

## The Mode of Co-ordination of the Quaternised 2,4'-Bipyridinium Cation. Crystal Structures of Trichloro(1'-methyl-2,4'-bipyridinium- $\kappa N^1$ )platinum(II) Dihydrate and Dichloro(1'-methyl-2,4'-bipyridin-3'-ylium- $\kappa C^3', N^1$ )platinum(II) ‡

Paule Castan, Françoise Dahan, and Smita Wimmer\*†

Laboratoire de Chimie de Coordination du CNRS (Unité 8241 liée par convention à l'Université Paul Sabatier), 205 route de Narbonne, 31077 Toulouse Cedex, France

Franz L. Wimmer†

Department of Chemical and Physical Sciences, Huddersfield Polytechnic, Queensgate, Huddersfield

The 1'-methyl-2,4'-bipyridinium ion (2,4'-mbipy<sup>+</sup>) reacts with  $K_2[MX_4]$  ( $M = Pt^{II}$  or  $Pd^{II}$ ;  $X = Cl$  or  $Br$ ) to give the zwitterionic compounds  $[M(2,4'-mbipy)X_3]$ . The crystal and molecular structure of  $[Pt(2,4'-mbipy)Cl_3]$  has been determined by single-crystal *X*-ray analysis. The compound crystallizes in the monoclinic system, space group  $P2_1/c$  with  $a = 12.319(2)$ ,  $b = 9.359(1)$ ,  $c = 13.665(2)$  Å, and  $\beta = 107.90(1)^\circ$ . From  $[M(2,4'-mbipy)X_3]$ , cyclometallated  $[ML^3X_2]$ , ( $M = Pt$  or  $Pd$ ,  $X = Cl$  or  $Br$ ,  $L^3 = 1'$ -methyl-2,4'-bipyridin-3'-ylium) has been synthesized and spectroscopically characterized. The crystal and molecular structure of  $[PtL^3Cl_2]$  has been determined by single-crystal *X*-ray analysis. The compound crystallizes in the orthorhombic system, space group  $Pbca$ ,  $a = 7.643(1)$ ,  $b = 17.726(2)$ , and  $c = 17.142(2)$  Å. 2,4'-Bipyridyl (2,4'-bipy) reacts with  $PdX_2$  ( $X = Cl$  or  $O_2CMe$ ) to yield *trans*- $[Pd(2,4'-bipy)_2X_2]$  and with  $K_2[PtCl_4]$  to give *cis*- $[Pt(2,4'-bipy)_2X_2]$ . Heating *trans*- $[Pd(2,4'-bipy)_2X_2]$  in acetic acid gives the cyclometallated dimer  $\{[PdL^2(\mu-O_2CMe)]_2\}$  ( $L^2 = 2,4'$ -bipyridin-3'-ylium).

The simplest and most convenient means of preparing an orthometallated complex of platinum(II) or palladium(II) is the initial co-ordination of the heteroatom followed by metallation.<sup>1</sup> The ease and the likelihood of such a process depends on various factors, notably (i) the nature of the heteroatom, (ii) the basicity, and (iii) the steric arrangement around the C-donor atom and metal atom. However, monodentate compounds of the type  $[M(HL)Cl_3]^-$  ( $HL =$  ligand) are rare and the species formed prior to cyclometallation are commonly  $[M(HL)_2Cl_2]$ . Further, mononuclear cyclometallated compounds of the type  $[MLCl_2]^-$  ( $L =$  cyclometallated ligand) are little known and the species formed on direct reaction of the metal salt with the ligand is the neutral binuclear complex,  $[LM(\mu-X)_2ML]$  ( $M = Pt$ ,  $X =$  halide;  $M = Pd$ ,  $X =$  halide or  $O_2CMe$ ). Mononuclear cyclometallated complexes are usually obtained on cleavage of the dinuclear complex with a neutral ligand ( $L'$ ) to form complexes of the type  $[ML(L')X]$ .

2,2'-Bipyridine (2,2'-bipy) can function as a monodentate, bidentate, or bridging ligand due to free rotation about the 2,2' bond. The formation of monodentate bipy ligands has been proposed to explain the photophysical and catalytic properties of metal complexes of polypyridines.<sup>2</sup> Although species containing monodentate bipy have been observed in the reaction of bipy with  $[Al(Me_2SO)_6]^{3+}$ ,<sup>3</sup> there are as yet no known compounds containing monodentate 2,2'-bipy in the solid state. Further, there are a very few examples of well characterised complexes in which 2,2'-bipy functions as a bridging ligand.<sup>4</sup>

We have been interested in the monodentate mode of co-ordination of 2,2'-bipy which was achieved by blocking one of the pyridine N atoms with an alkyl group. Reaction of the cationic ligand 1'-methyl-2,2'-bipyridinium  $[2,2'-mbipy]^+$  with platinum(II) and palladium(II) not only gives a monomer,  $[M(2,2'-mbipy)Cl_3]$ ,<sup>5,6</sup> but also a mononuclear cyclometallated complex,  $[ML^1Cl_2]$  ( $M = Pt$  or  $Pd$ ,  $L^1 = 1'$ -methyl-2,2'-bipyridin-3'-ylium). As a result of the metallation the ligand itself is zwitterionic.

Constable<sup>7</sup> has reported the preparation and characteris-

ation of cyclopalladated derivatives of 2,4'-bipyridine (2,4'-bipy). This is the only example known of a cyclopalladated complex of any of the isomers of bipyridine.<sup>8</sup>

A study of cyclometallation of quaternised 2,4'-bipy would enable us not only to compare this mode of co-ordination with unquaternised 2,4'-bipy but also with the  $[2,2'-mbipy]^+$  system.

### Results and Discussion

**Reactions of 2,4'-Bipyridine.**—The complex  $[Pd(2,4'-bipy)_2(O_2CMe)_2]$ , (1), separates as a pale yellow crystalline solid from the reaction of 2,4'-bipy with  $Pd(O_2CMe)_2$  in acetone, while 2,4'-bipy reacts with  $PdCl_2$  in acetonitrile to give a pale yellow powder of  $[Pd(2,4'-bipy)_2Cl_2]$ , (2). The i.r. spectra of the two compounds are essentially similar except for differences caused by the acetate groups in (1) and the chloro groups in (2) (see Table 1). The strong bands at 1 630, 1 585, 1 385, 1 371, and 1 305  $cm^{-1}$  and medium-intensity bands at 860, 705, and 630  $cm^{-1}$  of compound (1) [which are not present in the spectrum of (2)] are indicative of monodentate acetate groups.<sup>9</sup> The i.r. spectrum of (2) shows a sharp band at 355  $cm^{-1}$  (attributed to the Pd–Cl stretching vibration) suggesting that the compound is the *trans* isomer. This form is also ascribed to complex (1).

The compound 2,4'-bipy reacts with  $K_2[PtCl_4]$  in water to form bright yellow  $[Pt(2,4'-bipy)_2Cl_2]$ , (3). The bands at 330 and 340  $cm^{-1}$  in the i.r. spectrum of this compound are taken as indication of the *cis* configuration.<sup>9,10</sup> The ligating properties of 2,4'-bipy are essentially that of a substituted pyridine.

The compound 2,4'-bipy can co-ordinate as a monodentate ligand *via* the  $N^1$  atom or the  $N^1$  atom or as a bridging ligand *via* the two N atoms. The lack of solubility of complexes (1)–(3) hinders any further spectroscopic characterisation which would

† Present address: Department of Chemistry, Universiti Brunei Darussalam, Bandar Seri Begawan, Brunei.

‡ Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

Table 1. Analytical and physical data for the complexes

Complex	Colour	Yield/%	Analysis <sup>a</sup> /%			I.r. <sup>b</sup> /cm <sup>-1</sup>
			C	H	N	
[Pd(2,4'-bipy) <sub>2</sub> Cl <sub>2</sub> ]	Yellow	90	48.25 (49.00)	3.25 (3.25)	11.75 (11.45)	1 615s, 1 585s, 1 550m, 1 500m, 851s, 782s, 739m, 729s, 655m, 618m, 255m ν(Pd-Cl) 355m
[Pt(2,4'-bipy) <sub>2</sub> Cl <sub>2</sub> ].H <sub>2</sub> O	Light yellow	75	40.30 (40.25)	2.75 (3.00)	9.35 (9.40)	Essentially as above ν(Pt-Cl) 340m, 330m
[Pd(2,4'-bipy) <sub>2</sub> (O <sub>2</sub> CMe) <sub>2</sub> ].1.5H <sub>2</sub> O	Fawn-yellow	93	50.95 (51.10)	4.25 (4.80)	9.70 (9.95)	1 630s, <sup>c</sup> 1 610s, 1 585s, <sup>c</sup> 1 575s (br), 1 385s, <sup>c</sup> 1 371s, <sup>c</sup> 1 305s, <sup>c</sup> 855m, 779s, 730s, 700s, <sup>c</sup> 655m, 620m
[{PdL <sup>2</sup> (μ-O <sub>2</sub> CMe)} <sub>2</sub> ].4H <sub>2</sub> O	Cream-yellow	90	40.60 (40.40)	4.10 (3.95)	6.25 (7.85)	1 605m, 1 575s (br), <sup>d</sup> 1 460s (br), <sup>d</sup> 785m, 725m
[{PdL <sup>2</sup> (μ-Cl)} <sub>2</sub> ].1.5H <sub>2</sub> O	Yellow		38.50 (38.65)	2.65 (2.75)	8.20 (9.00)	1 605s, 1 580m, 1 565m, 1 400m, 792s, 755m, 720s ν(Pd-Cl) 280m, 245m
[Pd(2,4'-mbipy)Cl <sub>3</sub> ].2H <sub>2</sub> O	Orange	85	31.40 (31.45)	3.50 (3.55)	6.45 (6.65)	1 640s, 1 595m, 1 560m, 855s, 840m, 785s, 725m ν(Pd-Cl) 340s, 330m (br)
[Pt(2,4'-mbipy)Cl <sub>3</sub> ].2H <sub>2</sub> O	Orange-yellow	90	26.10 (25.95)	2.70 (2.75)	5.65 (5.55)	Essentially as above ν(Pt-Cl) 335s (br), 320s
[Pd(2,4'-mbipy)Br <sub>3</sub> ]	Brick-red	50	24.65 (25.50)	2.00 (2.10)	5.20 (5.40)	Same as above ν(Pd-Br) difficult to distinguish
[PtL <sup>3</sup> Cl <sub>2</sub> ]	Orange	95	29.95 (30.25)	2.25 (2.30)	6.35 (6.40)	1 610m, 1 600s, 1 200s, 820m, 755s, 745m, 710s, 410m ν(Pt-Cl) 330s, 270s
[PdL <sup>3</sup> Cl <sub>2</sub> ].H <sub>2</sub> O	Pale yellow	95	36.30 (36.10)	3.15 (3.55)	7.70 (7.65)	Essentially as above ν(Pd-Cl) 325m, 245m
[PdL <sup>3</sup> Br <sub>2</sub> ]	Pale orange	90	29.50 (30.25)	2.15 (2.30)	6.25 (6.40)	Essentially as above ν(Pd-Br) 265

<sup>a</sup> Required values are in parentheses. <sup>b</sup> As Nujol mull; s = strong, m = medium, and br = broad. <sup>c</sup> Monodentate acetate. <sup>d</sup> Bridging acetate.

enable one to make a distinction between the possible sites of co-ordination. However, it is thought that 2,4'-bipy would co-ordinate *via* the least-hindered nitrogen atom. This conclusion was also reached by Oishi<sup>11</sup> in a laser flash photolysis study of the photochemical substitution of [Cr(CO)<sub>6</sub>] by 2,4'-bipy.

When complex (1) is heated in acetic acid for 2 h the cyclometallated complex [{PdL<sup>2</sup>(μ-O<sub>2</sub>CMe)}<sub>2</sub>], (4; L<sup>2</sup> = 2,4'-bipyridin-3'-ylium), is obtained. The i.r. spectrum shows strong broad bands at 1 575 and 1 460 cm<sup>-1</sup> characteristic of bridging acetate groups.<sup>12</sup> This compound was first prepared by Constable<sup>7</sup> by the reaction of 2,4'-bipy with Pd(O<sub>2</sub>CMe)<sub>2</sub> in acetic acid. We found that when a slight excess of Pd(O<sub>2</sub>CMe)<sub>2</sub> relative to 2,4'-bipy in acetic acid is used a bright orange solid is formed which reacts further with more 2,4'-bipy to give the pale yellow complex (4). Further, Constable<sup>7</sup> observed bands at 1 708 and 1 830 cm<sup>-1</sup> in the i.r. spectrum of [{PdL<sup>2</sup>(μ-O<sub>2</sub>CMe)}<sub>2</sub>] which are not present in the spectrum of the compound prepared in this work. These bands are probably due to acetic acid.<sup>13</sup>

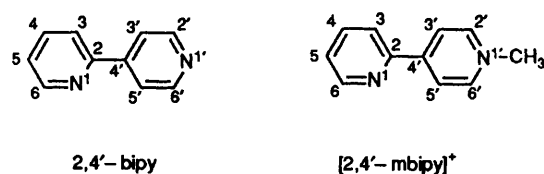
The acetato-bridged complex (4) can be readily converted into the chloro-bridged complex [{PdL<sup>2</sup>(μ-Cl)}<sub>2</sub>], (4a), using LiCl or dilute HCl. The i.r. spectrum of this compound shows the presence of bands at 280 and 245 cm<sup>-1</sup> which are not present in the spectrum of the acetato complex. These are assigned to the metal-chlorine stretching vibrations. The low frequency of these bands is indicative of bridging chloride ligands,<sup>14</sup> thus confirming Constable's proposition that (4a) has a bridged structure. The large separation between the two bands is due to the higher *trans* influence of a σ-bonded carbon atom compared to the nitrogen atom.<sup>15</sup>

When complex (2) is warmed in a dilute solution of HCl the initial pale yellow solid is gradually converted into a bright yellow solid with concomitant changes in the i.r. spectrum. The most significant changes are in the ring stretching (1 650—

1 500 cm<sup>-1</sup>) and the out-of-plane deformation (900—700 cm<sup>-1</sup>) modes. There is a new band at 1 600 cm<sup>-1</sup> and the band at 850 cm<sup>-1</sup> of complex (2) originally present has disappeared. The compound analyses as [Pd(2,4'-bipy)Cl<sub>2</sub>], (5). The absence of the band at 850 cm<sup>-1</sup> is also observed in the i.r. spectra of (4) and the cyclometallated complex of the cation [2,4'-mbipy]<sup>+</sup>, *viz.* [PdL<sup>3</sup>Cl<sub>2</sub>] (L<sup>3</sup> = 1'-methyl-2,4'-bipyridin-3'-ylium) (see below). Compound (5) can thus be either a cyclometallated complex in which the ligand is protonated at N<sup>1'</sup>, *viz.* [Pd(HL<sup>2</sup>)Cl<sub>2</sub>] (this type of co-ordination can be compared to that found for 2,2'-bipy in Watts' complex<sup>16</sup>) or 2,4'-bipy is behaving as a bridging ligand, *viz.* [Cl<sub>2</sub>Pd(μ-2,4'-bipy)<sub>2</sub>PdCl<sub>2</sub>].

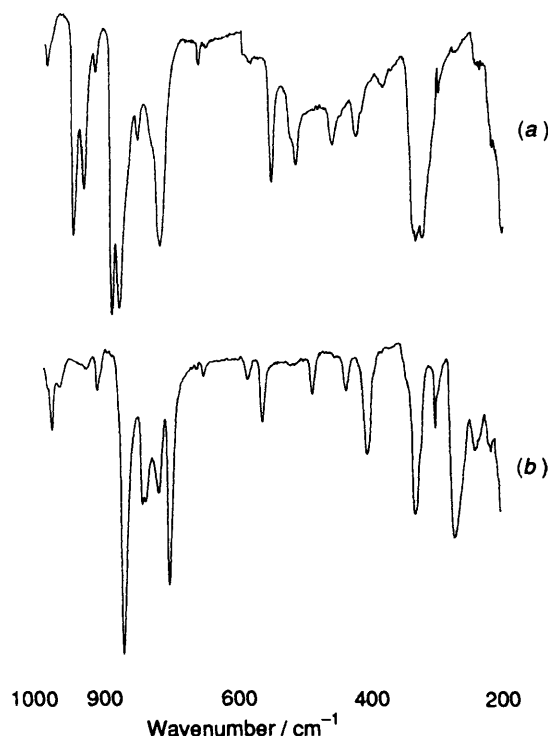
*Reactions of [2,4'-mbipy]<sup>+</sup>.*—Homer<sup>17</sup> isolated the mono- and di-methiodide salts by the reaction of 2,4'-bipy with a four-fold excess of methyl iodide in ethanol. We found that the formation of the dimethiodide is avoided if only a slight excess of methyl iodide is used and [2,4'-mbipy]I is then the unique product.

Monoquaternisation of 2,4'-bipy can lead to the formation of two isomers depending on the pyridine ring that is quaternised. A study of the N-methylation of 1,7- and 1,8-phenanthrolines and 1,5- and 1,6-benzonaphthapyridines<sup>18,19</sup> has shown that these azaheterocycles preferentially quaternise at the least sterically hindered N atoms, *viz.* at positions 7 and 8 for the phenanthrolines and at 5 and 6 for the benzonaphthapyridines. For 2,4'-bipy, preferential quaternisation is again at the less sterically hindered N<sup>1'</sup> atom as shown by the <sup>1</sup>H n.m.r. spectrum (see Table 2), *viz.* the protons of the 2-pyridyl ring are deshielded by approximately 0.1 p.p.m. whereas those of the 4'-pyridyl ring are deshielded by 0.33 (H<sup>2</sup>) and 0.72 p.p.m. (H<sup>3</sup>). Similar results have been observed for 5,5'-dimethylbipyridine<sup>20</sup> and 1,10-phenanthroline,<sup>21</sup> *i.e.* the protons of the N-methylated ring undergo a large deshielding and in addition

**Table 2.** N.m.r. spectral data<sup>a</sup>

Proton	$\delta$		$\Delta^d$
	b	c	
3	8.12	8.44	0.32
4	8.06	8.17	0.11
5	7.57	7.72	0.15
6	8.81	8.94	0.13
2'	8.75	9.08	0.33
3'	8.14	8.86	0.72
Me	—	4.54	—

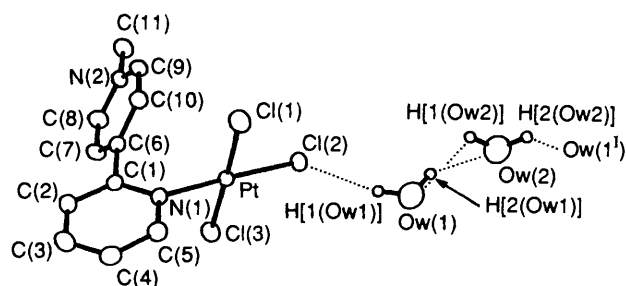
<sup>a</sup> In CD<sub>3</sub>OD solution. <sup>b</sup> 2,4'-bipy:  $J_{2,3}$  4.7,  $J_{2,5}$  1.7,  $J_{3,4}$  7.8,  $J_{3,5}$  1.6,  $J_{3,6}$   $\approx$  1,  $J_{4,5}$  7.1,  $J_{4,6}$  1.7, and  $J_{5,6}$  4.8 Hz. <sup>c</sup> [2,4'-mbipy]<sup>+</sup>:  $J_{2,3}$  6.8,  $J_{2,5}$  < 1,  $J_{3,4}$  8.0,  $J_{3,5}$  1.0,  $J_{3,6}$   $\approx$  1,  $J_{4,5}$  7.6,  $J_{4,6}$  1.7, and  $J_{5,6}$  4.7 Hz. <sup>d</sup> Change in chemical shift on methylation.

**Figure 1.** Infra-red spectra (CsI plates, Nujol mull) of (a) [Pt(2,4'-mbipy)Cl<sub>3</sub>] (**8**) and (b) [PtL<sup>3</sup>Cl<sub>2</sub>] (**10**)

some of the effect of the positive charge is transferred to the other ring.

On quaternisation, the initial ring stretching modes [ $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$ ] present at 1582 and 1545 cm<sup>-1</sup> shift to 1637, 1583, and 1559 cm<sup>-1</sup> which correspond to a molecule containing both a pyridine (1578, 1565 cm<sup>-1</sup>)<sup>22</sup> and a *N*-methylpyridinium (1632, 1582 cm<sup>-1</sup>) moiety.<sup>23</sup>

For complex formation, [2,4'-mbipy]NO<sub>3</sub> was prepared by metathesis of [2,4'-mbipy]I with AgNO<sub>3</sub> in acetone. Treatment of K<sub>2</sub>[PdCl<sub>4</sub>] with [2,4'-mbipy]NO<sub>3</sub> in water results in the gradual formation of [Pd(2,4'-mbipy)Cl<sub>3</sub>], (**6**), as orange

**Figure 2.** ORTEP plot of complex (**8**). Hydrogen bonds are drawn with dotted lines. Symmetry operation:  $I - x, -1 - y, 1 - z$ . Hydrogen atoms other than those of water molecules are omitted

needles. For the preparation of [Pd(2,4'-mbipy)Br<sub>3</sub>], (**7**), K<sub>2</sub>[PdBr<sub>4</sub>] in water has to be added to the ligand in a large quantity of acetone whereupon the complex gradually separates as red microcrystals. If the preparation was performed in the reverse manner, *i.e.* addition of the ligand to the metal salt, a buff coloured solid was produced and this was not studied further. Gentle warming is required to prepare the analogous platinum complex, [Pt(2,4'-mbipy)Cl<sub>3</sub>], (**8**), which separates from the solution as yellow-orange needles.

In the i.r. spectra of [M(2,4'-mbipy)X<sub>3</sub>] there is a new band at 1595 cm<sup>-1</sup>, not present in the spectrum of [2,4'-mbipy]I, which is indicative of complex formation *via* the pyridyl nitrogen atom<sup>24</sup> {see Figure 1 for the spectrum of [Pt(2,4'-mbipy)Cl<sub>3</sub>]}. The metal-halogen stretching frequencies are presented in Table 1. These values are indicative of terminal halogens. Hence we can discount the possibility of the formation of salts of the type [2,4'-mbipy]<sub>2</sub>[M<sub>2</sub>X<sub>6</sub>].<sup>25</sup>

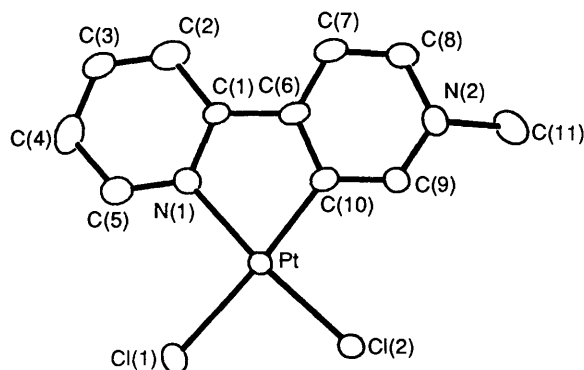
For neutral N-donor ligands, L, the formation of monoligand complexes of the type [MLX<sub>3</sub>]<sup>-</sup> is not straightforward; the compound that preferentially separates is the uncharged disubstituted complex, [ML<sub>2</sub>X<sub>2</sub>], on the direct reaction of [MX<sub>4</sub>]<sup>2-</sup> with the ligand.<sup>26</sup> If the formation of a neutral complex is the driving force, then for a positively charged ligand, L<sup>+</sup>, the production of a monoligand complex, [M(L<sup>+</sup>)X<sub>3</sub>] is actually favoured.

**Description of the Structure of Complex (8).**—The ORTEP plot of the molecule together with the labelling scheme is shown in Figure 2. Interatomic bond distances and angles are reported in Table 3. The crystal structure consists of zwitterionic trichloro(1'-methyl-2,4'-bipyridinium)platinum molecules together with two molecules of water of crystallisation. The co-ordination of the metal is square planar with three chlorine atoms and a nitrogen atom N<sup>1</sup> of the non-quaternised pyridine ring of [2,4'-mbipy]<sup>+</sup>. Deviations of Pt, Cl(1), Cl(2), Cl(3), and N(1) from the mean plane passing through them are -0.001(2), 0.019(1), 0.008(1), 0.017(1), and 0.065(4) Å. The extent of these deviations is slightly superior to those found for K[Pt(C<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>)Cl<sub>3</sub>]<sup>26</sup> but less than those of other zwitterionic complexes [PtLCl<sub>3</sub>] (L = ethylammonium, thiamine, or 9-methyladeninium).<sup>27</sup> The three Pt-Cl bonds are in the range 2.295(1)—2.310(1) Å. The bond angles about the platinum atom show little deviation from regular square-planar co-ordination. The Pt-N distance is 2.020(4) Å which is in the order of Pt-N bond distances of substituted-pyridine complexes of Pt<sup>II</sup>.<sup>28</sup>

The two pyridine rings are planar with a dihedral angle between them of 53°. In complexes where 2,2'-bipyridine behaves as a bridging ligand<sup>4</sup> or as a cation with the nitrogen atoms protonated<sup>29</sup> the dihedral angle between the two pyridine rings can vary from 36 to almost 90°, and the rotation about the rings is retained in solution. The dihedral angle between the co-ordinated pyridine plane and the platinum

**Table 3.** Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complexes (8) and (10)

	(8)	(10)	(8)	(10)
<b>Platinum environment</b>				
Pt-Cl(1)	2.295(1)	2.381(2)	Pt-Cl(3)	2.310(1)
Pt-Cl(2)	2.310(1)	2.299(2)	Pt-C(10)	—
Pt-N(1)	2.020(4)	2.036(6)		
Cl(1)-Pt-Cl(2)	91.50(5)	90.57(7)	Cl(2)-Pt-Cl(3)	91.03(5)
Cl(1)-Pt-Cl(3)	177.30(6)	—	Cl(2)-Pt-N(1)	177.6(1)
Cl(1)-Pt-N(1)	89.6(1)	95.7(2)	Cl(3)-Pt-N(1)	87.8(1)
Cl(1)-Pt-C(10)	—	175.1(2)	Cl(2)-Pt-C(10)	—
N(1)-Pt-C(10)	—	80.1(2)		
<b>2,4'-Bipyridine molecule</b>				
N(1)-C(1)	1.348(6)	1.372(9)	C(6)-C(7)	1.389(7)
C(1)-C(2)	1.387(8)	1.387(11)	C(7)-C(8)	1.371(8)
C(2)-C(3)	1.383(8)	1.345(12)	C(8)-N(2)	1.350(6)
C(3)-C(4)	1.373(8)	1.394(12)	N(2)-C(9)	1.334(6)
C(4)-C(5)	1.368(8)	1.392(12)	C(9)-C(10)	1.371(7)
C(5)-N(1)	1.350(7)	1.329(10)	C(10)-C(6)	1.392(6)
C(1)-C(6)	1.495(7)	1.470(10)	N(2)-C(11)	1.473(7)
Pt-N(1)-C(1)	124.5(4)	115.2(4)	C(1)-C(6)-C(7)	120.9(4)
Pt-N(1)-C(5)	117.2(3)	124.0(5)	C(1)-C(6)-C(10)	121.0(4)
C(1)-N(1)-C(5)	117.7(5)	120.7(6)	C(10)-C(6)-C(7)	117.9(5)
N(1)-C(1)-C(2)	122.0(5)	118.6(7)	C(6)-C(7)-C(8)	120.2(4)
C(1)-C(2)-C(3)	118.5(5)	119.3(8)	C(7)-C(8)-N(2)	120.3(5)
C(2)-C(3)-C(4)	120.0(6)	122.4(8)	C(8)-N(2)-C(9)	120.5(4)
C(3)-C(4)-C(5)	118.3(5)	115.0(8)	N(2)-C(9)-C(10)	121.2(4)
C(4)-C(5)-N(1)	123.5(5)	122.9(7)	C(9)-C(10)-C(6)	119.7(5)
N(1)-C(1)-C(6)	118.2(5)	112.9(6)	C(8)-N(2)-C(11)	119.9(4)
C(2)-C(1)-C(6)	119.8(4)	128.5(7)	C(9)-N(2)-C(11)	119.6(4)
Pt-C(10)-C(6)	—	117.1(5)	Pt-C(10)-C(9)	—

**Figure 3.** ORTEP plot of complex (10)

plane is  $79.1^\circ$ . Pyridine or substituted pyridine is usually twisted out of the co-ordination plane. The bond lengths in the co-ordinated pyridine ring average  $1.378(8)$  and  $1.349(7)$  Å for C-C and C-N respectively. For the quaternised pyridine ring, these bonds average  $1.381(7)$  and  $1.342(6)$  Å respectively. The mean values of the bond angles of the two rings are  $120.5(5)^\circ$ .

There are intermolecular contacts between the chloro ligands and the water molecules,  $3.392(6)$  and  $3.379(6)$  Å. The second one between Cl(2) and Ow(1) is most probably a hydrogen bond. Hydrogen bonds between the two water molecules [ $2.834(9)$  Å] enforce the crystal-packing stability.

\* Prolonged heating of  $[M(2,2'\text{-mbipy})Cl_3]$  in water for 22 and 72 h is necessary to prepare the respective cyclometallated complexes of Pd and Pt.<sup>5,14</sup>

**Cyclometallation.**—The complex  $[Pd(2,4'\text{-bipy})Cl_3]$  gradually dissolves in hot water to give an orange solution, from which pale yellow needles of the cyclometallated complex  $[PdL^3Cl_2]$ , (9), separate after approximately 2 min. To prepare the analogous bromo cyclometallated derivative (11) heating of  $[Pd(2,4'\text{-mbipy})Br_3]$  in water under reflux for 2 h is required. The slower reaction reflects the ease of substitution of a chloro compared to the bromo group.

When a suspension of  $[Pt(2,4'\text{-mbipy})Cl_3]$  in water is heated under reflux the complex gradually goes into solution, but at the same time the cyclometallated complex  $[PtL^3Cl_2]$ , (10), commences to separate out as orange needles; 6 h are required for complete reaction. The solutions at the end of these reactions are acidic and the filtrate after removal of the product contains ionic chloride (bromide).

The remarkable ease of cyclometallation of  $[2,4'\text{-mbipy}]^+$  compared to  $[2,2'\text{-mbipy}]^+$ \* is doubtless due to the lack of steric hindrance present in the latter ligand;  $[2,2'\text{-mbipy}]^+$  has the quaternised N atom in an *ortho* position which will give rise to an obstruction to ring closure.

The i.r. spectra of complexes (9)–(11) are almost identical except in the far-i.r. region. The most significant changes on cyclometallation are in the ring stretching and the out-of-plane deformation modes (see Figure 1). These changes suggest a modification of one of the pyridine rings; this is consistent with cyclometallation at C<sup>3'</sup> of the quaternised pyridine ring. The strongest bands in the far-i.r. spectra of these complexes, assigned as the M-Cl stretching modes, are presented in Table 1. The large separation between these bands is due to the halogens being *trans* to two different donor atoms.

**Description of the Structure of Complex (10).**—The ORTEP plot of the molecule, together with the labelling scheme, is

shown in Figure 3. Interatomic bond distances and angles are presented in Table 3. The structure is thus confirmed as dichloro(1'-methyl-2,4'-bipyridin-3'-ylium)platinum(II). The coordination about the platinum is square planar. On cyclometallation the bond angles around the metal approach those of the red form of  $[\text{Pt}(\text{bipy})\text{Cl}_2]$ . Thus the bite angle of  $\text{N}(1)\text{--Pt--C}(10)$  of  $80.1(2)^\circ$  compares well with  $80^\circ$  for  $[\text{Pt}(\text{bipy})\text{Cl}_2]$ .<sup>30</sup> The small bite of the chelate results in the opening of the angle  $\text{Cl}(2)\text{--Pt--C}(10)$   $93.7(2)^\circ$  and  $\text{Cl}(1)\text{--Pt--N}(1)$   $95.7(2)^\circ$ . The formation of the Pt–C bond has little influence on the Pt–Cl(2) distance *trans* to N, but the Pt–Cl(1) distance increases due to the *trans* influence of the carbon. The Pt–N(1) distance is comparable to that of  $[\text{Pt}(\text{bipy})\text{Cl}_2]$ .<sup>30</sup> The short Pt–C length, 1.963(7) Å, is similar to the Pt–C distance observed in a complex with such a bond *trans* to the chlorine atom (1.94 Å).<sup>31</sup>

Both the pyridyl and the cyclometallated ring are planar, with a dihedral angle of  $1.2^\circ$ . The dihedral angle between the plane of the complex and the pyridyl ring is  $3.6^\circ$ , while the same angle for the cyclometallated ring is  $4.7^\circ$ . Even allowing for the large estimated standard deviations (e.s.d.s) in this structure compared to those for  $[\text{Pt}(2,4\text{'-mbipy})\text{Cl}_3]$ , the C–C distance between the two pyridyl rings is shortened upon cyclometallation, indicating an increase in conjugation.

## Discussion

Blocking one of the N atoms of 2,2'-bipy and 2,4'-bipy by an alkyl group still leaves one pyridine free to co-ordinate to a metal ion, resulting in zwitterionic complexes of the type  $[\text{MLX}_3]$  ( $L = 2,2\text{'-mbipy}^+$ ,  $M = 3d$  metals,<sup>32</sup> Pt or Pd;<sup>5,32</sup>  $L = 2,4\text{'-mbipy}^+$ ,  $M = \text{Pt or Pd}$ ). Quaternised bipy would be a good model for a better understanding of the chemistry of monodentate bipy complexes. We found that the reaction of  $[2,2\text{'-mbipy}]^+$  with octahedral metal ions resulted in complexes of unidentified composition,<sup>33</sup> although rhodium(III) complexes of the nicotinium ion are known.<sup>34</sup> It is possible that the reaction is not clean due to steric hindrance imposed by the alkyl group on the N atom.<sup>35</sup> This problem would not arise for the quaternised 2,4'-bipy cation, and we are at present studying the ligating properties of this ligand with other platinum-group metal ions.

The chelating mode of co-ordination of the cationic bipy is not prevented and is in fact achieved by complexing *via* the pyridyl nitrogen atom and the  $\sigma$ -carbon atom of the quaternised ring. On cyclometallation the ligand is zwitterionic, whereas all other orthometallated ligands that have been reported are negatively charged. For mixed complexes containing halide ions the presence of a zwitterionic ligand results in a metal-to-halide ratio different to that of other cyclometallated complexes.

For the 2,2'-bipy system the chelating disposition of the two nitrogen atoms means that co-ordination *via* a pyridine nitrogen atom and  $\text{C}^{3'}$  atom is less likely, although examples of this mode of co-ordination are known.<sup>16</sup> The two nitrogens in 2,4'-bipy are unable to co-ordinate as a chelate, and this enables one to study and compare orthometallation of both the quaternised and non-quaternised ligand. Although a cyclopalladated complex of 2,4'-bipy can be prepared from  $\text{Pd}(\text{O}_2\text{CMe})_2$  in acetic acid, our attempts to prepare the platinum analogue were unsuccessful. Naturally initial co-ordination at the N' atom of 2,4'-bipy would preclude subsequent metallation. Blocking this atom with an alkyl group clearly directs co-ordination through the other nitrogen atom which is ideally situated for eventual ring closure *via*  $\text{C}^{3'}$ .

## Experimental

N.m.r. spectra were recorded on a WM250 Bruker Fourier-transform spectrometer, i.r. spectra ( $4\ 000\text{--}200\ \text{cm}^{-1}$ ) as Nujol

mulls on a Perkin-Elmer 983 spectrophotometer coupled with a Perkin-Elmer infrared data station. The C, H, N analyses were carried out by the Interuniversity Microanalytical Services, Ecole Nationale Supérieure de Chimie de Toulouse. The platinum and palladium salts were purchased from Johnson Matthey, 2,4'-bipyridine from Aldrich.

$[2,4\text{'-mbipy}]\text{I}$ .—This was prepared by a slight modification of the method of Homer.<sup>17</sup> A solution of 2,4'-bipy (6.55 mmol) and MeI (8.03 mmol) in absolute ethanol ( $10\ \text{cm}^3$ ) was heated under reflux for 6 h. The bright yellow needles that separated on cooling were isolated and recrystallised from warm ethanol-diethyl ether. M.p. =  $190\text{--}192^\circ\text{C}$  (lit.,<sup>17</sup>  $188\text{--}190^\circ\text{C}$ ). Yield = 70%.

$[2,4\text{'-mbipy}]\text{NO}_3$ .—For complex formation,  $[2,4\text{'-mbipy}]\text{NO}_3$  was prepared by metathesis of the iodide salt using  $\text{AgNO}_3$  in acetone. The precipitate of AgI was removed, and the solvent evaporated to give an oil which was then treated with the metal salt.

$[\text{Pd}(2,4\text{'-bipy})_2\text{Cl}_2]$  (1).—Palladium(II) chloride (1.26 mmol) was dissolved in hot MeCN ( $100\ \text{cm}^3$ ) by several extractions and the orange-red solution filtered. The ligand 2,4'-bipy (2.52 mmol) dissolved in hot MeCN was added to the hot stirred solution of  $[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$  whereupon a pale yellow precipitate separated. This solid was isolated, washed with MeCN, and air dried.

$[\text{Pt}(2,4\text{'-bipy})_2\text{Cl}_2]$  (3).—2,4'-Bipyridine (8.5 mmol) dissolved in acetone was added to a warm aqueous solution ( $25\ \text{cm}^3$ ) of  $\text{K}_2[\text{PtCl}_4]$  (4.27 mmol). The required compound precipitated almost instantaneously. After allowing the reaction mixture to digest for 1 h at room temperature, the pale yellow solid was filtered off, washed several times with water, and dried *in vacuo*.

$[\text{Pd}(2,4\text{'-bipy})_2(\text{O}_2\text{CMe})_2]\cdot 1.5\text{H}_2\text{O}$  (2).—Palladium(II) acetate (0.55 mmol) in acetone was added dropwise to a stirred solution of 2,4'-bipy (1.11 mmol) in acetone. Initially a clear pale yellow solution resulted, but as more of the metal complex was added the fawn-yellow complex (2) separated. The solid was collected, washed with acetone and dried *in vacuo*.

$\{[\text{PdL}^2(\mu\text{-O}_2\text{CMe})_2]\}_2\cdot 4\text{H}_2\text{O}$  (4).—The compound was prepared by Constable's method<sup>7</sup> using  $\text{Pd}(\text{O}_2\text{CMe})_2$  (0.333 g, 1.48 mmol) and 2,4'-bipy (0.284 g, 1.82 mmol).

$[\text{Pd}(2,4\text{'-mbipy})\text{Cl}_3]\cdot 2\text{H}_2\text{O}$  (6).—When a solution of  $[2,4\text{'-mbipy}]\text{NO}_3$  (0.44 mmol) and  $\text{K}_2[\text{PdCl}_4]$  (0.45 mmol) in water ( $15\ \text{cm}^3$ ) was allowed to stand at room temperature orange needles of complex (6) gradually formed. After digestion for 1 h the complex was collected by filtration, washed with water (in which the compound is slightly soluble) and acetone, and dried *in vacuo*.

$[\text{Pd}(2,4\text{'-mbipy})\text{Br}_3]$  (7).—A solution of  $\text{K}_2[\text{PdBr}_4]$  (0.95 mmol) in water ( $30\ \text{cm}^3$ ) was added dropwise to the solution of  $[2,4\text{'-mbipy}]\text{NO}_3$  (1.02 mmol) in acetone–water ( $30\ \text{cm}^3$ ). The solution appears deep red during the addition of the metal salt to the ligand, but if there was formation of a buff coloured precipitate during this addition acetone was added to redissolve this solid. Gradually, complex (7) separated as a brick-red solid. After digestion for 3 h at room temperature, the solid was collected, washed liberally with water and acetone, and dried *in vacuo*.

$[\text{Pt}(2,4\text{'-mbipy})\text{Cl}_3]\cdot 2\text{H}_2\text{O}$  (8).—A solution of  $[2,4\text{'-mbipy}]\text{NO}_3$  (0.83 mmol) and  $\text{K}_2[\text{PtCl}_4]$  (0.81 mmol) in water ( $40\ \text{cm}^3$ ) after 3 d at room temperature (or 2 h at  $50^\circ\text{C}$ ) furnished the

**Table 4.** Fractional atomic co-ordinates with e.s.d.s in parentheses for complex (8)

Atom	x	y	z
Pt	0.715 28(2)	0.133 39(2)	0.584 85(1)
Cl(1)	0.784 5(1)	0.022 1(2)	0.741 4(1)
Cl(2)	0.863 4(1)	0.045 3(2)	0.532 1(1)
Cl(3)	0.637 3(1)	0.246 0(2)	0.428 46(9)
N(1)	0.581 2(3)	0.206 0(4)	0.626 1(3)
C(1)	0.567 2(4)	0.342 8(5)	0.650 6(3)
C(2)	0.464 9(5)	0.392 2(6)	0.660 4(4)
C(3)	0.375 6(5)	0.296 9(7)	0.646 0(4)
C(4)	0.390 0(5)	0.156 3(6)	0.624 4(4)
C(5)	0.493 1(5)	0.115 3(6)	0.615 3(4)
C(6)	0.466 8(4)	0.441 9(5)	0.669 9(3)
C(7)	0.655 9(5)	0.573 8(6)	0.621 9(4)
C(8)	0.748 0(5)	0.663 4(6)	0.640 3(4)
N(2)	0.849 1(4)	0.626 2(4)	0.708 4(3)
C(9)	0.860 0(5)	0.502 9(5)	0.759 6(4)
C(10)	0.770 9(5)	0.408 7(5)	0.742 0(4)
C(11)	0.948 8(4)	0.720 2(6)	0.724 4(4)
Ow(1)	0.908 4(5)	-0.287 3(6)	0.456 5(5)
Ow(2)	1.115 9(5)	-0.428 9(6)	0.470 2(4)
H[1(Ow1)]	0.887(6)	-0.189(3)	0.465(6)
H[2(Ow1)]	0.989(2)	-0.291(7)	0.462(6)
H[1(Ow2)]	1.092(8)	-0.377(6)	0.522(4)
H[2(Ow2)]	1.154(6)	-0.516(5)	0.500(4)

**Table 5.** Fractional atomic co-ordinates with e.s.d.s in parentheses for complex (10)

Atom	x	y	z
Pt	0.288 69(4)	0.613 40(2)	0.666 72(2)
Cl(1)	0.301 5(3)	0.586 90(12)	0.530 43(11)
Cl(2)	0.167 1(3)	0.729 50(10)	0.641 59(10)
N(1)	0.404 2(8)	0.515 5(3)	0.701 4(3)
C(1)	0.414 8(9)	0.505 3(4)	0.780 7(4)
C(2)	0.483 5(12)	0.438 2(5)	0.808 9(6)
C(3)	0.556 9(10)	0.389 2(5)	0.758 6(5)
C(4)	0.537 6(12)	0.395 7(5)	0.677 9(6)
C(5)	0.461 5(11)	0.462 7(5)	0.652 6(5)
C(6)	0.340 9(10)	0.568 7(4)	0.825 2(4)
C(7)	0.339 7(11)	0.567 6(5)	0.904 8(5)
C(8)	0.263 9(10)	0.627 6(4)	0.942 0(5)
N(2)	0.200 5(9)	0.686 2(4)	0.899 0(3)
C(9)	0.201 6(10)	0.683 6(4)	0.821 9(4)
C(10)	0.276 9(9)	0.626 0(4)	0.780 6(4)
C(11)	0.108 9(11)	0.748 9(6)	0.937 1(4)

compound (8) as yellow-orange crystals which were isolated, washed with water and acetone, and dried *in vacuo*. Care should be taken that any heating is not too strong or too long to avoid formation of the cyclometallated complex.

[PtL<sup>3</sup>Cl<sub>2</sub>]-2H<sub>2</sub>O (9).—Complex (9) was prepared by heating an aqueous solution (30 cm<sup>3</sup>) of [2,4'-mbipy]NO<sub>3</sub> (0.72 mmol) and K<sub>2</sub>[PdCl<sub>4</sub>] (0.66 mmol) under reflux for 1.5 h. The pale yellow solid of [PtL<sup>3</sup>Cl<sub>2</sub>] was filtered off, washed with water and acetone and dried *in vacuo*. This compound can also be prepared by heating [Pd(2,4'-mbipy)Cl<sub>3</sub>] (0.15 mmol) in water (10 cm<sup>3</sup>) under reflux for 1 h.

[PtL<sup>3</sup>Cl<sub>2</sub>] (10).—The orange needles of complex (10) that separated from the reaction mixture when an aqueous solution (50 cm<sup>3</sup>) of [2,4'-mbipy]NO<sub>3</sub> (1.72 mmol) and K<sub>2</sub>[PtCl<sub>4</sub>] (1.48 mmol) was heated under reflux for 15 h were collected, washed with water, and dried *in vacuo*.

*X-Ray Crystal Structure Determination of [Pt(2,4'-mbipy)-*

Cl<sub>3</sub>]-2H<sub>2</sub>O (8).—*Crystal data.* C<sub>11</sub>H<sub>15</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>2</sub>Pt, *M* = 507.7, monoclinic, space group *P2<sub>1</sub>/c* (no. 14), *a* = 12.319(2), *b* = 9.359(1), *c* = 13.665(2) Å, β = 107.90(1)°, *U* = 1 499.2(6) Å<sup>3</sup> (by least-squares refinement of diffractometer angles for 25 automatically centred reflections in the range 13 < θ < 17°, λ = 0.710 73 Å), *D<sub>m</sub>* = 2.17 g cm<sup>-3</sup>, *Z* = 4, *D<sub>c</sub>* = 2.25 g cm<sup>-3</sup>. Yellow air-stable needles. Crystal dimensions (distance to faces from centre): 0.225 (010, 0 $\bar{1}$ 0) × 0.100 (100,  $\bar{1}$ 00) × 0.025 (001, 00 $\bar{1}$ ) mm, μ(Mo-K<sub>α</sub>) = 99.9 cm<sup>-1</sup>, *T* = 293 K.

*Data collection and processing.*<sup>36</sup> CAD4 diffractometer, ω—2θ scans with ω scan width = 0.80 + 0.35 tan θ, ω scan speed 1.1—8.2° min<sup>-1</sup>, graphite-monochromated Mo-K<sub>α</sub> radiation; 3 400 reflections measured (1.5 < θ < 27°, *h, k, ±l*), 3 258 unique [merging *R* = 0.015 after numerical absorption corrections<sup>37</sup> (maximum, minimum transmission factors = 0.90, 0.33)], giving 2 573 with *I* > 3σ(*I*). No significant variation of intensity standards.

*Structure analysis and refinement.* Heavy-atom method. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions (C—H 0.97 Å, *U* = 0.05 Å<sup>2</sup> for methyls, 0.04 Å<sup>2</sup> for others), but those of water molecules allowed to vary with *U* = 0.11 Å<sup>2</sup>, kept fixed. Sources of scattering factor data, including (*f'*, *f''*), are given in ref. 38. The weighting scheme *w* = [σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + 0.000 216 *F<sub>o</sub>*<sup>2</sup>]<sup>-1</sup>, with σ(*F<sub>o</sub>*) from counting statistics<sup>36</sup> gave satisfactory agreement analyses. An empirical isotropic extinction parameter was refined to the value 0.52 × 10<sup>-7</sup>. No shift/e.s.d. was greater than 0.01 for non-hydrogen parameters. Final *R* and *R'* values were 0.023 and 0.027. All calculations were performed on a VAX-11/730 DEC computer with SDP<sup>39</sup> and SHELX 76<sup>40</sup> programs. Atomic co-ordinates are listed in Table 4.

*X-Ray Crystal Structure Determination of [PtL<sup>3</sup>Cl<sub>2</sub>] (10).*—*Crystal data.* C<sub>11</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>Pt, *M* = 436.2, orthorhombic, space group *Pbca* (no. 61), *a* = 7.643(1), *b* = 17.726(2), *c* = 17.114(2) Å, *U* = 2 318.6(9) Å<sup>3</sup> (by least-squares refinement of diffractometer angles for 25 automatically centred reflections in the range 10 < θ < 13°, λ = 0.710 73 Å), *Z* = 8, *D<sub>c</sub>* = 2.50 g cm<sup>-3</sup>. Orange air-stable plates. Crystal dimensions (distance to faces from centre): 0.150 (100,  $\bar{1}$ 00) × 0.100 (001, 00 $\bar{1}$ ) × 0.025 (010, 0 $\bar{1}$ 0) mm, μ(Mo-K<sub>α</sub>) = 126.7 cm<sup>-1</sup>, *T* = 293 K.

*Data collection and processing.*<sup>36</sup> CAD4 diffractometer, ω—2θ scan mode with ω scan width = 1.00 + 0.35 tan θ, ω scan speed 1.0—5.5° min<sup>-1</sup>, graphite-monochromated Mo-K<sub>α</sub> radiation; 2 520 reflections measured (1.5 < θ < 27°, *h, k, ±l*), and corrected for numerical absorption<sup>37</sup> (maximum, minimum transmission factors = 0.88, 0.24), giving 1 124 with *I* > 3σ(*I*). No significant variation of intensity standards.

*Structure analysis and refinement.* Heavy-atom method. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions (C—H 0.97 Å, *U* = 0.07 Å<sup>2</sup>). The weighting scheme *w* = [σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + 0.001 *F<sub>o</sub>*<sup>2</sup>]<sup>-1</sup>, with σ(*F<sub>o</sub>*) from counting statistics<sup>36</sup> gave satisfactory agreement analyses. Maximum parameter shift/e.s.d. was equal to 0.05. Final *R* and *R'* values were 0.032 and 0.033. Sources of scattering data are given in ref. 38. Programs and computer used as for complex (8). Atomic co-ordinates are listed in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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