Platinum(II) phosphine complexes of dicarboxylates and ammonia: crystal structures of [{Pt(PPh₃)₂}₂{μ-1,3-(O₂C)₂C₆H₄}₂], [{Pt(PPh₃)₂(NH₃)}₂{μ-1,4-(O₂C)₂C₆H₄}][PF₆]₂ and *cis*-[Pt(PPh₃)₂(NH₃)₂][NO₃]₂

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The reaction of [Pt(PPh₃)₂(CO₃)] with a rigid dicarboxylic acid H₂L gave rise to dimeric compounds [{Pt(PPh₃)₂}₂(μ-L)₂] **1** [H₂L = C₆H₄(CO₂H)₂-1,4 (terephthalic acid) **a**, C₆H₄(CO₂H)₂-1,3 (isophthalic acid) **b**, *trans,trans*-HO₂CCH=CHCH=CHCO₂H (muconic acid) **c** or 4,4′-HO₂CC₆H₄C₆H₄CO₂H (biphenyldicarboxylic acid) **d**], which have been characterised spectroscopically and, in the case of **1b**, crystallographically. When the reaction was carried out in the presence of NH₄PF₆ the NH₄⁺ competed with the carboxylic acid and the major product from the reaction was [{Pt(PPh₃)₂(NH₃)}₂(μ-L)][PF₆]₂ **2**, which has been characterised crystallographically for L = terephthalate. This suggests that NH₄⁺ is acidic enough to react with [Pt(PPh₃)₂(CO₃)], which has been confirmed by the synthesis of *cis*-[PtL₂(NH₃)₂]X₂ [L = PPh₃, X = PF₆ **3a** or NO₃ **3b**; L = PEt₃, X = PF₆ **4a** or NO₃ **4b**; L₂ = Ph₂PCH₂CH₂PPh₂ (dppe), X = PF₆ **5a**] from [PtL₂(CO₃)]. The complex *cis*-[Pt(PPh₃)₂(¹⁵NH₃)₂][NO₃]₂ was synthesized from ¹⁵NH₄NO₃ and characterised by a combination of ³¹P-{¹H}, ¹⁵N-{¹H}, ¹⁹⁵Pt and ¹H NMR spectroscopy. The crystal structure of *cis*-[Pt(PPh₃)₂(NH₃)₂][NO₃]₂ **3b** has been determined and shows strong hydrogen bonding between the co-ordinated ammonia and the nitrate counter ions. The compound PhC₂CO₂H also reacted with [PtL₂(CO₃)], though the products were not the expected bifunctional carboxylates *cis*-[PtL₂(O₂CC₂Ph)₂] but the bis(phenylalkynyl) compounds *cis*-[PtL₂(C₂Ph)₂] (L = PPh₃ **6**, L₂ = dppe **7**).

For many years it was accepted that a mismatch of a soft metal and a hard ligand led to low-oxidation-state platinum-group metal–oxygen bonds being weak.[1] In consequence, complexes incorporating such bonds were believed to be unstable. However, as early as 1968 this was shown to be an oversimplification with the synthesis by Wilkinson and co-workers[2] of [Pt(PPh₃)₂(O₂CR)₂] (R = Me, CF₃ or Ph). Since this time other platinum(II) complexes of carboxylates[3,4] and alkoxides[5,6] have been prepared and studied, though only recently has a crystal structure of a platinum phosphine carboxylate been reported.[4] Platinum carboxylate complexes have been shown to be important medicinally, an important example being the anti-tumour agent carboplatin, [Pt(NH₃)₂(cbdca)] (cbdca = cyclo-butane-1,1-dicarboxylate).[7] In this paper we explore the possibilities of self-assembly within the platinum phosphine carboxylate system by the use of rigid dicarboxylates that, in contrast to cbdca and malonate, are unable to chelate to a single metal atom. This leads to the possibility of using transition-metal-directed assembly to generate molecules containing large rings,[8] which could provide sites for intercalation. In addition we examine the competition between carboxylic acids and ammonium cations, which has led to the realisation that the reaction of [Pt(PR₃)₂(CO₃)] with NH₄⁺ provides a simple and effective route to complexes of the general formula [Pt(PR₃)₂(NH₃)₂]²⁺ which have, perhaps surprisingly, not previously been fully characterised.

Results and Discussion

Synthesis and characterisation of complexes [{Pt(PPh₃)₂}₂(μ-L)₂] 1a–1d

On stirring [Pt(PPh₃)₂(CO₃)] with a rigid dicarboxylic acid in ethanol for several hours the dimeric species [{Pt(PPh₃)₂}₂(μ-L)₂] **1** [H₂L = C₆H₄(CO₂H)₂-1,4 (terephthalic acid) **a**, C₆H₄(CO₂H)₂-1,3 (isophthalic acid) **b**, *trans,trans*-HO₂CCH=CHCH=CHCO₂H (muconic acid) **c** or 4,4′-HO₂CC₆H₄C₆H₄CO₂H (biphenyldicarboxylic acid) **d**] were obtained as the only platinum-containing products. The compounds were obtained as colourless solids which were separated by filtration and recrystallised from dichloromethane and either hexane or diethyl ether. In all cases a singlet with ¹⁹⁵Pt satellites was observed in the ³¹P-{¹H} NMR spectrum, indicating equivalent phosphorus atoms. The ¹J(PPt) coupling constants vary from 3830 to 3876 Hz and are very similar in magnitude to those observed for the complexes [Pt(PPh₃)₂(O₂CR)₂] (R = Me, CF₃ or Ph),[4] and consistent with phosphorus *trans* to oxygen. The chemical shifts lie in a narrow range between δ 6.6 and 7.1 indicating very similar structures. No evidence was observed in the ¹H NMR spectra for protonated carboxylate groups. In the IR spectra the large separation between ν_asym- and ν_sym-(CO₂) (283–303 cm⁻¹) is characteristic of monodentate carboxylates.[9] Evidence for the dimeric nature of the complexes was obtained from the fast atom bombardment (FAB) mass spectra. With the exception of **1d**, the [Pt₂(PPh₃)₄L₂]⁺ ion was observed as the highest m/z peak. However, dimers can be observed in FAB mass spectra as a result of monomer aggregation during the experiment and hence their presence cannot be regarded as conclusive evidence for a dimeric structure. In addition, the absence of higher m/z peaks cannot definitively rule out higher oligomers. Consequently a single-crystal X-ray analysis of one of these complexes was undertaken in order to confirm the structure. Crystals of **1b** were obtained by the slow diffusion of hexane into a dichloromethane solution.

The X-ray analysis of complex **1b** confirms that the iso-phthalate ligands adopt a binucleating role bridging between two independent platinum centres to form a 16-membered

Table 1 Selected bond lengths (Å) and angles (°) for complex **1b**

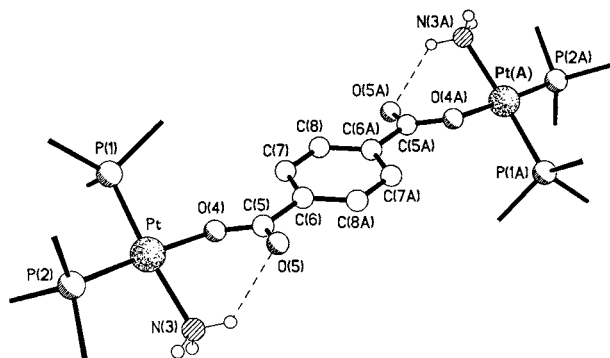|			
Pt(1)–O(2)	2.05(2)	Pt(1)–O(26)	2.08(2)
Pt(1)–P(46)	2.216(6)	Pt(1)–P(27)	2.241(8)
Pt(14)–O(13)	2.09(2)	Pt(14)–O(15)	2.09(2)
Pt(14)–P(84)	2.231(7)	Pt(14)–P(65)	2.239(8)
O(2)–Pt(1)–O(26)	83.3(7)	O(2)–Pt(1)–P(46)	92.2(5)
O(26)–Pt(1)–P(46)	173.3(5)	O(2)–Pt(1)–P(27)	169.6(5)
O(26)–Pt(1)–P(27)	87.5(5)	P(46)–Pt(1)–P(27)	97.4(3)
O(13)–Pt(14)–O(15)	84.6(6)	O(13)–Pt(14)–P(84)	170.9(5)
O(15)–Pt(14)–P(84)	86.4(5)	O(13)–Pt(14)–P(65)	90.5(5)
O(15)–Pt(14)–P(65)	174.3(5)	P(84)–Pt(14)–P(65)	98.4(3)

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Pt–O(4)	2.064(7)	Pt–N(3)	2.088(9)
Pt–P(2)	2.243(3)	Pt–P(1)	2.274(3)
O(4)–C(5)	1.295(13)	C(5)–O(5)	1.235(14)
C(5)–C(6)	1.51(2)		
O(4)–Pt–N(3)	85.0(3)	O(4)–Pt–P(2)	177.9(2)
N(3)–Pt–P(2)	93.0(3)	O(4)–Pt–P(1)	85.3(2)
N(3)–Pt–P(1)	169.3(3)	P(2)–Pt–P(1)	96.55(10)
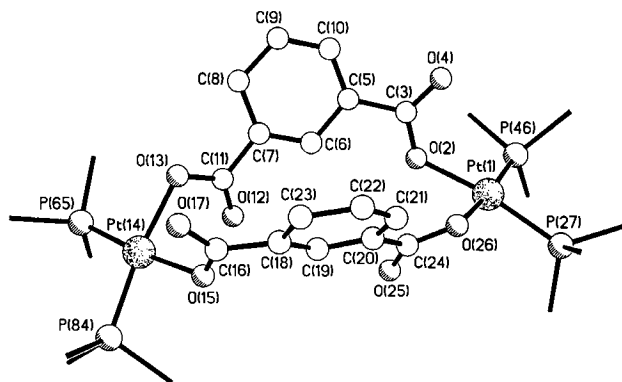
Fig. 1 Solid-state structure of the diplatinum complex **1b**. The trans-annular Pt · · · Pt distance is 8.9 Å

Fig. 2 Solid-state structure of the cationic complex present in **2**

metallocyclic ring (Fig. 1). Selected bond lengths and angles are given in Table 1. Of the possible bridging symmetries, a conformation with C_{2v} symmetry would be the intuitive choice, however a lower molecular symmetry (C_2) is adopted in the solid state. The geometries at the two platinum centres are essentially the same, being distorted square planar with *cis* angles ranging between 83.3(7) and 98.4(3)°; deviations from planarity are less than 0.1 Å. The Pt–P and Pt–O distances are unexceptional. The metallocyclic ring has a folded geometry with a cleft angle between the isophthalate rings of *ca.* 58°, the ring centroid · · · ring centroid distance being 4.77 Å. All four carboxylate groups are rotated out of the plane of their parent aromatic rings, the torsional twists about C(3)–C(5), C(7)–C(11), C(16)–C(18) and C(20)–C(24) being 17, 31, 16 and 12° respectively. The platinum co-ordination planes are both folded away from the open face formed by the isophthalate rings, subtending an angle of 121°. It is surprising that, with the bulky phosphine groups being folded away from the open face of the macro-cycle, there is no close approach of either symmetry-related complexes or solvent molecules (present in abundance) to this exposed cleft.

The structure of a related platinum(II) complex, [{Pt(NH₃)₂}₂-{μ-O₂C(CH₂)₃CO₂}₂], has been reported[10] which involves glutarates bridging between the two metal atoms. This complex was formed from the reaction of *cis*-[Pt(NH₃)₂(OH₂)₂]SO₄, glutaric acid and barium hydroxide in aqueous solution and also contains a 16-membered ring, though in this case the complex is centrosymmetric. In this compound, chelation of the dicarb-oxylate is geometrically possible, but this would have given rise to a sterically unfavourable eight-membered ring. A zirconium adduct of isophthalic acid, [{Zr(C₅H₄Me)₂}₂{μ-1,3-(O₂C)₂-C₆H₄}₂], has also been reported.[11] Like **1b**, this has a dimeric structure with two isophthalate ligands bridging the two metal centres. In contrast to **1b** though, each isophthalate exhibits two different co-ordination modes with one monodentate and one bidentate carboxylate. This allows each zirconium atom to bond to one of each type of carboxylate group and maintain a formal 18-electron configuration.

Synthesis and characterisation of [{Pt(PPh₃)₂(NH₃)}₂{μ-1,4-(O₂C)₂C₆H₄}][PF₆]₂ 2

When [Pt(PPh₃)₂(CO₃)] and terephthalic acid were stirred together in ethanol in the presence of NH₄PF₆ a colourless solid was produced in a similar manner to the syntheses of complexes **1a**–**1d**. The ³¹P-{¹H} NMR spectrum showed only one product to be present but in this case, in contrast to **1a**–**1d**, a pair of doublets with associated ¹⁹⁵Pt satellites were observed at δ 10.1 and 6.7 indicating two non-equivalent phosphorus environments. In addition a septet associated with PF₆⁻ was also observed and the integration suggested a Pt(PPh₃)₂:PF₆ ratio of 1:1. Absorptions in the IR spectrum at 1598 and 1313 cm⁻¹ showed the presence of terephthalate with the carboxyl-ates monodentate, whilst an absorption at 3356 cm⁻¹ suggested NH₃ to be present. Further evidence for the presence of NH₃ came from the observation of nitrogen in the microanalysis. This was unlikely to have arisen from NH₄⁺ since the presence of PF₆⁻ suggested a cationic complex. Taken together, the spectroscopic and analytical data are consistent with the formu-lation [{Pt(PPh₃)₂(NH₃)}₂{μ-1,4-(O₂C)₂C₆H₄}][PF₆]₂ **2**, in which the NH₃ has been derived from NH₄PF₆. Ammonium has there-fore competed with terephthalic acid for reaction with the car-bonate, acting as both an acid and a source of the NH₃ conjugate-base ligand. Although the M^+ peak was not observed in the FAB mass spectrum, there is evidence for a dimeric struc-ture, with observed peaks assigned to the species [Pt₂(PPh₃)₃-{1,4-(O₂C)₂C₆H₄}(NH₃)]⁺ and [Pt₂(PPh₃)₃{1,4-(O₂C)₂C₆H₄}]⁺. The identity of **2** has been confirmed by a single-crystal X-ray diffraction study, with the crystals obtained from the slow diffu-sion of hexane into a dichloromethane solution.

The X-ray analysis of complex **2** (Fig. 2) reveals a structure in which a single terephthalate ligand adopts a binucleating role, bridging two Pt(PPh₃)₂(NH₃) moieties in a C_i symmetric arrangement. Selected bond lengths and angles are given in Table 2. The co-ordination geometry at platinum is distorted square planar with *cis* angles in the range 85.0(3)–96.6(1)°, the platinum and its four co-ordinated atoms being coplanar to within 0.05 Å. The Pt–P distances differ significantly with that *trans* to oxygen being 0.031(3) Å shorter than that *trans* to nitrogen (Table 2). The carboxylate group is rotated by *ca.* 14° out of the plane of the terephthalate ring which is in turn inclined by 40° to the platinum co-ordination plane. The geom-etry of the complex is constrained by two intramolecular

N–H···O hydrogen bonds between one of the hydrogen atoms of each ammine group and their adjacent terephthalate carbonyl oxygen atoms (N···O, H···O distances 2.85, 2.17 Å; N–H···O angle 132°). There are no significant close approaches to the faces of the terephthalate ring, the ring being partially overlaid on both sides by phenyl rings of one of the phosphine ligands though at a distance too great for any significant π–π stacking interactions. There are no notable intermolecular contacts, the approach to the non-hydrogen-bonding ammine hydrogen atoms being shielded by one of the other phosphine rings of the complex.

The ability of NH_4^+ to compete with HO_2CR in the reaction with platinum(II) complexes was further illustrated by the reaction of $[\{Pt(PPh_3)_2\}_2\{\mu-1,4-(O_2C)_2C_6H_4\}_2]$ **1a** with an excess of NH_4PF_6 in ethanol. After 72 h the solvent was removed *in vacuo* and the $^{31}P-\{^1H\}$ NMR spectrum of the dichloromethane extract showed a 55:45 mixture of **1a** and $[\{Pt(PPh_3)_2(NH_3)\}_2\{\mu-1,4-(O_2C)_2C_6H_4\}][PF_6]_2$ **2**. This ratio of **1a**:**2** was unaltered by stirring with a further excess of NH_4PF_6 in ethanol for 48 h.

Synthesis and characterisation of $[PtL_2(NH_3)_2]^{2+}$ 3–5

The synthesis and characterisation of $[\{Pt(PPh_3)_2(NH_3)\}_2\{\mu-1,4-(O_2C)_2C_6H_4\}]^{2+}$ has demonstrated that NH_4^+ is acidic enough to react with $[Pt(PPh_3)_2(CO_3)]$. Therefore reaction without the presence of another acid should lead to the complex $[Pt(PPh_3)_2(NH_3)_2]^{2+}$. In view of the importance of NH_3 and PPh_3 as ligands in platinum chemistry it is somewhat surprising that this complex has not previously been well characterised.[12] Neutral complexes containing ammonia and a phosphine ligand, $[PtCl_2(PR_3)(NH_3)]$, were first prepared by Chatt *et al.*[13] from the reaction of $[Pt_2Cl_4(PR_3)_2]$ with NH_3 and the crystal structure of $[PtCl_2(PMe_3)(NH_3)]$ has been reported as an adduct with a crown ether[14] and β-cyclodextrin.[15] Kinetic studies[16] have demonstrated the existence in solution of $[Pt(PEt_3)_2(NH_3)_2]^{2+}$ but neither this complex nor indeed any of the general formula $[Pt(PR_3)_2(NH_3)_2]^{2+}$ has been fully characterised.

Quantitative conversion of $[Pt(PPh_3)_2(CO_3)]$ into *cis*-$[Pt(PPh_3)_2(NH_3)_2]X_2$ **3** (X = PF_6^- **a** or NO_3^- **b**) was achieved by stirring $[Pt(PPh_3)_2(CO_3)]$ with NH_4X in ethanol for several hours. The reaction was not limited to derivatives of PPh_3, and *cis*-$[Pt(PEt_3)_2(NH_3)_2]X_2$ **4** (X = PF_6^- **a** or NO_3^- **b**) and $[Pt(dppe)(NH_3)_2][PF_6]_2$ **5a** (dppe = $Ph_2PCH_2CH_2PPh_2$) were prepared in a similar manner from $[Pt(PEt_3)_2(CO_3)]$ and $[Pt(dppe)(CO_3)]$ respectively. However, reaction of $[Pt(dppe)(CO_3)]$ with NH_4NO_3 led to a mixture of products from which $[Pt(dppe)(NH_3)_2][NO_3]_2$ **5b** could not be isolated. As expected, the natures of both the phosphine and the anion have a strong effect on the solubility of the complexes. Complexes **3a**, **3b**, **4a** and **5a** are all soluble in dichloromethane whereas **4b** is insoluble in dichloromethane but soluble in water.

Complexes **3–5** were characterised by multinuclear NMR and IR spectroscopies, FAB mass spectrometry and microanalysis. In the $^{31}P-\{^1H\}$ NMR spectra singlets with ^{195}Pt satellites were observed with $^1J(PPt)$ between 3127 and 3428 Hz. As expected, $^1J(PPt)$ varies in the order $PPh_3 > dppe > PEt_3$, consistent with the decrease in π-back donation from PPh_3 to PEt_3. The coupling constants for **3a** and **3b** are both slightly larger than that observed for *cis*-$[Pt(PPh_3)_2(py)_2][ClO_4]_2$ (py = pyridine) [$^1J(PPt)$ 3276 Hz].[17] In the ^1H NMR spectra ($CDCl_3$) resonances due to the ammonia hydrogen atoms were observed as broad singlets at δ 3.15 for **3a** and at δ 4.28 for **3b**, with a 1:5 intensity ratio between these and the phenyl proton resonances. The large difference between the two values of δ is indicative of strong NH_3–anion hydrogen bonding present in solutions of the nitrate salt, **3b**. For complexes **4** and **5** δ was observed between 4.4 and 4.6, though in the cases of the hexafluorophosphate salts **4a** and **5a** hydrogen bonding to the solvent $(CD_3)_2CO$ is the likely cause of this shift (the complexes are not soluble in $CDCl_3$).

Table 3 Selected bond lengths (Å) and angles (°) for complex **3b**

Pt(1)–N(5)	2.092(8)	Pt(1)–N(4)	2.094(8)
Pt(1)–P(2)	2.264(4)	Pt(1)–P(3)	2.273(4)
Pt(6)–N(9)	2.096(8)	Pt(6)–N(10)	2.112(8)
Pt(6)–P(7)	2.260(4)	Pt(6)–P(8)	2.276(4)
N(5)–Pt(1)–N(4)	82.1(4)	N(5)–Pt(1)–P(2)	171.1(3)
N(4)–Pt(1)–P(2)	91.8(3)	N(5)–Pt(1)–P(3)	88.6(3)
N(4)–Pt(1)–P(3)	170.1(3)	P(2)–Pt(1)–P(3)	97.8(1)
N(9)–Pt(6)–N(10)	83.0(4)	N(9)–Pt(6)–P(7)	172.0(3)
N(10)–Pt(6)–P(7)	91.6(3)	N(9)–Pt(6)–P(8)	88.7(3)
N(10)–Pt(6)–P(8)	171.1(3)	P(7)–Pt(6)–P(8)	97.0(2)

The ^{15}N-labelled derivative, *cis*-$[Pt(PPh_3)_2(^{15}NH_3)_2][NO_3]_2$, can readily be prepared using $^{15}NH_4NO_3$. The additional coupling constants observed in the $^{31}P-\{^1H\}$ NMR spectrum that were not observable in the spectrum of the unlabelled complex are $^2J(PP)$ 22, $^2J(PN_{trans})$ 39 and $^2J(PN_{cis})$ −1 Hz. The $^{15}N-\{^1H\}$ NMR spectrum has a multiplet at δ −378.5 with $^1J(NPt)$ 194 Hz, whereas the ^{195}Pt NMR spectrum shows the expected triplet of triplets at δ −4452. In the ^1H NMR spectrum the broad singlet observed at δ 4.3 for the unlabelled complex is resolved into a multiplet with $^1J(HN)$ 72, $^2J(HPt)$ 32 and $^3J(HP_{trans})$ 3 Hz.

Infrared spectra, recorded as KBr pellets, showed bands at 3342s, 3274s [$\nu(NH_3)$], 1623m [$\delta(NH_3)$] and 833vs cm^{-1} [$\nu(PF_6)$] for **3a** and at 3436s, 3335m [$\nu(NH_3)$], 1625s [$\delta(NH_3)$] and 1384vs cm^{-1} [$\nu(NO_3)$] for **3b**. For **3a** and **3b** M^{2+} was observed in the FAB mass spectrum at m/z 377. Generally for the PF_6^- salts, **3a**, **4a** and **5a**, the most intense peaks were due to $[M - 2NH_3]^+$ and $[M + H]^+$, with $[M - NH_3]^+$ and $[M + PF_6]^+$ also observed, whereas for the nitrate salts, **3b** and **4b**, the most intense peaks were due to $[M - 2NH_3 + NO_3]^+$ and $[M - 2NH_3]^+$ with M^+ and $[M - NH_3]^+$ also observed.

In order to confirm the proposed structure and determine the nature of the hydrogen bonding present an X-ray analysis of complex **3b** was undertaken. Single crystals were prepared from the slow diffusion of hexane into a tetrahydrofuran (thf) solution. The structure analysis shows there to be two crystallographically independent cations in the asymmetric unit. Both molecules have essentially identical conformations and are each hydrogen bonded by N–H···O linkages to two nitrate anions. The hydrogen-bonding geometries are virtually identical for the two independent species (Fig. 3), with one nitrate hydrogen bonded to the two NH_3 ligands *via* lone pairs on two oxygen atoms and the other hydrogen bonded to the two NH_3 ligands *via* two lone pairs on the same oxygen atom.

Selected bond lengths and angles are given in Table 3. Both platinum atoms have significantly distorted co-ordination geometries with *cis* angles at Pt in the ranges 82.1(4)–97.8(1)° for the first molecule and 83.0(4)–97.0(2)° for the second, the principal distortions being due to a contraction of the N–Pt–N angles and an expansion of those for P–Pt–P. There are marked departures from planarity for the platinum co-ordination, *ca.* 0.1 Å for the two molecules. The Pt–N distances, which range between 2.092(8) and 2.112(8) and Pt–P distances, between 2.260(4) and 2.276(4) Å, are normal. There are no other significant intermolecular packing interactions other than normal van der Waals forces.

Reaction of $[Pt(PR_3)_2(CO_3)]$ with $PhC\equiv CCO_2H$

In an attempt to prepare carboxylate complexes containing additional functionalities, $[Pt(PPh_3)_2(CO_3)]$ and $[Pt(dppe)-(CO_3)]$ were treated with $PhC\equiv CCO_2H$ under the same conditions as those which gave rise to complexes **1a–1d**. In both cases only one product was observed in the $^{31}P-\{^1H\}$ NMR spectrum, though the magnitude of the $^1J(PPt)$ coupling constants (2331 Hz for the PPh_3 derivative and 2280 Hz for the dppe derivative) strongly suggested that the ligand *trans* to phosphorus was, in
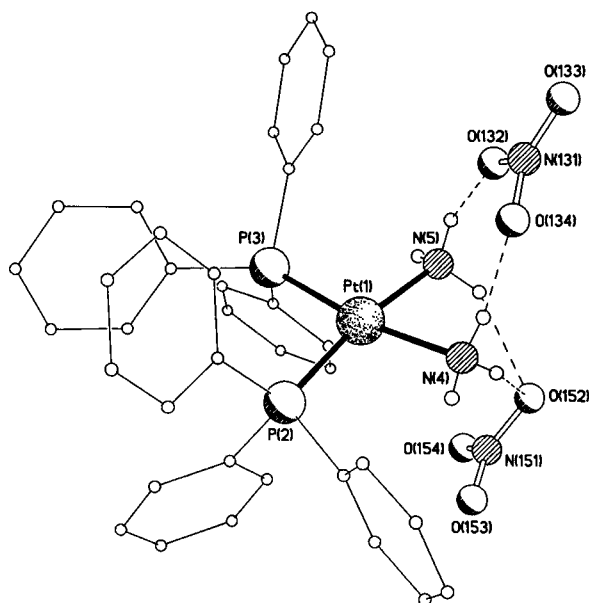
Fig. 3 Solid-state structure of one of the independent cation–anion groups in complex **3b**. The hydrogen-bond distances (Å) and angles (°) are N(5)···O(132) 2.84, H···O(132) 2.00 and N(5)–H···O(132) 157, N(4)···O(134) 2.99, H···O(134) 2.17 and N(4)–H···O(134) 152, N(4)···O(152) 2.89, H···O(152) 2.07 and N(4)–H···O(152) 153, N(5)···O(152) 2.96, H···O(152) 2.15 and N(5)–H···O(152) 150. For the other independent cation–anion grouping the equivalent hydrogen bond distances (Å) and angles (°) are N(9)···O(144) 2.87, H···O(144) 2.04 and N(9)–H···O(144) 156, N(10)···O(143) 2.94, H···O(143) 2.10 and N(10)–H···O(143) 158, N(10)···O(162) 2.92, H···O(162) 2.11 and N(10)–H···O(162) 151, N(9)···O(162) 3.00, H···O(162) 2.20 and N(9)–H···O(162) 149

both cases, exerting a considerably greater *trans* influence than that of a carboxylate oxygen. The NMR together with FAB mass spectral and microanalytical data has enabled the complexes to be identified as $[Pt(PPh_3)_2(C≡CPh)_2]$ **6** and $[Pt(dppe)(C≡CPh)_2]$ **7**. The previously reported [18] coupling constant for *trans*-$[Pt(PPh_3)_2(C≡CPh)_2]$ is larger than that observed here by over 650 Hz, suggesting that **6** is the previously unreported *cis* isomer. This is supported by the similarity of the coupling constants for **6** and **7**, the chelating dppe ligand constraining the phenylalkynyl ligands to a *cis* geometry in **7**. In the reactions loss of CO_2 has occurred from both the carbonate and the carboxylate to give rise to the bis(phenylalkynyl) complexes.

Conclusion

The above results demonstrate that it is possible to use the reaction of a platinum bis(phosphine) carbonate and a rigid dicarboxylic acid to give rise to dinuclear structures containing clefts which may be capable of interaction with another molecule, *via* the two π systems. However, not all carboxylic acids react to give bis(carboxylate) complexes: with $PhC≡CCO_2H$ loss of CO_2 occurs leading to bis(phenylalkynyl) complexes.

It has also been shown that NH_4^+ is acidic enough to compete with carboxylic acids in the reaction with $[PtL_2(CO_3)]$, so that in the presence of NH_4^+ reactions lead to dinuclear compounds which contain both ammonia and carboxylate ligands. This observation led to the prediction, subsequently realised, that the reaction of a platinum bis(phosphine) carbonate with NH_4^+ provides a general route to compounds of the type *cis*-$[Pt(PR_3)_2(NH_3)_2]^{2+}$. Such compounds, although containing perhaps the two most common ligands in platinum chemistry, have not previously been fully characterised.

Experimental

Reactions were routinely carried out using Schlenk-line tech-

niques under pure dry dinitrogen using dioxygen-free solvents, but no special precautions were taken to exclude oxygen during work-up procedures. Microanalyses (C, H and N) were carried out by the Imperial College Microanalytical Service. Infrared spectra were recorded on a Perkin-Elmer 1720 spectrometer as KBr pellets, ^{1}H and ^{31}P-{^{1}H} NMR spectra on a JEOL JNM-EX270 spectrometer operating at 270 MHz referenced to $SiMe_4$ and at 109.4 MHz referenced to H_3PO_4, respectively, [15]N-{[1]H} and [195]Pt spectra on a JEOL-EX400 spectrometer operating at 40.5 MHz referenced to $MeNO_2$ and at 85.6 MHz referenced to H_2PtCl_6·xH_2O, respectively and FAB mass spectra on a VG AutoSpec-Q spectrometer using 3-nitrobenzyl alcohol as the matrix.

The complexes $[Pt(PPh_3)_2(CO_3)]$,[2] $[Pt(PEt_3)_2(CO_3)]$[19] and $[Pt(dppe)(CO_3)]$[19] were prepared by the standard literature methods.

Reactions of $[Pt(PPh_3)_2(CO_3)]$

With $C_6H_4(CO_2H)_2$-1,4: synthesis of $[\{Pt(PPh_3)_2\}_2\{\mu-1,4-(O_2C)_2C_6H_4\}_2]$ 1a. The complex $[Pt(PPh_3)_2(CO_3)]$ (0.200 g, 0.26 mmol) and terephthalic acid (0.041 g, 0.25 mmol) were dissolved/suspended in ethanol (30 cm³) and the mixture stirred in darkness for 24 h. The solution was filtered and the colourless solid recrystallised from dichloromethane–diethyl ether to give crystals of $[\{Pt(PPh_3)_2\}_2\{\mu-1,4-(O_2C)_2C_6H_4\}_2]$ (Found: C, 56.7; H, 3.85. $C_{88}H_{68}O_8P_4Pt_2$·0.75CH_2Cl_2 requires C, 56.7; H, 3.8%); $\tilde{\nu}_{max}/cm^{-1}$ (CO_2) 1619s and 1325vs; $\delta_P(CDCl_3)$ 7.1 [s, $^1J(PPt)$ 3830 Hz]; $\delta_H(CDCl_3)$ 7.7–6.9 (m, aryl); m/z 1767 (M^+), 885 ($[Pt(PPh_3)_2\{1,4-(O_2C)_2C_6H_4\}H]^+$) and 718 $\{[Pt(PPh_3)_2]^+\}$.

With $C_6H_4(CO_2H)_2$-1,3: synthesis of $[\{Pt(PPh_3)_2\}_2\{\mu-1,3-(O_2C)_2C_6H_4\}_2]$ 1b. The complex $[Pt(PPh_3)_2(CO_3)]$ (0.200 g, 0.26 mmol) and isophthalic acid (0.041 g, 0.25 mmol) were dissolved/suspended in ethanol (30 cm³) and the mixture stirred in darkness for 24 h. The solution was filtered and the colourless solid recrystallised from dichloromethane–diethyl ether to give crystals of $[\{Pt(PPh_3)_2\}_2\{\mu-1,3-(O_2C)_2C_6H_4\}_2]$ (Found: C, 55.8; H, 3.85. $C_{88}H_{68}O_8P_4Pt_2$·2CH_2Cl_2 requires C, 55.8; H, 3.75%); $\tilde{\nu}/cm^{-1}$ (CO_2) 1624s and 1325vs; $\delta_P(CDCl_3)$ 6.9 [s, $^1J(PPt)$ 3876 Hz]; $\delta_H(CDCl_3)$ 7.7–6.9 (m, aryl); m/z 1768 (M^+), 885 ($[Pt(PPh_3)_2\{1,3-(O_2C)_2C_6H_4\}H]^+$) and 718 $\{[Pt(PPh_3)_2]^+\}$.

With *trans,trans*-muconic acid: synthesis of $[\{Pt(PPh_3)_2\}_2(\mu$-*trans,trans*-$O_2CCH=CHCH=CHCO_2)_2]$ 1c. The complex $[Pt(PPh_3)_2(CO_3)]$ (0.100 g, 0.13 mmol) and *trans-trans*-muconic acid (0.018 g, 0.13 mmol) were dissolved/suspended in ethanol (30 cm³) and the mixture stirred in darkness for 24 h. The solution was filtered and the colourless solid recrystallised from dichloromethane–hexane to give microcrystals of $[\{Pt(PPh_3)_2\}_2(\mu$-*trans,trans*-$O_2CCH=CHCH=CHCO_2)_2]$ (Found: C, 55.0; H, 3.95. $C_{84}H_{68}O_8P_4Pt_2$·2CH_2Cl_2 requires C, 54.7; H, 3.85%); $\tilde{\nu}_{max}/cm^{-1}$ (CO_2) 1624s and 1321vs; $\delta_P(CDCl_3)$ 6.6 [s, $^1J(PPt)$ 3832 Hz]; $\delta_H(CDCl_3)$ 7.8–7.0 (m, aryl and CH) and 6.4 (m, CH); m/z 1719 (M^+), 860 $\{[Pt(PPh_3)_2(O_2CCH=CHCH=CHCO_2)H]^+\}$ and 718 $\{[Pt(PPh_3)_2]^+\}$.

With 4,4′-biphenyldicarboxylic acid: synthesis of $[\{Pt(PPh_3)_2\}_2(\mu$-$O_2CC_6H_4C_6H_4CO_2)_2]$ 1d. The complex $[Pt(PPh_3)_2(CO_3)]$ (0.100 g, 0.13 mmol) and 4,4′-biphenyldicarboxylic acid (0.031 g, 0.13 mmol) were dissolved/suspended in ethanol (30 cm³) and the mixture stirred in darkness for 40 h. The solution was filtered and the colourless solid recrystallised from dichloromethane–diethyl ether to give crystals of $[\{Pt(PPh_3)_2\}_2(\mu$-$O_2CC_6H_4C_6H_4CO_2)_2]$ (Found: C, 57.8; H, 4.15. $C_{100}H_{76}O_8P_4Pt_2$·2.5CH_2Cl_2 requires C, 57.7; H, 3.85%); $\tilde{\nu}_{max}/cm^{-1}$ (CO_2) 1618s and 1335vs; $\delta_P(CDCl_3)$ 7.0 [s, $^1J(PPt)$ 3844 Hz]; $\delta_H(CDCl_3)$ 7.8–7.0 (m, aryl); m/z 718 $\{[Pt(PPh_3)_2]^+\}$.

With $C_6H_4(CO_2H)_2$-1,4 and NH_4PF_6: synthesis of $[\{Pt(PPh_3)_2(NH_3)\}_2\{\mu-1,4-(O_2C)_2C_6H_4\}][PF_6]_2$ 2. The complex

[Pt(PPh₃)₂(CO₃)] (0.200 g, 0.26 mmol), terephthalic acid (0.041 g, 0.25 mmol) and NH_4PF_6 (0.200 g, 1.2 mmol) were dissolved/suspended in ethanol (30 cm³) and the mixture stirred for 35 h. The solution was filtered and the colourless solid recrystallised from dichloromethane–diethyl ether to give crystals of [{Pt-(PPh₃)₂(NH₃)}₂{μ-1,4-(O₂C)₂C₆H₄}][PF₆]₂ (Found: C, 46.0; H, 3.3; N, 1.25. $C_{80}H_{70}N_2O_4P_4Pt_2 \cdot 3CH_2Cl_2$ requires C, 45.7; H, 3.5; N, 1.3%); $\tilde{\nu}_{max}/cm^{-1}$ 3356s (NH₃), 1598s and 1313s (CO₂), 838vs (PF₆); δ_P(CDCl₃) 10.1 [d, ^1J(PPt) 3530, ^2J(PP) 22] and 6.7 [d, ^1J(PPt) 3659, ^2J(PP) 22 Hz]; δ_H(CDCl₃) 7.8–6.8 (64 H, m, aryl) and 3.40 [6 H, s (br), NH]; m/z 1357 ([$M - PPh_3 - NH_3$]⁺), 1340 ([$M - PPh_3 - 2NH_3$]⁺), 883 ([Pt(PPh₃)₂{(O₂C)₂C₆H₄}]⁺), 736 {[Pt(PPh₃)₂(NH₃)]⁺} and 719 {[Pt(PPh₃)₂]⁺}.

With NH₄PF₆: synthesis of *cis*-[Pt(PPh₃)₂(NH₃)₂][PF₆]₂ 3a. The complex [Pt(PPh₃)₂(CO₃)] (0.100 g, 0.13 mmol) and NH_4PF_6 (0.200 g, 1.2 mmol) were dissolved in ethanol (30 cm³) and stirred for 24 h. The solvent was removed *in vacuo* and the product extracted with dichloromethane (3 × 5 cm³). The dichloromethane volume was then reduced *in vacuo* and hexane added to give colourless crystals of *cis*-[Pt(PPh₃)₂(NH₃)₂]-[PF₆]₂ Found: C, 41.2; H, 3.45; N, 2.55. $C_{36}H_{36}F_{12}N_2P_4Pt$ requires C, 41.4; H, 3.5; N, 2.7%); $\tilde{\nu}_{max}/cm^{-1}$ (NH₃) 3342s and 3274s; $\tilde{\delta}_{max}/cm^{-1}$ (NH₃) 1623s; $\tilde{\nu}_{max}/cm^{-1}$ (PF₆) 833vs; δ_P(CDCl₃) 7.8 [s, ^1J(PPt) 3428 Hz]; δ_H(CDCl₃) 7.5 (30 H, m, Ph) and 3.15 [6 H, s (br), NH]; m/z 898 ([$M + PF_6$]⁺), 754 ([$M + H$]⁺), 737 ([$M - NH_3 + H$]⁺), 719 ([$M - 2NH_3$]⁺) and 377 (M^{2+}).

With NH₄NO₃: synthesis of *cis*-[Pt(PPh₃)₂(NH₃)₂][NO₃]₂ 3b. The procedure was as above using [Pt(PPh₃)₂(CO₃)] (0.150 g, 0.19 mmol) and NH_4NO_3 (0.045 g, 0.56 mmol) (Found: C, 47.1; H, 4.3; N, 6.0. $C_{36}H_{36}N_4O_6P_2Pt \cdot 0.5CH_2Cl_2$ requires C, 47.6; H, 4.05; N, 6.1%); $\tilde{\nu}_{max}/cm^{-1}$ (NH₃) 3436s and 3335m; $\tilde{\delta}_{max}/cm^{-1}$ (NH₃) 1625s; $\tilde{\nu}_{max}/cm^{-1}$ (NO₃) 1384vs and 1313s; δ_P(CDCl₃) 9.3 [s, ^1J(PPt) 3361 Hz]; δ_H(CDCl₃) 7.4 (30 H, m, Ph) and 4.28 [6 H, s (br), NH]; m/z 781 ([$M - 2NH_3 + NO_3$]⁺), 737 ([$M - NH_3$]⁺), 719 ([$M - 2NH_3$]⁺) and 377 (M^{2+}).

With ¹⁵NH₄NO₃: synthesis of *cis*-[Pt(PPh₃)₂(¹⁵NH₃)₂][NO₃]₂. The procedure was as above using [Pt(PPh₃)₂(CO₃)] (0.100 g, 0.13 mmol) and $^{15}NH_4NO_3$ (0.030 g, 0.38 mmol). δ_P(CDCl₃) 9.3 [m, ^1J(PPt) 3361, ^2J(PP) 22, ^2J(PN$_{trans}$) 39, ^2J(PN$_{cis}$) −1]; δ_N(CDCl₃) −378.5 [m, ^1J(NPt) 194, ^2J(PP) 22, ^2J(PN$_{trans}$) 39, ^2J(PN$_{cis}$) −1]; δ_H(CDCl₃) 7.4 (30 H, m, Ph) and 4.28 [6 H, m, NH, ^1J(HN) 72, ^2J(HPt) 32, ^3J(HP$_{trans}$) 3]; δ_{Pt}(CDCl₃) −4452 [tt, ^1J(PPt) 3361, ^1J(NPt) 194 Hz].

With PhC≡CCO₂H: synthesis of *cis*-[Pt(PPh₃)₂(C≡CPh)₂] 6. The complex [Pt(PPh₃)₂(CO₃)] (0.100 g, 0.13 mmol) and phenyl-propiolic acid (0.050 g, 0.34 mmol) were dissolved/suspended in ethanol (30 cm³) and the mixture stirred in darkness for 16 h. The solution was filtered and the colourless solid recrystallised from dichloromethane–hexane to give crystals of *cis*-[Pt(PPh₃)₂-(C≡CPh)₂] (Found: C, 67.5; H, 4.35. $C_{52}H_{40}P_2Pt$ requires C, 67.7; H, 4.35%); $\tilde{\nu}_{max}/cm^{-1}$ (C≡C) 2119s; δ_P(CDCl₃) 17.3 [s, ^1J(PPt) 2331] {*cf.* sample prepared by literature method, *trans*-[Pt(PPh₃)₂(C≡CPh)₂], δ 17.3 [s, ^1J(PPt) 2988 Hz][18]}; δ_H(CDCl₃) 7.6–6.8 (m, aryl); m/z 922 ([$M + H$]⁺), 820 ([$M - C_2Ph$]⁺) and 719 ([$M - 2C_2Ph$]⁺).

Reactions of [Pt(PEt₃)₂(CO₃)]

With NH₄PF₆: synthesis of *cis*-[Pt(PEt₃)₂(NH₃)₂][PF₆]₂ 4a. The procedure was as for complex **3a** using [Pt(PEt₃)₂(CO₃)] (0.100 g, 0.20 mmol) and NH_4PF_6 (0.120 g, 0.74 mmol) (Found: C, 19.5; H, 4.5; N, 3.4. $C_{12}H_{36}F_{12}N_2P_4Pt$ requires C, 19.1; H, 4.8; N, 3.7%); $\tilde{\nu}_{max}/cm^{-1}$ (NH₃) 3356s and 3294s; $\tilde{\delta}_{max}/cm^{-1}$ (NH₃) 1637s; $\tilde{\nu}_{max}/cm^{-1}$ (PF₆) 837vs; δ_P(CDCl₃–CH₂Cl₂) 1.9 [s, ^1J(PPt) 3212 Hz]; δ_H(CD₃COCD₃) 4.4 [6 H, s (br), NH], 2.28 (12 H, dq, CH₂) and 1.31 (18 H, dt, CH₃); m/z 466 ([$M + H$]⁺), 448 ([$M - NH_3$]⁺) and 431 ([$M - 2NH_3$]⁺).

With NH₄NO₃: synthesis of *cis*-[Pt(PEt₃)₂(NH₃)₂][NO₃]₂ 4b. The complex [Pt(PEt₃)₂(CO₃)] (0.100 g, 0.20 mmol) and NH_4NO_3 (0.049 g, 0.61 mmol) were dissolved in ethanol (30 cm³) and stirred for 24 h. The solvent volume was reduced *in vacuo* and diethyl ether added to give colourless microcrystals of *cis*-[Pt(PEt₃)₂(NH₃)₂][NO₃]₂ (Found: C, 24.6; H, 5.9; N, 9.4. $C_{12}H_{36}N_4O_6P_4Pt$ requires C, 24.5; H, 6.15; H, 9.5%); $\tilde{\nu}_{max}/cm^{-1}$ (NH₃) 3252s, 3184s and 3116s; $\tilde{\delta}_{max}/cm^{-1}$ (NH₃) 1638s; $\tilde{\nu}_{max}/cm^{-1}$ (NO₃) 1383vs and 1327s; δ_P(CD₃OD) 3.1 [s, ^1J(PPt) 3127 Hz]; δ_H(CD₃COCD₃) 4.6 [6 H, s (br), NH], 2.23 (12 H, m, CH₂) and 1.29 (18 H, m, CH₃); m/z 493 ([$M - 2NH_3 + NO_3$]⁺), 466 ([$M + H$]⁺), 448 ([$M - NH_3$]⁺) and 431 ([$M - 2NH_3$]⁺).

Reactions of [Pt(dppe)(CO₃)]

With NH₄PF₆: synthesis of [Pt(dppe)(NH₃)₂][PF₆]₂ 5a. The procedure was as for complex **3a** using [Pt(dppe)(CO₃)] (0.100 g, 0.15 mmol) and NH_4PF_6 (0.200 g, 1.2 mmol) (Found: C, 34.0; H, 3.15; N, 2.85. $C_{26}H_{30}F_{12}N_2P_4Pt$ requires C, 34.0; H, 3.3; N, 3.05%); $\tilde{\nu}_{max}/cm^{-1}$ (NH₃) 3339s and 3286s; $\tilde{\delta}_{max}/cm^{-1}$ (NH₃) 1633s; $\tilde{\nu}_{max}/cm^{-1}$ (PF₆) 840vs; δ_P(CDCl₃–CH₂Cl₂) 40.2 [s, ^1J(PPt) 3340 Hz]; δ_H(CD₃COCD₃) 8.2–7.6 (20 H, m, Ph), 4.48 [6 H, s (br), NH] and 2.9 (4 H, m, CH₂); m/z 772 ([$M + PF_6$]⁺), 628 ([$M + H$]⁺), 610 ([$M - NH_3$]⁺) and 593 ([$M - 2NH_3$]⁺).

With PhC≡CCO₂H: synthesis of [Pt(dppe)(C≡CPh)₂] 7. The complex [Pt(dppe)(CO₃)] (0.100 g, 0.13 mmol) and phenyl-propiolic acid (0.050 g, 0.34 mmol) were dissolved/suspended in ethanol (30 cm³) and the mixture stirred in darkness for 16 h. The solution was filtered and the colourless solid recrystallised from dichloromethane–hexane to give crystals of [Pt(dppe)-(C≡CPh)₂] (Found: C, 63.6; H, 4.4. $C_{42}H_{34}P_2Pt$ requires C, 63.4; H, 4.3%); $\tilde{\nu}_{max}/cm^{-1}$ (C≡C) 2109s; δ_P(CDCl₃) 41.7 [s, ^1J(PPt) 2280] {*cf.* δ 41.1 [s, ^1J(PPt) 2280 Hz][18]}; δ_H(CDCl₃) 8.0–7.0 (m, 30 H, aryl) and 2.43 (m, 4 H, CH₂); m/z 796 ([$M + H$]⁺), 694 ([$M - C_2Ph$]⁺) and 593 ([$M - 2C_2Ph$]⁺).

Reaction of complex 1a with NH₄PF₆

Complex **1a** (0.100 g, 0.057 mmol) was dissolved in dichloromethane (20 cm³) and NH_4PF_6 (0.100 g, 0.61 mmol) in ethanol (5 cm³) added. The mixture was stirred for 72 h and the solvent removed *in vacuo*. The ^{31}P-{^1H} NMR spectrum showed a 55:45 mixture of **1a** and **2**. Repeating with more NH_4PF_6 (0.100 g) over 48 h led to no change in the product distribution.

Crystallography

Table 4 provides a summary of the crystal data, data collection and refinement parameters for complexes **1b**, **2** and **3b**. Structures **1b** and **2** were solved by the heavy-atom method, **3b** by direct methods and all three were refined by full-matrix least squares based on F^2. Despite collecting data at reduced temperature, the scattering of complex **1b** was very weak, and as a consequence only the platinum and phosphorus atoms could be refined anisotropically. For **2** and **3b**, however, all the full-occupancy non-hydrogen atoms of the ionic species were refined anisotropically; the single unique PF₆ anion in **2** was disordered and was refined isotropically in two alternative partial-occupancy orientations. All the structures contain a mixture of ordered and disordered, full and partial occupancy solvent molecules which were refined isotropically. The phenyl rings of the triphenylphosphine ligands were refined as idealised rigid bodies. The NH protons in **2** and **3b** were located from difference electron-density maps and optimised to tetrahedral geometries (N–H 0.90 Å). The C–H hydrogen atoms of each structure were placed in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system.[20]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallo-

Table 4 Crystal data, data collection and refinement parameters [a] for complexes **1b**, **2** and **3b**

	1b	**2**	**3b**
Formula	$C_{88}H_{68}O_8P_4Pt_2$	$C_{80}H_{70}F_{12}N_2O_4P_6Pt_2$	$C_{36}H_{36}N_4O_6P_2Pt$
Solvent	$CH_2Cl_2 \cdot 0.5Et_2O \cdot 0.5H_2O$	$4CH_2Cl_2$	$0.875thf$
M	2068.3	2267.1	940.8
Colour, habit	Clear blocky needles	Clear needles	Clear plates
Crystal size/mm	$0.20 \times 0.20 \times 0.17$	$0.63 \times 0.23 \times 0.23$	$0.63 \times 0.36 \times 0.07$
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
T/K	203	173	253
a/Å	21.154(3)	10.548(3)	26.63(3)
b/Å	17.518(10)	20.092(2)	26.93(3)
c/Å	27.114(4)	21.014(4)	24.77(3)
β/°	108.81(1)	99.40(2)	108.26(11)
U/Å^3	9512(6)	4394(2)	16 864(29)
Z	4	2 [b]	16 [c]
D_c/g cm^{-3}	1.444	1.714	1.482
$F(000)$	4112	2236	7536
μ/mm^{-1}	3.226	3.609	3.454
θ Range/°	1.9–22.5	2.0–23.0	1.8–23.0
No. measured reflections	12 441	6087	11 739
No. observed reflections $[|F_o| > 4\sigma(|F_o|)]$	5779	4671	7633
Absorption correction	Empirical	Gaussian	Gaussian
Maximum, minimum transmission	0.7878, 0.2570	0.4828, 0.4331	0.7981, 0.3273
No. variables	376	455	812
$R1$ [d]	0.105	0.052	0.059
$wR2$ [e]	0.211	0.111	0.134
Weighting factors a, b [f]	0.084, 187.876	0.000, 90.000	0.069, 126.433
Largest difference peak, hole/e Å^{-3}	1.45, -1.28	1.89, -1.56	1.32, -0.67

[a] Details in common: graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\ 73$ Å); ω scans; Siemens P4/PC diffractometer; monoclinic. [b] The molecule has crystallographic C_i symmetry. [c] There are two crystallographically independent molecules in the asymmetric unit. [d] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [e] $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [f] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

References

1 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984.
2 C. J. Nyman, C. E. Wymore and G. Wilkinson, *J. Chem. Soc. A*, 1968, 561.
3 J.-P. Laurant and B. Morvan, *J. Chem. Soc., Dalton Trans.*, 1993, 2141.
4 A. L. Tan, P. M. N. Low, Z.-Y. Zhou, W. Zheng, B.-M. Wu, T. C. K. Mak and T. S. A. Hor, *J. Chem. Soc., Dalton Trans.*, 1996, 2207.
5 M. A. Andrews, E. J. Voss, G. L. Gould, W. T. Klooster and T. F. Koetzle, *J. Am. Chem. Soc.*, 1994, **116**, 5730.
6 D. W. Dockter, P. E. Fanwick and C. P. Kubiak, *J. Am. Chem. Soc.*, 1996, **118**, 4846.
7 S. K. Mauldin, I. Husain, A. Sancar and S. G. Chang, *Cancer Res.*, 1986, **46**, 2876.
8 M. Fujita and K. Ogura, *Coord. Chem. Rev.*, 1996, **148**, 249.
9 C. Bird, B. L. Booth, B. N. Haszeldine, G. R. H. Neuss, M. A. Smith and A. Flood, *J. Chem. Soc., Dalton Trans.*, 1982, 1109.
10 M. V. Capparelli, D. M. L. Goodgame, R. T. Riley and A. C. Skapski, *Inorg. Chim. Acta*, 1982, **67**, L9.
11 U. Niemann, J. Diebold, C. Troll, U. Rief and H.-H. Brintzinger, *J. Organomet. Chem.*, 1993, **456**, 195.
12 M. I. Gel'fman and N. A. Kuslova, *Koord. Khim.*, 1979, **5**, 1402; *Chem. Abstr.*, 1979, **91**, 203546J.
13 J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 1956, 2712.
14 H. M. Colquhoun, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 847.
15 D. R. Alston, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams and R. Zarzycki, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1184.
16 R. G. Gunther and D. S. Martin, jun., *Inorg. Chim. Acta*, 1972, **6**, 81.
17 F. R. Hartley, S. G. Murray and A. Wilkinson, *Inorg. Chem.*, 1989, **28**, 549.
18 G. K. Anderson and G. J. Lumetta, *J. Organomet. Chem.*, 1985, **295**, 257.
19 C. Eaborn, A. Pidcock and B. R. Steele, *J. Chem. Soc., Dalton Trans.*, 1975, 809.
20 SHELXTL PC version 5.03, Siemens Analytical X-Ray Instruments, Madison, WI, 1994.