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 [$Pt{N(COMe)CHRC(0)O}L_2$] (R = H, Me, CH₂CH₂SMe or CH_2Ph) respectively, and with L-proline the complexes [$Pt{NCH_2CH_2CH_2CHC(0)O}L_2$] are produced. Similar treatment with the N-formyl or N-trifluoroacetyl derivatives of glycine gave the complexes $[\dot{P}t\{N(R)CH_2C(O)\dot{O}\}L_2]$ (R = CHO or COCF₃) respectively. An X-ray crystal structure study on the N-acetylglycinato(2-)-N,O complex [$Pt{N(COMe)CH_2C(O)O}(dppe)$] (dppe = $Ph_2PCH_2CH_2PPh_3$) 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 DLmandelic (x-hydroxybenzeneacetic) acid, 2-acetamidophenol, pyrrole-2-carboxylic acid, mercaptoacetic acid or oxamic acid in the presence of an excess of Ag₂O in refluxing dichloromethane afforded the complexes $[\dot{P}t{OC(H)PhC(O)\dot{O}}L_2]$, $[\dot{P}t{o-N(COMe)C_6H_4\dot{O}}L_2]$, $[\dot{P}t{NCH=C(H)CH=C(O)\dot{O}}L_2]$, $[\dot{P}t{SCH_2C(0)\dot{O}}L_2]$, $[\dot{P}t{N(H)C(0)C(0)\dot{O}}L_2]$ respectively. The cycloocta-1,5-diene (cod) ligand of [Pt{N(COMe)CH₂C(O)O}(cod)] and [Pt{N(COMe)CH(CH₂Ph)C(O)O}(cod)] is readily displaced by tertiary phosphines. One mole equivalent of Bu'NC stereospecifically displaces the PPh3 ligand opposite oxygen in the complex $[Pt{N(COMe)CH(CH_2Ph)C(O)O}(PPh_3)_2]$. Treatment of $[Pt{N(COMe)CH_2C(0)O}(PPh_3)_2]$ in refluxing ethanol with an excess of either diphenylacetylene or PPh_3 leads to the formation of $[Pt(PhC=CPh)(PPh_3)_2]$ or $[Pt(PPh_3)_4]$ respectively, in good yield. Treatment of the same metal complex in ethanol at room temperature with either SO₂ or CO led to the formation of the bis(ethanesulfonate) or bis(ethoxycarbonyl) complexes respectively. The

complex $[\dot{P}t{NCH_2CH_2CH_2CHC(0)O}(PPh_3)_2]$ 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 tin¹⁰ or germanium¹¹ 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.

Results and Discussion

Treatment of the complexes cis-[PtCl₂L₂] [L = PPh₃,

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









Scheme 1 (i) Refluxing CH_2Cl_2 , excess of Ag_2O



17d $L_2 = dppp$ 17e $L_2 = dppb$

/0 H₂ 19

Table 1 Select	ed bond dista	unces (Å) and ang	les (°) for
[Pt{N(COMe)CH	$L_C(O)O^{1}(dnne)$	Se with estimate	d standard
deviations (e.s.d.s) in parentheses	j oo, mini commute	u standard
	•		
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)PtN	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 $P(CH_2Ph)Ph_2$; $L_2 = Ph_2PCH_2PPh_2(dppm)$, $Ph_2P(CH_2)_2PPh_2(dppe), Ph_2P(CH_2)_3PPh_2(dppp), Ph_2P-$ (CH₂)₄PPh₂(dppb) or cycloocta-1,5-diene (cod)] {prepared in situ by the reaction of [PtCl₂(cod)] with either 2 mole equivalents of L or 1 equivalent of L_2 with 1 equivalent of Nacetylglycine 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 Nacetyl-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 Ntrifluoroacetylglycine as the source of the chelating fragment. Complexes 13, which contain a bicyclic skeleton, may be prepared using L-proline with silver(1) oxide in refluxing dichloromethane in the presence of cis-[PtCl₂L₂] (L = PPh₃;



 $L_2 = dppp$ 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(11) dichloride complexes and silver(11) oxide with other substrates containing 'acidic' hydrogen atoms in a 1,4 relationship in order to prepare new ring systems. Thus treatment of cis-[PtCl₂(PPh₃)₂] with 1 mole equivalent of DL-mandelic acid (α -hydroxybenzeneacetic acid) and an excess of silver(11) 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-[PtCl₂L₂] (L = PPh₃; L₂ = dppm, dppe, dppp or dppb) with 1 equivalent of mercaptoacetic acid and an excess of silver(1) 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 $78.8(5)^{\circ}$ 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 amidecontaining 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

¹H NMR Spectra.—The room-temperature ¹H 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 fivemembered 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-DLalaninato 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 fivemembered 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.

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

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



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 ${}^{1}J(PtP)$, 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 coordinated 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'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 [${}^{1}J(PtP)$ 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 ¹H NMR spectrum shows the presence of one Bu' group per phosphine ligand. Therefore, the substitution of a triphenylphosphine ligand in complex 11a by Bu'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 ³¹P-{¹H} 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 triphenyl-phosphine 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(SO₃Et)₂(PPh₃)₂] **26** in good yield. Comparison of ³¹P-{¹H} 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 ³¹P-{¹H} 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 ${}^{31}P{}_{1}$ 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 ³¹P-{¹H} NMR shift of δ 20.93 is significantly different to that of the bis(methoxycarbonyl) complex 27 (R =Me) made by Werner and Beck²⁵ (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 Kemmitt²³ 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

		Analysis (%)		$v(C=O)^{c}/cm^{-1}$		
Complex	M.p. (°C)	C	н	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 ₂ Cl 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
8ĥ	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,O	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,O	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 ₂ O	138	60.3 (59.9)	4.6 (4.6)	2.3 (1.5)	1660	1590
11b·H ₂ O	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 ₂ O	>220	53.7 (53.9)	4.4 (4.4)	1.5 (1.7)	1640	1570
11e-CH ₂ Cl ₂	> 220	51.2 (51.6)	4.0 (4.2)	1.7 (1.6)	1640	1580
IIf•H ₂ O	134	54.5 (54.9)	4.7 (4.7)	1.7 (1.7)	1650	1580
11g·H ₂ O	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
$12a \cdot CH_2Cl_2$	> 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 ₂ O	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	
$13c \cdot CH_2Cl_2$	158	49.9 (49.8)	4.7 (4.5)	1.7 (1.7)	1660	—

" Calculated values given in parentheses. " Recorded as KBr discs. " All bands strong.

shown to contain a single product, assigned as 27 (R = Me), whose ³¹P-{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 ³¹P-{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 metalnitrogen 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 nonnucleophilic 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 ³¹P-{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-acetylcontaining amino acidate(2-) compounds under analogous conditions.

Experimental

Table 2 shows m.p.s, analytical and selected IR data, and Table 3 shows ³¹P-{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 SiMe₄ (δ 0.0) as internal reference, positive values being to high frequency (low field), in CDCl₃ unless otherwise stated. The ¹³C-{¹H} NMR spectra were recorded on a Bruker AM300 spectrometer at 75.47 MHz with SiMe₄ (δ 0.0) as internal reference, in CDCl₃. The phenyl carbon region has been omitted for clarity. The ³¹P-{¹H} NMR spectra were recorded in dichloromethane on a JEOL-FX90 spectrometer at 36.21 MHz, with [P(OH)₄]⁺ in D₂O (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^tNC, diphenylacetylene,

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

Complex	δ P(1) ^b	¹ J[PtP(1)]/Hz	δ P(2) ^b	¹ <i>J</i> [PtP(2)]/H::	² <i>J</i> [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 ₂ Cl 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
9Ь	-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 ₂ O	- 53.85	2612	-67.38	3525	68
10e	38.42	3057	27.73	3906	15
10f·H ₂ O	-8.16	2849	-10.70	3694	35
10g	- 2.01	2905	9.69	3916	30
11a·H ₂ O	10.58	3047	5.75	4058	24
11b-H ₂ O	- 4.48	3052	-8.18	3938	27
11c	-16.24	3003	-23.30	3770	25
11d·H ₂ O	- 53.85	2639	-68.15	3574	78
11e-CH ₂ Cl ₂	38.40	3069	26.58	3931	15
11f·H ₂ O	- 8.17	2869	-12.15	3718	37
11g·H ₂ O	-3.83	2920	9.48	3960	30
11h					
$12a \cdot CH_2Cl_2$	12.86	3137	6.43	3730	24
12b	8.21	3184	4.92	3926	24
13a•H ₂ O	8.48	3316	6.06	3696	29
13b	10.34	3025	-12.55	3362	37
$13c \cdot CH_2Cl_2$	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*-formylglycine²⁹ and *N*-trifluoroacetyl-glycine³⁰ were prepared as described.

Preparation of New Platinacyclic Complexes using Silver(1) 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(1) oxide were added in succession to a stirred solution of $[PtCl_2(cod)]$ in dichloromethane (ca. 45 cm³), 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 cm³) 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*) [$Pt_{N(COMe)CH_{2}C(O)O_{}(PPh_{3})_{2}$] **8a**. The complex [PtCl₂(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: ¹H, δ 7.73–7.12 (m, 30 H, Ph), 4.25 [dd, 2 H, CH₂, ⁴J(PH) 1.3, ³J(PtH) 25], and 1.39 (s, 3 H, CH₃); ¹³C-{¹H}, δ 183.88 [d, CO, ³J(PC) 2], 170.84 (s, CO), 55.54 (s, CH₂) and 20.00 [d, Me, ⁴J(PC) 3 Hz].

(*ii*) [Pt{N(COMe)CH₂C(O)O}(PMePh₂)₂] **8b**. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with methyldiphenylphos-

phine (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: ¹H, δ 7.58–7.17 (m, 20 H, Ph), 4.30 [d, 2 H, CH₂, ⁴*J*(PH) 3, ³*J*(PtH) 23], 2.04 [d, 3 H, Me, PMePh₂, |²*J*(PH) + ⁴*J*(PH)| 11, ³*J*(PtH) 35], 1.76 [d, 3 H, Me, PMePh₂, |²*J*(PH) + ⁴*J*(PH)| 10, ³*J*(PtH) 24], and 1.60 (s, 3 H, Me); ¹³C-{¹H}, δ 184.10 [d, CO, ³*J*(PC) 3], 171.35 (s, CO), 55.41 (s, CH₂), 20.14 [d, Me, ⁴*J*(PC)] 4], 13.69 [d, Me, PMePh₂, |¹*J*(PC) + ³*J*(PC)| 45] and 13.40 [d, Me, PMePh₂, |¹*J*(PC) + ³*J*(PC)| 39 Hz].

(*iii*) [$\dot{P}t{N(COMe)CH_2C(O)O}{P(CH_2Ph)Ph_2}_2$] **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: ¹H, δ 7.72–6.11 (m, 30 H, Ph), 4.53 [d, 2 H, CH₂, ⁴*J*(PH) 3, ³*J*(PtH) 25], 3.85–3.62 [m, 4 H, CH₂, P(CH₂Ph)Ph₂] and 1.93 (s, 3 H, Me); ¹³C-{¹H}, δ 183.67 [d, CO, ³*J*(PC) 2], 171.78 (s, CO), 56.26 (s, CH₂), 38.09 [d, CH₂, P(CH₂Ph)Ph₂, |¹*J*(PC) + ³*J*(PC)| 36], 34.57 [d, CH₂, P(CH₂Ph)Ph₂, |¹*J*(PC) + ³*J*(PC)| 31 Hz] and 21.18 (s, Me).

(*iv*) [Pt{N(COMe)CH₂C(O)O}(dppm)] **8d**·CH₂Cl₂. The complex [PtCl₂(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**·CH₂Cl₂ (0.19 g, 90%). NMR spectra: ¹H, δ 7.80–7.28 (m, 20 H, Ph), 5.27 (s, 2 H, CH₂Cl₂), 4.33 [dd, 2 H, CH₂, dppm, ²J(PH) 9.11], 4.13 [d, 2 H, CH₂, ⁴J(PH) 2, ³J(PtH) 21] and 1.86 (s, 3 H, Me); ¹³C-{¹H}, δ 188.22 [d, CO, ³J(PC) 2], 172.07 (s, CO), 53.39 (s, CH₂), 53.27 (s, CH₂Cl₂), 49.11 [dd, CH₂, dppm, ¹J(PC) 31,32] and 19.56 [d, Me, ⁴J(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*-

cr₁stals of **8e** (0.18 g, 94%). NMR spectra: ¹H, δ 7.91–7.27 (m, 20 H, Ph), 4.22 [d, 2 H, CH₂, ⁴J(PH) 2, ³J(PtH) 18], 2.28–1.92 (m, 4 H, CH₂, dppe) and 1.70 (s, 3 H, Me); ¹³C-{¹H}, δ 187.24 (s, CO), 170.13 (s, CO), 54.10 (s, CH₂), 35.15 [dd, CH₂, dppe, ¹J(PC) 40, ³J(PC) 13], 24.40 [dd, CH₂, 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 [PtCl₂(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: ¹H, δ 7.83–7.28 (m, 20 H, Ph), 4.15 [d, 2 H, CH₂, ⁴J(PH) 3, ³J(PtH) 23], 2.32 (m, 4 H, PCH₂, dppp), 1.88 (m, 2 H, CH₂, dppp) and 1.39 (s, 3 H, Me); ¹³C-{¹H}, δ 184.86 [d, CO, ³J(PC) 3], 170.11 (s, CO), 55.12 (s, CH₂), 27.78 [dd, PCH₂, dppp, ¹J(PC) 41, ³J(PC) 9], 21.17 [dd, PCH₂, dppp, ¹J(PC) 38, ³J(PC) 7], 19.57 [d, Me, ⁴J(PC) 5 Hz] and 18.49 (s, CH₂, dppp).

(*vii*) [$^{h}t{N(COMe)CH_2C(O)O}{dppb}$] **8g**. The complex [PtCl₂(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, CH₂, $^{4}J(PH)$ 3, $^{3}J(PtH)$ 24], 2.87–1.43 (m, 8 H, CH₂, dppb) and 1.37 (s, 3 H, Me); $^{13}C-{^{1}H}$, δ 184.56 [d, CO, $^{3}J(PC)$ 3], 170.43 (s, CO), 54.76 (s, CH₂), 25.67 (m, PCH₂, dppb), 23.72 [d, PCH₂, dppb, $^{1}J(PC)$ 38], 21.57 (s, 2 × CH₂, dppb) and 19.54 [d, Me, $^{4}J(PC)$ 5 Hz].

(*viii*) [$\dot{P}t\{N(COMe)CH_2C(O)\dot{O}\}(cod)$] **8h**. The complex [PtCl₂(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: ¹H, 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, CH₂, ³J(PtH) 21], 2.74–2.21 (m, 8 H, CH₂, cod) and 2.00 (s, 3 H, Me); ¹³C-{¹H}, 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, CH₂), 32.20 (s, CH₂, cod), 27.81 (s, <u>CH₂, cod)</u> and 23.02 (s, Me).

(*ix*) [Pt{N(COMe)CH(Me)C(O)O}(PPh₃)₂] **9a**. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PPh₃ (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: ¹H, δ 7.87–7.12 (m, 30 H, Ph), 4.41 (m, 1 H, CH), 1.71 [d, 3 H, CHCH₃, ³J(HH) 7] and 1.44 [s, 3 H, C(O)Me]; ¹³C-{¹H}, δ 189.57 (s, CO), 170.50 (s, CO), 61.23 (s, CH), 21.81 (s, CHCH₃) and 19.66 [d, C(O)CH₃, ⁴J(PC) 3 Hz].

(x) [Pt{N(COMe)CH(Me)C(O)O}(PMePh₂)₂] **9b.** The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PMePh₂ (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: ¹H, δ 7.76–7.11 (m, 20 H, Ph), 4.50 (m, 1 H, CH), 1.98 [d, 3 H, Me, PMePh₂,]²J(PH) + ⁴J(PH)[11, ³J(PtH) 33], 1.77 [d, 3 H, Me, PMePh₂,]²J(PH) + ⁴J(PH)[11, ³J(PtH) 37], 1.71 [d, 3 H, CHCH₃, ³J(HH) 7] and 1.64 [s, 3 H, C(O)Me]; ¹³C-{¹H}, δ 187.25 [d, CO, ³J(PC) 3], 170.73 (s, CO), 61.36 (s, CH), 22.49 (s, CHCH₃), 19.47 [d, C(O)CH₃, ⁴J(PC) 4] and 13.59 [d, 2 × PMe, PMePh₂,]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 $P(CH_2Ph)$ -Ph₂ (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: ¹H, δ 7.72–6.30 (m, 30 H, Ph), 4.71 (m, 1 H, CH), 4.06 [m, 2 H, CH₂, $P(CH_2Ph)Ph_2$], 3.59 [m, 2 H, CH₂, $P(CH_2Ph)Ph_2$], 1.94 [s, 3 H, C(O)Me] and 1.82 [d, 3 H, CHCH₃, ³J(HH) 7]; ¹³C-{¹H}, δ 186.76 (s, CO), 171.09 (s, CO), 61.99 (s, CH), 37.78 [d, CH₂, $P(CH_2Ph)Ph_2$, $|^{1}J(PC) + {}^{3}J(PC)|$ 35], 34.50 [d, CH₂, $P(CH_2Ph)Ph_2$, $|^{1}J(PC) + {}^{3}J(PC)|$ 31], 22.52 (s, CHCH₃) and 20.45 [d, C(O)CH₃, 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: ¹H δ 7.83–7.17 (m, 20 H, Ph), 4.62 [ddd, 1 H, CH₂, dppm, ²*J*(PH) 9,11, ²*J*(HH) 16], 4.24 (m, 1 H, CH), 4.01 [ddd, 1 H, CH₂, dppm, ²*J*(PH) 10,12, ²*J*(HH) 16], i.88 [s, 3 H, C(O)Me] and 1.58 [d, 3 H, CHCH₃, ³*J*(HH) 7]; ¹³C-{¹H}, δ 190.76 (s, CO), 171.33 (s, CO), 58.65 (s, CH), 48.76 [dd, CH₂, dppm, ¹*J*(PC) 31,32], 23.55 (s, CHCH₃) and 18.53 [d, C(O)CH₃, ⁴*J*(PC) 2 Hz].

(*xiii*) [$\dot{P}t{N(COMe)CH(Me)C(O)O}{dpe}$] **9e**. The complex [PtCl₂(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: ¹H, 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, CH₂, dppe), 1.64 [s, 3 H, C(O)Me] and 1.47 [d, 3 H, CHCH₃, ³J(HH) 7]; ¹³C-{¹H}, δ 189.30 [d, CO, ³J(PC) 2], 169.15 (s, CO), 59.76 (s, CH), 35.00 [dd, CH₂, dppe, ¹J(PC) 40, ³J(PC) 13], 24.02 [dd, CH₂, dppe, ¹J(PC) 42, ³J(PC) 6], 23.25 (s, CHCH₃) and 18.34 [d, C(O)CH₃, ⁴J(PC) 4 Hz].

(*xiv*) [^{h}t {N(COMe)CH(Me)C(O)O}(dppp)] **9f**. The complex [PtCl₂(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: ¹H, δ 7.91–6.94 (m, 20 H, Ph), 4.33 (m, 1 H, CH), 2.68–2.05 (m, 6 H, CH₂, dppp), 1.55 [d, 3 H, CHCH₃, ³J(HH) 7] and 1.38 [s, 3 H, C(O)Me]; ¹³C-{¹H}, δ 187.93 [d, CO, ³J(PC) 3], 169.44 (s, CO), 61.06 (s, CH), 28.10 [dd, PCH₂, dppp, ¹J(PC) 38, ³J(PC)10], 23.17 [dd, PCH₂, dppp, ¹J(PC) 36, ³J(PC) 7], 22.34 (s, CHCH₃), 18.94 (s, CH₂, dppp) and 18.77 [d, C(O)CH₃, ⁴J(PC) 4 Hz].

(xv) [Pt{N(COMe)CH(Me)C(O)O}(dppb)] **9g**. The complex [PtCl₂(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: ¹H, δ 7.82–7.11 (m, 20 H, Ph), 4.36 (m, 1 H, CH), 2.70–2.15 (m, 8 H, CH₂, dppb), 1.62 [d, 3 H, CHCH₃, ³J(HH) 7] and 1.38 [s, 3 H, C(O)Me]; ¹³C-{¹H}, δ 187.78 [d, CO, ³J(PC) 3], 169.86 (s, CO), 60.61 (s, CH), 25.62 (m, PCH₂, dppb), 23.72 (m, PCH₂, dppb), 21.87 (s, 2 × CH₂, dppb), 21.66 (s, CHCH₃), and 18.95 [d, C(O)CH₃, ⁴J(PC) 4 Hz].

(*xvi*) [$Pt{N(COMe)CH(CH_2CH_2SMe)C(O)O}{(PPh_3)_2}$] **10a**. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PPh₃ (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: ¹H, δ 7.84–7.12 (m, 30 H, Ph), 4.34 (m, 1 H, CH), 2.42 (m, 2 H, SCH₂), 2.22 (m, 2 H, CHCH₂), 2.13 (s, 3 H, SMe), 1.56 [s, 3 H, C(O)Me]; ¹³C-{¹H}, δ 184.91 (m, CO), 171.87 (s, CO), 65.12 (s, CH), 36.29 (s, SCH₂), 31.03 (s, CHCH₂), 20.55 [d, C(O)CH₃, ⁴J(PC) 3 Hz] and 15.36 (s, SMe).

(xvii) [Pt{N(COMe)CH(CH₂CH₂SMe)C(O)O}(PMe-Ph₂)₂] **10b.** The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PMePh₂ (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: ¹H, δ 7.68–7.15 (m, 20 H, Ph), 4.45 (m, 1 H, CH), 2.70 (m, 1 H, SCH₂), 2.57 (m, 1 H, SCH₂), 2.42 (m, 1 H, CHCH₂), 2.27 (m, 1 H, CHCH₂), 2.17 (s, 3 H, sMe), 1.99 [d, 3 H, Me, PMePh₂, |²J(PH) + ⁴J(PH)| 11], 1.74 [s, 3 H, C(O)Me] and 1.72 [d, 3 H, Me, PMePh₂, |²J(PH) + ⁴J(PH) + ⁴J(PH) + ⁴J(PH)| 11]; ¹³C-{¹H}, δ 185.62 (m, CO), 171.65 (s, CO), 65.12 (s, CH), 36.77 (s, SCH₂), 30.87 (s, CHCH₂), 20.36 [d, C(O)CH₃, ⁴J(PC) 2 Hz], 15.40 (s, SMe) and 13.28 (m, 2 × Me, PMePh₂).

(xviii) [Pt{N(COMe)CH(CH₂CH₂SMe)C(O)O}{P(CH₂-Ph)Ph₂}_2] **10c**. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with P(CH₂Ph)Ph₂ (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: ¹H, δ 7.41–6.25 (m, 30 H, Ph), 4.68 (m, 1 H, CH), 4.05 [m, 2 H, PCH₂, P(CH₂Ph)Ph₂], 3.55 [m, 2 H, PCH₂, P(CH₂Ph)Ph₂], 2.83 (m, 2 H, SCH₂), 2.66–2.42 (m, 2 H, CHCH₂), 2.20 (s, 3 H, SMe) and 2.05 [s, 3 H, C(O)Me]; ¹³C-{¹H}, δ 185.22 (m, CO), 172.41 (s, CO), 65.99 (s, CH), 37.67 [d, CH₂, P(CH₂Ph)Ph₂], [¹J(PC) + ³J(PC)] 35], 36.86 (s, SCH₂), 34.30 [d, CH₂, P(CH₂Ph)Ph₂, [¹J(PC) + ³J(PC)] 31], 31.02

(s, CHCH₂), 21.45 [d, C(O)CH₃, ⁴J(PC) 2 Hz] and 15.64 (s, SMe).

(*xix*) [Pt{N(COMe)CH(CH₂CH₂SMe)C(O)O}(dppm)] **10d**·H₂O. The complex [PtCl₂(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**·H₂O (0.20 g, 94%). NMR spectra: ¹H, δ 7.84–7.30 (m, 20 H, Ph), 4.64 [ddd, 1 H, CH₂, dppm, ²J(PH) 9,11, ²J(HH) 16], 4.30 (m, 1 H, CH), 4.03 [ddd, 1 H, CH₂, dppm, ²J(PH) 10,12, ²J(HH) 16], 2.95 [ddd, 1 H, SCH₂, ²J(HH) 12, ³J(HH) 5,11], 2.69 [ddd, 1 H, SCH₂, ²J(HH) 12, ³J(HH) 6,11], 2.34 (s, br, 2 H, H₂O), 2.31–2.19 (m, 1 H, CHCH₂), 2.15–2.02 (m, 1 H, CHCH₂), 2.08 (s, 3 H, SMe), and 1.89 [s, 3 H, C(O)Me]; ¹³C-{¹H}, δ 188.58 (s, CO), 171.19 (s, CO), 62.22 (s, CH), 48.64 [dd, CH₂, dppm, ¹J(PC) 31,32], 36.01 (s, SCH₂), 29.22 (s, CHCH₂), 18.74 [d, C(O)CH₃, ⁴J(PC) 3 Hz] and 15.41 (s, SMe).

(xx) [Pt{N(COMe)CH(CH₂CH₂SMe)C(O)O}(dppe)] 10e. The complex [PtCl₂(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: ¹H, δ 8.05–7.30 (m, 20 H, Ph), 4.39 (m, 1 H, CH), 2.66–1.91 (m, 6 H, CH₂, dppe + SCH₂ + CHCH₂), 2.03 (s, 3 H, SMe), 1.68 [s, 3 H, C(O)Me] and 1.49 (m, 2 H, CH₂, dppe); ¹³C-{¹H}, δ 187.24 [d, CO, ³J(PC) 3], 169.33 (s, CO), 63.31 (s, CH), 36.36 (s, SCH₂), 34.66 [dd, PCH₂, dppe, ¹J(PC) 41, ³J(PC) 12], 29.56 (s, CHCH₂), 18.92 [d, C(O)CH₃, ⁴J(PC) 3], 17.78 [dd, PCH₂, dppe, ¹J(PC) 41, ³J(PC) 7 Hz] and 15.24 (s, SMe).

(*xxi*) [Pt{N(COMe)CH(CH₂CH₂SMe)C(O)O}{(dppp)] **10f**·H₂O. The complex [PtCl₂(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**·H₂O (0.20 g, 91%). NMR spectra: ¹H, δ 7.84–7.22 (m, 20 H, Ph), 4.27 (m, 1 H, CH), 2.65–1.92 (m, 12 H, 3 × CH₂, dppp + SCH₂ + CHCH₂ + H₂O), 2.13 (s, 3 H, SMe) and 1.48 [s, 3 H, C(O)Me]; ¹³C-{¹H}, δ 186.09 [d, CO, ³J(PC) 3], 169.93 (s, CO), 64.90 (s, CH), 36.96 (s, SCH₂), 30.58 (s, CHCH₂), 28.07 [dd, PCH₂, dppp, ¹J(PC) 40, ³J(PC) 9], 23.37 [dd, PCH₂, dppp, ¹J(PC) 38, ³J(PC) 5], 19.61 [d, C(O)CH₃, ⁴J(PC) 4 Hz], 18.75 (s, CH₂, dppp) and 15.17 (s, SMe).

(*x.xii*) [Pt{N(COMe)CH(CH₂CH₂SMe)C(O)O}(dppb)] **10g**. The complex [PtCl₂(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: ¹H, δ 7.75-7.17 (m, 20 H, Ph), 4.27 (m, 1 H, CH), 2.68-1.89 (m, 10 H, 3 × CH₂, dppb + SCH₂ + CHCH₂), 2.13 (s, 3 H, SMe), 1.58-1.26 (m, 2 H, CH₂, dppb) and 1.47 [s, 3 H, C(O)-Me]; ¹³C-{¹H}, δ 186.18 (m, CO), 170.73 (s, CO), 64.57 (s, CH), 36.57 (s, SCH₂), 30.91 (s, CHCH₂), 25.40 (m, PCH₂, dppb), 23.78 [dd, PCH₂, dppb, ¹J(PC) 41, ³J(PC) 3], 21.53 (s, 2 × CH₂, dppb), 19.86 [d, C(O)CH₃, ⁴J(PC) 3] and 15.17 (s, SMe).

(*xxiii*) [$^{h}t[N(COMe)CH(CH_2Ph)C(O)O](PPh_3)_2$] **11a**· H₂O. The complex [$^{P}tCl_2(cod)$] (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**·H₂O (0.23 g, 90%). NMR spectra: ¹H, δ 7.83–7.02 (m, 35 H, Ph), 4.62 (m, 1 H, CH), 3.50 [dd, 1 H, CH₂, ²J(HH) 14, ³J(HH) 5], 3.39 [dd, 1 H, CH₂, ²J(HH) 14, ³J(HH) 5], 3.39 [dd, 1 H, CH₂, ²J(HH) 14, ³J(HH) 5], 172.22 (s, CO), 67.44 (s, CH), 42.69 (s, CH₂) and 20.52 [d, Me, ⁴J(PC) 5 Hz].

(*xxiv*) [$\dot{P}t\{N(COMe)CH(CH_2Ph)C(O)\dot{O}\}(PMePh_2)_2$] **11b**·H₂O. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PMePh₂ (0.11 g, 0.55 mmol) and *N*-acetyl-L-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of **11b**·H₂O (0.20 g, 91%). NMR spectra: ¹H, δ 7.93–6.93 (m, 25 H, Ph), 4.85 (m, 1 H, CH), 3.53 [dd, 1 H, CH₂, ²J(HH) 14, ³J(HH) 5], 3.20 [dd, 1 H, CH₂, ²J(HH) 14, ³J(HH) 5], 2.24 (s, br, 2 H, H₂O), 1.94 [d, 3 H, Me, PMePh₂, |²J(PH) + ⁴J(PH)| 12, ³J(PtH) not discernible], 1.88 [s, 3 H, C(O)Me] and 1.30 [d, 3 H, Me, PMePh₂, |²J(PH) + ⁴J(PH)| 10, ³J(PtH) not discernible]; ¹³C-{¹H}, δ 186.15 [d, CO, ${}^{3}J(PC)$ 5], 172.81 (s, CO), 66.74 (s, CH), 41.50 (s, CH₂), 20.40 [d, C(O)CH₃, ${}^{4}J(PC)$ 4], 17.97 [d, Me, PMePh₂, | ${}^{1}J(PC)$ + ${}^{3}J(PC)$ | 48] and 12.83 [d, Me, PMePh₂, | ${}^{1}J(PC)$ + ${}^{3}J(PC)$ | 40 Hz].

(xxv) [Pt{N(COMe)CH(CH₂Ph)C(O)O}(PMe₂Ph)₂)] 11c. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PMe₂Ph (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: ¹H, δ 7.47–6.89 (m, 15 H, Ph), 4.90 (m, 1 H, CH), 3.50 [dd, 1 H, CH₂, ²J(HH) 13, ³J(HH) 6], 3.17 [dd, 1 H, CH₂, ²J(HH) 13, ³J(HH) 6], 3.17 [dd, 1 H, CH₂, ²J(HH) 13, ³J(HH) 5], 1.95 [s, 3 H, C(O)Me], 1.90 [d, 3 H, Me, PMe₂Ph, |²J(PH) + ⁴J(PH)| 12, ³J(PtH) 35], 1.49 [d, 3 H, Me, PMe₂Ph, |²J(PH) + ⁴J(PH)| 11, ³J(PtH) 22] and 1.38 [d, 3 H, Me, PMe₂Ph, |²J(PH) + ⁴J(PH)| 11, ³J(PtH) 21]; ¹³C-{¹H}, δ 186.11 [d, CO, ³J(PC) 3], 173.23 (s, CO), 67.24 (s, CH), 41.48 (s, CH₂), 20.58 [d, C(O)CH₃, ⁴J(PC) 4], 18.68 [d, Me, PMe₂Ph, |¹J(PC) + ³J(PC)| 47], 12.12 [d, Me, PMe₂Ph, |¹J(PC) + ³J(PC)| 42] and 11.40 [d, Me, PMe₂Ph, |¹J(PC) + ³J(PC)| 43 Hz].

(xxvi) [Pt{N(COMe)CH(CH₂Ph)C(O)O}(dppm)] 11d-H₂O. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with dppm (0.11 g, 0.29 mmol) and N-acetyl-t-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of 11d-H₂O (0.20 g, 92%). NMR spectra: ¹H, δ 7.90–7.16 (m, 25 H, Ph), 4.52 (m, 1 H, CH), 4.46 [ddd, 1 H, CH₂, dppm, ²J(PH) 9,11, ²J(HH) 16], 3.86 [ddd, 1 H, CH₂, dppm, ²J(PH) 9,12, ²J(HH) 16], 3.31 [dd, 1 H, CHCH₂, ²J(HH) 13, ³J(HH) 5], 3.09 [dd, 1 H, CHCH₂, ²J(HH) 13, ³J(HH) 5], 2.10 (s, br 2 H, H₂O) and 1.77 (s, 3 H, CH₃); ¹³C-{¹H}, δ 189.10 (s, CO), 171.47 (s, CO), 64.60 (s, CH), 49.01 [dd, CH₂, dppm, ¹J(PC) 31,32], 42.04 (s, CHCH₂) and 18.86 [d, Me, ⁴J(PC) 1 Hz].

(xxvii) [Pt{N(COMe)CH(CH₂Ph)C(O)O}(dppe)] 11e-CH₂Cl₂. The complex [PtCl₂(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-CH₂Cl₂ (0.21 g, 88%). NMR spectra: ¹H, δ 7.98–6.81 (m, 25 H, Ph), 5.24 (s, 2 H, CH₂Cl₂), 4.51 (m, 1 H, CH), 3.15 [dd, 1 H, CHCH₂, ²J(HH) 13, ³J(HH) 4], 3.03 [dd, 1 H, CHCH₂, ²J(HH) 13, ³J(HH) 7], 2.83– 2.23 (m, 2 H, PCH₂, dppe), 1.94 (m, 1 H, PCH₂, dppe), 1.42 (m, 1 H, PCH₂, dppe) and 1.29 (s, 3 H, Me); ¹³C-{¹H}, δ 187.88 [d, CO, ³J(PC) 2], 170.08 (s, CO), 66.02 (s, CH), 53.15 (s, CH₂Cl₂), 43.22 (s, CHCH₂), 34.99 [dd, PCH₂, dppe, ¹J(PC) 40, ³J(PC) 13], 17.80 [dd, PCH₂, dppe, ¹J(PC) 38, ³J(PC) 7] and 18.55 [d, Me, ⁴J(PC) 4 Hz].

(*xxviii*) [Pt{N(COMe)CH(CH₂Ph)C(O)O}(dppp)] **11f**. H₂O. The complex [PtCl₂(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**·H₂O (0.20 g, 89%). NMR spectra: ¹H, δ 7.84–6.89 (m, 25 H, Ph), 4.38 (m, 1 H, CH), 3.27 [dd, 1 H, CHCH₂, ²J(HH) 13, ³J(HH) 4], 3.00 [dd, 1 H, CHCH₂, ²J(HH) 13, ³J(HH) 8], 2.57–2.01 (m, 8 H, 3 × CH₂, dppp + H₂O) and 1.09 (s, 3 H, Me); ¹³C-{¹H}, δ 193.15 (m, CO), 170.49 (s, CO), 67.55 (s, CH), 43.48 (s, CHCH₂), 28.62 [dd, PCH₂, dppp, ¹J(PC) 40, ³J(PC) 10], 22.97 [dd, PCH₂, dppp, ¹J(PC) 33, ³J(PC) 5], 19.23 [d, Me, ⁴J(PC) 4 Hz] and 18.62 (s, CH₂, dppp).

(*xxix*) [Pt{N(COMe)CH(CH₂Ph)C(O)O}(dppb)] **11g**-H₂O. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with dppb (0.12 g, 0.28 mmol) and *N*-acetyl-t-phenylalanine (0.06 g, 0.29 mmol) gave white *microcrystals* of **11g**-H₂O (0.21 g, 92%). NMR spectra: ¹H, δ 7.79–7.04 (m, 25 H, Ph), 4.57 (m, 1 H, CH), 3.33 [dd, 1 H, CHCH₂, ²J(HH) 14, ³J(HH) 6], 3.22 [dd, 1 H, CHCH₂, ²J(HH) 14, ³J(HH) 5], 3.11–1.75 (m, br, 8 H, $3 \times$ CH₂, dppb + H₂O), 1.56 (m, 2 H, CH₂, dppb) and 1.38 (s. 3 H, Me); ¹³C-{¹H}, δ 186.57 [d, CO, ³J(PC) 3], 171.29 (s, CO). 66.26 (s, CH), 41.97 (s, CHCH₂), 25.57 (m, PCH₂, dppb), 22.72 [d, PCH₂, dppb, ¹J(PC) 35], 21.45 (s, 2 × CH₂, dppb) and 1.962 [d, Me, ⁴J(PC) 4 Hz]. (*x.x.*) [\dot{Pt} {N(COMe)CH(CH₂Ph)C(O)O}(cod)] **11h**. The complex [PtCl₂(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: ¹H, 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, CHCH₂Ph, ³J(HH) 36, ³J(PtH) 38], 4.57 [m, 1 H, CH, cod, ²J(PtH) 56], 3.31 [dd, 1 H, CHCH₂Ph, ²J(HH) 13, ³J(HH) 3], 2.96 [dd, 1 H, CHCH₂Ph, ²J(HH) 13, ³J(HH) 6 Hz], 2.73–1.63 (m, 8 H, CH₂, cod) and 2.12 (s, 3 H, Me); ¹³C-{¹H}, 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, CH₂, cod), 30.55 (s, CH₂, cod), 29.44 (s, CH₂, cod), 25.93 (s, CH₂, cod) and 22.15 (s, Me).

(*xxxi*) [$Pt{N(CHO)CH_2C(O)O}{(PPh_3)_2}$] **12a**-CH₂Cl₂. The complex [$PtCl_2(cod)$] (0.10 g, 0.27 mmol) with PPh₃ (0.15 g, 0.57 mmol) and *N*-formylglycine (0.03 g, 0.29 mmol) gave pale yellow *microcrystals* of **12a**-CH₂Cl₂ (0.24 g, 98%). NMR spectra: ¹H, δ 7.62–7.08 (m, 31 H, Ph + CHO), 5.22 (s, 2 H, CH₂Cl₂) and 4.33 [s, 2 H, CH₂, ³J(PtH) 23 Hz]; ¹³C-{¹H}, δ 184.25 (s, CO), 168.15 (s, CO), 53.36 (s, CH₂Cl₂) and 49.90 (s, CH₂).

(*xxxii*) [Pt{N(COCF₃)CH₂C(O)O}(PPh₃)₂] **12b.** The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PPh₃ (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: ¹H, δ 7.77–6.66 (m, 30 H, Ph) and 4.38 [d, 2 H, CH₂, ⁴J(PH) 3, ³J(PtH) 22]; ¹³C-{¹H}, δ 182.35 (s, CO) and 52.94 (s, CH₂); C(O)CF₃ were not discernible; ¹⁹F-{¹H}, δ –67.69 [d, CF₃, ⁵J(PF) 2. ⁴J(PtF) 21 Hz].

(xxxiii) [Pt{NCH₂CH₂CH₂CHC(O)O}(PPh₃)₂] 13a·H₂O.

The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PPh₃ (0.15 g, 0.57 mmol) and L-proline (0.035 g, 0.30 mmol) gave greeny yellow *microcrystals* of **13a**·H₂O (0.21 g, 92%). NMR spectra: ¹H δ 7.74–7.21 (m, 30 H, Ph), 4.88 (m, 1 H, CH), 2.70 (m, 2 H, CH₂), 2.46 (s, br, 2 H, H₂O), 2.02 (m, 2 H, CH₂) and 1.67 (m, 2 H, CH₂); ¹³C-{¹H}, δ 184.47 (m, CO), 64.11 (s, CH), 51.53 (s, CH₂), 30.16 (s, CH₂) and 24.88 (s, CH₂).

(xxxiv) [Pt{NCH₂CH₂CH₂CHC(O)O}(dppp)] 13b. The

complex [PtCl₂(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: ¹H, δ 8.42–7.25 (m, 20 H, Ph), 4.50 (m, 1 H, CH), 2.94 (m, 2 H, CH₂) and 2.52–1.26 (m, 10 H, 3 × CH₂, dppp + 2 × CH₂); ¹³C-{¹H}, δ 184.86 (m, CO), 63.03 (s, CH), 50.60 (s, CH₂), 29.85 (s, CH₂), 24.25 (s, CH₂), 23.59 (m, 2 × PCH₂, dppp) and 18.57 (s, CH₂, dppp).

(xxxv) [Pt{NCH₂CH₂CH₂CHC(O)O}(dppb)] 13c·CH₂Cl₂.

The complex [PtCl₂(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**·CH₂Cl₂ (0.20 g, 90%). NMR spectra: ¹H, δ 7.88–7.34 (m, 20 H, Ph), 5.29 (s, 2 H, CH₂Cl₂), 4.91 (m, 1 H, CH) and 2.91–1.20 (m, 14 H, 4 × CH₂, dppb + 3 × CH₂); ¹³C-{¹H}, δ 184.99 [d, CO, ³J(PC) 2], 63.00 (s, CH), 53.15 (s, CH₂Cl₂), 50.26 (s, CH₂), 29.43 (s, CH₂), 27.68 [d, PCH₂, dppb, ¹J(PC) 38], 25.45 [d, CH₂, dppb, ²J(PC) 4], 24.79 (s, CH₂), 23.80 [d, PCH₂, dppb, ¹J(PC) 40 Hz] and 20.74 (s, CH₂, dppb).

(*xxxvi*) [Pt{OC(H)PhC(O)O}(PPh₃)₂] **14**·H₂O. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PPh₃ (0.15 g, 0.57 mmol) and DL-mandelic acid (0.045 g, 0.29 mmol) gave white *microcrystals* of **14**·H₂O (0.22 g, 92%) (Found: C, 59.7; H, 4.3. C₄₄H₃₆O₃P₂Pt·H₂O requires C, 59.5; H, 4.3%), m.p. 123 C, v(C=O) at 1660s cm⁻¹. NMR spectra: ¹H (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, H₂O); ¹³C-{¹H}, δ 190.65 [dd, CO, ³J(PC) 4,7] and 81.65 [d, CH, ³J(PC) 2]; ³¹P-{¹H} (36.2 MHz), δ 10.87

{d, P(2), ${}^{1}J$ [PtP(2)] 3904, ${}^{2}J$ [P(1)P(2)] 27} and 9.69 {d, P(1), ${}^{1}J$ [PtP(1)] 3286, ${}^{2}J$ [P(2)P(1)] 27 Hz}.

(xxxvii) [Pt{o-N(COMe)C₆H₄O}(PPh₃)₂] **15**. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PPh₃ (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. C₄₄H₃₇NO₂P₂Pt requires C, 60.8; H, 4.3; N, 1.6%), m.p. above 220 °C, v(C=O) at 1600s cm⁻¹. NMR spectra: ¹H (90 MHz), δ 7.8–6.1 (m, 34 H, Ph) and 1.7 (s, 3 H, Me); ¹³C-{¹H}, δ 171.22 (s, CO) and 21.35 [d, Me, ⁴J(PC) 4]; ³¹P-{¹H} (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_2O.

The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PPh₃ (0.15 g, 0.57 mmol) and pyrrole-2-carboxylic acid (0.03 g, 0.27 mmol) gave white *microcrystals* of **16**·H₂O (0.22 g, 96%) (Found: C, 57.9; H, 3.9; N, 1.7. $C_{41}H_{33}NO_2P_2Pt\cdotH_2O$ requires C, 58.2; H, 4.1; N, 1.7%), m.p. above 220 °C; v(C=O) at 1650s cm⁻¹. NMR spectra: ¹H (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, H₂O); ¹³C-{¹H}, too insoluble; ³¹P-{¹H} (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}.

(*x.x.ix*) [$^{h}t{SCH_2C(O)O}{(PPh_3)_2}$] **17a**·CH₂Cl₂. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PPh₃ (0.15 g, 0.57 mmol) and mercaptoacetic acid (0.025 g, 0.27 mmol) gave yellow *microcrystals* of **17a**·CH₂Cl₂ (0.21 g, 87%) (Found: C, 53.3; H, 3.5. C₃₈H₃₂O₂P₂PtS·CH₂Cl₂ requires C, 52.4; H, 3.8%), m.p. 147 °C v(C=O) at 1650s cm⁻¹. NMR spectra: ¹H (300 MHz), δ 7.58–7.12 (m, 30 H, Ph), 5.33 (s, 2 H, CH₂Cl₂) and 3.60 [dd, 2 H, CH₂, ⁴J(PH) 1,2, ³J(PtH) 18]; ¹³C-{¹H}, δ 190.68 [d, CO, ³J(PC) 10], 53.25 (s, CH₂Cl₂) and 30.41 (s, CH₂); ³¹P-{¹H} (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{SCH₂C(O)O}(dppm)] **17b**·CH₂Cl₂. The complex [PtCl₂(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**·CH₂Cl₂ (0.18 g, 88%) (Found: C, 44.5; H, 3.4. C₂₇H₂₄O₂P₂PtS·CH₂Cl₂ requires C, 44.6; H, 3.4%), m.p. above 220 °C v(C=O) at 1610s cm⁻¹. NMR spectra: ¹H (300 MHz), δ 7.90–7.00 (m, 20 H, Ph), 5.30 (s, 2 H, CH₂Cl₂), 4.49 [dd, 2 H, CH₂, dppm, ²J(PH) 11,11, ³J(PtH) 53] and 3.70 [d, 2 H, CH₂, ⁴J(PH) 3, ³J(PtH) 20]; ¹³C-{¹H}, δ 192.44 [dd, CO, ³J(PC) 3,11] 53.29 (s, CH₂Cl₂), 43.06 [dd, CH₂, dppm, ¹J(PC) 31,36] and 28.34 (s, CH₂); ³¹P-{¹H} (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*) [$^{h}t{SCH_2C(O)O}(dppe)$] **17c**·CH₂Cl₂. The complex [PtCl₂(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**·CH₂Cl₂ (0.20 g, 96%) (Found: C, 45.0; H, 3.7. C₂₈H₂₆O₂P₂PtS·CH₂Cl₂ requires C, 45.3; H, 3.7%), m.p. 167 °C, v(C=O) at 1610s cm⁻¹. The complex was too insoluble for NMR studies.

(*xlii*) [Pt{SCH₂C(O)O}(dppp)] **17d**·CHCl₃. The complex [PtCl₂(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**·CHCl₃ (0.19 g, 86%) (Found: C, 43.6; H, 3.6. $C_{29}H_{28}O_2P_2PtS$ ·CHCl₃ requires C, 44.0; H, 3.6%), m.p. above 220 °C, v(C=O) at 1640s cm⁻¹. NMR spectra: ¹H (300 MHz), δ 7.93–7.11 (m, 21 H, Ph + CHCl₃), 3.37 (m, 2 H, CH₂), 2.99 (m, 4 H, PCH₂, dppp) and 2.44 (m, 2 H, CH₂, dppp); ¹³C-{¹H}, δ 190.89 [d, CO, ³*J*(PC) 11], 29.97 (s, CH₂), 23.43 [dd, PCH₂, dppp, ¹*J*(PC) 40, ³*J*(PC) 3], 21.93 [dd, PCH₂, dppp, ¹*J*(PC) 42, ³*J*(PC) 2] and 19.08 (s, CH₂, dppp); ³¹P-{¹H} (36.2 MHz), δ –1.10 {d, P(1),

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

(*xliii*) [Pt{SCH₂C(O)O}(dppb)] **17e**·CH₂Cl₂. The complex [PtCl₂(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**·CH₂Cl₂ (0.19 g, 88%) (Found: C, 46.9; H, 4.1. C₃₀H₃₀O₂P₂PtS·CH₂Cl₂ requires C, 46.7; H, 4.0%), m.p. above 220 °C; v(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, CH₂Cl₂), 3.37 [d, 2 H, CH₂. ⁴*J*(PH) 2, ³*J*(PtH) 18], 3.01 (m, 2 H, PCH₂, dppb), 2.35 (m, 4 H, CH₂ + PCH₂, dppb) and 1.66 (m, 2 H, CH₂, dppb); ¹³C-{¹H}, too insoluble; ³¹P-{¹H} (36.2 MHz), δ 11.70 {d, P(2), ¹*J*[PtP(2)] 3565, ²*J*[P(1)P(2)] 29} and 9.48 {d, P(1), ¹*J*[PtP(1)] 2817, ²*J*[P(2)P(1)] 29 Hz}.

(*xliv*) [$Pt{N(H)C(O)C(O)O}{(PPh_3)_2}$] **18a**·H₂O. The complex [PtCl₂(cod)] (0.10 g, 0.27 mmol) with PPh₃ (0.15 g, 0.57 mmol) and oxamic acid (0.025 g, 0.28 mmol) gave white *microcrystals* of **18a**·H₂O (0.21 g, 94%) (Found: C, 55.5; H, 3.8; N, 1.7. C₃₈H₃₁NO₃P₂Pt·H₂O requires C, 55.3; H, 4.0; N, 1.7%), m.p. above 220 °C, v(N–H) at 3360 cm⁻¹, v_{max} at 2140 cm⁻¹, v(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, H₂O); ¹³C-{¹H}, δ 168.01 (s, CO) and 166.17 (s, CO); ³¹P-{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 [PtCl₂(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. C₂₈H₂₅NO₃P₂Pt requires C, 49.4; H, 3.7; N, 2.1%), m.p. above 220 °C, v(N-H) at 3360 cm⁻¹, v_{max} at 2220 cm⁻¹, v(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, CH₂, dppe); ¹³C-{¹H}, too insoluble; ³¹P-{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**•CH₂Cl₂. The complex [PtCl₂(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**•CH₂Cl₂ (0.19 g, 90%) (Found: C, 44.7; H, 3.6; N, 1.8. $C_{29}H_{27}NO_3P_2Pt$ •CH₂Cl₂ requires C, 44.7; H, 3.7; N, 1.8%), m.p. above 220 °C, v(N–H) at 3360 cm⁻¹, v_{max} at 2240 cm⁻¹, v(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, CH₂Cl₂), 4.9 [m, 1 H, NH, ²J(PtH) 105] and 2.9–1.7 (m, 6 H, CH₂, dppp); ¹³C-{¹H}, δ 168.50 (s, CO) and 166.39 (s, CO), 53.31 (s, CH₂Cl₂), 24.20 (m, PCH₂, dppp) and 18.87 (s, CH₂, dppp); ³¹P-{¹H} (36.2 MHz), δ 7.7.26 {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 [PtCl₂(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 v(N-H) at 3370 cm⁻¹, v_{max} at 2200 cm⁻¹, v(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, PCH₂, dppb) and 2.31 (m, 4 H, CH₂, dppb); ¹³C-{¹H}, too insoluble; ³¹P-{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)CH₂C(O)O}(cod)] **8h** with PPh₃. A solution of [Pt{N(COMe)CH₂C(O)O}(cod)] **8h** (0.10 g, 0.24 mmol) in dichloromethane (ca. 30 cm³) with PPh₃ (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 dichloromethanelight petroleum to afford white *microcrystals* of $[Pt{N(COMe)CH_2C(O)O}{PPh_3}]$ 8a (0.19 g, 95%), identified by ³¹P-{¹H} NMR spectroscopy.

(b) $[Pt{N(COMe)CH_2C(O)O}(cod)]$ **8h** with PMePh₂. A solution of complex **8h** (0.10 g, 0.24 mmol) in dichloromethane (30 cm³) with PMePh₂ (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 ³¹P-{¹H} NMR spectroscopy.

(c) [Pt{N(COMe)CH₂C(O)O}(cod)] **8h** with dppp. A solution of complex **8h** (0.10 g, 0.24 mmol) in dichloromethane (30 cm³) 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)CH₂C(O)O}(dppp)] **8f** (0.17 g, 98%), identified by ³¹P-{¹H} NMR spectroscopy.

(d) [$\dot{P}t\{N(COMe)CH(CH_2Ph)C(O)\dot{O}\}(cod)$] 11h with PPh₃. A solution of [$Pt\{N(COMe)CH(CH_2Ph)C(O)O\}(cod)$] 11h (0.10 g, 0.20 mmol) in dichloromethane (30 cm³) with PPh₃ (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 ³¹P-{¹H} NMR spectroscopy.

(e) $[\dot{P}t{N(COMe)CH(CH_2Ph)C(O)O}(cod)]$ 11h with dppp. A solution of complex 11h (0.10 g, 0.20 mmol) in dichloromethane (30 cm³) 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 $[\dot{P}t{N(COMe)CH(CH_2Ph)C(O)O}(dpp)]$ 11f (0.16 g, 98%), identified by ³¹P-{¹H} and ¹H NMR spectroscopy.

(f) $[\dot{Pt}(N(COMe)CH(CH_2Ph)C(O)\dot{O})(PPh_3)_2]$ 11a·H₂O with Bu'NC. tert-Butyl isocyanide (0.02 g, 0.24 mmol) in dichloromethane (10 cm³) was added dropwise to a stirred solution of [Pt{N(COMe)CH(CH₂Ph)C(O)O}(PPh₃)₂] 11a. H_2O (0.20 g, 0.21 mmol) in dichloromethane (30 cm³), 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 solid sample а of $[\dot{Pt}{N(COMe)CH(CH_2Ph)C(O)O}(CNBu^t)(PPh_3)]$ 23·H₂O (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 (CHCl₃): v(C=N) at 2220s cm⁻¹, v(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, CH₂, ²*J*(HH) 13, ³*J*(HH) 5], 3.10 [dd, 1 H, CH₂, ²*J*(HH) 13, ${}^{3}J$ (HH) 5], 2.20 (s, br, 2 H, H₂O), 1.80 [s, 3 H, C(O)Me] and 1.08 (s, 9 H, Me, Bu'); ${}^{31}P{-}{}^{1}H$ (36.2 MHz), δ 8.08 [s, PPh₃, 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 cm³) 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 ³¹P-{¹H} NMR spectroscopy.

(b) At 60 °C. A solution of complex **8a** (0.10 g) in absolute ethanol (30 cm³) 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 ${}^{31}P{-}{}^{1}H$ NMR spectroscopy.

(c) $[\dot{P}t\{N(COMe)CH_2C(O)\dot{O}\}(PPh_3)_2]$ 8a with diphenylacetylene. Complex 8a (0.15 g, 0.18 mmol) with diphenylacetylene (0.12 g, 0.67 mmol) in absolute ethanol (25 cm³) 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, ${}^{31}P{-}{^{1}H} NMR$ spectroscopy showed the product to be [Pt(PhC=CPh)(PPh_3)_2] (0.13 g, 81°_o).

(d) [$\dot{P}t\{N(COMe)CH_2C(O)\dot{O}\}(PPh_3)_2]$ 8a with PPh₃. Complex 8a (0.15 g, 0.18 mmol) with PPh₃ (0.18 g, 0.69 mmol) in absolute ethanol (25 cm³) 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 $[\dot{P}t\{N(COMe)CH_2C(O)\dot{O}\}(PPh_3)_2]$ 8a with sulfur dioxide. In ethanol. A slow stream of SO₂ 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: v(SO₂) at 1260s and 1100s cm⁻¹. ³¹P-{¹H} NMR spectrum (36.2 MHz): δ 25.51 [s, PPh₃, ¹J(PtP) 2988 Hz].

(b) In dichloromethane. A slow stream of SO₂ 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); ³¹P-{¹H} (36.2 MHz), δ 6.33 [s, PPh₃, 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 ³¹P-{¹H} NMR spectroscopy, was shown to contain unreacted starting material.

(*b*) [$\dot{P}t\{N(COMe)CH_2C(O)\dot{O}\}(PPh_3)_2$] **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(CO₂Et)₂(PPh_3)₂] **27** (R = Et) (0.15 g, 72°_o). IR spectrum: v(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, CH₂, Et. ³J(HH) 7] and 0.26 [t, Me, Et. ³J(HH) 7]; ³¹P-{¹H} (36.2 MHz), δ 20.93 [s, PPh₃, ¹J(PtP) 3254 Hz].

(c) $[Pt_1N(COCF_3)CH_2C(O)O_1(PPh_3)_2]$ 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 ³¹P-{¹H} NMR spectrum was identical to that obtained for 27 (R = Et).

(d) cis-[Pt(O₂CMe)₂(PPh₃)₂] in methanol. A slow stream of carbon monoxide was passed through a stirred methanolic solution of cis-[Pt(O₂CMe)₂(PPh₃)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(CO₂Me)₂(PPh₃)₂] (0.09 g, 45°₀). The filtrate was evaporated to dryness to yield a pale brown oil which was crystallised from dichloromethanelight petroleum to give the pale brown solid cis-[Pt(CO₂-Me)₂(PPh₃)₂] **27** (R = Me) (0.09 g, 45%). NMR spectrum: ³¹P-{¹₁H¹₁ (36.2 MHz), δ 20.86 [s, PPh₃, ¹J(PtP) 3259]. (r) Attenuted insertion reactions. (a)

(v) <u>Attempted</u> insertion reactions. (a) [Pt{N(COMe)CH₂C(O)O}(PPh₃)₂] **8a** with dmad. Dimethyl acetylenedicarboxylate (0.10 g, 0.70 mmol) was added dropwise

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 ³¹P-{¹H} NMR spectroscopy, to contain unreacted **8a**. The reaction was repeated with the mixture being refluxed for an additional 6 h, however ³¹P-{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	Ξ	$U_{ m eq}/{ m \AA^2}$
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)	-0.0961(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)	-0.0116(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)	-0.0383(17)	0.070(6)
C(6)	0.172 8(11)	0.192 8(6)	-0.1708(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)	-0.0110(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)	-0.1026(10)	0.087(8)
C(25)	0.434 4(7)	0.356 6(3)	-0.0802(10)	0.087(7)
C(26)	0.366 9(7)	0.323 0(3)	-0.0232(10)	0.082(7)
C(31)	0.101 1(7)	0.098 0(4)	-0.0575(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)	-0.0898(7)	0.058 6(4)	0.003 8(12)	0.105(10)
C(35)	-0.0931(7)	0.076 8(4)	-0.1411(12)	0.102(9)
C(36)	0.002 4(7)	0.096 5(4)	-0.1717(12)	0.086(7)
C(41)	0.248 4(9)	0.095 1(4)	-0.2612(11)	0.072(6)
C(42)	0.193 2(9)	0.049 0(4)	-0.3228(11)	0.105(9)
C(43)	0.212 1(9)	0.026 9(4)	-0.4531(11)	0.122(11)
C(44)	0.286 3(9)	0.050 9(4)	-0.5219(11)	0.136(13)
C(45)	0.341 5(9)	0.097 0(4)	-0.4602(11)	0.144(14)
C(46)	0.322 5(9)	0.119 2(4)	-0.3299(11)	0.108(10)
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 U_{eq} = One third trace of the orthogonalised U.

(b) $[\dot{P}t{NCH_2CH_2CH_2CHC(O)O}(PPh_3)_2]$ **13a**·H₂O with excess of dmad. Dimethyl acetylenedicarboxylate (0.10 g, 0.70 mmol) was added dropwise to a dichloromethane solution of complex **13a**·H₂O (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 ³¹P-{¹H} NMR spectroscopy to contain numerous products.

(c) $[Pt{NCH_2CH_2CH_2CHC(O)O}(PPh_3)_2]$ **13a**·H₂O with hexafluorobut-2-yne. Hexafluorobut-2-yne (ca. 1.00 g, 6.17 mmol) was condensed onto a tetrahydrofuran (thf) solution of complex **13a**·H₂O (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. (C₄F₆)_n requires C, 29.6; F, 70.4%]. IR data (KBr): v(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 ${}^{31}P{}_{1}$ NMR spectroscopy.

X-Ray Crystal Structure of $[\dot{P}t{N(COMe)CH_2C(O)O}-$ (dppe)] 8e.—The crystal was mounted in air. The unit-cell parameters were determined by least-squares refinement of ωscan measurements for different layers. The intensities of 5663 unique reflections with $7 < 2\theta < 54^{\circ}$ 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 \times 0.08 mm, monoclinic, space group P2₁/n, a = 12.574(8), b =25.219(15), c = 9.165(3) Å, $\beta = 105.45(3)^{\circ}$, U = 2801.2 Å³, Z = 4, $D_c = 1.68$ g cm⁻³, F(000) = 1392.0, Mo-K α X-radiation, $\lambda = 0.7107$ Å, μ (Mo-K α) = 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 $w = 1/(\sigma^2 F + 1)$ gF^2) (g = 0.0007) and gave the final residual indices R = $\Sigma(|F_{o}| - |F_{c}|)/\Sigma|F_{o}| 0.058 \text{ and } R' = [\Sigma w(|F_{o}| - |F_{c}|)^{2}/\Sigma w|F_{o}|^{2}]^{\frac{1}{2}}$ 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 $(\sin \theta)/\lambda$ 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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References

- 1 Metal Ions in Biological Systems, ed. H. Sigel, Marcel Dekker, New York, 1974, vol. 1; 1982, vol. 14.
- 2 Amino acids, Peptides and Proteins, ed. R. C. Sheppard, Specialist Periodical Reports, Royal Society of Chemistry, London, 1969, vol. 1: 1983, vol. 14.

- 3 J. A. Kieft and K. Nakamoto, J. Inorg. Nucl. Chem., 1967, 29, 2561.
- 4 A. A. Grinberg and L. M. Volshtein, Dokl. Akad. Nauk SSSR, 1935,
- 7, 485. 5 F. W. Pinkard, E. Sharratt, W. Wardlaw and E. G. Cox, J. Chem.
- Soc., 1934, 1012. 6 L. M. Volshtein and L. F. Krylova, Russ. J. Inorg. Chem. (Engl.
- Transl.), 1972, 17, 1648. 7 L. M. Volshtein and L. D. Dikanskaya, Russ. J. Inorg. Chem. (Engl.
- Transl.), 1968, 13, 1304. 8 L. M. Volshtein and M. F. Mogilevkina, Russ. J. Inorg. Chem. (Engl. Transl.), 1963, 8, 304.
- 9 D. P. Graddon and L. Munday, Chem. Ind. (London), 1959, 122.
- 10 H. Preut, B. Mundus and F. Huber, Acta Crystallogr., Sect. C, 1989, 45. 728.
- 11 H. Lavayssiere, G. Dousse and J. Satge, J. Organomet. Chem., 1977, 137, C37.
- 12 A. I. Pochidaev, M. A. Simonov, A. I. Kruglik, N. A. Shestakova and G. D. Mal'chikov, Zh. Strukt. Khim., 1975, 16, 1080; I. A. Baidina, N. V. Podberezskaya, L. F. Krylova, S. V. Borisov and V. V. Bakakin, Zh. Strukt. Khim., 1980, 21, 106.
- 13 M. A. A. F. de C. T. Carrondo, D. M. L. Goodgame, C. R. Hadjioannou and A. C. Skapski, Inorg. Chim. Acta, 1980, 46, L32.
- 14 H. C. Freeman and M. L. Golomb, Acta Crystallogr., Sect. B, 1969, 25, 1203.
- 15 R. E. Marsh, Acta Crystallogr., 1958, 11, 654.
- 16 B. C. Challis and J. A. Challis, in Comprehensive Organic Chemistry, eds. D. Barton and W. D. Ollis, Pergamon, Oxford, 1979, vol. 2, p. 986.
- 17 D. H. Williams and I. Fleming, Spectroscopic Methods in Organic Chemistry, 3rd edn., McGraw-Hill, London, 1980.
- 18 A. J. Saraceno, I. Nakagawa, S. Mizushima, C. Curran and J. V. Quagliano, J. Am. Chem. Soc., 1958, 80, 5018.
- 19 L. J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London, 1960, p. 243.
- 20 W. Henderson, R. D. W. Kemmitt, L. J. S. Prouse and D. R. Russell, J. Chem. Soc., Dalton Trans., 1990, 781.
- 21 D. M. Blake and D. M. Roundhill, Inorg. Synth., 1978, 18, 120.
- 22 D. M. Adams and P. J. Chandler, J. Chem. Soc. A, 1969, 588.
- 23 D. M. Barlex and R. D. W. Kemmitt, J. Chem. Soc., Dalton Trans., 1972, 1436.
- 24 G. R. Hughes, P. C. Minshall and D. M. P. Mingos, Transition Met. Chem., 1979, 4, 147.
- 25 K. v. Werner and W. Beck, Chem. Ber., 1972, 105, 3947.
- 26 R. D. W. Kemmitt, S. Mason, M. R. Moore, J. Fawcett and D. R. Russell, J. Chem. Soc., Chem. Commun., 1990, 1535.
- 27 J. X. McDermott, J. F. White and G. M. Whitesides, J. Am. Chem. Soc., 1976, 98, 6521.
- 28 V. D. Bianco and S. Doronzo, Inorg. Synth., 1976, 16, 155. 29 I. Muramatsu, M. Murakami, T. Yoneda and A. Hagitani, Bull. Chem. Soc. Jpn., 1965, 38, 244.
- 30 F. Weygand and A. Röpsch, Chem. Ber., 1959, 92, 2095.
- 31 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.

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