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FULL PAPER

Insertion reactions of platinum(II) ureylene complexes

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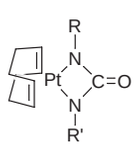
The reactivity of platinum(II) ureylene complexes towards various unsaturated molecules has been investigated. The complexes [Pt{NPhC(O)NPh}(cod)] **1a** (cod = cycloocta-1,5-diene) and [Pt{NMeC(O)NPh}(cod)] **1b** readily inserted phenyl isocyanate to give [Pt{NPhC(O)NPhC(O)NPh)}(cod)] and [Pt{NPhC(O)NMeC(O)NPh)}(cod)] respectively, with insertion taking place solely at the Pt–NMe linkage for the latter. When **1b** was treated with the isoelectronic diphenyl carbodiimide the product was characterised as [Pt{NPhC(O)NMeC(O)NPh}(cod)], presumably the result of hydrolysis. The biureto ligand in the latter was readily liberated by hydrochloric acid to give *N′*-methyl-*N*,*N″*-diphenylbiuret. Complex **1b** was also treated with various disubstituted acetylenes. Dimethyl acetylenedicarboxylate rapidly inserted into the Pt–NMe bond to give [Pt{C(CO_2Me)=C(CO_2Me)NMeC(O)NPh}(cod)]. Compound **1b** failed to react with diphenylacetylene, and was decomposed by methyl propiolate. Reaction of the more robust platinum ureylene [Pt{NMeC(O)NPh}(PPh_3)$_2$] with methyl propiolate displaced the urea dianion to give the diacetylide complex [Pt{C≡CC(O)OMe}$_2$(PPh_3)$_2$]. The compound [Pt{NMeC(O)NPh}(PPh_3)$_2$] was also treated with PhNSO and again the ureylene ligand was displaced to give the dimeric platinum sulfito complex [{Pt(SO_3)(PPh_3)$_2$}$_2$]·2PhNHC(O)NHMe. The crystal structure of the 2$CHCl_3$ solvate shows the complex to contain cocrystallised *N*-methyl-*N′*-phenylurea, hydrogen bonded from the NH moieties to the S(O)$_2$ groups. The compound presumably arises from hydrolysis of *N*-sulfinylaniline (or an intermediate insertion product thereof), and was also the only product characterised from the reaction of [Pt{NMeC(O)NPh}(PPh_3)$_2$] with sulfur dioxide. One of the chloroforms of crystallisation is also hydrogen bonded to the S(O)$_2$. The complex [Pt{NMeC(O)NPh}(PPh_3)$_2$] rapidly inserted carbon disulfide to give [Pt{S_2CNMeC(O)NPh}(PPh_3)$_2$] fully characterised by a single-crystal X-ray study. The complex contains a highly puckered six-membered ring, with the fold angle between the least-squares planes drawn through the co-ordination plane of the platinum and the remainder of the metallacycle being 56.8(1)°. In solution the compound slowly decomposes by loss of phenyl isocyanate to give [Pt(S_2C=NMe)(PPh_3)$_2$], also fully characterised by an X-ray crystallographic study. All the complexes reported have been subjected to extensive ^{1}H, ^{13}C and (where appropriate) ^{31}P NMR analysis. Further data from electrospray mass spectrometry, IR spectroscopy and elemental analysis are also given.

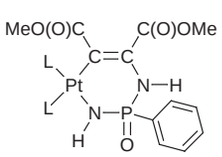
Insertion reactions into late transition metal–carbon bonds form a fundamental aspect of organometallic chemistry, and these important reactions and their applications to catalysis have been intensely studied. Despite this, the analogous chemistry of metal–nitrogen (and metal–oxygen) complexes has been largely unexplored, principally due to the relative scarcity and lower stability of precursor metal amide complexes compared with alkyl and aryl compounds.[1]

Recently, we reported the ready synthesis of (amongst others) the platinum(II) ureylene complexes **1a**–**1c**, formally derived from urea dianions, by the silver(I) oxide mediated reaction of [$PtCl_2L_2$] (L_2 = cod, L = PPh_3) with disubstituted ureas.[2] The synthesis requires at least one sufficiently acidic NH proton, with urea compounds possessing NH groups adjacent to electron-withdrawing substituents, such as aromatic or acetyl moieties, proving necessary for reaction to occur.

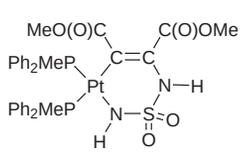
The previously reported palladium(II) ureylene complex [Pd{NPhC(O)NPh}(phen)] (phen = 1,10-phenanthroline) **2** readily undergoes insertion of phenyl isocyanate and carbon monoxide to give complexes [Pd{NPhC(O)NPhC(O)NPh}(phen)] **3** and [Pd{C(O)NPhC(O)NPh}(phen)] **4** respectively.[3] Additionally the reaction of dimethyl acetylenedicarboxylate with [Pt{NHP(O)PhNH}L_2] (L = tertiary phosphines) and [Pt{$NHS(O)_2NH$}($PMePh_2$)] gave the respective inserted products **5** and **6**.[4] The appreciable reactivity of these M–N systems led us to investigate the reactivity of our platinum ureylene complexes towards phenyl isocyanate, diphenylcarbodiimide, disubstituted acetylenes, *N*-sulfinylaniline, sulfur dioxide, and carbon disulfide. The results of these reactions are reported herein.



1a R = R′ = Ph
1b R = Ph, R′ = Me
1c R = Ph, R′ = 1-adamantyl



5 L = tertiary phosphine



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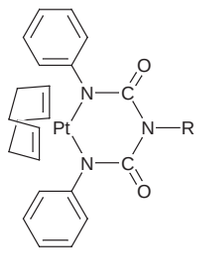
Results and Discussion

Insertion reactions with phenyl isocyanate and diphenylcarbodiimide

When a bright yellow dichloromethane solution of complex **1a** was treated with phenyl isocyanate at room temperature overnight the solution became almost colourless. Characterisation

using NMR and IR spectroscopy, electrospray mass spectrometry (ESMS) and elemental analysis confirmed the product as [Pt{NPhC(O)NPhC(O)NPh}(cod)] **7a**, analogous to the palladium(II) complex **3**[3] and to the nickel(II) and chromium(VI) biureto complexes [Ni{NPhC(O)NPhC(O)NPh}(PEt_3)$_2$][5] and [Cr{$NBu^tC(O)NBu^tC(O)NBu^t$}(NBu^t)$_3$][6] respectively.



7a R = Ph
7b R = Me

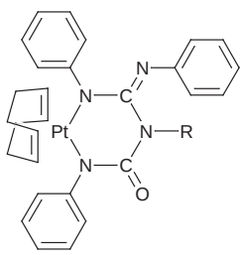
The ready formation of complex **7a** led us to examine the effect of using an unsymmetrical ureylene complex, introducing the possibility of two isomers forming. When the complex **1b** was treated with phenyl isocyanate in dichloromethane the solution decolorised rapidly from bright yellow to almost colourless. Completion was typically achieved in less than a minute. Both ^{1}H and ^{13}C NMR spectra of the crude reaction product showed the presence of only one CH=CH cycloocta-1,5-diene (cod) resonance, indicating reaction had taken place *exclusively* at the Pt–NMe linkage (reaction at Pt–NPh would result in two inequivalent cod CH=CH groups). Further evidence could be seen in the ^{1}H NMR spectrum where the absence of $^3J(^{195}Pt–^1H)$ coupling to the methyl group indicated the latter was now further removed from the platinum. The product was characterised as the biureto complex [Pt{NPhC(O)NMeC(O)NPh)}(cod)] **7b** also on the basis of NMR analysis, ESMS and elemental analysis.

The very rapid and exclusive insertion of phenyl isocyanate into only the Pt–NMe bond gives an indication of the relative reactivities of the Pt–NPh *versus* Pt–NMe groups. The increase in reactivity of complex **1b** indicates the Pt–N alkyl linkage is apparently weaker, also tentatively evidenced in the crystal structure of **1c**, where the Pt–N (adamantyl) bond length was slightly longer [2.048(8) Å] than Pt–NPh [2.021(8) Å],[2] although steric influences could be responsible in part.

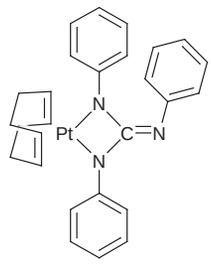
In light of successful 'one pot' insertion reactions described by Kemmitt *et al.*,[4] we wondered if this was also applicable to our isocyanate insertion reactions. When [$PtCl_2$(cod)], *N*-methyl-*N′*-phenylurea, an excess of phenyl isocyanate and silver(I) oxide were allowed to react in dichloromethane, **7b** was formed in excellent yield. The only reaction by-product appeared to be **7a**, formed presumably by the hydrolysis of phenyl isocyanate to diphenylurea, which subsequently reacts with any unchanged [$PtCl_2$(cod)] to give **1a**. This 'one-pot' synthesis provides an easy synthetic route (see later) to trisubstituted biurets RNHC(O)NR′C(O)NHR″ [with (potentially) R ≠ R′ ≠ R″], although other isocyanates were not tested.

When complex **1b** was treated with the closely related compound diphenylcarbodiimide (PhN=C=NPh) the biureto complex **7b** was still the only reaction product. This is presumably the result of the hydrolysis of either diphenylcarbodiimide or of the presumed guanidine intermediate derivative **8a**. To investigate when the hydrolysis occurred, the moisture-stable guanidine complex **9**[7,8] was treated with phenyl isocyanate. The product was characterised as the triphenylbiureto complex **7a**, by identical ^{1}H and ^{13}C NMR spectra. No detectable quantities of the expected complex **8b** was observed. This result suggests hydrolysis occurs *after* insertion.

In the absence of an excess of phenyl isocyanate, deinsertion



8a R = Me
8b R = Ph



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of the complexes **7a** and **7b** took place on standing to regenerate the respective starting complexes **1a** and **1b** and phenyl isocyanate, evidenced by NMR spectroscopy. This typically occurred over a few days, and for spectroscopic characterisation an excess of phenyl isocyanate was not necessary. However, a few drops of phenyl isocyanate were added to solutions of **7a** or **7b** prior to crystallisation to inhibit formation of crystals from the starting materials (**1a** or **1b**).

To examine the possible synthetic utility of the insertion reaction, a dichloromethane solution of complex **7b** was treated with concentrated hydrochloric acid. The diethyl ether extract of the residue contained pure *N′*-methyl-*N*,*N″*-diphenylbiuret, characterised by ^{1}H and ^{13}C NMR, elemental analysis and ESMS data. Integration of the ^{1}H NMR spectrum showed the expected phenyl : methyl and NH : methyl ratios of 2 : 1. Additionally, the methyl signal contained no splitting, indicating the absence of adjacent methyl and NH moieties that are present in *N*-methyl-*N′*-phenylurea. The ether-insoluble residue was characterised by NMR spectroscopy as almost pure [$PtCl_2$(cod)].

Characterisation of complexes 7a and 7b. In addition to the ^{1}H and ^{13}C NMR spectra already discussed, a further notable feature is evident. Upon insertion of phenyl isocyanate the carbonyl carbon undergoes a large upfield shift. For complex **7b** a chemical shift of δ 156.4 was noted, which compares with a value of δ 173.8 for the starting material **1b**. This is consistent with a release of steric strain on going from a four- to a six-membered ring system; indeed the platinum centre appears to have little bearing on the position of the carbonyl resonance of **7b**, since free *N′*-methyl-*N*,*N″*-diphenylbiuret shows the signal at δ 154.2.

The $^2J(^{195}Pt–^1H)$ and $^1J(^{195}Pt–^{13}C)$ coupling constants from the CH=CH part of the cod ligand are only slightly different from those of the starting materials. For complex **7a** a $^2J(^{195}Pt–^1H)$ value of 53.2 Hz and $^1J(^{195}Pt–^{13}C)$ of 145.2 Hz compare with respective values of 59.4 and 141.7 Hz for **1a**. Unsurprisingly, **7b** shows similar $^2J(^{195}Pt–^1H)$ and $^1J(^{195}Pt–^{13}C)$ coupling constants, with values of 56.1 and 143.1 Hz respectively.

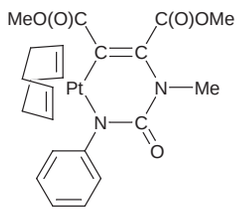
The carbonyl region (1700–1550 cm^{-1}) of the IR spectrum is the only area of diagnostic value. Upon insertion, the expected complication of bands arising from the addition of a carbonyl group was observed. For complex **7b**, five bands (1641, 1632, 1611, 1600 and 1584 cm^{-1}) are seen, compared to only two for the starting material **1b** (1650 and 1590 cm^{-1}).

Positive-ion electrospray (ES) mass spectra of the complexes **7a** and **7b** show very strong parent ions at low cone voltages (≈20 V), with increased fragmentation at higher voltages. The fragmentation pathway at moderate cone voltages (≈50 V) shows solely loss of phenyl isocyanate. Whether this process results in the four-membered ring system [Pt{NPhC(O)NR}(cod) + H]$^+$ (R = Ph or Me), *i.e.* [**1** + H]$^+$, or a ring-opened structure [Pt$^+$(NPhC(O)NHR}(cod)], cannot be determined, although the ready deinsertion of phenyl isocyanate to regenerate starting materials in solution suggests the former

as the most probable. In this case the most likely site for the protonation is the carbonyl group, as opposed to the NR moieties which are not expected to be sufficiently basic (sp^2 hybridised and conjugated).

Reaction with acetylenes

When dimethyl acetylenedicarboxylate ($MeO_2CC{\equiv}CCO_2Me$, dmad) was added to a dichloromethane solution of complex **1b** rapid decolorisation occurred. Recrystallisation produced flaky pale yellow crystals, which were characterised spectroscopically and by elemental analysis as the dmad-inserted product **10**. The ready formation of complex **10** is analogous to that reported for **5** and **6**.[4] Complex **1b** failed to react to any detectable extent with the more electron-rich diphenylacetylene, even after 2 d reflux.



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Unlike the phenyl isocyanate insertion products, the dmad-inserted complex remains unsymmetrical, thus giving rise to two cod CH=CH resonances. The $^2J(^{195}Pt-^1H)$ values of 58.3 and 36.2 Hz were observed for the signals at δ 5.06 and 4.77, and assigned as CH=CH *trans* to N and C respectively, on the basis of relative *trans* influences.[9] The ^{13}C NMR spectrum similarly showed $^1J(^{195}Pt-^{13}C)$ 155.8 and 67.2 Hz for the respective signals at δ 90.4 and 112.6. Like the phenyl isocyanate reactions, insertion took place solely at the Pt–NMe bond, readily witnessed by loss of $^3J(^{195}Pt-^1H)$ coupling on the methyl resonance. A $^1J(^{195}Pt-^{13}C)$ value of 982.0 Hz in the ^{13}C NMR spectrum of **10** unambiguously confirms formation of a Pt–C bond. As seen for complexes **7a** and **7b**, a large upfield shift in the ureylene carbonyl is observed going from δ 173.8 for **1b**, to δ 154.3 for **10**.

Like complexes **7a** and **7b**, **10** shows a very strong parent ion in its positive ion ES mass spectrum. Higher cone voltages induce fragmentation, which in this system could be expected to proceed *via* either loss of phenyl isocyanate, or by deinsertion of dmad. Examination of the spectrum at a cone voltage of 50 V revealed only the former, with no ions attributable to loss of dmad. This is not unexpected, since platinum prefers to bond to the softer carbon atom, and the electron-withdrawing groups on the alkene linkage should further enhance the Pt–C bond stability. At a higher voltage of 80 V, fragmentation of the ester units following loss of phenyl isocyanate yielded the principal ions $[M - PhNCO - MeO^-]^+$ and $[M - PhNCO - MeOC(O)^-]^+$.

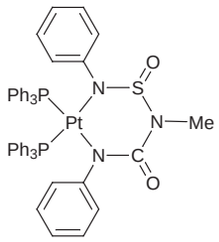
To examine the favoured orientation of an unsymmetrical acetylene upon insertion into a Pt–N of the ureylene ring, methyl propiolate [HC≡CC(O)OMe] was treated with complex **1b**. The ^1H NMR spectrum of the crude reaction mixture showed no signals attributable to the Pt(cod) moiety, indicating its complete decomposition. For this reason the more robust triphenylphosphine derivative $[\overline{Pt\{NMeC(O)N}Ph\}(PPh_3)_2]$ **11** was used. This compound had not been reported previously. Its preparation could be readily achieved directly from the silver oxide-mediated reaction of *cis*-$[PtCl_2(PPh_3)_2]$ and *N*-methyl-*N′*-phenylurea, by displacement of the cod ligand of **1b** with 2 equivalents of triphenylphosphine, or by reaction of *cis*-$[PtCl_2(PPh_3)_2]$ and *N*-methyl-*N′*-phenylurea in the presence of sodium hydride in thf. However, methyl propiolate proved too acidic and when the acetylene was added to a solution of **11**, rather than insertion into the Pt–N bond, loss of the ureylene ligand resulted to give the diacetylide complex *trans*-$[Pt\{C{\equiv}CC(O)OMe\}_2(PPh_3)_2]$ **12**. This was readily characterised by ^{31}P NMR spectroscopy which showed the formation of a symmetrical complex with $^1J(^{195}Pt-^{31}P)$ 2535 Hz. Acetylide complexes are well known and are found for most of the transition metals.[10] A number of platinum(II) examples have been structurally characterised.[11] Unsurprisingly, **12** could be readily synthesized from *cis*-$[PtCl_2(PPh_3)_2]$, methyl propiolate and silver(I) oxide. The NMR analysis of the crude reaction mixture from both the direct synthesis and by displacement of the ureylene ligand in **11** show the expected [11a] initial *cis* isomer with $^1J(^{195}Pt-^{31}P)$ 2365 Hz. This slowly converts into the *trans* isomer **12** on standing, and **12** is the only product isolated on crystallisation.

Attempted insertion reactions with *N*-sulfinylaniline and sulfur dioxide

Chemically similar to isocyanates, insertion reactions with sulfinylamines (RNSO) have attracted relatively little attention, with the isoelectronic sulfur dioxide [12,13] dominating the literature. Nonetheless, work describing sulfinylamines inserting into metal–carbon σ bonds [14] or giving co-ordination complexes from various ruthenium, osmium, rhodium and iridium compounds [15–18] has been published.

In a reaction analogous to the phenyl isocyanate insertions described above, reaction with *N*-sulfinylaniline was attempted, with the goal of forming insertion products of the type **13**. In contrast to phenyl isocyanate, the cod complex **1b** was decomposed by *N*-sulfinylaniline, although this is not surprising since the latter contains a soft sulfur atom, which would be expected to displace the labile cod ligand.

When *N*-sulfinylaniline was added to a dichloromethane solution of the triphenylphosphine derivative **11** and refluxed, a white powder was isolated. The connectivity of the product was initially not obvious, due to the continuing presence of resonances associated with a ureylene-type moiety in the ^1H and ^{13}C NMR spectra. Additionally when complex **11** was dissolved in liquid sulfur dioxide the same product was isolated, by similarity of ^{31}P, ^1H and ^{13}C NMR spectra. The complex was eventually characterised as $[\{Pt(SO_3)(PPh_3)_2\}_2]{\cdot}2PhNHC(O)NHMe$ **14**. This formulation was consistent with NMR and IR spectroscopies and elemental analysis. The absolute connectivity was determined by an X-ray crystallographic study. Compounds containing the $\overline{M-S-O-M-S-O}$ unit have been previously reported for palladium,[19] and the structure has been determined for the very closely related platinum(II) compound $[\{Pt(SO_3)(PMe_2Ph)_2\}_2]$ **15**.[20] This was formed by the hydrolysis of $[Pt(NSO)_2(PMe_2Ph)_2]$, and did not form in dry conditions even under an oxygen atmosphere. We believe it is unlikely the formation of **14** results from the *in situ* hydrolysis of *N*-sulfinylaniline to give sulfur dioxide (which could conceivably provide a source for the sulfite dianion which could subsequently displace the ureylene ligand). Although no insertion products were detected, simple attack of the ureylene ligand by free SO_3^{2-} would probably result in the formation of $[\overline{Pt\{O-S(O)-O}\}(PPh_3)_2]$, the reported reaction product of *cis*-$[PtCl_2(PPh_3)_2]$ and silver(I) sulfite.[20] Additionally, the reaction of **11** with sodium sulfite in methanol also did not give **14**. We speculate that the formation of **14** is the result of an initial insertion of *N*-sulfinylaniline or sulfur dioxide into the Pt–N bond, followed by metal-activated hydrolysis (similar to that suspected to occur for the formation of **7b** from **1b** and diphenylcarbodiimide), with the eventual extrusion of *N*-methyl-*N′*-phenylurea. Although a rigorously anhydrous protocol was not followed, even when freshly dried and distilled solvents were used, **14** was still the only significant reaction product.



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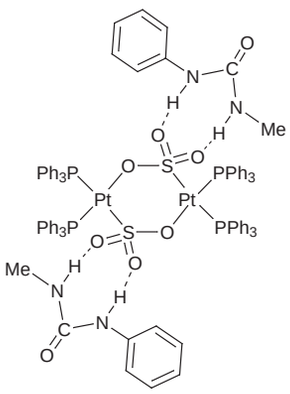

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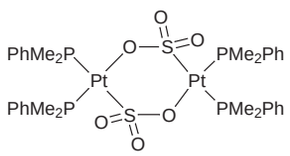

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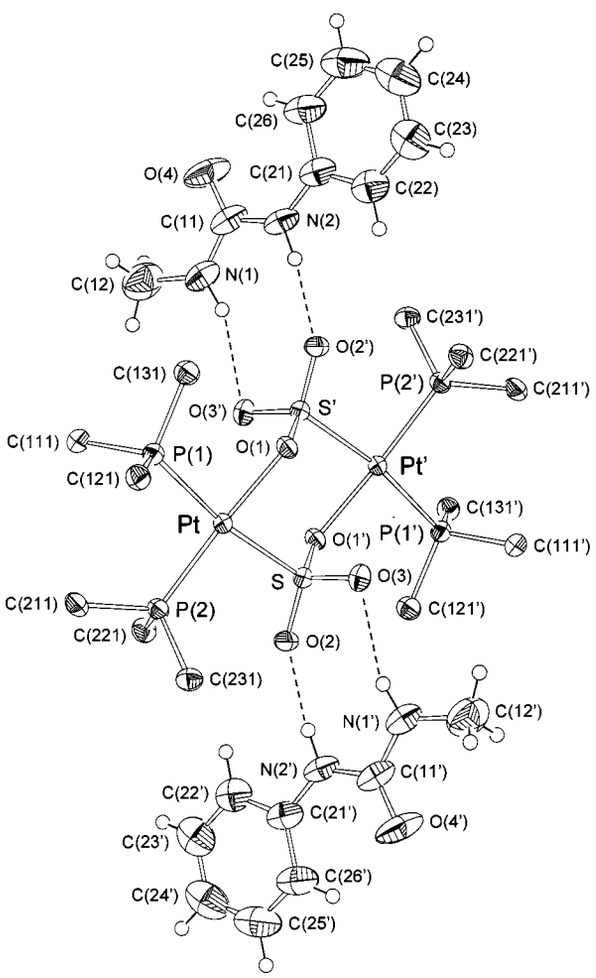


Fig. 1 Molecular structure of $[\{Pt(SO_3)(PPh_3)_2\}_2]\cdot 2PhNHC(O)NHMe\cdot 2CHCl_3$ **14**, showing the atom numbering scheme (primes denote symmetry-related atoms). Atoms are shown as thermal ellipsoids at the 50% probability level. For clarity, only the P-bonded carbons of the triphenylphosphine aromatic rings are shown, and the chloroforms of crystallisation have been omitted

Table 1 Selected bond lengths (Å) and angles (°) for complex $\mathbf{14}\cdot 2CHCl_3$ with estimated standard deviations in parentheses

Pt–P(1)	2.3404(7)	S–O(2)	1.474(2)
Pt–P(2)	2.2506(8)	S–O(3)	1.463(2)
Pt–O(1)	2.084(2)	Pt···Pt′	4.287(3)
Pt–S	2.3273(7)	S···S′	3.547(3)
S–O(1)	1.534(2)		
P(1)–Pt–P(2)	97.37(3)	Pt–S–O(2)	114.70(9)
S–Pt–O(1)	83.73(6)	Pt–S–O(3)	108.91(9)
P(1)–Pt–O(1)	87.01(6)	O(1)–S–O(2)	106.59(12)
P(2)–Pt–S	91.93(3)	O(1)–S–O(3)	109.41(12)
Pt–O(1)–S	121.82(12)	O(2)–S–O(3)	111.93(13)
Pt–S–O(1)	104.95(8)		
Cocrystallised PhNHC(O)NHMe			
C(11)–O(4)	1.233(5)	N(1)–C(12)	1.446(6)
C(11)–N(1)	1.355(6)	N(2)–C(21)	1.395(6)
C(11)–N(2)	1.367(5)		
N(1)–C(11)–N(2)	114.3(3)	C(11)–N(1)–C(12)	121.6(4)
N(1)–C(11)–O(4)	121.8(4)	C(11)–N(2)–C(21)	128.7(3)
N(2)–C(11)–O(4)	123.9(4)		
Hydrogen bonds			
O(2)···H(2)	1.944(5)	O(3)···H(1)	2.285(5)
O(2)···N(2)	2.860(5)	O(3)···N(1)	3.119(5)
N(2)–H(2)–O(2)	173.9(4)	N(1)–H(1)–O(3)	160.6(4)

Structure of complex $\mathbf{14}\cdot 2CHCl_3$. The structure shows the six-membered Pt–S–O–Pt–S–O ring system, identical to that previously reported for $\mathbf{15}\cdot 5CHCl_3$.[20] Fig. 1 shows the molecule, together with the atom numbering scheme (complex is centrosymmetric, and primes denote symmetry-related atoms). Selected bond lengths and angles are presented in Table 1.

The platinum atom has the typical distorted square-planar arrangement, with the maximum deviations for the least-square plane drawn through P(1), P(2), Pt, S and O(1) being 0.038(1) Å above and 0.034(1) Å below for S(1) and O(1) respectively. The core of the molecule has geometrical parameters almost identical to those of **15**. The chair conformation of the Pt–S–O–Pt–S–O ring is inclined 123.1(1)° between the S(1), O(1), S(1′) and O(1′) plane and the Pt, O(1) and S(1) plane; **15** shows a corresponding angle of 124°. The P–Pt bond lengths are not equal, as expected on *trans*-influence considerations,[9] with P *trans* to the higher *trans*-influence S being significantly longer [2.3404(7) Å] than P *trans* to O [2.2506(8) Å]. More detailed discussion regarding the geometry of this six-membered ring has been reported previously.[20]

The most structurally interesting feature of complex **14** is the hydrogen-bonded cocrystallised *N*-methyl-*N′*-phenylurea molecule. The hydrogen bonding occurs through the urea N–H groups and the $S(O)_2$ groups of the sulfite, as depicted in Fig. 1. The N···O contacts are markedly different in length, with N(2)···O(2) being significantly shorter [2.860(5) Å] than N(1)···O(3) [3.119(5) Å]. This is probably not due to geometric incompatibility of the urea and $S(O)_2$ groups, since the angles N(1)–C(11)–N(2) [114.3(3)°] and O(2)–S–O(3) [111.9(1)°] would suggest a good match. Rather, steric hindrance from the bulky triphenylphosphine ligands possibly restricts more optimised hydrogen bonding. Ureas hydrogen-bonded to $S(O)_2$ groups (the majority being sulfate dianions) in this way have been observed previously.[21] Additionally, hydrogen bonding between diarylureas and various cocrystallised hydrogen-bond acceptors,[22] and also between molecules of platinum(II) complexes[23,24] with various amide ligands, have attracted interest as model complexes exhibiting 'molecular recognition'. Remarkably, for the crystal structure of $[Pt(SO_3)(PMe_2Ph)_3]\cdot H_2O$ **16**[20] also containing a sulfite group, the

Table 2 Comparison of ^{1}H and ^{13}C NMR chemical shifts* of the hydrogen-bonded urea fragment of complex **14** and free *N*-methyl-*N′*-phenylurea

	δ (^{1}H)		δ (^{13}C)	
Group	**14**	MeNHC(O)-NHPh	**14**	MeNHC(O)-NHPh
PhN*H*	7.37	6.51	—	—
MeN*H*	5.59	4.86	—	—
Me	2.45	2.82	26.2	27.1
C=O	—	—	156.7	156.7
ipso-H/C	—	—	141.2	138.5
ortho-H/C	7.09	7.28	118.2	121.6
meta-H/C	7.19	7.32	128.1	129.4
para-H/C	6.80	7.09	120.0	124.1

* All data acquired in $CDCl_3$ solvent and referenced to $SiMe_4$ (δ 0.0).

authors report no hydrogen bonding between the SO_3 and the water of crystallisation. The *N*-methyl-*N′*-phenylurea of crystallisation is almost planar with no atom deviating from a least-squares plane drawn through every non-hydrogen atom of the molecule by more than 0.201(5) Å above for C(12) and 0.116(4) Å below the plane for O(4).

Attempts to remove the cocrystallised urea from complex **14** by repeated recrystallisation proved futile, and neither *N*-methyl-*N′*-phenylurea nor $[\{Pt(SO_3)(PPh_3)_2\}_2]$ could be isolated separately, indicating the hydrogen bonding has a substantial effect for this compound, persisting in solution (see NMR analysis) and directing the crystallisation.

One of the two chloroforms of crystallisation also forms a convincing hydrogen bond to O(3), with a C···O contact of 3.086(6) Å.

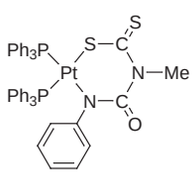
Spectroscopic properties of complex 14. The ^{31}P NMR spectrum of complex **14** shows the expected AB pattern, with chemical shifts of δ 21.3 and 10.5 showing ^{195}Pt–^{31}P coupling of 2459 and 4331 Hz. These were assigned as P *trans* to S and P *trans* to O respectively, on the basis of the *trans* influences associated with these atoms.[9] The related compound **15** shows similar coupling constants of 2329 and 3986 Hz, the discrepancy due to the electronically different phosphine moieties (PPh_3 and PMe_2Ph).

Interestingly, the *N*-methyl-*N′*-phenylurea present in solution shows different chemical shift values to those of the free urea (Table 2), indicating the persistence of the hydrogen-bonding interactions with the $S(O)_2$ unit in solution. The NH resonances are the most affected, as expected, with downfield differences in their chemical shifts of 0.86 and 0.73 ppm for the NH groups adjacent to the phenyl and methyl moieties respectively. This is consistent with the notion of decreased shielding of protons caused by a lowering of electron density associated with hydrogen-bond formation. Unexpectedly, the carbonyl carbon appears to be unaffected, showing a value of δ 156.7 for both **14** and free *N*-methyl-*N′*-phenylurea.

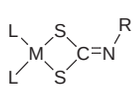
The IR values for complex **14** are significantly different to those reported for **15**, presumably due to the hydrogen bonding present in **14** only. Significant bands in the SO_3 stretching region (1200–900 cm^{-1}) appear at 1177, 1096, 1063 and 923 cm^{-1}, compared with values of 1168, 1156, 1048 and 1004 cm^{-1} given for **15**.[20] In the NH stretching region (3500–3000 cm^{-1}) bands are observed at 3082 and 3056 cm^{-1}, compared with bands at 3360 and 3316 cm^{-1} for free *N*-methyl-*N′*-phenylurea, thus showing a lowering in stretching frequency, as expected for hydrogen-bonded NH groups.[25]

Insertion reaction with carbon disulfide

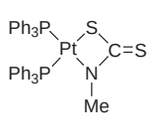
When carbon disulfide was added to a dichloroemethane solution of complex **11**, and stirred for 3 min, the carbon disulfide-inserted product $[Pt\{S_2CNMeC(O)NPh\}(PPh_3)_2]$ **17** was produced in quantitative yield according to ^{31}P NMR analysis of the residue. Large yellow blocks could be obtained on addition of diethyl ether to the chloroform solution. The compound was fully characterised by ^{31}P, ^{1}H and ^{13}C NMR, ESMS spectroscopy, elemental analysis and a single-crystal X-ray crystallographic study. Solutions of the complex slowly decompose to produce, in high yield, a second product **18a**, discussed later. As for the reaction involving *N*-sulfinylaniline, carbon disulfide readily decomposes the cod complex **1b**.



17



18a M = Pt, L = PPh_3, R = Me
18b M = Pt, L = PEt_3, R = CH_2Ph
18c M = Pd, L = PEt_3, R = CH_2Ph
18d M = Pt, L = PPh_3, R = Bu^n



19

Structure of complex 17·$CHCl_3$. The structure confirms the insertion of carbon disulfide into the Pt–NMe bond of complex **11** [Fig. 2(a), Table 3]. The most striking feature of the structure is the highly puckered six-membered metallacyclic ring, as depicted in Fig. 2(b). The butterfly angle between the least-squares planes drawn through Pt, S(2), N(2) and N(2), S(2), N(1) is 58.6(1)°. The reason for the puckering of the metallacycle is not entirely clear, but high fold angles have been observed previously for the M–S–C–C–C(O)–O six-membered ring in the platinum(II) and gold(III) thiosalicylate complexes $[Pt\{SC_6H_4(COO)\text{-}2\}(PPh_3)_2]$[26] and $[\{C_6H_4(CH_2NMe_2)\text{-}2\}Au\{SC_6H_4(COO)\text{-}2\}]$.[27] The planes Pt, S(2), N(2) and the phenyl ring [C(11)–C(16)] are almost at right angles [88.8(1)°].

The platinum has a distorted square-planar geometry. A least-squares plane drawn through P(1), P(2), Pt, S(2) and N(2) shows maximum deviations of 0.166(1) Å for S(2) above and

Table 3 Selected bond lengths (Å) and angles (°) for complex **17**·$CHCl_3$ with estimated standard deviations in parentheses

Pt–P(1)	2.2921(10)	Pt–N(2)	2.066(3)
Pt–P(2)	2.2686(10)	Pt–S(2)	2.3358(10)
P(1)–Pt–P(2)	97.21(4)	Pt–S(2)–C(1)	101.15(16)
S(2)–Pt–N(2)	83.53(10)	Pt–N(2)–C(2)	126.5(3)
P(1)–Pt–N(2)	94.20(10)	Pt–N(2)–C(11)	115.5(3)
P(2)–Pt–S(2)	86.17(4)		
$S_2CNMeC(O)NPh$ ligand			
C(1)–S(2)	1.736(5)	N(1)–C(2)	1.454(6)
C(1)–S(1)	1.672(6)	C(2)–O(1)	1.232(6)
C(1)–N(1)	1.360(6)	C(2)–N(2)	1.323(6)
N(1)–C(3)	1.470(6)	N(2)–C(11)	1.441(6)
S(2)–C(1)–S(1)	116.3(3)	C(3)–N(1)–C(2)	113.0(4)
S(2)–C(1)–N(1)	121.7(3)	N(1)–C(2)–N(2)	116.6(4)
S(1)–C(1)–N(1)	122.0(3)	N(1)–C(2)–O(1)	116.8(4)
C(1)–N(1)–C(2)	122.0(4)	O(1)–C(2)–N(2)	126.6(5)
C(1)–N(1)–C(3)	118.9(4)	C(2)–N(2)–C(11)	116.6(4)

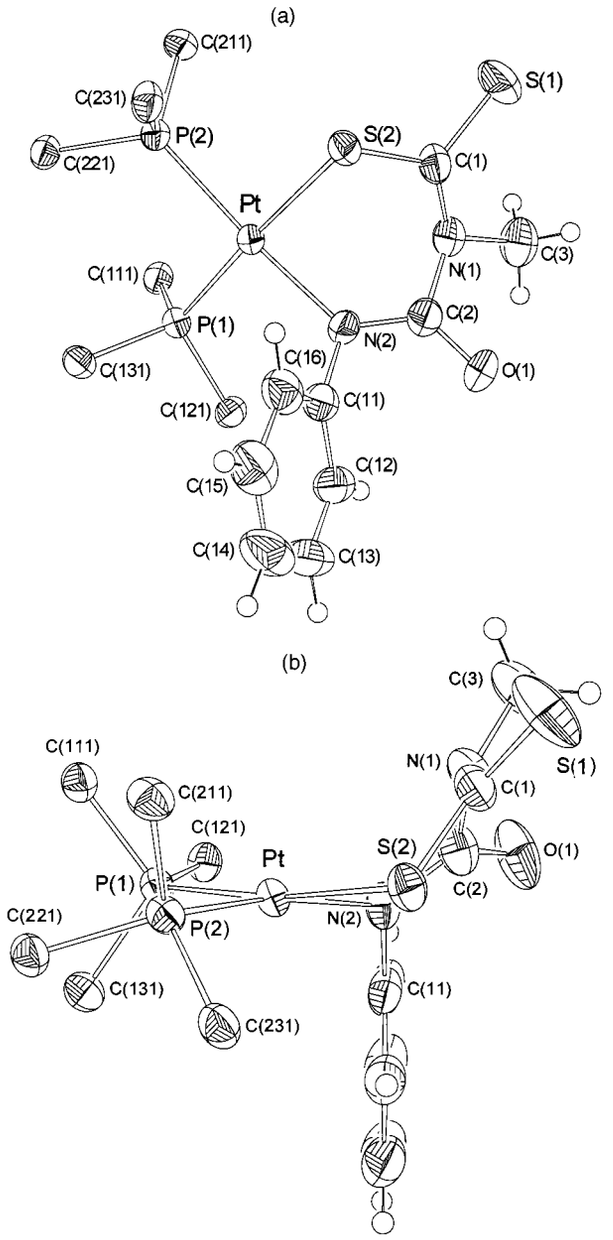


Fig. 2 (a) Perspective view of the molecular structure of $[Pt\{S_2CNMeC(O)NPh\}(PPh_3)_2]\cdot CHCl_3$ **17**, showing the atom numbering scheme. Atoms are shown as thermal ellipsoids at the 50% probability level. (b) Side view of **17**. For clarity, only the P-bonded carbons of the triphenylphosphine aromatic rings are shown, and the chloroform of crystallisation has been omitted

0.168(1) Å below the plane for N(2). The six-membered metallacyclic ring allows the platinum to adopt an N–Pt–S angle of 83.5(1)°, much closer to ideal square-planar geometry. For comparison, the N–Pt–N angle for **1c** (a complex closely related to the starting material **1b**), with a four-membered ring, is 64.7(3)°.

The N(1)–C(2)–N(2) angle of 116.6(4)° is larger than that of complex **1c** [104.1(7)°] as expected for a less constrained ligand. Indeed the angle is only marginally larger than the analogous N(1)–C(11)–N(2) angle of the free *N*-methyl-*N′*-phenylurea ligand present in **14**, which has an angle 114.3(3)°.

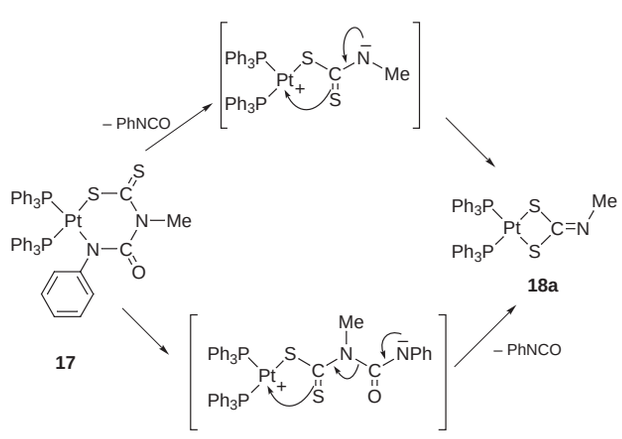
The Pt–P bonds are not equal [2.2921(10) and 2.2686(10) Å for Pt–P(1) and Pt–P(2) respectively], as expected for a non-symmetrical structure. The longer bond is *trans* to the higher *trans*-influence sulfur as predicted,[9] although the difference here is not as marked as that in the structure of **14**. The C–S bond lengths are also not equal [1.672(5) Å for C(1)=S(1) and 1.736(5) Å for C(1)–S(2)], and the difference [0.064(7) Å] is that expected for formally single and double bonds, with sp^2-hybridised C=S bond lengths averaging 1.67(2) Å and C–S averaging 1.76(2) Å.[28]

Spectroscopic properties of complex 17. The ^{31}P NMR spectrum of complex **17** shows the expected AB spin pattern with signals at δ 18.0 and 5.3 with $^1J(^{195}Pt–^{31}P)$ 3098 Hz and 3211 Hz, corresponding to PPh_3 *trans* to sulfur and nitrogen respectively. As for the phenyl isocyanate and dmad reactions, insertion took place only at the Pt–NMe bond, readily deduced from the ^1H NMR spectrum, with the methyl signal devoid of ^{195}Pt and ^{31}P coupling. In the ^{13}C NMR spectrum the carbonyl carbon again moved upfield from δ 176.9 to 155.0, consistent with the shifts observed for the inserted products **7b** (phenyl isocyanate) and **10** (dmad). The C=S carbon, at δ 205.1, is more deshielded than free CS_2, which appears at δ 192.6.

The infrared spectrum of complex **17** shows a number of bands in the carbonyl region (1700–1550 cm^{-1}) with absorbances at 1646, 1632 and 1586 cm^{-1}, and these have slightly higher energies than those of the starting ureylene complex **11** (1636, 1592 and 1571 cm^{-1}). The vibrations associated with the CS_2 group cannot be readily identified because of coupling and overlap with other peaks, but are probably found among the bands at 1265, 1096 and 1069 cm^{-1}.

The ESMS spectrum of complex **17** at a cone voltage of 20 V shows a very strong peak at *m*/*z* 945 attributable to the parent ion $[M + H]^+$. A number of other signals were also observed. At *m*/*z* 1434 a signal assigned as $[3M + 2NH_4]^{2+}$ is seen, its dicationic nature confirmed by a higher resolution acquisition showing an isotope peak spacing of 0.5 mass units. Loss of phenyl isocyanate was also observed, even at low cone voltages, with a peak at *m*/*z* 825. Loss of carbon disulfide was detected only at higher voltages (50 V), and only as additional fragmentation of the $[M + H - PhNCO]^+$ ion, to give *m*/*z* 751 assigned as $[M + H - PhNCO - CS_2]^+$, with $[M + H - CS_2]$ not observed. This result is consistent with the high relative stability of the Pt–S bond.

Decomposition of complex 17. When dichloromethane or chloroform solutions of complex **17** were left standing overnight, the ^{31}P NMR spectrum showed it was slowly decomposing to a second compound. Complete decomposition was effected after a week, during which time the solution became noticeably paler. Crystallisation of the yellow residue from chloroform gave colourless crystals and an X-ray crystallographic study revealed the compound to be the complex $[Pt(S_2C{=}NMe)(PPh_3)_2]$ **18a**. A range of these complexes has been reported previously by reaction of *cis*-$[PtCl_2L_2]$ (L = PPh_3 or PEt_3) with primary amines RNH_2 [R = Ph, CH_2Ph, Bu^n, Bu^t, cyclopentyl, CH_2CO_2H, CH_2CO_2Et, CH_2CH_2OH or CH(Me)-CO_2Et] and carbon disulfide in dichloromethane to give



Scheme 1

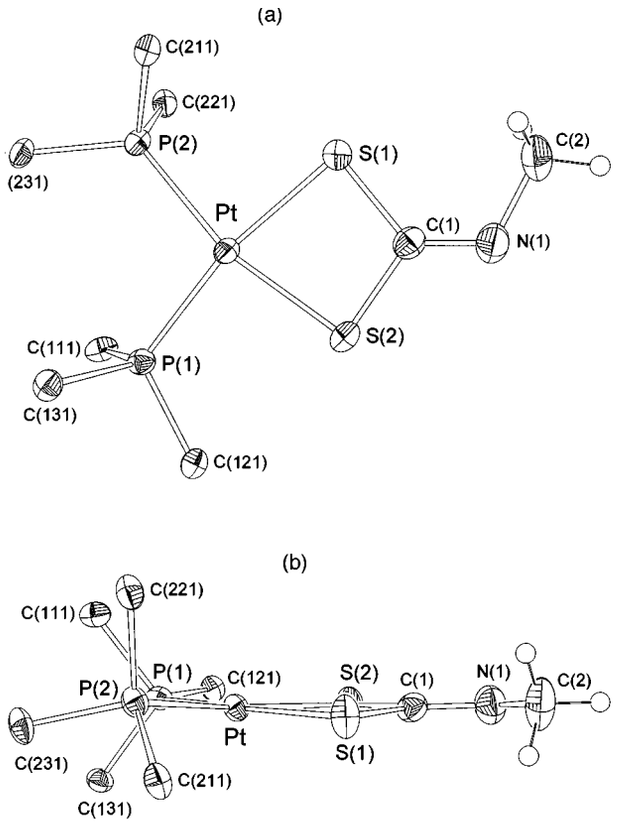


Fig. 3 (a) Perspective view of the molecular structure of [Pt(S_2C=N-Me)(PPh_3)$_2$] **18a**, showing the atom numbering scheme. Atoms are shown as thermal ellipsoids at the 50% probability level. (b) Side view of **18a**. For clarity, only the P-bonded carbons of the triphenylphosphine aromatic rings are shown

[Pt(S_2C=NR)L_2],[29] and **18a** could indeed be readily prepared by reacting *cis*-[$PtCl_2(PPh_3)_2$], methylamine and carbon disulfide.

The compound **18a** could arise either by loss of phenyl isocyanate to initially give intermediate **19** (analogous to the loss of phenyl isocyanate seen for the biureto systems both synthetically and in ES mass spectra), which rearranges to **18a** because of the relatively high lability of the Pt–NMe bond and the affinity of platinum(II) for the softer sulfur atom. However, more likely, the loss of phenyl isocyanate or simple ring opening of **17** could give either of the intermediate species **20** which, by a one-step process, could then rearrange to give **18a** (Scheme 1). The reaction by-product, phenyl isocyanate, was converted to *N*,*N*′-diphenylurea by adventitious water, and characterised by ^{1}H and ^{13}C NMR spectra of the crude residue. It was not isolated.

Structure of complex 18a. Fig. 3(a) illustrates the platinum(II) complex **18a** together with the atom numbering scheme. Selected bond lengths and angles are presented in Table 4. The structure is analogous to those previously reported for the platinum and palladium complexes[29] [Pt(S_2C=NCH_2Ph)(PEt_3)$_2$] **18b** and [Pd(S_2C=NCH_2Ph)(PEt_3)$_2$] **18c**. Owing to the restricted rotation about the C=N double bond, the molecule is asymmetrical, giving rise to non-equivalent Pt–P bond lengths: Pt–P(2) (phosphorus *cis* to Me) is slightly longer than Pt–P(1), although the difference [0.018(2) Å] is only small, since the locale of the asymmetry is quite removed from the metal centre. This is also witnessed in the ^{31}P NMR spectrum, which shows very similar chemical shifts and ^{31}P–^{195}Pt coupling constants for the two phosphorus atoms (see below). Similarly, the Pt–S bond lengths are not equal, with Pt–S(1) [2.342(2) Å] longer than Pt–S(2) [2.321(2) Å].

As seen in Fig. 3(b), the molecule (excluding the phenyl rings) is essentially planar, and least-squares analysis reveals the P(1), P(2), Pt, S(1) and S(2) plane to have maximum deviations of 0.046(1) Å [P(2)] above, and 0.051(1) Å [S(2)] below, the plane. For the plane drawn through the metallacycle and ligand [Pt, S(1), S(2), C(1), N(1) and C(2)] the largest deviations are 0.056(2) Å for Pt and 0.060(3) Å for S(1). Since the metallacycle is four-membered the S(1)–Pt–S(2) angle is only 75.46(6)°. However, the two co-ordinating sulfur atoms, being larger, are somewhat more accommodating than the nitrogen atoms in the ureylene complex **1c**, which has a N–Pt–N angle of 64.7(3)°.

Table 4 Selected bond lengths (Å) and angles (°) for complex **18a** with estimated standard deviations in parentheses

Pt–P(1)	2.280(2)	Pt–S(2)	2.321(2)
Pt–P(2)	2.298(2)	Pt···C(1)	2.902(2)
Pt–S(1)	2.342(2)		
P(1)–Pt–P(2)	100.59(6)	P(1)–Pt–S(2)	93.34(3)
S(1)–Pt–S(2)	75.46(6)	Pt–S(1)–C(1)	88.7(2)
P(2)–Pt–S(1)	90.55(6)	Pt–S(2)–C(1)	89.2(2)
S_2C=NMe ligand			
S(1)–C(1)	1.775(7)	C(1)–N(1)	1.285(9)
S(2)–C(1)	1.783(7)	N(1)–C(2)	1.483(11)
S(1)–C(1)–S(2)	106.6(4)	S(2)–C(1)–N(1)	124.4(6)
S(1)–C(1)–N(1)	129.0(6)	C(1)–N(1)–C(2)	116.9(7)

Comparing complex **18a** with the previously reported **18b**,[29] reveals the structures, as expected, to be very similar. The respective Pt–S, C=N and N–C bond length and P–Pt–P, S–Pt–S, S–C–S and Pt–S–C bond angles are essentially identical. However, the structure of **18a** is very accurate (*R* factor 0.024) and allows tentative determination of the relative *trans* influences of the two inequivalent sulfur atoms. Using bond length criteria [Pt–P(1) 2.280(2) Å and Pt–P(2) 2.298(2) Å], the sulfur [S(2)] *trans* to the methyl group has the higher *trans* influence, thus lengthening the Pt–P bond. This is consistent with the notion of Pt–S(2) being shorter than Pt–S(1) since S(1), being in a less sterically crowded position, can make a closer approach to the metal centre, thus acting as a slightly higher *trans*-influence ligand.

NMR and ESMS characterisation of complex 18a. The ^{31}P NMR spectrum shows the expected AB pattern fully consistent with two phosphorus atoms occupying very similar chemical environments, both *trans* to sulfur. On the basis of the *trans* influences suggested crystallographically, the resonances at δ 19.6 [^1J(^{195}Pt–^{31}P) 3107 Hz] and 18.8 [^1J(^{195}Pt–^{31}P) 3086 Hz] tentatively correspond to phosphorus atoms *trans* to S(1) and S(2) respectively (numbering scheme of crystal structure). These chemical shifts and the ^1J(^{195}Pt–^{31}P) coupling are very similar to those reported for the most closely related complex [Pt(S_2C=NBu^n)(PPh_3)$_2$] **18d**, which shows δ 20.9 [^1J(^{195}Pt–^{31}P) 3133 Hz] and 19.4 [^1J(^{195}Pt–^{31}P) 3103 Hz]. The central C=N carbon resonates at δ 171.5, significantly lower than for the S_2CN carbon in **17** with a chemical shift of δ 205.1, in the absence of the highly electronegative thiocarbonyl group. The value compares with δ 176.2 recorded for complex **18d**.

The ESMS spectrum of complex **18a** is completely consistent with that expected for [Pt(S_2C=NMe)(PPh_3)$_2$]. At low cone voltages the parent ion $[M + H]^+$ at *m*/*z* 826 is the only observed species. Significant fragmentation was not detected until a moderately high cone voltage of 80 V was used, when loss of triphenylphosphine was observed. This is not a typical fragmentation pathway for triphenylphosphine platinum derivatives, with (non-triphenylphosphine) ligand loss and subsequent cyclometallation to give [Pt{C_6H_4}PPh_2}(PPh_3)] (as seen for the acetylide complex **12**) more usual. This result suggests a high stability for the platinum ring system in **18a**.

More extensive fragmentation could only be induced with very high voltages >120 V.

Conclusion

The platinum(II) ureylene complexes investigated appear to be quite reactive compounds, readily inserting phenyl isocyanate, dmad and carbon disulfide. The Pt–NMe linkage displays much higher reactivity than Pt–NPh in the unsymmetrical ureylene systems **1b** and **11**, with insertion taking place exclusively in the Pt–NMe bond. In electrospray spectra of all the successful insertions loss of phenyl isocyanate was the major decomposition pathway, and this was also observed synthetically in the decomposition of **7a**, **7b** and **17**.

Experimental

Melting points were measured in air on a Reichert hostage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Bio-Rad FTS-40 spectrophotometer and electrospray mass spectra in positive-ion mode on a VG Platform II instrument using MeCN–water (1 : 1) as the mobile phase. Calculated isotope patterns were obtained using the ISOTOPE program.[30] Elemental analyses were performed by the Campbell Microanalytical Laboratory, University of Otago. All ^{1}H and ^{13}C-{^{1}H} NMR spectra and all normal mode (NOE) and two-dimensional (^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY and BIRDTRAP, bilinear rotational decoupling with two-step *J* filter purge) experiments were recorded on a Bruker AC300 spectrometer at 300.13 and 75.47 MHz for the proton and carbon channels respectively. Additional inverse two-dimensional experiments (HSQC, heteronuclear single quantum coherence; HMBC, heteronuclear multiple bond correlation; NOESY; and HOHAHA, homonuclear Hartmann–Hahn transfer) were recorded on a Bruker DRX 400 spectrometer at 400.13 and 100.61 MHz for the proton and carbon channels. All NMR work is referenced to $SiMe_4$ (δ 0.0) as the external standard, and all analyses were carried out in $CDCl_3$, with the exception of the ^{13}C NMR spectrum of *N*,*N*′-diphenylurea which was acquired in $CD_3S(O)CD_3$.

Dimethyl acetylenedicarboxylate, methyl propiolate, diphenylacetylene (all Aldrich), phenyl isocyanate, sulfur dioxide (both BDH) and carbon disulfide (May and Baker) were used as received. The sodium hydride (Koch-Light) used for the synthesis of complexes **1a** and **11** was oil-free and freshly powdered. *N*,*N*′-Diphenylurea [m.p. 239–240 °C (lit.,[31] 238 °C)] and *N*-methyl-*N*′-phenylurea [m.p. 178 °C (lit.,[31] 178 °C)] were prepared by the condensation of phenyl isocyanate and aniline or methylamine (33% in ethanol) respectively, in diethyl ether. The platinum ureylene[2] and guanidine[8] precursors were prepared by the literature procedure. *N*-Sulfinylaniline[32] and diphenyl carbodiimide[33] were also prepared by literature methods, distilled, and their purity checked by NMR spectroscopy.

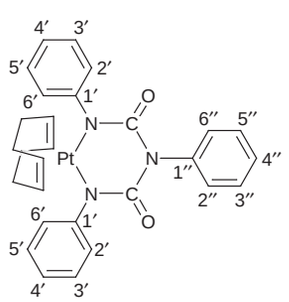
Preparations

Complex 11. To a flask containing dichloromethane (30 cm^3) was added *cis*-[$PtCl_2(PPh_3)_2$] (0.101 g, 0.128 mmol), *N*-methyl-*N*′-phenylurea (0.020 g, 0.133 mmol) and silver(I) oxide (0.12 g, excess) and the solution refluxed for 24 h. The silver salts were removed by filtration and the dichloromethane removed under reduced pressure. The resulting bright yellow residue was dissolved in dichloromethane and diethyl ether slowly added, to give bright yellow crystals of complex **11** (0.071 g, 64%).

Alternatively, to a flask containing dry thf (30 cm^3) was added *cis*-[$PtCl_2(PPh_3)_2$] (0.200 g, 0.253 mmol), *N*-methyl-*N*′-phenylurea (0.038 g, 0.253 mmol) and powdered sodium hydride (0.5 g, excess). The flask was stoppered and the suspension rapidly stirred at room temperature for 2 h, during which time the solution became bright yellow. The insoluble matter was filtered off and the thf removed under reduced pressure. Dichloromethane (10 cm^3) was added to the residue and any remaining solids filtered off. Diethyl ether was slowly added to the supernatant to give yellow crystals of complex **11** (0.160 g, 73%), and a cloudy suspension that could conveniently be separated from the crystals by decantation, m.p. 231–232 °C (melts with decomposition). IR: ν̃(CO region) 1636vs, 1592s and 1571w cm^{-1} (Found: C, 60.0; H, 4.5; N, 3.2. $C_{44}H_{38}N_2OP_2Pt$ requires C, 60.9; H, 4.4; N, 3.2%). ^{31}P NMR (121.49 MHz, $CDCl_3$): δ 13.5 (d, $^{2}J_{PP}$ = 21.9 Hz, $^{1}J_{PPt}$ = 3328.8, PPh_3 *trans* NPh) and 11.2 (d, $^{2}J_{PP}$ = 21.9, $^{1}J_{PPt}$ = 3249.1 Hz, PPh_3 *trans* NMe). ^{1}H NMR: δ 7.53–7.40 (12 H, m, PPh_3), 7.33 (3 H, t, $^{3}J_{HH}$ = 7.01, H-4, PPh_3), 7.18 (9 H, m, PPh_3), 7.03 (6 H, t, $^{3}J_{HH}$ = 7.67, PPh_3), 6.73 [2 H, d, $^{3}J(H^{2'}H^{3'})$ = 7.84, H-2′,6′], 6.62 [2 H, t, $^{3}J(H^{3'}H^{2'}/H^{4'})$ = 7.55, H-3′,5′], 6.53 [1 H, t, $^{3}J(H^{4'}H^{3'})$ = 7.02, H-4′] and 2.21 [s, $^{3}J_{HPt}$ = 34.64, $^{4}J_{HP}$ = 5.45 Hz, CH_3]. ^{13}C NMR: δ 176.9 (s, C=O), 146.8 (s, C-1′), 134.6 (d, $^{3}J_{CP}$ = 11.1 Hz, C-3,5, PPh_3), 134.0 (d, $^{3}J_{CP}$ = 11.2), C-3,5, PPh_3), 130.8 (d, C-4, PPh_3), 130.3 (s, $^{1}J_{CP}$ = 45.1, C-1, PPh_3), 130.0 (s, $^{1}J_{CP}$ = 34.9, C-1, PPh_3), 128.3 (d, $^{2}J_{CP}$ = 10.8, C-2,6, PPh_3), 127.9 (d, $^{2}J_{CP}$ = 10.9, C-2,6, PPh_3), 127.3 (d, C-2′, 6′,3′,5′), 121.0 (d, C-4′) and 31.4 (q, $^{2}J_{CPt}$ = 27.3, $^{3}J_{CP}$ = 3.3 Hz, CH_3).

Complex 1a. *N*,*N*′-Diphenylurea (0.116 g, 0.547 mmol) and [$PtCl_2$(cod)] (0.201 g, 0.537 mmol) were added to a flask containing thf (30 cm^3). Sodium hydride (1 g, excess) was added, the flask stoppered, and the suspension stirred vigorously for 45 min, during which time the suspension became bright yellow. Dichloromethane (30 cm^3) was added completely to effect dissolution of the product, and the insoluble sodium salts were filtered off. The solvent was removed under reduced pressure, and the residue recrystallised by addition of diethyl ether to a dichloromethane solution. The microcrystalline product was filtered off and dried under vacuum to give complex **1a** (0.154 g, 56%), characterised by spectroscopic properties as identical to an authentic sample prepared by the literature procedure.[2]

Complex 7a. To a dichloromethane (20 cm^3) solution of [Pt{PhNC(O)NPh}(cod)] **1a** (0.050 g, 0.097 mmol) was added phenyl isocyanate (5 drops, excess) and the mixture refluxed for 2 h, during which time it became markedly paler. Evaporation of the dichloromethane and recrystallisation of the residue (by vapour diffusion of diethyl ether into a chloroform solution) gave complex **7a** as colourless crystals (0.055 g, 90%), m.p. 140 °C (decomposes without melting) (Found: C, 47.0; H, 3.7; N, 5.6. $C_{28}H_{27}N_3O_2Pt\cdot CHCl_3$ requires C, 46.4; H, 3.8; N, 5.6%). IR: ν̃(CO region) 1642vs, 1610s and 1588m cm^{-1}. ESMS: (cone voltage = 20 V) *m*/*z* 1288 ([2*M* + Na]$^+$, 32), 1169 ([2*M* + Na − PhNCO]$^+$, 9), 971 ([3*M* + Na + H]$^{2+}$, 23), 868 ([4*M* + Na + 2H]$^{3+}$, 14), 696 ([*M* + Na + MeCN]$^+$, 23), 655 ([*M* + Na]$^+$, 100), 634 ([*M* + H]$^+$, 23), 536 ([*M* + Na − PhNCO]$^+$, 10) and 354 {[PhNHC(O)NPhC(O)NPh + Na]$^+$, 16}; (cone voltage = 50 V) 1288 ([2*M* + Na]$^+$, 30), 1169 ([2*M* + Na − PhNCO]$^+$, 33), 1050 ([2*M* + Na − 2PhNCO]$^+$, 56), 971 ([3*M* + Na + H]$^{2+}$, 5), 868 ([4*M* + Na + 2H]$^{3+}$, 29), 634 ([*M* + H]$^+$, 3), 577 ([*M* + Na − PhNCO + MeCN]$^+$, 27), 536 ([*M* + Na − PhNCO]$^+$,



100) and 514 ([*M* + H − PhNCO]$^+$, 11); (cone voltage = 80 V) 1050 ([2*M* + Na − 2PhNCO]$^+$, 10), 536 ([*M* + Na − PhNCO]$^+$, 100) and 354 {[PhNHC(O)NPhC(O)NHPh + Na]$^+$, 6%}. ^{1}H NMR: δ 7.35–7.30 (12 H, m, H-2′,6′,3′,5′,2″,6″,3″,5″), 6.74 [1 H, t, ^3J(H$^{4''}$H$^{3''}$) = 6.74, H-4″], 7.13 [2 H, t, ^3J(H$^{4'}$H$^{3'}$) = 6.81, H-4′], 4.61 (4 H, s, br, $^2J_{HPt}$ = 53.15 Hz, C*H*=CH), 2.50 (4 H, m, br, CH_2CH) and 2.12 (4 H, m, br, CH_2CH). ^{13}C NMR: δ 155.9 (s, C=O), 147.3 (s, C-1′), 140.9 (s, C-1″), 130.0 (d, C-2″), 129.3 (d, C-2′,6′), 128.4 (d, C-3′,5′), 128.1 (d, C-3″), 126.7 (d, C-4″), 125.7 (d, C-4′), 100.3 (d, $^1J_{CPt}$ = 145.2 Hz, *C*H=CH) and 29.6 (t, *C*H$_2$CH).

Alternatively, to a dichloromethane (20 cm^3) solution of [Pt{PhNC(=NPh)NPh}(cod)] **9**[8] (0.025 g, 0.042 mmol) was added phenyl isocyanate (5 drops, excess) and the mixture refluxed for 2 h. During this time the solution became noticeably paler. The solvent was removed under reduced pressure, and the residue crystallised by vapour diffusion of diethyl ether into a dichloromethane solution, to give colourless crystals, characterised as complex **7a** (0.024 g, 89%) by the NMR and ESMS spectra.

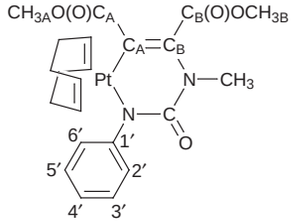
Complex 7b. To a dichloromethane solution of complex **1b** (0.032 g, 0.071 mmol) was added phenyl isocyanate (4 drops, excess), and stirred for 2 min. The solution became almost immediately paler. Evaporation of the solvent and crystallisation of the residue by vapour diffusion of diethyl ether into a dichloromethane solution containing two drops of phenyl isocyanate gave **7b** as almost colourless crystals (0.033 g, 82%). Slow deinsertion of phenyl isocyanate to regenerate **1b** was observed on standing solutions of **7b** in the absence of free isocyanate.

Alternatively, to dichloromethane (50 cm^3) was added [PtCl$_2$(cod)] (0.102 g, 0.273 mmol), *N*-methyl-*N′*-phenylurea (0.042 g, 0.280 mmol), silver(I) oxide (0.12 g, excess) and phenyl isocyanate (10 drops excess) and the mixture refluxed, with a drying tube fitted to the condenser, for 18 h. The silver salts were filtered off, and the solvent removed from the supernatant under reduced pressure. To the oily orange residue was added diethyl ether, to give a brown powder, revealed by NMR spectrometry to be a mixture of **7a** and **7b**, in a 1:6 ratio respectively. Pure **7b** could be readily achieved by the recrystallisation process detailed above (0.113 g, 74%), m.p. 167–168 °C (Found: C, 45.8; H, 4.2; N, 6.4. $C_{23}H_{25}N_3O_2Pt\cdot 0.5CH_2Cl_2$ requires C, 46.1; H, 4.3; N, 6.9%). IR: ν̃(CO region) 1641vs, 1632vs, 1611s, 1600s and 1584s cm^{-1}. ESMS: (cone voltage = 20 V) *m/z* 633 ([*M* + Na + MeCN]$^+$, 8), 588 ([*M* + NH$_4$]$^+$, 5), 571 ([*M* + H]$^+$, 100); (cone voltage = 50 V) 633 ([*M* + Na + MeCN]$^+$, 3), 571 ([*M* + H]$^+$, 91), 514 ([*M* + Na − PhNCO + MeCN]$^+$, 10), 473 ([*M* + Na − PhNCO]$^+$, 14) and 452 ([*M* + H − PhNCO]$^+$, 100%). ^{1}H NMR: δ 7.34 [4 H, t, ^3J(H$^{3'}$H$^{2'}$/H$^{4'}$) = 7.55, H-3′,5′], 7.27 [4 H, d, ^3J(H$^{2'}$H$^{3'}$) = 8.92, H-2′,6′], 7.15 [2 H, t, ^3J(H$^{4'}$H$^{3'}$) = 7.08, H-4′], 5.29 (1 H, s, CH_2Cl_2 of crystallisation), 4.53 (4 H, s, br, $^2J_{HPt}$ = 56.13 Hz, C*H*=CH), 3.14 (3 H, s, CH$_3$), 2.48 (4 H, m, br, CH_2CH) and 2.10 (4 H, m, br, CH_2CH). ^{13}C NMR: δ 156.4 (s, C=O), 147.7 (s, C-1′), 129.2 (d, C-3′,5′), 128.5 (d, C-2′,6′), 125.7 (d, C-4′), 99.9 (d, $^1J_{CPt}$ = 143.1, *C*H=CH), 32.6 (q, CH$_3$) and 29.5 (t, *C*H$_2$CH).

Reaction of complex 7b with HCl. The complex **7b** (0.025 g, 0.044 mmol) was dissolved in dichloromethane (5 cm^3) and three drops of concentrated hydrochloric acid added. The solution immediately became paler. After 5 min of stirring the volatiles were removed under vacuum. The residue was dissolved in the minimum quantity of dichloromethane, and an excess of diethyl ether was added. The white precipitate, characterised spectroscopically as [PtCl$_2$(cod)] (0.014 g, 88%), was removed by filtration. The solvent was removed from the supernatant to give a colourless residue. This was recrystallised from chloroform and pentane to give large colourless blocks of *N′*-methyl-*N*,*N″*-diphenylbiuret (0.009 g, 76%), m.p. 54–55 °C (Found: C, 66.6; H, 5.5; N, 15.7. $C_{15}H_{15}N_3O_2$ requires C, 66.9; H, 5.6; N, 15.6%). ESMS: (cone voltage = 20 V) *m/z* 561 ([2*M* + Na]$^+$, 50), 556 ([2*M* + NH$_4$]$^+$, 35), 333 ([*M* + Na + MeCN]$^+$, 11), 292 ([*M* + Na]$^+$, 12), 287 ([*M* + NH$_4$]$^+$, 39) and 270 ([*M* + H]$^+$, 100%); (cone voltage = 50 V) *m/z* 561 ([2*M* + Na]$^+$, 50), 424 (unidentified, 11), 333 ([*M* + Na + MeCN]$^+$, 26), 292 ([*M* + Na]$^+$, 56), 270 ([*M* + H]$^+$, 100) and 151 ([*M* + H − PhNCO]$^+$, 60%). ^{1}H NMR; δ 9.20 (2 H, s, NH), 7.46 [4 H, d, ^3J(H$^{2'}$H$^{3'}$) = 7.94, H-2′,6′], 7.34 [4 H, t, ^3J(H$^{3'}$H$^{2'}$/H$^{4'}$) = 7.74, H-3′,5′], 7.13 [2 H, t, ^3J(H$^{4'}$H$^{3'}$) = 7.30 Hz, H-4′] and 3.46 (3 H, s, NCH$_3$). ^{13}C NMR (75.47 MHz, CDCl$_3$): δ 154.2 (s, NC=O), 137.5 (s, C-1′), 129.1 (d, C-3′,5′), 124.6 (d, C-2′,6′), 121.3 (d, C-4′) and 30.6 (q, NCH$_3$).

Reaction of complex 1b with diphenylcarbodiimide. To a dichloromethane (20 cm^3) solution of [Pt{PhNC(O)NMe}(cod)] **1b** (0.025 g, 0.055 mmol) was added diphenylcarbodiimide (0.2 cm^3, excess) and the mixture refluxed for 15 h. During this time the solution became darker. Evaporation of the solvent gave an orange residue. This was dissolved in a small amount of dichloromethane and diethyl ether–pentane (1:1) added. Filtration of the resulting precipitate yielded a beige powder which upon recrystallisation from dichloromethane and diethyl ether gave almost colourless crystals, characterised as complex **7b** (0.018 g, 57%) according to NMR and ESMS spectra.

Complex 10. To a dichloromethane solution of [Pt{PhNC(O)NMe}(cod)] **1b** (0.030 g, 0.066 mmol) was added dmad (0.058 g, 50 μl, excess) and the resulting mixture refluxed for 2 h. During this time the solution became noticeably paler. Evaporation of the solvent and crystallisation of the residue by vapour diffusion of diethyl ether into a dichloromethane solution gave complex **10** as pale yellow plates (0.032 g, 81%), m.p. 200–204 °C (Found: C, 44.2; H, 4.6; N, 4.6. $C_{23}H_{25}N_3O_2Pt$ requires C, 44.5; H, 4.4; N, 4.7%). IR: ν̃(CO region) 1722s, 1698m, 1691s, 1616vs and 1584m cm^{-1}. ESMS: (cone voltage = 20 V) *m/z* 616 ([*M* + Na]$^+$, 10) and 594 ([*M* + H]$^+$, 100); (cone voltage = 50 V) 616 ([*M* + Na]$^+$, 8), 594 ([*M* + H]$^+$, 100) and 475 ([*M* + H − PhNCO]$^+$, 28); (cone voltage = 80 V) 616 ([*M* + Na]$^+$, 8), 594 ([*M* + H]$^+$, 40), 475 ([*M* + H − PhNCO]$^+$, 38), 443 ([*M* − PhNCO − MeO$^-$]$^+$, 100) and 415 {[*M* − PhNCO − MeOC(O)$^-$]$^+$, 95%}. ^{1}H NMR: δ 7.28 [2 H, t, ^3J(H$^{3'}$H$^{2'}$/H$^{4'}$) = 7.44, H-3′,5′], 7.21 [2 H, d, ^3J(H$^{2'}$H$^{3'}$) = 7.38, H-2′,6′], 7.07 [1 H, t, ^3J(H$^{4'}$H$^{3'}$) = 7.04, H-4′], 5.06 (2 H, t, $^3J_{HH}$ = 2.74, $^2J_{HPt}$ = 58.3, C*H*=CH *trans* N), 4.77 (2 H, t, $^3J_{HH}$ = 2.71, $^2J_{HPt}$ = 36.2 Hz, C*H*=CH *trans* C), 3.78 (3 H, s, CH$_{3B}$), 3.67 (3 H, s, CH$_{3A}$), 3.09 (3 H, s, NCH$_3$), 2.55–2.11 (8 H, m, CH_2CH). ^{13}C NMR: δ 172.9 (s, C$_A$=O), 165.1 (s, C$_B$=O), 154.3 (s, NC=O), 149.9 (s, C-1′), 138.7 (s, PtC=*C*$_B$), 129.3 (d, C-3′,5′), 127.9 (d, C-2′,6′), 125.3 (d, C-4′), 114.5 (s, $^1J_{CPt}$ = 982.0 Hz, Pt*C*$_A$=C), 112.6 (d, $^1J_{CPt}$ = 67.2, *C*H=CH *trans* C), 90.4 (d, $^1J_{CPt}$ = 155.8 Hz, *C*H=CH *trans* N), 52.4 (q, CH$_{3B}$), 52.0 (q, CH$_{3A}$), 36.3 (q, NCH$_3$), 31.4 (t, *C*H$_2$CH *trans* N) and 27.8 (t, *C*H$_2$CH *trans* C).



Complex 12. Methyl propiolate (5 drops, excess) was added to a dichloromethane solution of complex **11** (0.035 g, 0.040 mmol) and refluxed for 2 h. During this time the solution became almost colourless. Removal of the solvent and crystal-

lisation of the residue from dichloromethane and diethyl ether gave **12** as large colourless blocks. M.p. 235–238 °C (melts with decomposition) (Found: C, 60.0; H, 3.9. $C_{44}H_{36}O_4P_2Pt$ requires C, 59.7; H, 4.1%). IR: ṽ(C≡C region) 2116vs; ṽ(CO region) 1687vs cm^{-1}. ESMS: (cone voltage = 20 V) *m/z* 1789 ($[2M + NH_4]^+$, 75), 904 ($[M + NH_4]^+$, 100) and 886 ($[M + H]^+$, 33); (cone voltage = 50 V) 1789 ($[2M + NH_4]^+$, 33), 908 ($[M + Na]^+$, 29) and 886 ($[M + H]^+$, 100); (cone voltage = 80 V) 1789 ($[2M + NH_4]^+$, 10), 908 ($[M + Na]^+$, 32), 886 ($[M + H]^+$, 100), 802 (unidentified, 12), 759 {$[\overline{Pt(C_6H_4PPh_2)}(PPh_3) + MeCN]^+$, 22} and 718 {$[\overline{Pt(C_6H_4PPh_2)}(PPh_3)]^+$, 22%}. ^{31}P NMR: δ 18.1 (s, $^1J_{PPt}$ = 2535.6 Hz, PPh_3 *trans* P). Initial *cis* isomer (see main text): δ 15.7 (s, $^1J_{PPt}$ + 2364.6 Hz, PPh_3 *trans* C). ^1H NMR: δ 7.72–7.65 (12 H, m, PPh_3), 7.43–7.35 (18 H, m, PPh_3) and 2.45 (6 H, s, CH_3). ^{13}C NMR: δ 154.2 (s, C=O), 134.8 (d, $^3J_{CP}$ = 12.15, C-3,5, PPh_3), 134.5 (d, $^3J_{CP}$ = 10.88, C-3,5, PPh_3), 130.8 (d, C-4, PPh_3), 129.9 (s, $^1J_{CP}$ = 59.85, C-1, PPh_3), 116.0 (s, $^2J_{CP}$ = 29.2, $^1J_{CPt}$ = 988.6, Pt–*C*≡C), 104.6 (s, $^2J_{CPt}$ = 259.4 Hz, Pt-C≡*C*), 104.6 (s, $^2J_{CPt}$ = 259.4 Hz, Pt–C≡*C*) and 51.2 (q, CH_3).

Complex 14. To a dichloromethane (25 cm^3) solution of complex **11** (0.050 g, 0.058 mmol) was added *N*-sulfinylaniline (0.0087 g, 7.0 μl, 0.062 mmol) and refluxed for 2 h. During this time a noticeable change from bright to pale yellow was observed. The dichloromethane was removed under reduced pressure, and the residue dissolved in chloroform. This was slowly evaporated from a tube to give large colourless crystals of **14** (0.028 g, 51%), m.p. 202–206 °C (Found: C, 56.1; H, 4.5; N, 3.8. $C_{44}H_{40}N_2O_4P_2Pt_2S$ requires C, 55.6; H, 4.3; N, 3.0%). IR: ṽ(NH region) 3082w, 3056m; ṽ(CO region) 1693m, 1677w, 1609w, 1697w, 1554s, 1500s; ṽ(SO_3 region) 1177 (br) w, 1096s, 1063vs, 999w, 923 (br) vs cm^{-1}. ^{31}P NMR: δ 21.3 [d, $^2J_{PP}$ = 18.7, $^1J_{PPt}$ = 2458.9, PPh_3 *trans* $S(O)_2O$] and 10.5 [d, $^2J_{PP}$ = 19.0, $^1J_{PPt}$ = 4330.6 Hz, PPh_3 *trans* $OS(O)_2$]. ^1H NMR: δ 7.50–7.43 (24 H, m, PPh_3), 7.37 (2 H, s, br, PhN*H*), 7.19 [4 H, t, $^3J(H^{3'}H^{2'}/H^{4'})$ = 7.39, H-3′,5′], 7.09 [4 H, d, $^3J(H^{2'}H^{3'})$ = 6.93, H-2′,6′], 7.04–6.95 (36 H, m, PPh_3), 6.80 [2 H, t, $^3J(H^{4'}H^{3'})$ = 7.14, H-4′], 5.59 (2 H, s, br, MeN*H*) and 2.45 (6 H, d, $^3J_{HH}$ = 4.26 Hz, CH_3). ^{13}C NMR: δ 156.7 (s, C=O), 141.2 (s, C-1′), 134.8 (d, $^3J_{CP}$ = 10.79, C-3,5, PPh_3), 134.5 (d, $^3J_{CP}$ = 11.32 Hz, C-3,5 PPh_3), 130.6 (s, $^1J_{CP}$ = 67.09, C-1, PPh_3), 130.1 (d, C-4, PPh_3), 128.4 (s, $^1J_{CP}$ not resolved, C-1, PPh_3), 128.14 (d, $^2J_{CP}$ = 10.41, C-2,6, PPh_3), 128.07 (d, C-3′,5′), 127.5 (s, $^2J_{CP}$ = 11.39 Hz, C-2,6, PPh_3), 120.0 (d, C-4′), 118.2 (d, C-2′,6′) and 26.2 (q, CH_3).

Alternatively, complex **11** (0.025 g, 0.029 mmol) was placed in a glass ampoule, evacuated and sulfur dioxide (≈10 cm^3), which had previously been degassed by two cycles of freeze–pump–thawing, was condensed inside using standard vacuum-line techniques. The ampoule was sealed and placed in a Carius tube maintained at 55 °C for 16 h. At completion a white precipitate had formed. The sulfur dioxide was frozen, the ampoule opened, and the solvent slowly allowed to evaporate at room temperature. Recrystallisation of the residue from chloroform gave small crystals, characterised as **14** by NMR and IR spectra (0.012 g, 44%).

Complex 17. To a dichloromethane (15 cm^3) solution of complex **11** (0.025 g, 0.029 mmol) was added three drops of carbon disulfide, and the resulting mixture was stirred for 3 min. The volatiles were removed under reduced pressure to give a yellow oil. Large yellow crystals of **17** were grown by liquid–liquid diffusion of ether layered on a saturated chloroform solution of the residue (0.026 g, 96%), m.p. 129–130 °C (Found: C, 52.1; H, 3.4; N, 2.7. $C_{45}H_{38}N_2OP_2PtS_2{\cdot}CHCl_3$ requires C, 52.0; H, 3.7; N, 2.6%). IR: ṽ(CO region) 1646vs, 1632s, 1586m; ṽ(C=S region) 1265s, 1096s, 1069s, 749m, 727s and 693vs cm^{-1}. ESMS: (cone voltage = 20 V) *m/z* 1434 ($[3M + 2NH_4]^{2+}$, 12), 961 ($[M + NH_4]^+$, 29), 945 ($[M + H]^+$, 100) and 825 ($[M + H - PhNCO]^+$, 34); (cone voltage = 50 V) 945 ($[M + H]^+$, 100), 825 ($[M + H - PhNCO]^+$, 30) and 751 ($[M + H - PhNCO - CS_2]^+$, 13%). ^{31}P NMR δ 18.0 (d, $^2J_{PP}$ = 24.3, $^1J_{PPt}$ = 3097.6, PPh_3 *trans* S) and 5.3 (d, $^2J_{PP}$ = 24.3, $^1J_{PPt}$ = 3210.5 Hz, PPh_3 *trans* N). ^1H NMR: δ 7.39–6.96 (33 H, m, PPh_3, C-3′,5′,4′), 6.81 [2 H, d, $^3J(H^{2'}H^{3'})$ = 7.33 Hz, H-2′,6′] and 3.66 (3 H, s, CH_3). ^{13}C NMR: δ 205.1 (s, C=S), 155.0 (s, C=O), 147.8 (s, C-1′), 134.6 (d, $^3J_{CP}$ = 10.04, C-3,5, PPh_3), 133.6 (d, $^3J_{CP}$ = 11.09, C-3,5, PPh_3), 131.1 (d, C-4, PPh_3), 130.8 (d, C-4, PPh_3), 128.9 (s, $^1J_{CP}$ = 54.41, C-1, PPh_3), 128.8 (s, $^1J_{CP}$ not resolved, C-1, PPh_3), 128.4 (d, C-3′,5′), 128.3 (d, $^2J_{CP}$ = 10.64 Hz, C-2,6, PPh_3), 127.5 (d, C-2′,6′), 124.3 (d, C-4′) and 40.4 (q, CH_3).

Complex 18a. Dichloromethane and chloroform solutions of complex **17** prepared above were left standing for 1 week in the presence of an excess of carbon disulfide. During this time the solutions continually became paler. The ^{31}P NMR spectrum showed the gradual formation of a new species, which was recrystallised by slow evaporation of a chloroform solution to yield colourless crystals. This was characterised as **18a** on the basis of an X-ray crystallographic study (0.021 g, 88% based on 0.025 g of **11**). *N*,*N*′-Diphenylurea was detected by ^1H and ^{13}C NMR spectroscopy, but was not isolated.

Alternatively, in a preparation analogous to the literature procedure,[29] to a dichloromethane solution (20 cm^3) of *cis*-$[PtCl_2(PPh_3)_2]$ (0.098 g, 0.124 mmol) was added methylamine (0.046 cm^3, 33% in ethanol, 0.012 g, 0.380 mmol) and the solution stirred for 2 min. Carbon disulfide (0.0095 g, 7.6 μl, 0.125 mmol) was added, and after a few minutes a precipitate of methylamine hydrochloride formed. The mixture was stirred for 4 h, filtered, and solvent removed under reduced pressure. The residue was recrystallised from chloroform, to give complex **18a** (0.087 g, 85%), characterised by identical ^{31}P and ^1H NMR spectra to those observed for the previous preparation, m.p. 220 °C (decomposes without melting) (Found: C, 53.8; H, 3.4; N, 1.5. $C_{38}H_{33}NP_2PtS_2{\cdot}0.33CHCl_3$ requires: C, 53.3; H, 3.9; N, 1.6%). IR: ṽ(C=N region) 1583vs cm^{-1}. ESMS: (cone voltage = 20 V) *m/z* 826 ($[M + H]^+$, 100%); (cone voltage = 50 V) 826 ($[M + H]^+$, 100) and 563 ($[M + H - PPh_3]^+$, 4); (cone voltage = 80 V) 826 ($[M + H]^+$, 100) and 563 ($[M + H - PPh_3]^+$, 38); (cone voltage = 100 V) 826 ($[M + H]^+$, 20) and 563 ($[M + H - PPh_3]^+$, 100%). ^{31}P NMR: δ 19.6 (d, $^2J_{PP}$ = 23.1, $^1J_{PPt}$ = 3107.2, PPh_3 *trans* S) and 18.8 (d, $^2J_{PP}$ = 23.2, $^1J_{PPt}$ = 3086.2 Hz, PPh_3 *trans* S). ^1H NMR: δ 7.46–7.11 (30 H, m, PPh_3) and 3.15 (3 H, s, CH_3). ^{13}C NMR: δ 171.5 (s, C=N), 134.5 (d, $^3J_{CP}$ = 10.79, C-3,5, PPh_3), 130.7 (d, C-4, PPh_3), 130.8 (d, C-4, PPh_3), 130.1 (s, $^1J_{CP}$ = 54.34 Hz, C-1, PPh_3), 129.7 (s, $^1J_{CP}$ = 54.26, C-1, PPh_3), 128.04 (d, $^2J_{CP}$ = 10.64, C-2,6, PPh_3), 128.01 (d, $^2J_{CP}$ = 10.26 Hz, C-2,6, PPh_3) and 34.5 (q, CH_3). *N*,*N*′-Diphenylurea: ^1H NMR δ 8.93 (2 H, s, NH), 7.53 [4 H, d, $^3J(H^{2'}H^{3'})$ = 7.96, H-2′,6′] and 6.86 [2 H, t, $^3J(H^{4'}H^{3'})$ = 7.01 Hz, H-4′]; ^{13}C NMR δ 153.8 (s, C=O), 140.2 (s, C-1′), 128.5 (d, C-3′), 121.5 (d, C-2′) and 119.1 (d, C-4′).

Crystallography

Unit-cell dimensions and intensity data for all the structures were obtained on a Siemens CCD SMART diffractometer at 203(2) K, with monochromatic Mo-Kα X-rays (λ = 0.710 73 Å), at the University of Auckland. The data collections nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal to detector distance was 5.0 cm. The data sets were corrected empirically for absorption using SADABS.[34]

All the structures were solved by the Patterson methods option of SHELXS 96,[35] and the platinum positions determined. All further non-hydrogen atoms were located routinely (SHELXL 96[36]). In the final cycle of the full-matrix least-

Table 5 X-Ray data for the crystal structures of the complexes **14**, **17** and **18a**

	14·2$CHCl_3$	**17**·$CHCl_3$	**18a**
Empirical formula	$C_{36}H_{28}O_3P_2PtS·C_8H_{10}N_2O·2CHCl_3$	$C_{45}H_{38}N_2OP_2PtS_2·CHCl_3$	$C_{38}H_{33}NP_2PtS_2$
M_r	1186.59	1063.29	824.80
Crystal class	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$	$P2_1$
Crystal size/(mm)	0.40 × 0.11 × 0.10	0.56 × 0.40 × 0.20	0.30 × 0.11 × 0.08
a/Å	14.0378(2)	12.7698(2)	9.8358(1)
b/Å	14.0731(2)	16.7061(2)	9.3356(1)
c/Å	14.2127(2)	20.4585(2)	18.2494(1)
α/°	119.487(1)	—	—
β/°	94.800(1)	94.620(1)	99.008(1)
γ/°	93.597(1)	—	—
U_c/Å^3	2417.98(6)	4350.30(10)	1655.05(2)
D_c/g cm^{-3}	1.630	1.623	1.655
Z	2	4	2
F(000)	1176	2112	816
μ(Mo-Kα)/mm^{-1}	3.387	3.617	4.491
Unique reflections	10 569	9725	6285
Collection range/°	1.47 < θ < 28.11	1.58 < θ < 28.22	1.13 < θ < 28.22
$T_{max,min}$	0.67, 0.57	0.61, 0.39	0.70, 0.51
$R1[I \geqslant 2\sigma(I)]$	0.0251 for 9733 data	0.0322 for 8327 data	0.0242 for 5841 data
w*R*2	0.0617	0.0860	0.0821
Goodness of fit	1.030	1.051	1.074
Largest peak, deepest trough/e Å^{-3}	+1.65, −1.20	+2.27, −1.99	+0.73, −1.25

squares refinement based on F^2 all non-hydrogen atoms were assigned anisotropic thermal parameters, and hydrogen atoms included in calculated positions (SHELXL 96 [36]).

Data for the structures are summarised in Table 5. For complex **18a** the Flack *x* parameter refined to a value of 0.016(7), showing the correct polarity of the space group had been chosen.

CCDC reference number 186/939.

Acknowledgements

We thank the University of Waikato for financial support of this work and the New Zealand Lottery Grants Board for a grant-in-aid. We also thank Allen Oliver and Associate Professor C. E. F. Rickard (University of Auckland) for collection of the X-ray data sets and Professor B. K. Nicholson for assistance in the crystallography. Professor A. L. Wilkins is acknowledged for NMR assistance. We also thank Johnson-Matthey plc for a generous loan of platinum. M. B. D. thanks the University of Waikato and the William Georgetti Trust for scholarships.

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Received 10*th December* 1997; *Paper* 7/08879E