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Synthesis and characterisation of organo-platinum(II) complexes of the *N,O*-donor ligands hippuric acid (*N*-benzoylglycine) and *N*-phenylanthranilic acid

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Abstract

Reaction of $[PtCl_2(cod)]$ (cod = cyclo-octa-1,5-diene) with either hippuric acid $[PhC(O)NHCH_2COOH]$ or *N*-phenylanthranilic acid (*ortho*-$PhNHC_6H_4COOH$) in refluxing dichloromethane in the presence of silver(I) oxide gave the new organoplatinum derivatives $[Pt\{N(COPh)CH_2COO\}(cod)]$ and $[Pt\{N(Ph)C_6H_4COO\}(cod)]$ respectively. Ligand substitution reactions of the cod ligand in $[Pt\{N(COPh)CH_2COO\}(cod)]$ provided a facile route to a selection of phosphine-substituted analogues $[Pt\{N(COPh)CH_2COO\}L_2]$ [L = phosphatriazaadamantane (pta), PPh_3, or $L_2 = Ph_2PCH_2CH_2PPh_2$ or $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$] *via* displacement of the labile cod ligand. The complexes were characterised using NMR spectroscopy, IR spectroscopy, and ESI mass spectrometry. The X-ray structure of $[Pt\{N(COPh)CH_2COO\}(cod)]$ is also reported.

Keywords: Platinum complexes; Metallacyclic complexes; Silver(I) oxide; Hippuric acid; *N*-Phenylanthranilic acid; Crystal structure

Introduction

The coordination chemistry of amino acid ligands towards the platinum group metals has been extensively studied,[1,2,3] on account of the importance of such ligands in biological systems, and the utility of a number of platinum-based drugs for the treatment of cancer. However, there have been fewer studies on analogous complexes of ligands where the amine group of the amino acid is 'protected' by means of an acyl or sulfonyl [4] substituent. Both the NH and OH groups of the ligand can be readily deprotonated, allowing the ligand to bind as a dianion, typically forming a metallacyclic ring. The first examples of this type of complex resulted from reactions of the dipeptides L-val- L-val, L-leu- L-val and L-val- L-leu with Zeise's salt, $K[PtCl_3(C_2H_4)]$.[5] Kemmitt and co-workers prepared a substantial range of complexes by reaction of *cis*-$[PtCl_2L_2]$ (L = tertiary phosphine) with acetylated derivatives of the amino acids glycine, DL-alanine, DL-methionine, L-phenylalanine and L-proline, giving five-membered metallacyclic complexes $[Pt\{N(COMe)CHRC(O)O\}L_2]$ (R = H, Me, CH_2CH_2SMe or CH_2Ph).[6] Other prepared derivatives in this work included complexes of the *N*-formyl and *N*-trifluoroacetyl derivatives of glycine, together with the 1,5-cyclo-octadiene (cod) derivatives $[Pt\{N(COMe)CHRC(O)O\}(cod)]$ (R = H, CH_2Ph), which provide access to a range of other derivatives through facile ligand substitution reactions.[2] Related complexes derived from α-acetamidocinnamic acid produced a series of complexes $[Pt\{N(COMe)C(=CHR)C(O)O\}L_2]$ (L = tertiary phosphine).[7] Bauer *et al* have also reported three heterobimetallic complexes containing the $[Pt\{N(COR)CHR'C(O)O\}(PPh_3)_2]$ metallacyclic ring, where the R group is appended with an $Fe(CO)_3$(diene) group.[8]

In this paper we report the synthesis and characterisation of some analogous platinum(II) complexes derived from *N*-benzoylglycine (hippuric acid,

PhC(O)NHCH$_2$COOH). Although platinum complexes containing chelating hippurate dianions have not been described previously, some analogous complexes of this general type are known, for example the reaction of *N*-benzoyl-DL-α-valine (PhC(O)NHCH^{i}PrCOOH) with [PtCl$_2$(bipy)] (bipy = 2,2'-bipyridine) gave [Pt{N(COPh)CH^{i}PrC(O)O}(bipy)].[9] An analogue with an estrogen-like ligand has also been developed [10], together with a number of bipy-containing derivatives [11] that have been patented as precursors for the preparation of anti-tumour drugs.[12]

We also report herein a related platinum complex derived from *N*-phenylanthranilic acid (PhNHC$_6$H$_4$COOH), which can also form a dianionic *N,O*-bonded ligand, and a six-membered chelate ring. The focus in this current work is the cod complexes since the labile cod ligand allows a facile route to a range of ligand-substituted derivatives. Furthermore, it has recently been shown that a number of cod-platinum(II) complexes show higher anti-tumour activity than cisplatin towards HeLa cells,[13] suggesting that such organoplatinum complexes could also be of potential interest for their biological properties.

Results and discussion

Synthesis and X-ray structural characterisation of hippurate complexes

Reaction of [PtCl$_2$(cod)] with hippuric acid in refluxing dichloromethane in the presence of excess silver(I) oxide gave, on workup, the air- and moisture-stable organo-platinum hippurate complex **1a** in reasonable yield and purity (Scheme 1). The complex initially crystallised as a light purple solid due to contamination by silver, but a second recrystallisation gave almost colourless crystals that were analytically pure. Silver(I) oxide is well-recognised as a reagent in the chemistry of the platinum group metals, where it acts as

both a halide abstracting reagent and a strong base, with the first known example of its use being reported in 1977.[14] Silver(I) oxide is now widely established as a mediator for metallacyclic reactions, and for the formation of platinum group metal-ligand bonds [6,15,16,17], and more recently, the synthesis of *N*-heterocyclic carbene complexes.[18,19,20,21] However, in our experience the use of silver oxide can result in the product having a slight purple tinge, most likely due to colloidal silver, originating from decomposition of soluble silver-containing complexes which form during the reaction. The silver impurities can be removed by allowing the initially isolated sample to 'age'. Dissolution in the desired solvent (e.g. dichloromethane or chloroform) and filtering through Celite filter aid to remove the silver impurities, followed by crystallisation typically yields analytically pure products. An investigation into the potential applicability of alternative bases (copper(I) oxide or calcium hydroxide) in the synthesis of **1a** did not produce the desired product.

The presence of the labile cod ligand allowed the facile synthesis of a number of ligand-substituted derivatives. Thus, reaction of **1a** with PPh_3, dppe ($Ph_2PCH_2CH_2PPh_2$), pta (phosphatriazaadamantane) and dppf [$Fe(\eta^5\text{-}C_5H_4PPh_2)_2$] in dichloromethane solution gave (in high yield and good purity) the phosphine-substituted analogues **1b**-**1e**, Scheme 1. These complexes crystallise as white or yellow solids, which have relatively high melting points, and are generally readily soluble in dichloromethane and chloroform. The triphenylphosphine complex crystallises from the reaction mixture with dichloromethane of crystallisation, as confirmed by ^{1}H NMR spectroscopy.

In a similar fashion to the synthesis of the cod-Pt complex **1a**, reaction of the 2,2'-bipyridyl-palladium complex [$PdCl_2$(bipy)] with hippuric acid and silver(I) oxide in refluxing

dichloromethane gave the palladium complex [Pd{N(COPh)CH_2COO}(bipy)] **2** as an orange solid; this complex has much lower solubility than the platinum complexes.

In order to unambiguously confirm the structure of a hippurate complex, the X-ray structure of [Pt{N(COPh)CH_2COO}(cod)] **1a** was determined. The structure is shown in Figure 1 together with the atom numbering scheme, while Table 1 gives selected bond lengths and angles. Examination of the Cambridge Structural Database (version 5.36) confirms that there are no known X-ray structure determinations of metal complexes containing the hippurate dianion ligand, although the platinum complex of the related *N*-acetylglycine ligand, [Pt{N(COMe)CH_2COO}($Ph_2PCH_2CH_2PPh_2$)], has been structurally characterised,[6] together with a platinum complex containing a related benzoylated amino acid ligand, [Pt{N(COPh)CH($CH_2{}^i$Pr)COO}(bipy)].[11] Furthermore, there have only been three previous structure determinations of cod-Pt complexes containing chelating *N,O* ligands, none being amino acidate-type ligands.[22,23]

The geometry about the platinum atom of **1a** is the expected *pseudo*-square planar. The five-membered hippurate ring is not planar but has a slight envelope conformation, with a fold angle between the planes defined by Pt(1)-N(1)-O(2) and O(2)-C(10)-C(9)-N(1) of 10.3˚. The metallacyclic carbonyl lies roughly in the least-squares metallacycle plane defined by Pt(1), N(1), C(9), C(10) and O(2), with the distance of O(1) to the plane being 0.014 Å. The benzoyl carbonyl lies more out of the metallacycle least-squares plane, with O(3) lying 0.56 Å out of the plane. The phenyl ring is almost orthogonal to the metallacycle, as defined by an angle of 87.0˚ between the Pt(1)-N(1)-O(2) coordination plane and the least-squares plane of the phenyl ring [C(21)-C(26)].

As expected due to the lower *trans*-influence [24] of the carboxylate oxygen, the platinum-carbon distances *trans* to oxygen [Pt(1)-C(1) 2.157(4) and Pt(1)-C(2) 2.171(4) Å]

are shorter than the corresponding Pt-C distances *trans* to the amidate nitrogen [Pt(1)-C(5) 2.181(4), Pt(1)-C(6) 2.187(4) Å]. These bond distances can be compared to Pt-C bond distances of 2.161(4) to 2.171(5) Å, with an average of 2.166(4) Å, in a recent structural determination of $[PtCl_2(cod)]$.[13] The projection of the C(11)-O(3) bond of the benzoyl substituent towards the cod ligand appears to lengthen the Pt-C(2) distance relative to the Pt-C(1) distance. The cod ligand has a slightly skewed conformation.

Spectroscopic characterisation of hippurate complexes 1a - 1e

Each of the complexes was characterised using positive-ion ESI MS. For complex **1a**, only a relatively weak $[M + H]^+$ ion was observed at *m/z* 480.98 (calculated *m/z* 481.11), despite several attempts at varying the ionisation conditions and solvents (methanol and acetonitrile). In contrast, the phosphine-substituted derivatives **1b**-**1e** showed much more intense ions, typically showing a mixture of $[M + H]^+$, $[M + Na]^+$ and $[M + K]^+$ ions; the spectra were considerably simplified upon addition of a small quantity of NaCl, which resulted in the observation of solely the $[M + Na]^+$ ions. For example, the positive-ion spectrum of the triphenylphosphine complex **1b** (without added NaCl) showed $[M + H]^+$ (*m/z* observed 897.19 calculated 897.20), $[M + Na]^+$ (*m/z* observed 919.17, calculated 919.18) and $[M + K]^+$ (*m/z* observed 935.24, calculated 935.15) ions, with the $[M + Na]^+$ ion dominating the spectrum, as shown in Figure 2. The reasons for the apparent low ionisation efficiency of **1a** are not clear, since other cod-Pt complexes have been found to analyse well by ESI MS.[15] The bipyridine palladium complex **2** also showed the $[M + Na]^+$ ion as the base peak in the ESI mass spectrum (with added sodium formate), in addition to weaker ions due to $[M + H]^+$ (*m/z* 439.89), $[2M + Na]^+$ (*m/z* 461.88) and $[3M + Na]^+$ (*m/z* 902.77).

^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectroscopies have been employed to provide a full spectral assignment of the complexes. The ^{31}P{^{1}H} NMR spectra of the phosphine-substituted complexes **1b – 1e** give typical spectra for this type of complex, showing two doublets for the two inequivalent P nuclei (*trans* to O or N), showing mutual $^{2}J_{P\text{-}P}$ coupling. Satellites due to coupling to ^{195}Pt are also observed, with the magnitude of $^{1}J_{Pt\text{-}P}$ reflecting the *trans* influence of the *trans* donor atom (either higher *trans* influence N or lower *trans* influence O, producing respectively lower or higher $^{1}J_{Pt\text{-}P}$ values for the *trans* P atoms); data are summarised in Table 2. The pta complex has very upfield resonances (δ ^{31}P -67.0, -67.4 ppm) typical for pta-platinum(II) complexes.[25]

Full characterisation of the ^{1}H NMR spectrum of the cod complex **1a** was carried out using a combination of 1- and 2-dimensional NMR techniques. The ^{1}H NMR spectrum of **1a** is shown in Figure 3, a full assignment of the proton and carbon resonances is given in the Experimental section, and the atom numbering scheme is shown in Scheme 2.

Two signals are observed for the cod CH protons in the ^{1}H NMR spectrum (at δ 6.51 and 5.43) due to symmetry in the cod moiety which renders C_1 and C_2, and C_5 and C_6 spectroscopically equivalent. Consequently, the bonded hydrogens H_1 & H_2 and H_5 & H_6 are also equivalent. Each of the cod CH resonances has broad shoulders attributable to coupling to ^{195}Pt ($^{2}J_{Pt\text{-}H}$ ca. 70 Hz and 57 Hz, respectively).

As observed in the ^{31}P NMR spectra of the phosphine complexes, the differing *trans* influences of the N and O donors of the hippurate ligand in **1a** allows differentiation between CH groups *trans* to nitrogen/oxygen, based on their $^{2}J_{Pt\text{-}H}$ (and $^{1}J_{Pt\text{-}C}$) coupling constants. The cod CH resonance at δ 6.51 is assigned to H_1 & H_2, as it has the larger $^{2}J_{Pt\text{-}H}$ coupling constant (70 Hz), indicating that the bonded carbon (at δ 96.0, from the HSQC spectrum) is

trans to oxygen. Similarly, the resonance at δ 5.43 is assigned to H_5 & H_6, with a smaller $^2J_{Pt\text{-}H}$ of 57 Hz, which suggests that the attached carbon (δ 98.5) is *trans* to nitrogen. There are also notable differences between the two cod CH signals in terms of chemical shift, multiplicity and broadness. In particular, the broadness of the signal at δ 6.51 may be attributable to a proximity to lone pair electron density such as that on the N-C=O group on the hippurate moiety. This is consistent with the data, as the H_1 & H_2 signal at δ 6.51 is broader and downfield, while the H_5 & H_6 signal at δ 5.43 is sharper and more upfield. Density functional theory (DFT) was used to calculate theoretical NMR shifts; two different environments are calculated which, when averaged to account for vibrational motion on the time-scale of NMR spectroscopy, show a difference of 0.84 ppm (the chemical shifts for H_1/H_2 and H_5/H_6 are calculated to occur at δ 5.69 and 4.86 respectively). This is fairly consistent with the observed ^{1}H NMR data of **1a**, which shows a difference of 1.1 ppm between the signals for H_1/H_2 and H_5/H_6. Although these differ from the experimental chemical shifts of δ 6.51 and 5.43 (by 0.8 and 0.6 ppm respectively) they still suggest that the proton closest to the nitrogen is that in the H_1/H_2 environment.

Assuming that the two protons in the H_{22}/H_{26} environment are identical (due to free rotation about the C_{11}-C_{21} bond) there are three aromatic proton environments from the hippurate moiety (corresponding to H_{22} & H_{26}, H_{23} & H_{25}, and H_{24} in Scheme 2). These appear in the region from δ 7.36-7.18, and an expansion of this can be seen in the top left of the ^{1}H NMR spectrum of **1a** (Figure 3). Only one of the three aromatic proton environments was adequately resolved in the proton spectrum. The signal at δ 7.19 (essentially as a doublet of doublets with ^3J = 8.0, ^4J = 1.7 Hz) can be uniquely attributed to the H_{22}/H_{26} environment, since of the aromatic proton environments only this proton is expected to

show a ^{3}J coupling to its nearest neighbour (H_6) and a smaller ^{4}J coupling to H_7. A NOESY experiment confirmed this, showing an NOE from the H_{22}/H_{26} protons at δ 7.19 to the H_9 protons at δ 4.01, consistent with H_{22}/H_{26} being the closest of the aromatic protons to H_9. The H_{24} and H_{23}/H_{25} proton environments occur in the δ 7.36-7.27 region as complex second-order overlapped multiplets. Notwithstanding the complex nature of the overlapped signal, it was apparent from a high resolution COSY spectrum that the initial more intense correlation peaks are attributable to the larger ^{3}J couplings between H_{22} at δ 7.19 and the protons at δ 7.31, and later the smaller ^{4}J coupling correlations develop to the proton at δ 7.34. This allows tentative assignment for the higher chemical shift as H_{24} and the lower as the H_{23}/H_{25} environment.

The hippurate CH_2 protons at δ 4.01 also show significant coupling to ^{195}Pt ($^{3}J_{Pt\text{-}H}$ ~ 18.1 Hz), as expected. It is clearly recognisable as a methylene signal in a DEPT135 experiment. The observation of a single peak in the ^{1}H NMR spectrum indicates that the hippurate ligand lies in a plane of symmetry, which makes both protons chemically equivalent.

The cod CH_2 protons are observed as four complex multiplets around δ 2.5 and are easily distinguished as methylenes in a DEPT135 experiment. These protons are symmetry-paired (with H_{3a} & H_{8a}, H_{3b} & H_{8b}, H_{4a} & H_{7a} and H_{4b} & H_{7b} being the chemically equivalent pairs). In addition, there is both geminal ^{2}J coupling (between H_a and H_b for the CH_2 protons) and ^{3}J coupling between methylene and methyne protons, leading to complicated overlapping signals. Furthermore, each cod methylene couples to ^{195}Pt which adds to the complexity of the cod CH_2 signals. In the COSY spectrum the cod CH proton at δ 6.51 correlates to the protons at δ 2.72 and 2.42, whereas the proton at δ 5.43 shows correlations

to the protons at δ 2.60 and 2.28. In addition, the high-resolution COSY spectrum shows mutual correlations between the four adjacent methylene signals. Axial protons are generally higher in chemical shift than equatorial protons [26] which allows assignment of the cod CH_2 protons: H_{3a} & H_{8a} at δ 2.72, H_{3b} & H_{8b} at δ 2.42, H_{4a} & H_{7a} at δ 2.60, and H_{4b} & H_{7b} at δ 2.28.

The $^{13}C\{^{1}H\}$ NMR spectrum of complex **1a** shows a number of key resonances. The metallacycle ring CH_2 carbon appears at δ 56.9 as expected and exhibits broad shoulders due to coupling to ^{195}Pt ($^{2}J_{Pt-C}$ 15 Hz). The nitrogen-attached carbonyl (C_{11}) is observed at δ 176.7 and has slightly broad shoulders from coupling to ^{195}Pt ($^{2}J_{Pt-C}$ 32 Hz), while the metallacycle ring carbonyl (C_{10}) appears slightly upfield at δ 184.4, but no ^{195}Pt coupling could be resolved for this signal. The HMBC spectrum confirms these shifts since it shows correlations from the nitrogen-attached carbonyl to the aromatic protons, whereas the ring carbonyl displays no coupling to ^{1}H as it is too far away. The ^{1}H-coupled ^{13}C spectrum shows further evidence, with C_{10} appearing as a triplet at δ 184.4 (J_{C-H} 6 Hz) due to splitting by the neighbouring CH_2 protons, while the nitrogen-attached carbonyl C_{11} appears as a singlet at δ 176.7. Similarly, the quaternary carbon (C_{21}) of the phenyl ring shows broad shoulders due to coupling to ^{195}Pt ($^{3}J_{Pt-C}$ 42 Hz). As expected, it is further upfield in the aromatic region (δ 138.5), has a low intensity and shows no correlations to protons in the HSQC spectrum. In the aromatic region, two of the environments appear to overlap at δ 128.6, while the final signal occurs at δ 125.5. The latter is assigned as the C_{22}/C_{26} environment due to its correlation to the H_{22}/H_{26} signal at δ 7.19 in the HSQC spectrum. An expansion of the aromatic region allows the peaks at δ 128.6 to be almost fully separated to see the intensity ratio of 2:1. This enables clear assignment of C_{24} as the signal with the

lower chemical shift (δ 128.58) since it has a lower intensity attributable to its single carbon. In contrast, the signal with the higher chemical shift (δ 128.61) has a doubled intensity and therefore corresponds to the C_{23}/C_{25} environment.

The two cod CH resonances (the C_1/C_2 and C_5/C_6 environments in Scheme 2) are both seen in the $^{13}C\{^1H\}$ spectrum as singlets at δ 98.5 ($^1J_{Pt\text{-}C}$ 140 Hz) and 96.0 ($^1J_{Pt\text{-}C}$ 160 Hz), both displaying substantial coupling to ^{195}Pt. The HSQC spectrum showed that these are attached to the protons at δ 5.43 and 6.51, respectively. The signal at δ 96.0 can be assigned as the C_1 & C_2 environment due to its higher $^1J_{Pt\text{-}C}$ coupling constant (160 Hz) indicating it is *trans* to the metallacycle oxygen atom, while the δ 98.5 resonance can be correspondingly attributed to the C_5 & C_6 environment (*trans* to N) by its smaller $^1J_{Pt\text{-}C}$ coupling constant (140 Hz). In the ^1H-coupled ^{13}C NMR spectrum, the C_1/C_2 and C_3/C_4 resonances appear as doublets ($^1J_{C\text{-}H}$ *ca.* 165 Hz). These $J_{C\text{-}H}$ coupling constants are typical for CH environments of this type.[15,27,28]

The cod methylene carbons (C_3 & C_8, and C_4 & C_7) occur at δ 32.4 and 28.2 in the $^{13}C\{^1H\}$ NMR spectrum. In the proton-coupled spectrum, the C_3/C_8 and C_4/C_7 environments appears as triplets ($^1J_{C\text{-}H}$ 131 and 132 Hz respectively). As expected due to changes in *s*-character [27], the $J_{C\text{-}H}$ values for the cod methylene signals are approximately 35 Hz lower than those for the cod CH resonances. The HSQC spectrum shows that the CH_2 at δ 32.4 correlates to the proton signals centred at δ 2.72 and 2.42, while the CH_2 at 28.2 correlates to the proton signals centred at δ 2.60 and 2.28.

In comparison to its parent complex **1a**, the proton NMR spectrum of the triphenylphosphine complex **1b** appears rather straightforward, with only two regions. The complex multiplet from δ 7.81-6.75 corresponds to the aromatic protons, making

interpretation difficult, and no further assignment was undertaken. The ring methylene signal at δ 4.16 ($^3J_{Pt-H}$ 41 Hz) comes at an expected chemical shift, and is slightly more downfield than that of the ring methylene in the parent complex **1a** (δ 4.03). It appears as a doublet as a result of coupling to the *trans* phosphine. The ^{1}H NMR spectra of the other phosphine complexes were assigned in analogous fashion to those of **1a**, and showed typical features expected for these complexes.

The bipyridine palladium complex **2** had relatively poor solubility in $CDCl_3$ but was able to be characterised by ^{1}H NMR. In addition to the complex set of resonances due to the bipyridine and phenyl protons, a singlet at δ 4.26 is assigned to the CH_2 protons, by comparison with the chemical shift of the same protons in the analogous platinum complexes.

Synthesis and characterisation of the *N*-phenylanthranilate complex [Pt{OC(O)C$_6$H$_4$NPh}(cod)] 3

In a similar fashion to the synthesis of the hippurate complex **1a**, reaction of [$PtCl_2$(cod)], *N*-phenylanthranilic acid and silver(I) oxide in refluxing dichloromethane gave complex **3** on workup (Scheme 3). The complex, isolated in reasonable yield and purity, is an intense green-yellow coloured solid, in contrast to the platinum hippurate complexes, which are colourless (with of course the exception of the yellow ferrocene-derived complex **1e**). Somewhat surprisingly, there are no well-characterised complexes that contain dianionic *N*-phenylanthranilate ligands, although there are many examples of complexes containing monoanionic ligands [29,30,31] including complexes of the lanthanides,[32,33,34,35,36] and

other platinum group metals such as rhodium.[37,38] Platinum complexes of *N*-phenylanthranilate ligands have not been reported to date.

The IR spectrum of *N*-phenylanthranilic acid shows a very strong C=O stretch at 1660 cm^{-1}, as well as a very strong C-N stretch at 1263 cm^{-1}; these decrease to 1616 cm^{-1} and increase to 1338 cm^{-1} respectively, upon coordination to platinum(II) in complex **3**. Assignment of peaks was assisted by DFT calculations for both *N*-phenylanthranilic acid and complex **3**. As for complex **1a**, the *N*-phenylanthranilate complex **3** also did not give a simple ESI mass spectrum, though a weak $[M + H]^+$ ion was observed at *m/z* 515.17 (calculated *m/z* 515.12).

The ^1H NMR spectrum of **3** in $CDCl_3$ showed many similarities with that of the hippurate complex **1a**. The atom numbering is shown in Scheme 4; a full assignment of the various ^1H and ^{13}C resonances was able to be made following methods analogous to those used in the assignment of complex **1a**. The four cod CH protons are seen as two distinct signals in the ^1H NMR spectrum, due to the equivalence of C_1 and C_2, and of C_5 and C_6 (and their attached hydrogens). These resonances show different $^2J_{Pt\text{-}H}$ coupling constants (*ca.* 54 and 65 Hz), due to the differing *trans*-influence of the N and O donors. The resonance at δ 4.42 is assigned to the CH *trans* to O, as it shows the larger coupling constant. The DFT-calculated ^1H NMR shifts for the cod CH protons (δ 5.18 and 4.20) confirm these assignments, with the calculated difference in chemical shifts Δδ (0.98 ppm) being very close to the experimentally observed difference (1.0 ppm).

Conclusions

New platinum(II) complexes of the dianionic *N,O*-donor ligands hippurate and *N*-phenylanthranilate, which also contain ancillary cyclo-octadiene ligands, can be conveniently synthesised by the reaction of $[PtCl_2(cod)]$ with the parent hippuric acid or *N*-phenylanthranilic acid in the presence of silver(I) oxide. In the case of the hippurate complexes, the labile cod ligand allows access to a selection of phosphine-substituted derivatives by facile ligand substitution reactions.

Experimental

Instrumentation

High resolution ESI mass spectra were recorded on a Bruker MicrOTOF instrument, which was periodically calibrated using a solution of sodium formate. Samples of isolated products were typically prepared for analysis by dissolution in a few drops of dichloromethane followed by dilution with methanol and centrifugation. Typical parameters used a *Capillary Exit* voltage of 150 V and a *Skimmer 1* voltage of 50 V. Assignment of ions was assisted by comparison of experimental and theoretical isotope patterns, the latter calculated using an internet-based program [39] or proprietary instrument-based software.

All 1D and 2D NMR spectra (^{1}H, ^{13}C and ^{31}P, COSY, NOESY, DEPT, HSQC, HMBC and H2BC) were recorded on a Bruker AVIII-400 spectrometer in $CDCl_3$ (unless otherwise specified in-text) using BBI or BBFO probes, depending on the nucleus of the sample. Standard Bruker supplied pulse programmes were used for each experiment, with parameters including spectral window, number of increments, pulse angle and repetition rate altered as appropriate for each specific sample.

Elemental analyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. Melting points were recorded as finely ground samples in capillary tubes on a Buchi M-560 Melting Point instrument. IR spectra were recorded as KBr disks on a Perkin Elmer Spectrum 100 FTIR spectrometer.

Materials

Silver(I) oxide (BDH), hippuric acid (Sigma), 1,1'-bis(diphenylphosphino)ferrocene (dppf, Aldrich) and *N*-phenylanthranilic acid (BDH) were used as supplied. The complexes $[PtCl_2(cod)]$ [40] and $[PdCl_2(bipy)]$,[41] and the phosphines dppe [42] and pta [43] were prepared by the literature procedures. All solvents used were drum grade, with the exception of dichloromethane, which was passed through a solvent purification system to remove water, air and stabilisers.

Synthesis of [Pt{N(COPh)CH_2COO}(cod)] 1a

A mixture of $[PtCl_2(cod)]$ (201.2 mg, 0.538 mmol) and hippuric acid (96.7 mg, 0.540 mmol) with silver(I) oxide (611 mg, excess) in dichloromethane (30 mL) was refluxed for 3.5 h. After cooling to room temperature the mixture was filtered, giving a pale purple solution. Petroleum spirits (60 mL) was added and the mixture allowed to crystallise, giving pale purple crystals that were filtered, washed with petroleum spirits (10 mL) and dried under vacuum to give **1a** (124.3 mg, 48%). The product was dissolved in a minimal amount of dichloromethane, filtered through filter aid, and crystallised by vapour diffusion of diethyl ether to give almost colourless crystals. Found: C 42.5; H 4.0; N 2.9. $C_{17}H_{19}NO_3Pt$ requires C 42.5; H 4.0; N 2.9%. M.p. 162-163 °C (decomp.). IR ν(C=O) 1690(vs), 1604(vs) cm^{-1}.

ESI MS (capillary exit voltage 250 V) $[M + H]^+$ *m/z* 480.98 (calculated for $C_{17}H_{19}NO_3PtH$ *m/z* 481.11).

^{1}H NMR, δ 7.36-7.18 (m, 5H, H_{21}-H_{26}), 6.51 (s, 2H, H_1/H_2, $^2J_{Pt\text{-}H}$ 70), 5.43 (m, 2H, H_5/H_6, $^2J_{Pt\text{-}H}$ 57), 4.01 (s, 2H, H_{9a} & H_{9b}, $^3J_{Pt\text{-}H}$ 18), 2.77-2.23 (m, 8H, H_3, H_4, H_7 & H_8). ^{13}C{^{1}H} NMR, δ 184.4 (s, C_{10}), 176.7 (s, C_{11}, $^2J_{Pt\text{-}C}$ 32), 138.5 (s, C_{21}, $^3J_{Pt\text{-}C}$ 42), 128.6 (d, overlapping s + s, C_{23}/C_{25} & C_{24}), 125.5 (s, C_{22}/C_{26}), 98.5 [s, C_5/$C_{6(trans\ N)}$, $^1J_{Pt\text{-}C}$ 140], 96.0 [s, C_1/$C_{2(trans\ O)}$, $^1J_{Pt\text{-}C}$ 160], 56.9 [s, C_9, $^2J_{Pt\text{-}C}$ 15], 32.4 [s, C_3/C_8], 28.2 [s, C_4/C_7]. ^{13}C NMR, (excluding aromatic region) δ 184.4 (t, C_{10}, $^1J_{C\text{-}H}$ 6), 176.7 (s, C_{11}), 138.6 (t, C_{21}, $^1J_{C\text{-}H}$ 7), 98.5 [d, C_5/$C_{6(trans\ N)}$, $^1J_{C\text{-}H}$ 165], 96.0 [d, C_1/$C_{2(trans\ O)}$, $^1J_{C\text{-}H}$ 166], 56.9 (t, C_9, $^1J_{C\text{-}H}$ 140), 32.4 (t, C_3/C_8, $^1J_{C\text{-}H}$ 131), 28.2 (t, C_4/C_7, $^1J_{C\text{-}H}$ 132). Scheme 2 shows the atom numbering scheme of the complex.

Synthesis of $[Pt\{N(COPh)CH_2COO\}(PPh_3)_2]\cdot 1.5.CH_2Cl_2$ (1b·1.5CH_2Cl_2)

Complex **1b** was prepared by a ligand substitution reaction. A mixture of triphenylphosphine (51.8 mg, 0.197 mmol) and [Pt{N(COPh)CH_2COO}(cod)] **1a** (46.5 mg, 0.097 mmol) was dissolved in dichloromethane (4 mL) and left to stand for 5 min., then filtered through a cotton-plugged glass Pasteur pipette and washed through with a further 0.5 mL dichloromethane. Petroleum spirits (25 mL) was added, giving white needle crystals on standing overnight. Upon subsequent evaporation of around one third of the solvent, further product formed which, following removal of the supernatant, was washed with petroleum spirits (*ca.* 2 mL) and dried under vacuum for 3 h to give 95.7 mg (97%) of **1b**·1.5CH_2Cl_2. Found: C 54.3; H 4.0; N 1.4%. $C_{45}H_{37}NPtO_3P_2\cdot 1.5CH_2Cl_2$ requires C 54.5; H 4.0; N 1.4%.

M.p. 174-178 °C. IR: ν(C=O) 1647(vs) cm^{-1}. ESI MS (added NaCl, capillary exit voltage 160 V): $[M + Na]^+$ *m/z* 919.18 (100%), calculated for $C_{45}H_{37}NO_3P_2PtNa$ *m/z* 919.18.

^{1}H NMR, δ 7.81-6.75 (m, 35H, Ph), 5.32 (s, CH_2Cl_2), 4.16 (d, 2H, CH_2, $^3J_{Pt-H}$ 41). $^{31}P\{^1H\}$ NMR, δ 9.2 [d, $P_{A(trans\ N)}$, $^1J_{Pt-P}$ 3058, $^2J_{P-P}$ 24], 4.8 [d, $P_{B(trans\ O)}$, $^1J_{Pt-P}$ 4031, $^2J_{P-P}$ 23].

Synthesis of [Pt{N(COPh)CH$_2$COO}(dppe)] 1c

Complex **1c** was prepared by a ligand substitution reaction, following the same procedure as for **1b**, with a mixture of dppe (37.9 mg, 0.095 mmol) and [Pt{N(COPh)CH$_2$COO}(cod)] **1a** (44.4 mg, 0.092 mmol) in dichloromethane (4 mL) giving fluffy white crystals (41.1 mg, 57%) of **1c**. Found: C 54.7; H 4.1; N 1.8%. $C_{35}H_{31}NPtO_3P_2$ requires C 54.6; H 4.1; N 1.8%. M.p. 276-278 °C. IR ν(C=O) 1652(vs) cm^{-1}. ESI MS (added NaCl, capillary exit voltage 160 V): $[M + Na]^+$ *m/z* 793.13 (100%), calculated for $C_{35}H_{31}NO_3P_2PtNa$ *m/z* 793.13.

^{1}H NMR, δ 7.99-6.77 (m, 25H, Ph), 4.03 [d, 2H, CH_2(hippurate), $^3J_{Pt-H}$ 18], 2.39-1.99 [m, 4H, CH_2(dppe)]. $^{31}P\{^1H\}$ NMR, δ 37.4 [d, $P_{A(trans\ N)}$, $^1J_{Pt-P}$ 3085, $^2J_{P-P}$ 12], 28.1 [d, $P_{B(trans\ O)}$, $^1J_{Pt-P}$ 3876, $^2J_{P-P}$ 12].

Synthesis of [Pt{N(COPh)CH$_2$COO}(pta)$_2$] 1d

A mixture of pta (28.9 mg, 0.184 mmol) and [Pt{N(COPh)CH$_2$COO}(cod)] **1a** (45.7 mg, 0.095 mmol) was dissolved in dichloromethane (4 mL) and left for 5 min., resulting in the formation of fluffy white crystalline solid. Petroleum spirits (25 mL) was added and the mixture allowed to stand overnight. Following removal of the supernatant, the product was washed with petroleum spirits (*ca.* 2 mL) and dried under vacuum for 3 h to give **1d** (58.5

mg, 90%). Found: C 35.9; H 4.8; N 13.7%. $C_{21}H_{21}NPtO_2$ requires C 36.7; H 4.6; N 14.3%. M.p. 250-265 °C (decomp.). IR ν(C=O) 1638(vs) cm^{-1}. ESI MS (added NaCl, capillary exit voltage 160 V): $[M + Na]^+$ *m/z* 709.10 (100%), calculated for $C_{21}H_{31}N_7O_3P_2PtNa$ *m/z* 709.15.

^{1}H NMR, δ 7.35-7.27 (m, 5H, Ph), 5.28 (s, CH_2Cl_2), 4.58-4.27 [m, 24H, CH_2(pta)], 4.07 [d, 2H, CH_2(hippurate), $^3J_{Pt-H}$ 19]. $^{31}P\{^1H\}$ NMR, δ -67.0 [d, $P_{A(trans\ N)}$, $^1J_{Pt-P}$ 2800, $^2J_{P-P}$ 22], -67.4 [d, $P_{B(trans\ O)}$, $^1J_{Pt-P}$ 3484, $^2J_{P-P}$ 22].

Synthesis of [Pt{N(COPh)CH$_2$COO}(dppf)] 1e

Complex **1e** was prepared by a ligand substitution reaction, using a similar procedure to **1b**. A mixture of dppf (55.0 mg, 0.099 mmol) and [Pt{N(COPh)CH$_2$COO}(cod)] **1a** (46.0 mg, 0.096 mmol) was used in the same process as for **1b**, however additional petroleum spirits (10 mL) was added to further precipitate the product overnight. Reduction of volume by one third followed by addition of extra petroleum spirits (*ca.* 1 mL) was repeated once more. After removal of the supernatant, the yellow product was washed with petroleum spirits (*ca.* 2 mL) and dried under vacuum for 3 h to give **1e** (69.5 mg, 77%). Found: C 55.8; H 4.4; N 1.4%. $C_{42}H_{35}NPtO_3FeP_2$ requires C 55.7; H 3.8; N 1.5%. M.p. 204.5-210 °C (decomp.). IR: ν(C=O) 1654(s) cm^{-1}. ESI MS (added NaCl, capillary exit voltage 160 V): $[M + Na]^+$, *m/z* 949.10, calculated for $C_{42}H_{35}NFeO_3P_2PtNa$ *m/z* = 949.10.

^{1}H NMR ($CDCl_3$), δ 7.91-6.58 (m, 20H, Ph), 5.00 (br s, 2H, C_5H_4), 4.46 (s, 2H, C_5H_4), 4.18 (s, 2H, C_5H_4), 3.96 (d, 2H, H_{9a} & H_{9b}, $^3J_{Pt-H}$ 20), 3.58 (d, 2H, C_5H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ 9.44 [d, $P_{A(trans\ N)}$, $^1J_{Pt-P}$ 3131, $^2J_{P-P}$ 22], 6.47 [d, $P_{B(trans\ O)}$, $^1J_{Pt-P}$ 4102, $^2J_{P-P}$

23]. $^{13}C\{^{1}H\}$ NMR (DMSO), δ 182.1 (d, C_{10}), 171.6 (s, C_{11}), 138.4-127.2 (m, Ph), 76.8 (s, C_5H_4), 75.1 (d, C_5H_4), 74.8 (d, C_5H_4), 73.7 (d, C_5H_4), 56.5 (s, C_9, $^{2}J_{Pt\text{-}C}$ 47).

The atom numbering of **1e** is shown in Scheme 5.

Synthesis of [Pd{OC(O)CH$_2$N(COPh)}(bipy)] 2

A mixture of [$PdCl_2$(bipy)] (210 mg, 0.63 mmol) with hippuric acid (113 mg, 0.63 mmol) and silver(I) oxide (600 mg) in dichloromethane (30 mL) was refluxed for 3.5 h. Methanol (30 mL) was added, and the mixture filtered to give a clear yellow solution. The solid residue was extracted with an additional 40 mL of dichloromethane-methanol (1:1 v/v), and the filtrates combined. The solution was evaporated to dryness, redissolved in dichloromethane (40 mL) and the product precipitated by addition of petroleum spirits (40 mL). The solid was filtered, washed with petroleum spirits (10 mL) and dried under vacuum to give **2** as an orange solid (192 mg, 69%). Found: C 50.2; H 3.45; N 9.1. $C_{18}H_{15}N_3O_3Pd$ requires C 50.5; H 3.5; N 9.8%.

^{1}H NMR, δ 9.12-6.91 (m, bipy and Ph), 4.26 (s, CH_2). ESI MS (added $NaHCO_2$, capillary exit voltage 140 V): $[M + Na]^+$ *m/z* 461.88 (100%), calculated for $C_{19}H_{15}N_3O_3PdNa$ *m/z* 462.00.

Synthesis of [Pt{OC(O)C$_6$H$_4$NPh}(cod)] 3

Complex **3** was prepared using a similar procedure to the preparation of **1a**. Silver(I) oxide (1529.8 mg, excess) was added to a stirred mixture of [$PtCl_2$(cod)] (500.4 mg, 1.337 mmol) and *N*-phenylanthranilic acid (295.2 mg, 1.384 mmol) in dichloromethane (30 mL), and the mixture was refluxed for 3.5 h giving a dark green-yellow suspension. After cooling to room temperature the mixture was filtered twice through glass fibre filter paper to remove silver(I)

oxide, and the filter paper washed with dichloromethane (*ca.* 2 mL) each time. The resulting brown-yellow solution was reduced in volume (rotary evaporator) to *ca.* 5 mL. Petroleum spirits (*ca.* 95 mL) was added and the mixture allowed to crystallise overnight, giving green-yellow crystals which were filtered, washed with petroleum spirits (5 mL) and dried under vacuum overnight to give **3** (351 mg, 51%). Found: C 48.3; H 4.2; N 2.6%. $C_{21}H_{21}NPtO_2$ requires C 49.0; H 4.1; N 2.7%. M.p. 155-157 °C (decomp.). IR ν(C=O) 1616(vs) cm^{-1}. ESI MS (capillary exit voltage 160 V) $[M + H]^+$ *m/z* 515.17 (25%), calculated for $C_{21}H_{21}NO_2PtH$ *m/z* 515.12.

^{1}H NMR, δ 8.26-5.90 (m, 9H, H_{12}-H_{15} & H_{22}-H_{26}), 5.42 (m, 2H, H_5/H_6, $^2J_{Pt-H}$ 54), 4.42 (m, 2H, H_1/H_2, $^2J_{Pt-H}$ 65), 2.70-2.56 (m, 4H, H_{3a}, H_{4a}, H_{7a} & H_{8a}), 2.27-2.11 [m, 4H, H_{3b}, H_{4b}, H_{7b} & H_{8b}]. $^{13}C\{^1H\}$ NMR, δ 166.2 (s, C_9), 153.1 (s, C_{11}), 150.2 (s, C_{21}), 133.9 (s, C_{15}), 131.5 (s, C_{13}), 130.0 (s, C_{22}/C_{26}), 129.7 (s, C_{23}/C_{25}), 126.1 (s, C_{24}), 116.4 (s, C_{14}), 116.1 (s, C_{12}), 114.7 (s, C_{10}), 98.4 [s, C_5/$C_{6A(trans\ N)}$, $^1J_{Pt-C}$ 139], 93.7 [s, C_1/$C_{2B(trans\ O)}$, $^1J_{Pt-C}$ 198], 31.0 (s, C_3/C_8), 28.4 (s, C_4/C_7).

The atom numbering of the complex is shown in Scheme 4.

X-ray structure determination on [Pt{N(COPh)CH_2COO}(cod)] 1a

Crystals were obtained by vapour diffusion of diethyl ether into a dichloromethane solution, at room temperature. Data were acquired on a SuperNova, Single source at offset, Atlas diffractometer using a colourless block crystal of dimensions 0.19 × 0.11 × 0.06 mm. Empirical absorption corrections were made using spherical harmonics. Using Olex2 [44], the structure was solved with the olex2.solve [45] structure solution program using Charge Flipping and refined with the olex2.refine [45] refinement package using Gauss-Newton minimisation. All non-hydrogen atoms were refined as anisotropic except for C(1), C(5) and

C(6), which are close to the platinum atom, and for which unrealistic ellipsoids were obtained. All hydrogens were placed in calculated positions. *Crystal data:* $C_{17}H_{19}NO_3Pt$; M_r = 480.42 g mol^{-1}; monoclinic; space group $P2_1/n$; a = 12.30576(8) Å; b = 9.41089(6) Å; c = 12.54508(7) Å; β = 94.5941(6)°, V = 1448.154(16) Å^3; Z = 4; T = 100(1) K; λ(Cu-K$_\alpha$) = 1.54178 Å; μ(Cu-K$_\alpha$) = 18.236 mm^{-1}; d_{calc} = 2.203 g cm^{-3}; 27883 reflections collected; 2913 unique (R_{int} = 0.0480) giving R_1 = 0.0243, wR_2 = 0.0623 for data with [I>2σ(I)], and R_1 = 0.0246, wR_2 = 0.0627 for all data.

Theoretical calculations

Density functional theory (DFT) calculations were completed using Gaussian 09.[46] Unless specified, all calculations were completed using the B3LYP functional and the 6-311++G(2d,2p) basis set for all atoms excluding Pt, for which the LANL2DZ basis set and effective core potential was used instead. Geometry optimisations were completed for all structures. For those structures whose NMR shifts were calculated, geometry optimisations were carried out using chloroform as the solvent (unless otherwise specified). NMR chemical shifts were calculated using the GIAO approach with TMS as a reference. The geometrical optimisation and NMR chemical shifts of **1e** were calculated using DMSO as the solvent.

Supplementary material

Crystallographic data for the structure described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1465339. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road,

Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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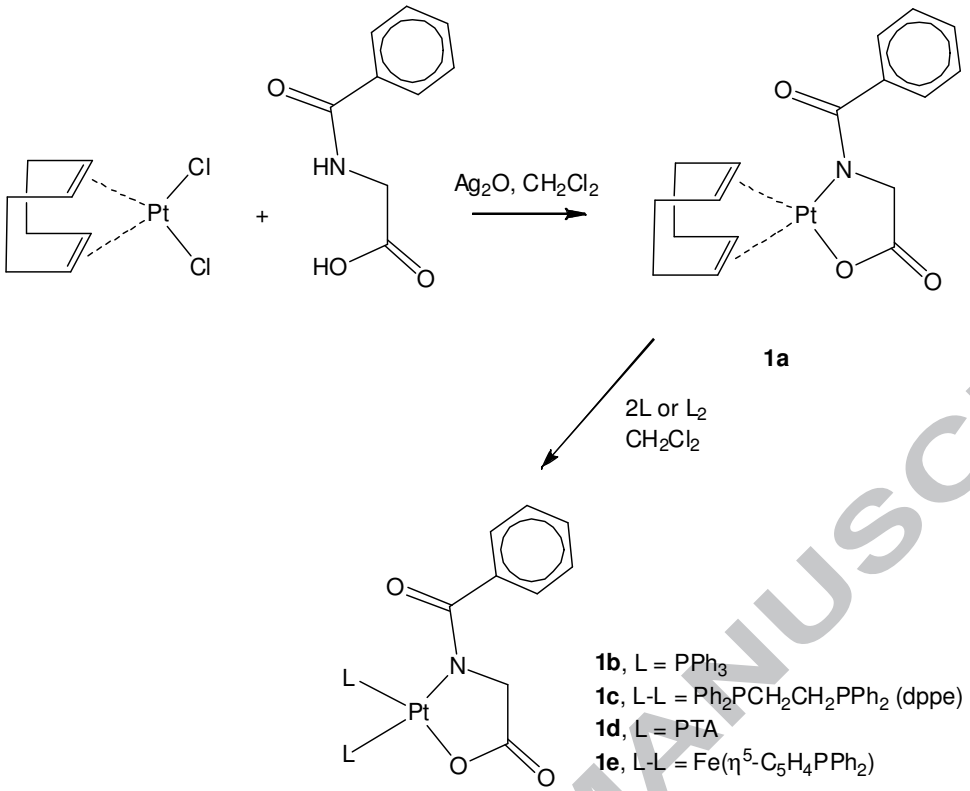
Table 1 Selected bond lengths (Å) and angles (°) for [Pt{N(COPh)CH_2COO}(cod)] **1a**

Pt(1)-N(1)	2.014(3)	Pt(1)-C(1)	2.157(4)
Pt(1)-C(2)	2.171(4)	Pt(1)-C(5)	2.181(4)
Pt(1)-C(6)	2.187(4)	C(1)-C(2)	1.392(5)
C(5)-C(6)	1.408(5)	C(9)-N(1)	1.469(5)
C(9)-C(10)	1.521(4)	C(10)-O(1)	1.215(5)
C(10)-O(2)	1.322(4)	C(11)-O(3)	1.232(5)
C(11)-N(1)	1.360(5)	C(11)-C(21)	1.511(5)

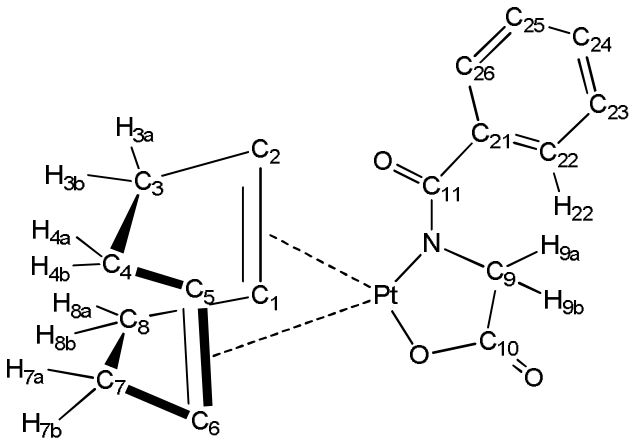
O(2)-Pt(1)-N(1)	81.81(11)	N(1)-C(9)-C(10)	111.0(3)
O(1)-C(10)-O(2)	122.4(3)	O(1)-C(10)-C(9)	121.5(3)
O(2)-C(10)-C(9)	116.0(3)	O(3)-C(11)-N(1)	123.8(3)
O(3)-C(11)-C(21)	117.83)	N(1)-C(11)-C(21)	118.4(3)
C(11)-N(1)-C(9)	120.0(3)	C(11)-N(1)-Pt(1)	127.3(3)
C(9)-N(1)-Pt(1)	112.6(2)	C(10)-O(2)-Pt(1)	116.2(2)

Table 2 Summary of $^{1}J_{Pt\text{-}P}$ NMR data for the phosphine-substituted hippurate complexes **1b**-**1e**

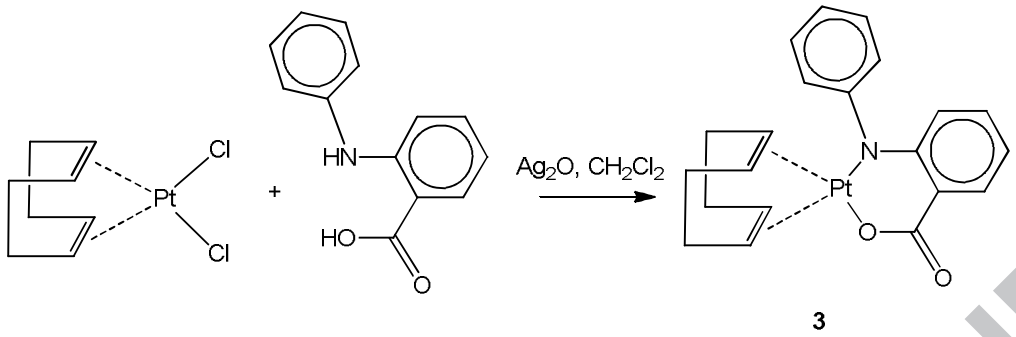
Complex	$^{1}J_{Pt\text{-}P}$ **(Hz)**	
	PPh_3 *trans* N	PPh_3 *trans* O
1b	3058	4031
1c	3085	3876
1d	2800	3484
1e	3131	4102



Scheme 1 Synthesis of the platinum(II) hippurate complexes **1a** – **1e**

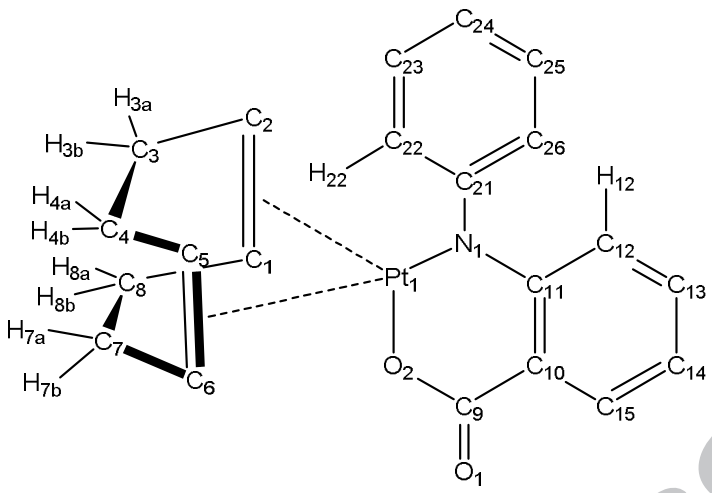


Scheme 2 The atom numbering scheme of [Pt{N(COPh)CH_2COO}(cod)] **1a**.

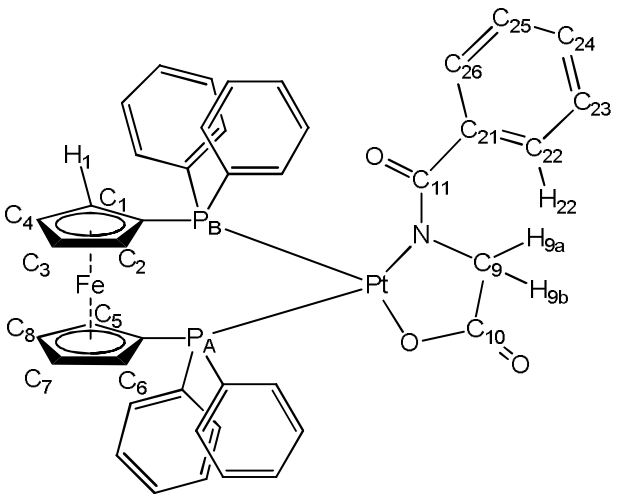


3

Scheme 3 Synthesis of the platinum(II) *N*-phenylanthranilate complex [Pt{OC(O)C_6H_4NPh}(cod)] **3**



Scheme 4 The atom numbering scheme of the *N*-phenylanthranilate complex [Pt{OC(O)C_6H_4NPh}(cod)] **3**



Scheme 5 The atom numbering scheme of **1e**, using the same numbering of the hippurate moiety as for **1a**. For simplicity, the dppf phenyl rings are not labelled.

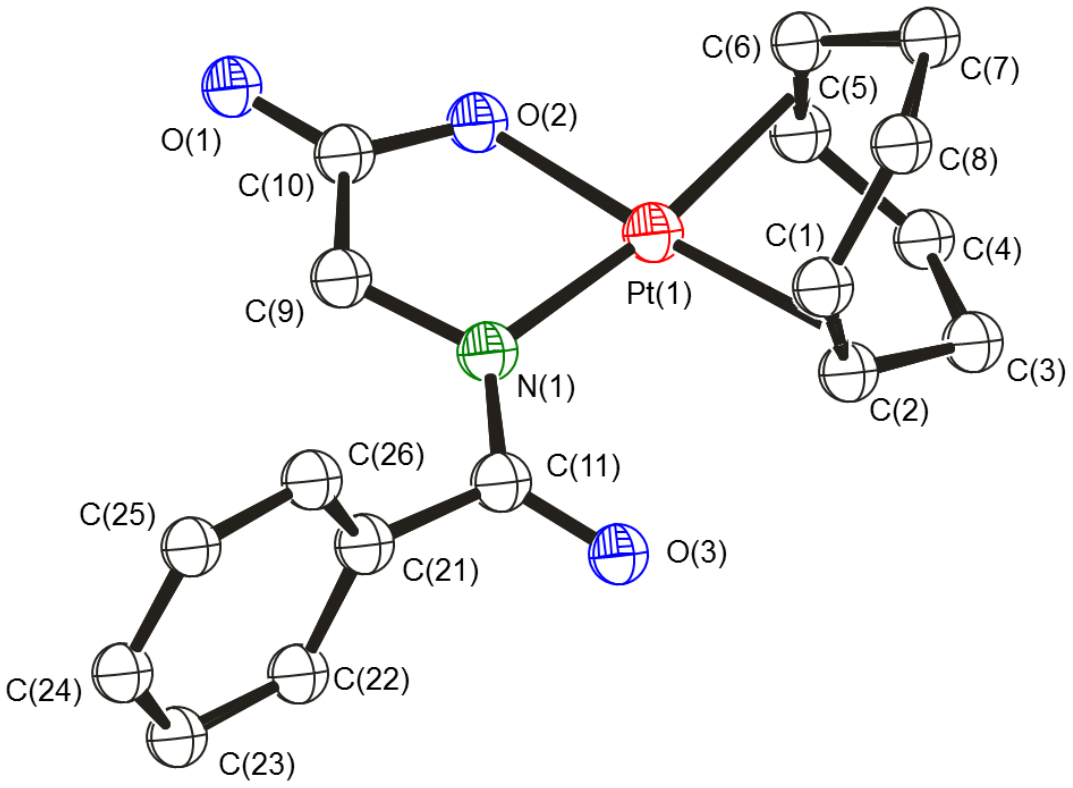


Figure 1 X-ray structure of the complex [Pt{N(COPh)CH_2COO}(cod)] **1a**, showing the atom numbering scheme

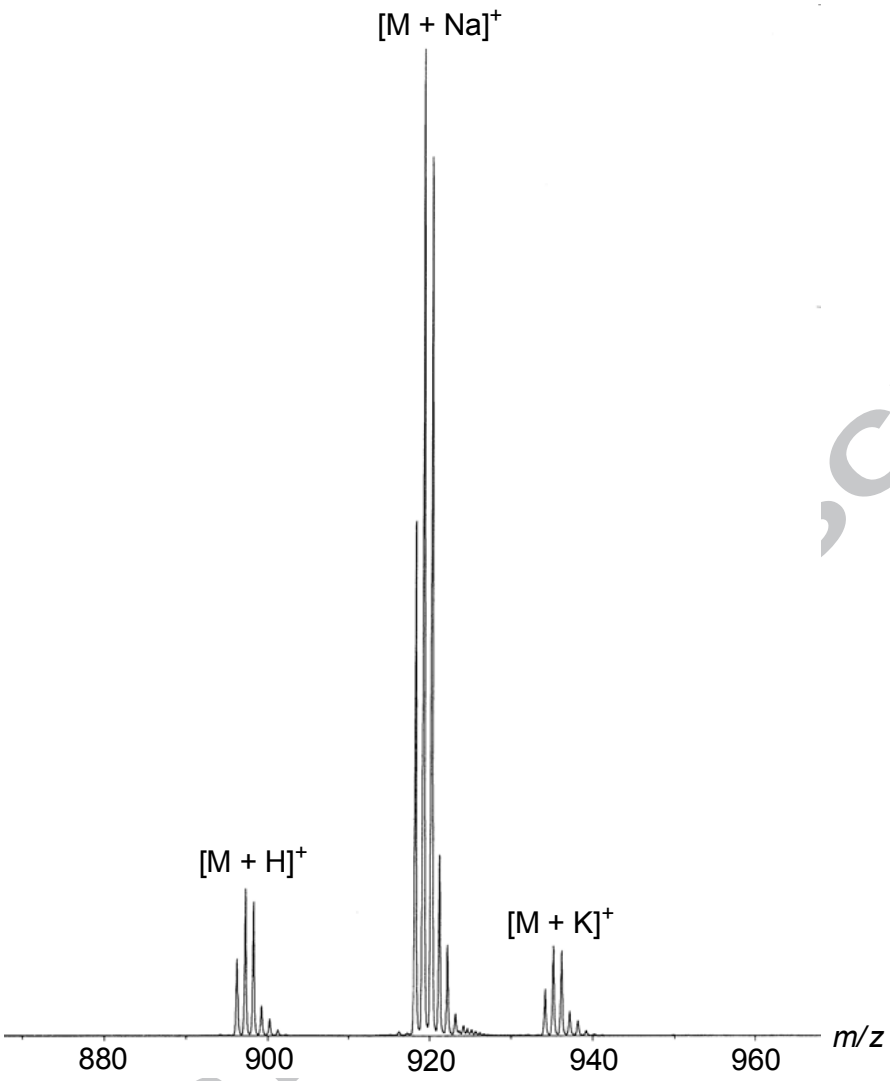


Figure 2 Positive ion ESI mass spectrum of the complex [Pt{N(COPh)CH_2COO}(PPh_3)$_2$] **1b**

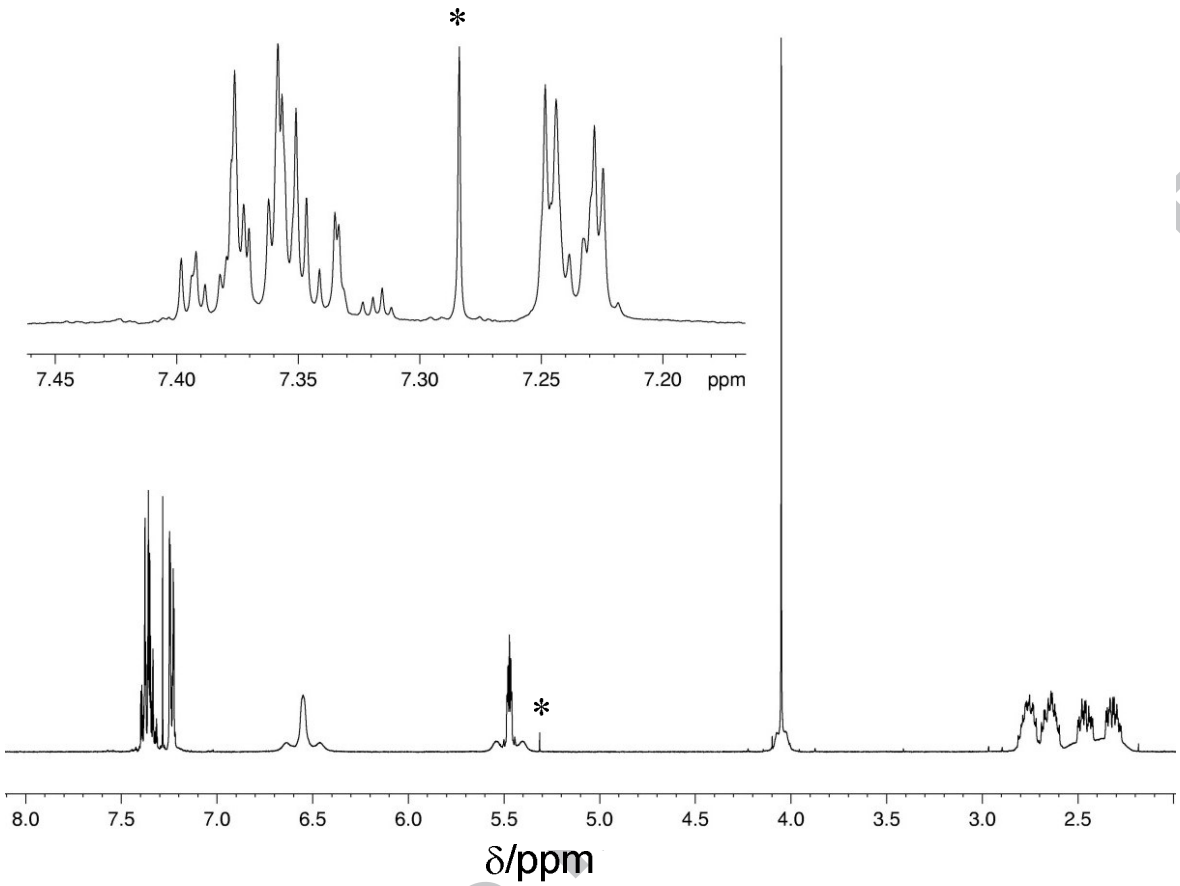


Figure 3 ^{1}H NMR spectrum of the complex [Pt{N(COPh)CH_2COO}(cod)]. The inset shows an expansion of the aromatic proton region, and the peaks marked * are due to solvent (δ 5.3 CH_2Cl_2, δ 7.28 $CHCl_3$)

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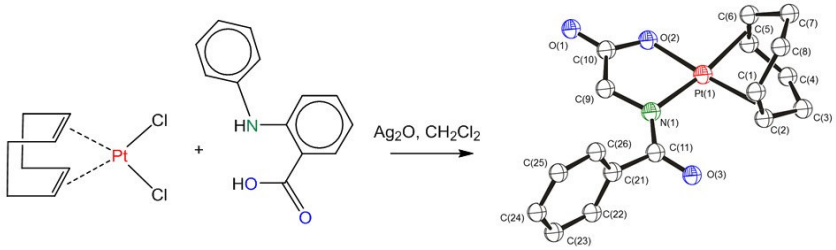

The new organoplatinum derivatives [Pt{N(COPh)CH_2COO}(cod)] and [Pt{N(Ph)C_6H_4COO}(cod)] (cod = cyclo-octa-1,5-diene) were synthesised by reaction of [$PtCl_2$(cod)] with hippuric acid [PhC(O)NHCH_2COOH] or *N*-phenylanthranilic acid (*ortho*-PhNHC_6H_4COOH). Ligand substitution reactions of the cod ligand in [Pt{N(COPh)CH_2COO}(cod)] provided a facile route to a selection of phosphine-substituted analogues. The complexes were characterised using NMR spectroscopy, IR spectroscopy, and ESI mass spectrometry. The X-ray structure of [Pt{N(COPh)CH_2COO}(cod)] is also reported.

Highlights

- New platinum complexes with hippurate and N-phenylanthranilate ligands
- X-ray structure of cyclo-octadiene complex [Pt{N(COPh)CH_2COO}(cod)]
- Phosphine platinum hippurate complexes synthesised by ligand substitution