

# Synthesis and characterisation of platinum(II) ureylene complexes, and the X-ray structure of $[\text{Pt}\{\text{PhNC}(\text{O})\text{NAd}\}(\text{COD})]$ (Ad = 1-adamantyl, COD = 1,5-cyclo-octadiene)

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## Abstract

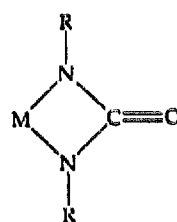
Reaction of  $[\text{PtCl}_2(\text{COD})]$  or  $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$  with a range of mono- and di-substituted ureas, together with urea itself, and an excess of silver(I) oxide gives ureylene complexes **3** and **4** containing the  $\text{Pt-N-C(O)-N}$  four-membered ring system. The complexes have been fully characterised by multinuclear NMR and IR spectroscopies, electrospray mass spectrometry, and a single-crystal X-ray structure of the complex  $[\text{Pt}\{\text{PhNC}(\text{O})\text{NAd}\}(\text{COD})]$  (Ad = 1-adamantyl, COD = 1,5-cyclo-octadiene).

**Keywords:** Platinum; Ureylene; Urea; Metallacycle; Crystal structure; Electrospray

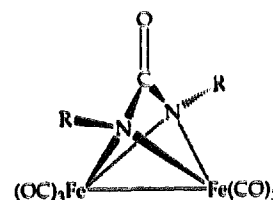
## 1. Introduction

Transition-metal ureylene complexes, containing the four-membered  $\text{M-N-C(O)-N}$  ring system **1** have been known for some years. Such complexes can be formulated as complexes of urea dianions, and a number of methods have been reported for their synthesis, which are summarised in two reviews [1,2]. These include reactions of low-valent ruthenium, palladium, platinum, rhodium and iridium complexes with isocyanates and organic azides [3] and the reactions of isocyanates with imido complexes of osmium [4] and rhenium [5,6], and with oxo-complexes of ruthenium and osmium [7]. Reaction of  $[\text{Pd}(\text{OAc})_2]$ , 1,10-phenanthroline (phen), and CO in  $\text{PhNO}_2$  solvent gave the complex  $[\text{Pd}\{\text{C}(\text{O})\text{NPhOC}(\text{O})\}(\text{phen})]$  which, upon reaction with phenyl isocyanate followed by heating, gave the palladaureylene complex  $[\text{Pd}\{\text{NPhC}(\text{O})\text{NPh}\}(\text{phen})]$  [8]. Dinuclear complexes **2** have also been prepared by the reaction of  $\text{Fe}_3(\text{CO})_{12}$  or  $\text{Fe}_2(\text{CO})_9$  with organic azides [9]. A number of tri- and tetra-nuclear palladium com-

plexes containing bridging urea dianions have also been recently reported [10].



**1**



**2**

R = Me, Ph, *p*-MeOC<sub>6</sub>H<sub>4</sub>

Synthetic routes to ureylene complexes starting from the appropriate parent urea have also been reported, including oxidative addition of 1,3-di-*p*-toluenesulphonylurea to low-valent metal complexes [2,3,11], and the reaction of  $[\text{Pd}(\text{OAc})_2(\text{phen})]$  with the dilithio salt of 1,3-diphenylurea [3]. In a recent communication [12] we reported that silver(I) oxide can be used to synthesise platinum(II) ureylene complexes, together with the first mononuclear examples of isoelectronic

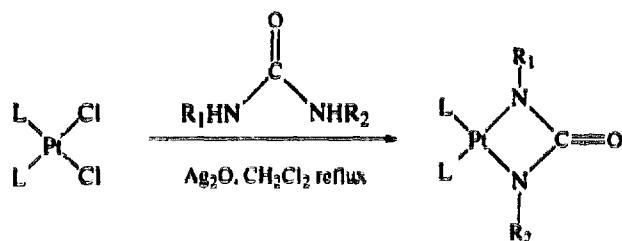
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triazatrimethylenemethane complexes formally derived from the *N,N',N''*-triphenylguanidine dianion. Related four-membered ring systems Pt–RN–X–NR (*X* = SO<sub>2</sub> or P(O)Ph) have also been synthesised using silver(I) oxide [13,14], and by the reaction of *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] with SO<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub> or SO<sub>2</sub>Cl<sub>2</sub> in liquid ammonia [15]. Here we report our detailed studies on the silver(I) oxide-mediated synthesis of platinum(II) ureylene complexes **3**, containing ancillary cyclo-octa-1,5-diene and triphenylphosphine ligands, together with the X-ray structure of one derivative.

## 2. Results and discussion

### 2.1. Syntheses

The silver(I) oxide-mediated reaction of platinum(II) halide complexes with ureas has been investigated as a general synthetic method for ureylene complexes. A wide range of ureas has been investigated in order to determine the general applicability of the method, which is shown here.



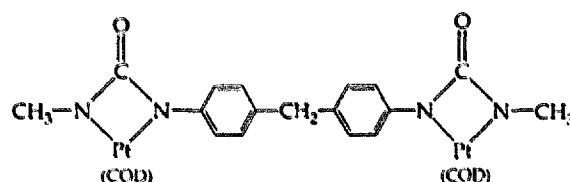
	L or L-L	R <sub>1</sub>	R <sub>2</sub>
<b>3a</b>	COD	Ph	Ph
<b>3b</b>	PPh <sub>3</sub>	Ph	Ph
<b>3c</b>	COD	Ph	2-Py
<b>3d</b>	COD	Ph	1-Ad
<b>3e</b>	COD	Ph	Me
<b>3f</b>	COD	Me	C(O)Me
<b>3g</b>	COD		
<b>3h</b>	PPh <sub>3</sub>	Ph	H
<b>3i</b>	PPh <sub>3</sub>	H	H

Thus, reaction of either [PtCl<sub>2</sub>(COD)] (COD = 1,5-cyclo-octadiene) or *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] with 1 mol equivalent of the appropriate urea and an excess of silver(I) oxide proceeds smoothly in refluxing dichloromethane, to give the platinum(II) ureylene complexes **3a–g** as yellow crystalline solids. Silver(I) oxide has been found to be a versatile reagent for the synthesis of a diverse range of metallacyclic complexes, con-

taining metal–carbon, –nitrogen, –oxygen or –sulphur bonds [16]. Typically, reactions can be carried out in air, without recourse to the use of air- and/or moisture-sensitive reagents, and the by-products (silver chloride and water) are readily removed, facilitating simple product isolation.

Typically, reactions of ureas containing at least one electron-withdrawing aromatic or acetyl substituent on nitrogen proceeded relatively quickly. Attempted synthesis of a ureylene complex derived from 1,3-dimethyl urea was unsuccessful by this methodology. This is presumably a consequence of the reduced acidity of the aliphatic-substituted ureas over their aromatic-substituted counterparts. Attempts at synthesising the unsubstituted parent ureylene complex [Pt(NHCO)NH](COD) led to a complex mixture of products. However, when the reaction is carried out using *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] the ureylene complex **3i** can be identified by <sup>31</sup>P NMR spectroscopy and electro-spray mass spectrometry (ESMS), though it decomposes to a mixture of unidentified products upon standing in dichloromethane solution. Presumably, complexes containing *N*-phenyl substituents have stabilised Pt–N bonds, though even in the case of phenyl urea, the bis(triphenylphosphine)platinum complex **3h** was still of marginal stability, and could not be fully characterised. This decreased stability of the unsubstituted metallacycles is in contrast with the related systems [Pt(NHXNH)(PPh<sub>3</sub>)<sub>2</sub>] (*X* = SO<sub>2</sub> or P(O)Ph), which have been reported to be stable [13–15].

The general methodology described above was also employed in the synthesis of a dinuclear ureylene complex. Reaction of diphenylmethane-4,4'-di-isocyanate with excess methylamine gave the bis(urea) (CH<sub>3</sub>NHC(O)NHC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CH<sub>2</sub> as an insoluble white solid, which, upon reaction with 2 mol equivalents of [PtCl<sub>2</sub>(COD)] yields the dinuclear complex **4**. There was no evidence of any monosubstituted complex being formed.



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In conclusion, the silver(I) oxide method for the synthesis of platinum(II) ureylene complexes is generally applicable for disubstituted ureas, particularly those containing at least one electron-withdrawing substituent. The procedure is particularly useful for the synthesis of

Table 1  
Final positional parameters and equivalent thermal parameters for [Pt(PhNC(O)NAd)(COD)] 3d, with estimated standard deviations in parentheses

Atom	x	y	z	$U_{eq}$
Pt	0.0176(1)	0.3286(1)	0.3615(1)	0.017(1)
O(1)	-0.3914(7)	0.2916(7)	0.3878(5)	0.026(1)
N(2)	-0.1498(8)	0.3206(8)	0.4516(5)	0.021(2)
N(1)	-0.1748(8)	0.3319(8)	0.2947(5)	0.021(2)
C(1)	-0.256(1)	0.3085(9)	0.3783(6)	0.021(2)
C(2)	-0.247(1)	0.3275(9)	0.1984(6)	0.019(2)
C(3)	-0.312(1)	0.4418(9)	0.1930(7)	0.023(2)
C(4)	-0.376(1)	0.1866(9)	0.1774(7)	0.025(2)
C(5)	-0.131(1)	0.355(1)	0.1184(7)	0.027(2)
C(11)	-0.193(1)	0.2618(9)	0.5433(6)	0.021(2)
C(12)	-0.086(1)	0.3082(9)	0.6217(7)	0.023(2)
C(13)	-0.122(1)	0.252(1)	0.7122(7)	0.032(2)
C(15)	-0.367(1)	0.101(1)	0.6513(7)	0.027(2)
C(14)	-0.263(1)	0.149(1)	0.7289(7)	0.032(2)
C(16)	-0.333(1)	0.1565(9)	0.5610(7)	0.025(2)
C(21)	-0.205(1)	0.352(1)	0.0177(7)	0.033(2)
C(22)	-0.268(1)	0.466(1)	0.0152(8)	0.034(2)
C(23)	-0.385(1)	0.440(1)	0.0930(7)	0.028(2)
C(24)	-0.516(1)	0.299(1)	0.0742(7)	0.030(2)
C(25)	-0.452(1)	0.186(1)	0.0770(7)	0.031(2)
C(26)	-0.332(1)	0.211(1)	-0.0009(7)	0.037(3)
C(31)	0.147(1)	0.267(1)	0.2552(7)	0.025(2)
C(32)	0.241(1)	0.193(1)	0.3007(7)	0.029(2)
C(33)	0.201(1)	0.153(1)	0.4058(7)	0.031(2)
C(34)	0.151(1)	0.253(1)	0.4600(7)	0.025(2)
C(35)	0.221(1)	0.397(1)	0.4565(7)	0.024(2)
C(36)	0.367(1)	0.474(1)	0.4042(7)	0.026(2)
C(37)	0.336(1)	0.513(1)	0.3004(7)	0.027(2)
C(38)	0.1927(9)	0.4099(9)	0.2542(6)	0.020(2)
C(1)	0.1989(5)	0.0225(4)	0.6476(4)	0.091(1)
C(2)	0.3409(8)	0.2023(6)	0.8109(4)	0.120(2)
C(4)	0.290(1)	0.181(1)	0.6880(9)	0.106(7)
C(9)	0.040(1)	0.931(1)	0.0790(9)	0.089(8)
C(9)	-0.076(1)	0.940(1)	0.0390(9)	0.13(1)
C(9)	-0.106(1)	0.958(1)	0.1390(9)	0.14(1)

## 2.2. X-ray crystal structure of [Pt(PhNC(O)NAd)(COD)] 3d

In order to assess the bonding in the platinaureylene system, a single-crystal X-ray diffraction study has been carried out on the asymmetrically substituted derivative 3d. The presence of two electronically and sterically different substituents (phenyl and 1-adamantyl) was desirable since there is only one other structural determination on an asymmetrically substituted ureylene complex [6], though a number of symmetric derivatives have been characterised. Fractional atomic coordinates for the structure are given in Table 1, while Table 2 gives selected intramolecular bond distances and angles.

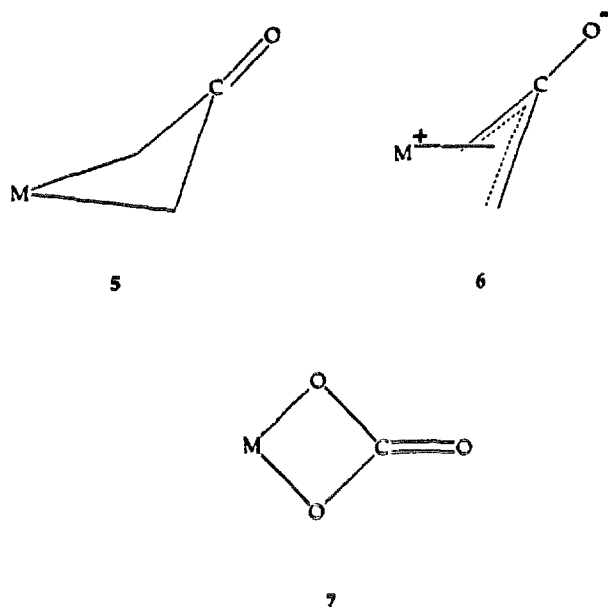
The structure (Fig. 1) confirms the expected platinaureylene structure 3d, which is analogous to other ureylene structures reported for Cr, Fe, Co, Mo, Ru, Pd, W, Re and Os. It is noteworthy that ureylene complexes are *N,N*-bonded, in marked contrast to platinum(II) complexes of *N,S*-chelated thiourea dianions [17], where the affinity of the soft sulphur atom for the metal centre dictates the coordination mode. As is normal with platinumacyclic complexes, the metal is coordinated in a distorted square-planar arrangement, with the bidentate ureylene and  $\eta^4$ -coordinated 1,5-cyclo-octadiene ligands lying in the plane. The main distortion is the N(1)–Pt–N(2) bite angle, which in this case is 64.7(3)°, deviating by 25.3° from a regular square-plane. This is due to the geometrical constraint set by the ligand, whose bonds have insufficient flexibility to adopt the 90° angle required for a regular square-planar arrangement. The metallacyclic is essentially planar (with no atom deviating from the least-squares plane by more than 0.068(5) Å, for C(1)), with the carbonyl group also lying in-plane as predicted. As expected for an unsymmetrical ureylene ligand, the N(1)–Pt and N(2)–Pt bond distances are not equal, with the former possibly being slightly longer (0.027(11) Å), though the estimated standard deviations do not permit an accurate comparison.

asymmetrically substituted complexes, which are not readily accessible by other routes, such as from isocyanates.

Table 2  
Selected bond lengths (Å) and angles (deg) for [Pt(PhNC(O)NAd)(COD)] 3d, with estimated standard deviations in parentheses

Bond lengths			
Pt–N(1)	2.048(8)	Pt–N(2)	2.021(8)
Pt–C(31)	2.177(9)	Pt–C(38)	2.178(9)
Pt–C(34)	2.185(9)	Pt–C(35)	2.191(9)
N(1)–C(1)	1.34(1)	N(2)–C(1)	1.39(1)
C(1)–O(1)	1.24(1)	N(1)–C(2)	1.47(1)
N(2)–C(11)	1.41(1)	C(31)–C(38)	1.38(1)
C(34)–C(35)	1.39(1)		
Bond angles			
N(1)–Pt–N(2)	64.7(3)	Pt–N(1)–C(1)	94.7(5)
Pt–N(2)–C(1)	95.5(5)	Pt–N(2)–C(11)	133.2(6)
Pt–N(1)–C(2)	142.4(6)	N(1)–C(1)–N(2)	104.1(7)
N(1)–C(1)–O(1)	128.4(8)	N(2)–C(1)–O(1)	127.3(8)

The metal–ureylene system is formally isoelectronic with the  $MCH_2C(O)CH_2$  oxodimethylenemethane system. Indeed, the former may be considered as oxadiazatrimethylenemethane complexes. However, a number of structural studies [18,19] on these complexes exclusively show the presence of highly puckered four-membered rings **5**, and the bonding is best rationalised in terms of an  $\eta^3$  contribution **6** to the bonding. Ureylene complexes accordingly more closely resemble the isoelectronic carbonato complexes **7**, which also have planar ring systems (see for example Ref. [20]).



The Pt–CH bond distances do not vary significantly (2.178(9) Å compared with 2.188(9) Å). However, the differing trans influences of the two inequivalent nitrogen atoms has an effect on the  $^1H$  and  $^{13}C$  NMR spectra of the  $CH=CH$  groups of the COD ligand. Further discussion on the NMR spectroscopic properties appears in Section 2.3.

The dihedral angle between the strictly planar phenyl ring and the metallacyclic ring is  $42.0(3)^\circ$ . The alkene moieties of the COD ligand are almost perpendicular to the metallacycle with a dihedral angle of  $87.0(4)^\circ$  between the planes defined by the platinum–carbon bonds, and the metallacycle. The remaining bond lengths and angles appear normal.

### 2.3. Spectroscopic and mass spectrometric characterisation

The complexes have been fully characterised by multinuclear NMR and IR spectroscopies, elemental analysis and ESMS. The  $^{31}P$ –( $^1H$ ) NMR spectrum of

the triphenylphosphine complex **3b** shows the expected single resonance, with coupling to  $^{195}Pt$  of 3337 Hz. This is characteristic of phosphine ligands trans to amide ligands, such as in the related complexes  $[Pt\{PhNS(O)_2NPh\}(PPh_3)_2]$  (3501 Hz) and  $[Pt\{PhNP(O)(Ph)NPh\}(PPh_3)_2]$  (3401 Hz) [13]. The trans influence of the diphenylureylene ligand is lower than that of the amide ligand in the related lactam complex  $[Pt\{CH(COMe)C(O)NPh\}(PPh_3)_2]$ , where the  $PPh_3$  ligand trans to the amide shows  $^1J(PtP)$  3709 Hz [18]. For the unsubstituted ureylene complex **3i**, the value of  $^1J(PtP)$  is 3291 Hz, while those for the unsymmetrical complex **3h** (3174 and 3423 Hz) lie outside the range defined by the two symmetrical structures **3a** and **3i**.

$^{13}C$  and  $^1H$  NMR data for the cyclo-octadiene olefinic resonances of the various ureylene complexes **3** are summarised in Table 3. It is evident that there is no obvious trend in both the  $^1H$  and  $^{13}C$  chemical shifts which range from 4.7 to 6.5 ppm and from 91 to 99 ppm respectively, regardless of the aromaticity or electron-withdrawing characteristics of the nitrogen substituent trans to it. However, if the  $^1H$  shift for any particular group is larger, the corresponding  $^{13}C$  is also greater, as is typical (although by no means necessary) in NMR generally. The coupling constants, however, are much more diagnostic. The more strongly electron-withdrawing groups (i.e. phenyl and acetyl) consistently induced higher  $^2J$  (for  $^{195}Pt$ – $^1H$ ) and lower  $^1J$  (for  $^{195}Pt$ – $^{13}C$ ) values to the coordinated COD ligand than their respective lesser electron-withdrawing (alkyl) counterparts, with the exception of  $[Pt(PhNC(O)NAd)(COD)]$  **3d** where the  $^1H$  coupling constants were identical within the experimental accuracy of the spectrometer.

The IR spectra of the ureylene complexes show two bands in the region  $1580$ – $1700\text{ cm}^{-1}$ . In comparison, other mononuclear ureylene complexes have been reported to have  $\nu(C=O)$  values in the range  $1608$ – $1698\text{ cm}^{-1}$  [4] including values of  $1615\text{ cm}^{-1}$  for  $[Pd(NPhC(O)NPh)(phen)]$  and  $1693\text{ cm}^{-1}$  for  $[Pt(NRC(O)NR)(PPh_3)_2]$  ( $R = p$ -toluenesulphonyl).

#### 2.3.1. ESMS

ESMS is a relatively recent ionisation technique, which is well-suited to the analysis of involatile transition metal complexes. The technique typically yields strong parent ions, providing the complex is either charged, or possesses 'basic' oxygen or nitrogen atoms which can associate with protons, giving parent ions of the  $[M+H]^+$  type. The ureylene complexes typically give  $[M+H]^+$  ions under a range of different cone voltages, though in several cases other ions were apparent. Generally, the strongest  $[M+H]^+$  ions were observed using cone voltages around 50 V. Complexes of  $[(COD)Pt(OH)]^+$ , alone, or with one or two molecules of MeCN mobile phase were also sometimes observed.

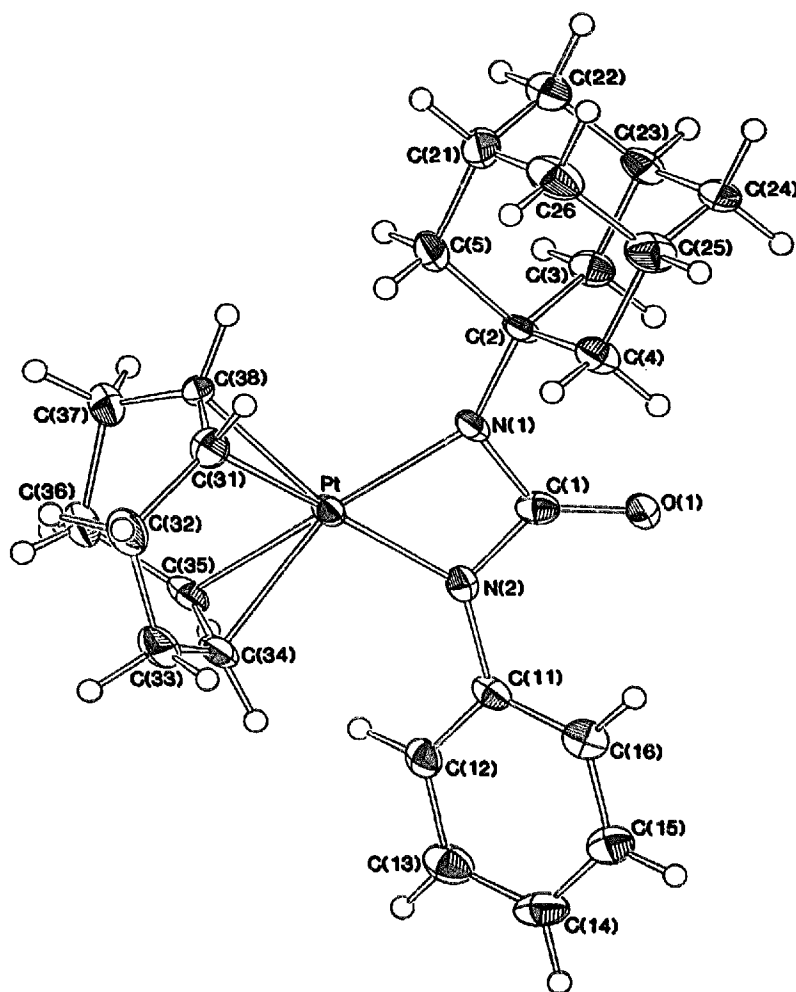


Fig. 1. ORTEP diagram of the molecular structure of the ureylene complex  $[\text{Pt}(\text{NPhC}(\text{O})\text{NAd})(\text{COD})]$  **3d**, showing the atom numbering scheme. Atoms are represented at the 50% probability level.

It is likely that these ions arise from incomplete reaction of the starting  $[\text{PtCl}_2(\text{COD})]$ , and that abstraction of chloride by  $\text{Ag}^+$  is the first step in the synthesis of the ureylene complexes. As expected, loss of acetonitrile proceeds with increased cone voltage.

For the diphenyl ureylene complex **3a**, loss of  $\text{Ph-NCO}$  occurred at higher cone voltages. Fig. 2 shows the positive-ion spectrum of this complex at a cone voltage of 50 V, together with a comparison of the observed and calculated isotope distributions for the parent  $[\text{M} + \text{H}]^+$

Table 3

A comparison of cyclo-octadiene olefinic  $^1\text{H}$  and  $^{13}\text{C}$  resonances and coupling constants for the various ureylene complexes  $[\text{Pt}(\text{NXC}(\text{O})\text{NY})(\text{COD})]$  **3**

Substituent (X,Y)	Pt-CH group trans to X substituent				Pt-CH group trans to Y substituent			
	$\delta$ (ppm)		$J$ (Hz)		$\delta$ (ppm)		$J$ (Hz)	
	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}-^{195}\text{Pt}$	$^{13}\text{C}-^{195}\text{Pt}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}-^{195}\text{Pt}$	$^{13}\text{C}-^{195}\text{Pt}$
X,Y = Ph <b>3a</b>	5.20	94.1	59.4	141.7	5.20	94.1	59.4	141.7
X = Ph; Y = Py <b>3c</b>	6.48	95.2	64.6	131.6	5.21	94.1	63.1	145.5
X = Ph; Y = Ad <b>3d</b>	4.73	90.7	60.8	128.6	5.63	93.8	61.0	142.8
X = Ph; Y = $\text{CH}_3$ <b>3e</b>	5.08	93.7 <sup>a</sup>	— <sup>b</sup>	133.1	5.13	92.1 <sup>a</sup>	53.9	143.5
X = COMe; Y = Me <b>3f</b>	5.17	93.5	62.4	128.7	6.08	93.9	61.3	141.1
X = $\text{SO}_2\text{C}_6\text{H}_4\text{Cl}$ ; Y = $\text{C}_3\text{N}_3(\text{OMe})\text{Me}$ <b>3g</b>	6.41	98.6	68.2	139.1	6.33	97.1	61.0	153.8

<sup>a</sup> Assigned following the basic trend in coupling constants observed for other related species.

<sup>b</sup> Not resolved.

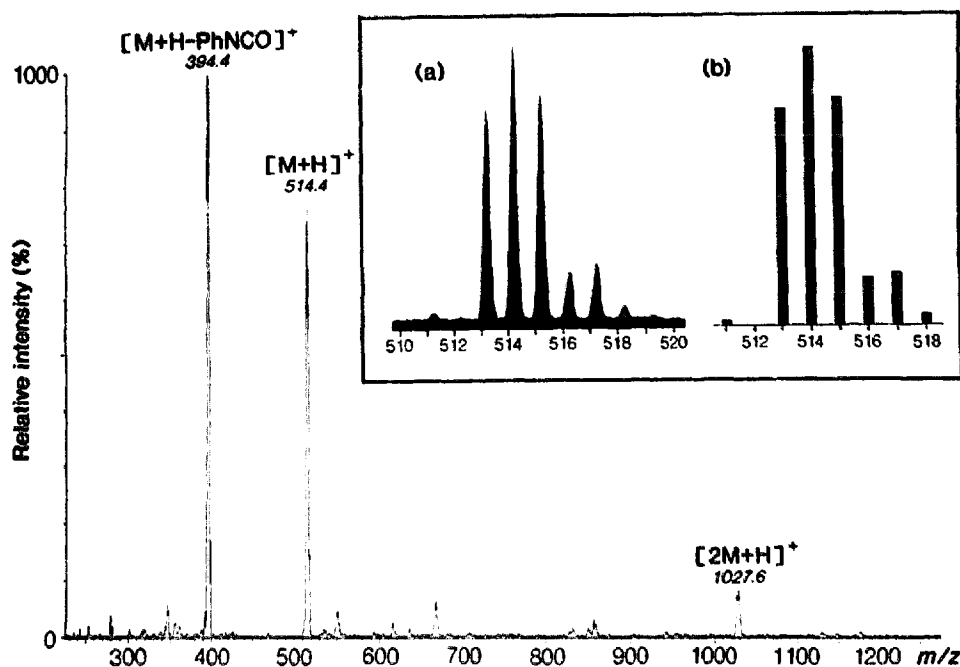


Fig. 2. Positive-ion electrospray mass spectrum of  $[Pt(PhNC(O)NPh)(COD)]$  **3a** ( $= M$ ), showing peak assignments. The inset shows a comparison of the (a) observed and (b) calculated isotope distribution patterns for the  $[M + H]^+$  parent ion at  $m/z$  514.

ion. Similar behaviour was observed for the sulphonylurea herbicide-derived product **3g**, which selectively lost chlorophenylsulphonylisocyanate at high cone voltages. Analogous loss of isocyanates from sulphonylurea herbicides has been described previously in desorption chemical ionisation studies of this class of compounds [21]. It is also noteworthy that the reactions of isocyanates with a range of metal complexes provide a synthetic route into ureylene complexes, as discussed in Section 1. ESMS thus appears to provide a rapid, convenient method for probing the decomposition pathways of such complexes.

### 3. Experimental details

$^1H$  and  $^{13}C$ - $\{^1H\}$  NMR spectra were recorded on a Bruker AC300P spectrometer, at 300.13 MHz and 75.47 MHz respectively, in  $CDCl_3$  (unless otherwise stated), with  $SiMe_4$  (0.0 ppm) as external reference. NMR spectra of ureylene complexes were fully assigned by a combination of  $^1H$ - $^1H$  COSY,  $^1H$ - $^{13}C$  COSY and nOe experiments.  $^{31}P$ - $\{^1H\}$  NMR spectra were recorded in  $CH_2Cl_2$  solution (unless otherwise stated) on a Jeol FX90Q spectrometer at 36.23 MHz, with 85%  $H_3PO_4$  (0.0 ppm) as external reference, and a glass capillary containing  $D_2O$  used to provide a lock signal. IR spectra were recorded as KBr disks on a BioRad FTS-40 spectrometer, with  $1\text{ cm}^{-1}$  resolution. Melting points were recorded on a Reichert Hotstage apparatus and are uncorrected. Electrospray mass spec-

tra were recorded in positive-ion mode on a VG Platform II instrument. The sample was delivered to the mass spectrometer source by a SpectraSystem P1000 HPLC pump, at a flow rate of  $0.1\text{ ml min}^{-1}$ , with  $MeCN-H_2O$  (1:1 v/v) as the mobile phase. The sample was introduced via a  $10\text{ }\mu\text{l}$  sample loop fitted to a Rheodyne injector. Nitrogen was employed as both the nebulising and drying gas, and the source temperature was  $60^\circ\text{C}$ . Cone voltages were typically varied between 20 and 80 V, in order to optimise formation of molecular ions, and investigate the effect of higher voltages on fragmentation of the parent species. Identification of all major species is aided by comparison of the observed and calculated [22] isotope distribution patterns.

The complex  $[PtCl_2(COD)]$  was prepared by the literature procedure [23] and *cis*- $[PtCl_2(PPh_3)_2]$  was prepared from this complex by ligand substitution with 2 mol equivalents of  $PPh_3$  in dichloromethane solution. Silver(I) oxide was prepared by a modification of the literature procedure. [24]

Urea (BDH), phenylurea (BDH), *N,N'*-dimethylurea (Aldrich), were obtained from commercial sources and used as-supplied. The sulphonylurea herbicide Chlorsulfuron was obtained from D. McNaughton, AgResearch Ltd., Hamilton, New Zealand, and used as-supplied.

*N*-acetyl-*N'*-methylurea was prepared by the literature procedure [25], m.p.  $178^\circ\text{C}$  (lit.  $178$ – $180^\circ\text{C}$ ).  $^1H$  NMR:  $\delta$  10.33 (s, 1H,  $CH_3CONH$ ), 8.40 (s, 1H,  $H_3CNH$ ), 2.84 (d, 3H,  $J_{H,H} = 5.49\text{ Hz}$ ,  $COCH_3$ ), 2.10 (s, 3H,  $CH_3$ ).  $^{13}C$  NMR:  $\delta$  172.6 (s,  $H_3C-C=O$ ), 155.6 (s,  $C=O$ ), 26.1 (q,  $NH-CH_3$ ), 23.9 (q,  $CO-CH_3$ ).

The various phenylureas were prepared via a minor modification of the general method recently described [26]; phenyl isocyanate (BDH) (0.5 ml) was added to a solution of the appropriate amine in diethyl ether (ca. 30 ml). The resulting solid was filtered, and washed with diethyl ether to yield the product urea.

*N*-Phenyl-*N'*-2-pyridyl urea, *PhNHC(O)NHPy*. M.p. 192–193 °C (194 °C [26]). <sup>1</sup>H NMR: δ 11.81 (s, 1H, br, PhNH), 9.23 (s, 1H, br, PyNH), 8.26 (dd, 1H, <sup>3</sup>J<sub>5'',4''</sub> = 5.07 Hz, <sup>4</sup>J<sub>5'',3''</sub> = 1.08 Hz, H-5''), 7.65 (td, 1H, <sup>3</sup>J<sub>3'',2''</sub> = 7.34 Hz, <sup>4</sup>J<sub>3'',5''</sub> = 1.85 Hz, H-3''), 7.63 (dd, 2H, <sup>3</sup>J<sub>2'',3''</sub> = 7.88 Hz, <sup>4</sup>J<sub>2'',4''</sub> = 1.08 Hz, H-2',6'), 7.36 (t, 2H, <sup>3</sup>J<sub>3',2'</sub> = 7.92 Hz, H-3',5'), 7.10 (tt, 1H, <sup>3</sup>J<sub>4',3'</sub> = 7.41 Hz, <sup>4</sup>J<sub>4',2'</sub> = 1.06 Hz, H-4'), 6.98 (d, 1H, <sup>3</sup>J<sub>2'',3''</sub> = 8.39 Hz, H-2''), 6.94 (tt, 1H, <sup>3</sup>J<sub>4',3'</sub> = 6.11 Hz, <sup>4</sup>J<sub>4',2'</sub> = 0.83 Hz, H-4''). <sup>13</sup>C NMR: δ 154.0 (s, C=O), 153.2 (s, C-1''), 145.9 (d, C-5''), 138.7 (s, C-1'), 138.7 (d, C-3''), 129.0 (d, C-3',5'), 123.4 (d, C-4'), 120.3 (d, C-2',6'), 117.2 (d, C-4''), 112.4 (d, C-2'').

*N*-1-Adamantyl-*N'*-phenyl urea, *PhNHC(O)NHAd*. M.p. 248 °C. <sup>1</sup>H NMR: δ 7.27 (m, 4H, H-2',3',5',6'), 7.05 (tt, 1H, <sup>3</sup>J<sub>4',3'</sub> = 6.26 Hz, <sup>4</sup>J<sub>4',2'</sub> = 2.38 Hz, H-4'), 6.22 (s, 1H, PhNH), 4.57 (s, 1H, AdNH), 2.08 (m, 3H, CH<sub>2</sub>-CH-CH<sub>2</sub>), 2.00 (d, 6H, C-CH<sub>2</sub>-CH), 1.67 (t, 6H, CH-CH<sub>2</sub>-CH). <sup>13</sup>C NMR: δ 154.4 (s, C=O), 139.0 (s, C-1'), 129.3 (d, C-3',5'), 123.6 (d, C-4'), 120.9 (d, C-2',6'), 51.4 (s, N-C-CH<sub>2</sub>), 42.3 (t, C-CH<sub>2</sub>-CH), 36.4 (t, CH-CH<sub>2</sub>-CH), 29.6 (d, CH<sub>2</sub>-CH-CH<sub>2</sub>).

*N*-Methyl-*N'*-phenyl urea, *PhNHC(O)NHMe*. M.p. 178 °C. <sup>1</sup>H NMR: δ 7.32–7.26 (m, 4H, H-2',3',5',6'), 7.09 (tt, 1H, <sup>3</sup>J<sub>4',3'</sub> = 6.48 Hz, <sup>4</sup>J<sub>4',2'</sub> = 2.21 Hz, H-4'), 6.54 (s, br, 1H, PhNH), 4.87 (s, br, 1H, H<sub>3</sub>CNH) 2.82 (d, 3H, <sup>3</sup>J<sub>11,10</sub> = 4.76 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR: δ 156.6 (s, C=O), 138.5 (s, C-1'), 129.4 (d, C-3',5'), 124.2 (d, C-4'), 121.6 (d, C-2',6'), 27.1 (q, CH<sub>3</sub>).

{CH<sub>3</sub>NHC(O)NHC<sub>6</sub>H<sub>4</sub>}<sub>2</sub>CH<sub>2</sub>. M.p. 280 °C. <sup>1</sup>H NMR: (D<sub>6</sub>-DMSO) δ 8.44 (s, 2H, br, C<sub>6</sub>H<sub>4</sub>-N-H), 7.36 (d, 4H, <sup>3</sup>J<sub>2',3'</sub> = 8.49 Hz, 2',6',2'',6''), 7.11 (d, 4H, <sup>3</sup>J<sub>3',2'</sub> =

8.47 Hz, H-3',5',3'',5''), 6.01 (q, 2H, <sup>3</sup>J<sub>H,H</sub> = 4.66 Hz, H<sub>3</sub>C-N-H), 3.82 (s, 2H, CH<sub>2</sub>), 2.70 (d, 6H, <sup>3</sup>J<sub>H,H</sub> = 4.63 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR: (D<sub>6</sub>-DMSO) δ 159.9 (s, C=O), 142.4 (s, C-1'), 138.2 (d, C-4'), 132.6 (d, C-3',6'), 121.8 (d, C-2',6'), 43.7 (t, CH<sub>2</sub>) 30.1 (q, CH<sub>3</sub>).

### 3.1. Preparation of ureylene complexes

Melting point, microanalytical and IR spectroscopic data for the ureylene complexes **3** and **4** are summarised in Table 4.

#### 3.1.1. Preparation of [Pt(PhNC(O)NPh)(COD)] **3a**

[PtCl<sub>2</sub>(COD)] (0.051 g, 0.136 mmol), *N,N'*-diphenylurea (0.029 g, 0.137 mmol) and silver(I) oxide (0.807 g, excess) were refluxed in dichloromethane (30 ml) for 18 h. Filtration to remove the silver salts gave a pale green-yellow solution. The solvent was removed by evaporation, and subsequent recrystallisation of the residue from dichloromethane–diethyl ether gave a pale green powder of **3a** (0.059 g, 84%).

<sup>1</sup>H NMR: δ 7.29–7.13 (m, 8H, Ph), 6.91 (t, 4H, <sup>3</sup>J<sub>4',3'</sub> = 7.13 Hz, H-4'), 5.20 (t, br, 4H, (d, <sup>2</sup>J<sub>H,Pt</sub> = 59.4 Hz), CH=CH), 2.61 (m, 4H, CH-CH<sub>2</sub>), 2.29 (m, 4H, CH-CH<sub>2</sub>). <sup>13</sup>C NMR: δ 129.1 (s, C-3',5'), 128.9 (s, C-3',5'), 123.6 (s, C), 122.6 (s, C), 120.6 (s, C), 94.1 (d, (d, <sup>1</sup>J<sub>C,Pt</sub> = 141.7 Hz), CH=CH), 30.2 (t, CH-CH<sub>2</sub>). ESMS: cone voltage 50 V (*m/z*, %) [2M + H]<sup>+</sup> (1027, 10%), [M + H]<sup>+</sup> (514, 80%), [MH - PhNCO]<sup>+</sup> (394, 100%).

#### 3.1.2. Preparation of [Pt(PhNC(O)NPh)(PPh<sub>3</sub>)<sub>2</sub>] **3b**

The compound was quantitatively prepared by ligand substitution from [Pt(PhNC(O)NPh)(COD)] **3a** prepared above, by addition of the appropriate molar amount of triphenylphosphine to a dichloromethane solution of **3a**.

The complex was also prepared directly from *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (generated in situ from [PtCl<sub>2</sub>(COD)] (0.050 g, 0.134 mmol) and triphenylphosphine (0.071 g, 0.271 mmol)), *N,N'*-diphenylurea (0.029 g, 0.137 mmol) and silver(I) oxide (0.843 g, excess). Yield 0.107 g (86%).

Table 4  
Melting point, microanalytical <sup>a</sup> and IR spectroscopic data for the platinum(II) ureylene complexes

Compound	M.p. (°C)	Microanalytical data			IR (carbonyl region, cm <sup>-1</sup> )
		C	H	N	
<b>3a</b>	150 <sup>b</sup>	48.57(49.12)	4.56(4.32)	5.43(5.46)	1648(vs),1594(s)
<b>3b</b>	240 <sup>b</sup>	62.55(63.29)	3.95(4.34)	2.65(3.01)	1639(vs),1589(m)
<b>3c</b> · 0.25 Et <sub>2</sub> O	240 <sup>b</sup>	46.66(46.11)	4.16(4.55)	8.13(8.07)	1662(vs),1548(s)
<b>3d</b> · 0.5CH <sub>2</sub> Cl <sub>2</sub> · 0.5Et <sub>2</sub> O	220 <sup>b</sup>	50.17(50.75)	5.95(5.89)	4.43(4.31)	1637(vs),1618(s)
<b>3e</b>	140 <sup>c</sup>	42.72(42.57)	4.84(4.47)	6.05(6.21)	1650(vs),1590(s)
<b>3g</b> · 0.33CH <sub>2</sub> Cl <sub>2</sub>	170 <sup>b</sup>	35.76(35.53)	3.40(3.32)	10.21(10.19)	1725(vs,br)
<b>4</b>	190 <sup>b</sup>	43.56(43.31)	4.96(4.41)	6.24(6.13)	1640(vs,br),1605(s)

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Decomposition point. <sup>c</sup> Melts without decomposition.

<sup>1</sup>H NMR: δ 7.47–7.32 (m, 14H, PPh<sub>3</sub>), 7.25–7.17 (m, 8H, PPh<sub>3</sub>), 7.09–7.04 (m, 8H, PPh<sub>3</sub>), 6.66 (d, 2H, <sup>3</sup>J<sub>2,3</sub> = 7.24 Hz, H-2',2''), 6.55 (t, 2H, <sup>3</sup>J<sub>3,2</sub> = 7.29 Hz, H-3',3''), 6.47 (t, 1H, <sup>3</sup>J<sub>4,3</sub> = 6.97 Hz, H-4',4''). <sup>13</sup>C NMR: δ 174.3 (s, C=O), 134.5–134.2 (m, PPh<sub>3</sub>), 131.2 (m, PPh<sub>3</sub>), 130.5 (m, PPh<sub>3</sub>), 128.6–128.4 (m, PPh<sub>3</sub>), 128.0–127.9 (m, PPh<sub>3</sub>), 127.5 (s, C-2',6'), 127.2 (s, C-3',5'), 121.2 (s, C-4'). <sup>31</sup>P–(<sup>1</sup>H) NMR: δ 10.0 (s, (d, <sup>1</sup>J<sub>P,Pt</sub> = 3337 Hz), Ph<sub>3</sub>P). ESMS: cone voltage 50 V (*m/z*, %) unidentified (957, 40%), [M + H]<sup>+</sup>, (930, 70%), unidentified, (772, 100%).

### 3.1.3. Preparation of [Pr(PhNC(O)NPy)(COD)] 3c

[PtCl<sub>2</sub>(COD)] (0.100 g, 0.266 mmol), *N*-phenyl-*N'*-2-pyridylurea (0.056 g, 0.264 mmol) and silver(I) oxide (0.129 g, excess) were refluxed in dichloromethane for 24 h. After workup as above, bright yellow crystals of **3c** (0.105 g, 77%) were obtained.

<sup>1</sup>H NMR: δ 7.98 (ddd, 1H, <sup>3</sup>J<sub>2',3'</sub> = 6.05 Hz, <sup>4</sup>J<sub>2',4'</sub> = 1.98 Hz, <sup>5</sup>J<sub>2',5'</sub> = 0.84 Hz, H-2''), 7.92 (dt, 1H, <sup>3</sup>J<sub>5',4'</sub> = 8.51 Hz, <sup>4</sup>J<sub>5',3'</sub> = 0.95 Hz, H-5''), 7.41 (ddd, 1H, <sup>3</sup>J<sub>4',3'/5'</sub> = 8.51 Hz, <sup>3</sup>J<sub>4',3'/5'</sub> = 7.08 Hz, <sup>4</sup>J<sub>4',2'</sub> = 2.02 Hz, H-4''), 7.21 (tt, 2H, <sup>3</sup>J<sub>3',2'</sub> = 7.71 Hz, <sup>4</sup>J<sub>3',5'</sub> = 1.70 Hz, H-3'), 7.12 (dt, 2H, <sup>3</sup>J<sub>2',3'</sub> = 9.2 Hz, <sup>4</sup>J<sub>2',4'</sub> = 1.79 Hz, H-2'), 6.91 (tt, 1H, <sup>3</sup>J<sub>4',3'</sub> = 7.13 Hz, <sup>4</sup>J<sub>4',2'</sub> = 1.29 Hz, H-4'), 6.50 (ddd, 1H, <sup>3</sup>J<sub>3',2'/4'</sub> = 7.11 Hz, <sup>3</sup>J<sub>3',2'/4'</sub> = 4.95 Hz, <sup>4</sup>J<sub>3',5'</sub> = 0.98 Hz, H-3''), 6.48 (2H, (t, <sup>3</sup>J<sub>H,H</sub> = 2.81 Hz), (d, <sup>2</sup>J<sub>H,Pt</sub> = 64.6 Hz), CH=CH *trans* NPh), 5.21 (2H, (t, <sup>3</sup>J<sub>H,H</sub> = 2.52 Hz), (d, <sup>2</sup>J<sub>H,Pt</sub> = 63.1 Hz), CH=CH *trans* NPy), 2.70–2.60 (m, 4H, CH=CH<sub>2</sub>), 2.40–2.14 (m, 4H, CH=CH<sub>2</sub>). <sup>13</sup>C NMR: δ 169.7 (s, C=O), 158.1 (s, C-1''), 147.5 (d, C-5''), 145.5 (s, C-1'), 136.9 (d, C-3''), 128.9 (d, C-3',5'), 122.6 (d, C-2',6'), 122.3 (d, C-4'), 115.6 (d, C-4''), 114.3 (d, (<sup>1</sup>J<sub>C,Pt</sub> = 45.8 Hz), C-2''), 95.2 (d, (d, <sup>1</sup>J<sub>C,Pt</sub> = 131.6 Hz), CH=CH *trans* NPh), 94.1 (d, (d, <sup>1</sup>J<sub>C,Pt</sub> = 145.5 Hz), CH=CH *trans* NPy), 30.7 (d, CH=CH<sub>2</sub>), 30.0 (d, CH=CH<sub>2</sub>). ESMS: cone voltage 15 V, (*m/z*, %) unidentified (747, 18%), [M + H<sub>2</sub>O]<sup>+</sup> (533, 100%), [(COD)Pt(OH)(MeCN)]<sup>+</sup> (361, 15%), [(COD)Pt(OH)(MeCN)<sub>2</sub>]<sup>+</sup> (402, 48%), Cone 50 V, (*m/z*, %) unidentified (665, 70%), [M + H<sub>2</sub>O]<sup>+</sup> (533, 100%), unidentified (427, 36%), [(COD)Pt(OH)(MeCN)]<sup>+</sup> (361, 72%), [(COD)Pt(OH)]<sup>+</sup> (320, 77%).

### 3.1.4. Preparation of [Pr(PhNC(O)NAd)(COD)] 3d

[PtCl<sub>2</sub>(COD)] (0.100 g, 0.266 mmol), *N*-1-adamantyl-*N'*-phenyl urea (0.073 g, 0.270 mmol) and silver(I) oxide (0.126 g, excess) were refluxed in dichloromethane for 24 h. After standard workup and recrystallisation from dichloromethane–diethyl ether, bright yellow crystals of **3d** (0.107 g, 70%) were obtained.

<sup>1</sup>H NMR: δ 7.17 (dt, 2H, <sup>3</sup>J<sub>2',3'</sub> = 6.52 Hz, <sup>4</sup>J<sub>2',4'</sub> = 1.79 Hz, H-2',6'), 7.11 (tt, 2H, <sup>3</sup>J<sub>3',2'</sub> = 8.20 Hz, <sup>4</sup>J<sub>3',5'</sub> = 1.30 Hz, H-3',5'), 6.88 (tt, 1H, <sup>3</sup>J<sub>4',3'</sub> = 7.10 Hz, <sup>4</sup>J<sub>4',2'</sub> =

1.48 Hz, H-4'), 5.63 (2H, (t, <sup>3</sup>J<sub>H,H</sub> = 2.77 Hz), (d, br, <sup>2</sup>J<sub>H,Pt</sub> = 61.0 Hz), CH=CH *trans* NAd), 4.73 (2H, (t, <sup>3</sup>J<sub>H,H</sub> = 2.79 Hz), (d, br, <sup>2</sup>J<sub>H,Pt</sub> = 60.8 Hz), CH=CH *trans* NPh), 2.54 (m, 4H, CH<sub>2</sub>–CH=CH), 2.26 (m, 4H, CH<sub>2</sub>–CH=CH), 2.01 (m, br, 9H, H-Ad), 1.66 (m, br, 6H, H-Ad). <sup>13</sup>C NMR: δ 174.2 (s, C=O), 146.7 (s, C-1'), 128.5 (d, C-3',5'), 124.7 (d, C-2',6'), 122.6 (d, C-4'), 93.8 (d, (d, <sup>1</sup>J<sub>C,Pt</sub> = 142.8 Hz), CH=CH *trans* NAd), 90.7 (d, (d, <sup>1</sup>J<sub>C,Pt</sub> = 128.6 Hz), CH=CH *trans* NPh), 57.6 (s, N–C–CH<sub>2</sub>), 44.2 (t, C–CH<sub>2</sub>–CH), 36.8 (t, CH–CH<sub>2</sub>–CH), 31.1 (t, CH<sub>2</sub>–CH=CH), 30.3 (CH<sub>2</sub>–CH–CH<sub>2</sub>), 29.4 (t, CH<sub>2</sub>–CH=CH).

### 3.1.5. Preparation of [Pr(PhNC(O)NCH<sub>3</sub>)(COD)] 3e

[PtCl<sub>2</sub>(COD)] (0.052 g, 0.139 mmol), *N*-methyl-*N'*-phenylurea (0.016 g, 0.138 mmol) and silver(I) oxide (0.11 g, excess) were refluxed in dichloromethane for 5 h. After standard workup, recrystallisation from dichloromethane–diethyl ether afforded pale yellow rosettes of **3e** (0.039 g, 81%). <sup>1</sup>H NMR: δ 7.18–7.05 (m, 4H, C-2',3',5',6'), 6.78 (t, 1H, <sup>3</sup>J<sub>4',3'</sub> = 7.07 Hz, H-4'), 5.13 ((s, br), 2H, (d, br, <sup>2</sup>J<sub>H,Pt</sub> = 53.9 Hz), CH=CH *trans* NCH<sub>3</sub>), 5.08 ((s, br), 2H, (d, br, <sup>2</sup>J<sub>H,Pt</sub> not discernible due to overlap), CH=CH *trans* NPh), 2.94 (s, 3H, (d, br, <sup>3</sup>J<sub>H,Pt</sub> = 38.3 Hz), CH<sub>3</sub>), 2.59 (m, br, 4H, CH<sub>2</sub>–CH), 2.22 (m, br, 4H, CH<sub>2</sub>–CH). <sup>13</sup>C NMR: δ 173.8 (s, (d, <sup>2</sup>J<sub>C,Pt</sub> = 97.0 Hz), C=O), 147.3 (s, C-1'), 128.8 (d, C-3',5'), 120.9 (d, C-2',6'), 118.8 (d, C-4'), 93.7 (d, (d, <sup>1</sup>J<sub>C,Pt</sub> = 133.1 Hz), CH=CH, *trans* NPh), 92.1 (d, (d, <sup>1</sup>J<sub>C,Pt</sub> = 143.5 Hz), CH=CH, *trans* NCH<sub>3</sub>), 31.7 (q, (d, <sup>2</sup>J<sub>C,Pt</sub> = 30.5 Hz), CH<sub>3</sub>), 30.4 (t, CH<sub>2</sub>–CH), 30.3 (t, CH<sub>2</sub>–CH).

### 3.1.6. Preparation of

### [Pr(CH<sub>3</sub>CONC(O)NCH<sub>3</sub>)(COD)] 3f

[PtCl<sub>2</sub>(COD)] (0.052 g, 0.139 mmol), *N*-acetyl-*N'*-methylurea (0.016 g, 0.138 mmol) and silver(I) oxide (0.11 g, excess) were refluxed in dichloromethane for 5 h. After standard workup, recrystallisation from dichloromethane–diethyl ether afforded a pale yellow oil of **3f** (0.049 g, which was ca. 95% pure by <sup>1</sup>H NMR).

<sup>1</sup>H NMR: δ 6.08 (2H, (t, <sup>3</sup>J<sub>H,H</sub> = 2.65 Hz), (d, br, <sup>2</sup>J<sub>H,Pt</sub> = 61.3 Hz), CH=CH *trans* NCH<sub>3</sub>), 5.17 (2H, (t, <sup>3</sup>J<sub>H,H</sub> = 2.48 Hz), (d, br, <sup>2</sup>J<sub>H,Pt</sub> = 62.4 Hz), CH=CH *trans* NCOCH<sub>3</sub>), 2.87 (s, 3H, (d, br, <sup>3</sup>J<sub>H,Pt</sub> = 40.0 Hz), CH<sub>3</sub>), 2.56 (m, br, 4H, CH<sub>2</sub>–CH), 2.37 (s, 3H, N–CH<sub>3</sub>), 2.32 (m, br, 4H, CH<sub>2</sub>–CH). <sup>13</sup>C NMR: δ 172.7 (s, H<sub>3</sub>C–C=O), 170.4 (s, C=O), 93.9 (d, (d, <sup>1</sup>J<sub>C,Pt</sub> = 141.1 Hz), CH=CH *trans* NCH<sub>3</sub>), 93.5 (d, (d, <sup>1</sup>J<sub>C,Pt</sub> = 128.7 Hz), CH=CH, *trans* NCOCH<sub>3</sub>), 31.1 (q, CO–CH<sub>3</sub>), 30.8 (t, CH<sub>2</sub>–CH), 30.0 (t, CH<sub>2</sub>–CH), 26.0 (q, (d, <sup>2</sup>J<sub>C,Pt</sub> = 41.5 Hz), CH<sub>3</sub>).

### 3.1.7. Preparation of 3g

[PtCl<sub>2</sub>(COD)] (0.053 g, 0.142 mmol), Chlorsulfuron (0.51 g, 0.143 mmol) and silver(I) oxide (0.765 g, ex-



cess) were refluxed in dichloromethane for 5 h. After standard workup, recrystallisation from dichloromethane–diethyl ether gave a cream solid of **3g** (0.074 g, 79%).

$^1\text{H}$  NMR:  $\delta$  8.29 (d, 1H,  $^3J_{\text{H,H}} = 7.15$  Hz, Ar-H), 7.42–7.35 (m, 3H, Ar-H), 6.41 ((s, br), 2H, (d, br,  $^2J_{\text{H,Pt}} = 68.2$  Hz), CH=CH *trans* *N*-chlorophenyl), 6.33 ((s, br), 2H, (d, br,  $^2J_{\text{H,Pt}} = 61.0$  Hz), CH=CH *trans* *N*-triazene), 3.86 (s, 3H, OCH<sub>3</sub>), 2.65 (m, br, 4H, CH<sub>2</sub>–CH), 2.42 (m, br, 4H, CH<sub>2</sub>–CH), 2.32 (s, 3H, CH<sub>3</sub>).  $^{13}\text{C}$  NMR:  $\delta$  178.7 (s, C=O), 171.5 (s), 168.1 (s), 161.3 (s), 139.0 (s), 133.6 (d), 133.0 (d), 131.5 (s), 131.3 (d), 127.2 (d, C-), 98.6 (d, (d, br,  $^1J_{\text{C,Pt}} = 139.1$  Hz), CH=CH *trans* *N*-chlorophenyl), 97.1 (d, (d, br,  $^1J_{\text{C,Pt}} = 153.8$  Hz), CH=CH *trans* *N*-triazene), 54.6 (q, OCH<sub>3</sub>), 30.9 (t, CH<sub>2</sub>–CH), 30.0 (t, CH<sub>2</sub>–CH), 25.6 (q, CH<sub>3</sub>). ESMS: cone voltage 50 V, (*m/z*, %) [M + H]<sup>+</sup> (659, 100). Cone voltage 100 V, (*m/z*, %) [M + H]<sup>+</sup> (659, 80), [M + H – OCNSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl]<sup>+</sup> (441, 100), unidentified (429, 63%).

### 3.1.8. Preparation of [Pt{PhNC(O)NH}(PPh<sub>3</sub>)<sub>2</sub>] 3h

[PtCl<sub>2</sub>(COD)] (0.050 g, 0.134 mmol), triphenylphosphine (0.071 g, 0.270 mmol), phenylurea (0.018 g, 0.132 mmol) and silver(I) oxide (0.122 g, excess) were added in succession to dichloromethane (25 ml) and refluxed for 5 h. Workup gave a pale orange oil which did not crystallise. On standing, the solution became noticeably darker, indicating possible decomposition. This was later confirmed by  $^{31}\text{P}$  NMR. Decomposition in chloroform was also noted.  $^{31}\text{P}$  NMR revealed that the oil was impure, precluding further NMR studies and elemental analysis.

$^{31}\text{P}$  NMR:  $\delta$  12.7 ((d,  $^2J_{\text{P,P}} = 22.0$  Hz), (d,  $^1J_{\text{P,Pt}} = 3174$  Hz), Ph<sub>3</sub>P *trans* NH), 11.7 ((d,  $^2J_{\text{P,P}} = 19.6$  Hz), (d,  $^1J_{\text{P,Pt}} = 3423$  Hz), Ph<sub>3</sub>P *trans* NPh), 6.53 (s, ( $^1J_{\text{P,Pt}} = 3699$  Hz), impurity).

### 3.1.9. Preparation of [Pt{HNC(O)NH}(PPh<sub>3</sub>)<sub>2</sub>] 3i

[PtCl<sub>2</sub>(COD)] (0.052 g, 0.139 mmol), triphenylphosphine (0.074 g, 0.282 mmol), urea (0.010 g, 0.167 mmol) and silver(I) oxide (0.113 g, excess) were refluxed in dichloromethane for 5 h. Workup gave a pale orange oil which did not crystallise.  $^{31}\text{P}$  NMR and ESMS revealed the oil was impure so further analysis was not pursued. A sample of the product in dichloromethane became dark orange on standing, with  $^{31}\text{P}$  NMR indicating decomposition.

$^{31}\text{P}$  NMR:  $\delta$  12.3 (s, (d,  $^1J_{\text{P,Pt}} = 3291$  Hz), Ph<sub>3</sub>P), 6.5 (s, (d,  $^1J_{\text{P,Pt}} = 3704$  Hz), impurity). On standing, the following additional impurity resonances resulted:  $\delta$  27.5 (s, impurity), 11.7 (s, (d,  $^1J_{\text{P,Pt}} = 3096$  Hz), impurity), 7.5 (s, (d,  $^1J_{\text{P,Pt}} = 3567$  Hz), impurity). ESMS (positive-ion mode, cone voltage 30 V) [M + H]<sup>+</sup>, (*m/z* 778, 100%), plus a number of other unidentified species.

### 3.1.10. Preparation of [(COD)Pt{CH<sub>3</sub>NC(O)NC<sub>6</sub>H<sub>4</sub>}]<sub>2</sub>CH<sub>2</sub> 4

[PtCl<sub>2</sub>(COD)] (0.102 g, 0.273 mmol), [CH<sub>3</sub>NHC(O)NHC<sub>6</sub>H<sub>4</sub>]<sub>2</sub>CH<sub>2</sub> (0.043 g, 0.138 mmol) and silver(I) oxide (0.11 g, excess) were refluxed in dichloromethane for 18 h. After standard workup, recrystallisation from dichloromethane–diethyl ether gave bright yellow pellets of **4** (0.094 g, 75%).

$^1\text{H}$  NMR:  $\delta$  6.93 (d, 4H,  $^3J_{2',3'} = 8.52$  Hz, 2',6',2'',6''), 6.88 (d, 4H,  $^3J_{3',2'} = 8.52$  Hz, H-3',5',3'',5''), 4.98 ((s, br), 8H, (d, br,  $^3J_{\text{H,Pt}}$  not discernible), CH=CH), 3.68 (s, 2H, CH<sub>2</sub>), 2.87 (s, 3H, (d, br,  $^2J_{\text{H,Pt}} = 38.3$  Hz), CH<sub>3</sub>), 2.41 (m, br, 4H, CH<sub>2</sub>–CH), 2.13 (m, br, 4H, CH<sub>2</sub>–CH).  $^{13}\text{C}$  NMR:  $\delta$  173.6 (s, C=O), 145.1 (s, C-1'), 133.9 (s, C-4'), 128.9 (d, C-3',5'), 120.8 (d, C-2',6'), 93.6 (d, (d, br,  $^1J_{\text{C,Pt}} = 127.5$  Hz), CH=CH), 91.9 (d, (d, br,  $^1J_{\text{C,Pt}} = 127.5$  Hz), CH=CH), 40.6 (t, CH<sub>2</sub>), 31.5 (q, CH<sub>3</sub>), 30.1 (t, CH<sub>2</sub>–CH), 30.0 (t, CH<sub>2</sub>–CH).

### 3.1.11. X-ray crystal structure of [Pt{PhNC(O)NAd}(COD)] · CH<sub>2</sub>Cl<sub>2</sub> 3d

Yellow rectangular blocks of **3d** were obtained on crystallisation by vapour diffusion of diethyl ether into a saturated dichloromethane solution at 4 °C. Preliminary precession photography indicated triclinic symmetry, so the space group was assumed to be *P* $\bar{1}$  which was confirmed by the successful refinement.

Accurate cell parameters and intensity data were collected on a Nicolet R3 automatic four-circle diffractometer at the University of Canterbury, using a crystal of dimensions 0.80 × 0.24 × 0.22 mm<sup>3</sup>, with monochromated Mo K $\alpha$  X-rays ( $\lambda = 0.71073$  Å).

*Crystal data.* C<sub>25</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>Pt · CH<sub>2</sub>Cl<sub>2</sub>, *M*<sub>r</sub> = 656.57, triclinic, space group *P* $\bar{1}$ . Unit cell dimensions: *a* = 9.55(2), *b* = 10.395(3), *c* = 13.761(7) Å,  $\alpha = 90.54(3)$ ,  $\beta = 91.21(7)$ ,  $\gamma = 112.26(5)^\circ$ , *U* = 1263(2) Å<sup>3</sup>, *D*<sub>c</sub> = 1.726 g cm<sup>-3</sup>, *Z* = 2, *F*(000) = 648,  $\mu(\text{Mo K}\alpha) = 5.79$  cm<sup>-1</sup>.

A total of 3937 reflections in the range  $2 < \theta < 24^\circ$  were collected at 130(2) K, of which 3881 were unique. These were subsequently corrected for Lorentz effects, polarisation effects, and for linear absorption by a  $\Psi$  scan method (*T*<sub>max,min</sub> = 0.85, 0.40). All non-hydrogen atom positions were located by the Patterson methods option of SHELXS-86 [27]. In the final cycle of the full-matrix least squares refinement based on *F*<sup>2</sup> using SHELXL-93 [28] all non-hydrogen atoms were assigned anisotropic temperature factors, with all hydrogen atom positions determined by calculation. A penultimate difference map showed some residual electron density which was modelled as three carbon atoms, with a tied occupancy factor which converged to 0.75. However, these could not be assigned to any chemically-sensible species, although it is most probably from a molecule of diethyl ether disordered across the inversion centre.

The refinement converged with  $R_1 = 0.0397$  for 3474 data with  $I \geq 2\sigma(I)$ ,  $0.0449$  for all data;  $wR_2 = 0.1056$ , and  $\text{GoF} = 1.088$ . No parameter shifted by more than  $1.3\sigma$  in the final cycle (for the disordered diethyl ether solvate), and the final difference map showed no peaks or troughs of electron density greater than  $+1.88 \text{ e } \text{\AA}^{-3}$  and  $-1.72 \text{ e } \text{\AA}^{-3}$  respectively (adjacent to the Pt atom).

Complete bond lengths and angles, final positional parameters, thermal parameters and calculated H-atom positions are available from the Cambridge Crystallographic Data Centre.

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