Reactions of Acetylenes with Noble-metal Carbonyl Halides. Part 7.[1] Synthesis and Chemical Characterization of Cationic and Neutral Tetrasubstituted Cyclobutadiene Complexes of Platinum(II). *X*-Ray Structure † of Dichloro(η^4-1,2-dimethyl-3,4-diphenylcyclobutadiene)-(triphenylphosphine)platinum(II)

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cis-[Pt(CO)$_2$Cl$_2$] reacts at 20 °C with 1-phenylpropyne, in non-polar solvents, to give ionic species of the type [Pt$_2$(C$_4$Me$_2$Ph$_2$)$_2$Cl$_3$][Pt(CO)Cl$_3$] (1) with the methyl groups of the η^4-cyclobutadiene ring in a *cis* configuration. Analytical and spectroscopic data of complex (1) show that the cation is a dimeric platinum(II) complex with three bridging chlorine atoms; each platinum is also co-ordinated to a tetrasubstituted cyclobutadiene ring. Complex (1) is easily transformed into the corresponding neutral tetrasubstituted-cyclobutadiene derivative [Pt$_2$(C$_4$Me$_2$Ph$_2$)$_2$Cl$_4$] (2). Complex (2) reacts with triphenylphosphine to give the monomeric derivative [Pt(C$_4$Me$_2$Ph$_2$)(PPh$_3$)Cl$_2$] (5a). Evidence for the formation of the isomer with *trans* methyl groups for reactions under different conditions is reported; organic by-products, obtained by dimerisation of acetylenes with CO insertion, and hexasubstituted benzene have been isolated. The crystal structure of complex (5a) has been solved by Patterson and Fourier methods from counter data and refined by diagonal least squares to a final conventional *R* of 0.046 for 4 358 independent observed reflections. Crystals of (5a) are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 10.900(4), b = 23.437(6), c = 13.289(4) Å, β = 113.5(5)°, and Z = 4. The crystals contain discrete molecules in which the co-ordination around the Pt atom is distorted tetrahedral. Selected bond lengths (Å) are: Pt–Cl(1) 2.425(3), Pt–Cl(2) 2.430(2), Pt–P 2.353(2). The cyclobutadiene ring is asymmetrically co-ordinated to platinum [Pt–C distances in the range 2.116(9)—2.214(8) Å]; the C–C bond distances in the ring, which is planar, are equal to within the estimated standard deviations [av. 1.47(1) Å].

We have previously reported reactions of *cis*-[Pt(CO)$_2$Cl$_2$] with symmetrical disubstituted dialkyl-[2,3] and diaryl-acetylenes,[4] to give cationic and neutral tetrasubstituted platinum(II) derivatives.

Dialkylacetylenes RC≡CR (R = Me,[2,3] Et,[2,3] or Pr^n [3]) react with *cis*-[Pt(CO)$_2$Cl$_2$] to give mainly ionic tetrasubstituted cyclobutadiene complexes which are easily transformed into the corresponding neutral cyclobutadiene derivatives, whereas diphenylacetylene reacts with *cis*-[Pt(CO)$_2$Cl$_2$] to give a neutral tetrasubstituted cyclobutadiene complex.[4] All attempts to obtain the ionic tetraphenylcyclobutadiene derivative as a reaction product from *cis*-[Pt(CO)$_2$Cl$_2$] and diphenylacetylene or reacting the preformed neutral cyclobutadiene complex with halide acceptors were unsuccessful.

Acetylenes containing electron-withdrawing groups such as RO$_2$CC≡CCO$_2$R (R = Me or Et) [5] show a different behaviour with the formation of σ-alkenylplatinum(II) compounds, while PhC≡CCO$_2$Et gives cyclocarbene complexes of platinum(II).[1]

Reactions of asymmetrical acetylenes, bearing moderately bulky substituents, with transition metal complexes lead mainly to tetrasubstituted cyclobutadiene derivatives and give, depending on the nature of the metal, its oxidation state, the substituents, and the experimental conditions, one of the two possible cyclobutadiene isomers or a mixture of both.[6]

In this paper we describe the reactions of an asymmetrical disubstituted acetylene having a bulky (phenyl) and a smaller (methyl) substituent, 1-phenylpropyne, with *cis*-[Pt(CO)$_2$Cl$_2$] to give an ionic tetrasubstituted cyclobutadiene derivative. Operating under mild conditions it is possible to obtain only one isomer, which has been characterized spectroscopically and chemically, and by an *X*-ray structure determination of a compound which is closely related to the main product. At higher temperature (60 °C) the formation, in low yield, of a second isomer is observed.

Results and Discussion

Synthesis and Chemical Characterization of [Pt$_2$(C$_4$Me$_2$Ph$_2$)$_2$-Cl$_3$][Pt(CO)Cl$_3$] (1).—Compound (1a) is the major product of the reaction of *cis*-[Pt(CO)$_2$Cl$_2$] with 1-phenylpropyne (Scheme). The reactivity of compound (1a) (see Scheme), the i.r., ^{1}H (Table 1) and ^{13}C n.m.r. data, and elemental analysis are in agreement with the presence of the same type of compound previously found in the case of symmetrical dialkylacetylenes.[3] These were found to contain ionic species: a dimeric cation [Pt$_2$(C$_4$R$_4$)$_2$Cl$_3$]$^+$ (R = Me, Et, or Pr^n) [3] and the anion [Pt(CO)Cl$_3$]$^-$.

In the dimeric cation the co-ordination around each Pt atom may be described as a distorted tetrahedron with the

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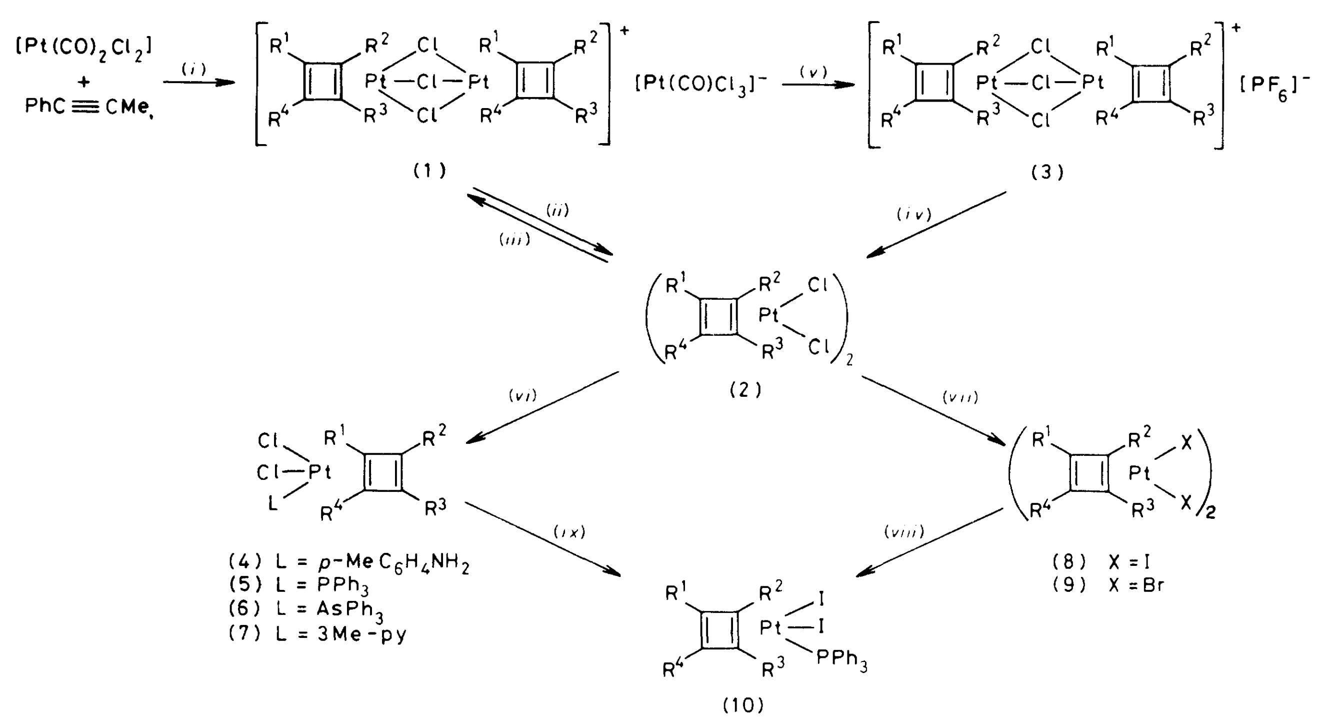
† *Supplementary data available* (No. SUP 23990, 32 pp.): H-atom co-ordinates, thermal parameters, structure factors, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



Scheme. Compounds (*n*a) $R^1 = R^4 = Ph$, $R^2 = R^3 = Me$; compounds (*n*b) $R^1 = R^3 = Ph$; $R^2 = R^4 = Me$. (*i*) $-CO$; (*ii*) $+MeCN$, $-[Pt(CO)(MeCN)Cl_2]$; $+[NEt_4]Cl$, $-[NEt_4][Pt(CO)Cl_3]$; (*iii*) $+[Pt(CO)_2Cl_2]$, $-CO$; (*iv*) $+[NEt_4]Cl$, $-[NEt_4][PF_6]$; (*v*) $+[NH_4][PF_6]$, $-[NH_4][Pt(CO)Cl_3]$; (*vi*) $+L$; (*vii*) $+LiX$, $-LiCl$; (*viii*) $+PPh_3$; (*ix*) $+LiI$

co-ordination positions defined by the three bridging chlorine atoms and the centre of the tetra-alkylcyclobutadiene ligand.

Compound (1a) is water sensitive and, dissolved in damp solvents, separates eventually metallic platinum; it is insoluble in aliphatic and aromatic hydrocarbons and Pr^iOH but soluble and stable for prolonged periods in $CHCl_3$ and CH_2Cl_2. In basic solvents (sol), such as MeCN and tetrahydrofuran (thf), (1a) reacts quantitatively according to equilibrium (i) with the formation of the insoluble orange

$$\underset{(1a)}{[Pt_2(C_4Me_2Ph_2)_2Cl_3][Pt(CO)Cl_3]} + \text{sol} \rightleftharpoons \underset{(2a)}{[Pt_2(C_4Me_2Ph_2)_2Cl_4]} + [Pt(CO)(\text{sol})Cl_2] \quad \text{(i)}$$

compound (2a). This type of reaction has previously been reported in the case of cyclocarbene complexes of platinum(II).[1] This behaviour prompted us to investigate the solutions obtained from compound (1a) dissolved in basic solvents. The i.r. spectra of solutions in different solvents show, in the CO stretching region, the presence of compound (1a) and of the solvated species $[Pt(CO)(sol)Cl_2]$ in different ratios, thus suggesting that an equilibrium between the ionic and the neutral tetrasubstituted cyclobutadiene complexes occurs.

The conductivity in dry acetone of compound (1a) (λ_m = 67.13 ohm^{-1} cm^{-1}; 1.65 × 10^{-3} mol dm^{-3} solution) is low for a 1 : 1 electrolyte compared with that found for the salt containing a σ-alkenylplatinum(II) anion;[7] nevertheless this conductivity agrees well with the value found for the ionic (η^4-tetrapropylcyclobutadiene)platinum(II) derivative[3] and this is in keeping with equilibrium (i).

The transformation of the complex (1a) into (3a) [see reaction (*v*) of the Scheme], obtained by metathetical reaction between compound (1a) and $[NH_4][PF_6]$, is further support for the ionic nature of (1a).

Table 1. Hydrogen-1 n.m.r. spectral data (δ/p.p.m.)[a]

Complex	CH_3[b]	Other signals	$J(^{195}Pt-H)$/Hz
(1a)[c]	1.85	7—8 (m, C_6H_5)	*d*
(1b)[c]	2.13	7—8 (m, C_6H_5)	*d*
(2a)[e]	1.94	7—8 (m, C_6H_5)	18.3
(2b)[e]	2.3	7—8 (m, C_6H_5)	5.9
(3a)[c]	1.97	7—8 (m, C_6H_5)	19.78
(3b)[c]	2.22	7—8 (m, C_6H_5)	*d*
(4a)[e]	1.75	2.24 (s, $CH_3C_6H_4NH_2$) 6.5—8 (m, aromatic)	17.3
(5a)[e]	1.77	7—8 (m, C_6H_5)	17.3[f]
(5b)[e]	1.87	7—8 (m, C_6H_5)	*d, g*
(6a)[e]	1.83	7—8 (m, C_6H_5)	16.1
(7a)[e]	1.91	2.61 (s, $CH_3C_5H_4N$)	15.4
(8a)[e]	1.96	7—8 (m, C_6H_5)	19.2
(9a)[e]	1.88	7—8 (m, C_6H_5)	18.8

[a] Values relative to internal $SiMe_4$. [b] All CH_3 signals are coupled with ^{195}Pt and appear as non-binomial triplets and, when coupled with ^{31}P as non-binomial triplets of doublets. [c] CD_2Cl_2 solution. [d] Not detected. [e] $CDCl_3$ solution. [f] $J(^{31}P-H)$ = 5.1 Hz. [g] $J(^{31}P-H)$= 4.5 Hz.

The ^1H n.m.r. spectra of both (1a) and (3a) (Table 1) show, in the region δ 1—3.6 p.p.m., only a non-binomial triplet due to the coupling of the two equivalent CH_3 groups with ^{195}Pt. The i.r. spectra of (1a) and (3a) are essentially identical in the region 625—4 000 cm^{-1} except for the presence of the strong absorption band at 2 080vs cm^{-1} (Nujol mull) for (1a). The far-i.r. spectrum of (1a) shows two absorption bands at 338m and 318w cm^{-1} (Nujol mull) arising from the Pt–Cl stretching mode in the $[Pt(CO)Cl_3]^-$ anion, and a band at 232m cm^{-1} (polyethylene pellet) due to Pt-μ-Cl deformation in the Pt_2Cl_3 unit[3] of the cationic part containing three bridging chlorine atoms. The i.r. spectrum of (3a) does not show any

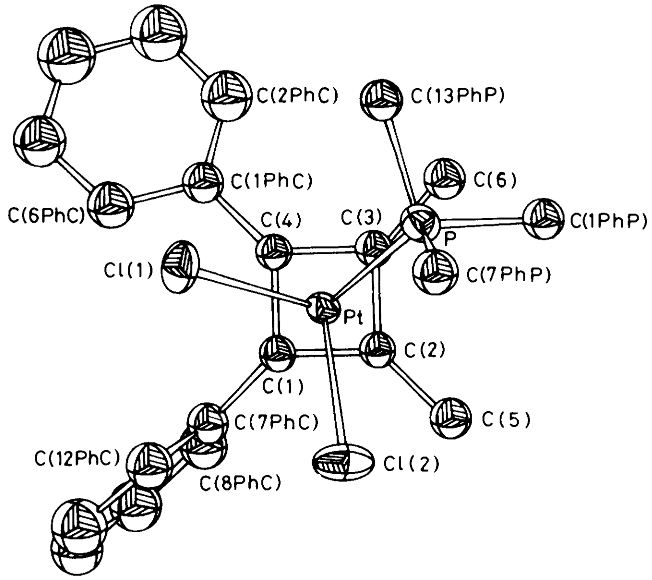


Figure. View of the co-ordination around the Pt atom of (5a) projected along the normal to the *cb* plane; the phenyl rings of the phosphine are omitted for clarity

band attributable to a $[Pt(CO)Cl_3]^-$ anion but only the absorption at 235m cm^{-1} (polyethylene pellet) arising from the Pt_2Cl_3 bridge deformations.

Synthesis and Chemical Characterization of $[Pt_2(C_4Me_2Ph_2)_2Cl_4]$ (2a).—By reacting with a large excess of chloride ions, compound (1a) is completely transformed into compound (2a) [see reaction (*ii*) of the Scheme]. When the mother-liquor is treated with $[N(PPh_3)_2]Cl$ the well known $[N(PPh_3)_2][Pt(CO)Cl_3]$ is isolated in agreement with the stoicheiometry of the reaction. On the other hand, complex (2a) can be obtained by a similar reaction from (3a) [see reaction (*iv*) of the Scheme]. The far-i.r. spectrum of (2a) shows bands at 315s and 295m cm^{-1} (Nujol mull) that can be assigned to terminal and bridging chlorine atoms respectively, suggesting that in the solid state dimeric species are present while the mass spectrum reveals peaks of monomeric species. The reaction leading from (1a) to (2a) can be reversed by treating (2a) with a stoicheiometric amount of *cis*-$[Pt(CO)_2Cl_2]$ in toluene. Compound (2a) reacts with a large excess of PPh_3 [molar ratio (2a) : PPh_3 = 1 : 5] in refluxing toluene to give the complex $[Pt(PPh_3)_2Ci_2]$, whereas reacting with a stoicheiometric amount of nitrogen-, phosphorus-, or arsenic-donor ligands gives the four-co-ordinate derivatives $[Pt(C_4Me_2Ph_2)(L)Cl_2]$ [L = *p*-$MeC_6H_4NH_2$ (4a), PPh_3 (5a), $AsPh_3$ (6a), or 3-methylpyridine (7a)] which were fully characterized by elemental analysis, i.r. and ^1H n.m.r. spectroscopy. On warming, the chloro-complex (2a) can, in turn, be transformed into the corresponding iodo- and bromo-complexes: $[Pt_2(C_4Me_2Ph_2)_2X_4]$ [X = I (8a) or Br (9a)] [see reaction (*vii*) of the Scheme] by metathetical reactions with lithium-iodide or -bromide respectively.

Compound (8a) reacts with PPh_3 in toluene, at room temperature, to give $[Pt(C_4Me_2Ph_2)(PPh_3)I_2]$ (10a) [see reaction (*viii*) of the Scheme]; the same product can be obtained by refluxing a methanolic suspension of (5a) with an excess of lithium iodide [see reaction (*ix*) of the Scheme].

Table 2. Some relevant bond distances (Å) and angles (°) for $[Pt(C_4Me_2Ph_2)(PPh_3)Cl_2]$ (5a) with e.s.d.s in parentheses

Pt–Cl(1)	2.425(3)	Pt–C–C [a]	70.2(2.5)
Pt–Cl(2)	2.430(2)	C–Pt–C [a]	39.8(5)
Pt–P	2.353(2)	Pt–P–C(1PhP)	110.6(3)
Pt–C(1)	2.116(9)	Pt–P–C(7PhP)	118.5(2)
Pt–C(2)	2.128(10)	Pt–P–C(13PhP)	113.4(2)
Pt–C(3)	2.203(8)	Cl(1)–Pt–Cl(2)	92.30(9)
Pt–C(4)	2.214(8)	Cl(1)–Pt–P	90.49(8)
C(1)–C(2)	1.47(1)	Cl(2)–Pt–P	93.07(8)
C(1)–C(4)	1.47(1)	Cl(1)–Pt–C(1)	105.9(2)
C(2)–C(3)	1.45(1)	Cl(1)–Pt–C(4)	96.6(2)
C(2)–C(5)	1.49(1)	Cl(2)–Pt–C(2)	97.1(2)
C(3)–C(4)	1.47(1)	Cl(2)–Pt–C(3)	134.5(1)
C(3)–C(6)	1.48(1)	C(1)–C(2)–C(3)	91.0(7)
C(1)–C(7PhC)	1.49(1)	C(1)–C(2)–C(5)	133.6(4)
C(4)–C(1PhC)	1.45(1)	C(1)–C(4)–C(3)	90.4(7)
P–C(1PhP)	1.814(9)	C(2)–C(1)–C(7PhC)	135.1(4)
P–C(7PhP)	1.832(8)	C(2)–C(3)–C(4)	89.6(7)
P–C(13PhP)	1.809(10)	C(2)–C(3)–C(6)	133.5(4)
C–C (phenyl) [a]	1.40(1)	C(2)–C(1)–C(4)	89.0(7)
Pt–cbd [b]	1.901(8)	C(3)–C(4)–C(1PhC)	134.3(4)
Cl(1) · · · C(1) [c]	3.629	C(4)–C(3)–C(6)	135.6(4)
Cl(1) · · · C(2) [c]	4.359	C(3)–C(2)–C(5)	133.8(4)
Cl(1) · · · C(3) [c]	4.201	C(1)–C(4)–C(1PhC)	135.0(4)
Cl(1) · · · C(4) [c]	3.465	C(4)–C(1)–C(7PhC)	132.1(4)
Cl(2) · · · C(1) [c]	3.500	C(1)–C(7PhC)–C(8PhC)	117.5(6)
Cl(2) · · · C(2) [c]	3.423	C(1)–C(7PhC)–C(12PhC)	121.1(6)
Cl(2) · · · C(3) [c]	4.273	C(4)–C(1PhC)–C(2PhC)	120.5(6)
Cl(2) · · · C(4) [c]	4.365	C(4)–C(1PhC)–C(6PhC)	119.5(7)
		C–P–C [a]	104.4(1.9)

[a] Average value; e.s.d.s (σ) on the average values are obtained from $\sigma = [\Sigma_i(d_i - \bar{d})/(n - 1)]^{\frac{1}{2}}$ where d_i is the *i*th bond length. [b] cbd refers to the unweighted centre of gravity of the cyclobutadiene ring. [c] Non-bonded distances: σ = 0.006—0.008 Å.

Crystal Structure of $[Pt(C_4Me_2Ph_2)(PPh_3)Cl_2]$ (5a).—The crystal structure consists of discrete $[Pt(C_4Me_2Ph_2)(PPh_3)Cl_2]$ molecules packed together by van der Waals forces with no unusual intermolecular contacts. An ORTEP view of the molecule is given in the Figure with the numbering scheme. Bond lengths and angles are in Table 2. The geometry around the Pt atom may be described as a distorted tetrahedral co-ordination defined by the two chlorine atoms, the phosphine ligand, and the centre of gravity of the η^4-cyclobutadiene ligand.

The two Pt–Cl distances [av. 2.427(3) Å] are equal to within the e.s.d.s and comparable with the value of 2.415(3) Å found in the anion $[Pt\{C(CO_2Me)=C(Cl)COO\}(CO)Cl]^-$.[8] In the related tetrapropylcyclobutadiene cation $[Pt_2(C_4Pr^n_4)_2Cl_3]^+$, Pt–Cl distances in the range 2.41—2.63 Å are found.[3] The Pt–P bond length [2.353(2) Å] is slightly longer than usually found in Pt^{II}-phosphine compounds [1,9,10] (2.24—2.33 Å). The tetrasubstituted cyclobutadiene ligand (cbd) is asymmetrically co-ordinated to the Pt atom with two shorter Pt–C(cbd) bonds [av. 2.122(9) Å] involving two carbon atoms [C(1) and C(2)] bearing a phenyl and a methyl substituent respectively; the remaining two cbd carbon atoms show longer distances, averaging 2.209(8) Å. This difference may be accounted for by the steric interference between the cbd ring, the atom Cl(1) and the phosphine ligand (see Figure). It may be noted that such a situation, in the solid state, is at variance with the n.m.r. results in solution where the carbon atoms bearing the same substituents are equivalent. Similar asymmetric co-ordination may be found when bulky substituents are present in the cbd ring, *e.g.* in the dimer $[Pd_2\{\eta^4-C_4(CH_2OPh)_4\}_2Cl_4]$ [11] [Pd–C bond lengths 2.09(1)—2.19(1) Å], and in the complexes $[Rh(C_5Me_5)(C_8H_2Ph_4)]$ [12] [Rh–C 2.11(1)—2.20(1) Å] and $[Rh(C_5Me_5)(C_4Ph_2HCPh=C_5Ph_2H_2)]$ [12] [Rh–C (av.) 2.103(7) and 2.146(6) Å]. Intramolecular packing forces are also responsible for asymmetric bonding in the cation [Pt(CF$_3$)-(η^4-C$_4$Me$_4$)(PMe$_2$Ph)$_2$]$^+$.[10] It is noteworthy that, as normally found in this class of compounds, the metal(ligand)$_3$ (ML$_3$) moiety is 'off axis' with the cbd ring;[10,13] the 'tilt angle' between the normal to the cbd plane and the axis passing through the Pt atom and the centre of the cyclobutadiene ligand is 3.8(4)°, a consequence of bonding interactions and intermolecular contacts due to the steric hindrance of the substituents. On the other hand, a symmetric situation is found in compounds where either an unsubstituted or methyl-substituted cbd moiety is present.[13,14]

The C$_4$ ring adopts an almost eclipsed configuration with respect to the ML$_3$ fragment as can be judged from the Figure and from the values of the torsion angles reported in Table 3; moreover due to the low barrier of rotation about the metal–C$_4$ axis,[15,16] it may be assumed that this configuration is dictated by the steric hindrance of the cbd substituents.

The C–C bond distances in the cbd ring are equal [av. 1.47(1) Å] and there is no significant variation of the angles from the ideal value of 90°; hence the ring is virtually square and planar while the atoms C(5), C(6), C(1PhC), and C(7PhC) are displaced from the plane defined by the atoms C(1)—C(4) (0.2—0.3 Å), away from the metal atom, an effect opposite to that observed for the hydrogen atoms in ferrocene.[17]

N.M.R. Studies and Evidence for a Second Isomer.—All the ^{1}H n.m.r. spectra of the dimethyldiphenylcyclobutadiene derivatives [compounds (1a)—(10a); see Table 1] show a non-binomial triplet in the region δ 1.7—2.3 p.p.m. downfield from SiMe$_4$ owing to the coupling of the equivalent *cis* methyl groups with ^{195}Pt and a multiplet in the region δ 6.5—8.0 p.p.m. due to the aromatic hydrogens. In the case of compound (5a) an additional coupling of the methyl groups with ^{31}P is observed.

Table 3. Relevant internal rotation angles (°) for [Pt(C$_4$Me$_2$Ph$_2$)-(PPh$_3$)Cl$_2$] (5a) with e.s.d.s in parentheses

Pt–C(1)–C(7PhC)–C(8PhC)	−171.0(1.2)
Cl(1)–Pt–C(1)–C(2)	175.8(8)
Cl(1)–Pt–C(4)–C(1PhC)	22.5(8)
Cl(2)–Pt–C(1)–C(2)	−88.7(9)
Cl(2)–Pt–C(1)–C(7PhC)	44.3(8)
Cl(2)–Pt–C(2)–C(5)	−31.8(8)
P–Pt–C(3)–C(6)	−1.7(8)
C(2)–C(1)–C(7PhC)–C(8PhC)	−67.8(1.9)
C(3)–C(4)–C(1PhC)–C(2PhC)	12.7(1.8)

These data confirm the equivalence of the methyl groups in solution in all the compounds isolated. They also confirm that there is no rearrangement of the organic fragment during the interconversion of complex (1a) through to (10a). The single signal found for the methyl groups does not support the presence of the other possible cyclobutadiene isomer in the crude product obtained under the present experimental conditions. The ^{13}C-{^{1}H} n.m.r. spectrum shows two sets of signals due to the cyclobutadiene carbon atoms bonded to platinum at δ 81.1 [^1J(^{195}Pt–C) = 160] and 108.9 p.p.m. [^1J(^{195}Pt–C) = 70 Hz]. On the basis of the ^{13}C n.m.r. spectrum (^{1}H non-decoupled), the signal at δ 108.9 p.p.m. is assigned to carbon atoms C(1) and C(4) bonded to the phenyl groups while the first resonance is assigned to carbon atoms C(2) and C(3) bonded to the methyl groups confirming the presence of the cyclobutadiene ring η^4-bonded to platinum (see Figure for numbering scheme). A further resonance at δ 14 p.p.m. is due to the carbon atoms C(5) and C(6) of the methyl groups and a multiplet at δ 130 p.p.m. is observed for the carbon atoms of the phenyl ring. In the low-temperature (−90 °C, CD$_2$Cl$_2$) ^{1}H n.m.r. spectrum of complex (6a) it was not possible to freeze out the inequivalence of carbons C(2) and C(3) and C(1) and C(4) which is present in the solid state.

The selectivity of dimerisation of 1-phenylpropyne induced by *cis*-[Pt(CO)$_2$Cl$_2$] with the formation of the cyclobutadiene-platinum(II) derivative with the methyl groups in a *cis* configuration is in agreement with the results obtained by Kelley and Maitlis[18] in a similar study of palladium(II) complexes with MeC≡CBu^t. The similarity of the results suggests that an extension of Maitlis's cyclisation mechanism[18] is applicable to the present platinum(II) complexes. It has been shown that the reactions of Fe^0 and Co^0 derivatives[6] with several asymmetric acetylenes do not lead to the formation of the pure *cis* isomer: either a mixture of the two isomers or the *trans* isomer only has been obtained.

The reaction between *cis*-[Pt(CO)$_2$Cl$_2$] and 1-phenylpropyne has been carried out over the temperature range 20—110 °C; the yield of compound (1) is not affected by the temperature. When the reaction of 1-phenylpropyne with *cis*-[Pt(CO)$_2$Cl$_2$] is carried out under very carefully controlled conditions, at 60 °C in toluene, the ^{1}H n.m.r. spectrum of the crude product

Table 4. Final atomic co-ordinates for [Pt(C$_4$Me$_2$Ph$_2$)(PPh$_3$)Cl$_2$] (5a) with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Pt	0.110 01(3)	0.318 49(1)	0.464 05(2)	C(11PhC)	−0.275 6(12)	0.181 1(5)	0.317 1(10)
Cl(1)	0.127 04(25)	0.276 36(10)	0.303 43(18)	C(12PhC)	−0.164 7(10)	0.217 9(4)	0.364 5(8)
Cl(2)	−0.090 57(23)	0.371 19(11)	0.353 39(22)	C(1PhP)	0.294 1(8)	0.438 1(4)	0.582 0(7)
P	0.252 79(20)	0.393 30(8)	0.461 67(17)	C(2PhP)	0.184 1(9)	0.458 8(4)	0.603 4(7)
C(1)	0.027 1(8)	0.254 6(3)	0.530 5(7)	C(3PhP)	0.207 0(11)	0.490 2(4)	0.696 4(9)
C(2)	0.061 2(8)	0.305 0(3)	0.602 2(6)	C(4PhP)	0.337 4(11)	0.502 4(5)	0.768 9(9)
C(3)	0.203 3(8)	0.293 0(3)	0.637 8(6)	C(5PhP)	0.444 2(11)	0.483 6(5)	0.748 5(9)
C(4)	0.170 6(8)	0.241 5(3)	0 569 0(7)	C(6PhP)	0 425 8(9)	0.450 3(4)	0.655 3(8)
C(5)	−0.017 4(9)	0.343 4(4)	0.642 9(7)	C(7PhP)	0.193 5(8)	0.443 8(4)	0.347 1(7)
C(6)	0.325 1(9)	0.316 5(4)	0.725 5(8)	C(8PhP)	0.208 6(10)	0.502 7(4)	0.365 6(8)
C(1PhC)	0.248 2(9)	0.194 3(4)	0.554 6(7)	C(9PhP)	0.175 9(12)	0.540 1(5)	0.278 4(10)
C(2PhC)	0.381 7(12)	0.185 5(5)	0.629 6(10)	C(10PhP)	0.123 1(15)	0.519 1(6)	0.170 8(12)
C(3PhC)	0.454 3(14)	0.138 9(6)	0.615 6(11)	C(11PhP)	0.108 7(17)	0.459 2(7)	0.151 6(13)
C(4PhC)	0.394 3(14)	0.102 4(6)	0.525 2(11)	C(12PhP)	0.140 2(13)	0.423 0(5)	0.241 0(10)
C(5PhC)	0.260 0(12)	0.108 7(5)	0.453 3(10)	C(13PhP)	0.410 0(8)	0.368 9(4)	0.461 0(7)
C(6PhC)	0.188 0(10)	0.155 6(4)	0.468 5(8)	C(14PhP)	0.446 5(10)	0.312 0(4)	0.485 1(8)
C(7PhC)	−0.095 0(8)	0.218 5(3)	0.477 4(7)	C(15PhP)	0.563 9(11)	0.291 5(5)	0.478 1(9)
C(8PhC)	−0.135 5(11)	0.185 4(4)	0.545 4(9)	C(16PhP)	0.642 3(12)	0.328 1(5)	0.442 0(10)
C(9PhC)	−0.247 7(12)	0.148 4(5)	0.498 5(10)	C(17PhP)	0.606 6(11)	0.383 6(5)	0.418 1(9)
C(10PhC)	−0.317 5(12)	0.148 1(5)	0.384 5(10)	C(18PhP)	0.489 1(10)	0.405 1(4)	0.426 3(9)

of compound (1) shows an additional resonance at δ 2.13 p.p.m. coupled with ^{195}Pt (corresponding to 8% of the total product) which has been assigned to complex (1b). The relative amount of this complex was determined by integrations of the methyl resonance against the methyl resonance of (1a). It proved impossible, even after several crystallizations, to obtain this compound pure.

By extracting the crude compound (2) with dichloromethane it is possible to obtain a sample 'enriched' with complex (2b) [(2a) 65% and (2b) 35%]. The ^{1}H n.m.r. spectrum of this enriched compound shows the expected resonance attributed to (2a) and the additional singlet at δ 2.3 p.p.m. [$^3J(^{195}\text{Pt-H}) = 10$ Hz] which can be assigned to (2b).

The mixture of (2a) and (2b) shows the same reactivity as (1a) when pure: thus the enriched sample can be transformed into compound (1) by reaction with *cis*-[Pt(CO)$_2$Cl$_2$] [see reaction (*iii*) of the Scheme] as demonstrated by its n.m.r. spectrum. The reaction with triphenylphosphine of the enriched sample (2) leads to the formation of compound (5) [see reaction (*vi*) of the Scheme].

The ^{1}H n.m.r. spectrum of this isomer mixture shows a set of three doublets with the expected intensity ratio 1 : 4 : 1 at δ 1.77 p.p.m. [$^4J(^{31}\text{P-H}) = 5.1$, $^3J(^{195}\text{Pt-H}) = 17.3$ Hz] for (5a) and a set of three doublets at δ 1.87 p.p.m. [$^4J(^{31}\text{P-H}) = 4.5$ Hz] for (5b).

The elemental analyses of the enriched sample and of some of its derivatives agree with the equivalent molecular formulae of complexes (1a), (2a), and (5a).

Organometallic and Organic By-products.—In the case of the reaction between *cis*-[Pt(CO)$_2$Cl$_2$] and 2-butyne, 3-hexyne, and 4-octyne it was possible to isolate the ionic cyclobutadiene-platinum(II) derivative,[2,3] a yellow Pt^{II} complex [Pt(η^4-C$_5$R$_4$O)Cl$_2$] (R = Et or Pr^n) [19] (containing a cyclopentadienone ligand), which has been fully characterized, and a white product [{Pt[C(O)–C(R)=C(R)–C(R)–C(R)Cl]Cl}$_2$] (R = Me, Et, or Pr^n).[19] The latter compound is probably produced by dimerisation of the acetylene and insertion of a CO group with the formation of a six-membered ring containing platinum. The two products containing a carbonyl group inserted into the organic fragment are not obtained in the case of the reaction of 1-phenylpropyne with *cis*-[Pt(CO)$_2$Cl$_2$]. From the mother-liquor from which complex (1) was separated, on addition of hexane it was possible to isolate in low yields two yellow compounds, (11) and (12), not yet fully characterized, containing a carbonyl group inserted into the organic fragment [ν(CO) = 1 700s cm^{-1} (Nujol mull)]. On the other hand, from the hexane solution, after separation of the organometallic compounds, the tetrasubstituted cyclopentadienone derivative and its Diels–Alder dimerisation product have been recognised and characterized by mass spectra, i.r. spectra, and elemental analyses. These organic species have also been isolated in the case of the reaction of diphenylacetylene [4] and 2-butyne [19] with *cis*-[Pt(CO)$_2$Cl$_2$], suggesting that during the reaction the unstable substituted-cyclopentadienone platinum(II) complex is formed as an intermediate product. Careful treatment of the hexane mother-liquor led to isolation of the trimerisation products of 1-phenylpropyne, characterized by elemental analyses and mass spectra ($m/e = 348$). The n.m.r. data are in agreement with a 2 : 1 mixture of 1,2,4-trimethyl-3,5,6-triphenylbenzene and 1,3,5-trimethyl-2,4,6-triphenylbenzene and there is no evidence for the formation of the 1,2,3-trimethyl-4,5,6-triphenylbenzene isomer. A mixture of the three isomers has been obtained by Maitlis and co-workers [20] by reacting bis(benzonitrile)dichloropalladium(II) in halogenated solvents (chloroform and dichloromethane) with 1-phenylpropyne.

Experimental

Microanalyses were determined by the Laboratorio Analisi Universita' di Milano. The ^{1}H and ^{13}C (internal standard SiMe$_4$) n.m.r. spectra were recorded on Bruker WP 80 (80 MHz) or Varian XL-200 (200 MHz) spectrometers and values are reported downfield of the standard. I.r. spectra were obtained on Perkin-Elmer 457 or 781 grating spectrophotometers and the far-i.r. spectra with Nicolet MX-1 FT-IR or with Perkin-Elmer 180 spectrometers using Nujol mulls, NaCl, CsI plates, or polyethylene pellets. Mass spectra were recorded on a Varian MAT 112 spectrometer.

All the reactions were carried out under an atmosphere of nitrogen and with anhydrous solvents although the products were rarely air sensitive. Solvents were purified and dried by standard methods. The complex *cis*-[Pt(CO)$_2$Cl$_2$] was prepared as described previously.[4] Crystals of compound (5a) suitable for *X*-ray analysis were obtained by slow diffusion of cyclohexane (20 cm^3) into a dichloromethane (5 cm^3) solution of the complex. The yellow crystals are stable in air and have an elongated prismatic habit. A crystal of approximate dimensions 0.2 × 0.1 × 0.2 mm was used for data collection.

Crystal Data.—C$_{36}$H$_{31}$Cl$_2$PPt, $M = 760.61$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.900(4)$, $b = 23.437(6)$, $c = 13.289(4)$ Å, $\beta = 113.5(5)^\circ$, $U = 3\,114(2)$ Å^3, $D_m = 1.63$ Mg m^{-3}, $Z = 4$, $D_c = 1.62$ Mg m^{-3}, $F(000) = 1\,496$, $\mu(\text{Mo-}K_\alpha) = 49.86$ cm^{-1}.

Data Collection.—Unit-cell parameters were obtained by least-squares fit of the 2θ values of 25 high-angle reflections accurately measured on a automatic diffractometer. Intensity data were collected with an automated four-circle diffractometer (Philips PW 1 100; graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å) up to $2\theta = 50^\circ$ using an ω-scan mode. A scan speed of 0.05° s^{-1} was used with a constant scan width of 1.20°. Two background counts were measured at each side of the peak for 6 s and the counts subsequently averaged. During the data collection three standard reflections were measured every two hours to check the stability of the experimental conditions and of the crystal: no significant variations were detected. A total of 5 480 independent reflections were measured and corrected for Lorentz and polarisation effects; σ(*I*) values were evaluated on counting statistics. 4 358 Reflections having $I_{net} \geqslant 3\sigma(I)$ were considered observed and used in the structure analysis. No absorption correction was considered necessary due to the small size and regular shape of the crystal; moreover the results of azimuthal ψ scans of general reflections at different 2θ values showed negligible variation in the transmission.

Structure Analysis.—The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares using anisotropic thermal parameters for the Pt, Cl, and P atoms, and isotropic for the others. The function minimized was $\Sigma w[F_o - (1/k)F_c]^2$ with weights chosen according to Cruickshank *et al.*[21] and atomic scattering factors taken from ref. 22; a correction for the real part of anomalous dispersion for the Pt, Cl, and P atoms was applied. The hydrogen atom contribution, held fixed in their calculated positions [r(C–H) = 1.08 Å, $B = 5.0$ Å^2], was taken into account during the last stages of the refinement. A final difference-Fourier map showed no significant features. The calculations were carried out using a UNIVAC version of programs written by Immirzi.[23] The final conventional agreement factor R was 0.046 (0.062 with unobserved reflections included). Fractional atomic co-ordinates are given in Table 4; relevant bond distances, angles, and internal rotation angles are reported in Tables 2 and 3.

Reaction of cis-$[Pt(CO)_2Cl_2]$ *with* 1-*Phenylpropyne at* 20 °C: *Synthesis of* (1a).—To a suspension of *cis*-$[Pt(CO)_2Cl_2]$ (8.25 g, 25.6 mmol) in anhydrous toluene (oxygen free) (140 cm^3), 1-phenylpropyne (11 cm^3, 89.2 mmol) was added. The solution was stirred at 20 °C until all the *cis*-$[Pt(CO)_2Cl_2]$ had reacted (*ca.* 192 h). The pale yellow precipitate was filtered off, washed with toluene (5 × 20 cm^3), and dried; yield 6.05 g (55.9%). Complex (1a) is insoluble in hydrocarbons, soluble in $CHCl_3$ and CH_2Cl_2, and reacts with thf and MeCN (Found: C, 34.9; H, 2.6; Cl, 16.1; Pt, 44.5. $C_{37}H_{32}Cl_6OPt_3$ requires C, 34.4; H, 2.5; Cl, 16.5; Pt, 45.3%).

The mother-liquor was reduced in volume *in vacuo* and treated with hexane (100 cm^3). The crude yellow-brown product was stirred with hexane (3 × 50 cm^3) and by fractional crystallisation from acetone two yellow-green organometallic complexes were separated: (11) and (12) [Found for (11): C, 38.4; H, 2.8. $C_{29}H_{24}Cl_4O_2Pt_2$ requires C, 37.2; H, 2.5%]; i.r.: ν(CO) = 1 700s cm^{-1} [Found for (12): C, 31.1; H, 2.2. $C_{10}H_8Cl_2OPt$ requires C, 29.2; H, 1.9%]; i.r.: ν(CO) = 1 700s cm^{-1}.

Reaction of cis-$[Pt(CO)_2Cl_2]$ *with* 1-*Phenylpropyne at* 60 °C.—To a suspension of *cis*-$[Pt(CO)_2Cl_2]$ (6.6 g, 20.5 mmol) in hot anhydrous toluene (80 cm^3), 1-phenylpropyne (5.5 cm^3, 44.6 mmol) was gradually added (*ca.* 5 h). The solution was kept at 60 °C until all the *cis*-$[Pt(CO)_2Cl_2]$ had reacted (*ca.* 24 h). The yellow precipitate, a mixture of (1a) and (1b), was filtered off, washed with toluene (5 × 30 cm^3) and dried; yield 8 g (91%) (Found: C, 34.1; H, 2.4; Cl, 16.1; Pt, 45.9. $C_{37}H_{32}Cl_6OPt_3$ requires C, 34.4; H, 2.5; Cl, 16.6; Pt, 45.3%).

Reaction of cis-$[Pt(CO)_2Cl_2]$ *with* 1-*Phenylpropyne* (*Molar Ratio* 1 : 5) *in refluxing Toluene*.—To a suspension of *cis*-$[Pt(CO)_2Cl_2]$ (4.2 g, 13 mmol) in toluene (100 cm^3), 1-phenylpropyne (8 cm^3, 64.9 mmol) was added. The solution was refluxed for 1 h. After cooling, the yellow-brown solid was filtered off, washed with toluene (5 × 20 cm^3) and dried. A mixture of (1a) and (1b) (92% and 8% respectively) was obtained, contaminated with (2a) and (2b) (Found: C, 35.1; H, 2.7; Cl, 15.8; Pt, 45.0%).

The volume of the toluene solution was reduced *in vacuo* (to 70 cm^3) and treated with hexane (100 cm^3). The yellow mixture of (11) and (12) was filtered off and dried; combined yield 0.9 g. The toluene–hexane solution was evaporated to dryness on a rotary evaporator at 30 °C leaving an oily residue which was washed with Pr^iOH (2 × 30 cm^3). The solid obtained was crystallized with MeOH. This solid (0.4 g) was a mixture of 1,2,4-trimethyl-3,5,6-triphenylbenzene and 1,3,5-trimethyl-2,4,6-triphenylbenzene in molar ratio 2 : 1 (Found: C, 91.9; H, 7.0. $C_{27}H_{24}$ requires C, 93.0; H, 7.0%). The parent ion was found at *m*/*e* = 348.

The Pr^iOH solution was taken to dryness leaving an orange oily residue which contained the tetrasubstituted cyclopentadienone and its Diels-Alder derivatives. The orange oil was dissolved in CH_2Cl_2 and chromatographed by t.l.c. [silica-gel plates; eluant, toluene–chloroform (3 : 1)]. Two well separated bands developed: the first was the tetrasubstituted-cyclopentadienone derivative (13) (R_f = 0.3), and the second the Diels-Alder dimerisation product (14) (R_f = 0.5) [Found for (13): C, 86.5; H, 5.8. $C_{19}H_{16}O$ requires C, 87.7; H, 6.2%]. I.r.: ν(CO) = 1 700s cm^{-1} (Nujol mull). ^1H N.m.r. ($CDCl_3$): δ 2.09(s, CH_3), 7—8(m, C_6H_5). The parent ion was found at *m*/*e* = 260 [Found for (14): C, 88.5; H, 6.6. $C_{38}H_{32}O_2$ requires C, 87.7; H, 6.2%]. I.r.: ν(CO) = 1 767s, 1 684s cm^{-1} (Nujol mull). ^1H N.m.r. ($CDCl_3$): several signals in the CH_3 region at δ 1—3, 7—8 p.p.m. (m, C_6H_5). The parent ion was found at *m*/*e* = 520.

Preparation of $[Pt_2(C_4Me_2Ph_2)_2Cl_4]$ (2a).—(*a*) *Reaction of* (1a) *with* MeCN. Complex (1a) (0.52 g, 0.4 mmol) was stirred with MeCN (20 cm^3) at room temperature. The colour of the solution changed from yellow to orange and, after 2 h, an orange precipitate was formed. The solid was filtered off, washed with MeCN (2 × 10 cm^3) and dried; yield 0.27 g (68%). Complex (2a) is insoluble in hydrocarbons, sparingly soluble in $CHCl_3$ and soluble in CH_2Cl_2 (Found: C, 43.4; H, 3.2; Cl, 14.0; Pt, 38.7. $C_{36}H_{32}Cl_4Pt_2$ requires C, 43.4; H, 3.2; Cl, 14.2; Pt, 39.1%). The parent ion occurs at *m*/*e* = 498 (calculated on ^{195}Pt and ^{35}Cl).

(*b*) *Reaction of* (1a) *with* $[NEt_4]Cl$. To a solution of $[NEt_4]Cl$ (1.75 g, 10.6 mmol) in MeOH (60 cm^3), was added (1a) (2.8 g, 2.2 mmol) and the suspension stirred at room temperature for 2 h. The orange solid was filtered off, washed with MeOH (2 × 10 cm^3) and dried; yield 2.1 g (98%) (Found: C, 43.2; H, 3.2%). The mother-liquor was treated with a MeOH (5 cm^3) solution of $[N(PPh_3)_2]Cl$ (2 g, 3.5 mmol). The reaction mixture was reduced in volume and after cooling at −20 °C the pale yellow solid was filtered off, washed with cold MeOH (3 × 5 cm^3) and dried; yield 1.4 g (77%). The compound was identified as the known $[N(PPh_3)_2][Pt(CO)Cl_3]$.

(*c*) *Reaction of* (3a) *with* $[NEt_4]Cl$. To a solution of $[NEt_4]Cl$ (0.19 g, 1.1 mmol) in MeOH (15 cm^3) was added (3a) (0.2 g, 0.18 mmol). The solution was stirred at room temperature for 15 min. The orange precipitate was filtered off, washed with MeOH (2 × 5 cm^3) and dried; yield 0.15 g (85%) (Found: C, 43.1; H, 3.3%).

Reaction of (2a) *with cis*-$[Pt(CO)_2Cl_2]$.—To a suspension of complex (2a) (1.46 g, 2.9 mmol) in anhydrous toluene (25 cm^3) was added *cis*-$[Pt(CO)_2Cl_2]$ (0.47 g, 1.45 mmol) and the mixture stirred at room temperature. The colour of the solid changed from orange to pale yellow and after 36 h the product was filtered off, washed with toluene (2 × 10 cm^3), dried and identified as (1a); yield 0.8 g (43%) (Found: C, 33.4; H, 2.3. $C_{37}H_{32}Cl_6OPt_3$ requires C, 34.4; H, 2.5%).

Preparation of $[Pt_2(C_4Me_2Ph_2)_2Cl_3][PF_6]$ (3a).—To a solution of $[NH_4][PF_6]$ (0.34 g, 2.1 mmol) in Pr^iOH (20 cm^3), was added (1a) (0.36 g, 0.5 mmol) and the suspension stirred at room temperature. The colour of the solid changed from pale yellow to yellow. After 3 h the complex was filtered off, washed with cold Pr^iOH (2 × 7 cm^3) and dried; yield 0.5 g, (93%). Complex (3a) is insoluble in hydrocarbons, sparingly soluble in $CHCl_3$ and soluble in CH_2Cl_2 (Found: C, 40.3; H, 2.8. $C_{36}H_{32}Cl_3F_6PPt_2$ requires C, 39.1; H, 2.9%). Conductivity: λ_m = 155.3 ohm^{-1} cm^{-1} (1.74 × 10^{-3} mol dm^{-3}, acetone solution).

Preparation of $[Pt(C_4Me_2Ph_2)(p\text{-}MeC_6H_4NH_2)Cl_2]$ (4a).—To a suspension of (2a) (0.47 g, 0.35 mmol) in toluene (20 cm^3) was added a solution of *p*-toluidine (0.163 g, 1.5 mmol) in toluene (10 cm^3). The solution was stirred at room temperature for 2 h, then filtered, and the yellow filtrate evaporated to dryness under reduced pressure; the residue was crystallised from CH_2Cl_2–hexane. A yellow solid was obtained, filtered off, washed with cold toluene (3 × 5 cm^3), and dried; yield 0.53 g (92%). The complex is insoluble in alphatic hydrocarbons, but soluble in toluene, $CHCl_3$, and CH_2Cl_2 (Found: C, 49.3; H, 4.3; N, 2.2. $C_{25}H_{25}Cl_2NPt$ requires C, 49.6; H, 4.2; N, 2.2%).

The complex $[Pt(C_4Me_2Ph_2)(3Me\text{-}py)Cl_2]$ (7a) (3Me-py = 3-methylpyridine) was prepared by a similar reaction starting from (2a) (0.257 g, 0.26 mmol) and 3Me-py (0.77 mmol); yield 0.17 g (55 %) (Found: C, 47.1; H, 3.9; N, 2.6. $C_{24}H_{23}Cl_2NPt$ requires C, 48.7; H, 3.9; N, 2.4%). The parent ion was found at *m*/*e* = 590.

Preparation of [Pt($C_4Me_2Ph_2$)(PPh_3)Cl_2] (5a).—A CH_2Cl_2 solution (10 cm^3) of PPh_3 (0.1 g, 0.38 mmol) was added to a solution of complex (2a) (0.16 g, 0.33 mmol) in CH_2Cl_2 (20 cm^3). After stirring at room temperature for 12 h the suspension was filtered and the yellow solution was treated with hexane (100 cm^3); the yellow-orange solid was filtered off, washed with cold toluene (2 × 10 cm^3), and dried; yield 0.15 g (52%). The product is insoluble in MeOH and hydrocarbons but soluble in thf, $CHCl_3$, and CH_2Cl_2 (Found: C, 58.6; H, 4.4; Cl, 9.1; Pt, 24.9. $C_{36}H_{31}Cl_2PPt$ requires C, 56.9; H, 4.1; Cl, 9.3; P, 4.1; Pt, 25.6%). The compound [Pt($C_4Me_2Ph_2$)(PPh_3)I_2] (10a) was prepared by a similar reaction starting from (8a) (0.11 g, 0.16 mmol) and PPh_3 (0.05 g, 0.19 mmol); yield 0.06 g (40%) (Found: C, 40.3; H, 3.1. $C_{36}H_{31}I_2PPt$ requires C, 45.8; H, 3.3%).

Preparation of [Pt($C_4Me_2Ph_2$)($AsPh_3$)Cl_2] (6a).—To a suspension of (2a) (0.19 g, 0.38 mmol) in toluene (10 cm^3), a toluene solution (8 cm^3) of $AsPh_3$ (0.13 g, 0.42 mmol) was gradually added (*ca.* 2 h). The suspension was kept at 50 °C for 3 h. After cooling, the yellow solid was filtered off, washed with hexane (2 × 10 cm^3), and dried; yield 0.27 g (88%). The product is insoluble in hydrocarbons and in alcohols, but soluble in $CHCl_3$ and CH_2Cl_2 (Found: C, 52.6; H, 3.5. $C_{36}H_{31}AsCl_2Pt$ requires C, 53.7; H, 3.9%).

Preparation of [Pt_2($C_4Me_2Ph_2$)$_2$$I_4$] (8a).—To a solution of LiI (1.5 g, 11.3 mmol) in MeOH (16 cm^3), was added (2a) (0.25 g, 0.5 mmol). After stirring at room temperature for 3 h the red solid was filtered off, washed with hexane (2 × 10 cm^3), and dried; yield 0.34 g (85%). The product is soluble in toluene, $CHCl_3$, CH_2Cl_2, and thf (Found: C, 31.8; H, 2.4. $C_{18}H_{16}I_2Pt$ requires C, 31.8; H, 2.4%). The compound [Pt_2($C_4Me_2Ph_2$)$_2$$Br_4$] (9a) was prepared by a similar reaction starting from (2a) (0.36 g, 0.72 mmol) and LiBr (1.3 g, 15 mmol); yield 0.39 g (92.4%) (Found: C, 37.7; H, 2.9. $C_{18}H_{16}Br_2Pt$ requires C, 36.8; H, 2.7%).

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