Platinum(II) and palladium(II) complexes derived from the monoanion of isatin (2,3-dihydroindole-2,3-dione, Hisat); crystal structure of cis-[Pt(isat)₂(PPh₃)₂]

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A number of platinum(II) and palladium(II) complexes containing the monoanion of isatin (2,3-dihydroindole-2,3-dione, Hisat) have been synthesized by reaction of the metal halide complex with isatin, in the presence of triethylamine. The complexes have been characterised by NMR and IR spectroscopies and elemental analysis. A single-crystal X-ray diffraction study has been carried out on cis-[Pt(isat)₂(PPh₃)₂], which shows two cis-isat ligands with their dicarbonyl functions pointing in opposite directions. Electrospray mass spectrometry was also used for characterisation; the complexes show a strong tendency to form aggregate ions with ammonium ions, and both mono- and di-cationic species are observed.
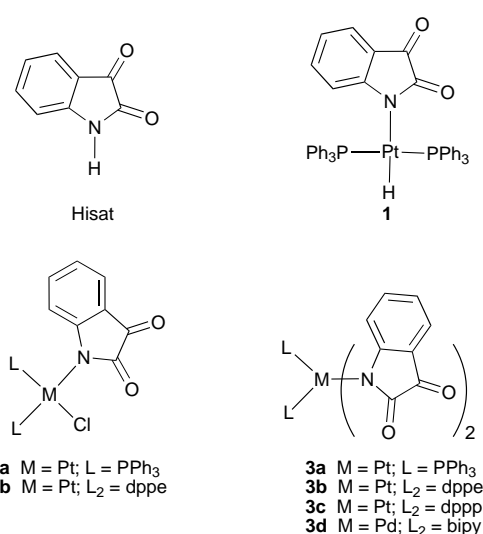
The amide functionality, RC(O)NHR′, is able to form a range of stable metal complexes bonding as its monoanion, and such ligands are able to stabilise transition-metal centres in high oxidation states.[1] There is current interest in the chemistry of transition-metal amides, since such complexes may possess biological activity, for example as second-generation antitumour drugs[2] and may be implicated in the interactions of platinum (and other transition-metal) complexes with biological molecules such as proteins and peptides.[3] Platinum–amide complexes are also intermediates in catalytic hydration reactions of nitriles.[4]

Isatin (2,3-dihydroindole-2,3-dione, Hisat) is a highly conjugated, intense orange compound, and hence may find potential application as a chromophoric labelling agent in its metal complexes. To the best of our knowledge, only one platinum-group-metal complex has been derived from isatin, the platinum hydride **1**, formed by oxidative addition of the N–H bond of isatin to a zerovalent platinum complex.[5] Gold(I) complexes of isatin, its 5-bromo derivative and some related dye molecules have also been recently reported.[6] Other isatin complexes have been synthesized with main-group metals, including the organotin compound SnBuⁿ₃(isat),[7] and a range of phenyl-antimony complexes.[8]

Additional interest in the synthesis of transition-metal complexes of isatin results from the presence of the carbonyl functions, which might themselves possess ligand properties towards other metals, leading to the formation of bi- and multi-metallic co-ordination assemblies. Recently, there has been interest in this field, where a range of multimetallic structures based upon amide complexes has been synthesized.[9] The related 2-pyridonate ligand also forms a diverse range of materials,[10] the chemistry of which is summarised in two recent reviews.[11] The presence of two adjacent carbonyl groups in isatin, both of which could potentially act as ligands towards other metal centres, offers a new dimension in this area; we note that metal complexes of the related α,β-diketo ligands oxalate[12] and oxamidate[13] are well known to form interesting co-ordination networks.

Results and Discussion

Initially, isatin (Hisat) was treated with some platinum dichloride complexes of the type cis-[PtCl₂L₂] [L = PPh₃, L₂ = 1,2-bis(diphenylphosphino)ethane (dppe) or cycloocta-1,5-diene (cod)] and one palladium complex, [PdCl₂(bipy)] (bipy = 2,2′-bipyridine), in a 1:1 ratio, with added triethylamine, in an

Hisat

1

2a M = Pt; L = PPh₃
2b M = Pt; L₂ = dppe

3a M = Pt; L = PPh₃
3b M = Pt; L₂ = dppe
3c M = Pt; L₂ = dppp
3d M = Pd; L₂ = bipy

attempt to synthesize the monosubstituted compounds of type **2**. This was successful for cis-[PtCl(isat)(PPh₃)₂] **2a**, but no other mono-isat compounds could be isolated pure. However, in the reaction between cis-[PtCl₂(dppe)] and isatin a mixture of the starting material, the monosubstituted **2b** and the di-substituted **3b** compounds was formed. It was decided therefore to repeat the reaction using 2 molar equivalents of isatin, and the four bis-isat complexes cis-[Pt(isat)₂(PPh₃)₂] **3a**, cis-[Pt(isat)₂(dppe)] **3b**, cis-[Pt(isat)₂(dppp)] **3c** (dppp = Ph₂PCH₂-CH₂CH₂PPh₂) and [Pd(isat)₂(bipy)] **3d** were thus prepared in moderate to high yields. All of these complexes are dark red crystalline or microcrystalline solids, and all except the palladium complex **3d** melt with decomposition at temperatures above 180 °C. The palladium complex did not melt below 320 °C, the limit of the apparatus used.

Crystal structure of cis-[Pt(isat)₂(PPh₃)₂] 3a

The crystal structure of complex **3a**, Fig. 1, showed the platinum atom co-ordinated to two triphenylphosphine and two isat ligands, in a cis-square planar geometry, as expected. The isat ligands co-ordinate through deprotonated nitrogen atoms. Selected bond lengths and angles are given in Table 1.

Analysis of the platinum co-ordination plane revealed that P(2) and N(1) were raised slightly above the plane (by 0.064 and 0.081 Å, respectively) while P(1) and N(2) were below the plane
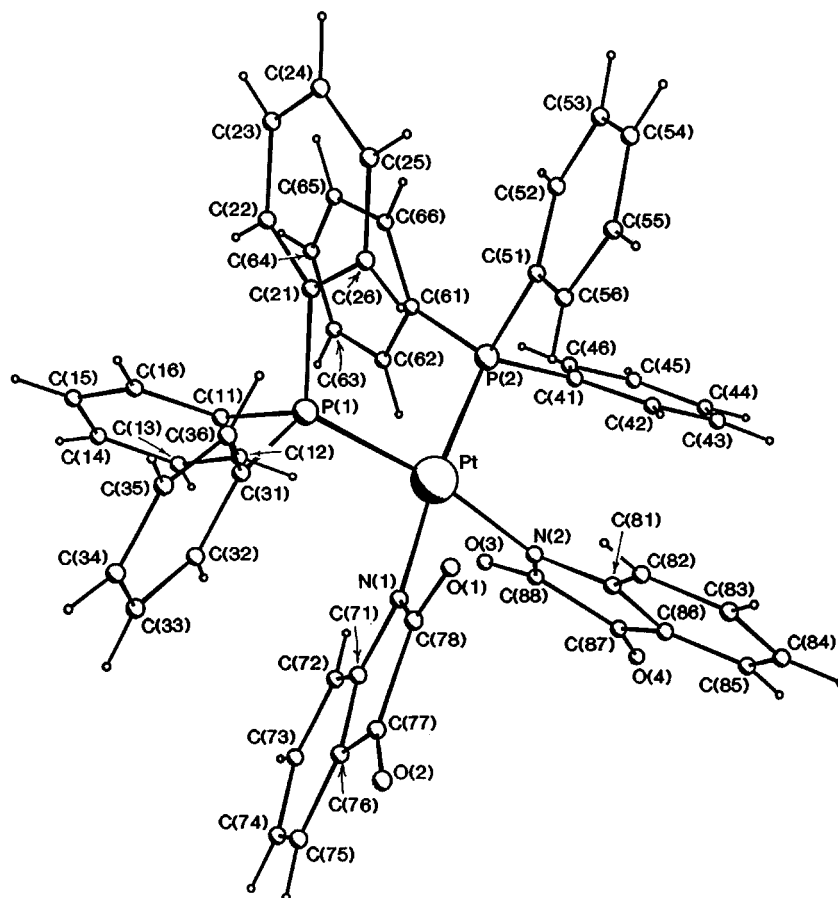
Fig. 1 Molecular structure of *cis*-[Pt(isat)$_2$(PPh$_3$)$_2$] **3a**, showing the atom numbering scheme

Table 1 Selected bond lengths (Å) and angles (°) for *cis*-[Pt(isat)$_2$-(PPh$_3$)$_2$] **3a**, with estimated standard deviations in parentheses

|			
Pt–N(1)	2.050(2)	Pt–N(2)	2.060(2)
Pt–P(2)	2.2956(7)	Pt–P(1)	2.2959(7)
N(1)–C(78)	1.358(4)	N(1)–C(71)	1.409(4)
N(2)–C(88)	1.357(4)	N(2)–C(81)	1.410(4)
O(1)–C(78)	1.221(4)	O(2)–C(77)	1.206(4)
O(3)–C(88)	1.218(4)	O(4)–C(87)	1.205(4)
N(1)–Pt–N(2)	84.71(9)	N(2)–Pt–P(2)	90.36(7)
N(1)–Pt–P(1)	99.48(7)	P(2)–Pt–P(1)	96.71(3)
C(71)–N(1)–Pt	127.3(2)	C(78)–N(1)–Pt	123.6(2)
C(88)–N(2)–Pt	124.0(2)	C(81)–N(2)–Pt	126.6(2)
C(78)–N(1)–C(71)	109.1(2)	C(88)–N(2)–C(81)	109.5(2)
O(1)–C(78)–N(1)	127.6(3)	O(1)–C(78)–C(77)	125.1(3)
O(2)–C(77)–C(76)	130.7(3)	O(2)–C(77)–C(78)	124.5(3)
O(3)–C(88)–N(2)	127.9(3)	O(3)–C(88)–C(87)	125.1(3)
O(4)–C(87)–C(86)	130.2(3)	O(4)–C(87)–C(88)	125.1(3)

(by 0.067 and 0.081 Å, respectively). This indicates a minor distortion of the co-ordination toward a tetrahedral geometry, presumably to relieve the steric crowding of the bulky ligands in this complex. The bulky phosphine ligands give a P(1)–Pt–P(2) angle of 96.71(3)°, and there is a correspondingly small N(1)–Pt–N(2) angle of 84.71(9)°. Similar angular deformations were observed for the azetidin-2-one complex **4**.[14]

The Pt–P bond lengths are equal [2.296(1) Å], but Pt–N(2) appears to be slightly longer than Pt–N(1) [2.060(2) and 2.050(2) Å, respectively]. Similar Pt–N bond lengths have been found for **4**[14] [2.03(1) and 2.05(1) Å], and also for the orotic acid (2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid) complex **5a** [2.056(6) Å].[15] However, the Pt–P distances for these two complexes were significantly shorter than those in **3a**, being 2.266(3) and 2.291(3) Å for **4** and 2.265(3) and 2.262(3) Å for **5a**.

The isat ligands are planar, with the greatest deviations from
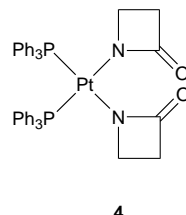
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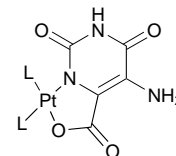
5a L = PPh$_3$
5b L–L = dppe

planarity being 0.021 Å for C(77) in the first isat ligand and 0.020 Å for C(88) in the second. Both of the ligand planes are almost perpendicular to the platinum co-ordination plane, with dihedral angles of 79.19(6) and 74.95(7)°, for the ligands co-ordinated through N(1) and N(2), respectively. As in complex **4**, these ligand planes are oriented so that the carbonyls of the two molecules point in opposite directions. This is illustrated in Fig. 2 which views complex **3a** parallel to the platinum co-ordination plane.

In the crystal structure of the free isatin molecule[16] a long C–C bond of 1.555(3) Å [*cf.* approximately 1.48 Å for a normal C(sp^2)–C(sp^2) single bond[17]] was observed between the two carbonyl groups. This was attributed to repulsion between the non-bonded lone pairs on the oxygen atoms, and is also seen in complex **3a**, with distances of 1.565(4) Å for C(77)–C(78) and 1.566(4) Å for C(87)–C(88).

NMR spectroscopy

(*a*) **31P-{1H}.** The ^{31}P-{^{1}H} NMR spectra of the isat complexes **2** and **3** are as expected; **3a** showed a single resonance with ^{195}Pt satellites, and a ^{195}Pt–^{31}P coupling constant of 3284 Hz. By comparison, the phthalimido complex **6** showed a similar value of 3340 Hz.[18] For the dppe complex **3b** a $^{1}J_{PtP}$ value of 3173 Hz was observed, which is slightly lower than the P *trans* to N values of 3322 Hz for the dppe platinum amide complex
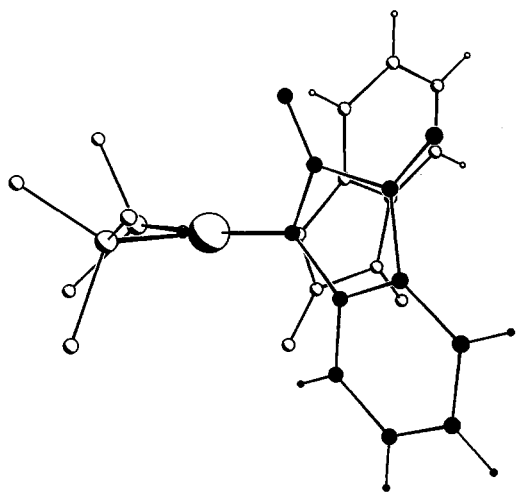
Fig. 2 Structure of *cis*-[Pt(isat)$_2$(PPh$_3$)$_2$] **3a** viewed parallel to the platinum co-ordination plane, showing how the carbonyl groups of the two isatin ligands point in opposite directions. Only P-bonded atoms of the phenyl rings are shown, and the atoms of the front isatin ligand are shown as black circles

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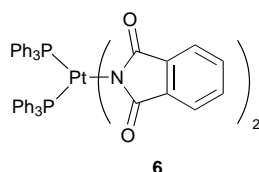
[PtMe{NHC(O)Me}(dppe)][19] and 3294 Hz for the 5-amino-orotic acid platinum complex **5b**.[15] In the spectrum of **3c** the $^1J_{PtP}$ value of 2963 Hz was small compared to that of the triphenylphosphine **3a** and dppe **3b** complexes, reflecting the pattern for the starting platinum dichloride complexes, and is the usual effect of increasing the chelate ring size from five atoms to six.

The mixed-ligand complex **2a** showed an AB spin system, indicative of two phosphorus atoms in different environments, coupling to each other (J_{PP} 18 Hz), with associated platinum satellites. The chloride ion has the lowest *trans* influence, and the phosphorus *trans* to this ligand showed the highest coupling to platinum (3832 Hz). Conversely, the amido ligand had a higher *trans* influence, resulting in a lower coupling constant, 3101 Hz, for the *trans* phosphorus atom. Also evident from this spectrum was the exaggerated difference in Pt–P coupling in asymmetric species. This effect has been observed previously[20] and is seen in *cis*-phosphine platinum complexes where two different groups occupy the sites *trans* to the phosphorus atoms. In such complexes, the lowest $^1J_{PtP}$ value is lowered relative to a symmetrical analogue, while the highest is raised, leading to an increase in the difference between the two coupling constants. The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] has a $^1J_{PtP}$ value of 3673 Hz, with P *trans* to Cl, while *cis*-[Pt(isat)$_2$(PPh$_3$)$_2$] **3a** has a coupling constant of 3284 Hz, with P *trans* to N. For the asymmetric species, *cis*-[PtCl(isat)(PPh$_3$)$_2$] **2a**, however, the value for P *trans* to Cl increases to 3832 Hz, and that for P *trans* to N decreases to 3101 Hz. Typical coupling constants for triphenylphosphine *trans* to chloride occur around 3700 Hz.[21]

The dppe platinum complex **2b** also showed the expected AB spin pattern, but with a lower $^2J_{PP}$ than that of the triphenylphosphine analogue **2a**, as expected.[15,22] A lower exaggeration in the $^1J_{PtP}$ difference was seen, on comparison with the triphenylphosphine analogue **2a**. The ^{31}P-{^{1}H} NMR spectrum of the crude product showed three complexes, namely the starting material, the intermediate monoamido complex **2b** and the bis-amido product **3b**. The complex **2b** showed coupling constants of 3656 Hz for the phosphorus *trans* to chloride, and 3126 Hz for phosphorus *trans* to nitrogen. On comparison with the

original dichloride and the bis-amido complexes, this showed an increase of 37 Hz for P *trans* to Cl, and a decrease of 46 Hz for P *trans* to N.

(*b*) ^{1}**H.** All of the complexes **2** and **3** showed the absence of the broad isatin amide proton resonance, at δ 7.93 in the ^{1}H NMR spectrum. The ^{1}H NMR spectrum of **2a** showed a complex multiplet between δ 7.9 and 7.1, due to the phenyl protons. A doublet and a triplet of doublets are seen at higher field due to the isat group, both showing $^3J_{HH}$ of *ca.* 7 Hz. The latter proton also showed $^4J_{HH}$ coupling of 0.7 Hz. Unfortunately, the other doublet and triplet of doublets expected were obscured by the phenyl resonances. The spectrum of complex **3a** was simpler than that of **2a**, as the phosphine ligands are now equivalent.

(*c*) ^{13}**C-{^{1}H}.** In the spectrum of complex **2a** the two isat carbonyls appeared at δ 192 and 168, respectively, with the high-field signal due to the carbonyl adjacent to the amido nitrogen. The two triphenylphosphine ligands are inequivalent, resulting in the observation of twice as many phenyl carbon signals as for a symmetrical complex. Additionally, carbons located close to one of the phosphorus atoms show coupling to that atom. All of the other phenyl carbons, with the exception of the *para* carbons, showed phosphorus–carbon coupling. One of these resonances appeared as a doublet, with a $^1J_{PC}$ value of 62 Hz. Another singlet, observed at slightly higher field, was assigned as half of the second doublet expected. The other half was assumed to be obscured under a larger, adjacent resonance. Both of these resonances were absent from the distortionless enhancement of polarisation transfer (DEPT) 135 spectrum, confirming their assignment as quaternary carbons. The *ortho* carbons appeared as two doublets, with $^2J_{PC}$ couplings of about 10 Hz for each.

For complexes **3a**–**3c** two carbonyl resonances for the isat ligand were seen, *e.g.* for **3a** at δ 188 and 166 with the latter being the amide carbonyl. The highest-field resonances in the spectra of **3b** and **3c** were for the methylene carbons of the dppe or dppp ligands. In the spectrum of **3b** the methylene carbons were observed as a doublet of doublets, due to coupling to two phosphorus atoms. A multiplet was seen for the dppp PCH$_2$ carbons of **3c**, as a result of coupling to both phosphorus atoms, while the central methylene carbon appeared as a higher-field singlet.

The bipy palladium complex **3d** showed the simplest of all the carbon NMR spectra, as it lacked phosphorus coupling. Hence, each of the thirteen carbon environments in the complex appeared as a singlet, with carbonyl resonances at δ 189 and 169, the latter being assigned to the amide carbonyl.

Infrared spectroscopy

In the infrared spectra of the isat complexes **2** and **3** the region 1750–1500 cm^{-1} is the most diagnostic. Free isatin shows three bands at 1748, 1728 and 1616 cm^{-1}, attributed to C=O and C=C stretches. For complexes of this ligand four strong bands are resolved in this region, *e.g.* 1732, 1685, 1605 and 1586 cm^{-1} for **2a** and these vary little for all of the complexes **2** and **3**. The overall lowering of frequency suggests that co-ordination of the nitrogen to the metal withdraws electron density from the C=C and C=O groups. Roundhill[23] noted corresponding weakening of carbonyl bonds for similar cyclic amide complexes of platinum and palladium, and frequencies in the range 1612–1578 cm^{-1} have been observed for platinum complexes with ligands of the type NHC(O)R (R = Me or Ph).[24]

Electrospray mass spectrometry (ESMS)

Electrospray mass spectrometry is finding increasing utility in the characterisation of inorganic complexes,[25] and several types of platinum(II) amide complexes have been investigated by ESMS.[14,26–28] The compounds described here were studied using
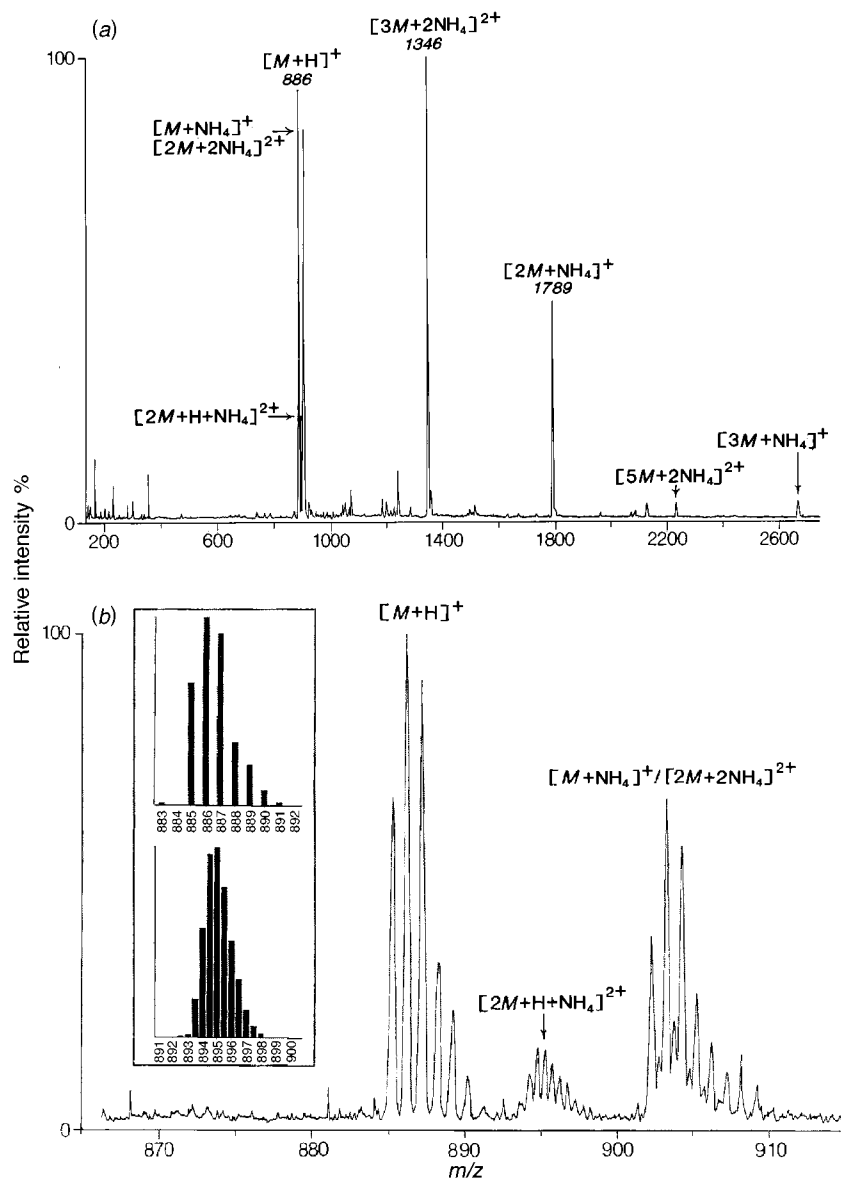
Fig. 3 Positive-ion electrospray mass spectrum (MeCN–water solution, cone voltage 20 V) of the bis(isat) complex **3b**: (*a*) full mass-range spectrum, with ion assignments, illustrating the strong propensity to aggregate with ammonium ions; (*b*) high-resolution expansion of the region *m*/*z* 865–915, showing contributions from various mono- and di-cationic species; the inset shows the calculated isotope patterns for the $[M + H]^+$ ion (upper) and the $[2M + H + NH_4]^{2+}$ ion (lower)

the positive-ion mode, and there are two ways that a molecule may obtain such a charge. First, a positively charged species, such as a proton or a metal ion, may attach itself to the complex. Hence, at low cone voltages, this method often shows a high abundance of molecular ions, $[M + H]^+$, where M is the original complex molecule. Secondly, a complex may lose a negatively charged group. This fragmentation mechanism is seen especially at higher cone voltages. Both of these methods can help in the characterisation of a complex. Additionally, comparison of the experimental and calculated isotope patterns can provide support for ion assignments.

Positive-ion ESMS data for complexes **2** and **3** are summarised in Table 2, and the general behaviour of the isat complexes is illustrated by discussion of the properties of the chloro–isat complex **2a** and the bis(isat) complexes **3a** and **3b**. The complexes show a very strong propensity to form aggregates with adventitious ammonium ions (from the acetonitrile mobile phase used), including multiply charged species. Presumably this behaviour results from the presence of the α,β-diketo moiety of the isatin ligand(s), which is expected to be an excellent hydrogen-bond acceptor from the ammonium ion donors.

The azetidinone complex **4** also showed a tendency to aggregate with ammonium ions, though to a far lesser extent.[14]

Overall, the ESMS behaviour of the bis(isat) complexes **3a** and **3b** were similar. For **3b** at a cone voltage of 5 V the main species present was an ammonium adduct, $[M + NH_4]^+$, and the dimeric form, $[2M + 2NH_4]^{2+}$, was observed as smaller peaks between those of the monomer. The protonated species $[M + H]^+$ was present at just under a quarter of the intensity of the major ion. Fig. 3(*a*) shows the 20 V spectrum of complex **3b**, while Fig. 3(*b*) shows a high-resolution expansion of the *m*/*z* 865–915 region. At 20 V, the main peak was the aggregate $[3M + 2NH_4]^{2+}$, together with $[M + H]^+$, $[M + NH_4]^+$, $[2M + NH_4]^+$ and $[3M + NH_4]^+$ ions. Several additional dicationic species were also observed, namely $[2M + 2NH_4]^{2+}$, $[2M + H + NH_4]^{2+}$ and $[5M + 2NH_4]^{2+}$. It is noteworthy that no $[2M + 2H]^{2+}$ ion was observed as small peaks of 0.5 mass unit separation superimposed on the $[M + H]^+$ pattern at *m*/*z* 886, presumably due to the poorer hydrogen-bond donor capacity, and smaller size, of a proton when compared to an ammonium ion. The $[2M + H + NH_4]^{2+}$ ion exists only as a 2+ ion, with no monocation of the same *m*/*z* possible, and this

Table 2 Positive-ion ESMS data for complexes **2a**, **3a** and **3b**, recorded in MeCN–water solution

Complex	Cone voltage/V	t^a/min	Observed ions (m/z, %)^b
2a	20	0	$[M + H]^+$ (902, 77), $[M - Cl + MeCN]^+$ (906, 35%), $[M + NH_4]^+/[2M + 2NH_4]^{2+}$ (919, 26), unidentified (1003, 9), $[3M + 2NH_4]^{2+}$ (1370, 100)
		27.5	$[M - Cl]^+$ (865, 14), $[M - Cl + NH_3]^+$ (882, 38), $[M + H]^+$ (902, 44), $[M - Cl + MeCN]^+$ (906, 100), $[3M + 2H]^{2+}$ (1352, 16), $[3M + 2NH_4]^{2+}$ (1370, 29)
	5	21	$[M - Cl + NH_3]^+$ (882, 25), $[M + H]^+$ (902, 54), $[M - Cl + MeCN]^+$ (906, 100), $[M + NH_4]^+/[2M + 2NH_4]^{2+}$ (919, 22), $[3M + 2H]^{2+}$ (1352, 12), $[3M + 2NH_4]^{2+}$ (1370, 47)
	60	16.8	$[Pt(o\text{-}C_6H_4PPh_2)(PPh_3)]^+$ (718, 32), $[M - isat]^+$ (755, 47), $[Pt(o\text{-}C_6H_4PPh_2)(MeCN)]^+$ (759, 29), $[M - isat + MeCN]^+$ (796, 22), $[M - Cl]^+$ (865, 100), $[M + H]^+$ (902, 29)
3a	5		$[M + H]^+$ (1012, 69), $[M + NH_4]^+/[2M + 2NH_4]^{2+}$ (1029, 100)
	20		$[M + H]^+$ (1012, 100), $[M + NH_4]^+/[2M + 2NH_4]^{2+}$ (1029, 79)
	40		$[M - isat]^+$ (865, 100), $[M + H]^+$ (1012, 32), unidentified (1393, 6), $[3M + 2NH_4]^{2+}$ (1536, 6), $[2M + NH_4]^+$ (2041, 6)
+ KCl	20		$[M + H]^+$ (1012, 18), $[M + K]^+$ (1051, 100)
+ KCl + NaCl	20		$[M + H]^+$ (1012, 21), $[M + Na]^+$ (1034, 89), $[2M + Na + K]^{2+}$ (1043, 27), $[M + K]^+$ (1051, 100)
	60		$[M + Na]^+$ (1034, 100), $[M + K]^+$ (1051, 69)
3b	5		$[M + H]^+$ (886, 23), $[M + NH_4]^+$ (903, 100), $[2M + 2NH_4]^{2+}$ (903.5, 27)
	20		$[M + H]^+$ (886, 93), $[2M + H + NH_4]^{2+}$ (895, 23), $[M + NH_4]^+$ (903, 85), $[2M + 2NH_4]^{2+}$ (903.5, 27), $[3M + 2NH_4]^{2+}$ (1347, 100), $[2M + NH_4]^+$ (1790, 48), $[5M + 2NH_4]^{2+}$ (2232, 3), $[3M + NH_4]^+$ (2674, 4)

^{a} Solvolysis was observed to occur with the chloro complex **2a**; times refer to time of spectrum acquisition after dissolution of the sample in the ESMS mobile phase. ^{b} The m/z values refer to the most abundant ion in the isotope distribution pattern. In isotope patterns of some of the higher- and lower-mass intensity, species contributions from aggregate species having higher m and z cannot be ruled out.
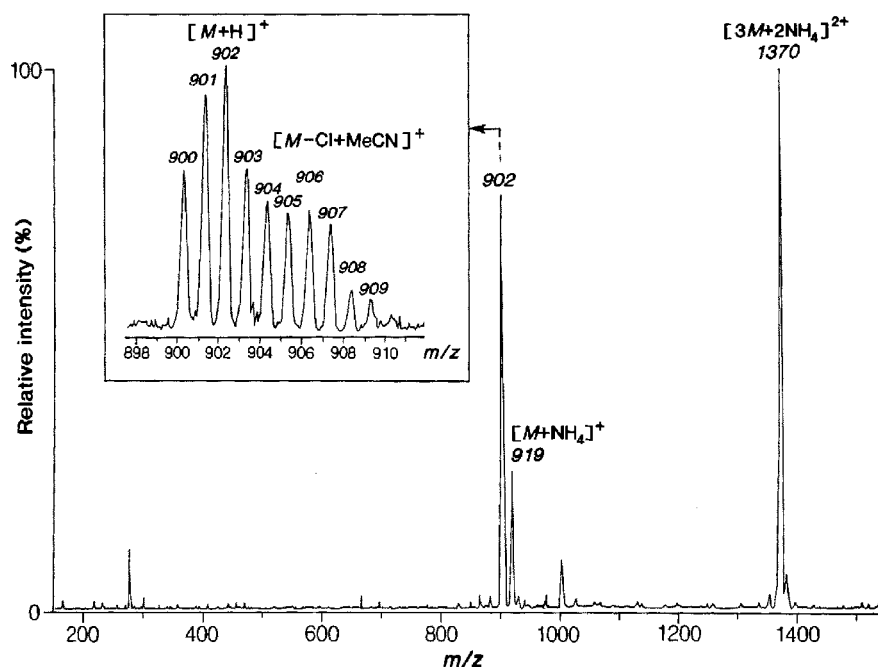
Fig. 4 Positive-ion electrospray mass spectrum (cone voltage 20 V) of a freshly prepared MeCN–water solution of complex **2a**, with ion assignments. The inset shows the high-resolution isotope pattern of the m/z 900–910 region, showing contributions from the ions $[M + H]^+$ (m/z 902) and $[M - Cl + MeCN]^+$ (m/z 906). On allowing the solution to stand the latter ion increases in intensity with a concomitant decrease in the former

is clearly observed in Fig. 3(*b*). No $[M + 2NH_4]^{2+}$ ion was observed, presumably because such an ion would have a relatively high charge density, and would tend to aggregate or fragment to form other ions.

For complex **2a** spectra were run at cone voltages between 5 and 60 V, producing varying amounts of fragmentation. Over the time of the experiment, the low-cone-voltage spectra showed changes due to solvolysis reactions. The spectrum of a freshly prepared solution, at a cone voltage of 20 V, illustrated in Fig. 4, showed a strong aggregate-ion peak corresponding to $[3M + 2NH_4]^{2+}$ (the same major species as observed for **3b** at 20 V) together with an $[M + H]^+$ ion. Over the course of several minutes the solvolysis product $[M - Cl + MeCN]^+$ increased in intensity, eventually becoming the dominant species in the

spectrum. The intensity of the $[3M + 2NH_4]^{2+}$ aggregate also decreased, while another aggregate, $[3M + 2H]^{2+}$, appeared, together with another solvolysis product, $[M - Cl + NH_3]^+$. A small peak, due to $[M - Cl]^+$, had also formed. After almost 30 min had elapsed after sample preparation the intensity of the ammonium aggregate and the $[M + H]^+$ ion had both fallen markedly, while the $[M - Cl + NH_3]^+$ ion had increased. The acetonitrile solvolysis product had increased to more than twice the intensity of any other peak. At the low cone voltage of 5 V fragmentation of ions is unlikely. The complex **2a** was dissolved in acetonitrile–water 21 min before the 5 V spectrum was obtained, hence the solvolysis reactions previously observed were already underway before the spectrum was run. This was seen in the spectrum, where the acetonitrile solvolysis product

was almost twice as intense as that of the $[M + H]^+$ ion. Along with these ions, the two aggregates $[3M + 2NH_4]^{2+}$ and $[3M + 2H]^{2+}$ were again observed. We have previously described analogous solvolysis reactions of related platinum(II) complexes containing chloride and anionic amide ligands derived from diethylbarbituric acid (1H,3H,5H-5,5-diethyl-pyrimidine-2,4,6-trione).[26]

At 60 V fragmentation of the various solvated ions began to occur. The predominant ions are $[M - Cl]^+$ (m/z 865) and $[M - isat]^+$ (m/z 755), followed in intensity by $[M + H]^+$ and $[M - isat + MeCN]^+$. Orthometallation of one of the phenyl rings of the triphenylphosphine ligands was observed by ions at m/z 718 $[Pt(o-C_6H_4PPh_2)(PPh_3)]^+$ and 754 $[Pt(o-C_6H_4PPh_2)(PPh_3) + MeCN]^+$, typical of other (triphenylphosphine)platinum complexes studied at high cone voltages.[26,27]

Owing to the apparent effectiveness of the isatin complexes to aggregate with ammonium cations, an investigation was carried out into the ability of the complexes **2a** and **3a** to co-ordinate alkali-metal cations. The spectrum of **2a** with added KCl contained most of the peaks seen in the previous 20 V spectrum, together with the K^{+} adducts $[M + K]^+$ and $[3M + K + NH_4]^{2+}$.

Addition of KCl to complex **3a** gave, at 20 V, $[M + K]^+$ as the main ion at m/z 1051; the isotope pattern of this ion appeared 'filled-in' suggesting that there was a small contribution from $[2M + 2K]^{2+}$, though individual peaks were not resolved. Addition of both KCl and NaCl to **3a** yielded three different alkali-metal adducts in the 20 V spectrum, with $[M + K]^+$ the most intense, followed by $[M + Na]^+$ at m/z 1034. The dication $[2M + K + Na]^{2+}$ was observed at m/z 1043, showing isotope peaks separated by m/z 0.5, with no contribution from a monocation possible. The isotope pattern for the $[M + Na]^+$ ion appeared more filled-in than that for $[M + K]^+$ suggesting a greater tendency of the higher charge-density Na^{+} to contribute to dicationic species. (It is worth noting that this trend is the opposite to that observed for proton *versus* ammonium aggregation for **3b**, though presumably in this case the extremely small size of the proton places constraints on aggregation.) On increasing the cone voltage to 60 V $[M + Na]^+$ became the major alkali-metal adduct, and the fragmentation of the dications was indicated by the observation of fully resolved isotope patterns for both $[M + Na]^+$ and $[M + K]^+$, and disappearance of the $[2M + Na + K]^{2+}$ ion.

In another experiment pyridine was added to a fresh solution of complex **2a**, to examine the effect of a strongly co-ordinating ligand. At 5 V the pyridine had replaced the chloride ion almost completely, yielding the $[M - Cl + pyridine]^+$ ion at m/z 944. A small peak due to $[M - Cl + NH_3]^+$ was also seen at m/z 882. Very little change was seen on increasing the cone voltage to 20 V. However, at 60 V, the principal ion was $[M - Cl]^+$, together with a small amount of the two orthometallated species observed earlier.

These experiments show that there is a strong tendency for the isatin complexes to aggregate about cations, at least under mass spectrometric conditions. The ESMS technique thus may provide an excellent small-scale, rapid screening mechanism for directing future studies aimed at isolating higher aggregates on a synthetic scale.

Experimental

Cycloocta-1,5-diene and 1,3-bis(diphenylphosphino)propane (Aldrich), isatin (BDH), and triphenylphosphine (Pressure Chemical Co.) were used as supplied. 1,2-Bis(diphenyl-phosphino)ethane[29] and [PdCl₂(bipy)][30] were prepared by literature methods. Triethylamine was distilled before use. The complex [PtCl₂(cod)] was synthesized by the literature procedure,[31] and the phosphineplatinum complexes *cis*-[PtCl₂(PPh₃)₂], [PtCl₂(dppe)] and [PtCl₂(dppp)] were prepared from it

by substitution with the stoichiometric amount of ligand in CH₂Cl₂ solution.[32]

AR grade solvents were used. Methanol was used as supplied, while others were distilled from the following drying agents: dichloromethane (calcium hydride), light petroleum, b.p. 40–60 °C (calcium hydride) and diethyl ether (sodium–benzophenone).

The NMR spectra were obtained on a Bruker AC300P spectrometer in CDCl₃ unless otherwise stated, ¹H spectra at 300.13 MHz, ¹³C-{¹H} at 75.47 MHz, and ³¹P-{¹H} at 121.5 MHz, the latter referenced to external 85% H₃PO₄ (δ 0.0). Electrospray mass spectra were obtained on a VG Platform II mass spectrometer, in positive-ion mode with acetonitrile–water (1:1 v/v) as the mobile phase. Theoretical isotope patterns were calculated using the ISOTOPE program, version 1.6.6 d1.[33] Melting points were determined on a Reichert Thermopan instrument, and are uncorrected. Infrared spectra were obtained as KBr discs, using a Perkin-Elmer 1600 Series FTIR instrument. Elemental analyses were carried out by the University of Otago Campbell Microanalytical Laboratory.

Syntheses

cis-**[PtCl(isat)(PPh₃)₂] 2a.** Isatin (0.019 g, 0.128 mmol) was added to a stirred suspension of *cis*-[PtCl₂(PPh₃)₂] (0.101 g, 0.128 mmol) in methanol (20 cm³). Triethylamine (0.5 cm³, excess) was added and the solution stirred and heated at 45–50 °C for 3.5 h. The solvent was removed under reduced pressure, and the red solid redissolved in dichloromethane (40 cm³). Water (2 × 70 cm³) was used to extract the NEt₃H⁺Cl⁻ produced in the reaction. The organic phase was separated, dried with anhydrous MgSO₄, filtered and the filtrate evaporated to dryness. The red solid was recrystallised from dichloromethane and light petroleum, washed with light petroleum and dried under vacuum, yielding 0.096 g (83%) of dark red crystals of complex **2a**, m.p. 262 °C (Found: C, 58.8; H, 3.9; N, 1.6. C₄₄H₃₄ClNO₂P₂Pt requires C, 58.6; H, 3.8; N, 1.6%). NMR: ³¹P-{¹H}, AB spin system, δ 17.0 (d, P *trans* Cl, $^1J_{PtP}$ 3832, $^2J_{PP}$ 18) and 7.8 (d, P *trans* N, $^1J_{PtP}$ 3101, $^2J_{PP}$ 18); ¹³C-{¹H} [in CDCl₃–(CD₃)₂SO], δ 192 (s, C=O, isat), 167.6 (s, amide C=O, isat), 164.0 (s, isat), 141.0 (s, isat), 138.5 (d, Ph *ortho*-C, $^2J_{PC}$ 9.9), 137.5 (d, Ph *ortho*-C, $^2J_{PC}$ 10.3), 135.0 (s, Ph *para*-C), 134.5 (s, Ph *para*-C), 132.9 (d, Ph *ipso*-C, $^1J_{PC}$ 61.5), 131.7 (pseudo-t, Ph *meta*-C), 131.0 [s, half of doublet (other half obscured by previous resonance), Ph *ipso*-C], 126.7 (s, isat), 124.4 (s, isat, quaternary carbon), 124.1 (s, isat) and 117.9 (s, isat); ¹H, δ 7.9–7.1 (m, Ph and isat), 6.97 (d, isat, $^3J_{HH}$ 6.9) and 6.61 (td, 1 H, isat, $^3J_{HH}$ 7.2, $^4J_{HH}$ 0.7 Hz). IR: $\tilde{\nu}_{max}$ = 1732vs, 1685vs, 1605vs and 1586vs cm⁻¹.

cis-**[Pt(isat)₂(PPh₃)₂] 3a.** The complex *cis*-[PtCl₂(PPh₃)₂] (0.100 g, 0.127 mmol), isatin (ca. 0.1 g, 0.7 mmol) and NEt₃ (0.5 cm³, excess) were allowed to react as above for 89 h. The product was worked up as above, although the dichloromethane solution was filtered before washing with water, to remove undissolved excess of isatin. Recrystallisation of the product from hot methanol, followed by addition of diethyl ether to complete precipitation, yielded 0.057 g (44%) of red crystals of **3a**, after washing with diethyl ether and drying under vacuum. A suitable crystal was characterised by X-ray crystallography. M.p. 268 °C (decomp.) (Found: C, 61.6; H, 4.0; N, 3.1. C₅₂H₃₈N₂O₄P₂Pt requires C, 61.7; H, 3.8; N, 2.8%). NMR: ³¹P-{¹H}, δ 3.76 (s, $^1J_{PtP}$ 3284); ¹³C-{¹H}, δ 187.8 (s, C=O, isat), 165.7 (s, amide C=O, isat), 159.8 (s, isat), 137.9 (s, isat), 134.7 (pseudo-t, Ph, J_{PC} 5.0), 130.9 (s, Ph), 128.0 (pseudo-t, Ph, J_{PC} 5.4), 127.8 (dd, Ph, $^1J_{PC}$ 66.7, $^3J_{PC}$ 8.9), 123.4 (s, isat), 121.4 (s, isat), 120.6 (s, isat) and 115.6 (s, isat); ¹H, δ 7.62–7.55 (m, Ph), 7.32–7.24 (m, Ph), 7,20 (dd, isat, $^3J_{HH}$ 7.2, $^4J_{HH}$ 1.3), 7.17–7.09 (m, Ph), 6.93 (d, 2 H, isat, $^3J_{HH}$ 7.2) and 6.56 (td,

2 H, isat, $^3J_{HH}$ 7.4, $^4J_{HH}$ 0.9 Hz). IR: $\tilde{v}_{max}$ = 1735vs, 1678vs, 1606vs and 1586vs cm^{-1}.

***cis*-[Pt(isat)$_2$(dppe)] 3b.** The complex *cis*-[PtCl$_2$(dppe)] (0.050 g, 0.076 mmol), isatin (*ca.* 0.1 g, 0.7 mmol) and NEt$_3$ (0.5 cm^3) were allowed to react as above, for *ca.* 2.5 d. The solvent was removed by rotary evaporation and the product redissolved in dichloromethane (70 cm^3). The solution was washed with ten portions (20–30 cm^3) of distilled water in a separating funnel, to remove triethylammonium chloride and some of the excess of isatin. The red solution was separated and dried as above, the solvent removed under reduced pressure, and the resulting red solid recrystallised by dissolving in hot methanol and allowing to cool. Crystallisation was aided by the addition of diethyl ether. The solid was filtered off, washed with diethyl ether and dried under vacuum to give 0.019 g (28%) of **3b** as dark red crystals, m.p. 315 °C (decomp.) (Found: C, 56.7; H, 3.8; N, 3.2. C$_{42}$H$_{32}$N$_2$O$_4$P$_2$Pt requires C, 57.0; H, 3.6; N, 3.2%). NMR: ^{31}P-{^{1}H}, δ 35.8 (s, $^1J_{PtP}$ 3173); ^{13}C-{^{1}H}, δ 189.5 (pseudo-t, C=O, isat), 165.7 (s, amide C=O, isat), 161.1 (s, isat), 137.9 (s, isat), 133.4 (s, Ph), 132.3 (s, Ph), 129.2 (pseudo-t, Ph, J_{PC} 5.7), 127.0 (d, Ph, J_{PC} 61.8), 123.4 (s, isat), 121.2 (s, isat), 120.2 (s, isat), 115.6 (s, isat) and 27.4 (dd, dppe CH$_2$, $^1J_{PC}$ 42.9, $^2J_{PC}$ 6.8); ^{1}H, δ 7.9–7.3 (m, 21 H, Ph), 7.1–6.9 (m, 6 H, isat), 6.51 (td, 2 H, isat, $^3J_{HH}$ 7.3, $^4J_{HH}$ 0.8) and 2.5–2.3 (m, 4 H, dppe CH$_2$). IR: $\tilde{v}_{max}$ = 1729vs, 1677vs, 1607vs and 1587vs cm^{-1}.

***cis*-[Pt(isat)$_2$(dppp)] 3c.** The complex *cis*-[PtCl$_2$(dppp)] (0.101 g, 0.149 mmol), isatin (0.044 g, 0.299 mmol) and NEt$_3$ (0.5 cm^3) were allowed to react as above, for 1 h. The product was worked up as above, although it was only washed with a single portion of distilled water. Recrystallisation, first by slow diffusion of pentane into dichloromethane and then from methanol and diethyl ether, yielded 0.074 g (55%) of dark red crystals of **3c**, after washing with diethyl ether and drying under vacuum, m.p. 180 °C (decomp.) (Found: C, 56.1; H, 4.3; N, 2.9. C$_{43}$H$_{34}$N$_2$-O$_4$P$_2$Pt requires C, 57.4; H, 3.8; N, 3.1%). Free isatin was observed in the NMR spectra of this complex. NMR: ^{31}P-{^{1}H}, δ −11.0 (s, $^1J_{PtP}$ 2963); ^{13}C-{^{1}H}, δ 188.4 (pseudo-t, C=O, isat, J_{PC} 2.8), 165.4 (s, amide C=O, isat), 160.5 (s, isat), 137.9 (s, isat), 133.4 (pseudo-t, Ph, J_{PC} 5.2), 132.2 (pseudo-t, Ph, J_{PC} 5.0), 131.3 (d, Ph, J_{PC} 31.3), 128.5 (pseudo-t, Ph, J_{PC} 5.4), 128.1 (s, unchanged isatin), 127.7 (s, unchanged isatin), 126.2 (s, unchanged isatin), 125.4 (s, unchanged isatin), 123.4 (s, isat), 121.1 (s, isat), 120.6 (s, isat), 115.8 (s, isat), 22.4 (m, dppp PCH$_2$) and 18.0 (s, dppp CCH$_2$C); ^{1}H, δ 7.8–7.2 (m, Ph), 7.20–7.00 (m, isat), 6.93 (d, isat, $^3J_{HH}$ 6.9), 6.59 (td, 2 H, isat, $^3J_{HH}$ 7.2, $^4J_{HH}$ 1.3 Hz), 2.97 (m, 4 H, dppp CH$_2$P) and 2.2 (m, 2 H, dppp CCH$_2$C). IR: $\tilde{v}_{max}$ = 1731vs, 1676vs, 1608vs and 1586vs cm^{-1}.

[Pd(isat)$_2$(bipy)] 3d. The complex [PdCl$_2$(bipy)] (0.099 g, 0.295 mmol), isatin (0.3 g, 2 mmol) and NEt$_3$ (0.5 cm^3) were allowed to react at 60–70 °C for *ca.* 5.5 d. The solvent was removed by rotary evaporation and the residue redissolved in dichloromethane (250 cm^3). The product was then washed with distilled water (200 cm^3). The organic layer was separated, dried and filtered, and the solvent removed. The product was recrystallised from hot methanol, with the addition of diethyl ether to complete the crystallisation. Filtration and washing with diethyl ether, followed by vacuum drying, yielded 0.11 g (65%) of **3d** as a dark red powder, m.p. >320 °C (Found: C, 54.9; H, 2.7; N, 9.8. C$_{26}$H$_{16}$N$_4$O$_4$Pd requires C, 56.3; H, 2.9; N, 10.1%). A broad methanol peak at δ 3.5 was seen in a ^{1}H NMR spectrum run in CDCl$_3$. The sample was not however concentrated enough to obtain an accurate integration of this peak (Calc. for C$_{26}$H$_{16}$N$_4$O$_4$Pd·CH$_3$OH: C, 55.3; H, 3.4; N, 9.6%). NMR [in (CD$_3$)$_2$SO]: ^{13}C-{^{1}H}, δ 189.1 (s, C=O, isat), 168.8 (s, amide C=O, isat), 162.6 (s, bipy), 157.4 (s, bipy), 153.1 (s, isat), 143.3 (s), 139.6 (s), 129.5 (s), 125.6 (s), 125.1 (s), 122.9

(s), 122.6 (s) and 117.1 (s, isat); ^{1}H, δ 8.74 (d, 2 H, bipy, $^3J_{HH}$ 7.8), 8.56 (dd, 2 H, bipy, $^3J_{HH}$ 5.6, $^4J_{HH}$ 1.4), 8.46 (td, 2 H, bipy, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.3), 7.78 (m, 2 H, bipy), 7.42 (td, 2 H, isat, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.3), 7.31 (d, 2 H, isat, $^3J_{HH}$ 7.9), 7.20 (dd, 2 H, isat, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.2) and 6.83 (t, 2 H, isat, $^3J_{HH}$ 7.5 Hz). IR: $\tilde{v}_{max}$ = 1727vs, 1676vs, 1605vs and 1587vs cm^{-1}.

Crystallography

Dark red crystals of complex **3a** were obtained from methanol–diethyl ether at 4 °C. Preliminary precession photography indicated a monoclinic lattice. Unit-cell dimensions and intensity data were collected using a Siemens SMART CCD diffractometer, with Mo-Kα X-radiation (λ = 0.710 73 Å). The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures with different φ angles. The crystal to detector distance was 5.0 cm. The data set was corrected empirically for absorption using SADABS [34] ($T_{max,min}$ 0.704, 0.479).

Crystal data. C$_{52}$H$_{38}$N$_2$O$_4$P$_2$Pt, M_r = 1011.87, monoclinic, space group $P2_1/c$, a = 11.2066(1), b = 18.0691(1), c = 21.1167(2) Å, β = 97.808(1)°, U = 4236.34(6) Å^3, Z = 4, D_c = 1.587 g cm^{-3}, μ(Mo-Kα) = 3.438 mm^{-1}, F(000) 2016, T = 293(2) K, crystal size = 0.14 × 0.28 × 0.32 mm.

A total of 26 163 reflections were collected, over a range of 1.49 < θ < 28.27°, of which 9527 were independent (R_{int} = 0.023). The structure was solved by direct methods (SHELXS 86) [35] and developed routinely. Refinement (SHELXL 93) [36] was by full-matrix least squares on F^2 and converged to $R1$ = 0.0242, $wR2$ = 0.0542 [for 8359 data with $I > 2σ(I)$], and $R1$ = 0.0316, $wR2$ = 0.0584 (all data), with goodness of fit = 1.089. In the final difference map the largest features were at +0.838 and −1.098 e Å^{-3}.

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