(2), C(1), C(2) and Pt(1), Pt(2), C(3), C(4) is 85.9°. A packing diagram for (4) is shown in Figure 4, and some least-squares planes in Table 4. There are no significantly short intermolecular contact distances.

TABLE 3

Bond lengths (Å) and angles (°) for complex (4)

(*a*) Distances

Pt(1)–Pt(2)	3.129(2)	Pt(1)–C(03)	2.22(2)
Pt(1)–C(1)	2.07(2)	Pt(1)–C(04)	2.27(2)
C(1)–C(2)	1.30(2)	Pt(1)–C(07)	2.26(2)
C(1)–C(11)	1.50(3)	Pt(1)–C(08)	2.30(2)
C(11)–F(11)	1.28(3)	C(01)–C(02)	1.52(2)
C(11)–F(12)	1.27(3)	C(02)–C(03)	1.48(3)
C(11)–F(13)	1.17(2)	C(03)–C(04)	1.38(2)
Pt(2)–C(2)	2.06(2)	C(04)–C(05)	1.51(3)
C(2)–C(21)	1.51(2)	C(05)–C(06)	1.53(2)
C(21)–F(21)	1.36(2)	C(06)–C(07)	1.47(3)
C(21)–F(22)	1.28(2)	C(07)–C(08)	1.39(2)
C(21)–F(23)	1.30(2)	C(08)–C(01)	1.47(2)
Pt(1)–C(3)	2.06(1)	Pt(2)–C(51)	2.27(2)
C(3)–C(4)	1.34(2)	Pt(2)–C(52)	2.32(2)
C(3)–C(31)	1.49(2)	Pt(2)–C(55)	2.23(1)
C(31)–F(31)	1.35(2)	Pt(2)–C(56)	2.25(1)
C(31)–F(32)	1.34(2)	C(51)–C(52)	1.35(3)
C(31)–F(33)	1.32(2)	C(52)–C(53)	1.52(2)
Pt(2)–C(4)	2.03(1)	C(53)–C(54)	1.58(4)
C(4)–C(41)	1.51(2)	C(54)–C(55)	1.49(3)
C(41)–F(41)	1.27(1)	C(55)–C(56)	1.41(3)
C(41)–F(42)	1.34(2)	C(56)–C(57)	1.50(3)
C(41)–F(43)	1.32(3)	C(57)–C(58)	1.52(2)
C(07,08)–Pt(1)	2.17(2)	C(58)–C(51)	1.51(3)
C(03,04)–Pt(1)	2.14(2)		
C(55,56)–Pt(2)	2.15(1)		
C(51,52)–Pt(2)	2.19(2)		

(*b*) Angles

(*i*) cod ligands

C(1)–Pt(1)–C(03)	163.3(6)	C(2)–Pt(2)–C(51)	165.5(6)
C(1)–Pt(1)–C(04)	160.4(6)	C(2)–Pt(2)–C(52)	160.3(7)
C(1)–Pt(1)–C(07)	96.3(6)	C(2)–Pt(2)–C(55)	91.9(6)
C(1)–Pt(1)–C(08)	101.6(6)	C(2)–Pt(2)–C(56)	99.2(6)
C(1)–Pt(1)–C(3)	81.5(6)	C(2)–Pt(2)–C(4)	82.2(5)
C(3)–Pt(1)–C(03)	92.2(5)	C(4)–Pt(2)–C(51)	95.0(5)
C(3)–Pt(1)–C(04)	99.1(6)	C(4)–Pt(2)–C(52)	100.2(5)
C(3)–Pt(1)–C(07)	165.4(5)	C(4)–Pt(2)–C(55)	163.5(7)
C(3)–Pt(1)–C(08)	159.1(5)	C(4)–Pt(2)–C(56)	159.6(7)
C(03)–Pt(1)–C(07)	93.6(6)	C(51)–Pt(2)–C(55)	94.5(6)
C(03)–Pt(1)–C(08)	79.0(6)	C(51)–Pt(2)–C(56)	78.6(6)
C(04)–Pt(1)–C(07)	78.1(6)	C(52)–Pt(2)–C(55)	80.4(6)
C(04)–Pt(1)–C(08)	84.8(7)	C(52)–Pt(2)–C(56)	85.4(6)
C(08)–C(01)–C(02)	114.3(16)	C(58)–C(51)–C(52)	126.3(13)
C(01)–C(02)–C(03)	115.1(12)	C(51)–C(52)–C(53)	125.6(16)
C(02)–C(03)–C(04)	125.3(15)	C(52)–C(53)–C(54)	113.3(18)
C(03)–C(04)–C(05)	124.4(16)	C(53)–C(54)–C(55)	114.0(17)
C(04)–C(05)–C(06)	113.5(19)	C(54)–C(55)–C(56)	127.0(20)
C(05)–C(06)–C(07)	114.9(14)	C(55)–C(56)–C(57)	125.6(18)
C(06)–C(07)–C(08)	124.2(17)	C(56)–C(57)–C(58)	115.2(14)
C(07)–C(08)–C(01)	124.7(19)	C(57)–C(58)–C(51)	112.7(19)

TABLE 3 (*Continued*)

(*ii*) hfb ligands

Pt(1)–C(1)–C(2)	115.7(12)	Pt(1)–C(3)–C(4)	117.3(8)
Pt(1)–C(1)–C(11)	117.2(12)	Pt(1)–C(3)–C(31)	117.5(10)
C(2)–C(1)–C(11)	126.5(17)	C(31)–C(3)–C(4)	124.8(13)
C(1)–C(11)–F(11)	115.2(22)	C(3)–C(31)–F(31)	112.5(12)
C(1)–C(11)–F(12)	118.0(18)	C(3)–C(31)–F(32)	113.3(14)
C(1)–C(11)–F(13)	117.7(15)	C(3)–C(31)–F(33)	114.9(13)
F(11)–C(11)–F(12)	93.3(19)	F(31)–C(31)–F(32)	104.1(12)
F(12)–C(11)–F(13)	107.5(25)	F(32)–C(31)–F(33)	107.6(12)
F(11)–C(11)–F(13)	101.5(21)	F(31)–C(31)–F(33)	103.4(14)
C(1)–C(2)–C(21)	125.0(16)	Pt(2)–C(4)–C(3)	115.0(9)
C(1)–C(2)–Pt(2)	116.8(12)	Pt(2)–C(4)–C(41)	120.0(9)
Pt(2)–C(2)–C(21)	117.9(10)	C(3)–C(4)–C(41)	124.8(10)
C(2)–C(21)–F(21)	111.6(16)	C(4)–C(41)–F(41)	118.9(14)
C(2)–C(21)–F(22)	115.8(11)	C(4)–C(41)–F(42)	111.2(15)
C(2)–C(21)–F(23)	114.3(16)	C(4)–C(41)–F(43)	112.0(12)
F(21)–C(21)–F(22)	102.5(16)	F(41)–C(41)–F(42)	101.8(12)
F(22)–C(21)–F(23)	109.2(18)	F(42)–C(41)–F(43)	103.3(15)
F(21)–C(21)–F(23)	102.0(11)	F(41)–C(41)–F(43)	108.2(17)

C(07,08) *–Pt(1)–C(1)	99.0(6)
C(1)–Pt(1)–C(3)	81.9(6)
C(3)–Pt(1)–C(03,04)	95.6(6)
C(03,04)–Pt(1)–C(07,08)	83.6(6)
C(55,56)–Pt(2)–C(2)	95.9(6)
C(2)–Pt(2)–C(4)	82.1(5)
C(4)–Pt(2)–C(51,52)	98.1(5)
C(51,52)–Pt(2)–C(55,56)	84.0(6)

* C(*n*,*m*) indicates the midpoint of the line joining atoms C(*n*) and C(*m*).

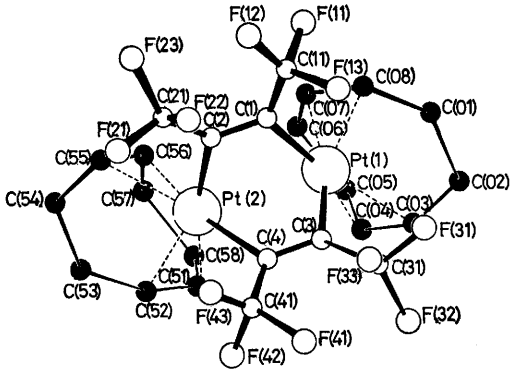

FIGURE 3 View of complex (4) $[\overline{\mathrm{Pt}\{\mathrm{C(CF_3)}\vdots\mathrm{C(CF_3)\cdot Pt\cdot C(CF_3)}\vdots\mathrm{C}}\mathrm{(CF_3)}\}\mathrm{(cod)_2}]$ down the *b* axis and showing the crystallographic numbering system

A possible insight into the mode of formation of (4) was provided when the reaction of the mononuclear complex (1) with carbon monoxide was examined. This reaction was studied, because we had previously[15] found that the nickel complex $[Ni(hfb)(CO)_2]$, formed from hfb and $[Ni(CO)_4]$, was the precursor of the tetranuclear complex $[Ni_4(hfb)_3(CO)_4]$. However, (1) with CO gave the binuclear species (3), which analysed as $[Pt_2(hfb)_2(CO)_2(cod)]$. The i.r. spectrum of (3) showed bands at 2 170vs and 2 140vs cm^{-1}, corresponding to the presence of terminally bonded carbonyl groups in a relative *cis* orientation as shown in the illustrated structure. In agreement, the ^{19}F n.m.r. spectrum showed two trifluoromethyl group environments, which appeared as multiplets with $^{195}Pt-^{19}F$ coupling from inequivalent ^{195}Pt nuclei.

A structurally related binuclear iridium complex $[Ir_2(hfb)_2(NO)_2(PPh_3)_2]$ has been described previously,[16] formed in the reaction of $[Ir(NO)(PPh_3)_3]$ with hfb. It was suggested that the binuclear complex was produced by dimerisation of a 1,3-dipolar species[17-20] initially formed in the stepwise reaction of the d^{10} iridium species with hfb. The formation of (3) from (1) is particularly interesting in that it suggests that such ionic intermediates can be formed from an acetylene complex such as (1) as illustrated in Scheme 2. It is reasonable to propose that in the reaction of (1), where hfb is symmetrically bonded to platinum, a five-co-ordinate intermediate is formed with carbon monoxide, in which the acetylene is skew-bonded. In valence-bond terms this can be interpreted as meaning that the 1,3-dipolar form represents a close approximation to the bonding between the acetylene and the platinum. Dimerisation of the skew-bonded (1,3-dipolar) species would then afford complex (3). Extension of these ideas also provides an explanation for the formation of (4). Although formation of the trinuclear molecule (2) could, in principle, be explained by a sequence of reactions involving ionic intermediates, our present understanding of such processes does not provide an explanation for the selective formation of this species. For this reason further consideration of the mechanism of formation of (2) is not appropriate at the present time.

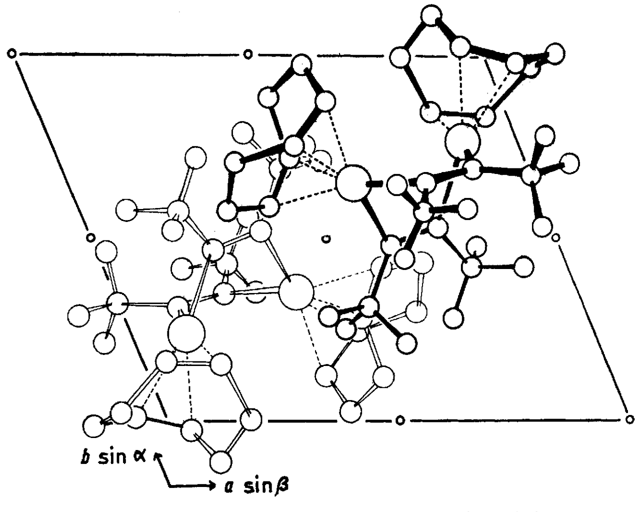

FIGURE 4 Contents of the unit cell of (4) viewed down the *c* axis towards the origin

TABLE 4

Molecular planes for complex (4) represented by $px + qy + rz = s$, where x, y, and z are the atomic fractional co-ordinates in direct space, and deviations (Å) from these planes (in square brackets)

Plane (1): Pt(1), C(1), C(3), C(03,04),* C(07,08)
$-4.439x - 6.308y + 7.965z = -2.366$
[Pt(1) 0.008, C(1) 0.05, C(3) −0.05, C(03,04) 0.05, C(07,08) −0.05]

Plane (2): Pt(2), C(2), C(4), C(51,52), C(55,56)
$10.813x - 4.759y - 2.418z = -0.610$
[Pt(2) 0.003, C(2) −0.05, C(4) 0.05, C(51,52) −0.05, C(55,56) 0.05]

Plane (3): Pt(1), Pt(2), C(1), C(2)
$-2.076x + 6.994y + 4.476z = 2.798$
[Pt(1) 0.007, Pt(2) −0.007, C(1) −0.018, C(2) 0.018]

Plane (4): Pt(1), Pt(2), C(3), C(4)
$5.730x - 6.718y + 11.303z = 2.224$
[Pt(1) 0.007, Pt(2) −0.007, C(3) −0.017, C(4) 0.017]

Dihedral angles (°)

Plane	(2)	(4)
(1)	72.5	
(3)		85.9

* C(n,m) indicates the midpoint of the line joining C(n) and C(m).

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra in $CDCl_3$ were recorded on a Varian Associates HA 100 spectrometer at 100 MHz with $SiMe_4$ (τ 10.00) as internal reference. Fluorine-19 n.m.r. spectra in $CDCl_3$ were measured on a JEOL PFT-100 spectrometer at 94.1 MHz; chemical shifts are relative to CCl_3F (0.0 p.p.m.). Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 457 spectrophotometer. Mass spectra were obtained on an A.E.I. 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 Hexafluorobut-2-yne.—Hexafluorobut-2-yne (0.7 g, 1.5 mmol) was condensed (−196 °C) into a thick-walled glass tube (*ca.* 100 cm^3) fitted with a Westef stopcock and containing a solution of $[Pt(cod)_2]$[2] (0.41 g, 1 mmol) in diethyl ether (80 cm^3). After 4 h at room temperature, volatile material was removed *in vacuo*, and the yellow solid was extracted with light petroleum (b.p. 40—60 °C). Reduction in volume of the solvent (*ca.* 10 cm^3) gave brown † *crystals* of [Pt(hfb)-

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* 1 eV ≈ 1.60×10^{-19} J.

† White crystals of (1) are only obtained after repeated recrystallisations from light petroleum.

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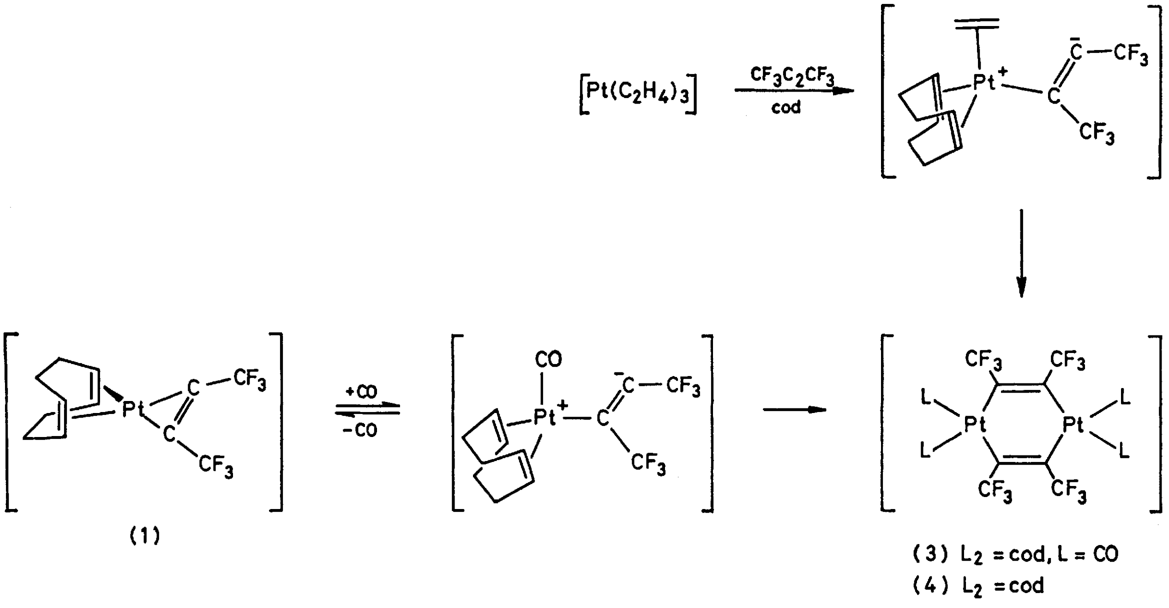
(cod)] (1) (0.46 g, 99%), m.p. 62 °C (Found: C, 31.2; H, 2.6. $C_{12}H_{12}F_6Pt$ requires C, 31.0; H, 2.6%); $\nu_{max.}$ at 3 050m, 3 030m, 1 790s, 1 515w, 1 475s, 1 440s, 1 435m, 1 345m, 1 312m, 1 278s, 1 240s, 1 225s, 1 190s, 1 165s, 1 140s, br, 1 110s, 1 015w, 1 005w, 1 000w, 985m, 960m, 942m, 902w, 872m, 865m, 832m, 822m, 792m, 775w, 760w, 732w, 702m, 658m, 610w, 575w, 548w, 510w, 472w, 458w, and 432vw cm^{-1}. The mass spectrum showed peaks at *m/e* 465 (*P*), 446 (*P* − F), and 303 (*P* − C_4F_6). N.m.r. spectra: ^1H, τ 4.30 (m, 4 H, CH=CH) and 7.63 (m, 8 H, CH_2); ^{19}F, 56.4 p.p.m. [s with ^{195}Pt satellites, *J*(PtF) 95.7 Hz].

Reactions of (*Cyclo-octa*-1,5-*diene*)(*hexafluorobut*-2-*yne*)-*platinum*.—(*a*) *With triphenylphosphine*. A solution of triphenylphosphine (0.22 g, 0.86 mmol) in diethyl ether (10 cm^3) was added dropwise with stirring to a solution of (1) (0.20 g, 0.43 mmol) in diethyl ether (20 cm^3). After 1 h at room temperature the volume of the solvent was reduced *in vacuo*, affording white *crystals* of (hexafluorobut-2-yne)-bis(triphenylphosphine)platinum (0.36 g, 95%), m.p. 212 °C (lit.,[5] m.p. 212—214 °C) (Found: C, 54.7; H, 3.5. Calc. for $C_{40}H_{30}F_6P_2$: C, 54.5; H, 3.4%).



(1)

(3) L_2 = cod, L = CO
(4) L_2 = cod

SCHEME 2

(*b*) *With hexafluorobut*-2-*yne*. An excess of hfb (1.29 g, 8 mmol) was condensed into a thick-walled tube containing a solution of (1) (0.46 g, 1.0 mmol) in diethyl ether (100 cm^3). After 24 h at room temperature the volatile material was removed *in vacuo*, and the residue was washed with light petroleum. The remaining solid was recrystallised from diethyl ether–light petroleum to give yellow *crystals* of $[Pt_3(hfb)_4(cod)_2]$ (2) (0.4 g, 27%), m.p. 155 °C [Found: C, 26.9; H, 1.9%; *M* 1 356 (in $CHCl_3$). $C_{32}H_{24}F_{24}Pt_3$ requires C, 26.5; H, 1.7%; *M* 1 450]; $\nu_{max.}$ at 2 990m, 1 632m, 1 590w, 1 570m, 1 480m, 1 432m, 1 350w, 1 345w, 1 320w, 1 280m, 1 250s, 1 235vs, 1 220vs, 1 202s, 1 195s, 1 185s, 1 168s, 1 148s, 1 138s, 1 118s, 1 098m, 1 085m, 1 030w, 1 010w, 1 005w, 992w, 972w, 955w, 880w, 870w, 860m, 850w, 835w, 825w, 798w, 795w, 702m, 658m, 652m, and 645m cm^{-1}. N.m.r. spectra: ^1H, τ 4.30 (m, 8 H, CH=CH) and 7.60—7.70 (m, 16 H, CH_2); ^{19}F in C_6D_6 at room temperature, 49.6(bm), 50.4(bm), 51.0(m), and 52.3(m) p.p.m.

(*c*) *With carbon monoxide*. A stream of carbon monoxide was bubbled through a solution of (1) (0.46 g, 1.0 mmol) in diethyl ether (30 cm^3). After 1 h at room temperature the volume of the solvent was reduced (10 cm^3) *in vacuo*. The resulting solid was collected and recrystallised from diethyl ether to give yellow *crystals* of $[Pt_2(hfb)_2(CO)_2(cod)]$ (3) (0.32 g, 70%), m.p. 191 °C (decomp.) (Found: C, 24.8; H, 1.5. $C_{18}H_{12}F_{12}O_2Pt_2$ requires C, 24.6; H, 1.4%); $\nu_{max.}$ at 2 170vs, 2 140vs, 1 612w, 1 440m, 1 355w, 1 325w, 1 258vs, 1 245vs, 1 230vs, 1 210m, 1 195w, 1 158vs, 1 138vs, 1 120vs, 1 100vs, 1 085s, 1 012m, 865m, 855m, 800m, 700m, 692m, 685w, and 670m cm^{-1}. N.m.r. spectra: ^1H, τ 4.3 (m, 4 H, CH=CH) and 7.6 (m, 8 H, CH_2); ^{19}F, two signals showing marked second-order effects at 53.1 [m, 6 F, *J*(FF) 12.5, ^3J(PtF) 131 Hz] and 54.0 p.p.m. [m, 6 F, *J*(FF) 12.5, ^3J(PtF) 129 Hz].

Reactions of Hexafluorobut-2-*yne*.—(*a*) *With bis*(*cyclo-octa*-1,5-*diene*)(*hexafluoroacetone*)*diplatinum*.— Hexafluorobut-2-yne (0.65 g, 4 mmol) was condensed into a thick-walled tube containing a suspension of $[\overline{Pt{\cdot}C(CF_3)_2{\cdot}O{\cdot}Pt}(cod)_2]$ [11] (0.40 g, 0.52 mmol) in diethyl ether (60 cm^3). After 48 h at room temperature, the volume of the solvent was reduced (20 cm^3) and the resulting yellow solid was collected. This was recrystallised from diethyl ether to give *crystals* of $[Pt_2(hfb)_2(cod)_2]$ (4) (0.30 g, 82%), m.p. 240 °C (decomp.) [Found: C, 31.0; H, 2.7; F, 24.2%; *M* 930 (mass spectrum). $C_{24}H_{24}F_{12}Pt_2$ requires C, 31.0; H, 2.6; F, 24.5%; *M* 930]; $\nu_{max.}$ at 1 600w, 1 590w, 1 575mw, 1 542w, 1 492m, 1 440m, 1 348w, 1 318w, 1 245vs, 1 228vs, 1 215vs, 1 135vs, 1 122vs, 1 110vs, 1 090vs, 1 045w, 1 020w, 1 008w, 995w, 982w, 845m, 792m, 698m, 688m, 655m, 535w, and 525w cm^{-1}. N.m.r. spectra: ^1H, τ 4.3 (m, 8 H, CH=CH) and 7.6 (m, 16 H, CH_2); ^{19}F, 52.3 p.p.m. [m, 12 F, ^3J(PtF) *ca.* 142; ^4J(PtF) < 25 Hz]. The ^{19}F spectrum was unchanged at −85 °C.

Evaporation of the mother liquors, after recovery of (4), afforded a brown solid, which on recrystallisation from diethyl ether–light petroleum gave brown crystals. Examination of the ^{19}F n.m.r. spectrum showed resonances at 52.3 p.p.m. [complex (4)] and multiplets centred at 55.3 and 56.5 p.p.m., the latter being assigned to $[\mathrm{Pt}\{\mathrm{C(CF_3)}{:}\mathrm{C(CF_3)}\cdot\mathrm{C(CF_3)}{:}\mathrm{C(CF_3)}\}(\mathrm{cod})]$.

(*b*) *With tris(ethylene)platinum in the presence of cyclo-octa-1,5-diene.* An excess of hexafluorobut-2-yne (1.3 g, 8 mmol) was condensed into a tube containing a solution of tris(ethylene)platinum (0.42 g, 1.5 mmol) and cyclo-octa-1,5-diene (0.65 g, 6 mmol) in light petroleum (30 cm^3). On warming to room temperature, yellow crystals of (2) (0.5 g, 80%) were deposited. Evaporation of the mother liquors gave white crystals of (1) and yellow crystals of (4).

TABLE 5

Atomic-positional parameters for complex (2) with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Pt(1)	0.068 97(7)	0.202 70(4)	0.035 29(7)
Pt(2)	0.155 93(6)	0.125 52(4)	0.031 54(6)
Pt(3)	0.286 43(6)	0.062 01(4)	0.056 18(6)
C(1)	0.097 8(16)	0.105 4(9)	0.146 9(19)
C(11)	0.021 5(21)	0.080 6(11)	0.151 1(23)
F(111)	−0.031 7(16)	0.107 0(14)	0.107 9(18)
F(112)	−0.012 9(15)	0.076 1(10)	0.225 4(13)
F(113)	0.025 0(21)	0.041 6(15)	0.117 6(32)
C(2)	0.153 6(15)	0.104 9(9)	0.213 7(16)
C(21)	0.137 1(26)	0.082 4(16)	0.307 1(22)
F(211)	0.079 9(14)	0.106 6(8)	0.352 4(11)
F(212)	0.111 3(13)	0.038 5(7)	0.296 6(12)
F(213)	0.204 7(15)	0.081 8(8)	0.352 9(12)
C(3)	0.234 2(15)	0.131 2(11)	0.204 2(15)
C(31)	0.254 6(22)	0.164 6(13)	0.277 7(19)
F(311)	0.185 0(13)	0.175 2(8)	0.324 0(10)
F(312)	0.308 6(12)	0.151 8(7)	0.333 6(10)
F(313)	0.277 7(11)	0.206 6(6)	0.245 7(13)
C(4)	0.285 4(17)	0.121 0(11)	0.140 7(19)
C(41)	0.363 7(19)	0.149 8(12)	0.124 2(20)
F(411)	0.401 2(12)	0.160 8(7)	0.197 8(14)
F(412)	0.417 9(11)	0.125 7(6)	0.077 2(13)
F(413)	0.345 3(13)	0.189 7(6)	0.083 6(14)
C(5)	0.011 8(18)	0.162 9(11)	−0.053 1(16)
C(51)	−0.063 8(21)	0.169 9(10)	−0.097 8(28)
F(511)	−0.080 6(17)	0.211 6(8)	−0.115 9(18)
F(512)	−0.125 8(17)	0.149 9(15)	−0.064 7(25)
F(513)	−0.062 3(19)	0.149 9(15)	−0.179 1(19)
C(6)	0.059 8(20)	0.123 0(9)	−0.052 0(15)
C(61)	0.056 8(20)	0.079 2(12)	−0.104 0(25)
F(611)	0.087 6(32)	0.089 1(16)	−0.183 5(22)
F(612)	0.094 7(21)	0.047 0(11)	−0.081 5(27)
F(613)	−0.015 6(17)	0.066 1(9)	−0.121 1(22)
C(7)	0.234 8(17)	0.137 8(9)	−0.063 3(17)
C(71)	0.231 8(26)	0.170 7(19)	−0.136 4(21)
F(711)	0.277 9(21)	0.208 8(10)	−0.118 7(20)
F(712)	0.263 1(19)	0.157 0(9)	−0.212 3(13)
F(713)	0.161 2(15)	0.187 6(13)	−0.153 4(17)
C(8)	0.291 6(15)	0.104 6(9)	−0.052 8(16)
C(81)	0.368 1(23)	0.099 8(13)	−0.107 3(25)
F(811)	0.432 6(10)	0.078 5(7)	−0.066 3(13)
F(812)	0.400 8(15)	0.140 6(9)	−0.133 1(18)
F(813)	0.357 5(14)	0.074 2(10)	−0.175 9(13)
C(01)	0.072 9(17)	0.312 1(11)	0.029 9(26)
C(02)	0.157 8(21)	0.294 6(17)	0.049 7(26)
C(03)	0.164 6(20)	0.247 5(12)	0.096 2(22)
C(04)	0.115 6(24)	0.231 9(9)	0.160 7(19)
C(05)	0.056 2(25)	0.262 6(12)	0.204 1(22)
C(06)	−0.033 9(23)	0.254 4(12)	0.167 1(21)
C(07)	−0.031 3(18)	0.247 1(10)	0.067 1(20)
C(08)	0.018 1(24)	0.271 9(12)	0.007 2(24)
C(91)	0.382 3(24)	−0.032 6(11)	0.043 6(21)
C(92)	0.407 1(25)	−0.008 5(15)	0.128 7(21)
C(93)	0.338 9(20)	0.017 8(10)	0.168 3(18)
C(94)	0.260 6(32)	0.010 1(16)	0.165 8(20)
C(95)	0.217 0(25)	−0.034 6(10)	0.128 0(24)
C(96)	0.188 8(23)	−0.030 7(12)	0.030 8(23)
C(97)	0.250 2(21)	−0.001 8(9)	−0.022 0(18)
C(98)	0.334 5(18)	−0.001 0(12)	−0.015 3(23)

Reaction of t-Butyl Isocyanide with Complex (4).—An excess of Bu^tNC (0.17 g, 2 mmol) in diethyl ether (10 cm^3) was added slowly to a stirred suspension of (4) (0.3 g, 0.32 mmol) in diethyl ether (80 cm^3). After 16 h at room temperature, the mixture was filtered and the volume of solvent was reduced (10 cm^3) *in vacuo*. Cooling (−10 °C) gave yellow crystals, which were collected and recrystallised from diethyl ether to give yellow *crystals* of (6) (0.22 g, 66%), m.p. 120 °C (decomp.) (Found: C, 32.1; H, 3.3; N, 5.3. $C_{28}H_{36}F_{12}N_4Pt_2$ requires C, 32.1; H, 3.5; N, 5.4%); $\nu_{max.}$ at 2 230s, 2 210(sh), 2 190s, and 2 140(sh) (NC) cm^{-1}.

TABLE 6

Atomic-positional parameters for complex (4) with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Pt(1)	0.393 79(5)	0.376 31(6)	0.221 49(3)
Pt(2)	0.118 30(5)	0.251 40(6)	0.285 61(4)
C(1)	0.235 1(14)	0.378 1(17)	0.139 5(9)
C(11)	0.265 9(19)	0.454 5(22)	0.063 0(12)
F(11)	0.303 5(24)	0.375 7(29)	−0.012 5(13)
F(12)	0.167 7(17)	0.442 1(32)	0.005 2(15)
F(13)	0.352 5(29)	0.594 5(19)	0.092 4(11)
C(2)	0.122 2(12)	0.330 9(14)	0.168 8(9)
C(21)	−0.000 9(15)	0.343 6(19)	0.129 9(12)
F(21)	−0.095 4(11)	0.308 9(18)	0.185 2(11)
F(22)	0.019 4(12)	0.491 3(15)	0.137 1(11)
F(23)	−0.068 4(13)	0.231 6(19)	0.037 6(9)
C(3)	0.365 9(13)	0.554 3(15)	0.339 2(9)
C(31)	0.468 0(14)	0.735 9(16)	0.375 9(11)
F(31)	0.562 5(10)	0.757 5(11)	0.320 8(9)
F(32)	0.539 6(12)	0.802 6(12)	0.473 1(8)
F(33)	0.418 5(11)	0.839 6(11)	0.369 4(8)
C(4)	0.251 0(13)	0.500 9(15)	0.368 8(9)
C(41)	0.210 5(15)	0.614 3(17)	0.451 1(11)
F(41)	0.296 3(13)	0.768 1(12)	0.504 0(10)
F(42)	0.180 2(15)	0.556 6(13)	0.523 9(8)
F(43)	0.096 9(16)	0.611 9(22)	0.414 8(9)
C(01)	0.631 2(17)	0.323 4(23)	0.133 3(13)
C(02)	0.689 5(16)	0.463 2(23)	0.241 4(14)
C(03)	0.596 0(14)	0.449 7(17)	0.311 1(11)
C(04)	0.508 3(16)	0.300 0(21)	0.315 8(11)
C(05)	0.500 7(19)	0.127 8(22)	0.255 0(13)
C(06)	0.397 1(19)	0.028 1(20)	0.151 6(14)
C(07)	0.380 3(16)	0.133 3(19)	0.101 4(10)
C(08)	0.487 2(15)	0.266 8(20)	0.092 5(11)
C(51)	0.164 1(17)	0.164 1(19)	0.406 3(12)
C(52)	0.047 0(18)	0.173 7(19)	0.416 6(11)
C(53)	−0.093 9(20)	0.024 1(23)	0.374 0(16)
C(54)	−0.162 7(19)	−0.010 7(26)	0.263 5(19)
C(55)	−0.068 5(16)	0.009 3(19)	0.194 0(13)
C(56)	0.041 2(18)	−0.030 1(18)	0.190 9(13)
C(57)	0.076 2(20)	−0.115 8(20)	0.250 7(15)
C(58)	0.178 6(19)	0.003 7(21)	0.353 4(13)

N.m.r. spectra: ^1H, τ 8.5 (s, 36 H, Bu^tN); ^{19}F, 52.0 p.p.m. [m, 12 F, $^3J(PtF)$ *ca.* 143, $^4J(PtF) < 22$ Hz].

X-*Ray Data Collection for Complexes* (2) *and* (4).—Crystals of (2) grow as small orange prisms, and the one selected for data collection was of dimensions *ca.* 0.15 × 0.10 × 0.45 mm, faces (021, $0\bar{2}\bar{1}$, $0\bar{1}1$, $01\bar{1}$, $\bar{1}00$, and $1\bar{1}1$). Preliminary photographs indicated systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$, consistent only with the centrosymmetric space group *Pbca* (D_{2h}^{15}, no. 61). Crystals of (4) grow as small yellow prisms from toluene, and the data crystal was of dimensions 0.10 × 0.15 × 0.20 mm with faces ($\bar{1}01$, $10\bar{1}$, $\bar{1}0\bar{2}$, 102, 010, and $0\bar{1}0$). Preliminary photographs indicated that the crystal was triclinic, *i.e.* space group either $P1$ or $P\bar{1}$. Diffracted intensities for both complexes were collected on a Syntex $P2_1$ four-circle diffractometer for $2.9 < 2\theta < 50°$ according to methods described earlier.[21] For a total of 6 436 [complex (2)] and

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

4 583 [complex (4)] independent measurements, 3 595 (2) and 3 451 (4) reflections were deemed observable according to the criterion $I \geqslant 2.5\sigma(I)$ where σ is the estimated standard deviation of the measured intensity based on counting statistics. No decay correction was required for either set of data. The observed reflections only, corrected for absorption in both cases, were used to solve and refine the structures.

Crystal data for complex (2). $C_{32}H_{24}F_{24}Pt_3$, $M = 1\,449.8$, Orthorhombic, space group *Pbca*, $a = 16.513(10)$, $b = 28.536(30)$, $c = 15.429(8)$ Å, $U = 7\,269.9$ Å^3, $D_m = 2.63$ g cm^{-3} (flotation), $Z = 8$,$D_c = 2.65$ g cm^{-3}, $F(000) = 5\,328$, Mo-K_α X-radiation, graphite monochromator ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 122.8 cm^{-1}.

Crystal data for complex (4). $C_{24}H_{24}F_{12}Pt_2$, $M = 930.6$, Triclinic, space group $P\bar{1}$, $a = 11.099(5)$, $b = 9.413(3)$, $c = 14.317(4)$ Å, $\alpha = 110.72(2)$, $\beta = 93.50(3)$, $\gamma = 113.08(3)°$, $U = 1\,251.9$ Å^3, $D_m = 2.43$ g cm^{-3} (flotation), $Z = 2$, $D_c = 2.47$ g cm^{-3}, $F(000) = 864$, Mo-K_α X-radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 118.5 cm^{-1}.

Solution and refinement of the structures. In both structure determinations the platinum-atom positions were located from a three-dimensional Patterson synthesis. Observed Fourier syntheses, phased on the platinum atoms only, led to location of all the non-hydrogen atoms. Hydrogen atoms were incorporated in the structure-factor calculations at calculated positions, and were not refined. The structures were refined using block-matrix least-squares techniques. In the final stages of refinement all the non-hydrogen atoms were refined anisotropically.

For crystal (2), weights were applied according to the scheme $w = PQ$, where $P = 1$ when $\sin\theta > b$ and $P = \sin\theta/b$ when $\sin\theta < b$, and $Q = 1$ when $c > F_o$ and $Q = c/F_o$ when $c < F_o$. The values of b and c used were 0.22 and 400, respectively, chosen from an analysis of the variations of $w\Delta^2$ with F_o and with $\sin\theta$. The final electron-density difference map showed no peaks > 2.0 or < -2.5 e Å^{-3}. These peaks were close to the platinum atoms, and the map was generally much flatter than these figures would indicate. The refinement converged at R 0.06 (R' 0.073) for 3 595 reflections (533 parameters). Positional parameters are given in Table 5.

For crystal (4) weights were applied according to the scheme $w = 1/(a + bF_o + cF_o^2 + dF_o^3)$, where $a = 4.255$, $b = -0.098$, $c = 0.001\,22$, and $d = -0.000\,003$. These values were chosen from an analysis of $w\Delta^2$ with F_o. The final electron-density difference maps showed no peaks >2.6 or < -2.1 e Å^{-3}, with these peaks lying very close to the platinum atoms, and the map being generally much flatter. Refinement converged at R 0.042 (R' 0.05) for 3 451 reflections (344 parameters). Positional parameters are given in Table 6.

For both crystals the subsequent function $\Sigma w(|F_o| - |F_o|)^2$ was not appreciably dependent on either $\sin\theta$ or on $|F_o|$, indicating correctly assigned weighting schemes. The atomic-scattering factors used were those of ref. 22 for Pt and F, of ref. 23 for C, and of ref. 24 for H. The scattering factors for Pt were corrected for the real and imaginary parts of anomalous dispersion.[22] All the computational work was carried out at the University of London Computing Centre using the ' X-Ray ' system of programs.[25] Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22059 (34 pp.).*

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

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