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Synthesis and electrospray mass spectrometry of platinum(II) complexes of 5,5-diethylbarbituric acid (Hdebarb); crystal structure of *cis*-[PtCl(debarb)(PPh_3)$_2$]·CH_2Cl_2

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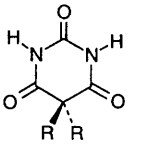
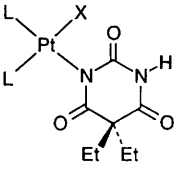
The reactions of 5,5-diethylbarbituric acid (Hdebarb; 1*H*,3*H*,5*H*-5,5-diethylpyrimidine-2,4,6-trione), either as the monosodium salt or free acid in the presence of ancillary base (silver oxide or triethylamine), with platinum(II) halide complexes yielded mono(barbiturato) complexes *cis*-[PtX(debarb)L_2] [X = Cl, Br or I; L = PPh_3; L_2 = 1,2-bis(diphenylphosphino)ethane (dppe) or 1,1′-bis(diphenylphosphino)ferrocene (dppf)]. A single-crystal structure determination of *cis*-[PtCl(debarb)(PPh_3)$_2$]·CH_2Cl_2 showed that the plane of the N-bonded barbiturate ligand is approximately perpendicular to the platinum co-ordination square plane, rendering the two ethyl substituents inequivalent. Electrospray mass spectrometry has also been used to study these complexes, with the major ions for *cis*-[PtX(debarb)L_2] being [Pt(debarb)L_2]$^+$ and [Pt(debarb)(NCMe)L_2]$^+$, though molecular ions [M + H]$^+$ are also observed for all complexes. A number of cationic derivatives of the type [Pt(debarb)L_2L']$^+$ (L = PPh_3 or L_2 = dppe; L′ = pyridine or PPh_3) are also reported.

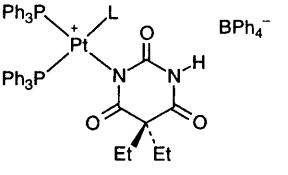
Over the years there has been a continuous interest in the chemistry of metal complexes of biologically important ligands. The study of such complexes may lead to a greater understanding of the role of the ligand in biological systems, and may also contribute to the development of new metal-based chemotherapeutic agents. The barbituric acids **I** are one such class of biologically active compounds the co-ordination chemistry of which has been investigated, since such metal complexes are important in the detection and identification of the barbiturate drugs. Barbituric acids can co-ordinate through one or both deprotonated nitrogen atoms, and/or ketone oxygens and, in the parent barbituric acid **Ia**, (1*H*,3*H*,5*H*-pyrimidine-2,4,6-trione), through a deprotonated CH_2 group, potentially giving a diverse range of metal complexes. Most studies have concentrated on the first-row transition metals,[1] and relatively few studies have concerned barbituric acid complexes of the platinum-group metals[2] or silver and gold.[3] A number of platinum-group metal and other transition-metal complexes of related ligands such as violuric acid (1*H*,3*H*-pyrimidine-2,4,5,6-tetrone 5-oxime) and purpuric {5-[hexahydro-2,4,6-trioxopyrimidin-5-yl)imino]-2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrione} acids have been reported.[4] Platinum barbiturato complexes containing ancillary amine ligands have been found to have antitumour activity.[5] In this paper we describe some platinum(II) complexes of 5,5-diethylbarbituric acid **Ib** (otherwise known as barbitone or veronal) containing ancillary phosphine ligands.



Ia R = H
Ib R = Et



1a L = PPh_3; X = Cl
1b L_2 = dppe; X = Cl
1c L_2 = dppf; X = Cl
1d L = PPh_3; X = Br
1e L = PPh_3; X = I



2a L = pyridine
2b L = PPh_3

Results and Discussion

The reactions between the platinum(II) halide complexes *cis*-[$PtCl_2L_2$] [L = PPh_3, L_2 = 1,2-bis(diphenylphosphino)-ethane (dppe) or 1,1′-bis(diphenylphosphino)ferrocene (dppf)] with the monosodium salt of 5,5-diethylbarbituric acid **Ib**, Na(debarb), proceeds smoothly in hot methanol or tetrahydrofuran (thf)–methanol, followed by evaporation and extraction from by-product NaCl, to give good yields of the monoamide complexes **1a**–**1c**. The analogous bromo and iodo complexes **1d** and **1e** can be prepared in analogous fashion, starting from the appropriate [$PtX_2(PPh_3)_2$] complex. The complexes have been characterised by their ^{31}P-{^1H}, ^{13}C-{^1H} and ^1H NMR and IR spectroscopic properties, electrospray mass spectrometry, elemental microanalysis, and by a single-crystal X-ray diffraction study carried out on the triphenylphosphine complex **1a**. Attempted metathetical displacement of the chloro ligand of **1a** by reaction with an excess of LiBr in acetone resulted in displacement of the barbiturate ligand, and the complex *cis*-[$PtBr_2(PPh_3)_2$] was identified by ^{31}P NMR spectroscopy. Similar one-pot reactions with pyridine (py) or triphenylphosphine with *cis*-[$PtCl_2(PPh_3)_2$], Na(debarb), and $NaBPh_4$ in methanol gave the cationic barbiturato complexes *cis*-[Pt(debarb)(py)(PPh_3)$_2$]BPh_4 **2a** and [Pt(debarb)-(PPh_3)$_3$]BPh_4 **2b** respectively.

Alternative syntheses of the barbiturato complexes have been investigated. Addition of an excess of triethylamine to a dichloromethane solution of *cis*-[$PtCl_2(PPh_3)_2$] to which 1

mol equivalent of **Ib** had been added resulted in rapid dissolution of the barbituric acid. After evaporation of the solvent, ^{31}P NMR spectroscopy showed the mono(barbiturato) complex **1a** to be the only phosphorus-containing product formed. We also wished to explore the use of silver(I) oxide in the synthesis of barbiturato complexes. This reagent has found utility in the synthesis of platinum(II) and palladium(II) amido complexes starting from metal halide complexes.[6] Reaction of *cis*-[$PtCl_2(PPh_3)_2$] with 1 mole equivalent of **Ib** and an excess of silver(I) oxide in refluxing dichloromethane proceeds slowly (presumably as a result of the insolubility of **Ib** in this solvent) giving a mixture of products. The major product, identified by ^{31}P NMR spectroscopy was **1a**. This can be isolated in a pure state from the mixture of products by several recrystallisations from CH_2Cl_2–light petroleum, and had identical NMR spectroscopic properties to those of samples prepared *via* the alternative routes described herein. Crystals of X-ray quality were obtained in this manner and subjected to a single-crystal X-ray diffraction study.

The molecular structure of the complex is shown in Fig. 1, which also gives the crystallographic atom numbering scheme. Selected bond distances and angles are in Table 1. The complex crystallises with one molecule of dichloromethane; there are no close contacts between them.

The barbiturate ligand is bonded to the platinum atom *via* one of the amide nitrogens (as opposed to the harder oxygen atoms), and the plane of the ligand is approximately perpendicular to the platinum co-ordination plane. This is illustrated by the torsion angles Cl(1)–Pt–N(1)–C(1) and Cl(1)–Pt–N(1)–C(4) which are −73.1 and 96° respectively. It seems reasonable that tipping of the barbiturate ligand out of perpendicularity occurs as a result of a steric interaction with a phenyl ring on P(2). A consequence of the perpendicularity of the two planes is that the two ethyl groups are inequivalent, one being directed towards the chloride ligand and the other towards a phenyl ring on P(2), as illustrated in Fig. 2. The P(1)–Pt and P(2)–Pt bond distances are different [2.274(2) and 2.241(2) Å], consistent with the amide [*trans* to P(1)] having the slightly larger *trans* influence. The remaining structural features are unexceptional. Barbituric acids are well known for their strong tendency to associate through hydrogen bonding.[7] However, examination of the packing diagram for **1a** did not reveal any apparent three-dimensional superstructure. This is possibly as a result of the steric bulk imposed by the two triphenylphosphine ligands.

Table 1 Selected intramolecular bond distances (Å) and angles (°) for *cis*-[$PtCl(debarb)(PPh_3)_2$]·CH_2Cl_2 **1a** with estimated standard deviations (e.s.d.s) in parentheses

Platinum barbiturato moiety			
Pt–P(1)	2.274(2)	Pt–P(2)	2.241(2)
Pt–Cl(1)	2.353(2)	Pt–N(1)	2.077(4)
C(1)–N(1)	1.378(7)	C(1)–O(1)	1.210(7)
C(1)–C(2)	1.523(8)	C(2)–C(3)	1.514(8)
C(3)–O(2)	1.216(7)	C(3)–N(2)	1.370(8)
C(4)–N(2)	1.384(7)	C(4)–N(1)	1.362(6)
C(4)–O(3)	1.220(6)	C(2)–C(8)	1.554(10)
C(7)–C(8)	1.485(12)	C(2)–C(6)	1.522(10)
C(5)–C(6)	1.490(12)		
Pt–N(1)–C(1)	115.8(3)	Pt–N(1)–C(4)	121.2(4)
C(1)–N(1)–C(4)	122.1(5)	N(1)–C(1)–C(2)	120.8(5)
N(1)–C(1)–O(1)	119.5(5)	C(2)–C(1)–O(1)	119.7(5)
C(1)–C(2)–C(3)	113.4(5)	C(1)–C(2)–C(8)	107.6(6)
C(1)–C(2)–C(6)	110.0(5)	C(3)–C(2)–C(8)	106.8(5)
C(6)–C(2)–C(8)	106.3(6)	C(8)–C(2)–C(3)	106.8(5)
C(6)–C(2)–C(3)	112.4(6)	C(2)–C(8)–C(7)	116.6(7)
C(2)–C(6)–C(5)	114.6(7)	C(2)–C(3)–O(2)	122.1(6)
C(2)–C(3)–N(2)	117.3(5)	O(2)–C(3)–N(2)	120.6(6)
C(3)–N(2)–C(4)	126.1(5)	N(1)–C(4)–N(2)	118.6(5)
N(2)–C(4)–O(3)	119.3(5)	N(1)–C(4)–O(3)	122.1(5)
Triphenylphosphine ligands			
P(1)–C(11)	1.823(6)	P(1)–C(21)	1.829(6)
P(1)–C(31)	1.842(6)	P(2)–C(41)	1.824(5)
P(2)–C(51)	1.820(6)	P(2)–C(61)	1.835(6)
P(1)–Pt–P(2)	99.97(5)	N(1)–Pt–P(2)	92.56(13)
Cl(1)–Pt–N(1)	85.17(13)	Cl(1)–Pt–P(1)	83.05(6)
Cl(1)–Pt–P(2)	171.89(5)	P(1)–Pt–N(1)	166.59(13)
Pt–P(1)–C(11)	109.6(2)	Pt–P(1)–C(21)	108.7(2)
Pt–P(1)–C(31)	124.4(2)	Pt–P(2)–C(41)	115.5(2)
Pt–P(2)–C(51)	108.4(2)	Pt–P(2)–C(61)	115.7(2)
C(11)–P(1)–C(21)	109.8(3)	C(11)–P(1)–C(31)	104.0(3)
C(21)–P(1)–C(31)	99.6(3)	C(41)–P(2)–C(51)	110.8(3)
C(41)–P(2)–C(61)	100.0(3)	C(51)–P(2)–C(61)	105.9(3)

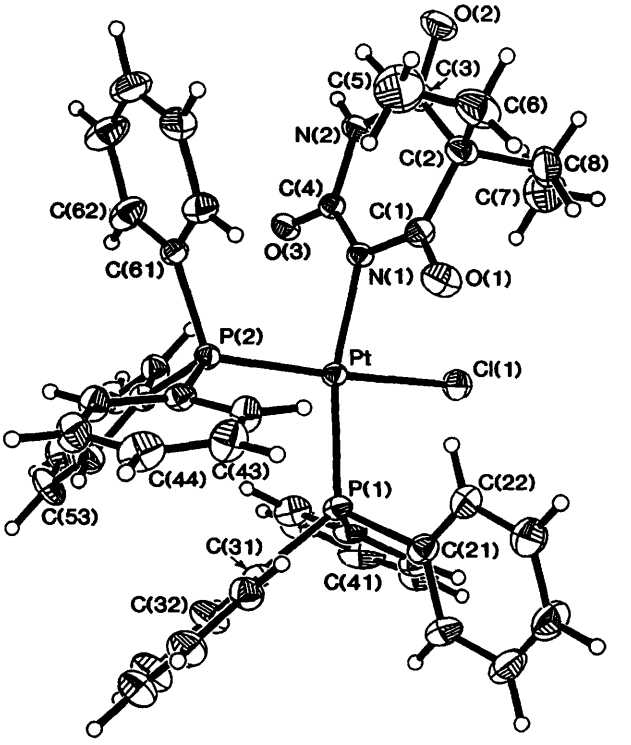


Fig. 1 Molecular structure of the complex *cis*-[$PtCl(debarb)(PPh_3)_2$]·CH_2Cl_2 **1a**, showing the atom numbering scheme. Atoms are shown as thermal ellipsoids at the 30% probability level, with the exception of the H atoms which are depicted as arbitrary spheres in their calculated positions. The dichloromethane molecule of crystallisation is not shown

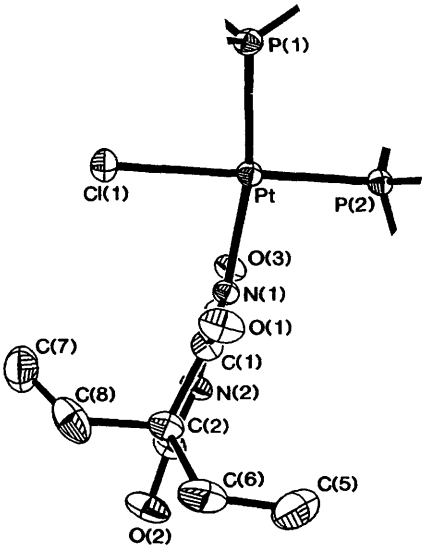


Fig. 2 Alternative view of the co-ordination geometry of the barbiturate ligand, clearly showing the inequivalence of the two ethyl groups. All phenyl rings have been removed for clarity

The ^{31}P-$\{^1H\}$ NMR spectra of the phosphine complexes show the expected AB patterns for two *cis*-phosphines *trans* to two ligands having differing *trans* influences. Thus for **1a** the two values of $^1J(PtP)$ are 3337 and 3950 Hz, and these are assigned to the phosphines *trans* to the barbiturate and chloride ligands respectively. The values of $^1J(PtP)$ for the phosphine ligands *trans* to the amide ligands are very comparable with those of other amido complexes. For example, for the complex *cis*-[PtMe{NHC(O)Me}(dppe)] the corresponding value of $^1J(PtP)$ is 3322 Hz.[8] It is noteworthy that the values of $^1J(PtP)$ for the phosphine ligands *trans* to the halide ligands increases in the order **1e** (I; 3196) < **1d** (Br, 3908) < **1a** (Cl, 3950 Hz), consistent with the iodide ligand having the highest *trans* influence in the series.

The ^1H and ^{13}C-$\{^1H\}$ NMR spectra of complexes **1a**–**1e** show two inequivalent ethyl substituents, consistent with restricted rotation about the Pt–N bond. In addition, the CH_2 resonances both show diastereotopism, and appear as two multiplets, rather than the expected simple quartet. This presumably arises as a result of the steric bulk of the barbiturate and triphenylphosphine ligands. Thus, in the ^1H NMR spectrum of **1a** CH_2 resonances were observed at δ 1.91 and 1.57, while methyl resonances were observed at δ 0.96 and 0.44. Similarly, in the ^{13}C-$\{^1H\}$ spectrum the CH_2 resonances appear at δ 33.4 and 26.5, while the difference in chemical shifts of the methyl carbons is smaller, appearing at δ 9.8 and 9.3. For comparison, the corresponding chemical shifts for CH_2 and CH_3 groups in the sodium salt of **1b** (recorded in D_2O solution) are as follows: ^1H; CH_2 (δ 2.05), CH_3 (δ 0.93). ^{13}C; CH_2 (δ 32.17) and CH_3 (δ 9.09). These data indicate that in the complex **1a** one of the ethyl groups is shielded. The solid-state structure indicates that one of the ethyl groups is directed towards a triphenylphosphine ligand, and therefore is likely to experience a ring-current shielding effect. Nuclear Overhauser effect (NOE) difference spectroscopy has been used to confirm this. For complex **1a**, irradiation of the methyl resonance at δ 0.45 produced a 2.2% NOE enhancement of the CH_2 resonance at δ 1.65, thus linking these two resonances to the same ethyl group. An enhancement of 2.1% was also observed for the phenyl protons. However, irradiation of the other methyl group at δ 0.96, while providing a 2.0% enhancement for the CH_2 resonance at δ 1.95 produced no enhancement of that of the phenyl protons. This clearly indicates that the former ethyl group is directed towards the phosphine ligand, and yields the more shielded resonances in the ^1H NMR spectrum. Variable-temperature ^1H NMR experiments were carried out, up to 65 °C, to try and induce fluxionality in the barbiturate ligand, however none was observed, suggesting a high barrier to rotation of the amide ligand.

The ^{13}C NMR resonance for the quaternary CEt_2 carbon appears for the triphenylphosphine complexes **1a**, **1d** and **1e** as a broadened doublet in the range δ 56.9–57.2. A weak four-bond coupling to one of the triphenylphosphine ligands, presumably the one *trans* to the barbiturate ligand, of 2.5–3.2 Hz was resolvable. No three-bond coupling to ^{195}Pt could be determined. These chemical shifts are similar to those observed for the sodium salt of 5,5-diethylbarbituric acid (in D_2O) which appears at δ 57.2. The complexes show the expected three carbonyl resonances in their ^{13}C-$\{^1H\}$ NMR spectra.

The NMR spectroscopic properties of the cationic complexes **2a** and **2b** are consistent with their proposed structures. For the pyridine derivative **2a** two ethyl resonances are again observed, however only one is found for the triphenylphosphine complex **2b** since this species posesses a plane of symmetry passing through the barbiturate ligand

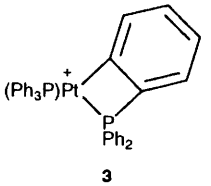
Electrospray mass spectrometry (ESMS)

We have investigated the barbiturato complexes by the relatively new technique of electrospray mass spectrometry which was initially developed for the analysis of large biomolecules.[9] While the number of inorganic systems which have been studied remains relatively small, the technique is finding increased application in the study of co-ordination, organometallic and bioinorganic systems.[10] It is particularly well suited for the analysis of large and/or highly polar molecules, and we have therefore undertaken an investigation into the ESMS behaviour of the platinum barbiturato complexes described herein. The data for the various complexes are summarised in Table 2.

Complexes **1a**, **1d** and **1e** show a relatively weak parent (protonated) molecular ion $[PtX(debarb)(PPh_3)_2 + H]^+$ (X = Cl, Br or I) at *m/z* 939, 983 and 1030 respectively. There are also two additional peaks in common, at *m/z* 902 and 943. These are assigned to the complexes $[Pt(debarb)(PPh_3)_2]^+$ and $[Pt(debarb)(NCMe)(PPh_3)_2]^+$ respectively. We also note that other platinum(II) phosphine halide complexes display a high propensity to form $[M - halide]^+$ as the major ions in their ESMS spectra.[11] A peak due to the ammine species $[Pt(debarb)(NH_3)(PPh_3)_2]^+$ is also observed in all three cases, as a result of ammonia being present in the mobile phase. Spectra were typically recorded on a freshly prepared solution, which showed protonated molecular ion peaks $[M + H]^+$. However, upon standing, the intensity of the $[M - Cl + NH_3]^+$ peak increased in intensity with a concomitant decrease in $[M + H]^+$, presumably due to slow solvolysis reactions. Certain platinum(II) complexes are known to catalyse the hydration of acetonitrile, and this might contribute to the formation of NH_3.[7] The chloro complex **1a** also showed a weak peak at *m/z* 1424. While the nature of this species is uncertain, one possibility is the aggregate $[\{Pt(debarb)(NCMe)(PPh_3)_2\}_3(OH)]^{2+}$ (M = 2847).

Variation of the skimmer cone voltage in the ESMS experiment is a versatile means of inducing fragmentation of parent molecular ions, and thus can be used to probe the strength of binding of the halide and barbiturate ligands to the platinum atom. Accordingly, a study of the behaviour of *cis*-$[PtCl(debarb)(PPh_3)_2]$ at a range of cone voltages has been carried out. At a low cone voltage of 10 V the peak due to $[Pt(debarb)(NCMe)(PPh_3)_2]^+$ was the major peak, whilst at 40 V $[Pt(debarb)(PPh_3)_2]^+$ was predominant. At a cone voltage of 60 V a new peak at *m/z* 718 is observed, and analysis of the isotope pattern indicates that this species is consistent with the complex containing an orthometallated triphenylphosphine ligand, *viz.* **3**. When the cone voltage is increased to 90 V species **3** is predominant, and the peaks due to $[Pt(debarb)(PPh_3)_2]^+$ were around 20% the intensity of **3**. As far as we are aware, cyclometallation reactions of PPh_3 ligands on platinum have not been observed previously by ESMS, though complexes of this type are well known from synthetic studies.[12]

The observation of platinum barbiturato species up to relatively high cone voltages indicates that the amide ligand is bonded to the metal centre relatively strongly. Thermal stability of platinum(II) and palladium(II) amides bearing electron-withdrawing groups has been noted previously.[13] Examination of the ESMS behaviour of the dppe complex **1b** reveals similar overall features to those of the related PPh_3 complex **1a**, however it is particularly noteworthy that there is a very strong peak for $[Pt(debarb)(dppe)]^+$ at far higher cone voltages than observed for the PPh_3 analogue. In this case it is possible that the five-membered platinum–diphosphine metallacycle may reduce the propensity for a phenyl ring to cyclometallate.



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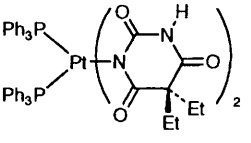
The mixed-ligand cationic complexes *cis*-[Pt(debarb)(py)(PPh_3)$_2$]$^+$ **2a** and [Pt(debarb)(PPh_3)$_3$]$^+$ **2b** also yield the expected features in their ESMS spectra, as indicated in Table 2, with predominant $[M]^+$ peaks observed for both complexes under low fragmentation (low cone voltage) conditions. Upon increasing the cone voltage the complexes lose a neutral donor ligand (py or PPh_3 respectively), giving the fragment [Pt(debarb)(PPh_3)$_2$]$^+$. Under conditions (cone voltage 40 V) where there was no orthometallation of a PPh_3 ligand (to produce **3** at *m*/*z* 718) selective loss of a PPh_3 ligand from **2b** {which would give the complex [Pt(debarb)(py)(PPh_3)]$^+$ (*m*/*z* 719)} was not observed. This is as expected, given the stronger preference of Pt^{II} to co-ordinate with phosphine ligands. The presence of three bulky PPh_3 ligands, together with the barbiturate ligand, in complex **2b** suggests that there is likely to be a degree of steric congestion. Consistent with this, addition of an excess of pyridine to a solution of **2b** in MeCN–water, followed by running the ESMS spectrum, yielded peaks due to the species [Pt(debarb)(py)(PPh_3)$_2$]$^+$ (*m*/*z* 981, 100%) as well as [Pt(debarb)(PPh_3)$_3$]$^+$ (*m*/*z* 1164/1165, 90%). No peak was observed due to the bis(pyridine) complex [Pt(debarb)(py)$_2$(PPh_3)]$^+$ in this case.

In situ generation of cationic barbiturato complexes can be achieved, for example [Pt(debarb)(py)(dppe)]$^+$, by addition of an excess of pyridine to the ESMS solution of **1b**, and ESMS data are summarised for this complex in Table 2.

An attempt at preparing a bis(barbiturato) complex, by reaction of *cis*-[$PtCl_2$(PPh_3)$_2$] with an excess of Na(debarb) in refluxing methanol, led mainly to the monoamide complex **1a**, as evidenced by ^{31}P NMR spectroscopy. However, a small peak observed at δ 28.5 showing coupling to ^{195}Pt of 3147 Hz is tentatively assigned as the bis(barbiturato) complex **4**. This value compares favourably with those of the other complexes described herein for the phosphine ligand *trans* to the barbiturato group, *e.g.* 3337 Hz for **1a**. No peak was observed in the ESMS spectrum of this reaction mixture, though this may not be unexpected due to possible dissociation of one barbiturate ligand to give *cis*-[Pt(debarb)(PPh_3)$_2$]$^+$ and debarb$^-$, which would be indistinguishable from the spectrum given by *cis*-[PtCl(debarb)(PPh_3)$_2$].



Experimental

Melting points were recorded on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Bio-Rad FTS-40 spectrophotometer, ^1H NMR spectra on a Bruker AC300P spectrometer at 300.13 MHz, with chemical shifts referenced to $SiMe_4$ (δ 0.0), ^{13}C-{^1H} NMR spectra on a Bruker AC300P spectrometer at 75.47 MHz relative to $SiMe_4$ (δ 0.0) and ^{31}P-{^1H} NMR spectra on a JEOL FX90Q spectrometer at 36.23 MHz respectively, with external 85% H_3PO_4 (δ 0.0) as reference. All NMR spectra were recorded in $CDCl_3$ solution; with the exception of the sodium salt of **Ib** which was recorded in D_2O solution.

All the compounds described are air-stable, and reactions were carried out in and products recrystallised from solvents without regard for the exclusion of air. Solvents were dried and distilled from appropriate drying agents prior to use. Light petroleum refers to the fraction of b.p. 40–60 °C. 5,5-Diethylbarbituric acid (barbitone) and its sodium salt and pyridine were used as received from BDH. 1,1′-Bis(diphenylphosphino)ferrocene was used as supplied from Aldrich. Triethylamine was distilled from KOH pellets prior to use. Other reagents were of laboratory grade and were used as supplied. The complexes *cis*-[$PtCl_2$(PPh_3)$_2$], [$PtCl_2$(dppe)] and [$PtCl_2$(dppf)] were generated from [$PtCl_2$(cod)] (cod = cycloocta-1,5-diene)[14] in a modification of the literature procedure[15] by addition of the appropriate molar amount of dppe, dppf or triphenylphosphine to a dichloromethane solution of the platinum complex, followed by addition of light petroleum to effect precipitation. Purity of the product was confirmed by ^{31}P NMR spectroscopy. The complexes *cis*-[$PtBr_2$(PPh_3)$_2$] and [PtI_2(PPh_3)$_2$] were prepared by metathesis of the chloride complex using an excess of LiBr or NaI in refluxing acetone, followed by evaporation, extraction with CH_2Cl_2 and crystallisation.

Electrospray mass spectra were obtained in positive-ion mode using a VG Platform II mass spectrometer and

Table 2 Positive-ion electrospray mass spectral data for the platinum(II) barbiturato complexes

Compound	Cone voltage (V)	Major ions[a] (*m*/*z*, relative intensity in %)
1a *cis*-[PtCl(debarb)(PPh_3)$_2$]	10	$[M - Cl]^+$ (902, 24), $[M - Cl + NH_3]^+$ (919, 7), $[M + H]^+$ (939, 12), $[M - Cl + MeCN]^+$ (943, 100), unidentified (1424, 3)
	20	$[M - Cl]^+$ (902, 100), $[M - Cl + NH_3]^+$ (919, 5), $[M + H]^+$ (939, 22), $[M - Cl + MeCN]^+$ (943, 50), unidentified (1424, 5)
	40	Unidentified (755, 3), $[M - Cl]^+$ (902, 100), $[M + H]^+$ (939, 4)
	60	$[Pt(C_6H_4PPh_2\text{-}o)(PPh_3)]^+$ (718, 25), unidentified (754, 10), $[M - Cl]^+$ (902, 100)
	90	$[Pt(C_6H_4PPh_2\text{-}o)(PPh_3)]^+$ (718, 100), unidentified (754, 10), $[M - Cl]^+$ (902, 20)
1d *cis*-[PtBr(debarb)(PPh_3)$_2$]	20	$[M - Br]^+$ (902, 100), $[M - Br + NH_3]^+$ (919, 5), $[M - Br + MeCN]^+$ (943, 50), $[M + H]^+$ (983, 11)
1e *cis*-[PtI(debarb)(PPh_3)$_2$]	20	$[M - I]^+$ (902, 100), $[M - I + NH_3]^+$ (919, 3), $[M - I + MeCN]^+$ (943, 50), $[M + H]^+$ (1030, 19)
2a *cis*-[Pt(debarb)(py)(PPh_3)$_2$]BPh_4[b]	20	$[M]^+$ (987, 100)
	40	$[M - py]^+$ (902, 100), $[M]^+$ (987, 100)
	60	$[M - py]^+$ (902, 100)
2b [Pt(debarb)(PPh_3)$_3$]BPh_4	20	$[M - PPh_3]^+$ (902, 29), $[M - PPh_3 + MeCN]^+$ (943, 26), $[M]^+$ (1164/1165, 100)
	40	$[M - PPh_3]^+$ (902, 100), $[M]^+$ (1164/1165, 48)
1b *cis*-[PtCl(debarb)(dppe)]	20	$[M - Cl]^+$ (776, 100), $[M - Cl + NH_3]^+$ (793, 18), $[M + H]^+$ (813, 2)
	120	$[Pt(C_6H_4PPhCH_2CH_2PPh_2\text{-}o)]^+$ **3** (592, 30), $[Pt(C_6H_4PPhCH_2CH_2PPh_2\text{-}o)(MeCN)]^+$ (633, 95), $[M - Cl]^+$ (776, 100), plus a number of minor unassigned peaks
cis-[Pt(debarb)(py)(dppe)]$^+$[c]	20	$[M]^+$ (854, 100)

[a] *m*/*z* Values given are those for the peak (or peaks) of greatest intensity in the isotope distribution pattern. [b] Counter ion BPh_4^- detected at *m*/*z* 319 in negative-ion ESMS spectrum. [c] Generated *in situ* by addition of an excess of pyridine to the solution for ESMS.

acetonitrile–water (1 : 1) as mobile phase. The compounds were dissolved in the mobile phase to give a solution typically of approximate concentration 0.1 mmol dm^{-3}, and spectra were routinely recorded on the freshly prepared solutions. The diluted solution was injected into the spectrometer *via* a Rheodyne injector fitted with a 10 μl sample loop. A Thermo Separation Products SpectraSystem P1000 LC pump delivered the solution to the mass spectrometer source (60 °C) at a flow rate of 0.01 cm^3 min^{-1}, and nitrogen was employed both as a drying and nebulising gas. Cone voltages were typically varied from 10 to 100 V, in order to investigate the effect of higher voltages on fragmentation of the parent ions. Confirmation of all species in this ESMS study is aided by comparison of the observed and predicted isotope distribution patterns. Theoretical isotope distribution patterns were calculated using the ISOTOPE computer program.[16]

Syntheses

***cis*-[PtCl(debarb)(PPh_3)$_2$] 1a.** To a solution of *cis*-[$PtCl_2(PPh_3)_2$] (152 mg, 0.192 mmol) in CH_2Cl_2 (20 cm^3) was added compound **Ib** (36 mg, 0.195 mmol). Triethylamine (five drops) was added, whereupon the barbituric acid dissolved giving a clear colourless solution. The mixture was stirred at room temperature for 21 h, and evaporated to dryness under reduced pressure. The ^{31}P-{^1H} NMR spectrum showed the presence of only complex **1a**. The product was extracted with CH_2Cl_2 (30 cm^3), washed with water (20 cm^3), and the CH_2Cl_2 layer separated, dried ($MgSO_4$), filtered and reduced in volume to *ca.* 5 cm^3. Addition of light petroleum (50 cm^3) gave a white microcrystalline solid, which was filtered off and dried *in vacuo* to give the product **1a** (130 mg, 72%) (Found: C, 55.7; H, 4.6; N, 3.0. $C_{44}H_{41}ClN_2O_3P_2Pt$ requires C, 56.3; H, 4.4; N, 3.0%), m.p. *ca.* 200 °C (decomp.); IR ν(CO) 1684s and 1618vs cm^{-1}. NMR: ^{31}P-{^1H}, AB spin system, δ 13.1 [d, PPh_3 *trans* to Cl, ^1J(PtP) 3950, ^2J(PP) 19.5] and 6.6 [d, PPh_3 *trans* to N, ^1J(PtP) 3337]; ^{13}C-{^1H}, δ 178.3 (s, CO), 174.6 (s, CO), 154.5 (s, CO), 135.3–127.8 (m, Ph), 57.2 [d, CEt_2, ^4J(PC) 2.5], 33.4 (s, CH_2), 26.5 (s, CH_2), 9.8 (s, CH_3) and 9.3 (s, CH_3); ^1H, δ 7.67–7.14 (m, 30 H, Ph), 1.91 (m, 2 H, CH_2), 1.57 (m, 2 H, CH_2), 0.96 [t, 3 H, CH_3, ^3J(HH) 7.4] and 0.44 [t, 3 H, CH_3, ^3J(HH) 7.4 Hz]. No CH_2Cl_2 of crystallisation was observed in this sample.

The complex can also be prepared as follows.

(*a*) *Using* Na(debarb). To [$PtCl_2$(cod)] (100 mg, 0.267 mmol) in thf (10 cm^3) was added triphenylphosphine (140 mg, 0.534 mmol), followed by methanol (10 cm^3) and Na(debarb) (58 mg, 0.281 mmol). The mixture was warmed to *ca.* 50 °C to yield a clear colourless solution which was stirred overnight at room temperature. The solvent was removed under reduced pressure and the product extracted with dichloromethane (30 cm^3) and filtered to remove NaCl by-product. Addition of light petroleum (60 cm^3) to the filtrate gave white microcrystals which were filtered off and dried *in vacuo* to give complex **1a** (195 mg, 78%) identified from its ^{31}P-{^1H} NMR spectrum.

(*b*) *Using* Ag_2O. To a solution of [$PtCl_2$(cod)] (200 mg, 0.535 mmol) in dichloromethane (25 cm^3) was added in succession triphenylphosphine (280 mg, 1.07 mmol), **Ib** (100 mg, 0.543 mmol) and silver(I) oxide (0.6 g, excess). The mixture was refluxed for 48 h. Filtration to remove the silver salts followed by removal of the solvent under reduced pressure gave a white solid, which was found to be a mixture of complex **1a** plus other by-products (^{31}P NMR spectroscopy). Crystallisation from CH_2Cl_2–light petroleum yielded colourless crystals (291 mg) of impure **1a**. Several recrystallisations from the same solvent mixture afforded colourless single crystals of pure **1a** (^{31}P NMR spectrum) which were used for the X-ray analysis. These were subsequently shown to contain one molecule of CH_2Cl_2 per platinum complex.

Reaction of *cis*-[$PtCl_2(PPh_3)_2$] with 2 mol equivalents of Na(debarb). To a suspension of *cis*-[$PtCl_2(PPh_3)_2$] (114 mg, 0.144 mmol) in methanol (10 cm^3) was added Na(debarb) (64 mg, 0.311 mmol). The white suspension of *cis*-[$PtCl_2(PPh_3)_2$] dissolved in about 10 min. The mixture was then refluxed for 5 h. The clear colourless solution was evaporated to dryness under reduced pressure. The ^{31}P-{^1H} NMR spectrum showed predominantly complex **1a**, together with a number of very minor impurities, one of which was tentatively assigned as the bis(barbiturato) complex **4** [δ 28.5, ^1J(PtP) 3147 Hz].

Reaction of complex 1a with LiBr. The crude reaction mixture above was dissolved in acetone (20 cm^3) and LiBr (0.5 g, excess) added. The mixture was stirred for 15 h, evaporated to dryness under reduced pressure, and extracted with CH_2Cl_2 (40 cm^3). After filtration and evaporation of the filtrate under reduced pressure, ^{31}P-{^1H} NMR spectroscopy showed the product to be mainly *cis*-[$PtBr_2(PPh_3)_2$], by comparison with the spectrum of an authentic sample.

***cis*-[PtCl(debarb)(dppf)] 1c.** A suspension of [$PtCl_2$(dppf)] (60 mg, 0.108 mmol) and Na(debarb) (23 mg, 0.112 mmol) in methanol (20 cm^3) was refluxed for 1 h. Work-up as for complex **1b** gave yellow microcrystals of **1c** (58 mg, 55%) (Found: C, 51.1; H, 4.0; N, 3.0. $C_{42}H_{39}ClFeN_2O_3P_2Pt$ requires C, 52.1; H, 4.1; N, 2.9%), m.p. > 230 °C. ^{31}P-{^1H} NMR: AB spin system, δ 13.6 [d, P *trans* to Cl, ^1J(PtP) 4031, ^2J(PP) 15] and 5.3 [d, P *trans* to N, ^1J(PtP) 3457 Hz].

***cis*-[PtBr(debarb)(PPh_3)$_2$] 1d.** A suspension of *cis*-[$PtBr_2(PPh_3)_2$] (150 mg, 0.171 mmol) in thf (10 cm^3) plus methanol (20 cm^3) with Na(debarb) (35 mg, 0.170 mmol) was stirred and warmed to *ca.* 50 °C to give a clear pale yellow solution, which was subsequently stirred overnight at room temperature. Evaporation to dryness under reduced pressure gave a pale yellow solid which was extracted with CH_2Cl_2 (30 cm^3), filtered to remove NaBr, and light petroleum (60 cm^3) added to the filtrate to give pale yellow microcrystals. These were filtered off and dried *in vacuo* to give complex **1d** (128 mg, 77%) (Found: C, 53.2; H, 4.3; N, 2.7. $C_{44}H_{41}BrN_2O_3P_2Pt$ requires C, 53.8; H, 4.2; N, 2.85%), m.p. > 250 °C; ν(CO) 1618vs (br) cm^{-1}. NMR: ^{31}P-{^1H}, AB spin system, δ 13.5 [d, PPh_3 *trans* to Br, ^1J(PtP) 3908, ^2J(PP) 17] and 5.3 [d, PPh_3 *trans* to N, ^1J(PtP) 3317]; ^{13}C-{^1H}, δ 178.1 (s, br, C=O), 174.4 (s, C=O), 154.2 (s, C=O), 135.5–127.7 (m, Ph), 57.0 [d, CEt_2, ^4J(PC) 3.0], 32.9 (s, CH_2), 26.2 (s, CH_2), 9.8 (s, CH_3) and 9.3 (s, CH_3); ^1H, δ 7.67–6.95 (m, 30 H, Ph), 1.90 (m, 2 H, CH_2), 1.59 (s, br, H_2O), 1.49 [dq, 2 H, CH_2, *J*(HH) 7.4, 3.1], 0.96 [t, 3 H, CH_3, *J*(HH) 7.4] and 0.45 [t, 3 H, CH_3, *J*(HH) 7.3 Hz].

***cis*-[PtI(debarb)(PPh_3)$_2$] 1e.** A suspension of *cis*-[$PtI_2(PPh_3)_2$] (77 mg, 0.079 mmol) in methanol (30 cm^3) with Na(debarb) (60 mg, excess) was stirred at room temperature for 3 d to give a pale yellow suspension. The mixture was evaporated to dryness under reduced pressure, and the resulting pale yellow solid extracted with CH_2Cl_2 (30 cm^3). After filtration to remove NaI the filtrate was evaporated to dryness to afford a pale yellow oil. Recrystallisation from CH_2Cl_2–light petroleum gave pale yellow microcrystals which were filtered off and dried *in vacuo* to give complex **1e**·0.5CH_2Cl_2 (55 mg, 65%) (Found: C, 49.9; H, 4.0; N, 2.6. $C_{44}H_{41}IN_2O_3P_2Pt$·0.5CH_2Cl_2 requires C, 49.9; H, 3.95; N, 2.6%) m.p. decomp. > 220 °C, ν(CO) 1716m, 1676m and 1618vs cm^{-1}. NMR: ^{31}P-{^1H}, AB spin system, δ 11.1 [d, ^1J(PtP) 3705, ^2J(PP) 14.7] and 2.0 [d, ^1J(PtP) 3196]; ^{13}C-{^1H}, δ 178.0 [d, C=O, ^3J(PC) 2.2, ^2J(PtC) not resolved], 174.5 (s, C=O), 154.3 (s, br, C=O), 135.8–127.5 (m, Ph), 56.9 [d, CEt_2, ^4J(PC) 3.2, ^3J(PtC) not resolved], 53.8 (s, CH_2Cl_2), 32.1 (s, CH_2), 26.0 (s, CH_2), 9.7 (s, CH_3) and 9.7 (s, CH_3); ^1H, δ 7.66–7.12 (m, 30 H, Ph), 5.29 (s, 0.5

CH_2Cl_2), 2.46 [dq, 2 H, CH_2, J(HH) 7.5, 3.0], 1.91 [dq, 2 H, CH_2, J(HH) 7.48, 2.8], 1.46 [t, 3 H, CH_3, J(HH) 7.4] and 1.00 [t, 3 H, CH_3, J(HH) 7.3 Hz].

***cis*-[PtCl(debarb)(dppe)]·CH_2Cl_2 1b.** A suspension of [$PtCl_2$(dppe)] (283 mg, 0.426 mmol) in methanol (30 cm^3) with Na(debarb) (88 mg, 0.427 mmol) was warmed to 50 °C for 20 min and then stirred at room temperature overnight. The clear colourless solution was evaporated to dryness under reduced pressure to afford a white solid which was extracted with CH_2Cl_2 and filtered to remove NaCl. The volume of the filtrate was reduced to *ca.* 5 cm^3 and light petroleum (60 cm^3) added to precipitate the product **1b** which was filtered off and dried *in vacuo*, yield 239 mg (63%) (Found: C, 47.1; H, 4.1; N, 3.1. $C_{34}H_{35}ClN_2O_3P_2Pt·CH_2Cl_2$ requires C, 46.9; H, 4.2; N, 3.1%), m.p. 174–177 °C; ν(CO) 1717m (sh), 1684s and 1626vs cm^{-1}. NMR: ^{31}P-{^1H}, AB spin system, δ 40.0 [d, P *trans* to Cl, ^1J(PtP) 3801, ^2J(PP) 10] and 33.6 [d, P *trans* to N, ^1J(PtP) 3330]; ^{13}C-{^1H}, δ 178.51 (s, br, C=O), 175.31 (s, C=O), 154.63 (s, C=O) 135.19–125.97 (m, Ph), 57.73 [d, CEt_2, ^4J(PC) 3.0, ^3J(PtC) not resolved], 53.8 (s, CH_2Cl_2), 33.98 (s, CH_2 of Et), 30.94 (s, CH_2 of Et), 30.0 [dd, CH_2 of dppe, J(PC) 42.7, 9.2, J(PtC) not resolved], 26.21 [dd, CH_2 of dppe, J(PC) 40.9, 9.3, J(PtC) not resolved], 9.60 (s, CH_3) and 9.43 (s, CH_3); ^1H, δ 8.40–7.26 (m, 20 H, Ph), 5.32 (s, 2 H, CH_2Cl_2), 2.5–1.6 (m, CH_2 of Et and dppe), 0.95 [t, 3 H, CH_3, J(HH) 7.3] and 0.21 [t, 3 H, CH_3, J(HH) 7.2 Hz].

***cis*-[Pt(debarb)(py)(PPh_3)$_2$]BPh_4 2a.** To a suspension of *cis*-[$PtCl_2$(PPh_3)$_2$] (200 mg, 0.253 mmol) in methanol (30 cm^3) was added Na(debarb) (53 mg, 0.257 mmol) and the mixture warmed to 50 °C for 20 min to effect conversion into complex **2a**. To the resulting solution was added $NaBPh_4$ (89 mg, 0.260 mmol) followed by pyridine (10 drops, excess). The clear solution was stirred at room temperature for 22 h, evaporated to dryness under reduced pressure and extracted with CH_2Cl_2 (2 × 20 cm^3) to remove NaCl by-product. After filtration the filtrate was reduced in volume to *ca.* 5 cm^3, and addition of ether (60 cm^3) effected precipitation of a white powder which was filtered off, washed with ether and dried *in vacuo* to yield product **2a** (280 mg, 85%) (Found: C, 67.0; H, 5.4; N, 3.1. $C_{73}H_{66}BN_3O_3P_2Pt$ requires C, 67.4; H, 5.1; N, 3.2%), m.p. 158–161 °C; ν(CO) 1718m, 1679m and 1618vs cm^{-1}. NMR: ^{31}P-{^1H} AB spin system, δ 3.8 [d, ^1J(PtP) 3552, ^2J(PP) 19.5] and 0.3 [d, ^1J(PtP) 3294]; ^{13}C-{^1H}, δ 178.56–121.75 (m, aromatic C), 57.24 [d, CEt_2, ^4J(PC) 2.8 Hz], 31.54 (s, CH_2), 27.27 (s, CH_2), 9.56 (s, CH_3) and 8.33 (s, CH_3).

***cis*-[Pt(debarb)(PPh_3)$_3$]BPh_4·CH_2Cl_2 2b.** A suspension of *cis*-[$PtCl_2$(PPh_3)$_2$] (141 mg, 0.178 mmol) and Na(debarb) (37 mg, 0.180 mmol) in methanol (30 cm^3) was warmed to *ca.* 60 °C to give an almost clear solution. To this was added in succession $NaBPh_4$ (62 mg, 0.181 mmol) and PPh_3 (47 mg, 0.179 mmol), and the solution kept at 60 °C for 10 min and then stirred for 24 h at room temperature. Evaporation to dryness under reduced pressure gave a white solid which was extracted with CH_2Cl_2 (30 cm^3), and filtered to remove the by-product NaCl. The

Table 3 Crystal data and intensity collection for *cis*-[PtCl(debarb)(PPh_3)$_2$]·CH_2Cl_2 **1a**

Empirical formula	$C_{44}H_{41}ClN_2O_3P_2Pt·CH_2Cl_2$
M	1023.19
Colour	Colourless
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.540(2)
b/Å	13.222(2)
c/Å	13.929(2)
α/°	106.08(1)
β/°	91.87(1)
γ/°	103.01(1)
U/Å^3	2151.0(6)
D_c/g cm^{-3}	1.580
Z	2
Radiation (λ/Å)	Mo-Kα (0.710 69 Å)
T/K	293
hkl ranges	−1 to 15, −15 to 13, −16 to 16
Reflections collected	8732
Unique reflections	7636 (R_{int} 0.0255)
F(000)	1020
μ/mm^{-1}	3.564

Table 4 Fractional atomic coordinates (× 10^4) for *cis*-[PtCl(debarb)(PPh_3)$_2$]·CH_2Cl_2 **1a**, with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Pt	2993(1)	2297(1)	2139(1)	C(26)	257(6)	3513(5)	4008(5)
Cl(1)	1872(1)	838(1)	2570(1)	C(31)	1401(5)	4309(5)	2231(4)
P(1)	1484(1)	2987(1)	2379(1)	C(32)	763(6)	4443(6)	1479(5)
P(2)	4042(1)	3523(1)	1511(1)	C(33)	700(8)	5471(7)	1453(7)
N(1)	4229(4)	1488(3)	2166(3)	C(34)	1299(7)	6377(6)	2173(7)
N(2)	5244(4)	241(4)	1382(4)	C(35)	1940(7)	6256(6)	2940(6)
O(1)	4451(4)	2164(4)	3839(3)	C(36)	1981(5)	5244(5)	2972(5)
O(2)	6285(4)	−478(4)	2223(4)	C(41)	4494(5)	4893(4)	2369(4)
O(3)	4077(3)	774(3)	479(3)	C(42)	4456(5)	5020(5)	3382(4)
C(1)	4642(5)	1516(5)	3104(4)	C(43)	4882(6)	6040(6)	4068(5)
C(2)	5301(5)	715(5)	3226(5)	C(44)	5311(6)	6909(6)	3738(6)
C(3)	5666(5)	115(5)	2250(5)	C(45)	5368(6)	6794(5)	2733(6)
C(4)	4477(5)	828(4)	1308(4)	C(46)	4975(6)	5773(5)	2031(5)
C(5)	7065(8)	2190(9)	3820(9)	C(51)	3307(5)	3528(5)	365(4)
C(6)	6259(7)	1285(7)	4036(6)	C(52)	2997(6)	4414(5)	215(5)
C(7)	3648(8)	−953(7)	2887(9)	C(53)	2369(6)	4317(6)	−665(6)
C(8)	4542(8)	−155(7)	3617(6)	C(54)	2090(7)	3342(7)	−1396(6)
C(11)	301(5)	2031(5)	1571(5)	C(55)	2382(6)	2444(6)	−1260(5)
C(12)	−581(5)	1459(5)	1924(6)	C(56)	2975(5)	2529(5)	−379(4)
C(13)	−1434(6)	719(6)	1241(7)	C(61)	5377(5)	3270(4)	1162(4)
C(14)	−1397(6)	544(6)	238(7)	C(62)	5608(6)	2868(5)	203(6)
C(15)	−528(6)	1085(6)	−108(6)	C(63)	6643(7)	2686(6)	8(7)
C(16)	332(6)	1829(5)	539(5)	C(64)	7433(7)	2905(7)	760(8)
C(21)	1219(5)	3210(5)	3696(5)	C(65)	7224(6)	3311(7)	1730(7)
C(22)	1990(6)	3171(6)	4407(5)	C(66)	6197(5)	3495(6)	1938(6)
C(23)	1820(7)	3448(7)	5410(6)	Cl(2)	1915(5)	788(4)	6040(3)
C(24)	875(8)	3728(7)	5712(6)	Cl(3)	1083(4)	−1065(4)	4412(5)
C(25)	96(7)	3743(6)	5016(6)	C(9)	1520(14)	315(10)	4830(9)

volume of the filtrate was reduced to *ca.* 6 cm^3, and addition of diethyl ether (60 cm^3) gave, on standing, an off-white microcrystalline solid which was filtered off and dried *in vacuo*. Yield 132 mg, 57%. A sample for elemental analysis was recrystallised from CH_2Cl_2–light petroleum (Found: C, 66.0; H, 5.0; N, 2.0. $C_{86}H_{76}BN_2O_3P_2Pt{\cdot}CH_2Cl_2$ requires C, 66.6; H, 5.0; N, 1.8%), m.p. > 200 °C; ν(CO) 1722m, 1674m and 1615vs cm $^{-1}$. NMR: ^{31}P-{^1H}, δ 17.5 [d, P_A, ^1J(PtP) 2605, ^2J(PP) 22] and 5.0 [t, P_B, ^1J(PtP) 3296]; ^1H, δ 7.68–6.67 (m, 45 H, PPh_3), 1.54 (s, br, 4 H, CH_2) and 0.44 [t, 6 H, CH_3, ^3J(HH) 7.35 Hz].

Crystallography

A colourless crystal of complex **1a** of approximate dimensions 0.39 × 0.29 × 0.15 mm was mounted in air. Accurate unit-cell parameters (see Table 3) were determined by least-squares refinement of the optimised setting angles for 23 centred reflections with $4.6 < \theta < 12.4°$. Data were collected on a Siemens P4 diffractometer with an ω-scan technique in the range θ 2.56–25.99°. The 7636 unique reflections were corrected for Lorentz and polarisation effects. A semiempirical absorption correction based on ψ scans was carried out with the maximum and minimum transmission factors 0.945 and 0.600 respectively (R_{int} = 0.0172). Subsequent calculations were carried out using the programs SHELXTL-PC [17] and SHELXL 93.[18]

The molecular structure was solved by conventional Patterson and Fourier-difference techniques. Scattering factors were taken from SHELXTL. In the final stages of full-matrix least-squares refinements all non-hydrogen atoms were given anisotropic displacement parameters. The hydrogen atom H(2) on N(2) was located and allowed to ride on N(2). All other hydrogens are included in calculated positions. The hydrogen atoms of the CH_2Cl_2 molecule were given a fixed isotropic displacement parameter while all others had isotropic thermal parameters refined as groups. The total number of refined parameters was 506, with a ratio of data : restraints : parameters of 7636 : 0 : 506. Final cycles employed a weighting factor w calculated from $1/[\sigma^2(F_o^2) + (0.0690P)^2 + 1.04P]$ where $P = [\max(F_o^2, 0) + (2F_c^2/3)]$. Final values of $R1$ and $wR2$ were 0.0442 and 0.1240 respectively. The maximum and minimum electron densities in the final ΔF map were 0.848 and −1.083 e Å $^{-3}$ respectively. Final atom coordinates are given in Table 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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