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Coordination isomerism in salicylhydroxamate complexes of platinum(II) and palladium(II)

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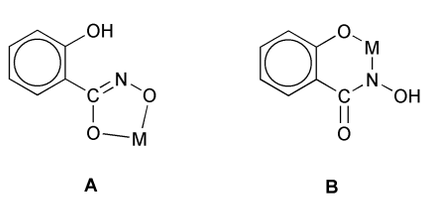
Received 25th March 2003, Accepted 12th May 2003
First published as an Advance Article on the web 28th May 2003

The syntheses of a range of platinum(II) and palladium(II) complexes containing salicylhydroxamate ligands are described. The ancillary ligands, together with the synthetic route, influence the coordination mode of the salicylhydroxamate ligand. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with salicylhydroxamic acid and trimethylamine in hot methanol gave O,O′-bonded $[Pt\{OC(=NO)C_6H_4OH\}(PPh_3)_2]$, but $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) gave N,O-bonded $[Pt\{OC_6H_4C(O)NOH\}(cod)]$. Ligand substitution gives other N,O bonded complexes, including $[Pt\{OC_6H_4C(O)NOH\}(PPh_3)_2]$. Reaction of K_2PtCl_4 with 2 equiv. of EPh_3 (E = As or Sb), salicylhydroxamic acid and excess trimethylamine gives products whose structures depend on E; $AsPh_3$ gives $[Pt\{OC(=NO)C_6H_4OH\}(AsPh_3)_2]$, while $SbPh_3$ gives $[Pt\{OC_6H_4C(O)NOH\}(SbPh_3)_2]$.

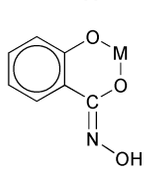
1 Introduction

Hydroxamic acids, containing the –C(O)NHOH functionality, are potent metal complexing agents, able to coordinate to a wide range of metal ions.[1–3] Nature has employed the hydroxamate functional group to great effect in, for example, microbial iron(III) complexing agents (siderophores), which, together with synthetic siderophores often have extremely high binding affinities for this metal ion.[4] Hydroxamate ligands typically coordinate as a bidentate chelating ligand, by coordination of the carbonyl oxygen and the deprotonated OH group to the metal centre. However, other binding modes are possible, such as through nitrogen, or an ancillary donor group in the ligand, and this is one of the features which has attracted interest in this class of ligand.[2,5] Following on from our recent studies into platinum group metal and gold complexes of the (sulfur–oxygen donor) thiosalicylate ligand,[6,7] we were interested in extending our studies to complexes of deprotonated salicylhydroxamic acid **1**. This ligand presents a number of potential binding modes to metal ions (Scheme 1) either in the traditional O,O′ binding mode **A**, or in alternative modes involving the nitrogen atom and/or the phenolic oxygen (**B**–**D**). Complexes of this ligand have been synthesised previously, for example, a range of first row transition metals,[8] copper(II)[9] and nickel(II).[10] Hambley and co-workers have recently reported some platinum(II) and palladium(II) complexes containing deprotonated salicylhydroxamic acid ligands.[11,12] In these studies, two different binding modes were highlighted. $[Pt\{OC(=NO)C_6H_4OH\}(PPh_3)_2]$ **2a**,[11] and the analogue $[Pt\{OC(=NO)C_6H_4OH\}(SOMe_2)_2]$[12] containing salicylhydroxamate dianion ligands, have the well-established O,O′ binding mode (**A**, Scheme 1). In contrast, the complex $[Pd\{(OC_6H_4C(OH)(=NOH)\}_2]$ contained the (monoanionic) ligand coordinated through the deprotonated phenolic oxygen, and the nitrogen atom, related to mode **B** in Scheme 1; this represented a unique binding mode for this ligand. In this paper, we have extended these studies, and report the syntheses of a range of complexes containing salicylhydroxamate dianion ligands. It is found that the ancillary ligands, and the synthetic route employed, bear a strong influence on the binding mode of the salicylhydroxamate ligand.

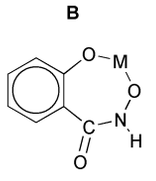


A

B

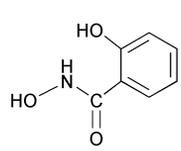


C

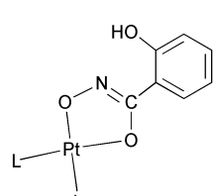


D

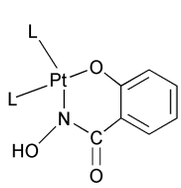
Scheme 1



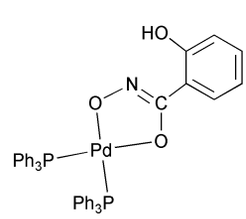
1



2a, L = PPh_3
2b, L_2 = dppf
2c, L = $AsPh_3$



3a, L_2 = cod
3b, L = PPh_3
3c, L_2 = dppf
3d, L = $P(OPh)_3$



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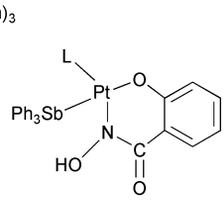

5a, L = $SbPh_3$
5b, L = 4-methylpyridine

DOI: 10.1039/b303367h

2 Results and discussion

Chemistry of the bis(triphenylphosphine)platinum(II) salicylhydroxamate system

The complex [Pt{OC(=NO)C_6H_4OH}(PPh_3)$_2$] **2a** has been previously synthesised by Hambley and co-workers, by the reaction of *cis*-[$PtCl_2(PPh_3)_2$] with salicylhydroxamic acid in methanol with aqueous NaOH, and has been characterised by an X-ray diffraction study.[11] However, ^{31}P NMR data were not reported for the complex. We find that the reaction, when carried out with trimethylamine as the base in hot methanol, gives the same product as an authentic sample prepared using the literature method, but does not require the pH to be monitored. The ^{31}P–{^{1}H} NMR spectrum of this complex shows a single species, with resonances at δ 11.1 and 9.5, showing coupling to ^{195}Pt of 3299 and 3786 Hz respectively. The difference between the two coupling constants is surprisingly large, and indicates that the two O donor groups have quite different *trans* influences.

When the complex [$PtCl_2$(cod)] (cod = cycloocta-1,5-diene) is reacted with salicylhydroxamic acid and trimethylamine base in hot methanol, a pale yellow microcrystalline solid **3a** was obtained, which analyses for [Pt(salicylhydroxamate)(cod)]. The complex shows two cod CH resonances in the ^{1}H NMR spectrum at δ 5.66 and 5.42, showing coupling to ^{195}Pt of *ca.* 69 and 62 Hz respectively. A broad peak at δ 10 is assigned to an OH proton, which exchanges on shaking with D_2O. Two cod CH and two CH_2 resonances were also observed in the ^{13}C–{^{1}H} NMR spectrum, with the CH resonances showing different ^1J(PtC) couplings of 157 and 171 Hz. Reaction of complex **3a** with 2 equiv. of triphenylphosphine in dichloromethane leads to a pale yellow complex **3b** which analyses as [Pt(salicylhydroxamate)(PPh_3)$_2$], but which has a different melting point and spectroscopic properties to complex **2a** prepared directly from *cis*-[$PtCl_2(PPh_3)_2$]. Thus, the ^{31}P–{^{1}H} NMR spectrum of complex **3b** shows two resonances at δ 22.2 and 6.0 with ^1J(PtP) 3455 and 3594 Hz respectively.

In order to unequivocally ascertain the mode of binding of the salicylhydroxamate ligand to the platinum centre in **3b**, an X-ray structure determination was carried out. Crystals of the complex were obtained from a $CDCl_3$ solution. The molecular structure and atom numbering scheme are shown in Fig. 1, while Table 1 gives selected bond lengths and angles.

The structure determination indicates that the salicylhydroxamate ligand coordinates to platinum through the phenolate oxygen and the nitrogen atom of the hydroxamic acid, forming a six-membered chelate ring system (**B**, Scheme 1). The O,O′ bonded isomer **2a** described by Hambley and coworkers[11] provides an excellent reference point for discussion of the structure, since the ancillary ligands are the same. The N,O isomer **3b** has both a shorter C–O bond distance [C(7)–O(2) 1.257(2) Å] and a longer C–N bond distance [C(7)–N(1) 1.334(3) Å] than the O,O′ isomer **2a**, which has C–O 1.322(6) and C–N 1.297(6) Å, consistent with the oxamate (as opposed to oximate) binding in **3a**. The palladium salicylhydroxamate monoanion complex [Pd{(OC_6H_4C(OH)(=NOH)}$_2$] likewise has a C=N double bond, with a bond length of 1.294(4) Å.[11] Unsurprisingly, the phenolic C–O bond has a similar bond length in **3b** [1.340(2) Å] to the uncoordinated version (with an OH group) in **2a** [1.349(7) Å].

Table 1 Selected bond lengths (Å) and bond angles (°) for [Pt{O-C_6H_4C(O)NOH}(PPh_3)$_2$] **3b**

Pt(1)–O(1)	2.0313(14)	Pt(1)–N(1)	2.0327(17)
N(1)–C(7)	1.334(3)	N(1)–O(3)	1.421(2)
O(1)–C(1)	1.340(2)	O(2)–C(7)	1.257(2)
C(6)–C(7)	1.492(3)		
P(1)–C(21)	1.817(2)	P(1)–C(31)	1.823(2)
P(1)–C(11)	1.833(2)	P(1)–Pt(1)	2.2648(5)
P(2)–C(41)	1.818(2)	P(2)–C(61)	1.824(2)
P(2)–C(51)	1.837(2)	P(2)–Pt(1)	2.2596(5)
O(1)–Pt(1)–N(1)	84.04(6)	N(1)–Pt(1)–P(2)	92.04(5)
O(1)–Pt(1)–P(1)	86.88(4)	P(2)–Pt(1)–P(1)	97.017(18)
C(7)–N(1)–O(3)	111.42(15)	C(7)–N(1)–Pt(1)	127.91(13)
O(3)–N(1)–Pt(1)	119.01(12)	C(1)–O(1)–Pt(1)	120.11(12)
O(1)–C(1)–C(2)	116.81(18)	O(1)–C(1)–C(6)	124.42(18)
O(2)–C(7)–N(1)	120.22(18)	O(2)–C(7)–C(6)	121.42(18)
N(1)–C(7)–C(6)	118.35(17)		

The platinum–phosphorus bond lengths also merit discussion. In the N,O isomer **3b**, the Pt–P bond distances are, on average, slightly longer [2.2648(5) and 2.2596(5) Å] than in the O,O′ isomer **2a** [2.2062(13) and 2.2335(17) Å], suggesting that the donor groups in the N,O binding mode have a slightly greater *trans* influence. In addition, the difference in the Pt–P bond distances for the O,O′ isomer **2a** (0.0273 Å) is greater than for the N,O isomer **3b** (0.0052 Å), which is consistent with the observation that difference in the ^1J(PtP) coupling constants (of the two PPh_3 ligands) in the NMR spectrum of the O,O′ isomer (3299 and 3786 Hz) are greater than for the N,O isomer (3455 and 3594 Hz).

The platinum–salicylhydroxamate system of **3b** is non-planar, being puckered along the O(1) ··· N(1) axis (Fig. 2a) with an angle between the platinum coordination plane [defined

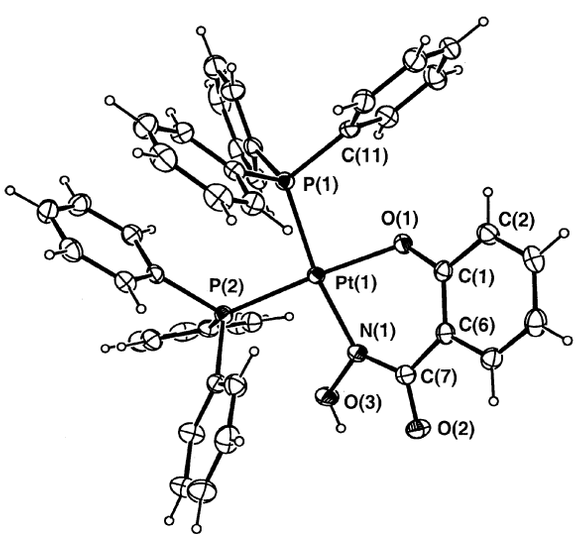

Fig. 1 Molecular structure of [Pt{OC_6H_4C(O)NOH}(PPh_3)$_2$] **3b**, showing the atom numbering scheme.

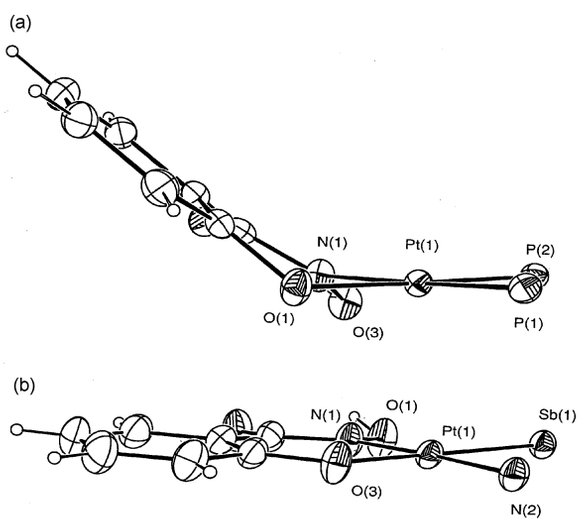

Fig. 2 The degree of puckering and twisting of the salicylhydroxamate–platinum system in (a) [Pt{OC_6H_4C(O)NOH}(PPh_3)$_2$] **3b** and (b) [Pt-{OC_6H_4C(O)NOH}($SbPh_3$)(*p*-NC_5H_4Me)] **5b**, with only the donor atoms of the ancillary ligands shown.

by the atoms P(1), P(2), Pt(1), O(1) and N(1)] and the salicylhydroxamate ligand [defined by atoms O(1), C(1)–C(6) and C(7)] being 41.87(5)°. The hydroxamic acid moiety is also twisted out of the plane of the benzene ring, Fig. 2a, with an angle of 14.9(2)° between the planes defined by the benzene ring (and associated phenolate oxygen) [C(1)–C(6) and O(2)] and the plane defined by C(7), O(2) and N(1). This puckering and twisting is reminiscent of that observed previously in platinum(II) thiosalicylate complexes,[7] and indicates somewhat of a mismatch in size between the metal centre and the preferred bite angle of the ligand, resulting in a ligand deformation. The salicylhydroxamate ligand binding in the N,O mode has a greater 'bite' angle [as indicated by the bond angle O(1)–Pt(1)–N(1) 84.04(6)°] compared to the O,O′ binding mode in **2a** [where the O–Pt–O bite angle is 79.21(13)°]. The greater bite angle results in a slight decrease in the P(1)–Pt(1)–P(2) bond angle in **3b** [97.017(18)°] compared with the corresponding angle in **2a** [100.59(5)°]. By comparison, [Pt{OC(=NO)C_6H_4OH}($SOMe_2$)$_2$] has an intermediate O–Pt–O bite angle of 82.16(14)°.[12]

The $CDCl_3$ of crystallisation is weakly hydrogen-bonded to oxygen O(1), with a D ⋯ O distance of 2.09 Å. Hydrogen H(3) is also weakly hydrogen-bonded intramolecularly to O(2) with a H(3) ⋯ O(2) distance of 2.03 Å; the O(2)–C(7)–N(1)–O(3) torsion angle is −0.59°, which facilitates this interaction. There are no unusual intermolecular interactions. By comparison, the O,O′ isomer contains a similar intramolecular hydrogen bond, between the phenolic OH proton and the oximate nitrogen.

The O,O′ bonded isomer **2a** appears to be the more stable of the two isomers, and several lines of evidence point towards this conclusion. Firstly, the bite angle of the salicylhydroxamate ligand in the O,O′ isomer is smaller than in the N,O isomer **3b** (which requires puckering of the ligand in order to coordinate more effectively). Secondly, the electrospray mass spectra of the two isomers at a low cone voltage (20 V) appear very similar, with $[M + H]^+$ the base peak (*m*/*z* 871), and $[2M + H]^+$ (*m*/*z* 1741) also seen as a lower intensity ion. However, at an elevated cone voltage (80 V), fragmentation is seen, giving the ion $[Pt(C_6H_4PPh_2)(PPh_3)]^+$ (*m*/*z* 718), formed by cyclometallation of a triphenylphosphine ligand, and loss of the salicylhydroxamate ligand. The intensity of this ion in the spectrum of the N,O isomer **3b** (*ca.* 85%) was significantly greater than that from the O,O′ isomer **2a** (*ca.* 33%), suggesting that the N,O isomer is more susceptible to fragmentation, as a result of reduced stability compared to the O,O′ isomer. Thirdly, the O,O isomer **2a** melts at 280–282 °C, while the N,O isomer **3b** initially melts at *ca.* 210 °C, resolidifies, and then remelts at 280–282 °C, suggesting that a thermal isomerisation reaction might be occuring to give the O,O′-isomer **2a**. Heating a sample of the N,O isomer to 250 °C for 5 min resulted in (incomplete) conversion to the O,O′ isomer **2a**, while heating a sample of **2a** under the same conditions resulted in no change to the ^{31}P NMR spectrum. A fourth piece of evidence pointing towards the greater stability of the O,O′ isomer is the fact that the reaction mixture between [Pt{OC_6H_4C(O)NOH}(cod)] and 2 equiv. of PPh_3 initially gives solely the N,O isomer [δ ^{31}P 22.3 and 6.1] but on prolonged standing (several days) in the $CDCl_3$ solution, a small amount of the O,O′ isomer [δ ^{31}P 11.1, 9.5] was seen to form. It is worth noting that theoretical calculations on the salicylhydroxamate *monoanion* complex [Pd{(OC_6H_4C(OH)(=NOH)}$_2$] indicated that the N,O isomer observed experimentally is the most stable in this case.[11] Hambley and coworkers have suggested that the O,O′ binding mode is stabilized by the presence of soft ligands *trans* to the hydroxamate ligand.[12]

^{13}C–{^{1}H} NMR spectroscopy can also be used to determine the binding mode of the salicylhydroxamate ligand. The O,O-bonded isomer **2a** shows a broad resonance at δ 167.5 and a singlet at δ 157.0. In contrast, the N,O isomer **3b** shows a much smaller separation of the two resonances, with a singlet at δ 163.0 and a doublet at δ 161.1 [with *J*(PC) 6.6 Hz]. The cod complex **3a** shows two resonances in the C–O region of the ^{13}C–{^{1}H} NMR spectrum, at δ 162.4, and at 160.0, the latter showing coupling to ^{195}Pt of 43.5 Hz, and this complex is thus assigned the N,O binding mode.

Table 2 Selected ^{13}C–{^{1}H} NMR data for platinum(II) and palladium(II) salicylhydroxamate complexes, with the assignment of the ligand binding mode[a]

Complex	δ ^{13}C	Assignment
2a	167.5, 157.0	O,O′
2b	167.3, 157.0	O,O′
2c	168.0, 157.0	O,O′
3a	162.4, 160.0	N,O
3b	163.0, 161.1	N,O
3c	162.9, 161.0	N,O
3d	162.6, 160.9	N,O
4	164.5, 157.1	O,O′
5a	164.0, 159.0	N,O

[a] Complexes with ^{13}C NMR resonances at *ca.* δ 157 and 168 are assigned the O,O′ binding mode **A**; those with resonances at *ca.* δ 159–160 and 163–164 are assigned the N,O mode **B**. Refer to Scheme 1.

Synthesis and characterisation of other salicylhydroxamate derivatives

Complexes of the salicylhydroxamate ligand, with platinum(II) or palladium(II), and various ancillary ligands, have been synthesised either directly (from the metal halide complex) or, in the case of platinum complexes, by ligand substitution of the cod ligand from **3a**. ^{13}C–{^{1}H} NMR spectroscopy has been used to assign the binding modes of other complexes described in this paper, with ^{31}P–{^{1}H} NMR spectroscopy also employed where possible. The appropriate ^{13}C NMR data and the ligand binding mode assignments are summarised in Table 2 for the various complexes reported in this paper.

The chemistry of the platinum(II)–1,1′-bis(diphenylphosphino)ferrocene (dppf)–salicylhydroxamate system mirrors that of the triphenylphosphine system. Thus, reaction of [$PtCl_2$(dppf)] with salicylhydroxamic acid and trimethylamine base gives the O,O′ isomer **2b**, which has resonances in the ^{31}P–{^{1}H} NMR spectrum at δ 10.7 and 8.5, with ^{195}Pt–^{31}P coupling constants of 3348 and 3862 Hz respectively. These values are very similar to the corresponding O,O′ isomer of the triphenylphosphine system, *i.e.* **2a**. Two resonances at δ 167.3 and 157.0 in the ^{13}C–{^{1}H} NMR spectrum confirm the O,O′ binding mode. In contrast, the reaction of [Pt{OC_6H_4-C(O)NOH}(cod)] **3a** with dppf gives the N,O isomer **3c**, which has ^{31}P NMR resonances at δ 20.3 and 5.0, with ^1J(PtP) values of 3497 and 3708 Hz respectively. The greater chemical shift separation of the two phosphine resonances, and the closer similarity of the corresponding ^{195}Pt–^{31}P coupling constants, by comparison with the triphenylphosphine analogue, indicates the N,O isomer in this case. Like the PPh_3 system, the N,O bonded dppf complex **3c** undergoes an isomerisation in $CDCl_3$ solution to the O,O′ isomer **2b** over the period of several days.

When [$PdCl_2$(PPh_3)$_2$] is reacted with salicylhydroxamic acid under the usual conditions, a maroon solid is obtained. Two ^{31}P NMR resonances are observed [δ 31.5 and 28.6], the chemical shift difference $\Delta\delta$ (2.9 ppm) being much closer to the small shift difference for the O,O′ bonded [Pt{OC(=NO)C_6H_4OH}-(PPh_3)$_2$] **2a** [$\Delta\delta$ 1.6 ppm] than the N,O bonded [Pt{OC_6-H_4C(O)NOH}(PPh_3)$_2$] **3b** [$\Delta\delta$ 16.2 ppm]. Hence the palladium complex is assigned the O,O′ bonded structure **4** (consistent with its preparation from the dichloride). The ^{13}C–{^{1}H} NMR spectrum of **4** shows a doublet of doublets at δ 164.5 [*J*(PC) 15.9 and 2.4] and a singlet at δ 157.1, consistent with O,O′ bonding (Table 2).

The reactions of $[PtCl_2(EPh_3)_2]$ (generated *in situ* from K_2PtCl_4 and EPh_3; E = As or Sb) with salicylhydroxamic acid and trimethylamine give yellow solids which analyse for [Pt(salicylhydroxamate)$(EPh_3)_2$]. However, $^{13}C–\{^1H\}$ NMR data suggest that these two complexes do not have the same structure. The $AsPh_3$ complex **2c** shows two singlets at δ 168.0 and 157.0, and is assigned the O,O′ binding mode (analogous to the lighter PPh_3 congener), but in contrast, the $SbPh_3$ complex shows signals at δ 164.0 and 159.7, and is assigned the N,O binding mode **5a** (Table 2). Supporting evidence for the assignment of the stibine complex comes from X-ray crystallographic characterisation of a ligand-substituted derivative, described in the next section.

The reaction of the cod complex **3a** with excess triphenylphosphite gave white microcrystals of the phosphite complex **3d**, which is proposed on the basis of ^{13}C NMR data to have the N,O bonded structure (refer to Table 2).

X-Ray structure determination of $[Pt\{OC_6H_4C(O)NOH\}(SbPh_3)(p\text{-}NC_5H_4Me)]$ 5b

Reaction of the bis(triphenylstibine) complex **5a** with excess 4-methylpyridine in dichloromethane solution resulted in formation of yellow crystals of the mono(stibine) complex $[Pt\{OC_6H_4C(O)NOH\}(SbPh_3)(p\text{-}NC_5H_4Me)]$ **5b**, which was characterised by elemental analysis, and an X-ray diffraction study.

The molecular structure and atom numbering scheme are shown in Fig. 3, while Table 3 gives selected bond lengths and angles. The structure determination confirms the N,O binding mode of the ligand, and allows comparison with the triphenylphosphine complex described above. The phenolate oxygen is *trans* to the $SbPh_3$ ligand, while the coordinated N(OH) group is *trans* to the 4-methylpyridine ligand. The stibine ligand *trans* to the N(OH) group of **5a** might be expected to be substituted more readily, because in the triphenylphosphine–platinum N,O structure **3b**, the phosphine *trans* to the N(OH) group has the longer Pt–P bond distance. This would account for the formation of the observed isomer of $[Pt\{OC_6H_4C(O)NOH\}(SbPh_3)(p\text{-}NC_5H_4Me)]$ **5b**.

The bond lengths within the salicylhydroxamate ligand are very similar to those of the N,O-bonded bis(triphenylphosphine) complex **3b**; the C(1)–O(2) and C(1)–N(1) bond distances of 1.263(6) and 1.333(7) Å are consistent with C=O double and C–N single bonds. The Pt(1)–O(3) [1.999(4) Å] and Pt(1)–N(1) [1.972(4) Å] distances are shorter than their counterparts in the triphenylphosphine analogue **3b** [2.0313(14) and 2.0327(17) Å respectively], due to the lower *trans* influence of triphenylstibine and 4-methylpyridine compared with triphenylphosphine.[13,14] In **5b** the O(3)–Pt(1)–N(1) bond angle [91.78(17)°] is even larger than in the N,O-triphenylphosphine complex [84.04(6)°], while the Sb(1)–Pt(1)–N(2) bond angle between the pyridine and stibine ligands is more acute, at 93.62(12)°. Compared with the N,O bonded bis(triphenylphosphine) complex **3b**, the stibine complex **5b** is much less puckered; the angle between the planes defined by the Pt coordination sphere [Sb(1), N(1), Pt(1), O(3), N(2)] and the ligand [O(3) and C(1)–C(7)] is only 3.2°, as shown in Fig. 2b. Likewise, the twist angle of the hydroxamate group [defined by N(1), C(1) and O(2)] and the plane of the ligand [O(3) and C(1)–C(7)] is 4.7°. The sterically less demanding ligands in the case of **5b** allow contraction of the Sb–Pt–N angle, with concomitant widening of the N–Pt–O salicylhydroxamate angle, so less puckering and twisting of the ligand is required to match the metal and ligand requirements.

Table 3 Selected bond lengths (Å) and bond angles (°) for $[Pt\{OC_6H_4C(O)NOH\}(SbPh_3)(p\text{-}NC_5H_4Me)]$ **5b**

Pt(1)–N(1)	1.972(4)	Pt(1)–O(3)	1.999(4)
Pt(1)–N(2)	2.049(4)	Pt(1)–Sb(1)	2.5060(7)
Sb(1)–C(19)	2.117(6)	Sb(1)–C(25)	2.122(5)
Sb(1)–C(13)	2.129(5)	O(1)–N(1)	1.421(6)
O(2)–C(1)	1.263(6)	O(3)–C(7)	1.317(6)
N(1)–C(1)	1.333(7)	C(1)–C(2)	1.481(8)
N(1)–Pt(1)–O(3)	91.78(17)	O(3)–Pt(1)–N(2)	83.05(16)
N(1)–Pt(1)–Sb(1)	91.57(13)	N(2)–Pt(1)–Sb(1)	93.62(12)
C(19)–Sb(1)–C(25)	102.6(2)	C(19)–Sb(1)–C(13)	98.8(2)
C(25)–Sb(1)–C(13)	100.5(2)	C(19)–Sb(1)–Pt(1)	115.59(15)
C(25)–Sb(1)–Pt(1)	122.85(15)	C(13)–Sb(1)–Pt(1)	112.90(15)
C(7)–O(3)–Pt(1)	125.4(3)	C(1)–N(1)–O(1)	113.9(4)
C(1)–N(1)–Pt(1)	130.9(4)	O(1)–N(1)–Pt(1)	115.1(3)
O(2)–C(1)–N(1)	120.6(5)	O(2)–C(1)–C(2)	119.9(5)
N(1)–C(1)–C(2)	119.5(5)		

The Pt–Sb distance of 2.5060(7) Å is similar to the Pt–Sb distance of 2.507(2) Å in the compound $[Bu_4N][PtI_3(SbPh_3)]$,[13] and the average Pt–Sb distance of 2.503(1) Å in two independent molecules in the structure of *cis*-$[PtCl_2(SbPh_3)_2]$.[15] It is worth noting that there have only been eight previous structure determinations on Pt–$SbPh_3$ complexes.[16] The Pt–N distance to the pyridine [2.049(4) Å] appears normal compared to Pt–N bond lengths of 2.01(1) and 2.04(1) Å in *cis*-$[PtCl_2(pyridine)_2]$.[17]

The complex dimerises by formation of two O–H ··· O hydrogen bonds between C=O and N–OH groups, as shown in Fig. 4. The O(1) ··· O(2) distance is 2.719 Å, and the O(1)–H(1) bond distance is 0.820 Å, with an O(1)–H(1)–O(2) angle of 158.4°. The O(1)–N(1)–C(1)–O(2) torsion angle is −1.6°. This dimerisation might be facilitated by the coplanarity of the NOH and C=O groups in this particular complex, a feature not present in the triphenylphosphine analogue **3b**.

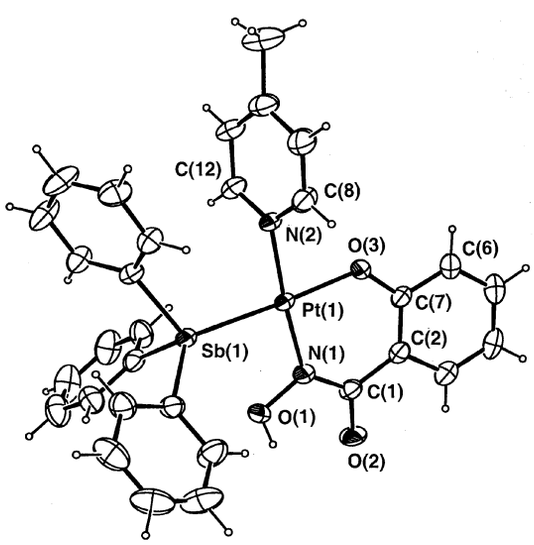

Fig. 3 Molecular structure of $[Pt\{OC_6H_4C(O)NOH\}(SbPh_3)(p\text{-}NC_5H_4Me)]$ **5b** showing the atom numbering scheme.

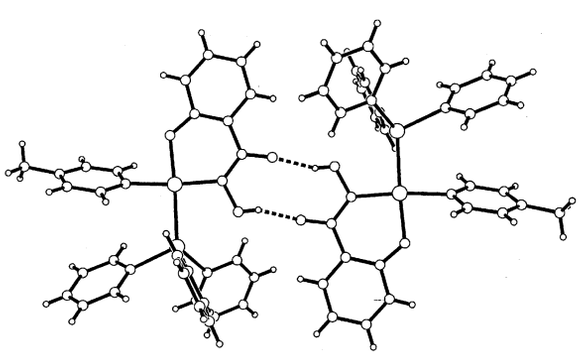

Fig. 4 Diagram showing the formation of hydrogen-bonded dimers between pairs of molecules of $[Pt\{OC_6H_4C(O)NOH\}(SbPh_3)(p\text{-}NC_5H_4Me)]$ **5b**.

Table 4 Biological activity data for selected salicylhydroxamate complexes

Complex	P388 IC_{50}[a]/ ng mL^{-1} (/μM)	Antimicrobial activity[b]					
		Eschericia coli	*Bacillus subtilis*	*Pseudomonas aeruginosa*	*Candida albicans*	*Trichophyton mentagrophytes*	*Cladosporium resinae*
2a	12898 (14.8)	0	0	0	0	0	0
2b	10788 (12.0)	0	0	0	0	0	0
3a	785 (1.7)	5	12	1	5	8	2
3b	1382 (1.6)	0	0	0	0	0	0
3c	16368 (18.1)	0	0	0	0	0	0
4	22712 (29.1)	0	1	0	0	0	0

[a] The concentration of sample in ng mL^{-1} (μM) required to reduce the cell growth of the P388 leukemia cell line (ATCC CCL 46) by 50%. [b] Inhibition zone as excess radius (mm) from a 6 mm diameter disc containing 2 mg of sample

Biological activity

The availability of different coordination isomers in the current work offered the opportunity to test the effect of this on the biological activity of the complexes. A selection of complexes was assayed for activity against P388 murine leukemia cells, and against 3 fungi and 3 bacteria, and data are summarised in Table 4. The N,O-bonded complexes **3a** and **3b** both show good activity against the P388 leukemia cells, with IC_{50} values of 1.7 and 1.6 μM respectively. The other complexes, including the triphenylphosphine-containing O,O′ isomer **2a**, and both dppf isomers **2b** and **3c**, are essentially inactive. In the antimicrobial screen, only the cyclooctadiene complex **3a** showed any activity, with some selectivity against *Bacillus subtilis*.

Discussion and conclusions

In this paper we have described syntheses of a series of platinum(II) and palladium(II) complexes containing salicylhydroxamate ligands. In some cases, complexes containing the ligand coordinated through the N and the deprotonated phenolic oxygen are obtained (the N,O binding mode **A**, Scheme 1) while in others, an alternative binding mode employing the two other oxygen atoms (the O,O′ binding mode **B**) is seen. $^{13}C–\{^1H\}$ and $^{31}P–\{^1H\}$ NMR spectroscopy can be used to determine the ligand binding mode in individual cases. The nature of the ancillary ligands appears to play a role in determining the isomer formed. When the ligand is a relatively bulky ligand, *viz.* triphenylphosphine, triphenylarsine or dppf, the O,O′ isomer is formed, possibly because the resulting five-membered chelate ring gives a more acute 'bite' at the metal centre, allowing the P–Pt–P or As–Pt–As bond angle to open out to relieve steric congestion. However, when a smaller ligand is used – *e.g.* cyclooctadiene, but also triphenylstibine, where the long Pt–Sb bond results in less effective steric bulk at the metal centre than for $AsPh_3$ or PPh_3 – the N,O isomer is formed. Ligand substitution of the cod ligand then allows access to a range of N,O bonded complexes which are not directly accessible from the phosphine–halide complexes. The salicylhydroxamate ligand has clearly produced some unanticipated results, and merits further investigation with other metal systems.

3 Experimental

3.1 Instrumentation

All NMR spectra were recorded in $CDCl_3$ solution on a Bruker AC300P instrument, as follows: ^1H (300.13 MHz), $^{13}C–\{^1H\}$ (75.47 MHz), $^{31}P–\{^1H\}$ (121.51 MHz). ^1H and ^{13}C NMR spectra were referenced relative to residual $CHCl_3$, while ^{31}P NMR spectra were referenced relative to external 85% H_3PO_4 (δ 0.0). Electrospray mass spectra were recorded on a VG Platform II instrument, using acetonitrile–water (1 : 1 v/v) as the mobile phase and solvent; further details have been described previously.[6,7] Assignment of major ions was aided by use of the ISOTOPE simulation program.[18] IR spectra were recorded as KBr disks on a Perkin Elmer 1500 series instrument. Melting points were recorded on a Reichert-Jung hotstage apparatus, and are uncorrected. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, New Zealand.

Biological assays were carried out by the commercial service offered by the Marine Chemistry Group, Department of Chemistry, Canterbury University, New Zealand. Samples were dissolved in 3 : 1 methanol–dichloromethane prior to testing. Antitumour assays were carried out by determining, by means of a two-fold dilution series, the concentration of sample in ng mL^{-1} required to reduce the cell growth of the P388 leukemia cell line (ATCC CCL 46) by 50%. The sample of interest was incubated for 72 h with the P388 Murine Leukemia cells. IC_{50} values were determined by measurement of the absorbance values when the yellow dye MTT tetrazolium is reduced by healthy cells to the purple dye MTT formazan. The antimicrobial assays were carried out by measuring the inhibition zone as an excess radius (mm) from a 6 mm diameter filter paper disk containing 2 mg of sample, which was placed on a seeded agar plate containing the organism tested.

Materials and methods

Reactions were carried out in air, in reagent grade methanol, with no further purification. Water was single-distilled prior to use. The following compounds were used as supplied from commercial sources: K_2PtCl_4 (Johnson Matthey), salicylhydroxamic acid (Sigma), triphenylphosphine (BDH), triphenylarsine (Aldrich), triphenylstibine (triphenylantimony) (Aldrich), triphenylphosphite (Aldrich), aqueous trimethylamine (33%, BDH), 4-methylpyridine (BDH), 1,1′-bis-(diphenylphosphino)ferrocene (Aldrich). The compounds $[PtCl_2(cod)]$[19] and $[PdCl_2(cod)]$[20] were prepared following the literature methods. The complexes *cis*-$[PtCl_2(PPh_3)_2]$ and $[PdCl_2(PPh_3)_2]$ were prepared by ligand substitution of the cod ligand in the appropriate $[MCl_2(cod)]$ complex with the stoichiometric quantity of the phosphine in dichloromethane.

Synthesis of $[Pt\{OC(=NO)C_6H_4OH\}(PPh_3)_2]$ 2a

A suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (300 mg, 0.380 mmol) and salicylhydroxamic acid (300 mg, 1.960 mmol) in methanol (30 mL) with trimethylamine solution (2 mL, excess) was refluxed for 1 h giving a yellow suspension. After cooling to room temperature, the yellow solid was filtered off, washed with water (10 mL) and diethyl ether (10 mL) and dried under vacuum to give **2a** (295 mg, 89%). Mp decomp. >240 °C, melting 280–282 °C. Found: C, 59.4; H, 3.8; N, 1.6. $C_{43}H_{35}NO_3P_2Pt$ requires C, 59.3; H, 4.05; N, 1.6%. $^{31}P–\{^1H\}$ NMR, δ 11.1 [d, ^1J(PtP) 3299, ^2J(PP) 23] and 9.5 [d, ^1J(PtP) 3786, ^2J(PP) 23 Hz]. $^{13}C–\{^1H\}$ NMR, δ 167.5 (s, br), 157.0 (s), 134.8–114.9 (m, Ph). ESMS: cone voltage 20 V, $[M + H]^+$ (*m*/*z* 871, 100%), $[2M + H]^+$ (*m*/*z* 1741, 38%). Cone voltage 80 V, $[Pt(C_6H_4PPh_2)(PPh_3)]^+$ (*m*/*z* 718, 33%), $[M + H]^+$ (*m*/*z* 871, 100%), $[2M + H]^+$ (*m*/*z* 1741, 5%).

Synthesis of [Pt{OC(=NO)C_6H_4OH}(dppf)] 2b

To a suspension of [$PtCl_2$(cod)] (300 mg, 0.802 mmol) in methanol (30 mL) was added dppf (444 mg, 0.802 mmol) and the mixture stirred and warmed gently, to generate [$PtCl_2$(dppf)] *in situ*. To the resulting orange suspension was added salicylhydroxamic acid (400 mg, 2.613 mmol) and trimethylamine solution (2 mL, excess) and the mixture refluxed for 2.5 h. After cooling to room temperature, the resulting orange solid product was filtered off, washed with water (10 mL) and diethyl ether (10 mL) and dried under vacuum to give **2b** (475 mg, 66%). Mp > 260 °C (decomp.). Found: C, 53.9; H, 3.5; N, 1.5. $C_{41}H_{33}NFeO_3P_2Pt$ requires C, 54.7; H, 3.7; N, 1.6%. ^{31}P–{^1H} NMR, δ 10.7 [d, ^1J(PtP) 3348, ^2J(PP) 24] and 8.5 [d, ^1J(PtP) 3862, ^2J(PP) 24]. ^{13}C–{^1H} NMR, δ 167.25 [dd, br, J(PC) *ca.* 10, 3 Hz], 157.0 (s), 135.1–114.9 (m, Ph), 76.4–73.2 (m, Cp). ESMS: cone voltage 20 V, $[M + H]^+$ (*m*/*z* 901, 100%), $[2M + H]^+$ (*m*/*z* 1800, 8%).

Synthesis of [Pt{OC(=NO)C_6H_4OH}($AsPh_3$)$_2$] 2c

To a solution of K_2PtCl_4 (300 mg, 0.723 mmol) in water (5 mL) and methanol (35 mL) was added triphenylarsine (442 mg, 1.444 mmol) and the mixture warmed with stirring to give a pale yellow suspension. Salicylhydroxamic acid (300 mg, 1.960 mmol) and aqueous trimethylamine (2 mL, excess) were added in succession, and the mixture refluxed for 1 h to give a yellow suspension. After cooling to room temperature, the product was filtered off, washed with water (10 mL), diethyl ether (10 mL) and dried under vacuum to give a yellow powder of **2c** (545 mg, 79%). Mp 248–250 °C. Found: C, 53.9; H, 3.6; N, 1.5. $C_{43}H_{35}NAs_2O_3Pt$ requires C, 53.9; H, 3.7; N, 1.5%. ^{13}C–{^1H} NMR, δ 168.0 (s), 157.0 (s), 133.6–115.0 (m, Ph). ESMS: cone voltage 20 V, $[M + H]^+$ (*m*/*z* 959, 100%), $[2M + H]^+$ (*m*/*z* 1916, 10%).

Synthesis of [Pt{OC_6H_4C(O)NOH}(cod)] 3a

To a suspension of [$PtCl_2$(cod)] (1.50 g, 4.01 mmol) and salicylhydroxamic acid (1.10 g, 7.2 mmol) in methanol (50 mL) was added trimethylamine solution (3 mL, excess), and the mixture refluxed for 1 h to give a yellow suspension. Water (50 mL) was added to the hot suspension which was cooled and allowed to stand overnight. The resulting pale yellow microcrystalline solid was filtered off, washed with water (2 × 10 mL) and diethyl ether (2 × 10 mL) and dried under vacuum to give **3a** (1.74 g, 96%). Mp 202–204 °C. Found: C, 39.8; H, 3.6; N, 3.1. $C_{15}H_{17}NO_3Pt$ requires C, 39.7; H, 3.8; N, 3.1%. ^1H NMR, δ 10.0 (s, br, OH), 8.20–6.79 (m, Ph), 5.66 [m, CH of cod, ^2J(PtH) 69], 5.42 [m, CH of cod, ^2J(PtH) 62], and 2.78–2.35 (m, CH_2 of cod). ^{13}C–{^1H} NMR, δ 162.4 (s), 160.0 [s, J(PtC) 43.5], 131.3, 130.5, 119.2, 117.8, 116.4 (s, Ph), 98.5 [s, CH of cod, ^1J(PtC) 157], 94.2 [s, CH of cod, ^1J(PtC) 171 Hz], 31.3 (s, CH_2 of cod), and 28.7 (s, CH_2 of cod). ESMS: cone voltage 20 V, $[M + H]^+$ (*m*/*z* 455, 100%), $[2M + H]^+$ (*m*/*z* 909, 65%), $[3M + H]^+$ (*m*/*z* 1363, 10%).

Synthesis of [Pt{OC_6H_4C(O)NOH}(PPh_3)$_2$] 3b

The complex [Pt{OC_6H_4C(O)NOH}(cod)] (100 mg, 0.220 mmol) and triphenylphosphine (116 mg, 0.443 mmol) were dissolved in dichloromethane (2 mL), and after several minutes, diethyl ether (*ca.* 20 mL) was added until the solution turned cloudy. On standing, a pale yellow microcrystalline solid formed, which was filtered off, washed with ether (10 mL) and dried under vacuum to give **3b** (185 mg, 96%). Mp > 210 °C, then resolidified to melt at 280–282 °C. Found: C, 58.6; H, 3.9; N, 1.6. $C_{43}H_{35}NO_3P_2Pt$ requires C, 59.3; H, 4.05; N, 1.6%. ^{31}P–{^1H} NMR, δ 22.2 [d, ^1J(PtP) 3455, ^2J(PP) 26] and 6.0 [d, ^1J(PtP) 3594, ^2J(PP) 26]. ^{13}C–{^1H} NMR, δ 163.0 (s, br), 161.1 [d, J(PC) 6.6 Hz], 134.8–115.8 (m, Ph). ESMS: cone voltage 20 V, $[M + H]^+$ (*m*/*z* 871, 100%), $[2M + H]^+$ (*m*/*z* 1741, 20%); cone voltage 80 V, $[Pt(C_6H_4PPh_2)(PPh_3)]^+$ (*m*/*z* 718, 85%), $[M + H]^+$ (*m*/*z* 871, 100%), plus several other low intensity ions.

Synthesis of [Pt{OC_6H_4C(O)NOH}(dppf)] 3c

The complex [Pt{OC_6H_4C(O)NOH}(cod)] (100 mg, 0.220 mmol) and dppf (122 mg, 0.220 mmol) were dissolved in dichloromethane (3 mL) to give an orange solution. Diethyl ether (*ca.* 10 mL) was added, giving orange microcrystals which were filtered off, washed with ether and dried under vacuum to give **3c** (179 mg, 90%). Mp > 260 °C. Found: C, 51.1 H, 4.0; N, 1.45. $C_{41}H_{33}NFeO_3P_2Pt{\cdot}CH_2Cl_2$ requires C, 51.2; H, 3.6; N, 1.4%; the presence of CH_2Cl_2 of crystallisation was confirmed by NMR spectroscopy. ^{31}P–{^1H} NMR, δ 21.6 [d, ^1J(PtP) 3497, ^2J(PP) 27] and 5.1 [d, ^1J(PtP) 3708, ^2J(PP) 27 Hz]. ^{13}C–{^1H} NMR, δ 162.9 (s), 161.0 (s), 135.0–113.4 (m, Ph), 73.1–70.1 (m, C_5H_4). ESMS: cone voltage 20 V, $[M + H]^+$ (*m*/*z* 901, 100%), $[2M + H]^+$ (*m*/*z* 1800, 3%).

Synthesis of [Pt{OC_6H_4C(O)NOH}{P(OPh)$_3$}$_2$] 3d

The complex [Pt{OC_6H_4C(O)NOH}(cod)] (100 mg, 0.220 mmol) was dissolved in dichloromethane (2 mL) and triphenylphosphite (3 drops) added. Addition of ether (2 mL) followed by partial evaporation of the solvent gave white microcrystals which were filtered off, washed with diethyl ether (5 mL) and dried under vacuum to give **3d** (90 mg, 42%). Mp 160–164 °C. Found: C, 53.4; H, 3.6; N, 1.5. $C_{43}H_{35}NO_9P_2Pt$ requires C, 53.4; H, 3.65; N, 1.45%. ^{31}P–{^1H} NMR, δ 67.44 [d, ^1J(PtP) 5277, ^2J(PP) 66.4], 62.04 [d, ^1J(PtP) 5649, ^2J(PP) 66.4]. ^{13}C–{^1H} NMR, δ 162.6 (s, br), 160.9 [d, J(PC) *ca.* 7.5 Hz], 150.9 (m), 129.9–116.4 (m). ESMS: cone voltage 20 V, $[M + H]^+$ (*m*/*z* 967, 100%).

Synthesis of [Pd{OC(=NO)C_6H_4OH}(PPh_3)$_2$] 4

To a suspension of [$PdCl_2$(PPh_3)$_2$] (400 mg, 0.570 mmol) and salicylhydroxamic acid (400 mg, 2.613 mmol) in methanol (30 mL) was added trimethylamine solution (2 mL, excess). The mixture was refluxed for 25 min giving deep maroon microcrystals in a red solution. After cooling to room temperature and standing overnight, the product was filtered off, washed with water (10 mL) and diethyl ether (10 mL) and dried under vacuum to give **4** (365 mg, 82%). Mp 224–226 °C. Found: C, 66.3; H, 4.5; N, 1.8. $C_{43}H_{35}NO_3P_2Pd$ requires C, 66.0; H, 4.5; N, 1.8%. ^{31}P–{^1H} NMR, δ 31.5 [d, ^2J(PP) 40.5], 28.6 [d, ^2J(PP) 40.5]. ^{13}C–{^1H} NMR, δ 164.5 [dd, J(PC) 15.9, 2.4 Hz], 157.1 (s), 134.7–114.9 (m, Ph). ESMS: cone voltage 20 V, $[M + H]^+$ (*m*/*z* 782, 100%), $[Pd_2\{OC(=NO)C_6H_4O\}(PPh_3)_4]^+$ (*m*/*z* 1412, 18%).

Synthesis of [Pt{OC_6H_4C(O)NOH}($SbPh_3$)$_2$] 5a

To a solution of K_2PtCl_4 (300 mg, 0.723 mmol) in water (5 mL) was added triphenylstibine (511 mg, 1.448 mmol) and methanol (35 mL), and the mixture warmed with stirring to give a yellow precipitate. Salicylhydroxamic acid (300 mg, 1.960 mmol) and aqueous trimethylamine (2 mL) were added and the mixture refluxed for 1 h to give a yellow suspension. After cooling to room temperature the product was filtered, washed with water (10 mL), diethyl ether (10 mL) and dried under vacuum to give a bright yellow powder, yield 549 mg (72%). Mp decomp. > 220 °C. Found: C, 49.3; H, 3.2; N, 1.3. $C_{43}H_{35}NO_3PtSb_2$ requires C, 49.1; H, 3.4; N, 1.3%. Mp decomp. > 220 °C. ESMS: cone voltage 20 V, $[M + H]^+$ (*m*/*z* 1054, 100%), $[2M + H]^+$ (*m*/*z* 2104, 5%).

Synthesis of [Pt{OC_6H_4C(O)NOH}($SbPh_3$)(*p*-NC_5H_4Me)] 5b

To a solution of complex **5a** (200 mg, 0.190 mmol) in distilled dichloromethane (5 mL) was added 4-methylpyridine (5 drops) and the solution allowed to stand for 3 days. The resulting yellow crystals were filtered, washed with diethyl ether (5 mL) and dried, yield 85 mg (56%). Mp decomp. > 190 °C. Found: C,

Table 5 Crystal, collection and refinement data for [Pt{$OC_6H_4C(O)NOH$}(PPh_3)$_2$] **3b** and [Pt{$OC_6H_4C(O)NOH$}($SbPh_3$)(*p*-NC_5H_4Me)] **5b**[a]

	3b	**5b**
Empirical formula	$C_{44}H_{36}Cl_3NO_3P_2Pt$	$C_{31}H_{27}N_2O_3PtSb$
Formula weight	990.12	792.39
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.5685(1)	10.0243(11)
b/Å	11.9897(1)	10.6353(9)
c/Å	17.6626(2)	14.590(3)
α/°	91.247(1)	106.725(19)
β/°	100.125(1)	100.613(15)
γ/°	116.025(1)	102.365(19)
V/Å^3	1967.42(3)	1404.0(3)
Z	2	2
Temperature/K	150(2)	200(2)
Reflections collected	17595	8032
Independent reflections [R_{int}]	7447 [0.0161]	7628 [0.0254]
Absorption coefficient/mm^{-1}	3.893	5.973
Final R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0148, 0.0372	0.0381, 0.0915
R_1, wR_2 indices (all data)	0.0156, 0.0375	0.0461, 0.0958

[a] Programs used: SHELX97[21] and SADABS.[22]

46.8; H, 3.4; N, 3.5. $C_{31}H_{27}N_2O_3PtSb$ requires C, 47.0; H, 3.4; N, 3.5%. ESMS: cone voltage 20 V, $[M + H]^+$ (*m*/*z* 793, 100%), $[2M + H]^+$ (*m*/*z* 1585, 20%).

X-ray structure determinations of [Pt{$OC_6H_4C(O)NOH$}(PPh_3)$_2$] 3b and [Pt{$OC_6H_4C(O)NOH$}($SbPh_3$)(*p*-NC_5H_4Me)] 5b

Crystals of **3b** were obtained by slow evaporation of a $CDCl_3$ solution. The complex crystallises with one molecule of $CDCl_3$ of crystallisation per molecule of complex. Found: C, 53.2; H, 3.35; N, 1.3. $C_{43}H_{35}NO_3P_2Pt{\cdot}CDCl_3$ requires C, 52.6; H, 3.7; N, 1.4%. Crystals of **5b** were obtained directly from the reaction mixture.

Crystal data, together with acquisition and refinement details for both structures are summarised in Table 5.

CCDC reference numbers 206449 (**3b**) and 206448 (**5b**).

See http://www.rsc.org/suppdata/dt/b3/b303367h/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Universities of Waikato and Leicester for financial support of this work. The New Zealand Lottery Grants Board is thanked for a grant in aid towards the mass spectrometer, and the generous loan of platinum from Johnson Matthey plc is acknowledged. We also thank Gill Ellis (University of Canterbury) for the biological assays, Dr. Ralph Thomson (University of Waikato) for some of the NMR spectra, Sarah Devoy for experimental assistance, and Associate Professor Cliff Rickard (University of Auckland) for collection of the data set of **3b**.

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