FULVENE—PLATINUM COMPLEXES: X-RAY CRYSTAL STRUCTURE OF [Pt(η^2-C$_5$H$_4$CPh$_2$)(PPh$_3$)$_2$]

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Summary

Bis(cycloocta-1,5-diene)platinum reacts with 2,3,4,5-tetraphenylfulvene to afford the complex [Pt(η^2-CH$_2$=C$_5$Ph$_4$)(cod)] (cod = C$_8$H$_{12}$) in which the metal atom is coordinated to the *exo*-cyclic double bond of the fulvene. Related compounds [Pt(η^2-CH$_2$=C$_5$Ph$_4$)L$_2$] (L = PPh$_3$, PMePh$_2$, PMe$_2$Ph, AsPh$_3$ or CNBu^t) have also been prepared and characterised. Reaction of the complexes [Pt-(C$_2$H$_4$)$_2$(L)] (L = P(cyclo-C$_6$H$_{11}$)$_3$, PPh$_3$ or AsPh$_3$) with 2,3,4,5-tetraphenyl-fulvene yields the compounds [Pt(C$_2$H$_4$)(η^2-CH$_2$=C$_5$Ph$_4$)(L)]. NMR data for the new species are reported and discussed. 6,6-Diphenylfulvene reacts with [Pt(cod)$_2$] and PPh$_3$ (1/2 mol ratio) to give the complex [Pt(η^2-C$_5$H$_4$CPh$_2$)-(PPh$_3$)$_2$] in which the metal atom is bonded to carbon atoms C(2) and C(3) of the fulvene ring. This was established by an X-ray diffraction study. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 13.761(4)$, $b = 21.653(13)$, $c = 17.395(6)$ Å, $\beta = 104.46(2)°$. The structure has been solved and refined to $R = 0.064$ ($R' = 0.064$) for 3139 independent diffracted intensities measured at room temperature. The platinum atom is in a trigonal environment formed by the two ligated phosphorus atoms and the C—C bond of the fulvene which is elongated to 1.52(3) Å. The C$_5$ fulvene ring is planar, and makes an angle of 108° with the coordination plane around the platinum. In this plane the metal atom is slightly asymmetrically bonded with Pt—C 2.15(2) and 2.24(2) Å, and Pt—P 2.280(6) and 2.301(6) Å.

Introduction

Following the development of a practical synthesis of [Pt(cod)$_2$] (cod = cycloocta-1,5-diene) [1], and discovery of the complexes [Pt(C$_2$H$_4$)$_2$(PR$_3$)] [2], we have been investigating reactions of these species with a variety of unsaturated compounds, in order to extend our knowledge of the organic chem-

istry of platinum. So far we have reported reactions of the platinum(0) compounds with olefins carrying electronegative substituents (tetrafluoroethylene [3], dimethyl or diethyl fumarate, dimethyl or diethyl maleate, or maleic anhydride [4]), methyl vinyl ketone [5], dienes [6], benzo-1,4-quinones [7,8], 2-methyl-2,4,6-tris(trifluoromethyl)pyran [9], alkynes [10—14], and allyl halides [15]. Herein we report some reactions with fulvenes.

There have been a number of previous studies of reactions between low-valent transition metal compounds and fulvenes, and the products of these reactions have established several different patterns of ligand behaviour. A fulvene molecule can η^2-interact with a metal centre via either a cyclic or an exo-cyclic double bond, or alternatively the two cyclic double bonds can coordinate to the metal in the η^4 mode. Moreover, in reactions with metal carbonyls there is a marked tendency for fulvene groups to transform into ring-substituted η^5-cyclopentadienyl ligands. These and other types of ligand bonding are exemplified in the various products obtained from reactions of [Fe$_2$(CO)$_9$] with 6,6-diethyl-, 6,6-dimethyl, or 6,6-diphenyl-fulvene [16]. Owing to the propensity with which platinum forms trigonal η^2-olefin complexes it was to be anticipated that any fulvene complexes formed from [Pt(cod)$_2$] or [Pt(C$_2$H$_4$)$_2$(PR$_3$)] would involve coordination of only one of the double bonds of the fulvene. However, whether a cyclic or the exo-cyclic double bond would coordinate could not be predicted with certainty in view of earlier results with other metals. Thus 6,6-diaryl fulvenes react with [RhCl(CO)$_2$]$_2$ to give adducts [RhCl-(CO)$_2$(fulvene)] in which the exo-cyclic double bond is bonded to the rhodium [17], whereas ultraviolet light irradiation of [Mn(CO)$_3$(η-C$_5$H$_5$)] with 6-methyl-or 6,6-methylphenylfulvene affords complexes in which a cyclic double bond is η^2-coordinated to manganese [18]. In contrast with the latter result, irradiation of [Mn(CO)$_3$(η-C$_5$H$_5$)] with 6-methylidenefulvene yields a product in which the manganese atom is attached to the exo-cyclic double bond [19]. No fulvene derivatives of metals of the nickel sub-group appear to have been reported previously in the journal literature, and so bonding patterns for the platinum sub-group metals were not known.

Results and discussion

Addition of [Pt(cod)$_2$] to a suspension of 2,3,4,5-tetraphenylfulvene (1/1 mol ratio) in hexane afforded a yellow crystalline complex I in essentially quantitative yield (Table 1). The ^{1}H NMR spectrum supports the structure shown wherein the platinum is coordinated to the exo-cyclic double bond. The chemical shifts of the CH$_2$ protons of the coordinated fulvene at τ 7.02 (J(PtH) 60 Hz) (Table 2) are shifted upfield by circa 2 ppm from their position in the spectrum of the free ligand. The observation of two CH signals for the cod ligand is also in agreement with the structure proposed [4,7,8], and the singlet resonance for the CH$_2$ group of the fulvene indicates the presence of a mirror plane through the molecule. The ^{13}C NMR spectrum of I (Experimental) shows resonances for the η^2-ligated carbon atoms of the fulvene at δ 81.6 and 34.4 ppm with ^{195}Pt satellites. In the free ligand, the signals for the carbon atoms of the

TABLE 1

MELTING POINTS, COLOUR, YIELDS AND ANALYSES

Compound	M.p. [a] (°C)	Colour	Yield (%)	Analyses (Found (calcd.) (%))	
				C	H
I	151—154	yellow	92	66.3 (66.6)	5.4 (5.0)
II	212—214	yellow	51	71.7 (71.9)	5.7 (4.8)
III	198—200	yellow	84	66.4 (66.1)	4.8 (4.4)
IV [b]	176	pale yellow	86	65.0 (64.6)	5.5 (5.4)
V	181—182	yellow	74	67.6 (68.8)	5.6 (5.0)
VI	153—154	pale brown	72	64.4 (64.7)	5.8 (5.2)
VII [c]	119—120	yellow	63	70.4 (70.3)	5.3 (5.0)
VIII	180—182	white	75	56.9 (57.0)	3.6 (3.6)
IX	150	yellow	79	67.3 (67.8)	6.7 (6.7)
X [d]	127	brown	94	73.8 (73.1)	5.1 (5.5)
XI	188	yellow	98	65.8 (65.9)	5.2 (4.5)

[a] With decomposition in vacuo, except for complexes VI and X. [b] N analysis 3.4(3.8)%. [c] Crystallised with one molecule of toluene. [d] Crystallised with two molecules of toluene.

exo-cyclic double bond occur at 133.0 and 123.7 ppm. There are four resonances for the cod ligand, as expected, since the four CH and the four CH_2 groups each give rise to two non-equivalent sets. The signals for the CH groups show [195]Pt satellite peaks (J(PtC) 151 and 86 Hz, respectively), but variation in the magnitude of the coupling suggests asymmetry in the bonding. A similar feature is observed for the fulvene resonances at 81.6 and 34.4 ppm which have J(PtC) 145 and 426 Hz, respectively. The NMR data thus provide conclusive evidence for coordination of the platinum atom to the *exo*-cyclic double bond so that I belongs to the extensive group of compounds of the type [Pt(alkene)-(cod)] [4,5], where the 'alkene' is electron withdrawing by virtue of the nature of the substituent(s), in this case a fulvene ring.

Attempts to displace the remaining cod ligand in I with excess 2,3,4,5-tetraphenylfulvene failed. However, reaction of I with PPh_3, $AsPh_3$ and $CNBu^t$ gave crystalline complexes II, III and IV, respectively. Data for these compounds is given in Tables 1 and 2, together with that for the complexes V and VI which were prepared by adding the stoichiometric amount of [Pt(cod)₂] to a mixture of the fulvene and $PMePh_2$ or PMe_2Ph, respectively.

The spectroscopic properties of compounds II—VI are in agreement with the structures proposed. Thus the [31]P{[1]H} spectra of II and VI show two doublet signals accompanied by [195]Pt satellite peaks, in accord with the non-equivalence of the two PPh_3 and PMe_2Ph groups in these species. For V only one central

TABLE 2

HYDROGEN-1 AND PHOSPHORUS-31 NMR DATA [a]

Complex	^{1}H [b]	^{31}P [c]
I	2,61—3,17 (m, 20 H, Ph), 5,38 (s, 2 H, CH(cod), J(PtH) 76), 5,12 (s, 2 H, CH(cod), J(PtH) 56], 7.02 (s, 2 H, CH_2, J(PtH) 60), 8.42 (m, 8 H, CH_2(cod))	
II [d,e]	2,78—3,26 (m, 50 H, Ph), 7,72 (d, 2 H, CH_2, J(PH) 13, J(PtH) 36)	34.1 J(PP) 40, J(PPt) 3 818; 25,0 J(PP) 40, J(PPt) 4 255,
III	2,30—3,10 (m, 50 H, Ph), 7,16 (s, 2 H, CH_2, J(PtH) 46)	
IV	2,16—2,94 (m, 20 H, Ph), 9,02 (s, 9 H, Bu^t), 9.26 (s, 9 H, Bu^t), 6.68 (s, 2 H, CH_2, J(PtH) 45)	
V [e]	2,50—3,08 (m, 40 H, Ph), 7,24 (d, 2 H, CH_2, J(PH) 4, J(PtH) 36), 8,24 (d, 3 H, MeP, J(PH) 8, J(PtH) 23), 8.54 (d, 3 H, MeP, J(PH) 8, J(PtH) 37)	8.9 J(PP) 38, J(PPt) 3 573; 8.9 J(PP) 38, J(PPt) 4 395
VI [e]	2,36—3,05 (m, 30 H, Ph), 7,26 (d, 2 H, CH_2, J(PH) 4, J(PtH) 35), 8,72 (d, 6 H, MeP, J(PH) 8, J(PtH) 27), 8.84 (d, 6 H, MeP, J(PtH) 9, J(PtH) 42)	−8.3 J(PP) 37, J(PPt) 3 456; −7.5 J(PP) 37, J(PPt) 4 392
VII	2,42—3,02 (m, 40 H, Ph), 4.50 (m, 2 H, CH), 4.85 (m, 2 H, CH)	35.4 J(PtP) 3 781; 26.2 J(PtP) 3 777
VIII	2,60—3,10 (m, 20 H, Ph), 7.12 (d, 2 H, CH_2, J(PH) 5, J(PtH) 46), 7,16 (s, 4 H, C_2H_4, J(PtH) 51), 8.30—9.05 (m, 33 H, C_6H_{11})	29.3 J(PP) 25, J(PPt) 3 387; 26.6 J(PP) 25, J(PPt) 4 553
IX	2,72—3,12 (m, 35 H, Ph), 7.04 (d, 2 H, C_2H_4, J(PH) 6, J(PtH) 45)	29.7 J(PPt) 3 879
X	2,60—3,10 (m, 35 H, Ph), 7,30 (s, J(PtH) 50), 7.38 (s, 4 H, C_2H_4, J(PtH) 64)	22.8 J(PPt) 4 004
XI [d]		

[a] Spectra measured in [^{2}H$_6$]benzene, unless otherwise stated. [b] Chemical shifts in τ, coupling constants in Hz. [c] Hydrogen-1 decoupled, chemical shifts in δ ppm, relative to external H_3PO_4 (85%), positive values representing signals to high frequency of the reference, coupling constants in Hz. [d] Hydrogen-1 spectrum measured in [^{2}H$_1$]chloroform. [e] The ^{1}H signals of the CH_2 and MeP groups are of the A_nXX' type, hence J(PH) = |J(PH) + J(P'H)|.

(I)

(II   L = PPh₃ ,
III ,   L = AsPh₃ ,
IV , L = CNBuᵗ ,
V   , L = PMePh₂ ,
VI   L = PMe₂Ph)
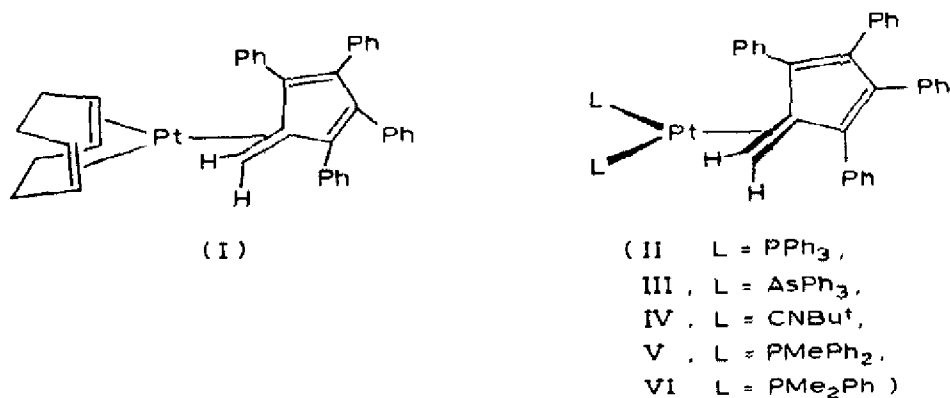
peak is observed in the spectrum, due to coincidence of the two ³¹P signals. However, the observation of two sets of ¹⁹⁵Pt satellites associated with this resonance confirms the presence of a Pt(PMePh₂)₂ group with non-equivalent phosphine ligands. In the ¹H NMR spectra of II—VI the CH₂ group of the fulvene ligand gives rise to a signal in the range τ 6.68—7.72, those for II, V and VI appearing as multiplets due to coupling with non-equivalent ³¹P nuclei. The tertiary butyl isocyanide complex IV shows two singlet ¹H resonances for the Buᵗ groups as expected for a cis-Pt(CNBuᵗ)₂ moiety, and in accord with this the IR spectrum has two NC stretching bands (2161 and 2128 cm⁻¹).

Since in complexes I—VI the platinum is coordinated to the exo-cyclic double bond of the 2,3,4,5-tetraphenylfulvene ligand, a reaction was next investigated using 6,6-diphenylfulvene Treatment of a mixture of the latter
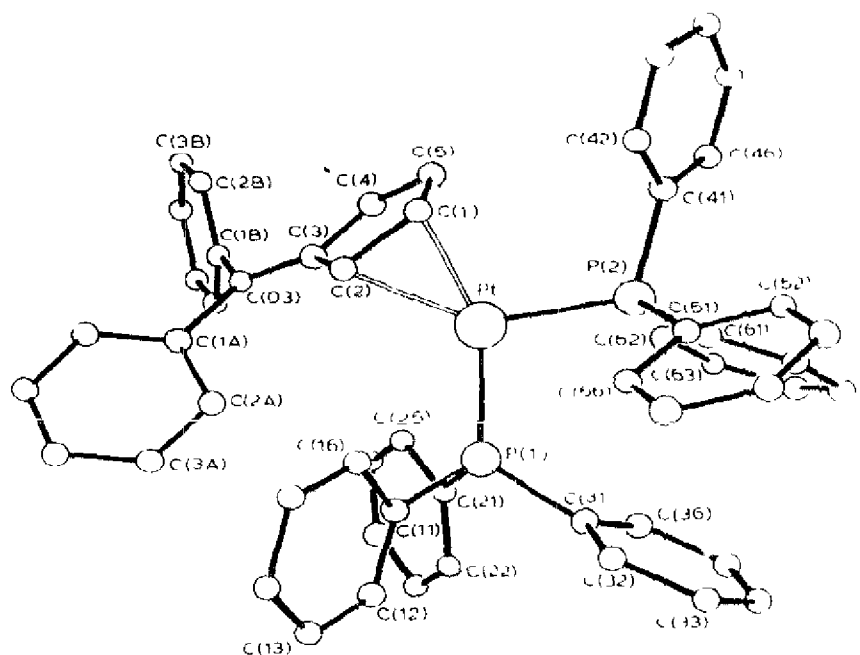

Fig 1 The molecular structure of [Pt(η²-C₅H₄CPh₂)(PPh₃)₂] with the atom numbering scheme

TABLE 3

ATOMIC POSITIONAL (FRACTIONAL COORDINATES) PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR THE COMPOUND $[Pt(\eta^2\text{-}C_5H_4CPh_2)(PPh_3)_2]$ (VII)

Atom	x	y	z
Pt	0.22432(6)	0.24027(3)	0.22028(5)
P(1)	0.3727(4)	0.2942(3)	0.2416(4)
P(2)	0.1181(5)	0.3071(3)	0.2595(4)
C(12)	0.5034(10)	0.3472(7)	0.1566(8)
C(13)	0.5430(10)	0.3536(7)	0.0906(8)
C(14)	0.5013(10)	0.3207(7)	0.0212(8)
C(15)	0.4199(10)	0.2815(7)	0.0178(8)
C(16)	0.3804(10)	0.2750(7)	0.0838(8)
C(11)	0.4221(10)	0.3079(7)	0.1532(8)
C(22)	0.5735(10)	0.2726(7)	0.3276(9)
C(23)	0.6462(10)	0.2412(7)	0.3845(9)
C(24)	0.6189(10)	0.1905(7)	0.4240(9)
C(25)	0.5190(10)	0.1713(7)	0.4066(9)
C(26)	0.4464(10)	0.2028(7)	0.3498(9)
C(21)	0.4737(10)	0.2534(7)	0.3103(9)
C(32)	0.4151(11)	0.3802(7)	0.3715(9)
C(33)	0.4137(11)	0.4382(7)	0.4059(9)
C(34)	0.3811(11)	0.4897(7)	0.3581(9)
C(35)	0.3498(11)	0.4830(7)	0.2758(9)
C(36)	0.3512(11)	0.4249(7)	0.2414(9)
C(31)	0.3838(11)	0.3735(7)	0.2892(9)
C(42)	−0.0326(13)	0.2320(8)	0.2894(9)
C(43)	−0.1307(13)	0.2109(8)	0.2793(9)
C(44)	−0.2083(13)	0.2369(8)	0.2209(9)
C(45)	−0.1877(13)	0.2840(8)	0.1727(9)
C(46)	−0.0895(13)	0.3052(8)	0.1828(9)
C(41)	−0.0120(13)	0.2792(8)	0.2412(9)
C(52)	0.0806(10)	0.3557(7)	0.3999(10)
C(53)	0.1032(10)	0.3649(7)	0.4818(10)
C(54)	0.1917(10)	0.3408(7)	0.5301(10)
C(55)	0.2575(10)	0.3076(7)	0.4964(10)
C(56)	0.2348(10)	0.2984(7)	0.4144(10)
C(51)	0.1464(10)	0.3225(7)	0.3662(10)
C(62)	0.1119(11)	0.3807(7)	0.1303(9)
C(63)	0.1050(11)	0.4361(7)	0.0883(9)
C(64)	0.0906(11)	0.4915(7)	0.1248(9)
C(65)	0.0830(11)	0.4916(7)	0.2032(9)
C(66)	0.0898(11)	0.4362(7)	0.2453(9)
C(61)	0.1043(11)	0.3808(7)	0.2088(9)
C(1)	0.1334(15)	0.1592(9)	0.1872(12)
C(2)	0.2389(15)	0.1429(9)	0.1818(12)
C(3)	0.2279(15)	0.1379(9)	0.0931(12)
C(4)	0.126(2)	0.1549(10)	0.0509(13)
C(5)	0.0699(15)	0.1669(9)	0.1049(12)
C(03)	0.294(2)	0.1096(10)	0.0589(13)
C(2A)	0.4543(11)	0.1294(6)	0.1614(9)
C(3A)	0.5522(11)	0.1127(6)	0.2000(9)
C(4A)	0.5932(11)	0.0582(6)	0.1793(9)
C(5A)	0.5363(11)	0.0203(6)	0.1200(9)
C(6A)	0.4384(11)	0.0370(6)	0.0813(9)
C(1A)	0.3974(11)	0.0916(6)	0.1020(9)
C(2B)	0.1838(12)	0.0551(8)	−0.0604(10)
C(3B)	0.1569(12)	0.0422(8)	−0.1415(10)
C(4B)	0.2087(12)	0.0699(8)	−0.1918(10)
C(5B)	0.2875(12)	0.1105(8)	−0.1609(10)
C(6B)	0.3143(12)	0.1234(8)	−0.0798(10)
C(1B)	0.2625(12)	0.0957(8)	−0.0295(10)

TABLE 3 (continued)

Atom	x	Y	z

Toluene solvent molecule (see Text and Fig. 2)

Atom	x	Y	z
C(1X)	0 28830(0)	0 06524(0)	0 53444(0)
C(10X)	0 20989(0)	0 06959(0)	0.46624(0)
C(3X)	0 13232(0)	0 02620(0)	0 45212(0)
C(6X)	0 13355(0)	−0.02154(0)	0 50620(0)
C(4X)	0 21216(0)	−0 02589(0)	0 57441(0)
C(5X)	0 28954(0)	0 01750(0)	0 58854(0)
C(7X)	0 13081(0)	0 07286(0)	0 40391(0)
C(8X)	0 20696(0)	0 11706(0)	0 42018(0)
C(9X)	0 28591(0)	J 11156(0)	0 48799(0)
C(2X)	0 21254(0)	0 01768(0)	0 52327(0)

(1 mmol) and PPh$_3$ (2 mmol) in hexane with [Pt(cod)$_2$] (1 mmol) afforded a yellow crystalline compound VII, which crystallised from toluene with one molecule of this solvent. The ^{1}H NMR spectrum of VII showed two complex multiplets due to CH groups, but this data did not establish whether the platinum atom was coordinated to the exo-cyclic double bond, or to one of the

TABLE 4

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE COMPLEX [Pt(η²-C₈H₁₂)(PPh₃)₂] (VII) [a]

Bond Lengths		Angles	
Pt—P(1)	2 301(6)	P(1)—Pt—P(2)	103 8(2)
Pt—P(2)	2 280(6)	P(1)—Pt—C(1)	151 1(6)
		P(1)—Pt—C(2)	112 6(5)
Pt—C(1)	2 15(2)	P(2)—Pt—C(1)	103 0(6)
Pt—C(2)	2 24(2)	P(2)—Pt—C(2)	143 2(6)
C(1)—C(2)	1 52(3)	C(1)—Pt—C(2)	40 5(7)
C(1)—C(5)	1 49(3)	Pt—C(1)—C(2)	73(1)
C(2)—C(3)	1 52(3)	Pt—C(2)—C(1)	67(1)
C(3)—C(4)	1 46(3)	C(1)—C(2)—C(3)	103(1)
C(4)—C(5)	1 38(4)	C(2)—C(3)—C(4)	109(2)
C(3)—C(03)	1 35(4)	C(2)—C(3)—C(03)	125(2)
		C(4)—C(3)—C(03)	123(2)
		C(3)—C(1)—C(5)	110(2)
		C(1)—C(5)—C(1)	110(2)
C(03)—C(1A)	1 18(3)	C(5)—C(1)—C(2)	108(2)
C(03)—C(1B)	1 52(3)	C(1A)—C(03)—C(3)	126(2)
		C(1B)—C(03)—C(3)	119(2)
		C(1A)—C(03)—C(1B)	114(2)
P(1)—C(11)	1 85(2)	C(11)—P(1)—C(21)	101 1(7)
P(1)—C(21)	1 82(1)	C(11)—P(1)—C(31)	102 2(7)
P(1)—C(31)	1 89(1)	C(21)—P(1)—C(31)	100 8(6)
P(2)—C(11)	1 81(2)	C(41)—P(2)—C(51)	100 8(7)
P(2)—C(51)	1 83(2)	C(41)—P(2)—C(61)	107 7(7)
P(2)—C(61)	1 81(1)	C(51)—P(2)—C(61)	103 1(7)

[a] All phenyl rings were refined as rigid groups with C—C 1 395 Å and interbond angle of 120.

TABLE 5

SOME LEAST-SQUARES PLANES FOR COMPLEX VII IN THE FORM $px + qy + rz = s$ WHERE x, y, AND z ARE FRACTIONAL CRYSTAL COORDINATES

Plane		p	q	r	s
(i)	Pt, P(1), P(2)	0.695	—7.944	15.427	1.646
(ii)	Pt, C(1), C(2)	0.029	—6.495	16.059	1.984
(iii)	Pt, C(1), C(2), P(1), P(2)	0.639	—7.157	15.676	1.918
(iv)	C(1), C(2), C(3), C(4), C(5)	3.682	20.862	—1.326	3.610
(v)	C(1A)—C(6A)	7.327	11.013	—13.710	2.530
(vi)	C(1B)—C(6B)	8.674	—16.465	—0.106	0.708

Dihedral angles (°) between planes:
(i)/(ii) 4.9; (iii)/(iv) 108.4; (iv)/(v) 50;
(iv)/(vi) 124; (v)/(vi) 99.

double bonds of the five-membered ring. Accordingly, since suitable crystals were available, an X-ray diffraction study was carried out. The results are summarised in Tables 3—5, and the molecular structure with the atom numbering scheme is shown in Fig. 1.

It will be seen immediately that the platinum atom is bonded to one of the cyclic double bonds [C(1)—C(2)] of the fulvene ring [*], and there is no significant interaction between the metal and the other carbon atoms; all the Pt—C distances being >2.95 Å. In common with many other η^2-alkene-like complexes, the C(1)—C(2) bond [1.52(3) Å] is elongated by coordination and may be compared with C(4)—C(5) 1.38(4) Å. The platinum atom is trigonally coordinated by P(1), P(2) and C(1)—C(2), the maximum deviation from planarity being 0.04 Å (Table 5). This results in only a small (5°) dihedral angle between the two planes defined by P(1), P(2), Pt and C(1), C(2), Pt. X-Ray crystallographic studies on a variety of complexes [Pt(alkene)(PPh$_3$)$_2$] have revealed dihedral angles between the PtP$_2$ and Pt—η^2-C$_2$ planes ranging from 1 to 12° [20]. The structure of VII is reminiscent of [Pt{η^2-C$_6$(CF$_3$)$_6$}(PEt$_3$)$_2$] in which the C—C distance of the two platinum-bonded carbon atoms is 1.51(3) Å and that between these carbon atoms and the platinum is 2.15(2) Å [21]. In VII, Pt—C(1) and Pt—C(2) are 2.15(2) and 2.24(2) Å, respectively. This slight asymmetry also reflected in the Pt—P(1) and Pt—P(2) separations (Table 4), is perhaps steric in origin since the closest intramolecular contacts (H····H, 2.56 Å) occur between the phenyl ring C(1A)—C(6A) and two of the phenyl rings on P(1) (Figure 1).

The C(1)—C(5) ring is essentially planar (maximum deviation ±0.03 Å), and makes an angle of 108° with the coordination plane around the platinum, defined by Pt, C(1), C(2), P(1) and P(2). The corresponding interplanar angle in [Pt{η-C$_6$(CF$_3$)$_6$}(PEt$_3$)$_2$] is 101.7° [21]. The exo-cyclic double bond [C(3)—C(03)] in VII has moved out of the C(1)—C(5) plane away from the metal, so that C(03) is 0.32 Å from this plane.

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[*] These are the C(2) and C(3) atoms of the ring, according to ring numbering convention.

The interbond angle P(1)PtP(2) [103.8(2)°] may be compared with that of 101.4(3)° in the compound [Pt{C$_2$(CN)$_4$}(PPh$_3$)$_2$] [22] and 111.6(1)° in the complex [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] [23]. The trigonal coordination of the metal found in VII may be compared with the similar geometry found for platinum in the complexes [Pt(C$_2$H$_4$)$_3$] [24], [Pt(C$_7$H$_{10}$)$_3$] [1], [Pt(C$_2$H$_4$)$_2$(C$_2$F$_4$)] [25], [Pt(C$_2$H$_4$)(C$_2$F$_4$){P(C$_6$H$_{11}$)$_3$}] [26], [Pt(C$_2$H$_4$)(η^2-C$_6$Me$_4$O$_2$){P(C$_6$H$_{11}$)$_3$}] [8], [Pt{η^2-C$_5$H$_2$Me(CF$_3$)$_3$O}(cod)] [9], and [Pt{η^2-C$_6$(CF$_3$)$_6$}(PEt$_3$)$_2$] [21].

During the investigation of fulvenes as ligands in platinum(0) chemistry, we also prepared complex VIII by adding [Pt(cod)$_2$] to a mixture of PPh$_3$ and 2,3,4,5-tetrachloro-6-phenylfulvene. This complex had a ^{31}P NMR spectrum (Table 2) as expected for the presence of a Pt(PPh$_3$)$_2$ group in which the ligands are non-equivalent. The structural assignment, in which the metal is coordinated to the *exo*-cyclic double bond of the fulvene, is made on the basis of the ^{13}C NMR data (Experimental). There are two doublet resonances at δ 71.4 ppm (*J*(PC) 26 Hz) and 57.2 ppm (*J*(PC) 44, *J*(PtC) 285 Hz) the chemical shifts of which, by comparison with the ^{13}C NMR spectra of I and V, suggest that the platinum is bonded to the C(1) and C(6) atoms of the tetrachlorofulvene.

(VII)   (VIII)
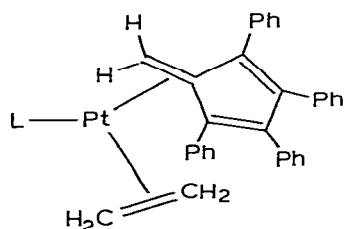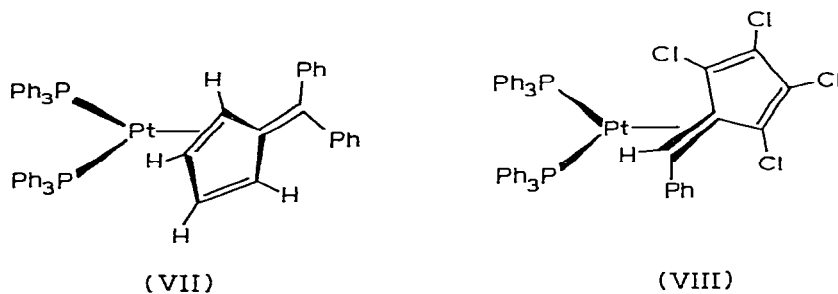
(IX . L = P(cyclo-C$_6$H$_{11}$) ;
  X , L = PPh$_3$;
  XI , L = AsPh$_3$)

We have previously shown that one ethylene molecule can be displaced from the complexes [Pt(C$_2$H$_4$)$_2$(PR$_3$)] by C$_2$F$_4$ [2] or benzo-1,4-quinones [8]. A similar reactivity pattern was shown by 2,3,4,5-tetraphenylfulvene in reactions with the species [Pt(C$_2$H$_4$)$_2$L] (L = P(C$_6$H$_{11}$)$_3$, PPh$_3$ or AsPh$_3$) affording the complexes IX—XI (Tables 1 and 2) in high yield. The ^{31}P{^{1}H} spectra of IX and X show the expected singlet resonance for a PtPR$_3$ group with the customary large ^{195}Pt coupling [2]. In the ^{1}H spectra of IX—XI the signal due to the coordinated C$_2$H$_4$ ligand is a singlet, indicating the molecules are undergoing dynamic

behaviour at room temperature with rotation of the ethylene groups about an axis through the platinum atom and the mid-point of the C=C double bonds of these groups [2]. This is supported by the ^{13}C NMR spectra of compounds IX and X where the C_2H_4 ligands give rise to one resonance with ^{195}Pt—^{13}C coupling. The ^{13}C spectra are also in accord with bonding of the metal atom to the *exo*-cyclic double bond. Resonances for the carbon atoms of the *exo*-cyclic double bond in the free ligand at δ 133.0 (C(1)) and 123.7 (C(6)) ppm are shifted upfield to appear at 77.5 ppm (C(1), J(PC) 22, J(PtC) 101 Hz) and 39.6 ppm (C(6), J(PC) < 2, J(PtC) 216 Hz) in the spectrum of IX, and at 79.5 ppm (C(1), J(PC) 11, J(PtC) 100 Hz) and 44.4 ppm (C(6), J(PC) 4, J(PtC) 208 Hz) in the spectrum of X. The resonances for C(1) in each spectrum have the larger J(PC) values implying structures in which the PR$_3$ ligands are *transoid* to the C$_5$-fulvene ring and *cisoid* to the CH$_2$ group of this ligand, a configuration which is perhaps not surprising since it would be expected to minimise steric interactions.

Experimental

General

All operations were carried out under dry oxygen-free nitrogen in Schlenk tubes. Infrared spectra were recorded as Nujol mulls on a Perkin—Elmer 457 spectrometer. ^{1}H-decoupled ^{31}P and ^{13}C NMR spectra were obtained with a JEOL PFT-100 spectrometer using a ^{2}H lock. ^{13}C chemical shifts (δ) are relative to internal Me$_4$Si, positive values representing signals to high frequency of the reference. ^{1}H NMR spectra were recorded on a JEOL PS-100 spectrometer. Analytical and other data for the new compounds are given in Table 1. Bis-(cyclo-octa-1,5-diene)platinum and the complexes [Pt(C$_2$H$_4$)$_2$L] (L = P(cyclo-C$_6$H$_{11}$)$_3$, PPh$_3$ and AsPh$_3$) were prepared as described previously [1,2], as were 2,3,4,5-tetraphenylfulvene, [27] and 2,3,4,5-tetrachloro-6-phenylfulvene [28]. 6,6-Diphenylfulvene was obtained commercially.

Synthesis of the complexes I—IV

2,3,4,5-Tetraphenylfulvene (0.19 g, 0.5 mmol) was suspended in hexane (10 cm^3) at —50°C, [Pt(cod)$_2$] (0.21 g, 0.5 mmol) was added portion-wise, and the mixture was stirred for 0.5 h. After warming to room temperature stirring was continued (10 h), and the yellow solid produced filtered, washed with hexane (2 × 3 cm^3) and crystallised from diethyl ether to give yellow crystals of [Pt-(H$_2$C=C$_5$Ph$_4$)(cod)] (I) (0.32 g), dried in vacuo.

A sample of I (0.34 g, 0.5 mmol) suspended in hexane (10 cm^3) was treated with AsPh$_3$ (0.3 g, 1 mmol). The mixture was stirred (1 h) at room temperature, and volatile material removed in vacuo. The residual solid was crystallised from tetrahydrofuran giving yellow crystals of [Pt(H$_2$C=C$_5$Ph$_4$)(AsPh$_3$)$_2$] (III) (0.5 g). The compounds [Pt(H$_2$C=C$_5$Ph$_4$)(PPh$_3$)$_2$] (II) and [Pt(H$_2$C=C$_5$Ph$_4$)(CNBu^t)$_2$] (IV) (ν_{max}(NC) 2161vs and 2128vs cm^{-1}) were prepared in the same manner, complex II being recrystallised from dichloromethane/hexane solutions.

Synthesis of the complexes VI—VIII

All the compounds were similarly prepared by adding the stoichiometric amount of [Pt(cod)$_2$] to a mixture of the fulvene and the tertiary phosphine in

the mol ratio 1/2. The following synthesis is representative.

Bis(cycloocta-1,5-diene)platinum (0.21 g, 0.5 mmol) was added portion-wise to a stirred suspension of 2,3,4,5-tetraphenylfulvene (0.19 g, 0.5 mmol) and PMe$_2$Ph (0.14 g, 1 mmol) in hexane (10 cm^3), and the mixture was stirred for 1 h. The supernatant liquid was removed and the light brown precipitate washed with hexane (2 × 3 cm^3). The residue was crystallised from tetrahydrofuran/hexane affording pale brown microcrystals of [Pt(H$_2$C=C$_5$Ph$_4$)(PMe$_2$Ph)$_2$] (VI) (0.31 g). For the preparation of compound VIII a longer period of stirring (10 h) was required.

Synthesis of the Complexes IX—XI

To a suspension of [Pt(C$_2$H$_4$)$_2${P(C$_6$H$_{11}$)$_3$}] (0.53 g, 1 mmol) in hexane (20 cm^3) was added H$_2$C=C$_5$Ph$_4$ (0.38 g, 1 mmol) at —50°C. The mixture was stirred for 0.5 h at this temperature and subsequently for 10 h at room temperature. The supernatant liquid was removed, and the residue washed with hexane (2 × 3 cm^3). Crystallisation from a toluene/hexane solution and drying in vacuo gave yellow microcrystals of [Pt(C$_2$H$_4$)(CH$_2$=C$_5$Ph$_4$){P(cyclo-C$_6$H$_{11}$)$_3$}] (IX) (0.7 g).

The compounds X and XI were prepared in a similar manner, the latter being purified by crystallisation from tetrahydrofuran/hexane solutions.

^{13}C NMR spectra

The spectra of the two ligands 2,3,4,5-tetraphenylfulvene and 6,6-diphenyl-fulvene gave rise to resonances for the fulvene-ring carbon atoms as follows [C(1) and C(6) refer to the *exo*-cyclic C(1)=C(6)H$_2$ bond]:
H$_2$C=C$_5$Ph$_4$, δ (ppm) C(3) and C(4) 152.4, C(2) and C(5) 143.5, C(1) 133.0, and C(6) 123.7.
Ph$_2$C=C$_5$H$_4$, δ (ppm) C(3) and C(4) 124.4, C(2) and C(5) 128.6, C(1) 143.9, and C(6) 151.9.
Due to an inability to obtain sufficiently concentrated solutions of the complexes, it was not possible to record satisfactory ^{13}C NMR spectra for all complexes. For those compounds which afforded spectra data were as follows:

I. δ (ppm) 138.3, 137.9, 137.6, 131.6, 135.9, 127.7 (Ph + *C*Ph), 98.6 (CH(cod), *J*(PtC) 86), 85.5 (CH(cod), *J*(PtC) 151), 81.6 (C(1), *J*(PtC) 145), 34.4 (C(6), *J*(PtC) 426 Hz), 31.4, 28.4 [CH$_2$(cod)].

V. δ (ppm) 138.9, 138.7, 133.8, 133.3, 132.6, 132.3, 131.9, 131.3, 130.5, 129.5, 129.4, 128.4, 128.2, 127.6, 127.2 (Ph + *C*Ph), 81.2 (C(1), *J*(PC) 5), 37.1 (C(6), *J*(PC) 16, *J*(PtC) 243), 18.1, 11.6 (MeP, | *J*(PC) + *J*(PC′) | 32 Hz).

VIII. δ (ppm), 135.0, 134.5, 134.1, 133.9, 133.3, 132.7, 132.0, 129.7, 128.4, 128.1, 125.2 (Ph + *C*Cl), 71.4 (C(1), *J*(PC) 26), 57.2 ((C(6), *J*(PC) 44, *J*(PtC) 285 Hz).

IX. δ (ppm) 141.1, 138.2, 136.2, 131.8, 131.2, 127.6, 127.3, 125.3 (Ph + *C*Ph), 77.5 (C(1), *J*(PC) 22, *J*(PtC) 101), 57.4 (C$_2$H$_4$, *J*(PtC) 121), 39.6 (C(6), *J*(PtC) 216), 37.0 (d, C(1) of C$_6$H$_{11}$, *J*(PC) 23, *J*(PtC) 62), 29.9 (*J*(PtC) 24), 27.8 (d, *J*(PC) 11 Hz), 26.8 (C$_6$H$_{11}$).

X. δ (ppm) 137.2, 133.9, 133.5, 133.0, 132.5, 131.2, 130.8, 130.2, 129.7, 128.9, 128.2, 127.8, 127.1, 126.5, 125.2, (Ph + *C*Ph), 79.5 (C(1), *J*(PC) 11, *J*(PtC) 100), 61.2 (C$_2$H$_4$, *J*(PtC), 118), 44.4 (C(6), *J*(PC) 4, *J*(PtC) 208 Hz).

Crystal-structure determination of $[Pt(\eta^2\text{-}C_5H_4CPh_2)(PPh_3)_2]$ (VII)

Crystals of VII grow from toluene solutions as yellow prisms and contain a molecule of solvent in the lattice. Intensity data were measured at ambient temperatures using a Nicolet P3m automated diffractometer to $2\theta \leqslant 45°$, on a crystal of dimensions ca. $0.28 \times 0.12 \times 0.12$ mm, bound by the faces $\langle 101 \rangle$ and $\langle 010 \rangle$. From the 6576 unique reflections, 3139 had $I \geqslant 3\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation of the measured intensity based on counting statistics. Corrections were applied for Lorentz and polarisation effects and for the effects of X-ray absorption.

Crystal data. $C_{54}H_{44}P_2Pt \cdot C_7H_8$, M 1087.7, Monoclinic, $a = 13.761(4)$, $b = 21.653(13)$, $c = 17.395(6)$ Å, $\beta = 104.46(2)°$, $U = 5019(4)$ Å^3, $Z = 4$, $D_c = 1.32$ g cm^{-3}, $F(000)$ 2384, Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda} = 0.710\ 69$ Å, μ(Mo-K_α) $= 29.3$ cm^{-1}, space group $P2_1/n$.

Structure solution and refinement

The structure was solved using Patterson and Fourier techniques and the 'SHELXTL' system of programs [29] on an 'Eclipse' (Data General) mini-computer, and refined by blocked-cascade least squares with anisotropic thermal parameters for all non-hydrogen atoms, except the carbon atoms of the disordered solvent molecule which were treated isotropically. All hydrogen atoms were assigned common isotropic temperature factors and were included at calculated positions (C—H 0.96 Å) except those on C(1), C(2), C(4), and C(5) (Fig. 1) which were not included in the refinement. Refinement for the structure converged at $R = 0.064$ ($R' = 0.064$). A weighting scheme of the form $w = [\sigma^2(F_o) + 0.00137|F_o|^2]^{-1}$ gave a satisfactory analysis, where $\sigma|F_o|$ is the estimated standard deviation based on counting statistics alone in the observed
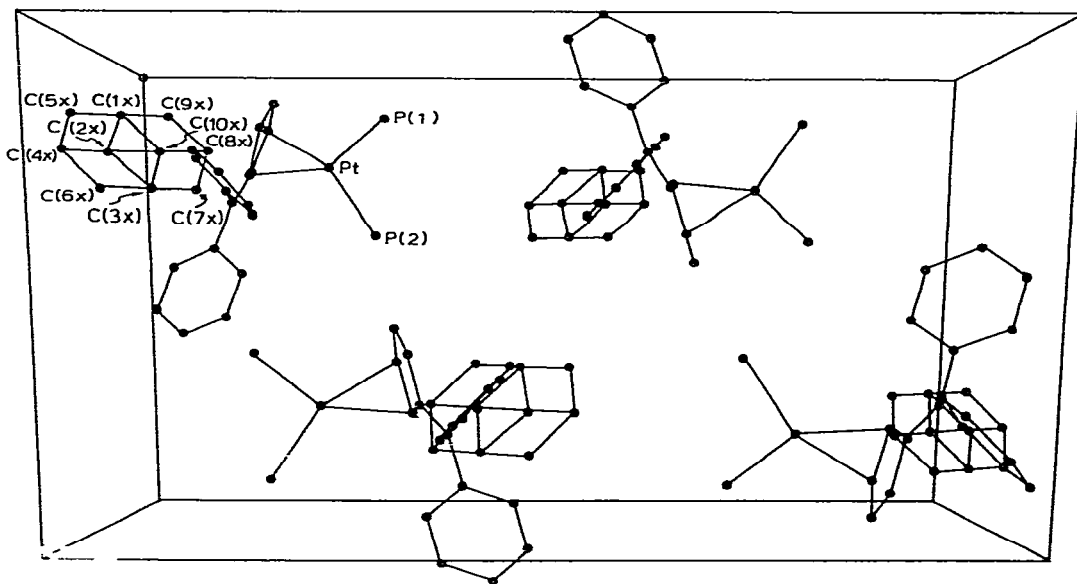

Fig. 2. Contents of the unit cell of $[Pt(\eta^2\text{-}C_5H_4CPh_2)(PPh_3)_2]$, with phenyl groups on phosphorus atoms omitted for clarity, and showing location of disordered toluene molecule.

structure factor $|F_o|$. The final difference electron density syntheses showed maxima and minima corresponding to ± 1 e Å^{-3} only in the region of the disordered solvent molecule. The latter, which co-crystallises in the unit cell, is disordered about a non-crystallographic centre of symmetry, thus the seven carbon atoms occupy six possible sites with occupation factor of 0 5 and four sites with occupancy of 1.0 (Fig. 2) Scattering factors for all atoms, including corrections for anomalous dispersion were taken from references [30—32]. The observed and calculated structure factors, atomic positional coordinates for the hydrogen atoms, thermal parameters, a full listing of bond distances and angles, and data for the toluene molecule are available from the authors.

Acknowledgement

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