Facile Synthesis of Four-membered Ring Platinalactam Complexes and the Single-crystal Structure of [Pt{CH(CN)C(O)N(CO$_2$Et)}(cod)] (cod = cycloocta-1,5-diene)†

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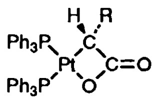
Treatment of the complexes [PtCl$_2$L$_2$] [L = PPh$_3$ or L$_2$ = cycloocta-1,5-diene (cod) or 1,2-bis(diphenylphosphino)ethane (dppe)] with 1 equivalent of ethyl *N*-cyanoacetylcarbamate and an excess of silver(I) oxide in refluxing dichloromethane afforded the new platinalactam complexes [Pt{CH(CN)C(O)N(CO$_2$Et)}L$_2$] (L = PPh$_3$; L$_2$ = cod or dppe) in high yield. A single-crystal X-ray diffraction study on the cod derivative confirms the presence of a planar four-membered platinalactam ring system. Molecular parameters and NMR spectroscopic properties of the metallacycles are discussed, in terms of the differing *trans* influences of the C- and N-donor atoms of the metallacycle.

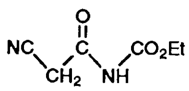
Silver(I) oxide has been shown to be a highly versatile reagent for the synthesis, from metal–halide complexes, of a range of metal–carbon and –nitrogen bonded compounds, including a number of metallacyclic complexes,[1,2] together with other σ-alkyl and alkynyl complexes.[3] The role of this reagent is to act both as a halide-abstracting reagent and as a strong base. These reactions typically proceed readily under mild conditions (refluxing dichloromethane), providing that electron-withdrawing substituents are present on the organic fragment to render the appropriate C–H or N–H bonds acidic. The silver(I) oxide-mediated synthesis of four-membered ring platinalactone complexes **1** has recently been described, starting from *cis*-[PtCl$_2$(PPh$_3$)$_2$] and either dialkyl malonate or PhSO$_2$CH$_2$CO$_2$H in the presence of an excess of silver(I) oxide.[4] We consequently reasoned that ethyl *N*-cyanoacetylcarbamate **I** should be a useful precursor for the synthesis of four-membered ring metallalactam complexes **2**. Relatively few examples of metallalactam complexes have been described previously, with five-membered nickelalactam rings of the type **3** being among the more common metallacycles of this class.[5] Metallalactams are of particular interest in the metal-mediated transformations of organic isocyanates,[5] and in the synthesis of β-lactams.[6]

The mode of binding of the organic fragment to the metal in metallalactams is also of interest. Related four-membered ring metallalactone complexes **1c**[7] and ureylene complexes **4**[8,9] of the platinum metals have been shown to contain planar ring systems. In contrast however, a number of four-membered ring metallacyclobutan-3-one complexes **5** contain highly non-planar metallacyclic rings, with fold angles typically around 50°.[1,10] The bonding of the organic fragment to the metal centre in these cases is subsequently best considered in terms of a significant contribution to the bonding from an η^3-oxodimethylenemethane representation **6**. It is therefore of interest to study the bonding in the formally isoelectronic four-membered metallalactam ring system.

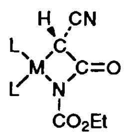
In this paper we report the facile synthesis, under very mild conditions, of a number of platinalactam complexes formed from compound **I** in the presence of silver(I) oxide.



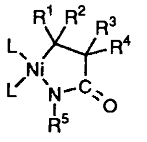
R
1a CO$_2$Me or CO$_2$Et
1b SO$_2$Ph
1c CO$_2$H



I



2a L$_2$ = cod
2b L = PPh$_3$
2c L$_2$ = dppe



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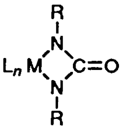

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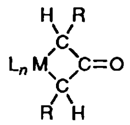

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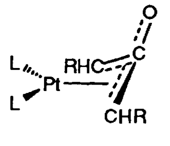

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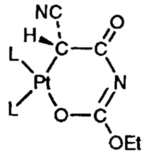

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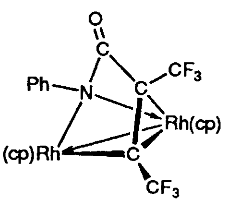

8 cp = η^5-C$_5$H$_5$

Results and Discussion

Treatment of the complexes [PtCl$_2$(cod)] (cod = cycloocta-1,5-diene), *cis*-[PtCl$_2$(PPh$_3$)$_2$] or [PtCl$_2$(dppe)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with 1 equivalent of compound **I** and an excess of silver(I) oxide in refluxing dichloromethane affords the

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

first examples of four-membered ring platinalactam complexes **2a**–**2c** respectively, in high yield. The complexes were isolated as air-stable off-white to pale-tan microcrystalline solids. The NMR spectroscopic evidence was, in our view, not fully conclusive in assigning the complexes as definitively containing a four-membered ring, as opposed to an isomeric six-membered C,O ring system **7**, which might be expected to possess somewhat similar spectroscopic properties, though this may be tentatively ruled out on the basis of the absence of a ^{13}C C=N resonance in the expected region of δ 220. Accordingly a single-crystal X-ray diffraction study was carried out on the cyclooctadiene complex **2a**.

The molecular structure of complex **2a**, together with the atom numbering scheme, is shown in Fig. 1. Intramolecular bond distances and angles are given in Table 1, atomic positional parameters in Table 2. The structure consists of individual platinalactam molecules with no unusual intermolecular contacts. There has only been one previous example of a structurally characterised complex containing the four-membered M–C–C(O)–N metallalactam-type unit, this being the dinuclear rhodium complex **8**.[11] Complex **2a** therefore represents the first structural characterisation of a four-membered metallalactam ring containing a transition metal. The Pt atom, in essentially square-planar geometry, is bonded in the normal fashion to the cod ligand, which adopts the expected twist-boat geometry. The other two co-ordination sites are occupied by the cyanoacetylurethane moiety, co-ordinated through the urethane nitrogen and the acetyl carbon to give a four-membered platinalactam ring system. The ring is virtually planar, with none of the ring atoms more than 0.027 Å from the least-squares plane formed by the Pt, N(1), C(3) and C(1) atoms. The torsion angles O(1)–C(3)–N(1)–Pt 2.6(8) and Pt–C(1)–C(3)–O(1) 2.5(8)° also clearly indicate the near planarity of the metallacycle. The platinalactam ring system thus appears to resemble very closely the planar platinalactone **1**[7] and ureylene **4**[8,9] ring systems, as opposed to the non-planar metallacyclobutan-3-one ring systems **5**.[1,10] Clearly, the presence of a metal-bonded heteroatom provides a strong driving force for planarity in these ring systems. The urethane ester substituent is largely coplanar with the metallacycle, as illustrated by the torsion angles O(1)–C(3)–N(1)–C(2) 2(1), O(3)–C(2)–N(1)–Pt 16(1), O(2)–C(2)–N(1)–Pt 19.7(6), and N(1)–C(2)–O(3)–C(5) 6.4(6)°. The C=O bond distances appear normal: C(3)=O(1) (lactam) 1.196(9) and C(2)=O(2) (ester) 1.215(9) Å. The metallacyclic C(3)–N(1) bond [1.391(10) Å] is comparable to the exocyclic C(2)–N(1) bond distance [1.374(10) Å].

The differing *trans* influences[12] of the CH(CN) and $N(CO_2Et)$ moieties can be clearly seen on examination of the

Table 1 Intramolecular bond lengths (Å) and selected angles (°) for $[Pt\{CH(CN)C(O)N(CO_2Et)\}(cod)]$ **2a**, with estimated standard deviations in parentheses

Pt–N(1)	2.016(6)	Pt–C(12)	2.236(8)
Pt–C(1)	2.069(8)	Pt–C(11)	2.263(7)
Pt–C(16)	2.162(7)	Pt···C(3)	2.634(8)
Pt–C(15)	2.162(8)		
C(1)–C(4)	1.448(12)	C(3)–O(1)	1.196(9)
C(1)–C(3)	1.538(11)	C(3)–N(1)	1.391(10)
C(2)–O(2)	1.215(9)	C(4)–N(2)	1.134(11)
C(2)–O(3)	1.351(9)	C(5)–O(3)	1.441(10)
C(2)–N(1)	1.374(10)	C(5)–C(6)	1.506(12)
Cyclooctadiene ligand			
C(11)–C(12)	1.391(11)	C(14)–C(15)	1.515(13)
C(11)–C(18)	1.499(11)	C(15)–C(16)	1.401(12)
C(12)–C(13)	1.492(11)	C(16)–C(17)	1.486(11)
C(13)–C(14)	1.538(11)	C(17)–C(18)	1.531(11)
N(1)–Pt–C(1)	67.0(3)	C(16)–Pt–C(12)	96.1(3)
N(1)–Pt–C(16)	156.6(3)	C(15)–Pt–C(12)	81.1(3)
C(1)–Pt–C(16)	99.4(3)	N(1)–Pt–C(11)	106.8(3)
N(1)–Pt–C(15)	159.6(3)	C(1)–Pt–C(11)	162.3(3)
C(1)–Pt–C(15)	102.7(3)	C(16)–Pt–C(11)	80.2(3)
N(1)–Pt–C(12)	102.4(3)	C(15)–Pt–C(11)	87.9(3)
C(1)–Pt–C(12)	158.8(3)		
C(4)–C(1)–C(3)	113.9(7)	N(1)–C(3)–C(1)	100.6(6)
C(4)–C(1)–Pt	118.6(5)	N(2)–C(4)–C(1)	178.0(9)
C(3)–C(1)–Pt	92.6(5)	O(3)–C(5)–C(6)	106.8(6)
O(2)–C(2)–O(3)	123.4(7)	C(2)–N(1)–C(3)	123.6(6)
O(2)–C(2)–N(1)	126.7(7)	C(2)–N(1)–Pt	136.5(5)
O(3)–C(2)–N(1)	109.8(6)	C(3)–N(1)–Pt	99.6(5)
O(1)–C(3)–N(1)	130.6(8)	C(2)–O(3)–C(5)	116.0(6)
O(1)–C(3)–C(1)	128.8(8)		
Cycloctadiene ligand			
C(12)–C(11)–C(18)	124.5(7)	C(16)–C(15)–C(14)	124.2(7)
C(12)–C(11)–Pt	70.9(4)	C(16)–C(15)–Pt	71.1(4)
C(18)–C(11)–Pt	110.7(5)	C(14)–C(15)–Pt	112.4(5)
C(11)–C(12)–C(13)	125.7(7)	C(15)–C(16)–C(17)	127.6(8)
C(11)–C(12)–Pt	73.1(4)	C(15)–C(16)–Pt	71.1(5)
C(13)–C(12)–Pt	107.3(5)	C(17)–C(16)–Pt	108.3(5)
C(12)–C(13)–C(14)	113.8(7)	C(16)–C(17)–C(18)	114.5(7)
C(15)–C(14)–C(13)	113.9(7)	C(11)–C(18)–C(17)	111.8(7)

Table 2 Atomic coordinates for $[Pt\{CH(CN)C(O)N(CO_2Et)\}(cod)]$ **2a**

Atom	*x*	*y*	*z*
Pt	0.1698(1)	0.1808(1)	0.0129(1)
C(1)	0.0283(7)	0.2705(8)	0.0598(7)
C(2)	0.1079(7)	−0.0475(7)	0.1670(6)
C(3)	0.0057(7)	0.1570(8)	0.1362(7)
C(4)	0.0459(7)	0.3919(9)	0.1204(7)
C(5)	0.2199(7)	−0.2372(8)	0.1706(7)
C(6)	0.3001(8)	−0.2973(8)	0.0998(9)
N(1)	0.0903(5)	0.0711(6)	0.1156(5)
N(2)	0.0620(7)	0.4852(7)	0.1704(7)
O(1)	−0.0664(5)	0.1469(5)	0.1952(5)
O(2)	0.0682(5)	−0.0859(5)	0.2487(5)
O(3)	0.1834(5)	−0.1157(5)	0.1173(4)
C(11)	0.2805(6)	0.0475(7)	−0.0726(6)
C(12)	0.3446(7)	0.0887(7)	0.0323(7)
C(13)	0.4325(7)	0.1940(7)	0.0482(7)
C(14)	0.3937(8)	0.3146(7)	−0.0241(8)
C(15)	0.2645(7)	0.3397(7)	−0.0427(8)
C(16)	0.1843(7)	0.2941(7)	−0.1373(7)
C(17)	0.2066(8)	0.2057(8)	−0.2296(7)
C(18)	0.2942(7)	0.0990(8)	−0.1880(7)

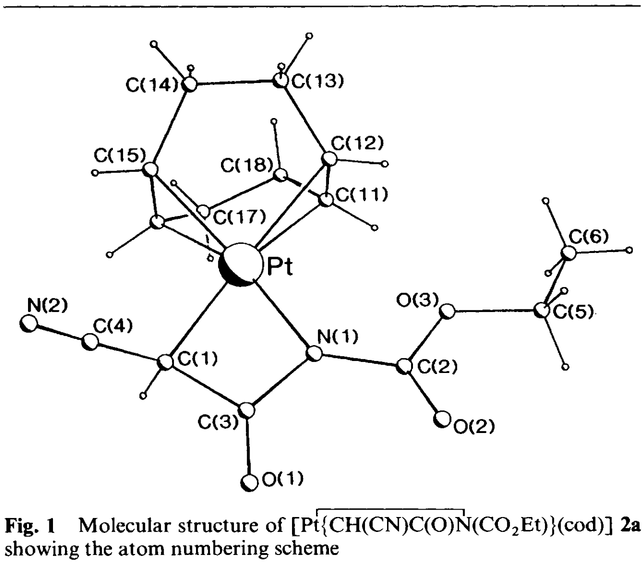

Fig. 1 Molecular structure of $[Pt\{CH(CN)C(O)N(CO_2Et)\}(cod)]$ **2a** showing the atom numbering scheme

Pt–C distances to the co-ordinated cyclooctadiene ligand. Thus, the Pt–C(11) and Pt–C(12) distances [2.263(7) and 2.236(8) Å respectively] opposite the higher *trans*-influence CH(CN) group are significantly longer than the Pt–C(15) and Pt–C(16) distances for the carbon atoms *trans* to the $N(CO_2Et)$ group [2.162(8) and 2.162(7) Å]. The remaining bond distances and angles are unremarkable.

The NMR spectra were consistent with the presence of the platinalactam ring system in solution. The $^{31}P-\{^1H\}$ spectrum of **2b** showed the expected AB pattern due to the two inequivalent triphenylphosphine ligands at δ 10.4 and 19.2, showing couplings to ^{195}Pt of 3801 and 2544 Hz respectively, assigned to phosphines Ph_3P_A and Ph_3P_B *trans* to low and high *trans*-influence $N(CO_2Et)$ and CH(CN) groups respectively. The value of $^1J(PtP_B)$ is very comparable to that observed in the related platinalactone complexes **1** (bearing a similar electron-withdrawing substituent, CO_2R, on the Pt–CH carbon).[7] Interestingly, the value of $^1J(PtP_A)$ resembles more closely those due to phosphine ligands opposite low *trans*-influence oxygen atoms rather than to nitrogen-bonded groups. Values of 2700–3300 Hz are typically observed[12–14] for phosphines *trans* to nitrogen-bonded ligands, including amides, whereas the value of $^1J(PtP_A)$ in **2a** closely resembles that of the platinalactone **1a** (4219 Hz).[7]

The $^{13}C-\{^1H\}$ NMR spectrum of the cod complex provides a large amount of information regarding the binding of the cyanoacetylurethane moiety to the platinum centre. The presence of four inequivalent cod olefinic carbons between δ 88 and 102, shown in Fig. 2, together with four inequivalent cod CH_2 groups is consistent with the asymmetry of the metallacycle. Both sets of resonances clearly divide into two pairs, according to whether they are *cis* or *trans* to the CH(CN) group, with the two CH groups *trans* showing significantly smaller values of *J*(PtC) (67.1 and 67.8, *cf.* 170.3 and 159.3 Hz) due to the high *trans* influence of the alkyl ligand. For comparison, the value of $^1J(PtC)$ for $[PtCl_2(cod)]$ is 152.6 Hz. It is also noteworthy that the two CH carbons *cis* to the asymmetric CH(CN) group show both a larger chemical shift difference, and the largest difference between their $^1J(PtC)$ values, due to their closer proximity to the CH(CN) group. The inequivalence of the pairs of cod CH_2 carbons is less pronounced, due to their greater distance from the asymmetric CH(CN) centre, but is still observable in the values of *J*(PtC) to these carbons, manifested in the shapes of the peaks. Those *trans* to the lower *trans*-influence $N(CO_2Et)$ group have larger values of *J*(PtC) and the satellites are therefore better 'resolved' at the base of these resonances. The PtCH carbon appears at δ 10.8 for **2a** and δ 16.1 for **2b**, showing the expected large one-bond couplings to ^{195}Pt of 503.3 and 386.6 Hz, respectively, consistent with the greater *trans* influence of the phosphine ligand. For **2b**, coupling to both the *trans* (72.9) and *cis* (1.9 Hz) phosphines is also evident, the resonance appearing as the expected doublet of doublets. Assignment of the individual lactam and ester CO resonances was readily accomplished by means of a long-range $^{13}C-^1H$ correlation experiment[15] employing the PtCH proton. The chemical shift of the lactam carbonyl, *e.g.* δ 168.9 for **2a**, is very similar to that for organic β-lactam rings, such as $PhCH_2NC(O)CH_2CH_2$ (1-benzylazetidin-2-one, δ 167.4).[16] The magnitude of $^2J(PtC)$ couplings to the carbonyl groups are much larger for the lactam carbonyl than for the ester (*e.g.* for **2a**; lactam, 147.2; ester, 22.0 Hz). The cyanide carbon appears as a distinctive resonance around δ 120, showing coupling to ^{195}Pt (54.6 Hz for **2a**, 58.7 Hz for **2b**), and in **2b**, coupling to the *trans* P atom of 7.4 Hz.

Similar asymmetries in the binding of the cod ligand to the Pt as a result of the differing *trans* influences of the metallacycle donor atoms are also observed in the ^1H NMR spectrum of complex **2a**. Two of the CH protons appeared to be concentration dependent; typically they overlap to a considerable extent, however in one recorded spectrum they were well resolved. Subsequent attempts to separate the two resonances by addition of a small quantity of the lanthanide shift reagent $[Eu(fod)_3]$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate) were unsuccessful. The PtCH resonance overlapped significantly with that of the cod CH_2 protons in **2a** but could still be resolved, although the ^{195}Pt satellites could not be observed. The methylene protons of the ethyl substituent, as a result of the asymmetric PtCH(CN) group, are diastereotopic, appearing as an ABX_3 multiplet (X = CH_3 protons). Similar behaviour was observed in the related platinalactone ring systems **1a**.[7]

The $^{195}Pt-\{^1H\}$ NMR spectra of the platinalactam complexes revealed the expected features;[17] the cod complex **2a** afforded a singlet at δ 940, whereas the PPh_3 complex **2b** displayed a doublet of doublets due to coupling to the two inequivalent P nuclei. Assignment of the peaks in this case was by means of comparison of the values of $^1J(PtP)$ from the $^{31}P-\{^1H\}$ NMR spectrum.

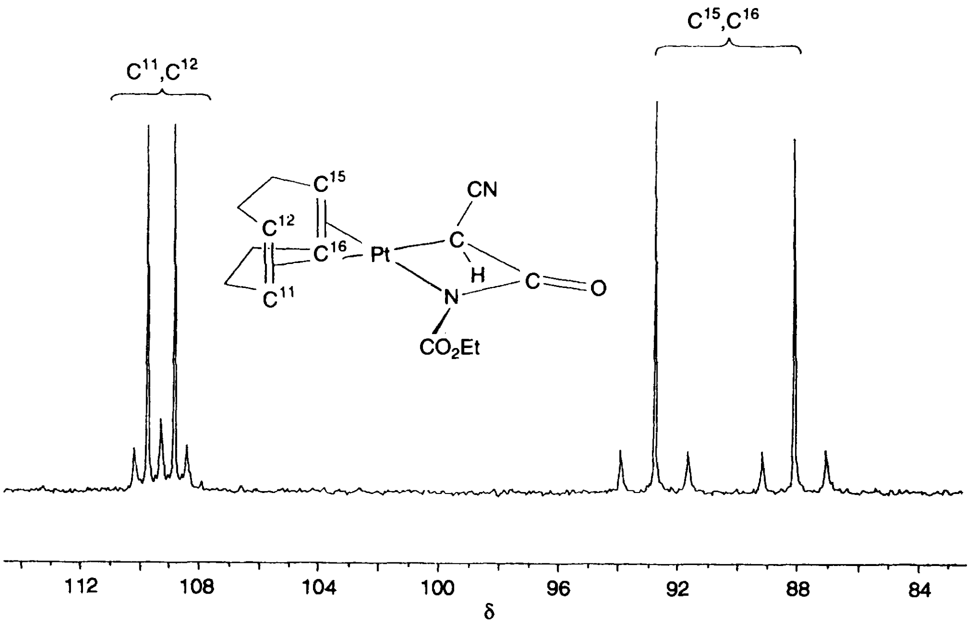

Fig. 2 The $^{13}C-\{^1H\}$ NMR spectrum of the co-ordinated cyclooctadiene alkene groups of $[Pt\{CH(CN)C(O)N(CO_2Et)\}(cod)]$ **2a**

The IR spectra of the platinalactam complexes showed weak bands due to the cyano group at 2186 cm^{-1} for **2a** and 2201 cm^{-1} for **2b**, shifted to lower frequency compared to the free urethane **I** (2259 cm^{-1}), presumably due to the substitution of two hydrogen atoms by a highly electron-rich platinum atom. A band attributable to the two C=O groups is also observed in the range 1728–1735 cm^{-1}. Carbonyl groups in four-membered ring organic lactams appear in the range 1730–1760 cm^{-1}. This is again consistent with the absence of any significant ring strain in compounds **2**, since the presence of ring strain in cyclic compounds is well known to increase the stretching frequency of exocyclic unsaturated groups.[18] In the urethane **I** the C=O groups appear at 1765 cm^{-1}, whereas for related transition metal–ureylene complexes **4** the carbonyl absorptions appear to somewhat lower frequency, in the range 1608–1698 cm^{-1}.[8,19] Fast atom bombardment (FAB) mass spectrometry of **2a** in a *m*-nitrobenzyl alcohol matrix confirmed the value of this technique in metallacyclic chemistry, showing a molecular ion due to $[M + H]^+$ at *m*/*z* 457. There was excellent agreement between the observed and calculated isotopomer distributions for this ion.

Preliminary studies indicate that the substitution labile cod ligand of complex **2a** can readily be displaced, allowing for the potential synthesis of a range of platinalactam derivatives. For example, treatment of a dichloromethane solution of **2a** with 2 mol equivalents of PPh_3 led to the isolation of **2b**, identified by $^{31}P-\{^1H\}$ NMR spectroscopy. Studies on the synthesis and chemistry of metallalactam complexes of other metals using urethane **I** and silver(I) oxide are in progress, and will be reported separately.

Experimental

General.—Triphenylphosphine (Pressure Chemical Co.), and ethyl *N*-cyanoacetylcarbamate **I** (Aldrich) were used as supplied; dppe[20] and silver(I) oxide[21] were prepared by minor modifications of the literature procedures. The complex $[PtCl_2(cod)]$ was prepared using a modification of the literature procedure,[22] with $PtCl_2$ in place of $K_2[PtCl_4]$; *cis*-$[PtCl_2(PPh_3)_2]$ and$[PtCl_2(dppe)]$ were prepared by ligand displacement of cod from $[PtCl_2(cod)]$ as described previously.[23] Reactions using silver(I) oxide were carried out under a nitrogen atmosphere (as a precautionary measure), in dichloromethane which was dried and distilled under nitrogen from P_4O_{10} prior to use. Other solvents were distilled from appropriate drying agents prior to use. The platinum complexes were air-stable and were recrystallised from solvents without exclusion of air. Melting points were recorded on a Reichert hot-stage apparatus and are uncorrected.

The IR spectra were recorded as KBr discs on a Bio-Rad FTS-40 spectrometer, ^1H and ^{13}C NMR spectra in $CDCl_3$ solution on a Bruker AC300P spectrometer at 300.13 and 75.47 MHz respectively, $^{31}P-\{^1H\}$ and $^{195}Pt-\{^1H\}$ spectra in CH_2Cl_2 solution, with a D_2O lock (by the concentric tube method) on a JEOL FX90Q spectrometer) $^{31}P-\{^1H\}$ spectra at 36.23 MHz with 85% H_3PO_4 as external reference and $^{195}Pt-\{^1H\}$ at 19.13 MHz with saturated aqueous $K_2[PtCl_4]$ as external reference.

Syntheses.—$[\overline{\mathrm{Pt\{CH(CN)C(O)N}}(\mathrm{CO_2Et})\}(\mathrm{cod})]$ **2a**. A mixture of $[PtCl_2(cod)]$ (0.4663 g, 1.25 mmol), urethane **I** (0.197 g, 1.26 mmol) and silver(I) oxide (1.19 g, excess) in dichloromethane (50 cm^3) was refluxed for 80 h under nitrogen. The solution was filtered by gravity to remove the insoluble silver salts. The resulting orange-tan solution was reduced in volume to *ca.* 3 cm^3 *in vacuo*, and diethyl ether (4 cm^3) added slowly, upon which precipitation commenced. The solution was allowed to stand overnight, yielding pale tan crystals of crystallographic quality. More ether (40 cm^3) was added to complete precipitation. The precipitate was filtered off and dried to give complex **2a** (0.43 g, 75%) (Found: C, 36.35; H, 3.60; N, 5.95. $C_{14}H_{18}N_2O_3Pt$ requires C, 36.75; H, 3.95; N, 6.10%), m.p. 193–195 °C. IR: ν(CN) at 2186s, ν(C=O) at 1728vs cm^{-1}. FAB mass spectrum (positive-ion mode, *m*-nitrobenzyl alcohol matrix): $[M + H]^+$ at *m*/*z* 457. NMR: ^1H, δ 6.20–5.98 (m, 2 H, CH of cod), 5.10 [m, 2 H, CH of cod, ^2J(PtH) 63.3], 4.15 [q, 2 H, CH_2 of Et, *J*(HH) 7.2], 2.61–2.28 (m, 8 H, CH_2 of cod), 2.45 [s, 1 H, CH of ring, ^2J(PtH) not discernible due to overlap], and 1.25 [t, 3 H, CH_3 of Et, *J*(HH) 7.2]; $^{13}C-\{^1H\}$, δ 168.9 [s, C=O of lactam, ^2J(PtC) 147.2], 155.4 [s, C=O of ester, ^2J(PtC) 22.0], 119.4 [s, CN, ^2J(PtC) 54.6], 109.7 [s, olefinic $CH_{trans\ C}$, ^1J(PtC) 67.1], 108.8 [s, olefinic $CH_{trans\ C}$, ^1J(PtC) 67.8], 92.8 [s, olefinic $CH_{trans\ N}$, ^1J(PtC) 170.3], 88.1 [s, olefinic $CH_{trans\ N}$, ^1J(PtC) 159.3], 62.1 (s, CH_2 of Et), 32.7 (s, CH_2 of cod), 30.4 (s, CH_2 of cod), 29.6 [s, CH_2 of cod), 28.8 (s, CH_2 of cod), 14.4 (s, CH_3 of Et) and 10.8 [s, CH, ^1J(PtC) 503.3 Hz]; $^{195}Pt-\{^1H\}$, δ 940 (s).

$[\overline{\mathrm{Pt\{CH(CN)C(O)N}}(\mathrm{CO_2Et})\}(\mathrm{PPh_3})_2]$ **2b**. A mixture of *cis*-$[PtCl_2(PPh_3)_2]$ (0.292 g, 0.369 mmol), urethane **I** (0.082 g, 0.0528 mmol) and silver(I) oxide (0.515 g, excess) in dichloromethane (50 cm^3) as above gave a tan solution. The reaction mixture was filtered to remove the silver salts and, after reduction in volume to 3 cm^3, addition of diethyl ether gave the product **2b** (0.254 g, 79%) (Found: C, 56.90; H, 4.10; N, 3.10. $C_{42}H_{36}N_2O_3P_2Pt$ requires C, 57.75; H, 4.15; N, 3.20%), m.p. 236–238 °C. IR: ν(CN) at 2201s, ν(C=O) at 1738vs cm^{-1}. NMR: ^1H, δ 7.54–7.15 (m, 30 H, Ph), 3.06 (m, 2 H, CH_2 of Et, diastereotopic protons), 1.67 [dd, 1 H, PtCH, $^3J(PH)_{trans}$ 7.01, $^3J(PH)_{cis}$ 3.71, ^2J(PtH) 51.2] and 0.27 [t, 3 H, CH_3 of Et, *J*(HH) 6.9]; $^{13}C-\{^1H\}$, δ 171.9 [d, C=O of lactam, ^2J(PtC) 124.2, $^3J(PC)_{trans}$ 26.6], 155.4 [d, C=O of ester, ^2J(PtC) not discernible due to overlap with main resonance, ^3J(PC) 7.4], 135–127 (m, Ph), 121.8 [d, CN, ^2J(PtC) 58.7, ^3J(PC) 7.4], 59.9 (s, CH_2 of Et), 16.1 [dd, PtCH, $^2J(PC)_{trans}$ 72.9, $^2J(PC)_{cis}$ 1.9, ^1J(PtC) 386.6], and 13.0 (s, CH_3 of Et); $^{31}P-\{^1H\}$, AB spin system, δ 19.2 [d, $P_{B(trans\ C)}$, ^1J(PtP) 2544, ^2J(PP) 17.1] and 10.4 [d, $P_{A(trans\ N)}$, ^1J(PtP) 3801, ^2J(PP) 17.1]; $^{195}Pt-\{^1H\}$, δ 50 [dd, ^1J(PtP) 3804, 2515 Hz].

$[\overline{\mathrm{Pt\{CH(CN)C(O)N}}(\mathrm{CO_2Et})\}(\mathrm{dppe})]$ **2c**. A mixture of $[PtCl_2(dppe)]$ (0.206 g, 0.310 mmol), the urethane **I** (0.049 g, 0.314 mmol) and silver(I) oxide (0.510 g, excess) reacted in dichloromethane (50 cm^3) as for complex **2a** above. The reaction yielded a tan solution after filtering off the silver salts, and addition of diethyl ether to the filtrate followed by filtration and drying *in vacuo* gave complex **2c** (0.224 g, 92%) (Found: C, 51.30; H, 3.80; N, 3.65. $C_{32}H_{30}N_2O_3P_2Pt$ requires C, 51.40; H, 4.05; N, 3.75%), m.p. 249–251 °C. IR: ν(CN) at 2211s, ν(C=O) at 1735 cm^{-1}. NMR: ^1H, δ 7.91–7.34 (m, 20 H, Ph), 3.48–3.36 (m, 2 H, CH_2 of ester, diastereotopic), 2.6–1.8 (m, 4 H, CH_2 of dppe), 2.23 [dd, PtCH, $^3J(PH)_{trans}$ 9.6, $^3J(PH)_{cis}$ 1.8, ^2J(PtH) 76.6], and 0.43 [t, 3 H, CH_3, *J*(HH) 7.1]; $^{31}P-\{^1H\}$, AB spin system, δ 36.6 [d, $P_{A(trans\ N)}$, ^1J(PtP) 3469, ^2J(PP) 5] and 45.5 [d, P_B, ^1J(PtP) 2600 Hz].

Complex **2b** *from* **2a**. Complex **2a** and triphenylphosphine (2 mol equivalents) were stirred in dichloromethane for 10 min. The solution was reduced in volume *in vacuo*, and precipitation enforced by the addition of diethyl ether. The tan precipitate was filtered off to give complex **2b**, which was identified from its $^{31}P-\{^1H\}$ NMR spectrum.

Crystal Structure Determination of $[\overline{\mathrm{Pt\{CH(CN)C(O)N}}(\mathrm{CO_2Et})\}(\mathrm{cod})]$ **2a**.—The space group and crystal quality were determined by precession photography.

Crystal data. $C_{14}H_{18}N_2O_3Pt$, $M = 457.4$, monoclinic, space group $P2_1/n$, $a = 11.737(2)$, $b = 10.409(2)$, $c = 11.798(2)$ Å, $\beta = 100.79(3)°$, $U = 1415.7(8)$ Å^3 (from 30 reflections, $10 < 2\theta < 25°$), $\lambda = 0.710\,73$ Å, $D_c = 2.146$ g cm^{-3}, $Z = 4$, $F(000)$ 872, μ(Mo-Kα) = 10 mm^{-1}, $T = 133$ K.

Data collection. Nicolet R3 automatic diffractometer, ω scans, on a crystal of dimensions 0.42 × 0.28 × 0.26 mm. A total of 2163 reflections were collected to $2\theta_{max}$ 45°, of which 1850 were unique ($R_{merge} = 0.0187$ after absorption correction; $T_{max,min}$ 0.825, 0.466), with 1643 observed $[I > 2\sigma(I)]$.

Structure analysis and refinement. The structure was solved by Patterson methods, and developed routinely. Full-matrix least-squares refinement was based on F^2 with all non-hydrogen atoms anisotropic and with hydrogen atoms included in calculated positions with isotropic thermal parameters 1.2 times the equivalent U_{iso} of the carbon atom to which they are attached. The refinement converged with $R_1 = 0.0312$, $wR^2 = 0.0773$, where $w = [\sigma^2(F_o^2) + (0.0593P)^2]^{-1}$, $P = (F_o^2 + 2F^2)/3$ and goodness of fit 1.047. A final difference map showed no feature greater than +1.69 or −1.22 e Å^{-3}, adjacent to the Pt atom. Programs used were SHELXS 86[24] and SHELXL 93.[25]

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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