

## Five-coordinate complexes of palladium(II) and platinum(II) with $\alpha$ -diimine and 1,5-cyclooctadiene ligands

Francesca Di Bianca,<sup>a</sup> Giuliano Bandoli,<sup>b</sup> Alessandro Dolmella,<sup>b</sup> Simonetta Antonaroli<sup>c</sup> and Bruno Crociani<sup>\*c</sup>

<sup>a</sup> Dipartimento di Chimica Inorganica, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy

<sup>b</sup> Dipartimento di Scienze Farmaceutiche, Università di Padova, Via Marzolo No. 5, 35131 Padova, Italy

<sup>c</sup> Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Via della Ricerca Scientifica, 00133 Roma, Italy. E-mail: crociani@stc.uniroma2.it; Fax: +39 06 72594328

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The five-coordinate complexes [PtMe(cod)(N–N')]BF<sub>4</sub> [cod =  $\eta^2, \eta^2$ -cyclooctadiene, N–N' = (6-R<sup>2</sup>)C<sub>5</sub>H<sub>3</sub>N-2-CH=NR<sup>1</sup> (R<sup>1</sup> = C<sub>6</sub>H<sub>4</sub>OMe-4, R<sup>2</sup> = H (1), Me (2); R<sup>1</sup> = CMe<sub>3</sub>, R<sup>2</sup> = H (3), Me (4); R<sup>1</sup> = (*R*)-bornyl, R<sup>2</sup> = Me (5))] are readily obtained from the reaction of [PtClMe(cod)] with N–N' in the presence of NaBF<sub>4</sub>. The preparation of [PtMe(cod)(6)]BF<sub>4</sub> (6 = 4-MeOC<sub>6</sub>H<sub>4</sub>N=CHCHN=C<sub>6</sub>H<sub>4</sub>OMe-4), [PdMe(cod)(N–N')]BF<sub>4</sub> and [PtCl(cod)(N–N')]BF<sub>4</sub> (N–N' = 2, 4) requires chloride abstraction by AgBF<sub>4</sub> from [PtClMe(cod)], [PdClMe(cod)] and [PtCl<sub>2</sub>(cod)], respectively, followed by coordination of N–N'. The NMR spectral data suggest a trigonal-bipyramidal structure with chelating cod and N–N' ligands, where the  $\alpha$ -diimine and one C=C bond are on the equatorial plane and the second C=C bond in an axial position. The complexes [PtMe(cod)(1)]BF<sub>4</sub> and [PtCl(cod)(2)]BF<sub>4</sub> undergo dynamic processes in solution which bring about N–N' ligand site exchange for the former, and exchange of all the olefinic protons for the latter. The X-ray diffraction analysis of [PtMe(cod)(2)]BF<sub>4</sub> indicates that in the solid state, the complex assumes a distorted trigonal-bipyramidal geometry, similar to that proposed to exist in solution. For the two independent molecules in the asymmetric unit cell, the differences in the structural parameters between the equatorial Pt–(CH=CH) bond [Pt–C 2.08(1), 2.09(2) Å, C=C 1.43(2) Å (molecule I); Pt–C 2.13(2), 2.10(2) Å, C=C 1.42(2) Å (molecule II)] and the axial Pt–(CH=CH) bond [Pt–C 2.35(1), 2.34(1) Å, C=C 1.39(2) Å (molecule I); Pt–C 2.37(2), 2.34(1) Å, C=C 1.38(2) Å (molecule II)] are related to the high *trans* influence of the methyl ligand and to greater d– $\pi$  back-donation in the equatorial bond.

### Introduction

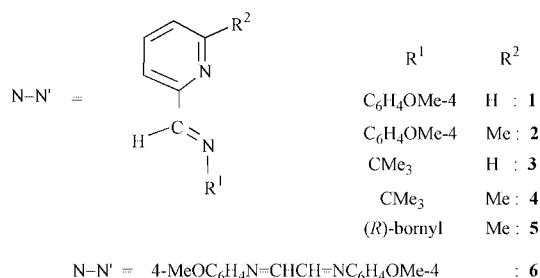
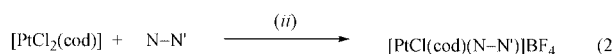
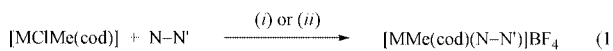
The ability of  $\alpha$ -diimine ligands, such as 1,2-bis(imino)ethanes, 2-(iminomethyl)pyridines, 2,2'-bipyridine and 1,10-phenanthroline, to give five-coordinate olefin complexes of palladium(II) and platinum(II) is well recognised and the subject has been reviewed.<sup>1</sup> Several neutral and cationic complexes of the type [MX<sub>2</sub>( $\eta^2$ -olefin)(N–N')], [MXR( $\eta^2$ -olefin)(N–N')] and [PtR(L)( $\eta^2$ -olefin)(N–N')] (M = Pd, Pt; X = halogen; R = alkyl or aryl group; L = monodentate ligand) have been prepared and characterised with a large variety of monoolefins and  $\alpha$ -diimines (N–N') in order to study the influence of the steric and electronic properties of these ligands in the stabilization of this unusual coordination mode.<sup>1,2</sup> In contrast, only a few five-coordinate derivatives with a chelating  $\eta^2, \eta^2$ -diolefin [MMe(cod)(N–N')] (M = Pd, Pt; cod = 1,5-cyclooctadiene) have been described, all containing rigid and sterically demanding 2,9-dimethyl- or 2,9-diaryl-1,10-phenanthrolines.<sup>3–5</sup> We wish to report here a convenient synthetic route to the latter type of complexes with the more flexible 2-(iminomethyl)pyridines as N–N' ligands, along with their structural characterisation in solution and in the solid state. This method can be also extended to the preparation of the analogous platinum(II) compounds with 1,2-bis(imino)ethanes and the chloro derivatives [PtCl(cod)(N–N')] (N–N' = rigid  $\alpha$ -diimine) have indeed been obtained from cod displacement in the reaction of

### Results and discussion

#### Synthesis and characterisation of the complexes

The five-coordinate complexes [MMe(cod)(N–N')]BF<sub>4</sub> (M = Pd, Pt) and [PtCl(cod)(N–N')]BF<sub>4</sub> are prepared according to reactions 1 and 2, respectively, of Scheme 1.

In both cases, the reaction involves replacement of a chloride anion in the starting compounds (already containing the  $\eta^2, \eta^2$ -bound cod ligand) by the  $\alpha$ -diimine, which then affords the five-coordinate products through N,N'-chelation. The synthetic routes, however, depend markedly on the initial substrate and the entering  $\alpha$ -diimine. Thus, the complexes [PtMe(cod)(N–N')]BF<sub>4</sub> (N–N' = 2-(iminomethyl)pyridines 1–5) are readily obtained from reaction 1 carried out in the presence of NaBF<sub>4</sub>, whereas for [PtMe(cod)(6)]BF<sub>4</sub>, it is necessary to generate a vacant coordination site in [PtClMe(cod)] through chloride abstraction by AgBF<sub>4</sub> owing to the lower ligating ability of the 1,2-bis(imino)ethane 6.<sup>6</sup> Chloride abstraction by AgBF<sub>4</sub> is also required for the preparation of [PdMe(cod)(N–N')]BF<sub>4</sub> and [PtCl(cod)(N–N')]BF<sub>4</sub> (N–N' = 2 and 4) because, in the presence of NaBF<sub>4</sub>, the complex [PdClMe(cod)] undergoes diolefin substitution by N–N', while no reaction takes place between [PtCl<sub>2</sub>(cod)] and N–N'. Square-planar derivatives of the type [PdClMe(N–N')] (N–N' = rigid  $\alpha$ -diimine) have indeed been obtained from cod displacement in the reaction of



**Scheme 1**  $\text{M} = \text{Pd}, \text{Pt}$ ; (i)  $+\text{NaBF}_4, -\text{NaCl}$ ; (ii)  $+\text{AgBF}_4, -\text{AgCl}$ ; (R)-bornyl = *endo*-(1R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl.

$[\text{PtClMe}(\text{cod})]$  with the appropriate  $\text{N}-\text{N}'$  ligand.<sup>7</sup> The versatile reactivity of  $[\text{PtClMe}(\text{cod})]$  is also worth noting. When this compound was allowed to react with 2-(iminomethyl)pyridines under an ethylene atmosphere, the neutral five-coordinate products  $[\text{PtClMe}(\eta^2\text{-C}_2\text{H}_4)(\text{N}-\text{N}')]^0$  were isolated.<sup>8</sup>

Reaction 1 with  $[\text{PtClMe}(\text{cod})]$  gives well-defined compounds  $[\text{PtMe}(\text{cod})(\text{N}-\text{N}')]\text{BF}_4$  with all the  $\alpha$ -diimines used in this study, independently of their steric requirements. However, the same reaction with  $[\text{PdClMe}(\text{cod})]$  yields the corresponding complexes  $[\text{PdMe}(\text{cod})(\text{N}-\text{N}')]\text{BF}_4$  only with the bulkier 2-(iminomethyl)pyridines **2** and **4**. With less sterically demanding  $\text{N}-\text{N}'$  ligands, a mixture of decomposition products is obtained, resulting from release of the initially bound diolefin. This finding is in line with previous observations on the relative stability toward olefin dissociation of the five-coordinate complexes  $[\text{MClMe}(\eta^2\text{-olefin})(\text{N}-\text{N}')]^+$ , which decreases considerably on going from  $\text{M} = \text{Pt}$  to  $\text{M} = \text{Pd}$ , and on the use of sterically crowded  $\alpha$ -diimines for the stabilization of five-coordinate methylpalladium(II) derivatives.<sup>3</sup> On the other hand, any attempt to isolate the complexes  $[\text{PdCl}(\text{cod})(\text{N}-\text{N}')]\text{BF}_4$  ( $\text{N}-\text{N}' = \mathbf{2}$  and **4**) by using  $[\text{PdCl}_2(\text{cod})]$  as the starting substrate in reaction 2 was unsuccessful. Evidently, the bulky  $\alpha$ -diimines **2** and **4** are unable to stabilise compounds of this type containing a Pd-Cl bond instead of a Pd-Me bond. Accordingly, for the complexes  $[\text{PdClX}(\eta^2\text{-olefin})(\text{N}-\text{N}')]^+$  ( $\text{X} = \text{Cl}, \text{Me}$ ; olefin =  $\text{CH}_2=\text{CH}_2$ ,  $\text{CH}_2=\text{CHMe}$ ;  $\text{N}-\text{N}' = 2,9$ -dimethyl-1,10-phenanthroline) the stability toward olefin dissociation was reported to decrease by *ca.* one order of magnitude (based on equilibrium constant values) on going from  $\text{X} = \text{Me}$  to  $\text{X} = \text{Cl}$ .<sup>3,9</sup>

The new complexes have been characterised by elemental analysis, IR spectroscopy, conductivity measurements (see Experimental), and by  $^1\text{H}$  and  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectroscopy. Some selected  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are listed in Tables 1 and 2, respectively.

All the compounds are conducting in  $\text{CH}_2\text{Cl}_2$  solution and contain a five-coordinate cationic species in which both the  $\text{N}-\text{N}'$  and the cod ligands are chelated to the central metal. The  $\text{N},\text{N}'$ -chelation of the  $\alpha$ -diimine is indicated by the downfield shifts (relative to the free ligands)<sup>†</sup> of the signals of the imino protons  $\text{N}=\text{CH}$  and  $\text{N}-\text{R}^1$ , of the pyridine protons 6-H or 6-Me, and by the  $^3J(\text{PtH})$  coupling constants (21–40 Hz) observed for the  $\text{N}=\text{CH}$  and 6-H resonances in the  $^1\text{H}$  NMR spectra.<sup>10,11</sup>

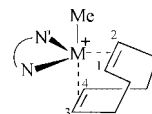
The  $\eta^2,\eta^2$ -bonding mode of the 1,5-cyclooctadiene is suggested by the upfield shifts of the olefinic proton and carbon

<sup>†</sup> For comparison, in the  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of ligand **3**, the  $\text{N}=\text{CH}$ , 6-H and  $\text{CMe}_3$  signals are observed at 8.28, 8.55 and 1.30 ppm, respectively, while in that of **4** the  $\text{N}=\text{CH}$ , 6-Me and  $\text{CMe}_3$  signals are detected at 8.30, 2.52 and 1.27 ppm respectively.

resonances relative to the corresponding resonances at 5.58 ( $^1\text{H}$ ) and 128.7 ppm ( $^{13}\text{C}$ ) of the free ligand in  $\text{CDCl}_3$ , and by their  $^2J(\text{PtH})$  and  $^1J(\text{PtC})$  coupling constants (see Tables 1 and 2).<sup>3</sup> The presence of M-Me bonds is clearly demonstrated by their characteristic high-field signals in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (flanked by the  $^{195}\text{Pt}$  satellites for  $\text{M} = \text{Pt}$ ), while the presence of a Pt-Cl bond in  $[\text{PtCl}(\text{cod})(\text{N}-\text{N}')]\text{BF}_4$  is inferred from the detection of a  $\nu(\text{PtCl})$  band at 314 ( $\text{N}-\text{N}' = \mathbf{2}$ ) and at 318  $\text{cm}^{-1}$  ( $\text{N}-\text{N}' = \mathbf{4}$ ) in the IR spectrum of the solid. The five-coordinate structure of the complexes is ultimately confirmed by the X-ray diffraction analysis of  $[\text{PtMe}(\text{cod})(\mathbf{2})]\text{BF}_4$  (*vide infra*).

### Stereochemistry in solution

As can be seen in Tables 1 and 2 for the complexes  $[\text{MMe}(\text{cod})(\text{N}-\text{N}')]\text{BF}_4$ , two olefinic protons are detected in the range 5.58–5.06 ppm [with  $^2J(\text{PtH})$  values of 29–25 Hz] and two in the range 4.92–3.28 ppm [with  $^2J(\text{PtH})$  values of 76–68 Hz]. A similar pattern is observed for the olefinic carbons, two of which resonate in the range 125.5–114.9 ppm [with  $^1J(\text{PtC})$  values of 36–27 Hz] and two in the range 86.2–57.5 ppm [with  $^1J(\text{PtC})$  values of 339–332 Hz]. These spectral features can be rationalised on the basis of the trigonal-bipyramidal structure reported in Fig. 1, where the  $\alpha$ -diimine and one of the cod C=C



**Fig. 1** Proposed structure for the cationic complexes  $[\text{MMe}(\text{cod})(\text{N}-\text{N}')]\text{BF}_4$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) in solution, with numbering scheme of the olefinic proton and carbon atoms.

bonds lie on the equatorial plane, while the methyl ligand and the second C=C bond are in the axial positions.

When  $\text{N}-\text{N}'$  is an unsymmetric 2-(iminomethyl)pyridine, the olefinic protons and carbons are non-equivalent and they appear as four (and sometimes three, for accidental degeneracy) distinct resonances. Moreover, a chiral centre is present on the metal, and therefore two enantiomers may exist in solution, which cannot be distinguished under the experimental conditions used for the NMR spectra. Consistently, two diastereoisomers in *ca.* 1 : 1 molar ratio are observed for  $[\text{PtMe}(\text{cod})(\mathbf{5})]\text{BF}_4$  where the 2-(iminomethyl)pyridine **5** has a chiral  $\text{N}-(R)$ -bornyl substituent. According to previous reports,<sup>3</sup> the two olefinic proton and carbon signals at lower field are assigned to the  $\text{HC}=\text{CH}$  unit in the axial position while those at higher field are assigned to the equatorial  $\text{HC}=\text{CH}$  unit, the much larger shielding of the latter nuclei being related to increased electron density caused by more extensive d- $\pi$  back-donation in the equatorial metal-olefin bond.<sup>1</sup> The above assignment is further confirmed by the NMR spectral changes upon replacement of the axial methyl group by a ligand of much lower electron-donating properties, such as the chloride anion in the complexes  $[\text{PdX}(\text{cod})(\mathbf{4})]\text{BF}_4$  ( $\text{X} = \text{Cl}, \text{Me}$ ). These changes mainly consist of a marked downfield shift for both the proton (*ca.* 1.5 ppm) and carbon (*ca.* 20 ppm) resonances of the equatorial  $\text{CH}=\text{CH}$  moiety, as a consequence of the decreased electron density on the metal (and hence of the lower d- $\pi$  back-donation), and of a marked increase in the  $^2J(\text{PtH})$  (*ca.* 25 Hz) and  $^1J(\text{PtC})$  (*ca.* 109 Hz) coupling constants for the axial  $\text{CH}=\text{CH}$  unit, as a consequence of the lower *trans* influence of the chloride ligand.

The structure of the complex  $[\text{PtMe}(\text{cod})(\mathbf{6})]\text{BF}_4$ , containing the symmetric 1,2-bis(imino)ethane **6**, has a plane of symmetry which bisects both the cod and the  $\alpha$ -diimine ligands. This results in the two axial olefinic protons being equivalent, detected as a single resonance at 5.17 ppm, and a similar situation for the two equatorial olefinic protons, detected as a single resonance at 3.47 ppm. A quite similar pattern is observed for

**Table 1** Selected  $^1\text{H}$  NMR data<sup>a</sup>/(ppm)

Complex	N–N' Protons		Olefinic protons		
	N=CH	Other signals	Axial (H <sup>3</sup> , H <sup>4</sup> )	Equatorial (H <sup>1</sup> , H <sup>2</sup> )	M–Me
[PtMe(cod)(1)]BF <sub>4</sub>	9.34 s (36.4)	9.10 m [6-H] (36.4); <sup>b</sup> 3.93 s [OMe]	5.15 m (29.0), 5.11 m, <sup>c</sup> 5.07 m <sup>c</sup>	3.44 m (73.9), 3.40 m <sup>c</sup>	0.51 s (63.6)
[PtMe(cod)(2)]BF <sub>4</sub>	9.28 s (34.1)	3.94 s [OMe]; 3.12 s [6-Me] <sup>b</sup>	5.20 m, 5.12 m, (26.0)	3.56 m, 3.52 m, (68.5)	0.58 s (62.5)
[PdMe(cod)(2)]BF <sub>4</sub> <sup>d</sup>	8.94 s	3.90 s [OMe]; 3.10 s [6-Me] <sup>b</sup>	5.37 m, 5.25 m	4.60 m	0.99 s
[PtMe(cod)(3)]BF <sub>4</sub>	9.18 s (36.5)	9.09 m [6-H] (21.0); <sup>b</sup> 1.67 s [CMe <sub>3</sub> ]	5.42 m, 5.07 m, (28.0)	3.34 m (75.0)	0.38 s (65.8)
[PtMe(cod)(4)]BF <sub>4</sub>	9.18 s (37.0)	3.10 s [6-Me]; <sup>b</sup> 1.67 s [CMe <sub>3</sub> ]	5.38 m, 5.06 m (28.5)	3.32 m (76.0)	0.48 s (63.6)
[PdMe(cod)(4)]BF <sub>4</sub> <sup>d</sup>	8.80 s	3.09 s [6-Me]; <sup>b</sup> 1.64 s [CMe <sub>3</sub> ]	5.58 m, 5.19 m	4.52 m, 4.45 m	0.93 s
[PtMe(cod)(5)]BF <sub>4</sub> <sup>d,e</sup>	9.30 s, (41.6)	5.05 m, 4.53 m [NCH];	5.47 m, 5.41 m, 5.35 m, 5.12 m	3.36 m, 3.28 m (71.0)	0.53 s, (63.4)
[PtMe(cod)(6)]BF <sub>4</sub> <sup>d</sup>	9.19 s (40.4)	3.08 s, 3.04 s [6-Me] <sup>b</sup>	5.17 m (25.5)	3.47 m (71.8)	0.35 s (63.4)
[PtMe(cod)(6)]BF <sub>4</sub> <sup>d</sup>	9.10 s (36.0)	3.91 s [OMe]	5.17 m (25.5)	3.47 m (71.8)	0.69 s (61.5)
[PtCl(cod)(2)]BF <sub>4</sub>	9.07 s (40.0)	3.96 s [OMe]; 3.34 s [6-Me] <sup>b</sup>	5.29 s (br); <sup>c</sup> 5.21 s (br) <sup>c</sup>	5.14 s (br) (59.0)	4.92 s (br); <sup>c</sup> 4.70 s (br) <sup>c</sup>
[PtCl(cod)(4)]BF <sub>4</sub>	9.10 s (42.0)	3.30 s [6-Me]; <sup>b</sup> 1.88 s [CMe <sub>3</sub> ]	5.52 m (50.9), 5.18 m (55.8)	4.87 m (71.6)	

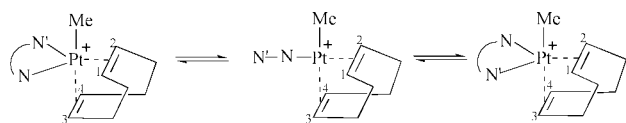
<sup>a</sup> In CD<sub>2</sub>Cl<sub>2</sub> at 25 °C, unless otherwise stated; satisfactory integration values are obtained; the coupling constants (Hz) with <sup>195</sup>Pt are given in round brackets, when measurable; s, singlet; m, multiplet; see Fig. 1 for the numbering of the olefinic protons. <sup>b</sup> Signal of the R<sup>2</sup> substituent on the pyridine ring. <sup>c</sup> At –60 °C. <sup>d</sup> In CDCl<sub>3</sub>. <sup>e</sup> Two diastereoisomers (see text).

**Table 2** Selected  $^{13}\text{C}$ -{ $^1\text{H}$ } NMR data<sup>a</sup>/(ppm)

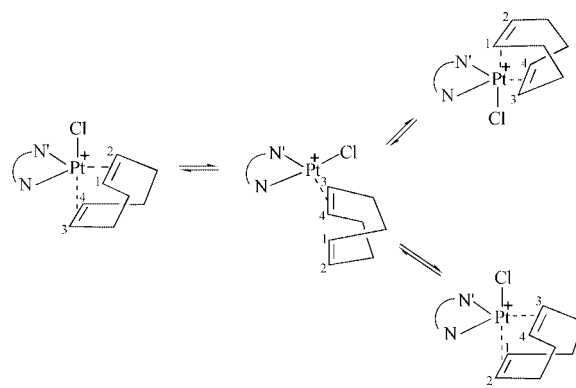
Complex	N–N' Carbons		Olefinic carbons		
	N=CH	Other signals	Axial (C <sup>3</sup> , C <sup>4</sup> )	Equatorial (C <sup>1</sup> , C <sup>2</sup> )	M–CH <sub>3</sub>
[PtMe(cod)(2)]BF <sub>4</sub>	160.9	161.3 [6-C]; <sup>b</sup> 152.8 [2-C]; <sup>b</sup> 56.1 [OCH <sub>3</sub> ]	118.6 (27.0), 117.2 (36.3)	59.4 (332.0), 58.5 (332.0)	–0.5 (538.5)
[PdMe(cod)(2)]BF <sub>4</sub>	157.3	158.4 [6-C]; <sup>b</sup> 149.2 [2-C]; <sup>b</sup> 54.6 [OCH <sub>3</sub> ]	125.0, 124.6	86.2, 85.3	11.4
[PtMe(cod)(3)]BF <sub>4</sub>	162.3	150.0 [6-C]; <sup>b</sup> 152.4 [2-C]; <sup>b</sup> 30.6 [C(CH <sub>3</sub> ) <sub>3</sub> ]	118.9 (27.2), 114.9 (33.9)	58.4 (337.1), 57.6 (331.8)	–0.7 (586.7)
[PtMe(cod)(4)]BF <sub>4</sub>	165.3	159.2 [6-C]; <sup>b</sup> 152.7 [2-C]; <sup>b</sup> 31.6 [C(CH <sub>3</sub> ) <sub>3</sub> ]	118.4 (31.1), 115.9 (32.2)	57.9 (339.1), 57.5 (339.4)	–1.6 (584.0)
[PdMe(cod)(4)]BF <sub>4</sub>	161.2	158.2 [6-C]; <sup>b</sup> 149.4 [2-C]; <sup>b</sup> 30.4 [C(CH <sub>3</sub> ) <sub>3</sub> ]	125.5, 124.0	85.9, 85.8	11.1
[PtCl(cod)(4)]BF <sub>4</sub>	165.0	160.7 [6-C]; <sup>b</sup> 151.7 [2-C]; <sup>b</sup> 32.3 [C(CH <sub>3</sub> ) <sub>3</sub> ]	107.0 (137.2), 103.8 (143.5)	77.6 (245.1), 77.2 (242.7)	

<sup>a</sup> In CDCl<sub>3</sub> at 25 °C; the couplig constants (Hz) with <sup>195</sup>Pt are given in round brackets, when measurable; see Fig. 1 for the numbering of the olefinic carbons. <sup>b</sup> Carbons of the pyridine ring at positions indicated by the number in parentheses.

the olefinic protons of the complex [PtMe(cod)(1)]<sup>+</sup> at 25 °C (see Table 1). At –60 °C, however, two rather close multiplets appear for the axial protons, while the equatorial ones remain unchanged. Some splitting of the cod CH<sub>2</sub> signals (in the range 3.0–1.8 ppm) also occurs at the lower temperature. These changes indicate that the complex undergoes a dynamic process which brings about a site exchange of the unsymmetric ligand **1**. This may occur through pseudorotation<sup>12</sup> or Pt–N bond dissociation–association *via* a four-coordinate transient with a monodentate N–N' ligand, as shown in Scheme 2.

**Scheme 2** Proposed mechanism for the N–N' ligand site exchange in the complex [PtMe(cod)1]<sup>+</sup>.

Dissociation of a Pt–N bond was proposed as the initial step in the mechanism of olefin or *a*-diimine ligand exchange and substitution for the five-coordinate complexes [PtCl<sub>2</sub>(η<sup>2</sup>-olefin)(*a*-diimine)].<sup>13</sup> The solution behaviour of the complex [PtCl(cod)(2)]<sup>+</sup> is particularly interesting in the sense that at 25 °C, a single resonance is observed for the four olefinic protons, whereas at –60 °C, four distinct signals are present. When the temperature is progressively increased, the signals broaden and eventually coalesce at –31 °C. This kind of fluxionality can be explained by the mechanism reported in Scheme 3, whereby the dissociation–association of a Pt–olefin bond involves the exchange of all the olefinic protons *via* a four-coordinate transient with an η<sup>2</sup>-bound cod ligand.

**Scheme 3** Proposed mechanism for the fluxional behaviour of the complex [PtCl(cod)2]<sup>+</sup>.

Other possible dynamic processes, such as the Pt–N bond dissociation–association shown in Scheme 2 or Pt–Cl bond association–dissociation,<sup>13</sup> cannot be taken into account since they would give rise to pair exchanges of the olefinic protons 1 ⇌ 2 and 3 ⇌ 4 or 1 ⇌ 4 and 2 ⇌ 3, respectively. In the mechanism of Scheme 3, we propose preferential cleavage of the equatorial Pt–(CH=CH) bond, in line with previous findings on the stability toward dissociation of the equatorial olefin in [PtClX(η<sup>2</sup>-olefin)(N–N')], which was found to increase on going from X = Cl to X = Me<sup>9,11</sup> (stabilization of the five-coordinate structure) and on increasing the steric requirements of the N–N' ligand<sup>8,11</sup> (destabilization of the four-coordinate species resulting from olefin dissociation). As a matter of fact, the dynamic process observed for [PtCl(cod)(2)]<sup>+</sup> is slow on the NMR time scale, if it occurs, for [PtMe(cod)(2)]<sup>+</sup> (*i.e.* when

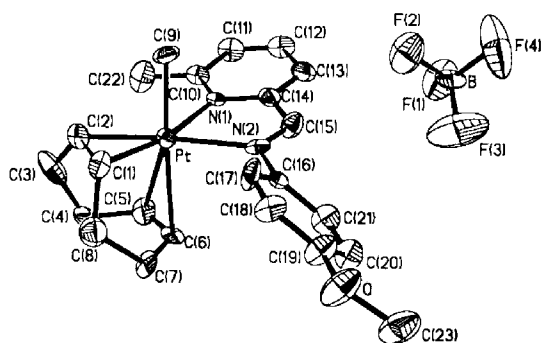
**Table 3** Selected bond distances (Å) and angles (°) of [PtMe(cod)(2)]<sup>+</sup>

	Molecule I	Molecule II		Molecule I	Molecule II
Pt–C(1)	2.08(1)	2.13(2)	C(1)–Pt–C(2)	40.3(5)	39.3(6)
Pt–C(2)	2.09(1)	2.10(2)	C(5)–Pt–C(6)	34.6(4)	34.1(5)
Pt–C(5)	2.35(1)	2.37(2)	N(1)–Pt–N(2)	73.2(4)	74.7(4)
Pt–C(6)	2.34(1)	2.34(1)	C(9)–Pt–C(5)	160.8(6)	163.3(7)
Pt–N(1)	2.28(1)	2.26(1)	C(9)–Pt–C(6)	163.1(5)	161.2(6)
Pt–N(2)	2.26(1)	2.28(1)	C(9)–Pt–N(1)	84.9(5)	88.2(5)
Pt–C(9)	2.08(1)	2.11(2)	C(9)–Pt–N(2)	88.1(5)	88.1(5)
C(1)–C(2)	1.43(2)	1.42(2)	C(9)–Pt–C(1)	91.1(6)	90.7(6)
C(5)–C(6)	1.39(2)	1.38(2)	C(9)–Pt–C(2)	87.9(6)	89.5(6)

the chloride ligand is replaced by a methyl group), and for [PtCl(cod)(4)]<sup>+</sup> (*i.e.* when the imino substituent C<sub>6</sub>H<sub>4</sub>OMe-4 is replaced by the bulkier CMe<sub>3</sub> group). On the other hand, the occurrence of slow dissociation equilibria of a Pt–N and/or a Pt–olefin bond for the complexes [PtMe(cod)(N–N')]<sup>+</sup> is suggested by the slow diolefin displacement by carbon monoxide to yield the four-coordinate derivatives [PtMe(CO)(N–N')]<sup>+</sup> (see Experimental).

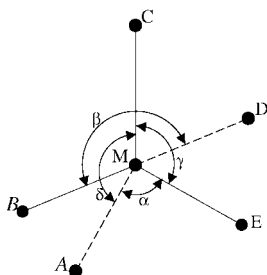
### Crystal structure of [PtMe(cod)(2)]BF<sub>4</sub>

The solid state structure of this compound was determined by X-ray diffraction analysis. The unit cell comprises two independent molecules (I and II) of the cationic complex, which are superimposable, the r.m.s. being only 0.06 Å when the fitting is performed using the Pt, N(1), N(2) and C(1)–C(15) atoms. The molecules show no anomalies in their structural data, summarised in Table 3, and the major difference resides in the relative orientation of the phenyl group at N(2) (for example, the C(15)N(2)C(16)C(17) torsion angle is 140.0 and 149.9° in I and II, respectively). An ORTEP<sup>14</sup> view of molecule I is presented in Fig. 2.



**Fig. 2** ORTEP drawing of molecule I of [PtMe(cod)(2)]BF<sub>4</sub> with atom numbering scheme. For clarity, molecule II and hydrogen atoms are omitted.

If both the CH=CH units of the diolefin are considered as monodentate ligands, the coordination geometry around the Pt atom can be assigned from the value of the index  $\tau = (\beta - \alpha) / 60$ <sup>15</sup> or, better, the modified index  $\chi = (\beta + \gamma + \delta - 2\alpha) / 180$ <sup>16</sup> (Chart 1).



**Chart 1** A, B = midpoints of the cod C=C bonds; C, D, E = three donor atoms.

It is easy to demonstrate that the  $\tau$  and  $\chi$  values are zero for an ideal square pyramid and that they become unity for an ideal trigonal bipyramid. The  $\tau$  and  $\chi$  values of [PtMe(cod)(2)]<sup>+</sup> are listed in Table 4, along with the corresponding values for five-coordinate complexes of d<sup>8</sup> metal ions containing the  $\eta^2, \eta^2$ -bound cyclooctadiene ligand.

As can be seen, the coordination environment is generally intermediate between the square-pyramidal and the trigonal-bipyramidal geometries. Another common feature is the presence of longer M–B and shorter M–A distances [*i.e.*, the axial and the equatorial M–(CH=CH) bonds in a trigonal-bipyramidal structure], the largest difference (0.26–0.30 Å) being observed for the palladium(II) and platinum(II) derivatives. For [PtMe(cod)(2)]<sup>+</sup>, as well as for [PdMe(cod)(phen)]<sup>+</sup>, however, the  $\tau$  and  $\chi$  values of < 1 are mostly due to the small bite angle N(1)–M–N(2) (angle  $\gamma$  in Chart 1): 73.2 and 74.7° for molecules I and II, respectively, and 74.7° for the palladium(II) complex.<sup>5</sup> This observation and the bond angles C(9)–Pt–B (174.8 and 175.0° in I and II, respectively) and A–Pt–B (85.2 and 85.1° in I and II, respectively), together with the angles C(9)–Pt–N(1), C(9)–Pt–N(2), C(9)–Pt–C(1) and C(9)–Pt–C(2), which lie in the range 84.9–91.1°, suggest that the coordination geometry in [PtMe(cod)(2)]<sup>+</sup> is better described as a distorted trigonal-bipyramid, with the methyl C(9) and the midpoint B of the C(5)=C(6) bond in axial positions. The  $\alpha$ -diimine nitrogen atoms N(1), N(2) and the olefinic carbons C(1), C(2) are on the equatorial plane (with a maximum deviation of 0.02 Å), while the Pt atom is 0.06 Å out of this plane, being shifted toward the C(5)=C(6) bond. The equatorial plane makes dihedral angles of 40.9 and 26.7° in I and II, respectively, with the phenyl ring at N(2). Thus, the structural data show that the complex [PtMe(cod)(2)]<sup>+</sup> has a solid state coordination geometry similar to that proposed in solution. The CH=CH units of the cod molecule are almost symmetrically coordinated to the platinum atom. The much longer Pt–C axial bonds are essentially due to the strong *trans* influence of the methyl ligand, while the shorter Pt–C equatorial bonds and the slight elongation, at the level of twice the standard deviation, of the equatorial C=C bond are related to greater d– $\pi$  back-donation from the central metal. These findings are consistent with the larger upfield shifts of the <sup>1</sup>H and <sup>13</sup>C signals and with the greater <sup>2</sup>J(PtH) and <sup>1</sup>J(PtC) values for the equatorial CH=CH unit. Similar structural and spectral features have been reported for the five-coordinate *tbp* complexes [PdMe(cod)(phen)]<sup>+</sup>,<sup>5</sup> [RhCl(nbd)(N–N')]<sup>22</sup> and [Rh(nbd)(PPh<sub>3</sub>)(N–N')]<sup>+</sup><sup>23</sup> (nbd =  $\eta^2, \eta^2$ -norbornadiene; N–N' =  $\alpha$ -diimine). To the best of our knowledge, the Pt–C(equatorial) and Pt–C(axial) bond lengths in [PtMe(cod)(2)]<sup>+</sup> are the shortest and the longest values, respectively, so far observed for 1,5-cyclooctadiene-platinum complexes. In square-planar complexes of the type [PtX<sub>2</sub>(cod)] (X = Cl, alkyl or aryl group)<sup>24–26</sup> and [PtClR(cod)] (R = alkyl group),<sup>25</sup> the Pt–C(olefin) bonds *trans* to chloride are in the range 2.15–2.18 Å, and those *trans* to an alkyl or aryl group are in the range 2.22–2.30 Å. In [PtMe(cod)(2)]<sup>+</sup>, the Pt–N bonds with the pyridine nitrogen N(1) and the imine nitrogen N(2) have comparable lengths [2.27(1) Å, average value], in contrast with the slightly different values of 2.239(5) (pyridine nitrogen) and 2.188(5) Å

**Table 4** Some metrical parameters in five-coordinate complexes of d<sup>8</sup> metal ions containing the η<sup>2</sup>,η<sup>2</sup>-bound cod ligand

Complex <sup>a</sup>	M–A <sup>b</sup> /Å	M–B <sup>b</sup> /Å	τ <sup>c</sup>	χ <sup>d</sup>	Ref.
[Rh(cod)(tacn)] <sup>+</sup>	1.95(1)	2.05(1)	0.56	0.56	17
[Rh(cod)(bpma)] <sup>+</sup>	1.95(1)	2.02(1)	0.38	0.44	17
[Rh(cod)(bpba)] <sup>+</sup> <sup>e</sup>	1.97(1)	2.05(1)	0.33	0.38	17
	1.97(1)	2.04(1)	0.27	0.32	
[Rh(cod)(bpbza)] <sup>+</sup> <sup>e</sup>	1.97(2)	2.05(2)	0.28	0.31	17
	1.98(2)	2.03(2)	0.29	0.32	
[Rh(cod)(tpzm)] <sup>+</sup>	1.95(1)	2.02(1)	0.62	0.64	18
[IrMe(cod)(dppp)]	2.03(1)	2.13(1)	0.52	0.66	19
[IrMe(cod)(dppe)]	2.01(1)	2.11(1)	0.55	0.65	20
[IrMe(cod)(PMe <sub>2</sub> Ph) <sub>2</sub> ]	2.08(1)	2.12(1)	0.64	0.75	21
[PdMe(cod)(phen)] <sup>+</sup>	2.01(1)	2.31(1)	0.50	0.57	5
[PtMe(cod)(2)] <sup>+</sup> <sup>e</sup>	1.95(1)	2.24(1)	0.48	0.54	Present
	1.99(2)	2.25(2)	0.47	0.53	work

<sup>a</sup> bpba = *N-n*-butyl-*N,N*-bis[(6-methyl-2-pyridyl)methyl]amine; bpbza = *N*-benzyl-*N,N*-bis[(6-methyl-2-pyridyl)methyl]amine; bpma = *N,N*-bis(2-pyridylmethyl)amine; dppp = 1,3-bis(diphenylphosphino)propane; phen = 2,9-bis(4-*tert*-butylphenyl)-1,10-phenanthroline; tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane; tpzm = tris(pyrazol-1-yl)methane. <sup>b</sup> A and B are the midpoints of the cod C(1)=C(2) and C(5)=C(6) bonds, respectively. <sup>c</sup> τ = (β – α)/60; for the meaning of α and β, see Chart 1. <sup>d</sup> χ = (β + γ + δ – 2α)/180; for the meaning of γ and δ, see Chart 1. <sup>e</sup> Two independent molecules in the asymmetric unit.

(imine nitrogen) reported for the structurally related five-coordinate derivative [PtClMe(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)(N–N')] [N–N' = (6-Me)C<sub>5</sub>H<sub>3</sub>N-2-CH=N-(*S*)-CHMePh] where the N–N' and the ethylene ligands are on the equatorial plane.<sup>8</sup> A comparison with the structural data of the latter compound [Pt–C(olefin) 2.053(6), C=C 1.415(11) and Pt–Me 2.055(6) Å] shows that the corresponding bonds in [PtMe(cod)(2)]<sup>+</sup> (also including the Pt–N bonds) are slightly but significantly longer, with the exception of the equatorial C=C bond length, which is comparable.

## Experimental

### General

The <sup>1</sup>H and <sup>13</sup>C-{<sup>1</sup>H} NMR spectra were recorded on a Bruker AM 400 spectrometer operating at 400.13 and 100.61 MHz, respectively. The chemical shifts were referenced to internal solvent and reported in ppm downfield from SiMe<sub>4</sub>. The IR spectra of solid samples were recorded in the range 4000–200 cm<sup>-1</sup> on a Perkin-Elmer 983G instrument using Nujol mulls and CsI windows. The electric conductivity was measured with a CDM83 conductivity meter. All reactions were performed under an atmosphere of dry nitrogen, unless otherwise stated.

### Materials

The solvents (acetone, dichloromethane and diethyl ether) were dried and freshly distilled under nitrogen prior to use.<sup>27</sup> The *α*-diimines N–N'<sup>28</sup> and the complexes [PdClMe(cod)],<sup>29</sup> [PtClMe(cod)],<sup>30</sup> and [PtCl<sub>2</sub>(cod)],<sup>31</sup> were prepared according to literature procedures. All other chemicals were commercial grade and were purified by standard methods,<sup>27</sup> when required. The elemental analysis and selected IR data of the complexes [MX(cod)(N–N')]BF<sub>4</sub> (M = Pd, Pt; X = Cl, Me) are listed in Table 5.

For these ionic compounds, the molar conductivity values were found to lie in the range 19.6–44.8 S cm<sup>2</sup> mol<sup>-1</sup> for 1 × 10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub> solutions at 25 °C.

### Preparations

**(6-Me)C<sub>5</sub>H<sub>3</sub>N-2-CH=N-(*R*)-bornyl (5).** The 6-methyl-2-pyridinecarboxaldehyde (0.727 g, 6 mmol) and (*R*)-bornylamine (0.920 g, 6 mmol) were dissolved in 80 cm<sup>3</sup> of a CH<sub>2</sub>Cl<sub>2</sub>–MeOH solvent mixture (3 : 1 v/v) at room temperature. The progress of the condensation was monitored by TLC. After 3 h, the solvents were removed under reduced pressure at 20 °C. The pale-yellow solid product (1.520 g, 98.8% yield, based on the theoretical amount) was used and analysed without further purification (Found: C, 79.7; H, 9.5; N, 10.8%. C<sub>17</sub>H<sub>24</sub>N<sub>2</sub> requires C, 79.64; H, 9.44; N, 10.93%; ν<sub>max</sub>/cm<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub>)

(C=N) 1638 ms; δ<sub>H</sub> (CDCl<sub>3</sub>) 8.32 (1H, s, N=CH), pyridine protons: 7.93 (1H, d), 7.62 (1H, t), 7.15 (1H, d), (*R*)-bornyl protons: 3.52 (1H, m, NCH), 2.15–2.10 (2H, m), 1.85–1.65 (2H, m), 1.45–1.20 (3H, m), 0.98 (3H, s, Me), 0.93 (3H, s, Me), 0.72 (3H, s, Me).

**[PtMe(cod)(N–N')]BF<sub>4</sub> (N–N' = 1–5).** The ligand N–N' (1 mmol) and NaBF<sub>4</sub> (0.220 g, 2 mmol) dissolved in acetone (30 cm<sup>3</sup>) were added to a solution of [PtClMe(cod)] (0.354 g, 1 mmol) in 30 cm<sup>3</sup> of acetone. Precipitation of NaCl readily occurred. After stirring for 1 h, the solvent was evaporated to dryness at reduced pressure and the solid residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>). Filtration on Celite gave a clear solution which was concentrated then diluted with Et<sub>2</sub>O to precipitate the yellow products (yields in the range 75.1–87.6%). The complexes were recrystallised from a CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O solvent mixture.

**[PtMe(cod)(6)]BF<sub>4</sub>, [PdMe(cod)(N–N')]BF<sub>4</sub> and [PtCl(cod)(N–N')]BF<sub>4</sub> (N–N' = 2, 4).** Addition of AgBF<sub>4</sub> (0.098 g, 0.5 mmol) to an acetone solution of the starting compound [PtClMe(cod)], [PdClMe(cod)] and [PtCl<sub>2</sub>(cod)], respectively, (0.5 mmol in 20 cm<sup>3</sup> of solvent) caused the immediate precipitation of AgCl. After 10 min stirring, the appropriate ligand N–N' was added, and the resulting mixture was worked up as described above for [PtMe(cod)(N–N')]BF<sub>4</sub> to yield the yellow to red complexes (68.3–96.0%).

**Reaction of [PtMe(cod)(N–N')]BF<sub>4</sub> with carbon monoxide.** When dichloromethane solutions of the five-coordinate complexes were saturated with CO at 1 atm pressure, slow displacement of the cod ligand took place to give the square-planar derivatives [PtMe(CO)(N–N')]BF<sub>4</sub>. The progress of the reaction was monitored by IR spectroscopy, which showed the progressive increase of a ν(CO) band of the coordinated carbon monoxide at 2101–2109 cm<sup>-1</sup>, and by <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) spectroscopy, which showed the formation of increasing amounts of free 1,5-cyclooctadiene. In a typical experiment, carbon monoxide was allowed to react with [PtMe(cod)(1)]BF<sub>4</sub> (0.123 g, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) at room temperature. The IR spectra at different times showed the presence of a ν(CO) band of increasing intensity at 2109 cm<sup>-1</sup>. After 24 h the solution was concentrated at reduced pressure, and diluted with Et<sub>2</sub>O to give the product [PtMe(CO)(1)]BF<sub>4</sub> as a yellow microcrystalline solid (0.085 g, 79.1%); ν<sub>max</sub>/cm<sup>-1</sup> (Nujol) (CO) 2107 s, (C=N) 1600 m, (BF) 1075 s (br); δ<sub>H</sub> (CDCl<sub>3</sub>) 9.61 (1H, s, N=CH, <sup>3</sup>J(PtH) 38.4 Hz), 8.75 (1H, m, pyridine 6-H, <sup>3</sup>J(PtH) 34.5 Hz), 3.87 (3H, s, OMe), 1.37 (3H, s, PtMe, <sup>2</sup>J(PtH) 67.6 Hz); A<sub>M</sub> 17.1 S cm<sup>2</sup> mol<sup>-1</sup> for a 1 × 10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub> solution at 25 °C.

**Table 5** Analytical<sup>a</sup> and selected IR data

Complex	Analysis (%)			$\nu(\text{C}=\text{N})^b/\text{cm}^{-1}$	$\nu(\text{BF})^b/\text{cm}^{-1}$
	C	H	N		
[PtMe(cod)(1)]BF <sub>4</sub>	42.4 (42.80)	4.3 (4.41)	4.4 (4.54)	1624 ms	1052 vs(br)
[PtMe(cod)(2)]BF <sub>4</sub>	43.5 (43.75)	4.6 (4.63)	4.4 (4.44)	1624 m	1064 vs
[PdMe(cod)(2)]BF <sub>4</sub>	50.9 (50.90)	5.5 (5.39)	5.1 (5.16)	1622 ms	1056 vs(br)
[PtMe(cod)(3)]BF <sub>4</sub>	40.4 (40.22)	5.3 (5.15)	5.0 (4.98)	1627 mw	1067 vs(br)
[PtMe(cod)(4)]BF <sub>4</sub>	41.5 (41.32)	5.4 (5.37)	4.9 (4.82)	1632 m	1064 vs(br)
[PdMe(cod)(4)]BF <sub>4</sub>	48.8 (48.75)	6.5 (6.34)	5.6 (5.69)	1629 m	1056 vs
[PtMe(cod)(5)]BF <sub>4</sub>	47.3 (47.21)	5.8 (5.94)	4.2 (4.24)	1639 mw	1083 vs(br)
[PtMe(cod)(6)]BF <sub>4</sub>	44.7 (44.59)	4.6 (4.64)	4.1 (4.16)	1622 w	1060 vs(br)
[PtCl(cod)(2)]BF <sub>4</sub>	40.6 (40.54)	4.1 (4.02)	4.3 (4.30)	1628 ms	1054 vs(br)
[PtCl(cod)(4)]BF <sub>4</sub>	37.9 (37.92)	4.8 (4.70)	4.6 (4.66)	1629 m	1048 vs(br)

<sup>a</sup> Required values are given in parentheses. <sup>b</sup> In Nujol mulls.

### Crystal structure determination of complex [PtMe(cod)(2)]BF<sub>4</sub>

Single crystals of [PtMe(cod)(2)]BF<sub>4</sub> were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex.

**Crystal data.** C<sub>23</sub>H<sub>29</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>pt</sub>,  $M = 631.38$ , monoclinic,  $a = 30.387(9)$ ,  $b = 7.940(3)$ , and  $c = 20.650(8)$  Å,  $\beta = 105.61(3)^\circ$ ,  $U = 4798(3)$  Å<sup>3</sup>, space group  $P2(1)/c$ ,  $Z = 8$ ,  $\mu(\text{Mo-K}\alpha) = 5.90$  mm<sup>-1</sup>,  $T = 293(2)$  K, 6224 reflections measured, 5351 unique. The final  $R$  and  $wR(F^2)$  were 0.0505 and 0.1304 (observed data), respectively. X-Ray data were collected on a Nicolet-Siemens R3m/V diffractometer. All hydrogen atoms were included at calculated positions and constrained to ride on the atoms to which they are bonded, with  $U_{\text{iso}}$  1.5 greater than that of the parent atom. Their contributions were added to the structure factor calculations, but their positions were not refined. The non-hydrogen atoms were refined anisotropically and the final difference map was featureless.

CCDC reference number 176254.

See <http://www.rsc.org/suppdata/dt/b1/b106247f/> for crystallographic data in CIF or other electronic format.

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