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Organometallic complexes of platinum-group metals incorporating substituted guanidine dianion (triazatrimethylenemethane) ligands

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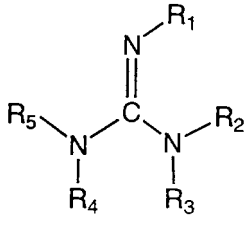
Abstract

Reactions of the platinum-group metal halide complexes $[PtCl_2(COD)]$ (COD = 1,5-cyclo-octadiene), $[Cp^*RhCl_2(PPh_3)]$ ($Cp^* = \eta^5$-C_5Me_5), $[Cp^*IrCl_2(PPh_3)]$, $[(p\text{-cymene})RuCl_2(PPh_3)]$ and $[(p\text{-cymene})OsCl_2(PPh_3)]$ with symmetrically trisubstituted (acetyl or phenyl) guanidines, mediated by silver(I) oxide, give complexes formally containing the triazatrimethylenemethane ligand. A full X-ray crystal structure determination is reported for the *N*,*N*′,*N*″-triphenylguanidine dianion complex [Pt{NPhC(=NPh)NPh}(COD)] **4a** which shows the presence of a planar Pt-NR-C(=NR)-NR four-membered platinacycle. At room temperature (r.t.), the ^1H- and $^{13}C\{^1H\}$-NMR spectra of **4a** yield a single set of COD CH and CH_2 resonances. At 240 K however, two sets of resonances are observed, interpreted in terms of fluxionality of the C=N-Ph moiety. Attempted synthesis of the analogous platinum triacetylguanidine complex yields the new ureylene complex [Pt{NAcC(=O)NAc}(COD)], via a hydrolysis reaction. Starting with the osmium compound, both the guanidine complex $[(p-\text{cymene})Os\{NAcC(=NAc)NAc\}(PPh_3)]$ **9** and the ureylene complex $[(p-\text{cymene})Os\{NAcC(=O)NAc\}(PPh_3)]$ **10** were formed; similar results were obtained for the iridium system.

Keywords: Guanidine; Triazatrimethylenemethane; Metallacycle; Silver oxide; Platinum group metal

1. Introduction

Guanidines, with the general structure **1**, are versatile



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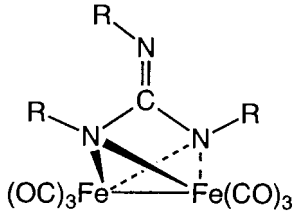
ligands and are capable of bonding to metal centres in a variety of coordination modes, the most common being as neutral donor ligands [1,2] or as monoanions [1]. Bailey et al. have recently reported some ruthenium [3] and dimolybdenum [4] complexes of the *N*,*N*′,*N*″-triphenylguanidine monoanion. However, transition-metal complexes containing the guanidine dianion ligand $[C(NH)_3]^{2-}$, or substituted derivatives, are much less common. To the best of our knowledge only one transition-metal complex containing a guanidine dianion has been previously reported, the dinuclear iron carbonyl complex **2**, formed by the reaction of dicyclo-



2; R = Cy

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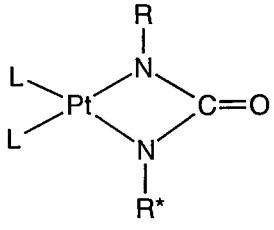
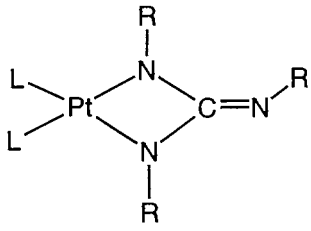
hexylcarbodiimide and $Fe(CO)_5$ ([5]a); a very recent Sb example also contains a formally dianionic guanidine ligand ([5]b). The guanidine dianion ligand is of interest, since it is formally isoelectronic with the trimethylenemethane (TMM) ligand $[C(CH_2)_3]^{2-}$, for which there are numerous reports of complexes [6,7]. Complexes of monoazatrimethylenemethane have recently been described [8]. The recent synthesis of the dilithio-salt of *N*,*N*′,*N*″-triphenylguanidine [9] and its reaction to form a heterobimetallic cadmium–lithium complex [10] suggests that a diverse range of metal complexes containing guanidine dianion ligands should be accessible from this reagent. Reactions of 1,3-dianions with metal halide complexes have been shown to be versatile, general synthetic routes to a wide range of metallacyclic complexes [11]. Complexes containing oxodimethylenemethane [12] and trimethylenemethane [7] ligands have also been prepared using such types of reagent.

We have adopted a complementary strategy for the synthesis of platinum group metal complexes of guanidine dianion ligands, using the reagent silver(I) oxide. This reagent simultaneously acts as a halide-abstracting reagent and a base, and a variety of complexes containing metal–oxygen, –nitrogen, –carbon and –sulfur bonds have been synthesised under mild reaction conditions [13]. We have recently reported the use of silver(I) oxide in the synthesis of a range of platinum(II) ureylene complexes **3** [14] which are derived from urea dianion ligands $[RNC(O)NR]^{2-}$, formally isoelectronic with the guanidine dianion $[RNC(NR)NR]^{2-}$. Complexes of the urea-derived ligand are more widely reported in the literature [14–16].



3; L = PPh_3 or L_2 = COD
R = Ph or Ac; R* = alkyl or aryl

The use of silver(I) oxide as a general synthetic reagent is limited to moisture-stable complexes (in particular those of the platinum group metals described herein), since water is a by-product of the reaction. Its advantage lies in the ease of product isolation. Using the silver oxide method, we recently reported the synthesis of the first mononuclear complex of a guanidine dianion, this being the cyclo-octadiene platinum complex **4a** [17]. In this paper, we report our detailed



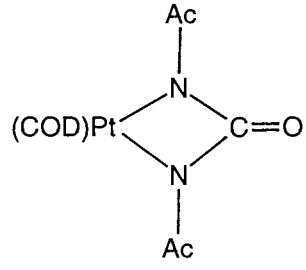
4a: R = Ph, L_2 = COD
4b: R = Ac; L_2 = COD
4c: R = Ph; L = PPh_3

studies into the synthesis of organometallic platinum(II), rhodium(III), iridium(III), ruthenium(II) and osmium(II) complexes containing triphenyl- and triacetyl-guanidine dianion ligands.

2. Results and discussion

2.1. Syntheses

The ready availability of *N*,*N*′,*N*″-triphenyl- and *N*,*N*′,*N*″-triacetylguanidines suggested that their reaction with platinum-group metal–dihalide complexes might form a general synthetic route into the synthesis of guanidine dianion (triazatrimethylenemethane) complexes. Thus, the complex $[PtCl_2(COD)]$ readily reacts with *N*,*N*′,*N*″-triphenylguanidine in refluxing dichloromethane in the presence of excess silver(I) oxide to give the guanidine dianion complex **4a** in 94% yield [17]. In marked contrast however, the attempted synthesis of the analogous *N*,*N*′,*N*″-triacetylguanidine platinum complex **4b** was unsuccessful. In this case, the *N*,*N*′-diacetylureylene complex [Pt{NAcC(=O)NAc}(COD)] **5**



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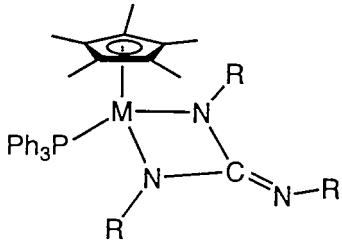
was isolated and characterised in 87% yield as a white crystalline solid. The silver(I) oxide-mediated reaction appears to be only applicable to the synthesis of platinum complexes of phenyl-substituted guanidines, since the attempted synthesis of analogous platinum complexes with alkyl-substituted guanidines led either to significant decomposition of the starting $[PtCl_2(COD)]$ (with methyldiphenylguanidine and 1-adamantyldiphenylguanidine) or to recovery of unreacted

$[PtCl_2(COD)]$, in the case of the reaction with trimethylguanidine.

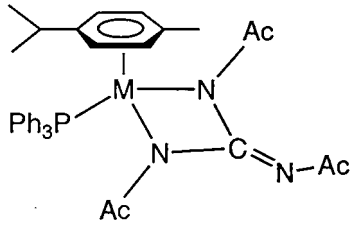
When *N*,*N*′,*N*″-triacetylguanidine was reacted under the same conditions (as for the platinum complex **5**) with the metal complexes $[Cp^*RhCl_2(PPh_3)]$ ($Cp^* = \eta^5$-C_5Me_5), $[Cp^*IrCl_2(PPh_3)]$, and [(*p*-cymene)-$RuCl_2(PPh_3)$] the corresponding complexes **6a**, **7** and **8**, containing the triacetylguanidine dianion ligand could be isolated. However, the attempted synthesis of the osmium complex **9** was less successful, with the ^{31}P-NMR of the crude reaction mixture showing two products in almost equal amounts. These were characterised as being the desired product, $[(p-\text{cymene})\overline{Os\{NAcC(=NAc)NAc\}}(PPh_3)]$ **9** and the ureylene complex, $[(p-\text{cymene})\overline{Os\{NAcC(=O)NAc\}}(PPh_3)]$ **10**.

When the complex $[Cp^*IrCl_2(PPh_3)]$ was reacted with *N*,*N*′,*N*″-triacetylguanidine under the same standard conditions, there was NMR and electrospray mass spectrometric evidence for the corresponding ureylene complex **11** being formed. Pure samples of the osmium and iridium ureylene complexes (**10** and **11**, respectively) were subsequently obtained by the silver(I) oxide-mediated reactions of the dihalide complexes with *N*,*N*′-diacetylurea in refluxing CH_2Cl_2. This subsequently facilitated unambiguous NMR spectroscopic characterisation of the osmium complex **9**, which was not obtained in a pure state.

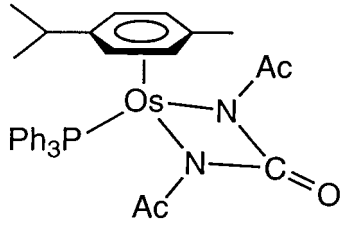
The formation of the diacetylureylene complexes clearly arises as a result of hydrolysis of the triacetylguanidine ligand. Additionally, the hydrolysis reaction occurs to variable extent with the different metal centres. For example, rhodium gives solely the guanidine complex **6a**, while iridium gives ca. 25% ureylene complex **11** in the crude product **7**. Similarly, a higher degree of hydrolysis occurs for the osmium complex **9** when compared to the ruthenium analogue **8**. Platinum gives solely the ureylene complex **5**. The relative amounts of **9** and **10** remained constant when the reaction was carried out by refluxing the triacetylguanidine and Ag_2O for 18 h, with and without added water, before adding a stoichiometric amount of $[(p\text{-cymene})OsCl_2(PPh_3)]$. However, if the reaction mixture containing $[(p\text{-cymene})OsCl_2(PPh_3)]$, silver oxide and the guanidine was refluxed for 20 h, a 42:58 distribution of **9**:**10** was obtained. When the reaction time was decreased to 2 h, a ca. 50:50 mixture was obtained. These observations suggests that the free guanidine and the final guanidine dianion product **9** essentially resist hydrolysis under the reaction conditions, and so conversion to the ureylene ligand requires coordination to the metal in an intermediate species. A possible mechanism explaining the formation of differing amounts of ureylene and guanidine dianion products is shown in Scheme 1. Initial reaction of the metal–dihalide complex with triacetylguanidine mediated by silver(I) oxide gives the monodentate guanidine intermediate **X**, which can then react by two different pathways, **A** and **B**. Pathway **A** involves simple cyclisation to give the guanidine dianion complex. It is suggested that the greater lability of the second-row metals (Ru and Rh) over their third-row counterparts results in pathway **A** being rapid for these metals, resulting in the isolation of solely the guanidine dianion complexes. For the metals Pt, Ir and Os however, pathway **B** becomes competitive with pathway **A** (entirely so for Pt). These third-row metals are less labile, cyclisation



6a: M = Rh; R = Ac
6b: M = Rh; R = Ph
7: M = Ir; R = Ac



8: M = Ru
9: M = Os



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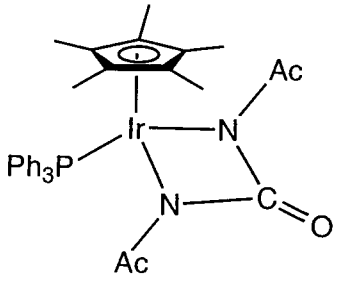

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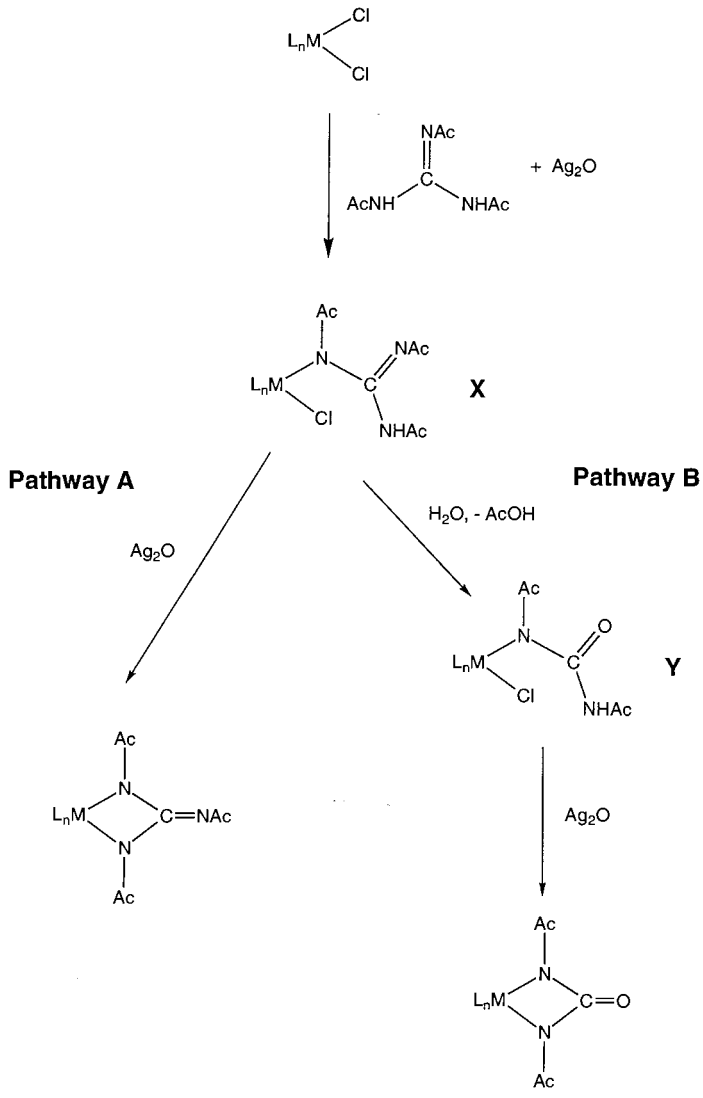


Scheme 1. A possible mechanism explaining the formation of differing amounts of ureylene and guanidine dianion products.

by pathway **A** is slower, and thus metal-promoted hydrolysis of the coordinated guanidine monoanion to the coordinated urea monoanion, intermediate **Y** in Scheme 1, may occur. The formation of the ureylene complexes then simply proceeds by silver(I) oxide-mediated cyclisation of intermediate **Y**.

The preparations of the rhodium and ruthenium complexes (**6** and **8**, respectively) had to be carried out under a nitrogen atmosphere, while the platinum complexes **4b** and **5** could also be prepared successfully in air. All the complexes are air- and moisture-stable once isolated, and are typically bright yellow to orange in colour. Freshly-prepared solutions of the ruthenium complex **8** are initially orange in colour, but rapidly turn dark green upon standing in air. Since NMR spectra essentially only show resonances due to **8**, it was concluded that the crude product is contaminated with a small quantity of a highly coloured impurity. After recrystallisation by diffusion of diethyl ether and pentane into a dichloromethane solution, stable orange crystals were obtained.

The synthesis of the triphenylphosphine complex **4c** was also attempted. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with *N*,*N*′,*N*″-triphenylguanidine and silver(I) oxide led to very little product formation after 24 h reaction, while the attempted ligand substitution reaction of the COD ligand of **4a** with PPh_3 surprisingly led to recovery of unreacted starting material.

2.1.1. X-ray crystal structure determinations

A single-crystal X-ray analysis was carried out in order to ascertain the nature of the bonding of the ligand to the metal centre in the platinum complex **4a**. The molecular structure and atom numbering scheme are shown in Fig. 1, while Table 1 gives atomic

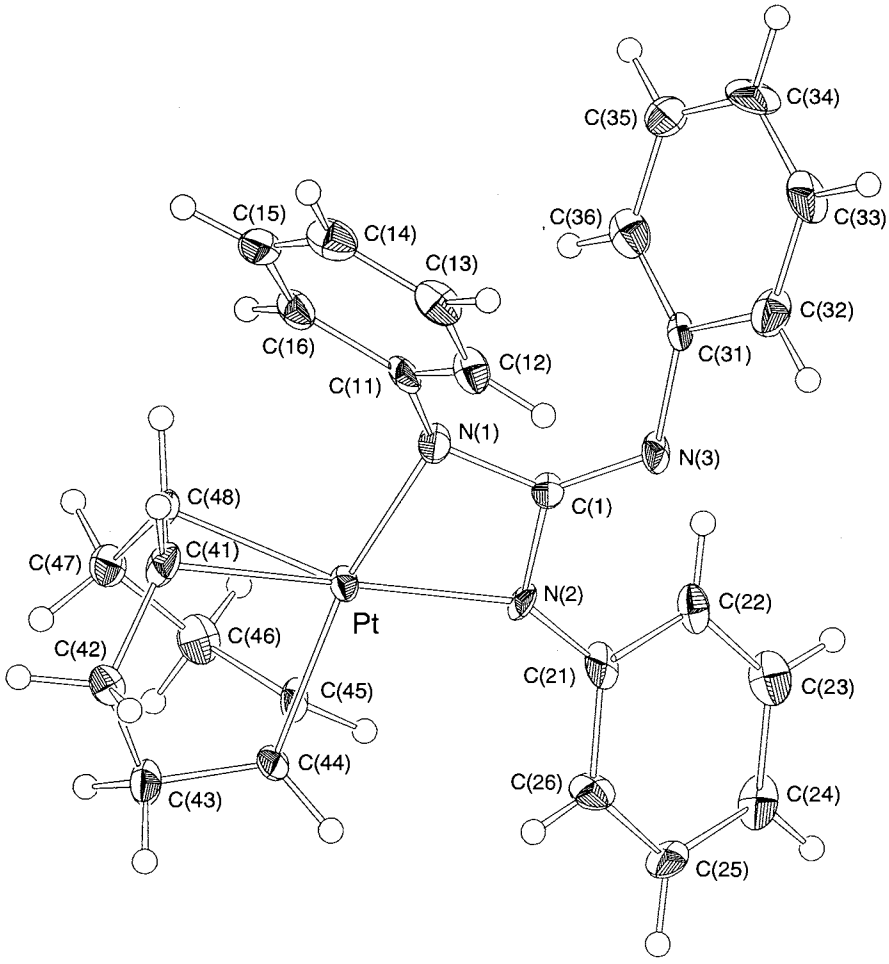


Fig. 1. Molecular structure of [Pt{NPhC(=NPh)NPh}(COD)] **4a**, showing the atom numbering scheme. The dichloromethane and disordered diethyl ether of crystallisation have been omitted for clarity.

coordinates for the structure, and Table 2 gives selected bond lengths and angles.

The complex contains an η^2-triazatrimethylenemethane (guanidine dianion) ligand, coordinated to platinum via two nitrogen atoms, forming an essentially planar Pt–N–C–N metallacycle. No atom deviates from the least-squares plane of this metallacycle by more than 0.054(12) Å, for N(2). The C(1)–N(3) bond distance, at 1.30(1) Å, is significantly shorter than the C(1)–N(1) and C(1)–N(2) bond distances, which are both 1.40(1) Å. This indicates the presence of localised single [C(1)–N(1) and C(1)–N(2)] and double [C(1)–N(3)] bonds in the complex. By comparison, the average C–N bond distance to the central carbon in the delocalised dianion of $Li_2[C(NPh)_3]$ is 1.36(1) Å [9]. The X-ray structure of *N*,*N*′,*N*″-triphenylguanidine has also been reported [18] and the C–N bond lengths in this structure are equal at ca. 1.34 Å. The difference between the Pt–N(1) and Pt–N(2) bond distances in **4a**, 2.034(8) and 2.002(7) Å, respectively, can be attributed to steric interactions between the phenyl substituents on nitrogens N(1) and N(3), which permits a closer approach of N(2) to the platinum. The orientation of the phenyl substituent on the imino group presumably precludes a fully symmetrical binding of the ligand to the platinum centre. The phenyl substituents are tipped out of the metallacyclic plane, again presumably to minimise steric interactions. Thus, carbon atoms C(11), C(21) and C(31) are 0.84(1) Å above, 0.62(1) Å below and 0.34(1) Å below the metallacyclic plane, respectively, as depicted in the orientation of Fig. 1.

The triphenylguanidine dianion complex **4a** overall bears a very strong resemblance to formally isoelectronic carbonato complexes. Thus, a number of platinum(II)–phosphine complexes, e.g. $[Pt(CO_3)(PPh_3)_2]$, $[Pt(CO_3)(PMe_3)_2]\cdot 2H_2O$ and $[Pt(CO_3)(Ph_2PCH_2CH_2CH_2PPh_2)]$ also contain essentially planar $\overline{Pt-O-C(O)-O}$ metallacycles [19]. Metal–ureylene complexes, containing $\overline{M-N-C(O)-N}$ ring systems (of the type **3**) also have planar ring systems [14,16]. In marked contrast, the palladium η^3-trimethylenemethane complex $[Pd\{\eta^3\text{-}CH_2C\{C(CO_2Me)_2\}$-

$CH_2\}(PPh_3)_2$] (also formally isoelectronic with the guanidine dianion platinum complex) shows a highly non-planar metal–ligand arrangement [20].

An X-ray structure determination of the ruthenium complex **8** was also attempted. A reasonable data set was obtained and solved, but the refinement was bedeviled by extensive disorder of the guanidine dianion ligand and possibly by unresolved twinning, so that an R_1 factor of only 0.145 was obtained. The analysis can therefore only be taken to confirm the atom connectivity and the overall conformation (as shown in Fig. 2) and so no bond parameters are given or discussed here. The molecule does contain the expected triacetylguanidine dianion ligand attached to the ruthenium via two nitrogen atoms to give the expected four-membered ring complex.

2.1.2. Characterisation by NMR spectroscopy and electrospray mass spectrometry (ESMS)

Unambiguous NMR assignments were made using a combination of NOE, ^{1}H-^{13}C COSY, and long range BIRDTRAP (^1J suppression) ^{1}H-^{13}C COSY experiments.

Since most of the starting materials contained the triphenylphosphine ligand, ^{31}P-NMR was conveniently used to monitor reaction progress and outcomes. Detailed NMR assignments are given in the experimental section, while significant and diagnostic NMR features of the starting materials and prepared complexes are summarised in Table 3.

A number of general conclusions can be drawn. In the ^{31}P-NMR, a downfield shift of the PPh_3 (relative to the starting material) is observed on coordination of the guanidine dianion ligand, consistent with a decreased availability of electron density about the metal (and hence the phosphorus) centre. A downfield shift (relative to the starting material) of the ^{13}C-NMR resonance of the central guanidine carbon is produced on coordination, largely independent of metal.

In the triacetyl- and triphenyl-guanidine complexes the ^{13}C and ^{1}H spectra indicate that the substituents on the metal-coordinated N atoms are equivalent, despite the expected inequivalence arising from the *syn* or *anti*-arrangement of the substituents on the third N atom. A variable-temperature ^{1}H- and ^{13}C$\{^1$H$\}$-NMR study was therefore undertaken on the COD complex **4a**. The ^{1}H-NMR spectra of **4a** at four temperatures ranging from 300–240 K are shown in Fig. 3. At r.t., a single slightly broadened COD CH=CH resonance is observed at δ 4.92, which broadens further at 280 K, before forming two CH resonances at 260 K, which sharpen at 240 K. The ^{13}C$\{^1$H$\}$-NMR spectra of **4a** at the same temperatures show analogous behaviour, with two CH and two CH_2 resonances being observed at 240 K. These observations are interpreted as a r.t. fluxional process (Scheme 2), which serves to interchange the

Table 1
Final positional and equivalent thermal parameters for [Pt{NPhC(=NPh)NPh}(COD)] **4a**

Atom	*x*	*y*	*z*	U_{eq}
Pt(1)	0.2226(1)	0.0701(1)	0.0871(1)	0.014(1)
N(1)	0.3042(8)	−0.0580(5)	0.1128(4)	0.019(2)
N(2)	0.2096(8)	−0.0111(5)	−0.0071(4)	0.017(2)
N(3)	0.3009(8)	−0.1638(5)	0.0011(4)	0.019(2)
C(1)	0.2777(9)	−0.0871(6)	0.0343(5)	0.016(2)
C(11)	0.3004(9)	−0.1149(7)	0.1773(6)	0.018(2)
C(12)	0.2362(10)	−0.1996(7)	0.1710(6)	0.025(2)
C(13)	0.2323(10)	−0.2533(7)	0.2362(6)	0.023(2)
C(14)	0.2901(9)	−0.2221(8)	0.3109(6)	0.026(2)
C(15)	0.3517(10)	−0.1338(8)	0.3179(6)	0.027(2)
C(16)	0.3595(9)	−0.0832(7)	0.2534(5)	0.021(2)
C(21)	0.2012(10)	0.0065(6)	−0.0873(6)	0.021(2)
C(22)	0.3017(10)	−0.0247(7)	−0.1273(6)	0.021(2)
C(23)	0.2855(10)	−0.0051(7)	−0.2067(6)	0.027(2)
C(24)	0.1725(12)	0.0446(6)	−0.2474(6)	0.025(2)
C(25)	0.0725(10)	0.0764(7)	−0.2087(5)	0.024(2)
C(26)	0.0859(10)	0.0558(7)	−0.1301(6)	0.022(2)
C(31)	0.3928(9)	−0.2312(6)	0.0412(5)	0.015(2)
C(32)	0.3548(11)	−0.3239(7)	0.0254(6)	0.027(2)
C(33)	0.4452(12)	−0.3934(7)	0.0574(6)	0.030(2)
C(34)	0.5767(11)	−0.3718(8)	0.1060(6)	0.032(3)
C(35)	0.6125(10)	−0.2820(7)	0.1201(5)	0.025(2)
C(36)	0.5218(10)	−0.2112(8)	0.0875(6)	0.025(2)
C(41)	0.1865(9)	0.1157(7)	0.1996(5)	0.021(2)
C(42)	0.0552(9)	0.1707(6)	0.1887(5)	0.017(2)
C(43)	0.0229(10)	0.2263(7)	0.1136(6)	0.024(2)
C(44)	0.0805(9)	0.1847(6)	0.0461(5)	0.018(2)
C(45)	0.2101(10)	0.2043(6)	0.0328(5)	0.019(2)
C(46)	0.3161(10)	0.2674(7)	0.0828(6)	0.025(2)
C(47)	0.3341(10)	0.2513(7)	0.1712(6)	0.021(2)
C(48)	0.3155(9)	0.1509(7)	0.1914(5)	0.019(2)
O(111)	1.0000	0.5000	0.0000	0.210(19)
C(111)	0.9406(46)	0.5278(27)	0.0581(19)	0.249(25)
C(112)	0.9605(22)	0.6002(12)	0.0909(10)	0.084(6)

Table 2
Selected bond lengths (Å) and angles (°) for [Pt{NPhC(=NPh)NPh}(COD)] **4a**, with estimated standard deviations in parentheses

Pt(1)–N(2)	2.002(7)	Pt(1)–N(1)	2.034(8)
Pt(1)–C(41)	2.173(9)	Pt(1)–C(44)	2.188(9)
Pt(1)–C(45)	2.155(9)	Pt(1)–C(48)	2.183(9)
N(1)–C(1)	1.398(11)	N(2)–C(1)	1.402(11)
N(3)–C(1)	1.298(11)	N(1)–C(11)	1.402(12)
N(2)–C(21)	1.406(12)	N(3)–C(31)	1.406(11)
Pt(1)···C(1)	2.561(9)		
N(2)–Pt(1)–N(1)	65.9(3)	C(1)–N(1)–Pt(1)	94.7(5)
C(1)–N(2)–Pt(1)	96.0(5)	C(11)–N(1)–Pt(1)	129.2(6)
C(21)–N(2)–Pt(1)	133.5(6)	N(1)–C(1)–N(2)	103.3(7)
N(3)–C(1)–N(1)	133.0(8)	N(3)–C(1)–N(2)	123.7(8)
C(1)–N(3)–C(31)	122.1(8)	C(1)–N(1)–C(11)	125.1(8)
C(1)–N(2)–C(21)	124.8(7)	N(3)–C(1)–Pt(1)	174.7(7)
N(2)–N(1)–C(11)	36.8(7)		
N(1)–N(2)–C(21)	26.2(5)		

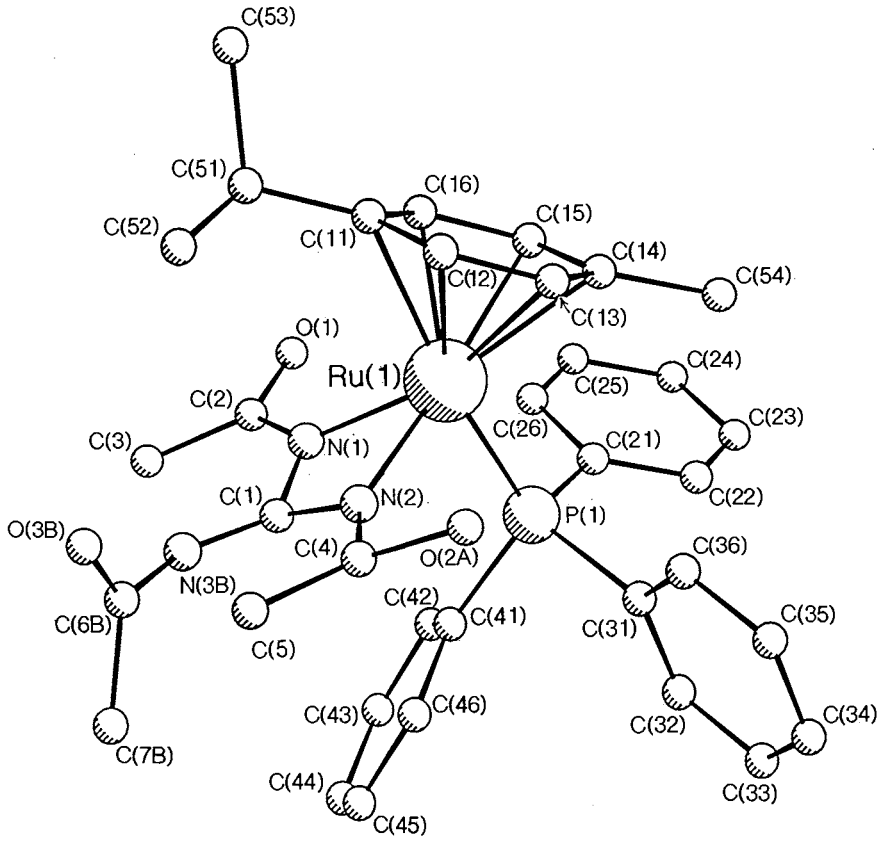


Fig. 2. Molecular structure of [(*p* − cymene)Ru{NAcC(=NAc)NAc}(PPh_3)] **8**. Only one component of the disordered triacetylguanidine dianion ligand is shown.

lone pair and phenyl substituent on the C=N nitrogen N(3). At 240 K, this process is frozen out, leading to the structure also observed in the solid state, with the phenyl on N(3) rendering the two sides of the COD ligand inequivalent. Unfortunately, it was not possible to resolve ^1J(PtC) or ^2J(PtH) couplings in the frozen-out structure, though small differences would be expected for CH groups *trans* to N(1) and N(3).

Electrospray mass spectrometry (ESMS) can be successfully used as an additional characterisation technique for the new complexes reported herein. ESMS is finding increased use in the characterisation of a range of organometallic and coordination complexes, and generally leads to observation of strong parent ions [21]. As an example, the platinum complex **4a** gives the parent ion $[MH]^+$ as the base peak at a cone voltage of 50 V when recorded in MeCN–H_2O solution; the other guanidine dianion complexes show similar behaviour. However, for the rhodium, iridium, ruthenium and osmium complexes, which contain a coordinated triphenylphosphine ligand, ions of the type $[MH - PPh_3]^+$ and $[MH - PPh_3 + MeCN]^+$ were typically observed. Presumably the sterically crowded environment around the metal labilises the phosphine ligand in these complexes. We have previously reported analogous behaviour for a series of Cp* rhodium(III) oxolene complexes [22]. It is also worth noting that the triacetylguanidine dianion complexes typically showed some loss of MeCN in their ES spectra and, since no ureylene complexes were formed in the cases of rhodium and ruthenium, this loss is interpreted in terms of a hydrolysis reaction occurring in the mass spectrometer.

2.1.3. Conclusions

A number of platinum-group metal complexes containing guanidine dianion (triazatrimethylenemethane) ligands have been successfully synthesised using the silver(I) oxide method. X-ray crystallography reveals that the ligand bonds in a planar η^2-type arrangement, reminiscent of ureylene and carbonate complexes.

3. Experimental details

^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded on a Bruker AC300P spectrometer, at 300.13 and 75.47 MHz, respectively, in $CDCl_3$, with $SiMe_4$ (δ 0.0) as the external reference. ^{31}P{^{1}H}-NMR spectra were recorded, unless stated otherwise, in $CDCl_3$ solution at 121.49 MHz on a Bruker AC300P spectrometer with 85% H_3PO_4 (δ 0.0) as the external reference. The ^{31}P-NMR

Table 3
A comparison of significant NMR spectroscopic properties of the guanidine dianion complexes

Compound	^{13}C=N (ppm)	Product PPh$_3$ (δ/ppm), ($^1J_{P-M}$/Hz)	Starting material PPh$_3$ (δ/ppm), ($^1J_{P-M}$/Hz)
PhNHC(NPh)NHPh	145.2	–	–
4a	166.4	–	–
4c	Not observed	8.1 (3344)	14.0 (3750)
6b	154.6	35.6 (158.7)	30.0 (144.0)
AcNHC(NAc)NHAc	150.3	–	–
7	166.0	15.4	2.2
6a	164.8	40.9 (150.2)	30.0 (144.0)
8	161.9	44.2	24.9
9	164.0	11.6 (301.5)	−12.4 (281.8)

spectrum of the rhodium complex **6b** was recorded on a JEOL FX90 spectrometer at 36.23 MHz. IR spectra were recorded as KBr disks on a BioRad FTS-40 spectrometer; only major peaks in the region 1700–1500 cm^{-1} are reported as distinctive fingerprints. Melting points were recorded on a Reichert Hotstage apparatus and are uncorrected.

Electrospray mass spectra were recorded in positive-ion mode on a VG Platform II instrument, using MeCN–H_2O (1:1 v/v) as the mobile phase. Fragmentation was investigated by varying the skimmer cone voltage, typically from 10 to 80 V. Isotope patterns for major species were recorded and compared to calculated patterns obtained using the Isotope simulation program [23].

N,*N*′,*N*″-triphenylguanidine was prepared by reaction of aniline with diphenylcarbodiimide [24]. ESMS data for triphenylguanidine: cone voltage + 10 V, *m*/*z* 288 (MH$^+$, 100%). Cone voltage 100 V, *m*/*z* 288 (MH$^+$, 3%), 196 ([PhN=C=NPh]H$^+$, 100%)]. *N*,*N*′,*N*″-triacetylguanidine [25] was prepared by the literature procedure, while *N*,*N*′-diacetylurea was prepared by reaction of urea with acetyl chloride, by modification of the literature procedure for propionylurea [26]. The complex [PtCl$_2$(COD)] was prepared via a minor modification of the literature procedure [27] and the complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] was prepared from this complex by displacement of the labile COD ligand by reaction with two mole equivalents of PPh$_3$ in CH_2Cl_2. The complexes [Cp*RhCl$_2$(PPh$_3$)] (Cp* = η^5-C$_5$Me$_5$) [28], [Cp*IrCl$_2$(PPh$_3$)] [28], [(*p*-cymene)RuCl$_2$(PPh$_3$)] [29] and [(*p*-cymene)OsCl$_2$(PPh$_3$)] [30] were prepared by the appropriate literature procedures and their purities checked by ^{31}P{^{1}H}-NMR.

3.1. Preparation of [Pt{NPhC(=NPh)NPh}(COD)] 4a

[PtCl$_2$(COD)] (0.050 g, 0.134 mmol), *N*,*N*′,*N*″-triphenylguanidine (0.039 g, 0.136 mmol) and silver(I) oxide (0.103 g, excess) were refluxed in dichloromethane (20 ml) for 3 h. Filtration to remove the silver salts gave a bright yellow solution. The solvent was removed by evaporation and subsequent recrystallisation of the residue from dichloromethane–diethyl ether gave bright yellow crystals of **4a**, (0.074 g, 94%). This complex was further characterised by an X-ray structure analysis (see below). M.p. 175°C (decomp.). Found: C, 54.4; H, 5.1; N, 6.8%. $C_{27}H_{27}N_3Pt \cdot Et_2O \cdot 0.5CH_2Cl_2$ requires: C, 54.3; H, 5.1; N, 6.5%. ESMS: (Cone voltage + 50 V): *m*/*z* 589 (MH$^+$, 100%). IR: ν_{max} 1609(s), 1590(s), 1574(s) and 1565(vs) cm^{-1}. ^{1}H-NMR: δ 7.05 (4H, t, br, $^3J_{3',2'} = 7.33$ Hz, H-3′,5′), 6.97 (4H, s, br, H-2′,6′), 6.86–6.73 (6H, m, H–Ar), 6.51 (1H, tt, $^3J_{4',3'} = 7.01$ Hz, $^4J_{4',2'} = 1.48$ Hz H-4″), 4.92 (4H, (s, br), (d, $^2J_{H,Pt} = 57.3$ Hz), C*H*=CH), 2.59 (4H, m, CH–CH_2), 2.21 (4H, m, CH–CH_2). ^{13}C-NMR: δ 166.4 (s, C=N), 148.0 (s, 1″), 147.7 (s, C-1′), 129.4 (d, C-3′,5′), 128.3 (d, C-3″,5″), 123.2 (d, C-2′,6′), 123.0 (d, C-2″,6″), 122.0 (s, C-4′), 119.9 (s, C-4″), 93.8 (d, (d, $^1J_{C,Pt} = 140.5$ Hz), *C*H=CH), 30.1 (t, CH–*C*H$_2$).The atom numbering scheme is shown for the r.t. ^{1}H- and ^{13}C-NMR spectra in Scheme 2.

3.2. Attempted preparation of [Pt{NPhC(=NPH)NPh}(PPh$_3$)$_2$] 4c

A mixture of [PtCl$_2$(COD)] (0.052, 0.139 mmol), triphenylphosphine (0.073 g, 0.278 mmol), *N*,*N*′,*N*″-triphenylguanidine (0.082 g, 0.139 mmol), and silver(I) oxide (0.987 g, excess) was refluxed in dichloromethane (20 ml) for 4 h. Filtration to remove the silver salts gave a dark orange solution. The solvent was removed by evaporation, to give a solid residue that failed to crystallise. NMR studies revealed the reaction does not proceed cleanly, with considerable quantities of an unknown impurity present. ESMS: (Cone voltage + 10 V): *m*/*z* 1019 (unidentified, 39%), 1005 (MH$^+$, 88%), 771 ([(Ph$_3$P)$_2$Pt(OH)$_2$]NH$_4^+$, 100%), 754 ([(Ph$_3$P)$_2$Pt(OH)$^+$ + H$_2$O], 20%). ^{31}P-NMR: (36.23 MHz) ($CDCl_3$) δ 8.14 (s, (d, $^1J_{P,Pt} = 3344$ Hz), Ph$_3$P), 6.06 (s, (d, $^1J_{P,Pt} = 3709$ Hz), impurity). ^{1}H-NMR: δ 7.42–7.07 (45H, m, H–Ar).

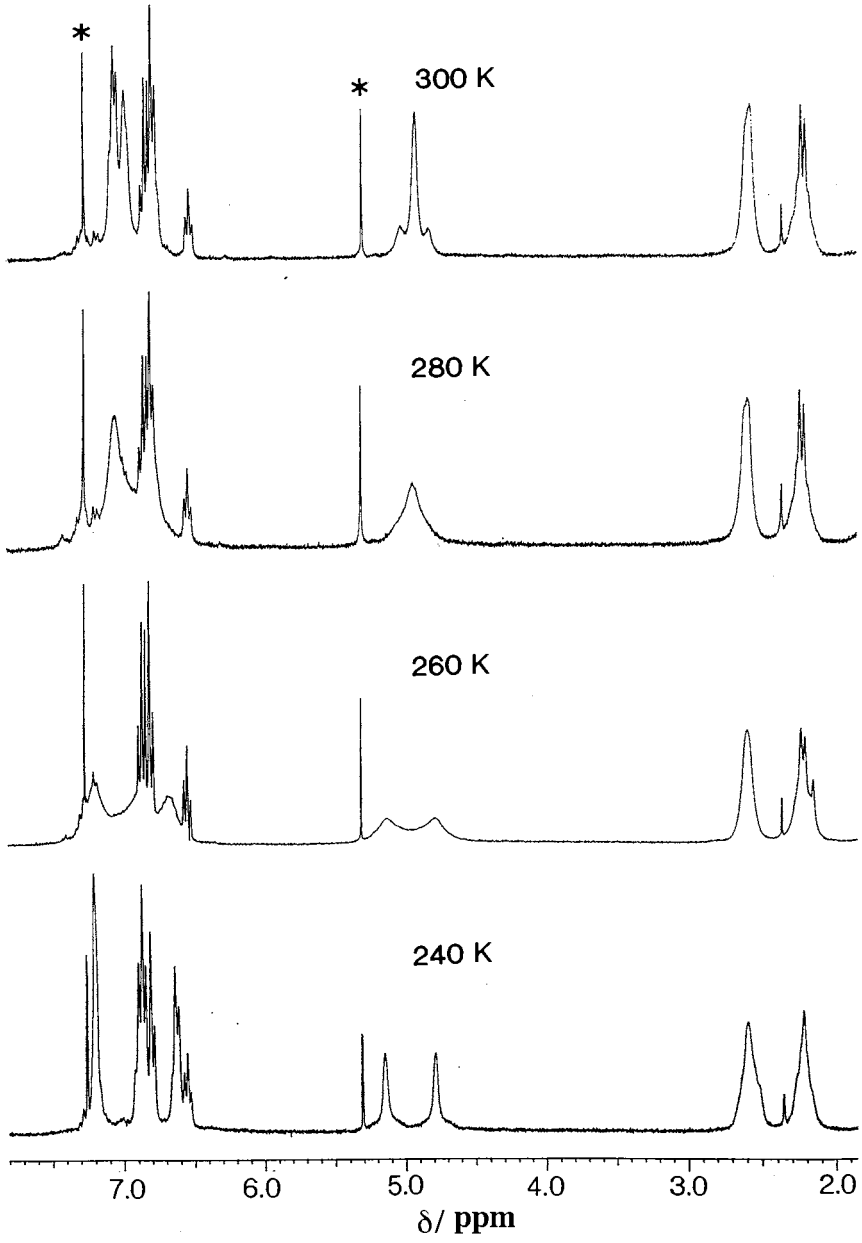
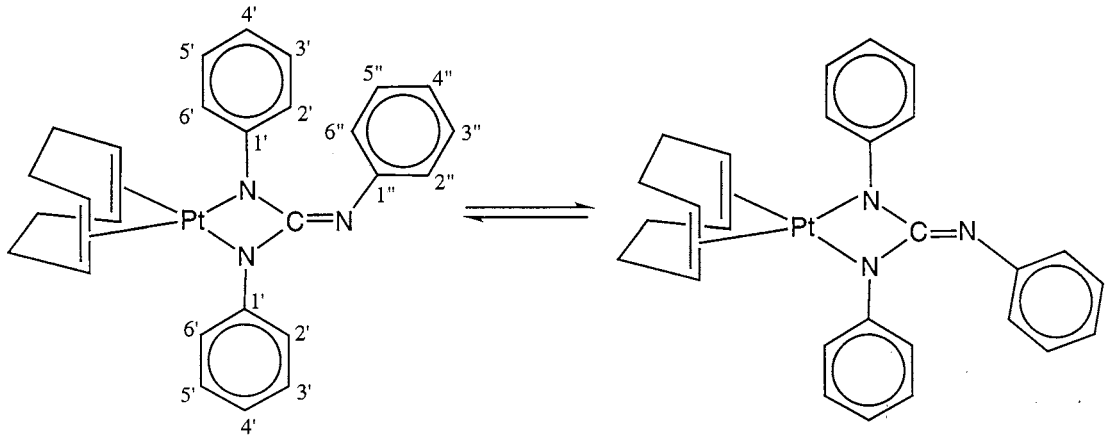


Fig. 3. ^{1}H-NMR spectra of the complex [Pt{NPhC(=NPh)NPh}(COD)] **4a** at temperatures of 300, 280, 260 and 240 K, in $CDCl_3$ solution. The COD alkene protons (δ 4.92 at 300 K) become inequivalent at the lowest temperature due to freezing out of the fluxional process involving the C=NPh moiety, see Scheme 2. The peaks marked * are due to $CHCl_3$ (δ 7.27) and CH_2Cl_2 (δ 5.32), respectively.

An alternative synthesis of **4c**, by ligand substitution of the COD complex **4a** was also attempted. Complex **4a** (0.035 g, 0.059 mmol) and triphenylphosphine (0.032 g, 0.122 mmol) were refluxed in dichloromethane (25 ml) for 3 h. No colour change was noted and upon removing the solvent under reduced pressure, the distinctive smell of free COD was not detected. ^{1}H- and ^{31}P-NMR showed only starting materials, indicating no reaction had taken place.

3.3. Preparation of [Pt{NAcC(=O)NAc}(COD)] 5

The complex [$PtCl_2$(COD)] (0.050 g, 0.134 mmol), *N*,*N*′,*N*″-triacetylguanidine (0.025 g, 0.135 mmol) and silver(I) oxide (0.08 g, excess) were refluxed in dichloromethane (20 ml) for 2 h. Filtration to remove the silver salts gave a colourless solution. The solvent was removed by evaporation and subsequent recrystallisation of the residue from dichloromethane–diethyl



Scheme 2. Fluxional process interconverting the Pt–NR groups, and COD CH and CH_2 groups.The NMR numbering scheme for the phenyl substituents is also shown for the r.t. spectrum with identical Pt–NPh moieties.

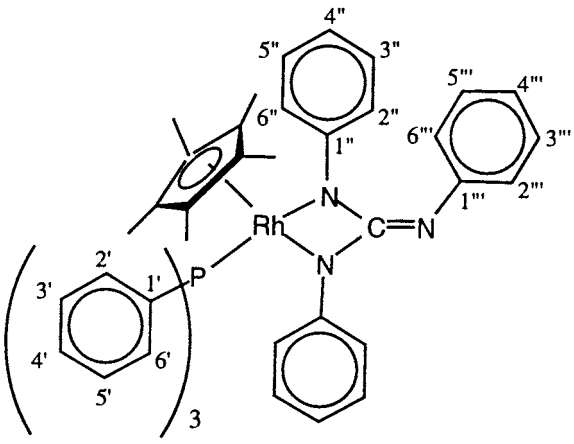
ether gave white crystals of **5** (0.052 g, 87%). M.p. 264°C (decomp.). Found: C, 35.1; H, 3.9; N, 6.2%. $C_{15}H_{21}N_3O_3Pt$ requires: C, 35.1; H, 4.1; N, 6.3%. ESMS: (Cone voltage + 50 V): m/z 446 (MH^+, 100%), 360 ($CODPt(OH)^+ + CH_3CN$, 28%). IR: ν_{max} 1726(vs), 1641(vs, br) cm^{-1}. ^{1}H-NMR: δ 6.17 (4H, (s, br), (d, br, $^2J_{H,Pt} = 64.0$ Hz), C*H*=CH), 2.50 (4H, m, CH-CH_2), 2.39 (6H, s, CH_3) 2.31 (4H, m, CH-CH_2). ^{13}C-NMR: δ 174.6 (s, CH_3C=O), 165.3 (s, NC(O)N), 96.7 (d, (d, $^1J_{C,Pt} = 132.7$ Hz), *C*H=CH), 30.4 (t, CH-*C*H_2), 26.7 (q, (d, $^3J_{C,Pt} = 36.5$ Hz), *C*H_3).

3.4. Preparation of *[Cp*Rh{NAcC(=NAc)NAc}(PPh$_3$)]* **6a**

The complex [Cp*$RhCl_2(PPh_3)$] (0.051 g, 0.089 mmol), *N*,*N*′,*N*″-triacetylguanidine (0.017 g, 0.092 mmol) and silver(I) oxide (0.05 g, excess) were added to dichloromethane (25 ml), which had previously been degassed and flushed with nitrogen. The mixture was refluxed under nitrogen for 1 h, during which time a marked colour change from orange to bright yellow was observed. An inert atmosphere appears to be essential, with attempts at carrying out the reaction in air proving unsuccessful. At completion, with no further efforts at excluding air, the silver salts were filtered off and the solvent removed under reduced pressure. Recrystallisation from dichloromethane–pentane gave **6a** as bright yellow crystals (0.051 g, 85%). M.p. 153–155°C. Found: C, 59.7; H, 5.6; N, 5.7%. $C_{35}H_{38}N_3O_3PRh \cdot 0.5CH_2Cl_2$ requires: C, 58.8; H, 5.4; N, 5.0%. IR: ν_{max} 1669(w), 1610(m) cm^{-1}. ESMS: (Cone voltage + 15 V): m/z 1368 ($2MH^+$, 3%), 684 (MH^+, 100%). (Cone voltage + 50 V): m/z 684 (MH^+, 90%), 643 ($[MH - CH_3CN]^+$, 30%), 422 ($[MH - PPh_3]^+$, 100%). ^{31}P-NMR: δ 40.9 (d, $^1J_{P,Rh} = 150.2$ Hz, *P*Ph_3). ^{1}H-NMR: δ 7.53 (6H, t, $^3J_{3',2'} = 8.88$, C-3′, 5′), 7.43–7.35 (9H, m, br, C-2′,4′,6′), 1.97 (6H, s, RhNC(O)CH_3), 1.83 (3H, s, C=NC(O)CH_3), 1.56 (15H, d, $^4J_{H,P} = 3.17$ Hz, Cp-CH_3). ^{13}C-NMR: δ 177.8 (s, RhNC(O)CH_3), 174.1 (s, C=NC(O)CH_3), 164.8 (s, *C*=N), 134.7 (d, (d, $^3J_{C,P} = 11.17$ Hz), C-3′,5′), 131.3 (d, C-4′), 130.1 (s, $^1J_{C,P} = 45.35$ Hz, C-1′), 128.2 (d, (d, $^2J_{C,P} = 10.49$ Hz), C-2′,6′), 99.9 (s, Cp), 26.7 (q, RhNC(O)*C*H_3), 26.1 (q, C=NC(O)*C*H_3), 8.8 (q, Cp–*C*H_3).

3.5. Preparation of *[Cp*Rh{NPhC(=NPh)NPh}(PPh$_3$)]* **6b**

The complex [Cp*$RhCl_2(PPh_3)$] (0.050 g, 0.088 mmol), *N*,*N*′,*N*″-triphenylguanidine (0.026 g, 0.091 mmol) and silver(I) oxide (0.06 g, excess) were added to dichloromethane (25 ml), which had previously been degassed and flushed with nitrogen. The mixture was refluxed under nitrogen for 1 h, during which time no colour change was noted. At completion, with no further efforts at excluding air, the silver salts were filtered off and the solvent removed under reduced pressure, to give a bright yellow oil which did not crystallise. ^{31}P-NMR revealed product with $< 50\%$ purity, with a very broad singlet (> 100 Hz) indicating substantial decomposition. ESMS: (Cone = + 20 V) 978 (unidentified, 8%), 937 (unidentified, 10%), 834 (unidentified, 20%), 787 (MH^+, 100%), 566 ($[MH - PPh_3 + CH_3CN]^+$, 32%). ^{31}P-NMR: (36.23 MHz) δ 35.6 (d, $^1J_{P,Rh} = 158.7$ Hz, *P*Ph_3), 9.6 (s, br, impurity). ^{1}H-NMR: δ 7.48–6.64 (m, Ar–H), 1.61 (15H, s, Cp–CH_3). ^{13}C-NMR: δ 154.6 (s, *C*=N), 144.9 (s, C-1″), 138.3 (s, C-1‴), 134.1 (d, (d, $^3J_{C,P} = 16.45$ Hz), C-3′,5′), 132.0 (s, $^1J_{C,P} = 29.51$ Hz, C-1′), 130.3 (d, C-4′), 129.3 (d, Ar), 128.8 (d, $^2J_{C,P} = 10.04$ Hz, C-2′,6′), 128.6 (d, C-3″,5″), 128.2 (d, Ar), 124.2 (d, C-2″,6″), 122.3 (d, Ar), 120.9 (d, Ar), 99.9 (s, (d, $^2J_{C,P} = 8.53$ Hz), Cp), 9.2 (q, Cp–*C*H_3).



3.6. Preparation of [Cp*Ir{NAcC(=NAc)NAc}(PPh3)] 7 and [Cp*Ir{NAcC(=O)NAc}(PPh3)] 11

The complex [Cp*$IrCl_2$(PPh_3)] (0.050 g, 0.076 mmol), *N*,*N*′,*N*″-triacetylguanidine (0.014 g, 0.076 mmol) and silver(I) oxide (0.05 g, excess) were added to dichloromethane (20 ml), which had previously been degassed and flushed with nitrogen, and the mixture was refluxed under nitrogen for 6 h. At completion, with no further efforts at excluding air, the silver salts were filtered, and the solvent removed from the filtrate under reduced pressure to give a yellow oil, shown by NMR to be a mixture of **7** and **11** in a 3:1 ratio. Recrystallisation from dichloromethane and pentane gave **7** as bright yellow crystals (0.036 g, 61%). M.p. 224–226°C. Found: C, 52.3; H, 4.9; N, 5.2%. $C_{35}H_{39}N_3O_3PIr\cdot 0.5CH_2Cl_2$ requires: C, 54.3; H, 5.1; N, 5.4%. IR: ν_{max} 1616(m), 1590(w), 1525(s, br) cm^{-1}. ESMS: (Cone voltage + 15 V): *m*/*z* 774 (MH^+, 100%), 732 ($[M-CH_3CN]H^+$, 10%). (Cone voltage + 50 V): *m*/*z* 774 (MH^+, 100%), 732 ($[\mathbf{11}+H]^+$, 5%), 512 ($[MH-PPh_3]^+$, 20%). ^{31}P-NMR: δ 15.4 (s, *P*Ph_3). ^{1}H-NMR: δ 7.51 (6H, m, Ar–H), 7.43–7.26 (9H, m, Ar–H), 1.96 (6H, s, IrNC(O)CH_3), 1.83 (3H, s, C=NC(O)CH_3), 1.56 (15H, s, (d, $^4J_{P,H}=1.51$ Hz), Cp–CH_3). ^{13}C-NMR: δ 176.3 (s, IrN*C*(O)CH_3), 174.4 (s, C=N*C*(O)CH_3), 166.0 (s, *C*=N), 134.9 (d, (d, $^3J_{C,P}=$ 10.79 Hz), C-3′,5′), 130.8 (d, C-4′), 130.0 (s, (d, $^1J_{C,P}=54.72$ Hz), C-1′), 128.1 (d, (d, $^2J_{C,P}=10.49$ Hz), C-2′,6′), 93.6 (s, Cp), 26.3 (q, C=NC(O)*C*H_3), 26.1 (q, IrNC(O)*C*H_3), 9.3 (q, Cp–*C*H_3). Atom numbering scheme as for complex **6b**.

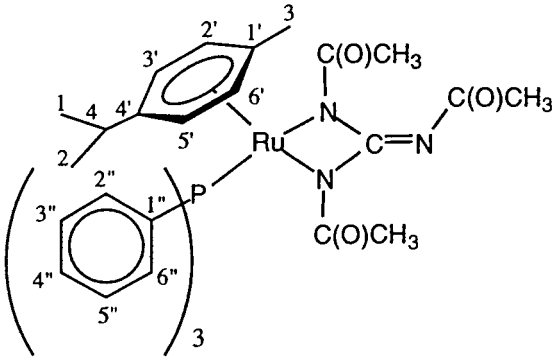
3.7. Preparation of [Cp*Ir{NPhC(=O)NAc}(PPh3)] 11

The complex [Cp*PPh_3IrCl_2] (0.051 g, 0.077 mmol), *N*,*N*′-diacetylurea (0.011 g, 0.076 mmol) and silver(I) oxide (0.08 g, excess) were refluxed in dichloromethane (25 ml) under nitrogen for 2 h. Workup gave a yellow oil that readily crystallised by vapour diffusion of pentane into a saturated chloroform solution at r.t., to give large yellow blocks of **11** (0.047 g, 84%). M.p. decomposed without melting. Found: C, 48.3; H, 4.5; N, 3.4%. $C_{33}H_{36}N_2O_3PIr\cdot CHCl_3$ requires: C, 48.0; H, 4.4; N, 3.3%. IR: ν_{max} 1694(s), 1616(s), 1600(s) cm^{-1}. ESMS: (Cone voltage + 20 V) 733 (MH^+, 100%). (Cone voltage + 50 V) 731 (MH^+, 100%), 471 ($[MH-PPh_3]^+$, 22%), 263 ($[PPh_3H]^+$, 12%). (Cone voltage + 80 V) 733 (MH^+, 20%), 493 ($[MNa-PPh_3]^+$, 22%), 471 ($[MH-PPh_3]^+$, 100%), 427 ($[M-CH_3C(O)-PPh_3]^+$, 12%), 386 (unidentified, 80%), 263 ($[PPh_3H]^+$, 38%). ^{31}P-NMR: δ 17.6 (s, PPh_3). ^{1}H-NMR: δ 7.61 (6H, m, br, Ar–H), 7.41–7.37 (9H, m, Ar–H), 2.16 (6H, s, IrNC(O)CH_3), 1.56 (15H, s, (d, $^4J_{P,H}=1.51$ Hz), Cp–CH_3).^{13}C-NMR: δ 175.9 (s, IrN*C*(O)CH_3), 165.0 (s, *C*=O), 134.9 (d, (d, $^3J_{C,P}=10.79$ Hz), C-3′,5′), 130.7 (d, C-4′), 130.0 (s, (d, $^1J_{C,P}=54.72$ Hz), C-1′), 127.9 (d, (d, $^2J_{C,P}=10.49$ Hz), C-2′,6′), 92.9 (s, Cp), 27.5 (q, IrNC(O)CH_3), 9.3 (q, Cp–*C*H_3).

3.8. Preparation of [(p − cymene)Ru{NAcC(=NAc)NAc}(PPh3)] 8

To a Schlenk flask containing dichloromethane (20 ml) (which had previously been degassed and flushed with nitrogen) was added [(*p*-cymene)$RuCl_2]_2$ (0.0.30 g, 0.049 mmol) and triphenylphosphine (0.026 g, 0.099 mmol). The solution was refluxed for 15 min. To this was added *N*,*N*′,*N*″-triacetylguanidine (0.018 g, 0.097 mmol) and silver(I) oxide (0.07 g, excess) and the mixture was refluxed under nitrogen for a further 2 h, during which time a marked colour change from bright orange to pale yellow was observed. Without exclusion of air, the silver salts were filtered off and solvent was evaporated under reduced pressure to give a yellow oil. Solutions of the compound became dark green, although NMR revealed no decomposition, implying the colouration is probably due to trace impurities. Recrystallisation by vapour diffusion of pentane and ether into dichloromethane over 3 months gave bright orange blocks of **8** (0.040 g, 60%). M.p. 188–189°C. Found: C, 58.8; H, 5.6; N, 5.9%. $C_{35}H_{38}N_3O_3PRu\cdot 0.5CH_2Cl_2$ requires: C, 59.0; H, 5.4; N, 5.8%. IR: ν_{max} 1673(m), 1651(m), 1590(m), 1577(m), 1569(m). ESMS: (Cone voltage + 20 V): *m*/*z* 682 (MH^+, 100%). (Cone voltage + 50 V): *m*/*z* 682 (MH^+, 70%), 419 ($[MH-PPh_3]^+$, 100%). (Cone voltage + 80 V): *m*/*z* 419 ($[MH-PPh_3]^+$, 22%), 335 ($[(p\text{-cymene})Ru+2CH_3CN+H_2O]^+$, 100%), 294 ($[(p\text{-cymene})Ru+CH_3CN+H_2O]^+$, 80%). ^{31}P-NMR: δ 44.2 (s, *P*Ph_3). ^{1}H-NMR: δ 7.56 (6H, t, $^3J_{3'',2''}=8.63$ Hz, C-3″,5″), 7.43–7.35 (9H, m, C-2″, 4″, 6″), 5.95 (2H, d, $^3J_{2'',3''}=$ 6.12 Hz, C-2′,6′), 5.05 (2H, d, $^3J_{3'',2''}=5.98$ Hz, C-3′,5′), 2.74 (1H, q, $^3J_{4,1}=6.87$ Hz, C-4), 1.93 (6H, s, RuNC(O)CH_3), 1.82 (3H, s, C=NC(O)CH_3), 1.68 (3H, s, C-3), 1.16 (6H, d, $^3J_{1,4}=6.90$ Hz, C-1, 2). ^{13}C-NMR: δ177.9 (s, RuN*C*(O)CH_3), 174.4 (s, C=N*C*(O)CH_3), 161.9 (s, *C*=NC(O)CH_3), 134.6 (d, (d, $^3J_{C,P}=10.94$ Hz),

C-3″,5″), 131.8 (s, (d, $^1J_{C,P} = 45.58$ Hz), C-1″), 130.5 (d, C-4″), 128.2 (d, (d, $^2J_{C,P} = 9.96$ Hz), C-2″,6″), 112.4 (s, (d, $^2J_{C,P} = 8.75$ Hz), C-1′), 102.6 (s, C-4′), 88.4 (d, C-2′,6′), 86.8 (d, C-3′,5′), 30.9 (d, C-4), 26.4 (q, C=NC(O)CH_3), 25.8 (q, RuNC(O)CH$_3$), 22.5 (q, C-1,2), 18.7 (q, C-3).



3.9. Preparation of [(p − cymene)-Os{NAcC(=NAc)NAc}(PPh$_3$)] **9** and [(p − cymene)Os{NAcC(=O)NAc}(PPh$_3$)] **10**

To a Schlenk flask containing dichloromethane (20 ml) (which had previously been degassed and flushed with nitrogen) was added [(*p*-cymene)OsCl$_2$(PPh$_3$)] (0.050 g, 0.076 mmol), *N*, *N*′, *N*″-triacetylguanidine (0.014 g, 0.076 mmol) and silver(I) oxide (0.10 g, excess) and the mixture was refluxed under nitrogen for 2 h, during which time the colour changed from bright yellow to almost colourless. The silver salts were filtered off and solvent was evaporated under reduced pressure to give a pale yellow oil which, despite repeated efforts, did not crystallise. NMR spectroscopy revealed the material to be a ca. 50:50 mixture of **9** and **10**. ESMS: (Cone voltage + 15 V) *m*/*z* 772 ([**9** + H]$^+$, 100%), 731 ([**10** + H]$^+$, 28%).

3.9.1. [(p − cymene)Os{NAcC(=NAc)NAc}(PPh$_3$)] **9**

^{31}P-NMR: δ 11.6 (s, (d, $^1J_{P,Os} = 301.5$ Hz), PPh$_3$). ^{1}H-NMR: δ 7.60 (6H, m, Ar–H), 7.38–7.33 (9H, m, Ar–H), 5.99 (2H, d, $^3J_{2',3'} = 5.58$ Hz, C-2′,6′), 5.13 (2H, d, $^3J_{3',2'} = 5.58$ Hz, C-3′,5′), 2.61 (1H, quintet, $^3J_{4,1} = 6.87$ Hz, C-4), 1.92 (6H, s, OsNC(O)CH_3), 1.84 (3H, s, C-3), 1.81 (3H, s, C=NC(O)CH_3), 1.12 (3H, d, $^3J_{1,4} = 6.89$ Hz, C-1,2). ^{13}C-NMR: δ 177.0 (s, OsNC(O)CH$_3$), 174.6 (s, C=NC(O)CH$_3$), 164.0 (s, C=NC(O)CH$_3$), 134.9 (d, (d, $^3J_{C,P} = 10.72$ Hz), C-3″,5″), 131.4 (s, (d, $^1J_{C,P} = 52.45$ Hz), C-1″), 130.6 (d, C-4″), 128.1 (d, (d, $^2J_{C,P} = 9.58$ Hz), C-2″,6″), 105.5 (s, (d, $^2J_{C,P} = 8.98$ Hz), C-1′), 94.7 (s, C-4′), 80.0 (d, C-2′,6′), 77.8 (d, C-3′,5′), 31.0 (d, C-4), 25.2 (q, OsNC(O)CH$_3$), 22.6 (q, C-1,2), 22.1 (q, C=NC(O)CH$_3$), 18.4 (q, C-3). Atom numbering scheme as for **8** above.

3.9.2. Preparation of [(p − cymene)Os{NAcC(=O)NAc}(PPh$_3$)] **10**

The complex [(*p*-cymene)OsCl$_2$(PPh$_3$)] (0.052 g, 0.079 mmol), *N*,*N*′-diacetylurea (0.012 g, 0.083 mmol) and silver(I) oxide (0.13 g, excess) were refluxed in dichloromethane (25 ml) under nitrogen for 2 h. Workup gave a very pale yellow oil that resisted crystallisation. Evacuation of all solvent, however, gave **10** as a pale yellow solid of sufficient purity (0.055 g, 95%). M.p. 235–238°C. Found: C, 53.6; H, 5.0; N, 4.0%. $C_{33}H_{35}N_2O_3POs$ requires: C, 54.4; H, 4.8; N, 3.8%. IR: ν_{max} 1692(s), 1616(s), 1599(s) cm^{-1}. ESMS: (Cone voltage + 20 V) 731 (MH$^+$, 100%). (Cone = + 50 V) 731 (MH$^+$, 100%), 510 ([MH − PPh$_3$ + CH$_3$CN]$^+$, 3%), 469 ([MH − PPh$_3$]$^+$, 10%), 263 ([PPh$_3$H]$^+$, 22%). (Cone voltage + 80 V) 731 (MH$^+$, 20%), 510 ([MH − PPh$_3$ + CH$_3$CN]$^+$, 22%), 469 ([MH − PPh$_3$]$^+$, 48%), 425 ([M − CH$_3$C(O)–PPh$_3$]$^+$, 48%), 384 (unidentified, 80%), 263 ([PPh$_3$H]$^+$, 100%). ^{31}P-NMR: δ 13.9 (s, (d, $^1J_{P,Os} = 301.1$ Hz), PPh$_3$). ^{1}H-NMR: δ 7.62–7.55 (6H, m, Ar–H), 7.42–7.33 (9H, m, Ar–H), 6.03 (2H, d, $^3J_{2',3'} = 5.77$ Hz, C-2′,6′), 5.15 (2H, d, $^3J_{3'',2''} = 5.73$ Hz, C-3′,5′), 2.53 (1H, quintet, $^3J_{4,1} = 6.90$ Hz, C-4), 2.10 (6H, s, OsNC(O)CH_3), 1.80 (3H, s, C-3), 1.04 (3H, d, $^3J_{1,4} = 6.93$ Hz, C-1, 2). ^{13}C-NMR: δ 176.7 (s, OsNC(O)CH$_3$), 164.6 (s, C=O), 134.9 (d, (d, $^3J_{C,P} = 10.64$ Hz), C-3″,5″), 131.3 (s, (d, $^1J_{C,P} = 52.15$ Hz), C-1″), 130.5 (d, C-4″), 128.4 (d, (d, $^2J_{C,P} = 9.58$ Hz), C-2″,6″), 104.0 (s, (d, $^2J_{C,P} = 9.89$ Hz), C-1′), 94.2 (s, C-4′), 79.8 (d, C-2′,6′), 76.7 (d, C-3′,5′), 31.2 (d, C-4), 26.6 (q, OsNC(O)CH_3), 22.6 (q, C-1, 2), 18.4 (q, C-3). Atom numbering scheme as for **8** above.

3.10. X-ray structure determination of [(p − cymene)Pt{NPhC(=NPh)NPh}(COD)] **4a** · CH_2Cl_2 · 0.5Et_2O

Yellow rectangular blocks were obtained on crystallisation by vapour diffusion of diethyl ether into a saturated dichloromethane solution of **4a** at 4°C. Accurate cell parameters and intensity data were collected on a Nicolet R3 diffractometer, using a crystal of dimensions 0.80 × 0.24 × 0.22 mm, and Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Crystal data: $C_{27}H_{27}N_3Pt \cdot CH_2Cl_2 \cdot 0.5Et_2O$, $M = 625.67$, monoclinic, space group $P2_1/c$ with $a = 9.862(1)$, $b = 14.497(3)$, $c = 17.436(3)$ Å, $\beta = 103.02(1)°$, $U = 2428.7(6)$ Å^3, $D_{calc.} = 1.711$ g cm^{-3}, $Z = 4$, μ(Mo–K$_\alpha$) = 5.80 mm^{-1}, $F(000) = 1236$. A total of 4291 reflections in the range $2 < \theta < 25$ Å were collected at 130(2) K, of which 4270 were unique. These were subsequently corrected for Lorentz and polarisation effects, and for linear absorption by a Ψ scan method ($T_{max,\ min} = 0.49,\ 0.18$). The structure was solved by Patterson interpretation [31] and developed routinely. A penultimate difference map revealed electron density which was attributed to a disordered diethyl ether molecule lying across an inversion centre in the lattice. In the final cycle of full-matrix least-squares refinement based on F^2 using SHELXL-93 [32] all non-H atoms were assigned anisotropic temperature factors, with all H-

atoms in calculated positions. The refinement converged with $R_1 = 0.0456$ for 3197 data with $I \leq 2\sigma(I)$, 0.0612 for all data; $wR_2 = 0.1147$, and GOF = 0.933. The largest parameter shift was 0.4σ (for the disordered diethyl ether solvent molecule) in the final cycle, and in the final difference map the largest features were +2.58 and −1.97 e Å^{-3} near the platinum atom.

Full tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, and can be obtained from the authors on request.

3.11. X-Ray structure determination of [(p − cymene)Ru{NAcC(=NAc)NAc}(PPh$_3$)] **8**

An orange rosette of **8** was obtained on crystallisation by vapour diffusion of diethyl ether and pentane into a saturated dichloromethane solution at 4°C, from which a rectangular block (dimensions 0.88 × 0.34 × 0.14 mm) suitable for X-ray analysis was cleaved. Preliminary precession photography indicated orthorhombic symmetry, with space group *Pbcn*. Crystal data: $C_{35}H_{38}N_3O_3PRu$, $M = 682.58$, orthorhombic, space group *Pbcn*, $a = 25.174(4)$, $b = 14.847(2)$, $c = 16.913(9)$ Å, $U = 6322(4)$ Å^3, $D_{calc.} = 1.435$ g cm^{-3}, $Z = 8$, μ(Mo–K$_\alpha$) = 5.86 mm^{-1}, $F(000) = 2832$. A total of 5445 reflections in the range $2.41 < \theta < 22.50°$ were collected at 130(2)K, of which 4131 were unique ($R_{int} = 0.056$). These were corrected for Lorentz and polarisation effects, and for linear absorption by a Ψ scan method ($T_{max,\ min}$ = 0.35, 0.32). Solution (direct methods, SHELXS-86) [31] gave the positions of the Ru and P atoms. Subsequent difference maps slowly revealed the rest of the structure, though with extensive disorder of the acetyl substituents on the metallacyclic ring. No satisfactory refinement model could be developed, the best giving R_1 0.1455 (2σ data), Rw_2 0.2896 (all data). Although the overall connectivity is unambiguous, detailed parameters are unreliable so are not reported in this paper.

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