Synthesis and Reactivity of *N*-Acetylamino acidate(2−) and Related Complexes of Platinum(II)†

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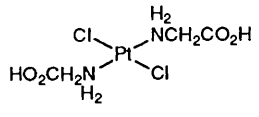
Treatment of the complexes $[PtCl_2L_2]$ (L = P-donor ligand) with the *N*-acetyl derivatives of the amino acids glycine, DL-alanine, DL-methionine or L-phenylalanine in the presence of an excess of silver(I) oxide in refluxing dichloromethane affords $[Pt\{N(COMe)CHRC(O)O\}L_2]$ (R = H, Me, CH_2CH_2SMe or CH_2Ph) respectively, and with L-proline the complexes $[Pt\{NCH_2CH_2CH_2CHC(O)O\}L_2]$ are produced. Similar treatment with the *N*-formyl or *N*-trifluoroacetyl derivatives of glycine gave the complexes $[Pt\{N(R)CH_2C(O)O\}L_2]$ (R = CHO or $COCF_3$) respectively. An X-ray crystal structure study on the *N*-acetylglycinato(2−)-*N*,*O* complex $[Pt\{N(COMe)CH_2C(O)O\}(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) indicated the presence of an almost planar five-membered ring with substantial electron delocalisation within the carboxylate and amide functionalities. Treatment of the complexes $[PtCl_2L_2]$ with DL-mandelic (α-hydroxybenzeneacetic) acid, 2-acetamidophenol, pyrrole-2-carboxylic acid, mercaptoacetic acid or oxamic acid in the presence of an excess of Ag_2O in refluxing dichloromethane afforded the complexes $[Pt\{OC(H)PhC(O)O\}L_2]$, $[Pt\{o\text{-}N(COMe)C_6H_4O\}L_2]$, $[Pt\{NCH{=}C(H)CH{=}CC(O)O\}L_2]$, $[Pt\{SCH_2C(O)O\}L_2]$, $[Pt\{N(H)C(O)C(O)O\}L_2]$ respectively. The cycloocta-1,5-diene (cod) ligand of $[Pt\{N(COMe)CH_2C(O)O\}(cod)]$ and $[Pt\{N(COMe)CH(CH_2Ph)C(O)O\}(cod)]$ is readily displaced by tertiary phosphines. One mole equivalent of Bu^{t}NC stereospecifically displaces the PPh_3 ligand opposite oxygen in the complex $[Pt\{N(COMe)CH(CH_2Ph)C(O)O\}(PPh_3)_2]$. Treatment of $[Pt\{N(COMe)CH_2C(O)O\}(PPh_3)_2]$ in refluxing ethanol with an excess of either diphenylacetylene or PPh_3 leads to the formation of $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$ or $[Pt(PPh_3)_4]$ respectively, in good yield. Treatment of the same metal complex in ethanol at room temperature with either SO_2 or CO led to the formation of the bis(ethanesulfonate) or bis(ethoxycarbonyl) complexes respectively. The complex $[Pt\{NCH_2CH_2CH_2CHC(O)O\}(PPh_3)_2]$ induces the polymerisation of hexaflurobut-2-yne.

Platinum(II) complexes of the amino acids, where the latter can act either as a neutral or monoanionic ligand, have been well studied and their relative inertness makes them of considerable interest in the investigation of the bonding of metal ions to peptides and proteins.[1,2] Many examples of monodentate and chelate complexes are known, with bonding to the metal being able to occur through both the N and C terminii, or where appropriate through the basic sulfur or nitrogen atoms of an α-carbon side chain.[1,2]

Platinum(II) complexes with glycine seem to have received the most attention and the variety of such complexes **1**,[3] **2**,[4] **3**,[5] and **4**[6] shows the versatility of this ligand. Also shown are complexes of histidine **5**[7] and methionine **6**,[8] in which the preference of the metal to bond to the heteroatom of the side chain rather than the anionic carboxylate group is of interest.

However, in spite of the relatively large number of known complexes of the amino acids with transition metals in general, there are surprisingly few in which these ligands act as chelating dianionic fragments. Copper is the only transition metal for which such complexes have been described,[9] although examples containing either tin[10] or germanium[11] have also been prepared.

The present work describes the synthesis and characterisation of the first examples of platinum(II) complexes containing chelating dianionic amino acid derivatives **7**. In addition to these complexes, various other substrates were used to prepare similar five-membered metallacycles containing metal bonds to either oxygen, nitrogen or sulfur.



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$K_2[Pt(NH_2CH_2CO_2)_4]$

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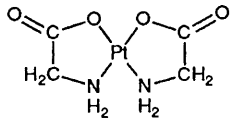

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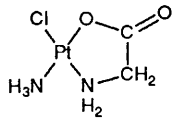

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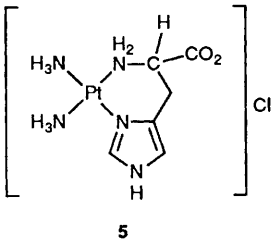

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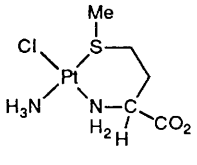

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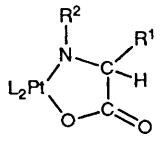
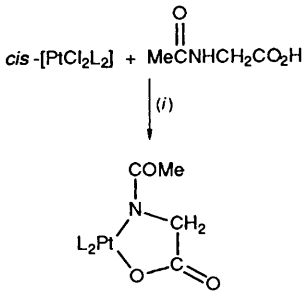
Results and Discussion

Treatment of the complexes *cis*-$[PtCl_2L_2]$ [L = PPh_3,

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

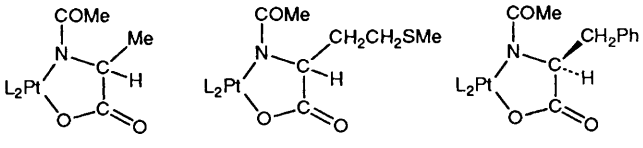


7 L = donor ligand



8a L = PPh_3
8b L = $PMePh_2$
8c L = $P(CH_2Ph)Ph_2$
8d L_2 = dppm
8e L_2 = dppe
8f L_2 = dppp
8g L_2 = dppb
8h L_2 = cod

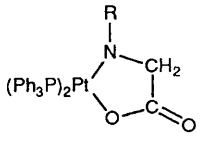
Scheme 1 (*i*) Refluxing CH_2Cl_2, excess of Ag_2O



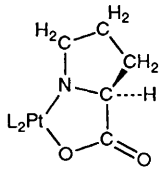
9a L = PPh_3
9b L = $PMePh_2$
9c L = $P(CH_2Ph)Ph_2$
9d L_2 = dppm
9e L_2 = dppe
9f L_2 = dppp
9g L_2 = dppb

10a L = PPh_3
10b L = $PMePh_2$
10c L = $P(CH_2Ph)Ph_2$
10d L_2 = dppm
10e L_2 = dppe
10f L_2 = dppp
10g L_2 = dppb

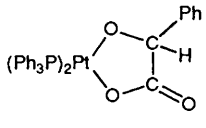
11a L = PPh_3
11b L = $PMePh_2$
11c L = PMe_2Ph
11d L_2 = dppm
11e L_2 = dppe
11f L_2 = dppp
11g L_2 = dppb
11h L_2 = cod



12a R = CHO
12b R = $COCF_3$



13a L = PPh_3
13b L_2 = dppp
13c L_2 = dppb



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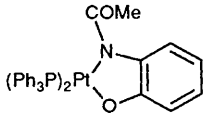

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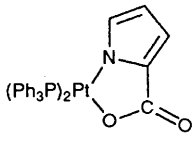

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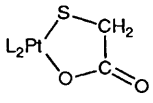
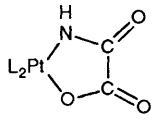


17a L = PPh_3
17b L_2 = dppm
17c L_2 = dppe
17d L_2 = dppp
17e L_2 = dppb



18a L = PPh_3
18b L_2 = dppe
18c L_2 = dppp
18d L_2 = dppb

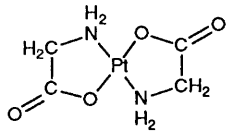


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Table 1 Selected bond distances (Å) and angles (°) for [Pt{N(COMe)CH_2C(O)O}(dppe)] **8e**, with estimated standard deviations (e.s.d.s) in parentheses

Pt–P(1)	2.245(4)	C(2)–O(2)	1.245(19)
Pt–P(2)	2.240(4)	N–C(3)	1.258(19)
Pt–N	2.060(11)	C(3)–O(3)	1.278(16)
Pt–O(1)	2.097(10)	C(3)–C(4)	1.538(22)
N–C(1)	1.433(18)	P(1)–C(5)	1.811(13)
C(1)–C(2)	1.485(22)	P(2)–C(6)	1.847(14)
C(2)–O(1)	1.232(19)	C(5)–C(6)	1.533(19)
P(1)–Pt–P(2)	86.3(1)	O(1)–C(2)–O(2)	125.0(19)
P(1)–Pt–O(1)	94.4(3)	Pt–N–C(3)	127.8(12)
P(2)–Pt–N	100.6(4)	C(1)–N–C(3)	120.0(14)
O(1)–Pt–N	78.8(5)	N–C(3)–O(3)	122.4(18)
Pt–O(1)–C(2)	117.8(11)	C(4)–C(3)–O(3)	114.5(16)
O(1)–C(2)–C(1)	116.2(15)	N–C(3)–C(4)	123.1(15)
C(2)–C(1)–N	114.6(13)	Pt–N–C(1)–H(1A)	127.59
Pt–N–C(1)	112.1(9)	Pt–N–C(1)–H(1B)	−114.05
C(1)–C(2)–O(2)	118.7(17)	Pt–N–C(3)–O(3)	4.07

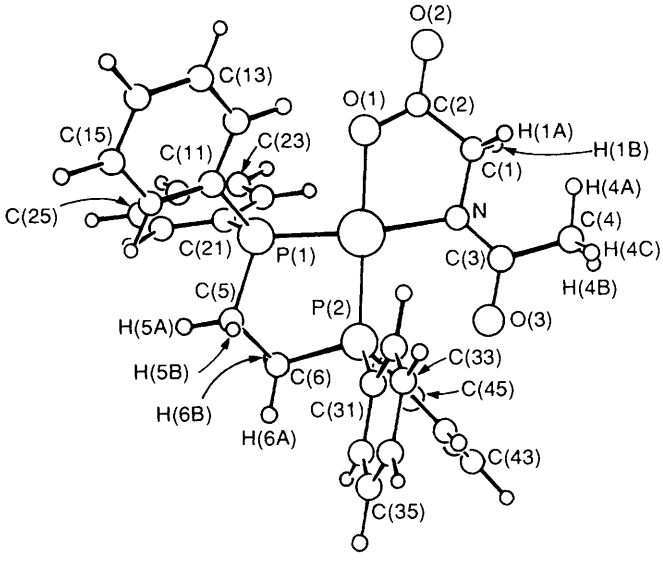
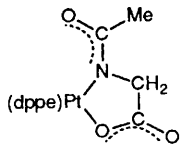


Fig. 1 Molecular structure of [Pt{N(COMe)CH_2C(O)O}(dppe)] **8e**, showing the atom numbering scheme

$PMePh_2$, or $P(CH_2Ph)Ph_2$; L_2 = $Ph_2PCH_2PPh_2$(dppm), $Ph_2P(CH_2)_2PPh_2$(dppe), $Ph_2P(CH_2)_3PPh_2$(dppp), Ph_2P-$(CH_2)_4PPh_2$(dppb) or cycloocta-1,5-diene (cod)] {prepared *in situ* by the reaction of $[PtCl_2(cod)]$ with either 2 mole equivalents of L or 1 equivalent of L_2} with 1 equivalent of *N*-acetylglycine and an excess of silver(I) oxide in refluxing dichloromethane afforded, in high yield, the new complexes **8**, Scheme 1. Similarly, complexes **9** may be prepared using *N*-acetyl-DL-alanine, **10** using *N*-acetyl-DL-methionine and **11** using *N*-acetyl-L-phenylalanine instead of *N*-acetylglycine. Also **12a** or **12b** may be synthesised using *N*-formylglycine or *N*-trifluoroacetylglycine as the source of the chelating fragment. Complexes **13**, which contain a bicyclic skeleton, may be prepared using L-proline with silver(I) oxide in refluxing dichloromethane in the presence of *cis*-$[PtCl_2L_2]$ (L = PPh_3;



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L_2 = dppp or dppb). All the new complexes were isolated as air-stable, white to pale yellow microcrystalline solids with the exception of **13a** which is greeny yellow.

The success of these preparations led to the investigation of platinum(II) dichloride complexes and silver(I) oxide with other substrates containing 'acidic' hydrogen atoms in a 1,4 relationship in order to prepare new ring systems. Thus treatment of *cis*-$[PtCl_2(PPh_3)_2]$ with 1 mole equivalent of DL-mandelic acid (α-hydroxybenzeneacetic acid) and an excess of silver(I) oxide in refluxing dichloromethane afforded complex **14** in high yield. Similarly, complex **15** may be prepared using 2-acetamidophenol and complex **16** using pyrrole-2-carboxylic acid.

Treatment of the complexes *cis*-$[PtCl_2L_2]$ (L = PPh_3; L_2 = dppm, dppe, dppp or dppb) with 1 equivalent of mercaptoacetic acid and an excess of silver(I) oxide in refluxing dichloromethane afforded, in high yield, complexes **17**. Complexes **18** may be prepared using oxamic acid in place of mercaptoacetic acid.

Previous structural studies on the glycinate chelate complexes **3**,[12] **4**[13] and **19**[14] have established the presence of almost planar five-membered rings with substantial intermolecular hydrogen bonding. A single-crystal X-ray diffraction study was thus carried out on the *N*-acetylglycinato(2−) complex **8e** in order to investigate its molecular geometry and to compare the structure with those of the other platinum(II) glycinate compounds. Important bond lengths and angles are presented in Table 1 whilst the molecular structure is illustrated in Fig. 1.

The structure consists of a chelating *N*-acetylglycinato(2−) ligand co-ordinated to a Pt(dppe) fragment through nitrogen and oxygen so as to give the metal a square-planar environment. The Pt–N(1)–C(1)–C(2)–O(1) ring is close to planarity, C(1) deviating most from the least-squares plane of the ring at a distance of 0.041 Å. The acetyl group is attached to N(1) such that the carbonyl oxygen O(3) sits closer to the phosphine ligand than does the methyl group, presumably for steric reasons. The atoms C(3), O(3) and C(4) lie close to the Pt–N(1)–C(1)–C(2)–O(1) plane, the torsion angle O(3)–C(3)–N(1)–Pt being 4.1°.

The Pt–N(1) and Pt–O(1) distances compare well to those of other glycinate complexes of platinum(II).[12–14] Within the *N*-acetylglycinato(2−) ligand, the N(1)–C(1) and C(1)–C(2) distances are slightly shorter than the corresponding distances in the other glycinate complexes,[12–14] and are also shorter than those of free glycine itself.[15] However a significant difference arises in the comparison of the carboxylate bond distances. The structure of **8e** shows that the C(2)–O(2) 'double bond' and the C(2)–O(1) 'single bond' are of comparable length, whereas in the structures of **3**, **4** and **19** the former bond length is significantly shorter than the latter.[12–14] The bond distances within the *N*-acetyl function also indicate significant electron delocalisation in this group, which suggests that the resonance form **20** makes a significant contribution to the structure.

The bond angles in the *N*-acetylglycinato(2−) chelate ring agree well with those of previously reported structures, apart from the chelate angle at the platinum, which at 78.8(5)° is smaller than those found in prior investigations.[12–14] This is probably due to the presence of a relatively large chelating phosphine ligand opposing the dianionic fragment.

The bond angles at N(1) add up to 359.9°, indicating a planar hybridisation for this atom, with its lone pair occupying a 2p orbital. Crystal structure determinations of other amide-containing compounds have also shown substantial electron delocalisation within this group, with both the C–O and C–N bonds having significant double-bond character.[16]

^{1}H *NMR Spectra*.—The room-temperature ^{1}H NMR spectra for all the new complexes are consistent with the structures shown above. The spectra of complexes **8**, which contain an *N*-acetylglycine residue, all contain a signal in the region δ 4.15–4.53 which can be assigned to the methylene group of the five-membered ring. The two protons of this group are equivalent in solution, due to rapid inversion of the ring, and in the spectrum of complex **8h**, in which there are no phosphines present, they appear as a singlet with ^3J(PtH) 21 Hz. When phosphines are present in the complexes the signal appears as a doublet with platinum-195 satellites. Also, in complex **8d**, the dppm methylene protons are equivalent and are observed as a doublet of doublets due to phosphorus-31 coupling.

The spectra of complexes **9**, which contain an *N*-acetyl-DL-alaninato fragment, all show a complex signal in the region δ 4.24–4.71 which contains platinum-195, phosphorus-31 and proton coupling, assignable to the methine proton of the five-membered ring. The adjacent α-methyl group appears as a doublet in the range δ 1.47–1.82. The dppm methylene protons in **9d** are not equivalent, one being *cis* to the α-methyl group and the other *trans*. Thus, two separate resonances are observed as doublets of doublets of doublets with coupling to each other and to both phosphorus nuclei.

The signal for the ring methine proton of complexes **10**, **11** and **13** is distinctive due to its low-field position with respect to the signals for the other non-aromatic substituents, and generally appears as a multiplet between δ 4.2 and 5.0. These complexes all contain diastereotopic methylene protons, however only those in **11** can be resolved and each is observed as a doublet of doublets. The spectra of complexes **18** show the NH proton as a broad multiplet between δ 4.42 and 5.63, with ^2J(PtH) in the range 100–106 Hz.

^{13}C-{^{1}H} *NMR Spectra*.—The ^{13}C-{^{1}H} NMR spectra of the new amino acidate(2−) complexes which contain an *N*-acetyl function show the presence of two non-equivalent carbonyl groups. The signal for the C(2) carboxylate carbonyl group appears in the range δ 182.35–193.15 and usually shows coupling to either one or both phosphine ligands in the respective complexes, although any coupling to platinum-195 is not discernible. The C(3) acetyl carbonyl group appears to higher field, between δ 168.15 and 175.55, and is observed as a singlet, even though its attached methyl group sometimes appears as a doublet, with ^4J(PC) in the range 1–5 Hz.

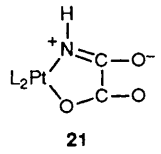
For complexes **8**, the ring methylene group appears as a singlet between δ 49.90 and 56.26. The spectrum for the cod derivative **8h** shows two distinct resonances with platinum-195 satellites for the alkene carbons of the co-ordinated ligand indicating the apparent planarity of the *N*-acetylglycinato(2−) chelate ring.

In the spectra of complexes **9**–**11** the ring methine carbon appears as a singlet in the range δ 58.65–67.55. For the *N*-acetyl-L-phenylalaninato(2−) complexes the chiral nature of this carbon is clearly shown in the spectrum of **11c**, where the four methyl carbons of the two dimethylphenylphosphine ligands occur as doublets at four different chemical shifts. The methyl and methylene carbons of the α-carbon side chains in complexes **9**–**11** all appear as singlets.

For complexes **13** the bridgehead carbon atom appears as a singlet in the range δ 63.00–64.11. The other three carbon atoms in the L-proline ring also appear as singlets and the carbonyl carbon appears as a weak signal between δ 184.47 and 184.99.

As with the ^{1}H NMR spectra, the ^{13}C-{^{1}H} NMR spectra of the other new complexes are consistent with the structures shown.

^{31}P-{^{1}H} *NMR Spectra*.—The ^{31}P-{^{1}H} NMR spectra of



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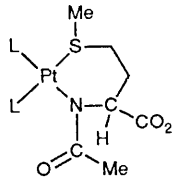

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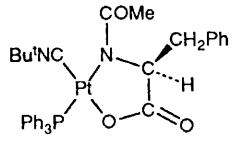

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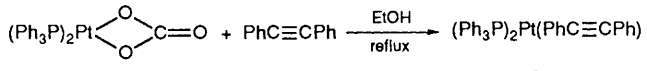

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Scheme 2

the new complexes containing phosphine ligands indicate the presence of two non-equivalent phosphorus nuclei in each case. Hence the spectra show second-order AB spin patterns with corresponding platinum-195 satellites. Assigning the signals is facilitated by the large difference in the one-bond coupling constants ^1J(PtP), such that the phosphorus lying opposite the carboxylate oxygen, P(2), always experiences a larger platinum-195 coupling than P(1), which is *trans* to either nitrogen or sulfur, or in the case of **14**, opposite oxygen.

Infrared Spectra.—The IR spectra of all the new compounds are dominated by the carbonyl absorptions, which occur within the range 1570–1700 cm^{-1}. With the exception of complexes **12b** and **13a**–**13c**, the amino acidate(2−) compounds show two intense bands in this region, due to the carboxylate and amide stretches. The higher-frequency band can be assigned to the carboxylate stretch and lies between 1640 and 1680 cm^{-1}, about 60 cm^{-1} higher than the amide band.[17] For compound **12b** the two bands overlap due to the higher frequency of the amide stretch of the trifluoroacetyl group.[17] Complexes **13a**–**13c** show just one band in this region, between 1660 and 1670 cm^{-1}. The carboxylate stretching frequencies compare well to those of compounds **3** and **19** (1639 and 1640 cm^{-1} respectively) in which the monoanion of glycine is acting as a chelate ligand.[18]

The spectra for the new compounds **17** and **18** are consistent with the structures shown. Interestingly, complexes **18** show, in addition to the two carbonyl bands, an N–H stretch between 3370 and 3360 cm^{-1} and also a band between 2240 and 2140 cm^{-1}. This latter absorption may be due to a coupling of two vibrations which appear in other parts of the spectrum, or it may be related to the zwitterionic structure **21**. A similar band has been noted in the spectra of simple amino acids, and has been associated with their dipolar form.[19]

The NMR and IR studies confirm the attachment of the *N*-acetyl-DL-methionine fragment in complexes **10** as being through nitrogen and the carboxylate oxygen, rather than through the sulfur atom as in **22**. The ^{31}P-{^{1}H} NMR and IR spectra in particular indicate, by their similarity to those of the other amino acidate(2−) complexes, that **10a**–**10g** are co-ordinated in a similar fashion. The differing co-ordination of the methionine residue in **10a**–**10g** compared with **6** can be accounted for by the contrasting methods of preparation of the complexes. The latter was prepared *via* the initial co-ordination, through nitrogen and sulfur, of a neutral methionine molecule, followed by deprotonation of the acid group, which failed to produce any reorganisation of the existing chelate ring.[8] Complexes **10a**–**10g** were presumably formed by initial deprotonation of *N*-acetyl-DL-methionine followed by co-ordination to the metal through the nitrogen and oxygen, on which the anionic charges resided.

The cycloocta-1,5-diene complexes **8h** and **11h** readily undergo simple ligand-displacement reactions with mono- or bi-dentate tertiary phosphines to yield the corresponding phosphine complexes. Thus, treatment of **8h** with 2 mole equivalents of triphenylphosphine or methyldiphenylphosphine in dichloromethane afforded complex **8a** or **8b** respectively, whereas treatment of **8h** with dppp yielded complex **8f**. Complexes **11a** and **11f** may be obtained from **11h** by a similar methodology.

Treatment of the triphenylphosphine complex **11a** with 1 mole equivalent of Bu^{t}NC in dichloromethane afforded complex **23** as a pale brown oil in good yield. The ^{31}P-{^{1}H} NMR spectrum of the product shows a single peak with corresponding platinum-195 satellites [^1J(PtP) 2913 Hz], which indicates that the remaining phosphine is bound *trans* to nitrogen rather than oxygen. The IR spectrum shows two carbonyl stretches and a band at 2220 cm^{-1}, indicative of a terminal isocyanide ligand.[20] The ^{1}H NMR spectrum shows the presence of one Bu^t group per phosphine ligand. Therefore, the substitution of a triphenylphosphine ligand in complex **11a** by Bu^{t}NC is stereospecific, the isocyanide ligand co-ordinating *trans* to the oxygen atom of the chelating fragment, as shown.

At room temperature, the phosphine complexes **8a** and **10a** do not react with ethanol, being quantitatively retrievable after stirring for 24 h in this solvent. However, if the solution is warmed to over 50 °C, decomposition of the complexes occurs, with the formation of numerous products as indicated by ^{31}P-{^{1}H} NMR spectroscopy.

The formation of the acetylene complex **25** from the carbonato complex **24** by refluxing in ethanol in the presence of diphenylacetylene, Scheme 2,[21] led to an investigation of the reactions of the amino acidate(2−) complexes in ethanol with donor ligands. Thus, the reaction of diphenylacetylene with **8a** in ethanol at 60 °C led to the formation of complex **25**[21] in good yield. A similar reaction using excess of triphenylphosphine instead of an acetylene led to the precipitation of bright yellow tetrakis(triphenylphosphine)platinum(0), identified by IR spectroscopy.[22]

The reaction of complex **8a** with sulfur dioxide in ethanol led to the formation of the bis(ethane sulfonate) complex $[Pt(SO_3Et)_2(PPh_3)_2]$ **26** in good yield. Comparison of ^{31}P-{^{1}H} NMR and IR spectra with those of an authentic sample, made by the method of Barlex and Kemmitt,[23] led to the identification of the product. The *cis* or *trans* nature of the product was not investigated, although it should be noted that an X-ray crystal structure determination of a sample shown to be identical to that made by Barlex and Kemmitt showed the complex to have *trans* stereochemistry.[24] Reaction of complex **8a** with sulfur dioxide in dichloromethane led to the formation of an unknown product whose ^{31}P-{^{1}H} NMR spectrum showed a singlet at δ 6.33 with ^1J(PtP) 3870 Hz.

Treatment of complex **8a** with carbon monoxide in dichloromethane led to the recovery of starting material as shown by ^{31}P-{^{1}H} NMR spectroscopy. However, the reaction of complex **8a** or **12b** with carbon monoxide in ethanol led to the formation of a product, tentatively assigned as the bis(ethoxycarbonyl) complex $[Pt(CO_2R)_2(PPh_3)_2]$ **27** (R = Et) in good yield. Again, the *cis* or *trans* nature of the product was not determined, although its ^{31}P-{^{1}H} NMR shift of δ 20.93 is significantly different to that of the bis(methoxycarbonyl) complex **27** (R = Me) made by Werner and Beck[25] (δ 16.4), which was assigned *trans* stereochemistry on the basis of a dipole moment measurement. Interestingly, a complex formulated as **27** (R = Me) could also be isolated from the reaction of *cis*-$[Pt\{OC(O)Me\}_2(PPh_3)_2]$ with carbon monoxide in methanol. This reaction was initially carried out by Barlex and Kemmitt[23] who obtained the product *trans*-$[Pt(CO_2Me)\{OC(O)Me\}(PPh_3)_2]$ as a precipitate in less than 50% yield. This result was confirmed in the present study and, in addition, the filtrate was

Table 2 M.p.s, analytical[a] and selected IR[b] data for the *N*-acetylamino acidate(2−) complexes **8**–**13**

Complex	M.p. (°C)	Analysis (%)			ν(C=O)[c]/cm^{-1}	
		C	H	N	Carboxylate	Amide
8a	185	57.0 (57.5)	4.1 (4.2)	1.8 (1.7)	1650	1600
8b	>220	50.7 (50.7)	4.7 (4.4)	1.8 (2.0)	1650	1590
8c	142	57.9 (58.5)	4.5 (4.5)	1.6 (1.6)	1660	1590
8d·CH_2Cl_2	>220	46.2 (46.2)	3.8 (3.7)	1.9 (1.8)	1640	1590
8e	>220	50.5 (50.9)	3.9 (4.1)	2.0 (2.0)	1650	1600
8f	>220	50.9 (51.4)	4.4 (4.3)	2.1 (1.9)	1650	1600
8g	217	52.2 (52.2)	4.5 (4.3)	1.9 (1.9)	1650	1600
8h	171	34.4 (34.5)	3.9 (4.1)	3.4 (3.4)	1670	1620
9a	>220	58.1 (58.0)	4.6 (4.4)	1.7 (1.7)	1660	1600
9b	128	50.9 (51.4)	4.6 (4.6)	2.0 (1.9)	1650	1570
9c	>220	58.8 (58.9)	4.9 (4.7)	1.4 (1.6)	1660	1570
9d	>220	50.5 (50.8)	4.0 (4.1)	2.0 (2.0)	1650	1570
9e	>220	51.2 (51.5)	4.3 (4.3)	2.0 (1.9)	1650	1580
9f	218	52.0 (52.2)	4.7 (4.5)	1.9 (1.9)	1650	1580
9g	>220	52.7 (52.8)	4.6 (4.7)	1.6 (1.9)	1650	1570
10a	138	56.6 (56.8)	4.8 (4.5)	1.4 (1.5)	1660	1580
10b	118	50.2 (50.5)	4.8 (4.7)	1.9 (1.8)	1660	1570
10c	170	57.8 (57.7)	4.6 (4.8)	1.5 (1.5)	1660	1570
10d·H_2O	121	48.5 (48.8)	4.3 (4.4)	1.8 (1.8)	1640	1570
10e	154	50.2 (50.6)	4.3 (4.5)	1.8 (1.8)	1650	1580
10f·H_2O	127	50.3 (50.1)	4.8 (4.8)	1.7 (1.7)	1650	1580
10g	>220	51.6 (51.9)	4.9 (4.8)	1.9 (1.7)	1650	1570
11a·H_2O	138	60.3 (59.9)	4.6 (4.6)	2.3 (1.5)	1660	1590
11b·H_2O	123	54.2 (54.3)	4.8 (4.8)	1.9 (1.7)	1650	1580
11c	188	48.0 (47.9)	4.8 (4.9)	2.3 (2.1)	1650	1580
11d·H_2O	>220	53.7 (53.9)	4.4 (4.4)	1.5 (1.7)	1640	1570
11e·CH_2Cl_2	>220	51.2 (51.6)	4.0 (4.2)	1.7 (1.6)	1640	1580
11f·H_2O	134	54.5 (54.9)	4.7 (4.7)	1.7 (1.7)	1650	1580
11g·H_2O	200	55.5 (55.5)	4.9 (4.9)	1.7 (1.7)	1650	1570
11h	167	44.8 (44.9)	4.5 (4.5)	2.8 (2.8)	1680	1590
12a·CH_2Cl_2	>220	52.7 (53.0)	3.7 (3.9)	1.6 (1.6)	1670	1660
12b	>220	53.9 (54.1)	3.5 (3.6)	1.5 (1.6)	1660(br)	—
13a·H_2O	159	57.4 (57.9)	4.7 (4.6)	1.3 (1.6)	1670	—
13b	148	53.3 (53.3)	4.5 (4.6)	1.8 (1.9)	1660	—
13c·CH_2Cl_2	158	49.9 (49.8)	4.7 (4.5)	1.7 (1.7)	1660	—

[a] Calculated values given in parentheses. [b] Recorded as KBr discs. [c] All bands strong.

shown to contain a single product, assigned as **27** (R = Me), whose ^{31}P-$\{^1H\}$ NMR spectrum was almost identical to that of **27** (R = Et) obtained above, but significantly different to that of *trans*-**27** (R = Me) as synthesised by Werner and Beck. Hence, on the basis of this ^{31}P-$\{^1H\}$ NMR data, the product **27** (R = Et) obtained by the action of carbon monoxide in ethanol on complex **8a** or **12b** can be assigned *cis* stereochemistry.

The ability of dimethyl acetylenedicarboxylate (dmad) to insert into the metal–nitrogen bonds of four-membered metallacycles has been described.[26] This led to an investigation of whether the same acetylene would insert into the metal–nitrogen bonds of the new five-membered metallacycles. Treatment of complex **8a** with excess of dmad in dichloromethane, at room temperature or at reflux, resulted in no reaction. This lack of reactivity is probably due to the non-nucleophilic character of the nitrogen lone pair as it is delocalised over the acetyl moiety. Treatment of the L-prolinato(2−) complex **13a**, which does not contain an acetyl group, with excess of dmad in dichloromethane at room temperature gave a number of products as shown by ^{31}P-$\{^1H\}$ NMR spectroscopy. However, no pure products could be isolated from the mixture.

Complex **13a** was also treated with hexafluorobut-2-yne in order to try and effect an acetylene insertion into the metallacycle. However, unlike the reaction with dmad, an orange gel-like substance was formed in the reaction mixture. On desiccation the gel yielded a pale brown powder whose elemental analysis indicated that it was comprised of only carbon and fluorine in a 1:1.5 ratio and whose IR spectrum showed strong bands attributable to C–F stretches.[17] The powder was highly insoluble in all common organic and inorganic solvents and is presumably a polymer of hexafluorobut-2-yne. This acetylene did not react with the new *N*-acetyl-containing amino acidate(2−) compounds under analogous conditions.

Experimental

Table 2 shows m.p.s, analytical and selected IR data, and Table 3 shows ^{31}P-$\{^1H\}$ NMR data for complexes **8**–**13** respectively. Melting points were measured in air on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 580 spectrophotometer, Proton NMR spectra on a Varian EM390 spectrometer at 90 MHz or on a Bruker AM300 spectrometer at 300.13 MHz with $SiMe_4$ (δ 0.0) as internal reference, positive values being to high frequency (low field), in $CDCl_3$ unless otherwise stated. The ^{13}C-$\{^1H\}$ NMR spectra were recorded on a Bruker AM300 spectrometer at 75.47 MHz with $SiMe_4$ (δ 0.0) as internal reference, in $CDCl_3$. The phenyl carbon region has been omitted for clarity. The ^{31}P-$\{^1H\}$ NMR spectra were recorded in dichloromethane on a JEOL-FX90 spectrometer at 36.21 MHz, with $[P(OH)_4]^+$ in D_2O (δ 0.0) as external reference.

Experiments were carried out using a dry, oxygen-free, dinitrogen atmosphere, using solvents which were dried and distilled under dinitrogen prior to use. Light petroleum refers to the fraction of b.p. 40–60 °C. All compounds were recrystallised in air. The compounds *N*-acetylglycine, *N*-acetyl-DL-methionine, *N*-acetyl-L-phenylalanine, L-proline, DL-mandelic acid, 2-acetamidophenol, pyrrole-2-carboxylic acid, mercaptoacetic acid, oxamic acid, Bu^{t}NC, diphenylacetylene,

Table 3 ^{31}P-{^{1}H} NMR data[a] for the complexes **8**–**13**.

Complex	δ P(1)[b]	^{1}J[PtP(1)]/Hz	δ P(2)[b]	^{1}J[PtP(2)]/Hz	^{2}J[P(1)P(2)]/Hz
8a	10.39	3047	3.92	4063	24
8b	−2.32	3027	−11.30	3896	30
8c	9.92	3108	2.59	3982	22
8d·CH_2Cl_2	−54.70	2608	−68.33	3512	78
8e	40.14	3071	26.72	3931	13
8f	−7.67	2869	−10.57	3731	34
8g	−2.01	2900	10.29	3945	29
8h	—	—	—	—	—
9a	10.39	3025	5.55	4043	24
9b	−2.12	3018	−10.39	3887	25
9c	9.66	3101	2.32	3943	22
9d	−53.70	2612	−67.70	3530	78
9e	38.60	3062	27.53	3922	14
9f	−7.95	2847	−10.07	3704	34
9g	−2.22	2895	10.48	3926	30
10a	10.36	3044	6.09	4060	25
10b	−2.66	3022	−9.99	3889	26
10c	8.92	3105	1.80	3936	25
10d·H_2O	−53.85	2612	−67.38	3525	68
10e	38.42	3057	27.73	3906	15
10f·H_2O	−8.16	2849	−10.70	3694	35
10g	−2.01	2905	9.69	3916	30
11a·H_2O	10.58	3047	5.75	4058	24
11b·H_2O	−4.48	3052	−8.18	3938	27
11c	−16.24	3003	−23.30	3770	25
11d·H_2O	−53.85	2639	−68.15	3574	78
11e·CH_2Cl_2	38.40	3069	26.58	3931	15
11f·H_2O	−8.17	2869	−12.15	3718	37
11g·H_2O	−3.83	2920	9.48	3960	30
11h	—	—	—	—	—
12a·CH_2Cl_2	12.86	3137	6.43	3730	24
12b	8.21	3184	4.92	3926	24
13a·H_2O	8.48	3316	6.06	3696	29
13b	−10.34	3025	−12.55	3362	37
13c·CH_2Cl_2	−4.43	3140	9.28	3569	30

[a] At 36.2 MHz in dichloromethane, at room temperature. [b] See Fig. 1.

dimethyl acetylenedicarboxylate (Aldrich), *N*-acetyl-DL-alanine (Sigma), carbon monoxide (BOC), sulfur dioxide (BDH) and hexafluorobut-2-yne (Fluorochem) were used as supplied. Absolute ethanol and methanol (BDH) were dried over activated molecular sieves prior to use. The compounds $[PtCl_2(cod)]$,[27] *cis*-$[Pt\{OC(O)Me\}_2(PPh_3)_2]$,[23] benzyldiphenylphosphine,[28] *N*-formylglycine[29] and *N*-trifluoroacetylglycine[30] were prepared as described.

Preparation of New Platinacyclic Complexes using Silver(I) *Oxide; General Method.*—Two equivalents of tertiary phosphine or 1 equivalent of chelating tertiary phosphine followed by 1 equivalent of the respective organic substrate and an excess of silver(I) oxide were added in succession to a stirred solution of $[PtCl_2(cod)]$ in dichloromethane (*ca.* 45 cm^3), and the mixture refluxed for 6 h. The mixture was filtered through Celite and the filtrate evaporated to dryness under reduced pressure. Dissolution of the residual oil in dichloromethane (*ca.* 5 cm^3) followed by addition of light petroleum afforded, on standing, a white to pale yellow microcrystalline solid which was recrystallised from dichloromethane–light petroleum and dried *in vacuo*.

(*i*) $[Pt\{N(COMe)CH_2C(O)O\}(PPh_3)_2]$ **8a**. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with triphenylphosphine (0.15 g, 0.57 mmol) and *N*-acetylglycine (0.035 g, 0.30 mmol) gave white *microcrystals* of **8a** (0.21 g, 93%). NMR spectra: ^{1}H, δ 7.73–7.12 (m, 30 H, Ph), 4.25 [dd, 2 H, CH_2, ^{4}J(PH) 1.3, ^{3}J(PtH) 25], and 1.39 (s, 3 H, CH_3); ^{13}C-{^{1}H}, δ 183.88 [d, CO, ^{3}J(PC) 2], 170.84 (s, CO), 55.54 (s, CH_2) and 20.00 [d, Me, ^{4}J(PC) 3 Hz].

(*ii*) $[Pt\{N(COMe)CH_2C(O)O\}(PMePh_2)_2]$ **8b**. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with methyldiphenylphosphine (0.11 g, 0.55 mmol) and *N*-acetylglycine (0.035 g, 0.30 mmol) gave white *microcrystals* of **8b** (0.17 g, 89%). NMR spectra: ^{1}H, δ 7.58–7.17 (m, 20 H, Ph), 4.30 [d, 2 H, CH_2, ^{4}J(PH) 3, ^{3}J(PtH) 23], 2.04 [d, 3 H, Me, $PMePh_2$, $|^{2}J(PH) + {}^{4}J(PH)|$ 11, ^{3}J(PtH) 35], 1.76 [d, 3 H, Me, $PMePh_2$, $|^{2}J(PH) + {}^{4}J(PH)|$ 10, ^{3}J(PtH) 24], and 1.60 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 184.10 [d, CO, ^{3}J(PC) 3], 171.35 (s, CO), 55.41 (s, CH_2), 20.14 [d, Me, ^{4}J(PC) 4], 13.69 [d, Me, $PMePh_2$, $|^{1}J(PC) + {}^{3}J(PC)|$ 45] and 13.40 [d, Me, $PMePh_2$, $|^{1}J(PC) + {}^{3}J(PC)|$ 39 Hz].

(*iii*) $[Pt\{N(COMe)CH_2C(O)O\}\{P(CH_2Ph)Ph_2\}_2]$ **8c**. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with benzyldiphenylphosphine (0.16 g, 0.58 mmol) and *N*-acetylglycine (0.035 g, 0.30 mmol) gave white *microcrystals* of **8c** (0.22 g, 94%). NMR spectra: ^{1}H, δ 7.72–6.11 (m, 30 H, Ph), 4.53 [d, 2 H, CH_2, ^{4}J(PH) 3, ^{3}J(PtH) 25], 3.85–3.62 [m, 4 H, CH_2, $P(CH_2Ph)Ph_2$] and 1.93 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 183.67 [d, CO, ^{3}J(PC) 2], 171.78 (s, CO), 56.26 (s, CH_2), 38.09 [d, CH_2, $P(CH_2Ph)Ph_2$, $|^{1}J(PC) + {}^{3}J(PC)|$ 36], 34.57 [d, CH_2, $P(CH_2Ph)Ph_2$, $|^{1}J(PC) + {}^{3}J(PC)|$ 31 Hz] and 21.18 (s, Me).

(*iv*) $[Pt\{N(COMe)CH_2C(O)O\}(dppm)]$ **8d**·CH_2Cl_2. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with dppm (0.11 g, 0.29 mmol) and *N*-acetylglycine (0.035 g, 0.30 mmol) gave white *microcrystals* of **8d**·CH_2Cl_2 (0.19 g, 90%). NMR spectra: ^{1}H, δ 7.80–7.28 (m, 20 H, Ph), 5.27 (s, 2 H, CH_2Cl_2), 4.33 [dd, 2 H, CH_2, dppm, ^{2}J(PH) 9.11], 4.13 [d, 2 H, CH_2, ^{4}J(PH) 2, ^{3}J(PtH) 21] and 1.86 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 188.22 [d, CO, ^{3}J(PC) 2], 172.07 (s, CO), 53.39 (s, CH_2), 53.27 (s, CH_2Cl_2), 49.11 [dd, CH_2, dppm, ^{1}J(PC) 31,32] and 19.56 [d, Me, ^{4}J(PC) 3 Hz].

(*v*) $[Pt\{N(COMe)CH_2C(O)O\}(dppe)]$ **8e**. The complex $[PtCl_2(cod)]$ (0.10 g, 0.27 mmol) with dppe (0.11 g, 0.28 mmol) and *N*-acetylglycine (0.035 g, 0.30 mmol) gave white *micro-*

crystals of **8e** (0.18 g, 94%). NMR spectra: ^{1}H, δ 7.91–7.27 (m, 20 H, Ph), 4.22 [d, 2 H, CH_2, ^4J(PH) 2, ^3J(PtH) 18], 2.28–1.92 (m, 4 H, CH_2, dppe) and 1.70 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 187.24 (s, CO), 170.13 (s, CO), 54.10 (s, CH_2), 35.15 [dd, CH_2, dppe, ^1J(PC) 40, ^3J(PC) 13], 24.40 [dd, CH_2, dppe, ^1J(PC) 36, ^3J(PC) 6] and 19.57 [d, Me, ^4J(PC) 5 Hz]. X-Ray quality crystals of **8e** were grown slowly from dichloromethane–light petroleum, in air.

(*vi*) [Pt{N(COMe)CH_2C(O)O}(dppp)] **8f**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and *N*-acetylglycine (0.035 g, 0.30 mmol) gave white *microcrystals* of **8f** (0.18 g, 92%). NMR spectra: ^{1}H, δ 7.83–7.28 (m, 20 H, Ph), 4.15 [d, 2 H, CH_2, ^4J(PH) 3, ^3J(PtH) 23], 2.32 (m, 4 H, PCH_2, dppp), 1.88 (m, 2 H, CH_2, dppp) and 1.39 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 184.86 [d, CO, ^3J(PC) 3], 170.11 (s, CO), 55.12 (s, CH_2), 27.78 [dd, PCH_2, dppp, ^1J(PC) 41, ^3J(PC) 9], 21.17 [dd, PCH_2, dppp, ^1J(PC) 38, ^3J(PC) 7], 19.57 [d, Me, ^4J(PC) 5 Hz] and 18.49 (s, CH_2, dppp).

(*vii*) [Pt{N(COMe)CH_2C(O)O}(dppb)] **8g**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and *N*-acetylglycine (0.035 g, 0.30 mmol) gave white *microcrystals* of **8g** (0.19 g, 95%). NMR spectra: ^{1}H, δ 7.74–7.20 (m, 20 H, Ph), 4.20 [d, 2 H, CH_2, ^4J(PH) 3, ^3J(PtH) 24], 2.87–1.43 (m, 8 H, CH_2, dppb) and 1.37 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 184.56 [d, CO, ^3J(PC) 3], 170.43 (s, CO), 54.76 (s, CH_2), 25.67 (m, PCH_2, dppb), 23.72 [d, PCH_2, dppb, ^1J(PC) 38], 21.57 (s, 2 × CH_2, dppb) and 19.54 [d, Me, ^4J(PC) 5 Hz].

(*viii*) [Pt{N(COMe)CH_2C(O)O}(cod)] **8h**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with *N*-acetylglycine (0.035 g, 0.30 mmol) gave white *microcrystals* of **8h** (0.10 g, 89%). NMR spectra: ^{1}H, δ 6.39 [m, 2 H, CH, cod, ^2J(PtH) 74], 5.38 [m, 2 H, CH, cod, ^2J(PtH) 56], 4.19 [s, 2 H, CH_2, ^3J(PtH) 21], 2.74–2.21 (m, 8 H, CH_2, cod) and 2.00 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 184.55 (s, CO), 175.55 (s, CO), 97.63 [s, CH, cod, ^1J(PtC) 139], 95.67 [s, CH, cod, ^1J(PtC) 161 Hz], 55.58 (s, CH_2), 32.20 (s, CH_2, cod), 27.81 (s, CH_2, cod) and 23.02 (s, Me).

(*ix*) [Pt{N(COMe)CH(Me)C(O)O}(PPh_3)$_2$] **9a**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with PPh_3 (0.15 g, 0.57 mmol) and *N*-acetyl-DL-alanine (0.04 g, 0.29 mmol) gave white *microcrystals* of **9a** (0.22 g, 96%). NMR spectra: ^{1}H, δ 7.87–7.12 (m, 30 H, Ph), 4.41 (m, 1 H, CH), 1.71 [d, 3 H, $CHCH_3$, ^3J(HH) 7] and 1.44 [s, 3 H, C(O)Me]; ^{13}C-{^{1}H}, δ 189.57 (s, CO), 170.50 (s, CO), 61.23 (s, CH), 21.81 (s, $CHCH_3$) and 19.66 [d, C(O)CH_3, ^4J(PC) 3 Hz].

(*x*) [Pt{N(COMe)CH(Me)C(O)O}($PMePh_2$)$_2$] **9b**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with $PMePh_2$ (0.11 g, 0.55 mmol) and *N*-acetyl-DL-alanine (0.04 g, 0.30 mmol) gave white *microcrystals* of **9b** (0.18 g, 92%). NMR spectra: ^{1}H, δ 7.76–7.11 (m, 20 H, Ph), 4.50 (m, 1 H, CH), 1.98 [d, 3 H, Me, $PMePh_2$, $|^2J(PH) + {}^4J(PH)|$ 11, ^3J(PtH) 33], 1.77 [d, 3 H, Me, $PMePh_2$, $|^2J(PH) + {}^4J(PH)|$ 11, ^3J(PtH) 37], 1.71 [d, 3 H, $CHCH_3$, ^3J(HH) 7] and 1.64 [s, 3 H, C(O)Me]; ^{13}C-{^{1}H}, δ 187.25 [d, CO, ^3J(PC) 3], 170.73 (s, CO), 61.36 (s, CH), 22.49 (s, $CHCH_3$), 19.47 [d, C(O)CH_3, ^4J(PC) 4] and 13.59 [d, 2 × PMe, $PMePh_2$, $|^1J(PC) + {}^3J(PC)|$ 39 Hz].

(*xi*) [Pt{N(COMe)CH(Me)C(O)O}{$P(CH_2Ph)Ph_2$}$_2$] **9c**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with $P(CH_2Ph)Ph_2$ (0.16 g, 0.58 mmol) and *N*-acetyl-DL-alanine (0.04 g, 0.30 mmol) gave white *microcrystals* of **9c** (0.22 g, 93%). NMR spectra: ^{1}H, δ 7.72–6.30 (m, 30 H, Ph), 4.71 (m, 1 H, CH), 4.06 [m, 2 H, CH_2, $P(CH_2Ph)Ph_2$], 3.59 [m, 2 H, CH_2, $P(CH_2Ph)Ph_2$], 1.94 [s, 3 H, C(O)Me] and 1.82 [d, 3 H, $CHCH_3$, ^3J(HH) 7]; ^{13}C-{^{1}H}, δ 186.76 (s, CO), 171.09 (s, CO), 61.99 (s, CH), 37.78 [d, CH_2, $P(CH_2Ph)Ph_2$, $|^1J(PC) + {}^3J(PC)|$ 35], 34.50 [d, CH_2, $P(CH_2Ph)Ph_2$, $|^1J(PC) + {}^3J(PC)|$ 31], 22.52 (s, $CHCH_3$) and 20.45 [d, C(O)CH_3, ^4J(PC) 2 Hz].

(*xii*) [Pt{N(COMe)CH(Me)C(O)O}(dppm)] **9d**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppm (0.11 g, 0.29 mmol) and *N*-acetyl-DL-alanine (0.04 g, 0.30 mmol) gave white *microcrystals* of **9d** (0.18 g, 94%). NMR spectra: ^{1}H δ 7.83–7.17 (m, 20 H, Ph), 4.62 [ddd, 1 H, CH_2, dppm, ^2J(PH) 9,11, ^2J(HH) 16], 4.24 (m, 1 H, CH), 4.01 [ddd, 1 H, CH_2, dppm, ^2J(PH) 10,12, ^2J(HH) 16], 1.88 [s, 3 H, C(O)Me] and 1.58 [d, 3 H, $CHCH_3$, ^3J(HH) 7]; ^{13}C-{^{1}H}, δ 190.76 (s, CO), 171.33 (s, CO), 58.65 (s, CH), 48.76 [dd, CH_2, dppm, ^1J(PC) 31,32], 23.55 (s, $CHCH_3$) and 18.53 [d, C(O)CH_3, ^4J(PC) 2 Hz].

(*xiii*) [Pt{N(COMe)CH(Me)C(O)O}(dppe)] **9e**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppe (0.11 g, 0.28 mmol) and *N*-acetyl-DL-alanine (0.04 g, 0.30 mmol) gave white *microcrystals* of **9e** (0.18 g, 92%). NMR spectra: ^{1}H, δ 8.07–7.22 (m, 20 H, Ph), 4.38 [ddq, 1 H, CH, ^4J(PH) 1.5, ^3J(HH) 7], 2.69–2.35 (m, 4 H, CH_2, dppe), 1.64 [s, 3 H, C(O)Me] and 1.47 [d, 3 H, $CHCH_3$, ^3J(HH) 7]; ^{13}C-{^{1}H}, δ 189.30 [d, CO, ^3J(PC) 2], 169.15 (s, CO), 59.76 (s, CH), 35.00 [dd, CH_2, dppe, ^1J(PC) 40, ^3J(PC) 13], 24.02 [dd, CH_2, dppe, ^1J(PC) 42, ^3J(PC) 6], 23.25 (s, $CHCH_3$) and 18.34 [d, C(O)CH_3, ^4J(PC) 4 Hz].

(*xiv*) [Pt{N(COMe)CH(Me)C(O)O}(dppp)] **9f**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and *N*-acetyl-DL-alanine (0.04 g, 0.30 mmol) gave white *microcrystals* of **9f** (0.18 g, 95%). NMR spectra: ^{1}H, δ 7.91–6.94 (m, 20 H, Ph), 4.33 (m, 1 H, CH), 2.68–2.05 (m, 6 H, CH_2, dppp), 1.55 [d, 3 H, $CHCH_3$, ^3J(HH) 7] and 1.38 [s, 3 H, C(O)Me]; ^{13}C-{^{1}H}, δ 187.93 [d, CO, ^3J(PC) 3], 169.44 (s, CO), 61.06 (s, CH), 28.10 [dd, PCH_2, dppp, ^1J(PC) 38, ^3J(PC)10], 23.17 [dd, PCH_2, dppp, ^1J(PC) 36, ^3J(PC) 7], 22.34 (s, $CHCH_3$), 18.94 (s, CH_2, dppp) and 18.77 [d, C(O)CH_3, ^4J(PC) 4 Hz].

(*xv*) [Pt{N(COMe)CH(Me)C(O)O}(dppb)] **9g**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and *N*-acetyl-DL-alanine (0.04 g, 0.30 mmol) gave white *microcrystals* of **9g** (0.19 g, 94%). NMR spectra: ^{1}H, δ 7.82–7.11 (m, 20 H, Ph), 4.36 (m, 1 H, CH), 2.70–2.15 (m, 8 H, CH_2, dppb), 1.62 [d, 3 H, $CHCH_3$, ^3J(HH) 7] and 1.38 [s, 3 H, C(O)Me]; ^{13}C-{^{1}H}, δ 187.78 [d, CO, ^3J(PC) 3], 169.86 (s, CO), 60.61 (s, CH), 25.62 (m, PCH_2, dppb), 23.72 (m, PCH_2, dppb), 21.87 (s, 2 × CH_2, dppb), 21.66 (s, $CHCH_3$), and 18.95 [d, C(O)CH_3, ^4J(PC) 4 Hz].

(*xvi*) [Pt{N(COMe)CH(CH_2CH_2SMe)C(O)O}(PPh_3)$_2$] **10a**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with PPh_3 (0.15 g, 0.57 mmol) and *N*-acetyl-DL-methionine (0.055 g, 0.29 mmol) gave white *microcrystals* of **10a** (0.24 g, 98%). NMR spectra: ^{1}H, δ 7.84–7.12 (m, 30 H, Ph), 4.34 (m, 1 H, CH), 2.42 (m, 2 H, SCH_2), 2.22 (m, 2 H, $CHCH_2$), 2.13 (s, 3 H, SMe), 1.56 [s, 3 H, C(O)Me]; ^{13}C-{^{1}H}, δ 184.91 (m, CO), 171.87 (s, CO), 65.12 (s, CH), 36.29 (s, SCH_2), 31.03 (s, $CHCH_2$), 20.55 [d, C(O)CH_3, ^4J(PC) 3 Hz] and 15.36 (s, SMe).

(*xvii*) [Pt{N(COMe)CH(CH_2CH_2SMe)C(O)O}($PMePh_2$)$_2$] **10b**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with $PMePh_2$ (0.11 g, 0.55 mmol) and *N*-acetyl-DL-methionine (0.055 g, 0.29 mmol) gave white *microcrystals* of **10b** (0.20 g, 94%). NMR spectra: ^{1}H, δ 7.68–7.15 (m, 20 H, Ph), 4.45 (m, 1 H, CH), 2.70 (m, 1 H, SCH_2), 2.57 (m, 1 H, SCH_2), 2.42 (m, 1 H, $CHCH_2$), 2.27 (m, 1 H, $CHCH_2$), 2.17 (s, 3 H, sMe), 1.99 [d, 3 H, Me, $PMePh_2$, $|^2J(PH) + {}^4J(PH)|$ 11], 1.74 [s, 3 H, C(O)Me] and 1.72 [d, 3 H, Me, $PMePh_2$, $|^2J(PH) + {}^4J(PH)|$ 11]; ^{13}C-{^{1}H}, δ 185.62 (m, CO), 171.65 (s, CO), 65.12 (s, CH), 36.77 (s, SCH_2), 30.87 (s, $CHCH_2$), 20.36 [d, C(O)CH_3, ^4J(PC) 2 Hz], 15.40 (s, SMe) and 13.28 (m, 2 × Me, $PMePh_2$).

(*xviii*) [Pt{N(COMe)CH(CH_2CH_2SMe)C(O)O}{$P(CH_2Ph)Ph_2$}$_2$] **10c**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with $P(CH_2Ph)Ph_2$ (0.16 g, 0.58 mmol) and *N*-acetyl-DL-methionine (0.055 g, 0.29 mmol) gave white *microcrystals* of **10c** (0.24 g, 95%). NMR spectra: ^{1}H, δ 7.41–6.25 (m, 30 H, Ph), 4.68 (m, 1 H, CH), 4.05 [m, 2 H, PCH_2, $P(CH_2Ph)Ph_2$], 3.55 [m, 2 H, PCH_2, $P(CH_2Ph)Ph_2$], 2.83 (m, 2 H, SCH_2), 2.66–2.42 (m, 2 H, $CHCH_2$), 2.20 (s, 3 H, SMe) and 2.05 [s, 3 H, C(O)Me]; ^{13}C-{^{1}H}, δ 185.22 (m, CO), 172.41 (s, CO), 65.99 (s, CH), 37.67 [d, CH_2, $P(CH_2Ph)Ph_2$, $|^1J(PC) + {}^3J(PC)|$ 35], 36.86 (s, SCH_2), 34.30 [d, CH_2, $P(CH_2Ph)Ph_2$, $|^1J(PC) + {}^3J(PC)|$ 31], 31.02

(s, $CHCH_2$), 21.45 [d, C(O)CH_3, ^4J(PC) 2 Hz] and 15.64 (s, SMe).

(*xix*) [Pt{N(COMe)CH(CH_2CH_2SMe)C(O)O}(dppm)] **10d**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppm (0.11 g, 0.29 mmol) and *N*-acetyl-DL-methionine (0.055 g, 0.29 mmol) gave white *microcrystals* of **10d**·H_2O (0.20 g, 94%). NMR spectra: ^{1}H, δ 7.84–7.30 (m, 20 H, Ph), 4.64 [ddd, 1 H, CH_2, dppm, ^2J(PH) 9,11, ^2J(HH) 16], 4.30 (m, 1 H, CH), 4.03 [ddd, 1 H, CH_2, dppm, ^2J(PH) 10,12, ^2J(HH) 16], 2.95 [ddd, 1 H, SCH_2, ^2J(HH) 12, ^3J(HH) 5,11], 2.69 [ddd, 1 H, SCH_2, ^2J(HH) 12, ^3J(HH) 6,11], 2.34 (s, br, 2 H, H_2O), 2.31–2.19 (m, 1 H, $CHCH_2$), 2.15–2.02 (m, 1 H, $CHCH_2$), 2.08 (s, 3 H, SMe), and 1.89 [s, 3 H, C(O)Me]; ^{13}C-{^{1}H}, δ 188.58 (s, CO), 171.19 (s, CO), 62.22 (s, CH), 48.64 [dd, CH_2, dppm, ^1J(PC) 31,32], 36.01 (s, SCH_2), 29.22 (s, $CHCH_2$), 18.74 [d, C(O)CH_3, ^4J(PC) 3 Hz] and 15.41 (s, SMe).

(*xx*) [Pt{N(COMe)CH(CH_2CH_2SMe)C(O)O}(dppe)] **10e**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppe (0.11 g, 0.28 mmol) and *N*-acetyl-DL-methionine (0.055 g, 0.29 mmol) gave white *microcrystals* of **10e** (0.20 g, 95%). NMR spectra: ^{1}H, δ 8.05–7.30 (m, 20 H, Ph), 4.39 (m, 1 H, CH), 2.66–1.91 (m, 6 H, CH_2, dppe + SCH_2 + $CHCH_2$), 2.03 (s, 3 H, SMe), 1.68 [s, 3 H, C(O)Me] and 1.49 (m, 2 H, CH_2, dppe); ^{13}C-{^{1}H}, δ 187.24 [d, CO, ^3J(PC) 3], 169.33 (s, CO), 63.31 (s, CH), 36.36 (s, SCH_2), 34.66 [dd, PCH_2, dppe, ^1J(PC) 41, ^3J(PC) 12], 29.56 (s, $CHCH_2$), 18.92 [d, C(O)CH_3, ^4J(PC) 3], 17.78 [dd, PCH_2, dppe, ^1J(PC) 41, ^3J(PC) 7 Hz] and 15.24 (s, SMe).

(*xxi*) [Pt{N(COMe)CH(CH_2CH_2SMe)C(O)O}(dppp)] **10f**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and *N*-acetyl-DL-methionine (0.055 g, 0.29 mmol) gave white *microcrystals* of **10f**·H_2O (0.20 g, 91%). NMR spectra: ^{1}H, δ 7.84–7.22 (m, 20 H, Ph), 4.27 (m, 1 H, CH), 2.65–1.92 (m, 12 H, 3 × CH_2, dppp + SCH_2 + $CHCH_2$ + H_2O), 2.13 (s, 3 H, SMe) and 1.48 [s, 3 H, C(O)Me]; ^{13}C-{^{1}H}, δ 186.09 [d, CO, ^3J(PC) 3], 169.93 (s, CO), 64.90 (s, CH), 36.96 (s, SCH_2), 30.58 (s, $CHCH_2$), 28.07 [dd, PCH_2, dppp, ^1J(PC) 40, ^3J(PC) 9], 23.37 [dd, PCH_2, dppp, ^1J(PC) 38, ^3J(PC) 5], 19.61 [d, C(O)CH_3, ^4J(PC) 4 Hz], 18.75 (s, CH_2, dppp) and 15.17 (s, SMe).

(*xxii*) [Pt{N(COMe)CH(CH_2CH_2SMe)C(O)O}(dppb)] **10g**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and *N*-acetyl-DL-methionine (0.055 g, 0.29 mmol) gave white *microcrystals* of **10g** (0.20 g, 91%). NMR spectra: ^{1}H, δ 7.75–7.17 (m, 20 H, Ph), 4.27 (m, 1 H, CH), 2.68–1.89 (m, 10 H, 3 × CH_2, dppb + SCH_2 + $CHCH_2$), 2.13 (s, 3 H, SMe), 1.58–1.26 (m, 2 H, CH_2, dppb) and 1.47 [s, 3 H, C(O)Me]; ^{13}C-{^{1}H}, δ 186.18 (m, CO), 170.73 (s, CO), 64.57 (s, CH), 36.57 (s, SCH_2), 30.91 (s, $CHCH_2$), 25.40 (m, PCH_2, dppb), 23.78 [dd, PCH_2, dppb, ^1J(PC) 41, ^3J(PC) 3], 21.53 (s, 2 × CH_2, dppb), 19.86 [d, C(O)CH_3, ^4J(PC) 3] and 15.17 (s, SMe).

(*xxiii*) [Pt{N(COMe)CH(CH_2Ph)C(O)O}(PPh_3)$_2$] **11a**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with PPh_3 (0.15 g, 0.57 mmol) and *N*-acetyl-L-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of **11a**·H_2O (0.23 g, 90%). NMR spectra: ^{1}H, δ 7.83–7.02 (m, 35 H, Ph), 4.62 (m, 1 H, CH), 3.50 [dd, 1 H, CH_2, ^2J(HH) 14, ^3J(HH) 5], 3.39 [dd, 1 H, CH_2, ^2J(HH) 14, ^3J(HH) 7], 2.13 (s, br, 2 H, H_2O) and 1.43 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 185.61 [d, CO, ^3J(PC) 3], 172.22 (s, CO), 67.44 (s, CH), 42.69 (s, CH_2) and 20.52 [d, Me, ^4J(PC) 5 Hz].

(*xxiv*) [Pt{N(COMe)CH(CH_2Ph)C(O)O}($PMePh_2$)$_2$] **11b**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with $PMePh_2$ (0.11 g, 0.55 mmol) and *N*-acetyl-L-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of **11b**·H_2O (0.20 g, 91%). NMR spectra: ^{1}H, δ 7.93–6.93 (m, 25 H, Ph), 4.85 (m, 1 H, CH), 3.53 [dd, 1 H, CH_2, ^2J(HH) 14, ^3J(HH) 5], 3.20 [dd, 1 H, CH_2, ^2J(HH) 14, ^3J(HH) 5], 2.24 (s, br, 2 H, H_2O), 1.94 [d, 3 H, Me, $PMePh_2$, $|^2J$(PH) + ^4J(PH)| 12, ^3J(PtH) not discernible], 1.88 [s, 3 H, C(O)Me] and 1.30 [d, 3 H, Me, $PMePh_2$, $|^2J$(PH) + ^4J(PH)| 10, ^3J(PtH) not discernible]; ^{13}C-{^{1}H}, δ 186.15 [d, CO, ^3J(PC) 5], 172.81 (s, CO), 66.74 (s, CH), 41.50 (s, CH_2), 20.40 [d, C(O)CH_3, ^4J(PC) 4], 17.97 [d, Me, $PMePh_2$, $|^1J$(PC) + ^3J(PC)| 48] and 12.83 [d, Me, $PMePh_2$, $|^1J$(PC) + ^3J(PC)| 40 Hz].

(*xxv*) [Pt{N(COMe)CH(CH_2Ph)C(O)O}(PMe_2Ph)$_2$)] **11c**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with PMe_2Ph (0.08 g, 0.58 mmol) and *N*-acetyl-L-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of **11c** (0.17 g, 93%). NMR spectra: ^{1}H, δ 7.47–6.89 (m, 15 H, Ph), 4.90 (m, 1 H, CH), 3.50 [dd, 1 H, CH_2, ^2J(HH) 13, ^3J(HH) 6], 3.17 [dd, 1 H, CH_2, ^2J(HH) 13, ^3J(HH) 5], 1.95 [s, 3 H, C(O)Me], 1.90 [d, 3 H, Me, PMe_2Ph, $|^2J$(PH) + ^4J(PH)| 12, ^3J(PtH) 37], 1.55 [d, 3 H, Me, PMe_2Ph, $|^2J$(PH) + ^4J(PH)| 12, ^3J(PtH) 35], 1.49 [d, 3 H, Me, PMe_2Ph, $|^2J$(PH) + ^4J(PH)| 11, ^3J(PtH) 22] and 1.38 [d, 3 H, Me, PMe_2Ph, $|^2J$(PH) + ^4J(PH)| 11, ^3J(PtH) 21]; ^{13}C-{^{1}H}, δ 186.11 [d, CO, ^3J(PC) 3], 173.23 (s, CO), 67.24 (s, CH), 41.48 (s, CH_2), 20.58 [d, C(O)CH_3, ^4J(PC) 4], 18.68 [d, Me, PMe_2Ph, $|^1J$(PC) + ^3J(PC)| 47], 12.12 [d, Me, PMe_2Ph, $|^1J$(PC) + ^3J(PC)| 40], 11.95 [d, Me, PMe_2Ph, $|^1J$(PC) + ^3J(PC)| 42] and 11.40 [d, Me, PMe_2Ph, $|^1J$(PC) + ^3J(PC)| 43 Hz].

(*xxvi*) [Pt{N(COMe)CH(CH_2Ph)C(O)O}(dppm)] **11d**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppm (0.11 g, 0.29 mmol) and *N*-acetyl-L-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of **11d**·H_2O (0.20 g, 92%). NMR spectra: ^{1}H, δ 7.90–7.16 (m, 25 H, Ph), 4.52 (m, 1 H, CH), 4.46 [ddd, 1 H, CH_2, dppm, ^2J(PH) 9,11, ^2J(HH) 16], 3.86 [ddd, 1 H, CH_2, dppm, ^2J(PH) 9,12, ^2J(HH) 16], 3.31 [dd, 1 H, $CHCH_2$, ^2J(HH) 13, ^3J(HH) 5], 3.09 [dd, 1 H, $CHCH_2$, ^2J(HH) 13, ^3J(HH) 5], 2.10 (s, br 2 H, H_2O) and 1.77 (s, 3 H, CH_3); ^{13}C-{^{1}H}, δ 189.10 (s, CO), 171.47 (s, CO), 64.60 (s, CH), 49.01 [dd, CH_2, dppm, ^1J(PC) 31,32], 42.04 (s, $CHCH_2$) and 18.86 [d, Me, ^4J(PC) 1 Hz].

(*xxvii*) [Pt{N(COMe)CH(CH_2Ph)C(O)O}(dppe)] **11e**·CH_2Cl_2. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppe (0.11 g, 0.28 mmol) and *N*-acetyl-L-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of **11e**·CH_2Cl_2 (0.21 g, 88%). NMR spectra: ^{1}H, δ 7.98–6.81 (m, 25 H, Ph), 5.24 (s, 2 H, CH_2Cl_2), 4.51 (m, 1 H, CH), 3.15 [dd, 1 H, $CHCH_2$, ^2J(HH) 13, ^3J(HH) 4], 3.03 [dd, 1 H, $CHCH_2$, ^2J(HH) 13, ^3J(HH) 7], 2.83–2.23 (m, 2 H, PCH_2, dppe), 1.94 (m, 1 H, PCH_2, dppe), 1.42 (m, 1 H, PCH_2, dppe) and 1.29 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 187.88 [d, CO, ^3J(PC) 2], 170.08 (s, CO), 66.02 (s, CH), 53.15 (s, CH_2Cl_2), 43.22 (s, $CHCH_2$), 34.99 [dd, PCH_2, dppe, ^1J(PC) 40, ^3J(PC) 13], 17.80 [dd, PCH_2, dppe, ^1J(PC) 38, ^3J(PC) 7] and 18.55 [d, Me, ^4J(PC) 4 Hz].

(*xxviii*) [Pt{N(COMe)CH(CH_2Ph)C(O)O}(dppp)] **11f**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and *N*-acetyl-L-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of **11f**·H_2O (0.20 g, 89%). NMR spectra: ^{1}H, δ 7.84–6.89 (m, 25 H, Ph), 4.38 (m, 1 H, CH), 3.27 [dd, 1 H, $CHCH_2$, ^2J(HH) 13, ^3J(HH) 4], 3.00 [dd, 1 H, $CHCH_2$, ^2J(HH) 13, ^3J(HH) 8], 2.57–2.01 (m, 8 H, 3 × CH_2, dppp + H_2O) and 1.09 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 193.15 (m, CO), 170.49 (s, CO), 67.55 (s, CH), 43.48 (s, $CHCH_2$), 28.62 [dd, PCH_2, dppp, ^1J(PC) 40, ^3J(PC) 10], 22.97 [dd, PCH_2, dppp, ^1J(PC) 33, ^3J(PC) 5], 19.23 [d, Me, ^4J(PC) 4 Hz] and 18.62 (s, CH_2, dppp).

(*xxix*) [Pt{N(COMe)CH(CH_2Ph)C(O)O}(dppb)] **11g**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and *N*-acetyl-L-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of **11g**·H_2O (0.21 g, 92%). NMR spectra: ^{1}H, δ 7.79–7.04 (m, 25 H, Ph), 4.57 (m, 1 H, CH), 3.33 [dd, 1 H, $CHCH_2$, ^2J(HH) 14, ^3J(HH) 6], 3.22 [dd, 1 H, $CHCH_2$, ^2J(HH) 14, ^3J(HH) 5], 3.11–1.75 (m, br, 8 H, 3 × CH_2, dppb + H_2O), 1.56 (m, 2 H, CH_2, dppb) and 1.38 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 186.57 [d, CO, ^3J(PC) 3], 171.29 (s, CO), 66.26 (s, CH), 41.97 (s, $CHCH_2$), 25.57 (m, PCH_2, dppb), 22.72 [d, PCH_2, dppb, ^1J(PC) 35], 21.45 (s, 2 × CH_2, dppb) and 19.62 [d, Me, ^4J(PC) 4 Hz].

(*xxx*) [Pt{N(COMe)CH(CH$_2$Ph)C(O)O}(cod)] **11h**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with *N*-acetyl-L-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of **11h** (0.11 g, 80%). NMR spectra: ^{1}H, δ 7.41–7.18 (m, 5 H, Ph), 6.51 [m, 1 H, CH, cod, ^2J(PtH) 76], 5.80 [m, 1 H, CH, cod, ^2J(PtH) 63], 5.16 [m, 1 H, CH, cod, ^2J(PtH) 52], 4.70 [dd, 1 H, C*H*CH$_2$Ph, ^3J(HH) 3,6, ^3J(PtH) 38], 4.57 [m, 1 H, CH, cod, ^2J(PtH) 56], 3.31 [dd, 1 H, CHC*H*$_2$Ph, ^2J(HH) 13, ^3J(HH) 3], 2.96 [dd, 1 H, CHC*H*$_2$Ph, ^2J(HH) 13, ^3J(HH) 6 Hz], 2.73–1.63 (m, 8 H, CH$_2$, cod) and 2.12 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 185.67 (s, CO), 174.77 (s, CO), 98.38 (s, CH, cod), 97.29 (s, CH, cod), 96.99 (s, CH, cod), 91.72 (s, CH, cod), 67.24 (s, *C*HCH$_2$Ph), 41.19 (s, CH*C*H$_2$Ph), 32.94 (s, CH$_2$, cod), 30.55 (s, CH$_2$, cod), 29.44 (s, CH$_2$, cod), 25.93 (s, CH$_2$, cod) and 22.15 (s, Me).

(*xxxi*) [Pt{N(CHO)CH$_2$C(O)O}(PPh$_3$)$_2$] **12a**·CH$_2$Cl$_2$. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PPh$_3$ (0.15 g, 0.57 mmol) and *N*-formylglycine (0.03 g, 0.29 mmol) gave pale yellow *microcrystals* of **12a**·CH$_2$Cl$_2$ (0.24 g, 98%). NMR spectra: ^{1}H, δ 7.62–7.08 (m, 31 H, Ph + CHO), 5.22 (s, 2 H, CH$_2$Cl$_2$) and 4.33 [s, 2 H, CH$_2$, ^3J(PtH) 23 Hz]; ^{13}C-{^{1}H}, δ 184.25 (s, CO), 168.15 (s, CO), 53.36 (s, CH$_2$Cl$_2$) and 49.90 (s, CH$_2$).

(*xxxii*) [Pt{N(COCF$_3$)CH$_2$C(O)O}(PPh$_3$)$_2$] **12b**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PPh$_3$ (0.15 g, 0.57 mmol) and *N*-trifluoroacetylglycine (0.05 g, 0.29 mmol) gave white *microcrystals* of **12b** (0.23 g, 96%). NMR spectra: ^{1}H, δ 7.77–6.66 (m, 30 H, Ph) and 4.38 [d, 2 H, CH$_2$, ^4J(PH) 3, ^3J(PtH) 22]; ^{13}C-{^{1}H}, δ 182.35 (s, CO) and 52.94 (s, CH$_2$); *C*(O)*C*F$_3$ were not discernible; ^{19}F-{^{1}H}, δ −67.69 [d, CF$_3$, ^5J(PF) 2, ^4J(PtF) 21 Hz].

(*xxxiii*) [Pt{NCH$_2$CH$_2$CH$_2$CHC(O)O}(PPh$_3$)$_2$] **13a**·H$_2$O. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PPh$_3$ (0.15 g, 0.57 mmol) and L-proline (0.035 g, 0.30 mmol) gave greeny yellow *microcrystals* of **13a**·H$_2$O (0.21 g, 92%). NMR spectra: ^{1}H δ 7.74–7.21 (m, 30 H, Ph), 4.88 (m, 1 H, CH), 2.70 (m, 2 H, CH$_2$), 2.46 (s, br, 2 H, H$_2$O), 2.02 (m, 2 H, CH$_2$) and 1.67 (m, 2 H, CH$_2$); ^{13}C-{^{1}H}, δ 184.47 (m, CO), 64.11 (s, CH), 51.53 (s, CH$_2$), 30.16 (s, CH$_2$) and 24.88 (s, CH$_2$).

(*xxxiv*) [Pt{NCH$_2$CH$_2$CH$_2$CHC(O)O}(dppp)] **13b**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and L-proline (0.035 g, 0.30 mmol) gave pale yellow *microcrystals* of **13b** (0.18 g, 92%). NMR spectra: ^{1}H, δ 8.42–7.25 (m, 20 H, Ph), 4.50 (m, 1 H, CH), 2.94 (m, 2 H, CH$_2$) and 2.52–1.26 (m, 10 H, 3 × CH$_2$, dppp + 2 × CH$_2$); ^{13}C-{^{1}H}, δ 184.86 (m, CO), 63.03 (s, CH), 50.60 (s, CH$_2$), 29.85 (s, CH$_2$), 24.25 (s, CH$_2$), 23.59 (m, 2 × PCH$_2$, dppp) and 18.57 (s, CH$_2$, dppp).

(*xxxv*) [Pt{NCH$_2$CH$_2$CH$_2$CHC(O)O}(dppb)] **13c**·CH$_2$Cl$_2$. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and L-proline (0.035 g, 0.30 mmol) gave pale yellow *microcrystals* of **13c**·CH$_2$Cl$_2$ (0.20 g, 90%). NMR spectra: ^{1}H, δ 7.88–7.34 (m, 20 H, Ph), 5.29 (s, 2 H, CH$_2$Cl$_2$), 4.91 (m, 1 H, CH) and 2.91–1.20 (m, 14 H, 4 × CH$_2$, dppb + 3 × CH$_2$); ^{13}C-{^{1}H}, δ 184.99 [d, CO, ^3J(PC) 2], 63.00 (s, CH), 53.15 (s, CH$_2$Cl$_2$), 50.26 (s, CH$_2$), 29.43 (s, CH$_2$), 27.68 [d, PCH$_2$, dppb, ^1J(PC) 38], 25.45 [d, CH$_2$, dppb, ^2J(PC) 4], 24.79 (s, CH$_2$), 23.80 [d, PCH$_2$, dppb, ^1J(PC) 40 Hz] and 20.74 (s, CH$_2$, dppb).

(*xxxvi*) [Pt{OC(H)PhC(O)O}(PPh$_3$)$_2$] **14**·H$_2$O. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PPh$_3$ (0.15 g, 0.57 mmol) and DL-mandelic acid (0.045 g, 0.29 mmol) gave white *microcrystals* of **14**·H$_2$O (0.22 g, 92%) (Found: C, 59.7; H, 4.3. C$_{44}$H$_{36}$O$_3$P$_2$Pt·H$_2$O requires C, 59.5; H, 4.3%), m.p. 123 °C, ν(C=O) at 1660s cm^{-1}. NMR spectra: ^{1}H (300 MHz), δ 7.87–6.96 (m, 35 H, Ph), 5.53 [d, 1 H, CH, ^4J(PH) 8, ^3J(PtH) 43] and 2.20 (s, br 2 H, H$_2$O); ^{13}C-{^{1}H}, δ 190.65 [dd, CO, ^3J(PC) 4,7] and 81.65 [d, CH, ^3J(PC) 2]; ^{31}P-{^{1}H} (36.2 MHz), δ 10.87 {d, P(2), ^1J[PtP(2)] 3904, ^2J[P(1)P(2)] 27} and 9.69 {d, P(1), ^1J[PtP(1)] 3286, ^2J[P(2)P(1)] 27 Hz}.

(*xxxvii*) [Pt{*o*-N(COMe)C$_6$H$_4$O}(PPh$_3$)$_2$] **15**. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PPh$_3$ (0.15 g, 0.57 mmol) and 2-acetamidophenol (0.045 g, 0.30 mmol) gave white *microcrystals* of **15** (0.20 g, 85%) (Found: C, 60.9; H, 4.4; N, 1.8. C$_{44}$H$_{37}$NO$_2$P$_2$Pt requires C, 60.8; H, 4.3; N, 1.6%), m.p. above 220 °C, ν(C=O) at 1600s cm^{-1}. NMR spectra: ^{1}H (90 MHz), δ 7.8–6.1 (m, 34 H, Ph) and 1.7 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 171.22 (s, CO) and 21.35 [d, Me, ^4J(PC) 4]; ^{31}P-{^{1}H} (36.2 MHz), δ 10.80 {d, P(1), ^1J[PtP(1)] 3184, ^2J[P(2)P(1)] 22} and 3.40 {d, P(2), ^1J[PtP(2)] 3798, ^2J[P(1)P(2)] 22 Hz}.

(*xxxviii*) [Pt{NCH=C(H)CH=CC(O)O}(PPh$_3$)$_2$] **16**·H$_2$O. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PPh$_3$ (0.15 g, 0.57 mmol) and pyrrole-2-carboxylic acid (0.03 g, 0.27 mmol) gave white *microcrystals* of **16**·H$_2$O (0.22 g, 96%) (Found: C, 57.9; H, 3.9; N, 1.7. C$_{41}$H$_{33}$NO$_2$P$_2$Pt·H$_2$O requires C, 58.2; H, 4.1; N, 1.7%), m.p. above 220 °C; ν(C=O) at 1650s cm^{-1}. NMR spectra: ^{1}H (300 MHz), δ 7.49–7.11 (m, 30 H, Ph), 6.64 (m, 1 H, CH), 5.28 (m, 1 H, CH) and 1.91 (s, br, 2 H, H$_2$O); ^{13}C-{^{1}H}, too insoluble; ^{31}P-{^{1}H} (36.2 MHz); δ 14.87 {d, P(1), ^1J[PtP(1)] 3313, ^2J[P(2)P(1)] 24} and 5.95 {d, P(2), ^1J[PtP(2)] 3599, ^2J[P(1)P(2)] 24 Hz}.

(*xxxix*) [Pt{SCH$_2$C(O)O}(PPh$_3$)$_2$] **17a**·CH$_2$Cl$_2$. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with PPh$_3$ (0.15 g, 0.57 mmol) and mercaptoacetic acid (0.025 g, 0.27 mmol) gave yellow *microcrystals* of **17a**·CH$_2$Cl$_2$ (0.21 g, 87%) (Found: C, 53.3; H, 3.5. C$_{38}$H$_{32}$O$_2$P$_2$PtS·CH$_2$Cl$_2$ requires C, 52.4; H, 3.8%), m.p. 147 °C ν(C=O) at 1650s cm^{-1}. NMR spectra: ^{1}H (300 MHz), δ 7.58–7.12 (m, 30 H, Ph), 5.33 (s, 2 H, CH$_2$Cl$_2$) and 3.60 [dd, 2 H, CH$_2$, ^4J(PH) 1,2, ^3J(PtH) 18]; ^{13}C-{^{1}H}, δ 190.68 [d, CO, ^3J(PC) 10], 53.25 (s, CH$_2$Cl$_2$) and 30.41 (s, CH$_2$); ^{31}P-{^{1}H} (36.2 MHz), δ 21.68 {d, P(1), ^1J[PtP(1)] 2898, ^2J[P(2)P(1)] 23} and 11.20 {d, P(2), ^1J[PtP(2)] 3743, ^2J[P(1)P(2)] 23 Hz}.

(*xl*) [Pt{SCH$_2$C(O)O}(dppm)] **17b**·CH$_2$Cl$_2$. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppm (0.11 g, 0.29 mmol) and mercaptoacetic acid (0.025 g, 0.27 mmol) gave yellow *microcrystals* of **17b**·CH$_2$Cl$_2$ (0.18 g, 88%) (Found: C, 44.5; H, 3.4. C$_{27}$H$_{24}$O$_2$P$_2$PtS·CH$_2$Cl$_2$ requires C, 44.6; H, 3.4%), m.p. above 220 °C ν(C=O) at 1610s cm^{-1}. NMR spectra: ^{1}H (300 MHz), δ 7.90–7.00 (m, 20 H, Ph), 5.30 (s, 2 H, CH$_2$Cl$_2$), 4.49 [dd, 2 H, CH$_2$, dppm, ^2J(PH) 11,11, ^3J(PtH) 53] and 3.70 [d, 2 H, CH$_2$, ^4J(PH) 3, ^3J(PtH) 20]; ^{13}C-{^{1}H}, δ 192.44 [dd, CO, ^3J(PC) 3,11] 53.29 (s, CH$_2$Cl$_2$), 43.06 [dd, CH$_2$, dppm, ^1J(PC) 31,36] and 28.34 (s, CH$_2$); ^{31}P-{^{1}H} (36.2 MHz), δ −44.87 {d, P(1), ^1J[PtP(1)] 2344, ^2J[P(2)P(1)] 73} and −55.37 {d, P(2), ^1J[PtP(2)] 3086, ^2J[P(1)P(2)] 73 Hz}.

(*xli*) [Pt{SCH$_2$C(O)O}(dppe)] **17c**·CH$_2$Cl$_2$. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppe (0.11 g, 0.28 mmol) and mercaptoacetic acid (0025 g, 0.27 mmol) gave yellow *microcrystals* of **17c**·CH$_2$Cl$_2$ (0.20 g, 96%) (Found: C, 45.0; H, 3.7. C$_{28}$H$_{26}$O$_2$P$_2$PtS·CH$_2$Cl$_2$ requires C, 45.3; H, 3.7%), m.p. 167 °C, ν(C=O) at 1610s cm^{-1}. The complex was too insoluble for NMR studies.

(*xlii*) [Pt{SCH$_2$C(O)O}(dppp)] **17d**·CHCl$_3$. The complex [PtCl$_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and mercaptoacetic acid (0.025 g, 0.27 mmol) gave yellow *microcrystals* which were recrystallised from a saturated chloroform solution to give yellow *crystals* of **17d**·CHCl$_3$ (0.19 g, 86%) (Found: C, 43.6; H, 3.6. C$_{29}$H$_{28}$O$_2$P$_2$PtS·CHCl$_3$ requires C, 44.0; H, 3.6%), m.p. above 220 °C, ν(C=O) at 1640s cm^{-1}. NMR spectra: ^{1}H (300 MHz), δ 7.93–7.11 (m, 21 H, Ph + CHCl$_3$), 3.37 (m, 2 H, CH$_2$), 2.99 (m, 4 H, PCH$_2$, dppp) and 2.44 (m, 2 H, CH$_2$, dppp); ^{13}C-{^{1}H}, δ 190.89 [d, CO, ^3J(PC) 11], 29.97 (s, CH$_2$), 23.43 [dd, PCH$_2$, dppp, ^1J(PC) 40, ^3J(PC) 3], 21.93 [dd, PCH$_2$, dppp, ^1J(PC) 42, ^3J(PC) 2] and 19.08 (s, CH$_2$, dppp); ^{31}P-{^{1}H} (36.2 MHz), δ −1.10 {d, P(1),

^1J[PtP(1)] 2832, ^2J[P(2)P(1)] 34} and −7.76 {d, P(2), ^1J[PtP(2)] 3374, ^2J[P(1)P(2)] 34 Hz}.

(*xliii*) [Pt{$SCH_2C(O)O$}(dppb)] **17e**·CH_2Cl_2. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and mercaptoacetic acid (0.025 g, 0.27 mmol) gave yellow *microcrystals* of **17e**·CH_2Cl_2 (0.19 g, 88%) (Found: C, 46.9; H, 4.1. $C_{30}H_{30}O_2P_2PtS$·CH_2Cl_2 requires C, 46.7; H, 4.0%), m.p. above 220 °C; ν(C=O) at 1620s cm^{-1}. NMR spectra: ^1H (300 MHz), δ 7.78–7.29 (m, 20 H, Ph), 5.27 (s, 2 H, CH_2Cl_2), 3.37 [d, 2 H, CH_2, ^4J(PH) 2, ^3J(PtH) 18], 3.01 (m, 2 H, PCH_2, dppb), 2.35 (m, 4 H, CH_2 + PCH_2, dppb) and 1.66 (m, 2 H, CH_2, dppb); ^{13}C-{^1H}, too insoluble; ^{31}P-{^1H} (36.2 MHz), δ 11.70 {d, P(2), ^1J[PtP(2)] 3565, ^2J[P(1)P(2)] 29} and 9.48 {d, P(1), ^1J[PtP(1)] 2817, ^2J[P(2)P(1)] 29 Hz}.

(*xliv*) [Pt{N(H)C(O)C(O)O}$(PPh_3)_2$] **18a**·H_2O. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with PPh_3 (0.15 g, 0.57 mmol) and oxamic acid (0.025 g, 0.28 mmol) gave white *microcrystals* of **18a**·H_2O (0.21 g, 94%) (Found: C, 55.5; H, 3.8; N, 1.7. $C_{38}H_{31}NO_3P_2Pt$·H_2O requires C, 55.3; H, 4.0; N, 1.7%), m.p. above 220 °C, ν(N–H) at 3360 cm^{-1}, ν_{max} at 2140 cm^{-1}, ν(C=O) at 1700s and 1640s cm^{-1}. NMR spectra: ^1H (90 MHz), δ 7.9–6.6 (m, 30 H, Ph), 4.7 [m, 1 H, NH, ^2J(PtH) 105] and 2.0 (s, br, 2 H, H_2O); ^{13}C-{^1H}, δ 168.01 (s, CO) and 166.17 (s, CO); ^{31}P-{^1H} (36.2 MHz); δ 11.40 {d, P(1), ^1J[PtP(1)] 3184, ^2J[P(2)P(1)] 25} and 9.90 {d, P(2), ^1J[PtP(2)] 3784, ^2J[P(1)P(2)] 25 Hz}.

(*xlv*) [Pt{N(H)C(O)C(O)O}(dppe)] **18b**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppe (0.11 g, 0.28 mmol) and oxamic acid (0.025 g, 0.28 mmol) gave white *microcrystals* of **18b** (0.18 g, 98%) (Found: C, 49.0; H, 3.8; N, 2.2. $C_{28}H_{25}NO_3P_2Pt$ requires C, 49.4; H, 3.7; N, 2.1%), m.p. above 220 °C, ν(N–H) at 3360 cm^{-1}, ν_{max} at 2220 cm^{-1}, ν(C=O) at 1690s and 1640s cm^{-1}. NMR spectra: ^1H (300 MHz), δ 7.88–7.26 (m, 20 H, Ph), 5.63 [m, 1 H, NH, ^2J(PtH) 106] and 2.61–2.33 (m, 4 H, CH_2, dppe); ^{13}C-{^1H}, too insoluble; ^{31}P-{^1H} (300 MHz), δ 32.56 {d, P(2), ^1J[PtP(2)] 3605, ^2J[P(1)P(2)] 11} and 31.70 {d, P(1), ^1J[PtP(1)] 3150, ^2J[P(2)P(1)] 11 Hz}.

(*xlvi*) [Pt{N(H)C(O)C(O)O}(dppp)] **18c**·CH_2Cl_2. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppp (0.12 g, 0.29 mmol) and oxamic acid (0.025 g, 0.28 mmol) gave white *microcrystals* of **18c**·CH_2Cl_2 (0.19 g, 90%) (Found: C, 44.7; H, 3.6; N, 1.8. $C_{29}H_{27}NO_3P_2Pt$·CH_2Cl_2 requires C, 44.7; H, 3.7; N, 1.8%), m.p. above 220 °C, ν(N–H) at 3360 cm^{-1}, ν_{max} at 2240 cm^{-1}, ν(C=O) at 1690s and 1640s cm^{-1}. NMR spectra: ^1H (90 MHz), δ 7.7–6.8 (m, 20 H, Ph), 5.25 (s, 2 H, CH_2Cl_2), 4.9 [m, 1 H, NH, ^2J(PtH) 105] and 2.9–1.7 (m, 6 H, CH_2, dppp); ^{13}C-{^1H}, δ 168.50 (s, CO) and 166.39 (s, CO), 53.31 (s, CH_2Cl_2), 24.20 (m, PCH_2, dppp) and 18.87 (s, CH_2, dppp); ^{31}P-{^1H} (36.2 MHz), δ −7.26 {d, P(2), ^1J[PtP(2)] 3447, ^2J[P(1)P(2)] 35} and −9.38 {d, P(1), ^1J[PtP(1)] 2949, ^2J[P(2)P(1)] 35 Hz}.

(*xlvii*) [Pt{N(H)C(O)C(O)O}(dppb)] **18d**. The complex [$PtCl_2$(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and oxamic acid (0.025 g, 0.28 mmol) gave white *microcrystals* of **18d** (0.17 g, 89%) (Found: C, 50.5; H, 4.1; N, 2.0. $C_{30}H_{29}NO_3P_2Pt$ requires C, 50.8; H, 4.1; N, 2.0%), m.p. above 220 °C ν(N–H) at 3370 cm^{-1}, ν_{max} at 2200 cm^{-1}, ν(C=O) at 1690s and 1650s cm^{-1}. NMR spectra: ^1H (300 MHz), δ 7.78–7.10 (m, 20 H, Ph), 4.42 [m, 1 H, NH, ^2J(PtH) 100], 2.76 (m, 4 H, PCH_2, dppb) and 2.31 (m, 4 H, CH_2, dppb); ^{13}C-{^1H}, too insoluble; ^{31}P-{^1H} (36.2 MHz), δ 12.10 {d, P(2), ^1J[PtP(2)] 3660, ^2J[P(1)P(2)] 29} and −2.30 {d, P(1), ^1J[PtP(1)] 2988, ^2J[P(2)P(1)] 29 Hz}.

Reactions of [*Amino acidate*(2−)-N,O]*bis*(*ligand*)*platinum*(II) *Complexes.*—(*i*) *Ligand substitution reactions.* (*a*) [Pt{N(COMe)$CH_2C(O)O$}(cod)] **8h** *with* PPh_3. A solution of [Pt{N(COMe)$CH_2C(O)O$}(cod)] **8h** (0.10 g, 0.24 mmol) in dichloromethane (*ca.* 30 cm^3) with PPh_3 (0.13 g. 0.50 mmol) was stirred for 15 min at room temperature. The mixture was then evaporated to dryness under reduced pressure to afford a colourless oil which was crystallised from dichloromethane–light petroleum to afford white *microcrystals* of [Pt{N(COMe)$CH_2C(O)O$}$(PPh_3)_2$] **8a** (0.19 g, 95%), identified by ^{31}P-{^1H} NMR spectroscopy.

(*b*) [Pt{N(COMe)$CH_2C(O)O$}(cod)] **8h** *with* $PMePh_2$. A solution of complex **8h** (0.10 g, 0.24 mmol) in dichloromethane (30 cm^3) with $PMePh_2$ (0.1 g, 0.50 mmol) was stirred for 30 min at room temperature. Work-up as in (*a*) afforded white *microcrystals* of [Pt{N(COMe)$CH_2C(O)O$}$(PMePh_2)_2$] **8b** (0.16 g, 94%), identified by ^{31}P-{^1H} NMR spectroscopy.

(*c*) [Pt{N(COMe)$CH_2C(O)O$}(cod)] **8h** *with dppp.* A solution of complex **8h** (0.10 g, 0.24 mmol) in dichloromethane (30 cm^3) with dppp (0.11 g, 0.27 mmol) was stirred for 20 min at room temperature. Work-up as in (*a*) afforded white *microcrystals* of [Pt{N(COMe)$CH_2C(O)O$}(dppp)] **8f** (0.17 g, 98%), identified by ^{31}P-{^1H} NMR spectroscopy.

(*d*) [Pt{N(COMe)$CH(CH_2Ph)C(O)O$}(cod)] **11h** *with* PPh_3. A solution of [Pt{N(COMe)$CH(CH_2Ph)C(O)O$}(cod)] **11h** (0.10 g, 0.20 mmol) in dichloromethane (30 cm^3) with PPh_3 (0.11 g, 0.42 mmol) was stirred for 30 min at room temperature. Work-up as in (*a*) afforded white *microcrystals* of [Pt{N(COMe)$CH(CH_2Ph)C(O)O$}$(PPh_3)_2$] **11a** (0.18 g, 97%), identified by ^{31}P-{^1H} NMR spectroscopy.

(*e*) [Pt{N(COMe)$CH(CH_2Ph)C(O)O$}(cod)] **11h** *with dppp.* A solution of complex **11h** (0.10 g, 0.20 mmol) in dichloromethane (30 cm^3) with dppp (0.09 g, 0.22 mmol) was stirred for 15 min at room temperature. Work-up as in (*a*) afforded white *microcrystals* of [Pt{N(COMe)$CH(CH_2Ph)C(O)O$}(dppp)] **11f** (0.16 g, 98%), identified by ^{31}P-{^1H} and ^1H NMR spectroscopy.

(*f*) [Pt{N(COMe)$CH(CH_2Ph)C(O)O$}$(PPh_3)_2$] **11a**·H_2O *with* Bu^{t}NC. *tert*-Butyl isocyanide (0.02 g, 0.24 mmol) in dichloromethane (10 cm^3) was added dropwise to a stirred solution of [Pt{N(COMe)$CH(CH_2Ph)C(O)O$}$(PPh_3)_2$] **11a**·H_2O (0.20 g, 0.21 mmol) in dichloromethane (30 cm^3), and the mixture was stirred for 4 h at room temperature. Evaporation to dryness under reduced pressure afforded a pale brown oil (0.15 g, 84%) which resisted attempts using numerous solvent mixtures to yield a solid sample of [Pt{N(COMe)$CH(CH_2Ph)C(O)O$}(CNBu^t)(PPh_3)] **23**·H_2O (Found: C, 53.3; H, 4.6; N, 3.1. $C_{34}H_{35}N_2O_3PPt$·H_2O requires C, 53.5; H, 4.8; N, 3.7%). IR ($CHCl_3$): ν(C≡N) at 2220s cm^{-1}, ν(C=O) at 1660s and 1610s cm^{-1}. NMR spectra: ^1H (300 MHz), δ 7.74–7.00 (m, 20 H, Ph), 4.61 (m, 1 H, CH), 3.21 [dd, 1 H, CH_2, ^2J(HH) 13, ^3J(HH) 5], 3.10 [dd, 1 H, CH_2, ^2J(HH) 13, ^3J(HH) 5], 2.20 (s, br, 2 H, H_2O), 1.80 [s, 3 H, C(O)Me] and 1.08 (s, 9 H, Me, Bu^t); ^{31}P-{^1H} (36.2 MHz), δ 8.08 [s, PPh_3, ^1J(PtP) 2913 Hz].

(*ii*) *Reactions with ethanol.* (*a*) *At room temperature.* A solution of either [Pt{N(COMe)$CH_2C(O)O$}$(PPh_3)_2$] **8a** (0.10 g) or [Pt{N(COMe)$CH(CH_2CH_2SMe)C(O)O$}$(PPh_3)_2$] **10a** (0.10 g) in absolute ethanol (30 cm^3) was stirred for 24 h at room temperature. Evaporation to dryness under reduced pressure afforded a colourless oil which contained the respective starting materials, as shown by ^{31}P-{^1H} NMR spectroscopy.

(*b*) *At* 60 °C. A solution of complex **8a** (0.10 g) in absolute ethanol (30 cm^3) was stirred and heated to 60 °C for 1 h. Evaporation to dryness under reduced pressure afforded a brown oil, shown to contain numerous products by ^{31}P-{^1H} NMR spectroscopy.

(*c*) [Pt{N(COMe)$CH_2C(O)O$}$(PPh_3)_2$] **8a** *with diphenylacetylene.* Complex **8a** (0.15 g, 0.18 mmol) with diphenylacetylene (0.12 g, 0.67 mmol) in absolute ethanol (25 cm^3) was stirred and heated to 60 °C for 1.5 h. The mixture was cooled to 0 °C and the pale yellow precipitate was filtered off. By

comparison with data for an authentic sample, $^{31}P-\{^1H\}$ NMR spectroscopy showed the product to be $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$ (0.13 g, 81%).

(*d*) $[Pt\{N(COMe)CH_2C(O)O\}(PPh_3)_2]$ **8a** *with* PPh_3. Complex **8a** (0.15 g, 0.18 mmol) with PPh_3 (0.18 g, 0.69 mmol) in absolute ethanol (25 cm^3) was stirred and heated to 60 °C for 2 h. The mixture was cooled to 0 °C and a bright yellow precipitate (0.19 g, 84%) was filtered off, identified as tetrakis(triphenylphosphine)platinum by IR spectroscopy.

(*iii*) *Reactions of* $[Pt\{N(COMe)CH_2C(O)O\}(PPh_3)_2]$ **8a** *with sulfur dioxide. In ethanol.* A slow stream of SO_2 was passed through an ethanol solution of complex **8a** (0.15 g, 0.18 mmol) for 20 min at room temperature. Evaporation to dryness under reduced pressure afforded a colourless oil which was crystallised from dichloromethane–light petroleum to afford the white solid $[Pt(SO_3Et)_2(PPh_3)_2]$ **26** (0.14 g, 83%). IR spectrum: $\nu(SO_2)$ at 1260s and 1100s cm^{-1}. $^{31}P-\{^1H\}$ NMR spectrum (36.2 MHz): δ 25.51 [s, PPh_3, ^1J(PtP) 2988 Hz].

(*b*) *In dichloromethane.* A slow stream of SO_2 was passed through a dichloromethane solution of complex **8a** (0.15 g, 0.18 mmol) for 20 min at room temperature. Work-up as in (*a*) afforded a white solid (0.14 g). NMR spectra: ^1H (90 MHz), δ 7.8–7.0 (m, Ph); $^{31}P-\{^1H\}$ (36.2 MHz), δ 6.33 [s, PPh_3, ^1J(PtP) 3870 Hz].

Reactions with carbon monoxide. (*a*) *In dichloromethane.* A slow stream of carbon monoxide was passed through a dichloromethane solution of $[Pt\{N(COMe)CH_2C(O)O\}(PPh_3)_2]$ **8a** (0.10 g) for 5 h at room temperature. Evaporation to dryness under reduced pressure yielded a colourless oil which, by $^{31}P-\{^1H\}$ NMR spectroscopy, was shown to contain unreacted starting material.

(*b*) $[Pt\{N(COMe)CH_2C(O)O\}(PPh_3)_2]$ **8a** *in ethanol.* A slow stream of carbon monoxide was passed through an ethanol solution of complex **8a** (0.20 g, 0.24 mmol) for 5 h at room temperature. Removal of the solvent under reduced pressure afforded a pale orange oil which was crystallised from dichloromethane–light petroleum to give a pale brown powdery solid, formulated as *cis*-$[Pt(CO_2Et)_2(PPh_3)_2]$ **27** (R = Et) (0.15 g, 72%). IR spectrum: ν(C=O) at 1805s and 1840s cm^{-1}. NMR spectra: ^1H (300 MHz), δ 7.74–6.71 (m, 30 H, Ph), 2.84 [q, CH_2, Et, ^3J(HH) 7] and 0.26 [t, Me, Et, ^3J(HH) 7]; $^{31}P-\{^1H\}$ (36.2 MHz), δ 20.93 [s, PPh_3, ^1J(PtP) 3254 Hz].

(*c*) $[Pt\{N(COCF_3)CH_2C(O)O\}(PPh_3)_2]$ **12b** *in ethanol.* A slow stream of carbon monoxide was passed through an ethanol solution of complex **12b** (0.15 g, 0.17 mmol) for 5 h at room temperature. Evaporation to dryness under reduced pressure yielded a pale brown oil whose $^{31}P-\{^1H\}$ NMR spectrum was identical to that obtained for **27** (R = Et).

(*d*) *cis*-$[Pt(O_2CMe)_2(PPh_3)_2]$ *in methanol.* A slow stream of carbon monoxide was passed through a stirred methanolic solution of *cis*-$[Pt(O_2CMe)_2(PPh_3)_2]$ (0.20 g, 0.24 mmol) for 5 h at room temperature. The solution was then filtered to separate white *microcrystals* of *trans*-$[Pt(CO_2Me)_2(PPh_3)_2]$ (0.09 g, 45%). The filtrate was evaporated to dryness to yield a pale brown oil which was crystallised from dichloromethane–light petroleum to give the pale brown solid *cis*-$[Pt(CO_2Me)_2(PPh_3)_2]$ **27** (R = Me) (0.09 g, 45%). NMR spectrum: $^{31}P-\{^1H\}$ (36.2 MHz), δ 20.86 [s, PPh_3, ^1J(PtP) 3259].

(*e*) *Attempted insertion reactions.* (*a*) $[Pt\{N(COMe)CH_2C(O)O\}(PPh_3)_2]$ **8a** *with dmad.* Dimethyl acetylenedicarboxylate (0.10 g, 0.70 mmol) was added dropwise to a stirred dichloromethane solution of complex **8a** (0.10 g, 0.12 mmol) and the mixture was stirred for 15 h at room temperature. Evaporation of the solvent under reduced pressure afforded a colourless oil, which was shown, by $^{31}P-\{^1H\}$ NMR spectroscopy, to contain unreacted **8a**. The reaction was repeated with the mixture being refluxed for an additional 6 h, however $^{31}P-\{^1H\}$ NMR spectroscopy again indicated the presence of unreacted **8a**.

Table 4 Fractional atomic coordinates and thermal parameters for $[Pt\{N(COMe)CH_2C(O)O\}(dppe)]$ **8e** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	U_{eq}/Å^2
Pt	0.366 40(4)	0.141 10(2)	0.106 47(6)	0.058 9(2)
P(1)	0.312 02(29)	0.226 20(14)	0.090 0(4)	0.060 8(14)
P(2)	0.223 8(3)	0.126 85(15)	−0.096 1(4)	0.063 9(15)
O(1)	0.506 3(8)	0.154 3(4)	0.287 2(13)	0.083(5)
O(2)	0.641 5(10)	0.116 7(6)	0.458 4(17)	0.136(7)
O(3)	0.291 6(9)	0.021 7(4)	−0.011 6(14)	0.094(5)
N	0.426 3(10)	0.065 1(4)	0.150 9(16)	0.071(5)
C(1)	0.527 6(14)	0.063 7(7)	0.268 4(20)	0.089(8)
C(2)	0.561 0(13)	0.115 4(8)	0.344 6(23)	0.094(8)
C(3)	0.381 9(12)	0.022 6(8)	0.093 5(20)	0.088(8)
C(4)	0.432 0(14)	−0.032 4(7)	0.142 1(24)	0.107(9)
C(5)	0.175 1(10)	0.230 3(6)	−0.038 3(17)	0.070(6)
C(6)	0.172 8(11)	0.192 8(6)	−0.170 8(17)	0.074(6)
C(11)	0.300 9(9)	0.259 3(4)	0.261 7(11)	0.066(6)
C(12)	0.370 6(9)	0.244 7(4)	0.401 6(11)	0.092(8)
C(13)	0.363 5(9)	0.270 8(4)	0.532 9(11)	0.100(9)
C(14)	0.286 6(9)	0.311 3(4)	0.524 4(11)	0.110(11)
C(15)	0.216 9(9)	0.325 9(4)	0.384 6(11)	0.116(11)
C(16)	0.224 1(9)	0.299 8(4)	0.253 3(11)	0.099(9)
C(21)	0.398 0(7)	0.270 5(3)	0.011 4(10)	0.057(5)
C(22)	0.496 6(7)	0.251 4(3)	−0.011 0(10)	0.066(6)
C(23)	0.564 2(7)	0.285 0(3)	−0.068 0(10)	0.078(7)
C(24)	0.533 0(7)	0.337 6(3)	−0.102 6(10)	0.087(8)
C(25)	0.434 4(7)	0.356 6(3)	−0.080 2(10)	0.087(7)
C(26)	0.366 9(7)	0.323 0(3)	−0.023 2(10)	0.082(7)
C(31)	0.101 1(7)	0.098 0(4)	−0.057 5(12)	0.067(6)
C(32)	0.104 4(7)	0.079 7(4)	0.087 3(12)	0.067(6)
C(33)	0.009 0(7)	0.060 0(4)	0.117 9(12)	0.093(8)
C(34)	−0.089 8(7)	0.058 6(4)	0.003 8(12)	0.105(10)
C(35)	−0.093 1(7)	0.076 8(4)	−0.141 1(12)	0.102(9)
C(36)	0.002 4(7)	0.096 5(4)	−0.171 7(12)	0.086(7)
C(41)	0.248 4(9)	0.095 1(4)	−0.261 2(11)	0.072(6)
C(42)	0.193 2(9)	0.049 0(4)	−0.322 8(11)	0.105(9)
C(43)	0.212 1(9)	0.026 9(4)	−0.453 1(11)	0.122(11)
C(44)	0.286 3(9)	0.050 9(4)	−0.521 9(11)	0.136(13)
C(45)	0.341 5(9)	0.097 0(4)	−0.460 2(11)	0.144(14)
C(46)	0.322 5(9)	0.119 2(4)	−0.329 9(11)	0.108(10)

U_{eq} = One third trace of the orthogonalised *U*.

(*b*) $[Pt\{NCH_2CH_2CH_2CHC(O)O\}(PPh_3)_2]$ **13a**·H_2O *with excess of dmad.* Dimethyl acetylenedicarboxylate (0.10 g, 0.70 mmol) was added dropwise to a dichloromethane solution of complex **13a**·H_2O (0.10 g, 0.12 mmol) and the mixture was stirred for 4 h at room temperature. Evaporation of the solvent under reduced pressure afforded a pale brown oil, which was shown by $^{31}P-\{^1H\}$ NMR spectroscopy to contain numerous products.

(*c*) $[Pt\{NCH_2CH_2CH_2CHC(O)O\}(PPh_3)_2]$ **13a**·H_2O *with hexafluorobut-2-yne.* Hexafluorobut-2-yne (*ca.* 1.00 g, 6.17 mmol) was condensed onto a tetrahydrofuran (thf) solution of complex **13a**·H_2O (0.10 g, 0.12 mmol) at −78 °C. The stirred reaction mixture was allowed to warm to room temperature, during which time a pale orange gel formed in the solution. Desiccation of the gel under vacuum yielded a pale brown powder (0.80 g) which was washed with dichloromethane and dried in air [Found: C, 29.3; H, <0.03; F, 66.1; N, <0.03. $(C_4F_6)_n$ requires C, 29.6; F, 70.4%]. IR data (KBr): ν(C–F) between 1150 and 1300(br) cm^{-1}.

(*d*) $[Pt\{N(COMe)CH(Me)C(O)O\}(PPh_3)_2]$ **9a** *with hexafluorobut-2-yne.* Hexafluorobut-2-yne (*ca.* 1.00 g, 6.17 mmol) was condensed onto a thf solution of complex **9a** (0.10 g, 0.12 mmol) at −78 °C. The stirred solution was allowed to warm to room temperature with no evident reaction. Evaporation of the solvent under reduced pressure afforded a colourless oil, which was shown to contain unreacted **9a** by $^{31}P-\{^1H\}$ NMR spectroscopy.

X-Ray Crystal Structure of [Pt{N(COMe)CH_2C(O)O}(dppe)] **8e**.—The crystal was mounted in air. The unit-cell parameters were determined by least-squares refinement of ω-scan measurements for different layers. The intensities of 5663 unique reflections with $7 < 2\theta < 54°$ and $(\pm h, +k, +l)$ were collected at room temperature on a Stöe Stadi-2 Weissenberg diffractometer. The data were corrected for Lorentz and polarisation effects to yield 2916 reflections with $[I > 3\sigma(I)]$. An absorption correction was also applied to the data, the maximum and minimum transmission factors being 0.676 and 0.291 respectively. All subsequent computations were carried out using the computer program SHELX 76.[31]

Crystal data. $C_{30}H_{29}NO_3P_2Pt$, $M = 708.60$, 0.60 × 0.28 × 0.08 mm, monoclinic, space group $P2_1/n$, $a = 12.574(8)$, $b = 25.219(15)$, $c = 9.165(3)$ Å, $\beta = 105.45(3)°$, $U = 2801.2$ Å^3, $Z = 4$, $D_c = 1.68$ g cm^{-3}, $F(000) = 1392.0$, Mo-Kα X-radiation, $\lambda = 0.7107$ Å, μ(Mo-Kα) = 49.3 cm^{-1}.

The structure was solved using Patterson and Fourier techniques. Phenyl rings were included as rigid groups with D_{6h} symmetry, and C–C distances of 1.395 Å. Hydrogen atoms were not located on the Fourier difference map, and all hydrogens were included in calculated positions (C–H 1.08 Å). The isotropic thermal parameters of the phenyl hydrogen atoms were refined as groups. For the remaining hydrogen atoms a single fixed thermal parameter was employed. All other atoms were refined with anisotropic thermal parameters. Final cycles of refinement employed a weighting parameter $w = 1/(\sigma^2F + gF^2)$ ($g = 0.0007$) and gave the final residual indices $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ 0.058 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ 0.056. The final Fourier difference map was featureless except for +2.5e peaks at < 1 Å from the platinum atom. An analysis of the weighting scheme over $|F_o|$ and (sin θ)/λ was satisfactory. The atomic coordinates for the structure are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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