Chemistry of Acetoacetanilide and Derivatives with Zero- and Di-valent Platinum and Palladium Complexes; Crystal Structure of the Four-membered Ring Palladalactam Complex [Pd{CH(COMe)C(O)NPh}(bipy)] (bipy = 2,2′-bipyridyl)†

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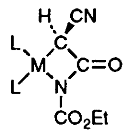
Reaction of the complexes *cis*-[MCl_2L_2] [M = Pd, L_2 = 2,2′-bipyridyl (bipy); M = Pt, L = PPh_3 or L_2 = cycloocta-1,5-diene or $Ph_2P(CH_2)_3PPh_2$] with acetoacetanilide, *o*- or *p*-acetoacetanisidide mediated by silver(I) oxide gave, under mild conditions, high yields of the metallalactam complexes [M{CH(COMe)C(O)NR}L_2] (R = Ph, C_6H_4OMe-*o* or *p*). The complexes have been fully characterised by multinuclear NMR spectroscopy, fast atom bombardment mass spectrometry, and by a single-crystal X-ray diffraction study carried out on the 2,2′-bipyridyl palladium derivative [Pd{CH(COMe)C(O)NPh}(bipy)]. The complex contains a slightly puckered palladalactam ring system (fold angle 17.5°). Reaction of acetoacetanilide with the zerovalent platinum complex [Pt(*trans*-PhCH=CHPh)$(PPh_3)_2$] in air gives exclusively the peroxometallacyclic complex [Pt{OOC(Me)[$CH_2C(O)NHPh$]O}$(PPh_3)_2$], while reaction with [Pt$(PPh_3)_4$] gave a mixture of the peroxometallacycle plus the platinalactam complex [Pt{CH(COMe)C(O)NPh}$(PPh_3)_2$].

Silver(I) oxide has been found to be a very convenient reagent for the synthesis of metal–carbon σ bonds starting from readily available metal–halide complexes.[1] Using appropriately functionalised organic precursors, containing activating electron-withdrawing groups, a wide range of small-ring metallacyclic complexes can be prepared.[2–4] In view of the interest in the chemistry of small-ring metallacyclic complexes[5] we are undertaking a detailed study of the chemistry of four-membered ring metallalactam complexes. Such ring systems have potential for use in the development of new synthetic reagents, *viz*. the metal-mediated synthesis of carbon–carbon and –nitrogen bonds. Metallalactam complexes are of interest in transformations of organic isocyanates,[6] and in the synthesis of the important β-lactam class of organic compounds.[7] Related metallalactone complexes are likewise attracting interest,[8] and have been considered as intermediates in various metal-directed transformations generating, or involving, organic lactones.[9] We have previously described the high yield silver(I) oxide-mediated synthesis of the four-membered ring platina- and pallada-lactam complexes **1a**–**1c** starting from ethyl *N*-cyanoacetylcarbamate,[10,11] and have now extended this study to the synthesis of related ring systems derived from other amides containing activated 'acidic' hydrogens. In this paper we report the synthesis of four-membered ring metallalactam complexes derived from acetoacetanilide and phenyl-functionalised derivatives, together with the first structural determination of a four-membered palladalactam ring complex. An investigation of the reactions of zerovalent platinum complexes with acetoacetanilide as a potential route to platinalactam complexes is also presented.



	M	L or L_2
1a	Pt	PPh_3
1b	Pt	cod
1c	Pd	dppe

Results and Discussion

Reaction of the platinum or palladium dichloride complexes *cis*-[MCl_2L_2] [M = Pd, L_2 = 2,2′-bipyridyl (bipy); M = Pt, L = PPh_3 or L_2 = cycloocta-1,5-diene (cod) or $Ph_2P(CH_2)_3PPh_2$ (dppp)] with either acetoacetanilide [$C_6H_5NHC(O)CH_2C(O)Me$], *o*- or *p*-acetoacetanisidide [$MeOC_6H_4NHC(O)CH_2C(O)Me$] in refluxing dichloromethane, in the presence of an excess of silver(I) oxide gives high yields of the metallalactam complexes **2a**–**2h**, as shown in Scheme 1. The complexes are isolated as white (Pt) or orange (Pd) crystalline compounds, which are air-stable, both in solution and in the solid state. The synthesis of these metallalactam complexes is analogous to the syntheses described previously for metallalactams derived from ethyl *N*-cyanoacetylcarbamate.[10,11] This work thus extends the range of substrates which can be employed in this extremely facile synthesis of this class of ring system.

The complexes have been characterised by multinuclear NMR and IR spectroscopies, fast atom bombardment mass spectrometry (FABMS), elemental analysis, and by a single-crystal X-ray diffraction study carried out on the 2,2′-bipyridyl

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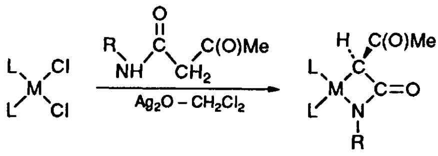
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



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	M	L or L$_2$	R
2a	Pd	bipy	Ph
2b	Pt	PPh$_3$	Ph
2c	Pt	cod	Ph
2d	Pt	PPh$_3$	C$_6$H$_4$OMe-*p*
2e	Pt	PPh$_3$	C$_6$H$_4$OMe-*o*
2f	Pt	dppp	Ph
2g	Pt	dppp	C$_6$H$_4$OMe-*p*
2h	Pt	dppp	C$_6$H$_4$OMe-*o*

Scheme 1

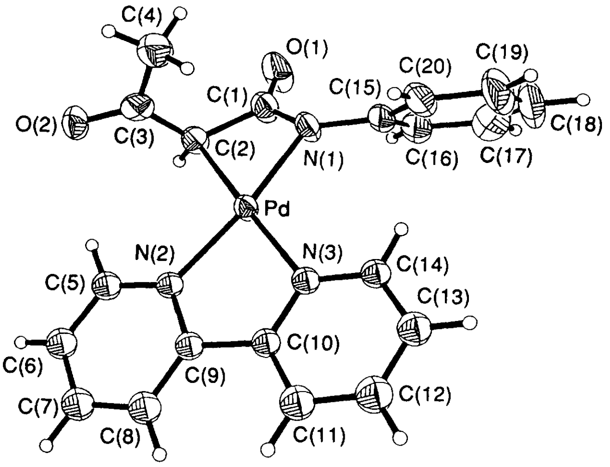


Fig. 1 Molecular structure of [Pd{CH(COMe)C(O)NPh}(bipy)] **2a** showing the atom numbering scheme. Atoms are shown as thermal ellipsoids at the 50% probability level

Table 1 Crystal data for [Pd{CH(COMe)C(O)NPh}(bipy)] **2a**

Empirical formula	C$_{20}$H$_{17}$N$_3$O$_2$Pd
M	437.8
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	10.629(2)
b/Å	11.018(2)
c/Å	18.046(2)
α/°	99.16(1)
β/°	91.29(1)
γ/°	117.96(1)
U/Å^3	1831.5(4)
D_c/g cm^{-3}	1.59
Z	4
F(000)	880
μ/mm^{-1}	1.032

Table 2 Fractional atomic coordinates (× 10^4) for one of the two independent molecules (molecule 1) of [Pd{CH(COMe)C(O)NPh}(bipy)] **2a**

Atom	*x*	*y*	*z*
Pd	2746(1)	3496(1)	934(1)
O(1)	−900(8)	3240(8)	1053(6)
O(2)	280(7)	−88(6)	1017(4)
N(1)	1546(8)	4340(7)	1409(5)
N(2)	3602(7)	2365(7)	361(3)
N(3)	4942(7)	5018(7)	1062(3)
C(1)	294(12)	3274(10)	1116(7)
C(2)	584(9)	2069(9)	827(5)
C(3)	468(9)	1069(10)	1290(6)
C(4)	619(12)	1505(11)	2126(6)
C(5)	2855(10)	1037(9)	−13(5)
C(6)	3474(10)	376(10)	−460(5)
C(7)	4865(11)	1064(10)	−523(5)
C(8)	5688(11)	2458(10)	−140(5)
C(9)	5040(9)	3068(8)	307(4)
C(10)	5793(9)	4541(8)	724(4)
C(11)	7246(11)	5377(10)	756(5)
C(12)	7830(12)	6748(11)	1156(5)
C(13)	7003(10)	7237(10)	1494(5)
C(14)	5541(9)	6329(8)	1441(4)
C(15)	1824(7)	5736(5)	1631(4)
C(16)	1295	6348	1179
C(17)	1656	7755	1394
C(18)	2546	8551	2061
C(19)	3075	7939	2513
C(20)	2714	6531	2298

Table 3 Intramolecular bond lengths (Å) and selected angles (°) for one of the two independent molecules (molecule 1) of [Pd{CH(COMe)C(O)NPh}(bipy)] **2a** with estimated standard deviations in parentheses

Palladalactam ring system			
Pd–N(1)	2.033(9)	Pd–N(2)	2.036(8)
Pd–N(3)	2.120(6)	Pd • • • C(1)	2.535(13)
Pd–C(2)	2.070(7)	O(1)–C(1)	1.254(17)
O(2)–C(3)	1.210(13)	N(1)–C(1)	1.317(11)
N(1)–C(15)	1.409(10)	C(1)–C(2)	1.517(17)
C(2)–C(3)	1.448(16)	C(3)–C(4)	1.489(14)
2,2′-Bipyridyl ligand			
N(2)–C(5)	1.342(10)	N(2)–C(9)	1.366(11)
N(3)–C(10)	1.355(13)	N(3)–C(14)	1.328(10)
C(5)–C(6)	1.379(16)	C(6)–C(7)	1.326(14)
C(7)–C(8)	1.406(12)	C(8)–C(9)	1.365(16)
C(9)–C(10)	1.486(10)	C(10)–C(11)	1.371(12)
C(11)–C(12)	1.394(13)	C(12)–C(13)	1.340(18)
C(13)–C(14)	1.389(12)		
N(1)–Pd–N(2)	169.6(2)	N(1)–Pd–N(3)	110.9(3)
N(2)–Pd–N(3)	79.1(3)	N(1)–Pd–C(2)	67.0(3)
N(2)–Pd–C(2)	103.0(3)	N(3)–Pd–C(2)	177.9(4)
Pd–N(1)–C(1)	96.0(7)	Pd–N(1)–C(15)	132.2(5)
C(1)–N(1)–C(15)	125.2(10)	Pd–N(2)–C(5)	125.3(7)
Pd–N(2)–C(9)	116.3(5)	C(5)–N(2)–C(9)	118.1(8)
Pd–N(3)–C(10)	113.9(4)	Pd–N(3)–C(14)	127.4(7)
C(10)–N(3)–C(14)	118.6(7)	Pd–C(1)–O(1)	166.3(10)
Pd–C(1)–N(1)	52.9(6)	O(1)–C(1)–N(1)	128.5(11)
Pd–C(1)–C(2)	54.7(5)	O(1)–C(1)–C(2)	125.7(8)
N(1)–C(1)–C(2)	105.8(10)	Pd–C(2)–C(1)	88.5(5)
Pd–C(2)–C(3)	105.4(6)	C(1)–C(2)–C(3)	121.5(9)
O(2)–C(3)–C(2)	121.9(9)	O(2)–C(3)–C(4)	119.7(11)
C(2)–C(3)–C(4)	118.4(9)	N(2)–C(5)–C(6)	122.6(8)
N(2)–C(9)–C(8)	121.0(7)	N(2)–C(9)–C(10)	115.1(8)
N(3)–C(10)–C(9)	115.3(7)	N(3)–C(10)–C(11)	121.9(8)
N(3)–C(14)–C(13)	122.6(10)	N(1)–C(15)–C(16)	121.4(5)

palladium derivative **2a**, the first structural characterisation of a four-membered ring palladalactam complex. The molecular structure of complex **2a** is shown in Fig. 1, together with the atom numbering scheme. Crystal data and fractional atomic coordinates for the structure are presented in Tables 1 and 2 respectively, while Table 3 gives selected bond distances and angles. The complex crystallises with two independent molecules in the unit cell, however there are only minor structural differences between them (specifically in the orientation of the phenyl rings) and only one molecule will be discussed subsequently. The palladium atom has the expected square-planar geometry, with no atom in the palladium co-ordination sphere being more than 0.030 Å from the least-

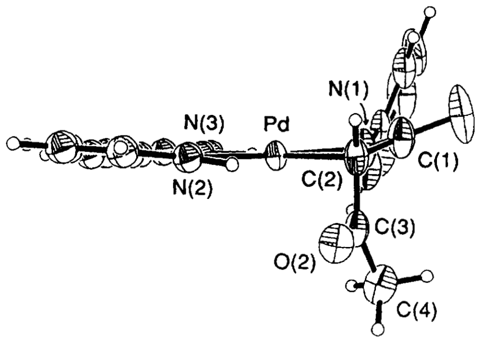
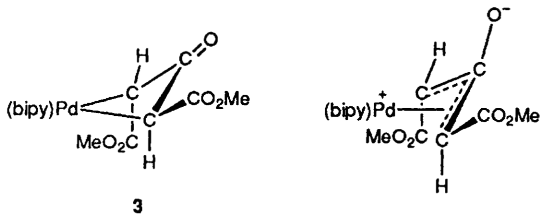


Fig. 2 Side view of [Pd{CH(COMe)C(O)NPh}(bipy)] **2a**, showing the puckering of the palladalactam ring



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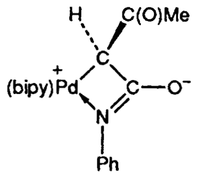
squares plane defined by Pd, N(1), N(2), N(3) and C(2). The four-membered palladacycle is slightly puckered, as shown in Fig. 2, with a fold angle of 17.5° between the Pd–N(1)–C(2) and C(2)–C(1)–N(1) planes. It is worth noting that a number of structural studies[2,12–15] on related four-membered ring metallacyclobutan-3-one complexes such as the bipyridyl palladium derivative **3**[12] have shown these complexes to be highly non-planar, with fold angles around 50° being typically observed, and with the carbonyl oxygen tipped out of the C–C–C plane towards the metal by around 12°. A substantial contribution to the bonding from a η^3-oxodimethylenemethane form has been invoked to account for these structural characteristics. It has also been found that the palladium complexes are more non-planar than their platinum counterparts.[2,12–14] It is therefore possible that there is a small contribution to the bonding in the palladalactam complex **2a** from an analogous η^3-bonding representation. However, a more likely explanation for the ring puckering is relief of strain caused by interaction of the metallacycle C(O)Me and N-phenyl substituents, with the bipyridyl hydrogens *ortho* to the donor nitrogens. This can be clearly seen in a model of the complex. It is noteworthy that the N-phenyl ring adopts a conformation tending towards perpendicularity to the palladium co-ordination plane, as can be seen in Fig. 2. The carbonyl group is essentially coplanar with the remainder of the organic fragment, with a small tip angle of 1.96° between the C(1)–O(1) bond and the N(1)–C(1)–C(2) plane.

The Pd–C bond distance, 2.070(7) Å, is identical to that of the previously structurally characterised platinalactam **1b** [2.069(8) Å],[10] both being shorter than the palladacyclobutan-3-one (η^3-oxodimethylenemethane) complex **3** [average 2.094(3) Å].[12] Similarly, the C–C bonds of pallada- and platinalactams **2a** and **1b** [1.517(17) and 1.538(11) Å respectively] are comparable, within experimental error, and are longer than in **3** [1.471(5) Å], these observations being consistent with the substantial η^3 contribution to the bonding in complex **3**.

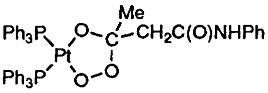
There appears to be several interesting features on comparison of the C–N and C=O metallacycle bonds of the platina- and pallada-lactam complexes **1b** and **2a**. The C–N bond of the Pd complex is significantly shorter [1.317(11) Å] than that of the Pt complex [1.391(10) Å]. Furthermore, on examination of the C=O bonds, that for the palladalactam [1.254(17) Å] appears to be significantly longer at the 3σ probability level than the platinalactam [1.196(9) Å], and is more comparable to the significantly lengthened C=O bond of the palladacyclobutan-3-one (η^3-oxodimethylenemethane) complex **3** [1.242(4) Å].[12] Although not significant at the 3σ level, the Pd–N(1) bond of **2a** tentatively appears to be slightly longer than that of the Pt complex **1b** [2.033(9) *vs.* 2.016(6) Å].[10] Although these individual comparisons may not be fully conclusive, taken together they appear to suggest a possible contribution to the metallacyclic bonding of **2a** from an imidato-type representation as shown below.



The ^{1}H, ^{13}C-{^{1}H} and, where appropriate, ^{31}P-{^{1}H} NMR spectra of the metallalactam complexes **2a**–**2h** show the expected features by comparison with the previously reported platinum and palladium derivatives of ethyl *N*-cyanoacetylcarbamate **1a**–**1c**.[10,11] Confirmation of the formation of a metallated carbon in the palladium complex **2a** was accomplished by means of a ^{13}C distortionless enhancements by polarisation transfer (DEPT) NMR spectrum which clearly displayed the absence of any CH_2 resonances. Assignment of the Pd–CH and CH_3 singlets was completed by a comparison with the analogous resonances for the cod platinum complex, which were readily assigned, by availability of ^{195}Pt coupling on the metallacyclic CH group. The lactam carbonyl was observed in the region δ 171.9–174.8, with the platinum complexes **2b** and **2c** showing the characteristically large coupling to ^{195}Pt of 142.2 and 161.7 Hz respectively. These coupling constants are comparable to that observed for the lactam carbonyl of **1b** (147.2 Hz)[10] and the lactone carbonyl of the complex [Pt{CH(CO$_2$Me)C(O)O}(PPh$_3$)$_2$] (175.5 Hz).[4] The C(O)Me carbonyl groups of **2a**–**2c** appear in the expected region of δ 205.2–206.7, the platinum complexes **2b** and **2c** showing the expected small ^2J(PtC) couplings of 41.0 and 48.5 Hz respectively, by comparison with **1a** and **1b**.[10]

Fast atom bombardment mass spectrometry also proved to be a useful tool for characterising these metallacyclic systems, with a molecular ion routinely being observed as a characteristic cluster of peaks, with the distribution of these closely matching the predicted isotopomer distribution.

The reactions of acetoacetanilide with the zerovalent platinum complexes [Pt(*trans*-PhCH=CHPh)(PPh$_3$)$_2$] and [Pt(PPh$_3$)$_4$] have also been investigated, as a possible route to platinalactam complexes. A number of metallacyclobutan-3-one (η^3-oxodimethylenemethane) complexes of platinum(II)[2] and palladium(II)[12] have been prepared *via* this methodology. Thus, reaction of the *trans*-stilbene complex with acetoacetanilide in the presence of air gave a moderate yield of a white complex, identified by its ^{31}P-{^{1}H}, ^{13}C-{^{1}H} and ^{1}H NMR spectra as the peroxometallacyclic complex **4**. The product is formed *via* reaction of the ketone group exclusively, and we find no evidence for the participation of the amide carbonyl group in this reaction. The ^{31}P-{^{1}H} NMR spectrum of **4** showed the expected AB spin system with values of ^1J(PtP) of 3679 and 3328 Hz being observed. The latter compares very favourably with the values of ^1J(PtP) observed for PPh$_3$ ligands *trans* to peroxo groups in the complexes [Pt{OOCR$_2$C(CN)$_2$}(PPh$_3$)$_2$] (R = CN, *J* 3392 and R = Me, *J* 3309 Hz).[16] Diagnostic of an N–H proton was a single, rather broad resonance in the ^{1}H NMR spectrum at δ 9.91, which is similar to the position of this proton in free acetoacetanilide (δ 9.23). In addition, lack of ^{31}P or ^{195}Pt coupling to the resonances at δ 2.98 and 1.64 in the ^{1}H NMR and at δ 46.8 and 23.3 in the ^{13}C-{^{1}H} NMR spectrum were consistent with the presence of CH_2 and CH_3 groups respectively, remote from the Pt(PPh$_3$)$_2$ moiety. The assignment



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of these was confirmed by a ^{13}C-DEPT experiment, and by comparison with acetoacetanilide (CH$_2$: ^{1}H δ 3.50, ^{13}C δ 50.8; CH$_3$: ^{1}H δ 2.20, ^{13}C δ 30.8). The peroxometallacyclic carbon appeared as a doublet of doublets due to coupling to the two ^{31}P nuclei, though coupling to ^{195}Pt could not be resolved. It is noteworthy that complex **4** is stable and can be readily isolated and characterised without decomposition or loss of oxygen, though gas evolution was noted upon melting. Several other examples of related peroxoplatinacycles formed by reaction of the dioxygen complex [Pt(O$_2$)(PPh$_3$)$_2$] with aldehydes and ketones,[17] fluorinated ketones[18] and alkenes[16,19] have been described previously. Such compounds are believed to be important intermediates in metal-mediated oxidations of organic substrates,[19] and there is considerable interest in the chemistry of such processes.[20]

The reaction between [Pt(PPh$_3$)$_4$] and acetoacetanilide in the presence of air for 24 h gave a white solid which, on the basis of ^{31}P-{^{1}H} NMR spectroscopy, was found to be a *ca.* 2:1 mixture of the peroxoplatinacycle **4** and the platinalactam complex **2b**. On stirring the mixture in dichloromethane solution with additional triphenylphosphine for 22 h, very little further conversion to the platinalactam occurred, indicating that the major route to this complex from [Pt(PPh$_3$)$_4$] does not proceed *via* the peroxoplatinacycle **4**. However, upon prolonged stirring in air for several weeks with triphenylphosphine, the mixture was converted exclusively to the lactam complex **2b** plus triphenylphosphine oxide. A previous study[2] has shown that the reaction of [Pt(PPh$_3$)$_4$] with RCH$_2$C(O)CH$_2$R (R = CO$_2$Me or CO$_2$Et) in air gives a mixture of the platinacyclobutan-3-one (η^3-oxodimethylenemethane) complex [Pt{RCHC(O)CHR}(PPh$_3$)$_2$] plus a peroxoplatinacycle analogous to **4**. It is highly likely, based on the similar natures of the organic starting reagents, that the synthesis of the platinalactam complex **4** proceeds *via* a similar mechanism.

Experimental

Melting points were recorded on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs, either on a Perkin-Elmer 580 or on a Bio-Rad FTS-40 spectrophotometer. Proton NMR spectra were recorded in CDCl$_3$ solution, on Bruker AM300 or AC300P spectrometers at 300.13 MHz, with chemical shifts referenced to SiMe$_4$ (δ 0); ^{13}C-{^{1}H} NMR spectra were recorded in CDCl$_3$ on a Bruker AC300P spectrometer at 75.47 MHz relative to SiMe$_4$ (δ 0); ^{31}P-{^{1}H} NMR spectra were recorded either on a JEOL JNM-FX60 or FX90Q spectrometer at 24.15 or 36.23 MHz respectively, with external 85% H$_3$PO$_4$ (δ 0) as reference; ^{195}Pt-{^{1}H} NMR spectra were recorded on a Bruker AM300 spectrometer at 64.52 MHz with K$_2$[PtCl$_4$] as external reference. Fast atom bombardment mass spectra were recorded in a *m*-nitrobenzyl alcohol matrix on a Kratox Concept double-focussing sector spectrometer.

Experiments were carried out under a nitrogen atmosphere as a routine precaution, however, all the compounds described are air-stable, and were recrystallised from solvents without regard for the exclusion of air. Solvents were dried and distilled from appropriate drying agents prior to use. Light petroleum refers to the fraction of b.p. 40–60 °C. Acetoacetanilide, and *o*- and *p*-acetoacetanisidides, together with 1,3-bis(diphenylphosphino)propane (dppp) were purchased from Aldrich and used as supplied. The compounds [PtCl$_2$(cod)],[21] [PdCl$_2$(bipy)],[22] [Pt(PPh$_3$)$_4$],[23] [Pt(*trans*-PhCH=CHPh)(PPh$_3$)$_2$],[24] and silver(I) oxide[25] were prepared *via* the literature procedures.

Syntheses.—[Pd{CH(COMe)C(O)NPh}(bipy)] **2a**. A mixture of [PdCl$_2$(bipy)] (0.250 g, 0.749 mmol), acetoacetanilide (0.133 g, 0.751 mmol), and silver(I) oxide (0.9 g, excess) in dichloromethane (30 cm^3) was refluxed for 24 h. Filtration to remove the silver salts followed by evaporation of the filtrate under reduced pressure gave a bright yellow oil. Dissolution of the oil in dichloromethane (5 cm^3) followed by addition of light petroleum (70 cm^3) gave a yellow solid which was filtered off and dried *in vacuo* to give **2a** (0.270 g, 82%). Slow recrystallisation from dichloromethane–diethyl ether yielded bright yellow-orange crystals of crystallographic quality (Found: C, 54.25; H, 3.80; N, 9.35. $C_{20}H_{17}N_3O_2Pd$ requires C, 54.85; H, 3.90; N, 9.60%), m.p. 240–245 °C (decomp.). IR: ν(C=O) at 1620vs cm^{-1}. NMR: ^{1}H, δ 9.02–7.11 (m, Ph + bipy), 3.15 (s, 1 H, Pd–CH), 2.45 (s, 3 H, CH$_3$); ^{13}C-{^{1}H}, δ 206.7 (s, *C*OCH$_3$), 171.9 (s, *C*ONPh), 154.6–121.8 (m, Ph + bipy), 37.6 (s, Pd–CH), and 27.1 (s, CO*C*H$_3$). A DEPT-135 ^{13}C NMR spectrum (acquired using a 135 θ pulse) clearly showed the absence of any CH$_2$ resonances.

[Pt{CH(COMe)C(O)NPh}(PPh$_3$)$_2$] **2b**. To a solution of [PtCl$_2$(cod)] (0.200 g, 0.535 mmol) in dichloromethane (30 cm^3) was added in succession triphenylphosphine (0.280 g, 1.070 mmol), acetoacetanilide (0.099 g, 0.559 mmol) and silver(I) oxide (0.9 g, excess), and the mixture was refluxed for 12 h. Filtration to remove the silver salts afforded a pale yellow solution which was evaporated to dryness under reduced pressure to give a pale yellow oil. Dissolution of the oil in dichloromethane (5 cm^3) followed by addition of light petroleum (70 cm^3) gave an off-white solid which was filtered off and dried *in vacuo* to give **2b** (0.438 g, 92%). Slow recrystallisation from dichloromethane–light petroleum gave pale yellow needles (Found: C, 60.95; H, 4.25; N, 1.45. $C_{46}H_{39}NO_2P_2Pt$ requires C, 61.75; H, 4.40; N, 1.55%), m.p. 246–248 °C (decomp.). FABMS: *M*$^+$ at *m*/*z* 895. IR: ν(C=O) at 1635vs and 1590s cm^{-1}. NMR: ^{31}P-{^{1}H} (36 MHz), AB spin system at δ 17.2 [dd, $P_{trans\ C}$, ^1J(PtP) 2402, ^2J(PP) 17] and 10.8 [dd, $P_{trans\ N}$, ^1J(PtP) 3709]; ^{13}C-{^{1}H}, δ 206.0 [d, *C*(O)CH$_3$, $^3J(PC)_{trans}$ 4.8, ^2J(PtC) 41.0], 174.8 [d, *C*(O)NPh, ^3J(PC) 6.3, ^2J(PtC) 142.2], 144.0–123.4 (m, Ph), 50.4 [dd, Pt–CH, $^2J(PC)_{trans}$ 61.1, $^2J(PC)_{cis}$ 2.2, ^1J(PtC) 363.7] and 29.0 (s, CH$_3$); ^{1}H, δ 7.48–6.43 (m, 35 H, Ph), 2.77 [dd, 1 H, Pt–CH, $^3J(PH)_{trans}$ 6.1, $^3J(PH)_{cis}$ 4.2, ^2J(PtH) 45.1 Hz] and 2.09 (s, 3 H, CH$_3$).

[Pt{CH(COMe)C(O)NPh}(cod)] **2c**. A mixture of [PtCl$_2$(cod)] (0.300 g, 0.802 mmol), acetoacetanilide (0.145 g, 0.818 mmol), and silver(I) oxide (0.9 g, excess) in dichloromethane (25 cm^3) was refluxed for 4 h and then stirred at room temperature for 17 h. Filtration to remove the silver salts followed by evaporation of the filtrate to dryness under reduced pressure gave a light brown oil. Dissolution of the oil in dichloromethane (5 cm^3), followed by addition of light petroleum (60 cm^3) gave fine off-white needles which were filtered off and dried *in vacuo* to give **2c** (0.267 g, 70%) (Found: C, 45.05; H, 4.20; N, 2.85. $C_{18}H_{21}NO_2Pt$ requires C, 45.20; H, 4.40; N, 2.95%), m.p. 181–183 °C. IR: ν(C=O) at 1671vs and 1642vs cm^{-1}. NMR: ^{1}H, δ 7.29–7.00 (m, 5 H, Ph), 5.53 [m, 1 H, CH of cod, ^2J(PtH) *ca.* 44.2], 5.47 [m, 1 H, CH of cod, ^2J(PtH) *ca.* 48.7], 4.95 [m, 1 H, CH of cod, ^2J(PtH) *ca.* 62.7], 4.33 [m, 1 H, CH of cod, ^2J(PtH) 59.9], 3.05 [s, 1 H, Pt–CH, ^2J(PtH) 98.7], 2.60–2.26 (m, 8 H, CH$_2$ cod) and 2.20 (s, 3 H, CH$_3$); ^{13}C-{^{1}H}, δ 205.2 [s, *C*OCH$_3$, ^2J(PtC) 48.5], 173.8 [s, *C*(O)NPh, ^2J(PtC) 161.7], 144.4 [s, Ph, C^1, ^2J(PtC) *ca.* 10], 129.0 (s, Ph, C^3), 124.8 (s, Ph, C^4), 123.8 [s, Ph, C^2, ^3J(PtC) 23.7], 106.7 [s, CH of cod, ^1J(PtC) 62.9], 106.5 [s, CH of cod, ^1J(PtC) 63.2], 90.5 [s, CH of cod, ^1J(PtC) 169.0], 87.1 [s, CH of cod, ^1J(PtC) 155.7], 45.6 [s, Pt–CH, ^1J(PtC) 425.2 Hz], 31.9 (s, CH$_2$ of cod), 30.5 (s, CH$_2$ of cod), 29.4 (s, CH$_2$ of cod), 28.5 (s, CH$_2$ of cod) and 27.9 (s, CH$_3$ of cod).

The following metallalactam derivatives were also prepared by an analogous procedure: $[Pt\{CH(COMe)C(O)N(C_6H_4OMe\text{-}p)\}(PPh_3)_2]\cdot CH_2Cl_2$ **2d** from $[PtCl_2(cod)]$, PPh_3, *p*-acetoacetanisidide and silver(I) oxide: yield 78%, m.p. 195 °C (Found: C, 57.85; H, 4.20; N, 1.05. $C_{47}H_{41}NO_3P_2Pt\cdot CH_2Cl_2$ requires C, 57.10; H, 4.30; N, 1.40%). IR: $\nu(C{=}O)$ at 1650vs (br) cm^{-1}. FABMS: M^+ at m/z 925. NMR: $^{31}P\text{-}\{^1H\}$ (24 MHz), AB spin system, δ 17.5 [dd, $P_{trans\ C}$, $^1J(PtP)$ 2402, $^2J(PP)$ 17] and 11.0 [dd, $P_{trans\ N}$, $^1J(PtP)$ 3667 Hz].

$[Pt\{CH(COMe)C(O)N(C_6H_4OMe\text{-}o)\}(PPh_3)_2]\cdot 0.5CH_2Cl_2$ **2e** from $[PtCl_2(cod)]$, PPh_3, *o*-acetoacetanisidide and silver(I) oxide: yield 70%, m.p. 140 °C (Found: C, 58.65; H, 4.45; N, 1.45. $C_{47}H_{41}NO_3P_2Pt\cdot 0.5CH_2Cl_2$ requires C, 59.00; H, 4.40; N, 1.45%). IR: $\nu(C{=}O)$ at 1635vs (br) cm^{-1}. FABMS: M^+ at m/z 925. NMR: $^{31}P\text{-}\{^1H\}$ (24 MHz), AB spin system, δ 17.3 [dd, $P_{trans\ C}$, $^1J(PtP)$ 2410, $^2J(PP)$ 17] and 10.9 [dd, $^1J(PtP)$ 3669 Hz].

$[Pt\{CH(COMe)C(O)NPh\}(dppp)]\cdot 2CH_2Cl_2$ **2f** from $[PtCl_2(cod)]$, dppp, acetoacetanilide and silver(I) oxide: yield 66%, m.p. 135 °C (decomp.) (Found: C, 49.90; H, 4.10; N, 1.30. $C_{37}H_{35}NO_2P_2Pt\cdot 2CH_2Cl_2$ requires C, 49.30; H, 4.15; N, 1.45%). IR: $\nu(C{=}O)$ at 1710s and 1635vs (br) cm^{-1}. FABMS: M^+ at m/z 783. NMR: $^{31}P\text{-}\{^1H\}$ (24 MHz), AB spin system, δ −2.3 [dd, $P_{trans\ C}$, $^1J(PtP)$ 2339, $^2J(PP)$ 27] and −6.9 [dd, $^1J(PtP)$ 3347 Hz].

$[Pt\{CH(COMe)C(O)N(C_6H_4OMe\text{-}p)\}(dppp)]\cdot CH_2Cl_2$ **2g** from $[PtCl_2(cod)]$, dppp, *p*-acetoacetanisidide and silver(I) oxide: yield 70%, m.p. 140 °C (decomp.) (Found: C, 51.80; H, 4.25; N, 1.85. $C_{38}H_{37}NO_3P_2Pt\cdot CH_2Cl_2$ requires C, 52.15; H, 4.40; N, 1.55%). IR: $\nu(C{=}O)$ at 1610m (sh) and 1590vs (br) cm^{-1}. FABMS: M^+ at m/z 813. NMR: $^{31}P\text{-}\{^1H\}$(24 MHz), AB spin system, δ −2.3 [dd, $P_{trans\ C}$, $^1J(PtP)$ 2349, $^2J(PP)$ 27] and −6.9 [dd, $^1J(PtP)$ 3291 Hz]; $^{195}Pt\text{-}\{^1H\}$, δ −4536 [dd, $^1J(PtP)$ 3275, 2335 Hz].

$[Pt\{CH(COMe)C(O)N(C_6H_4OMe\text{-}o)\}(dppp)]\cdot 0.5CH_2Cl_2$ **2h** from $[PtCl_2(cod)]$, dppp, *o*-acetoacetanisidide and silver(I) oxide: yield 58%, m.p. 148–150 °C (decomp.) (Found: C, 54.20; H, 4.65; N, 1.40. $C_{38}H_{37}NO_3P_2Pt\cdot 0.5CH_2Cl_2$ requires C, 54.05; H, 4.50; N, 1.65%). IR: $\nu(C{=}O)$ at 1635vs (br) cm^{-1}. FABMS: M^+ at m/z 813. NMR: $^{31}P\text{-}\{^1H\}$(24 MHz), AB spin system, δ −2.9 [dd, $P_{trans\ C}$, $^1J(PtP)$ 2354, $^2J(PP)$ 27] and −7.2 [dd, $^1J(PtP)$ 3321 Hz].

Reactions of Zerovalent Platinum Complexes with Acetoacetanilide.—Synthesis of $[Pt\{OOC(Me)[CH_2C(O)NHPh]O\}(PPh_3)_2]$ **4**. A suspension of $[Pt\{trans\text{-}PhCH{=}CHPh\}(PPh_3)_2]$ (0.200 g, 0.222 mmol) with acetoacetanilide (0.120 g, 0.677 mmol) in diethyl ether (20 cm^3) was stirred in air for 21 h, to give a white suspension which was filtered off, washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo* to give **4** (0.084 g, 41%) (Found: C, 58.65; H, 4.30; N, 1.40. $C_{46}H_{41}NO_4P_2Pt$ requires C, 59.50; H, 4.45; N, 1.50%), m.p. 158–168 °C (decomp. with gas evolution). IR: $\nu(C{=}O)$ at 1679s cm^{-1}. NMR: $^{31}P\text{-}\{^1H\}$(36 MHz), AB spin system, δ 11.4 [dd, $^1J(PtP)$ 3679, $^2J(PP)$ 20] and 8.5 [dd, $^1J(PtP)$ 3328 Hz]; $^{13}C\text{-}\{^1H\}$, δ 170.2 [s, *C*(O)NHPh], 138.7–119.6 (m, Ph), 106.4 [m, Pt–O–C, $^2J(PtC)$ not resolved], 46.8 (s, CH_2) and 23.3 (s, CH_3) (the CH_2 and CH_3 resonances were unambiguously assigned by means of a DEPT-135 NMR spectrum); ^1H, δ 9.91 (s, 1 H, NH), 7.60–6.65 (m, 35 H, Ph), 2.98 (s, 2 H, CH_2) and 1.64 (s, 3 H, CH_3).

Reaction of $[Pt(PPh_3)_4]$ *with Acetoacetanilide.*—A mixture of $[Pt(PPh_3)_4]$ (0.540 g, 0.434 mmol) and acetoacetanilide (0.150 g, 0.847 mmol) in diethyl ether (30 cm^3) was stirred in air for 24 h. The resulting white suspension was filtered off, washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo* to give 0.383 g of a *ca.* 2 : 1 mixture of complexes **4** and **2b**, identified by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The product was then stirred in dichloromethane (25 cm^3) with triphenylphosphine (0.250 g) for 22 h, after which $^{31}P\text{-}\{^1H\}$ NMR showed that very little further reaction had occurred. The mixture was then allowed to stand at room temperature for several weeks, whereupon complete conversion to the platinalactam complex **2b** had occurred, as evidenced by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy, which also showed the presence of Ph_3PO.

Crystal Structure Determination of Complex **2a**.—An orange crystal of approximate dimensions 0.38 × 0.26 × 0.09 mm was glued to the end of a thin glass fibre using epoxy resin. Accurate unit-cell dimensions were determined by least-squares refinement of ω angles for 35 centred reflections with $9 < 2\theta < 25°$. Crystal data are reported in Table 1. Intensity data were measured on a Siemens P4 diffractometer at 293 K, using Mo-Kα radiation (λ = 0.710 73 Å), using an ω scan method. 7189 Reflections were measured over the range $5 < 2\theta < 50°$ with $-1 < h < 9$, $-12 < k < 12$ and $-22 < l < 22$. The reflections were corrected for Lorentz and polarisation effects and merged to give 5877 independent reflections (R_{int} = 0.03) with 4201 having $I > 2\sigma(I)$ regarded as observed. Only two reflections were available for ψ scans which was insufficient for an empirical absorption correction. The crystal was small and a weak scatterer, with a low μ coefficient, and it was deemed unnecessary to perform an analytical absorption correction.

The structure was solved by direct methods using the program SHELXTL-PC.[26] Two unique molecules were found (*i.e.* $Z = 2$ for each molecule) which could be approximately superimposed, the greatest discrepancy being between the phenyl positions. All hydrogen atoms were included in calculated positions (C–H 0.96 Å), with a common fixed isotropic thermal parameter (0.08 Å^2). The atoms of the bipyridyl group were refined with isotropic thermal parameters. On refining the bipyridyl ligand anisotropically there was no improvement in the *R* factor, but the estimated standard deviations of the bond lengths increased. This group was therefore returned to isotropic refinement. All other atoms were refined with anisotropic thermal parameters. Final cycles of refinement gave $R = 0.0626$, $R' = 0.0815$ ($w^{-1} = \sigma^2F + 0.0012F^2$). The maximum and minimum electron densities in the final ΔF map were 1.40 and −1.42 e Å^{-3} respectively. The mean and maximum shift/error in the final refinement cycle were 0.000 and 0.002.

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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