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Oxidative addition of methyl iodide to dimethylplatinum (II) compounds containing bulky and/or chiral ligands. Crystal structure of compound [$PtMe_3I${1-($Me_2NCH_2CH_2NCH$)$C_{10}H_7$}]

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Abstract

Compound [$PtMe_2${1-($Me_2NCH_2CH_2NCH$)C_{10} H_7}] (**2a**) gave upon reaction with methyl iodide platinum (IV) compound [$PtMe_3I${1-($Me_2NCH_2CH_2NCH$)$C_{10}H_7$}] (**3a**) as a single isomer which was characterised structurally. Upon standing in solution, two isomers of **3a** were detected by ^1H NMR. New chiral compounds [$PtMe_2$(*N*,*N*′-chelate)] (*N*,*N*′ = 2-((*S*)-CHNCH(Me)C_6H_5)C_9H_6N (**2b**), 2-((*R*)-CHNCH(Me)$C_{10}H_7$)C_5H_4N (**2c**) and 2-((*R*)-CHNCH(Me)$C_{10}H_7$)C_9H_6N (**2d**)) were obtained from [$Pt_2Me_4(\mu$-$SMe_2)_2$] and the corresponding diimines. The oxidative addition of methyl iodide to compounds **2b**–**2d** gave two diastereomers each of compounds [$PtMe_3I$(*N*,*N*′-chelate] in nearly equal amounts. All new platinum (II) and platinum (IV) compounds were fully characterised.

Keywords: Platinum; Imine ligands; Chiral compounds; Oxidative addition; Steric effects; Crystal structure

1. Introduction

The oxidative addition reaction is one of the most fundamental processes in transition metal chemistry. Studies of this reaction involving Pt (II)/Pt (IV) systems indicate that nitrogen donor ligands impart high nucleophilicity to the metal centre, increasing its reactivity, which is, however, moderated by the presence of bulky ligands that might hinder or even inhibit the reaction [1]. In most cases, the oxidative addition of alkyl halides to organoplatinum (II) complexes gives *trans* stereochemistry, although subsequent isomerisation can yield products, that appear to arise from *cis*-oxidative addition [2]. The geometrical isomerism of complexes [$PtMe_2RX$(*N*,*N*′)] has been examined [3]. Moreover high degrees of stereoselectivity in which steric effects of ligands play an important role have been reported for both intra- [4] and intermolecular [5,6] oxidative additions to chiral platinum complexes.

Here we attempt to assess the influence of ligand steric effects on: (1) the reactivity of organoplatinum (II) compounds towards methyl iodide and (2) the stereoselectivity of the process. Two distinct types of dinitrogen ligands were selected for this study: amine–imine ligand **1a** containing a bulky naphthyl substituent and diimine chiral ligands containing sterically demanding groups such as quinoline or naphthyl (**1b**–**1d**).

2. Results and discussion

2.1. Oxidative addition of methyl iodide to compound **2a**

Compound [$PtMe_2${1-($Me_2NCH_2CH_2NCH$)$C_{10}H_7$}] (**2a**) has been previously synthesised from [Pt_2Me_4

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(μ-$SMe_2)_2$] and ligand **1a** as a precursor for a cyclometallated compound containing a terdentate [C,*N*,*N*′] ligand [7]. Compound **2a** is also an appropriate substrate to study whether oxidative addition of methyl iodide is plausible when bulky naphthyl groups are present. 2D-NOESY NMR spectra were taken for **1a** and **2a**. In both cases, the ligand adopts the E form shown in Chart 1 as shown by the cross-peak between imine and methylene protons. Therefore, co-ordination of the ligand as a (*N*,*N*′) chelate takes place without isomerisation of the imine.

Upon addition of methyl iodide to a solution of compound **2a** in acetone the colour of the solution changed from orange to light yellow and work-up of the final solution allowed isolation of a platinum (IV) compound $[PtMe_3I\{1\text{-}(Me_2NCH_2CH_2NCH)C_{10}H_7\}]$ (**3a**) in high yield. The new compound was characterised by elemental analysis, FAB-MS, ^1H, ^{13}C and ^{195}Pt NMR spectroscopies, and was also characterised crystallographically.

Compound **3a** consists of a single isomer for which three distinct methyl-platinum resonances coupled to platinum are observed. The values of the ^2J(Pt–H) coupling constants are smaller than those for the corresponding platinum (II) compound, which is consistent with the higher oxidation state of platinum, and the values obtained indicated the expected *fac*-$PtMe_3$ geometry as shown in Chart 1. In agreement with co-ordination through both nitrogen atoms, the diastereotopic methyl groups of the NMe_2 unit and the imine proton are also coupled to platinum. The ^{195}Pt NMR spectrum confirms the presence of a single isomer of the obtained platinum (IV) compound.

After **3a** has been allowed to stand in solution, a second isomer (**3a**′) is formed and after several hours both isomers are present in similar amounts. Assignment of the ^1H (500 MHz) spectrum of the final mixture was based on a COSY ^1H–^1H experiment. For both isomers, the value of the coupling constant of the imine proton with ^{195}Pt (J(H–Pt) = 32–34 Hz) is in the range expected for a trans arrangement (E-conformation) across the C=N bond [10]. This was confirmed by the cross-peak signals between the imine and the two lower field methylene protons (H^e) observed for both isomers in a 2D-NOESY NMR spectrum. Therefore, the two species present in the final mixture might be assigned to two

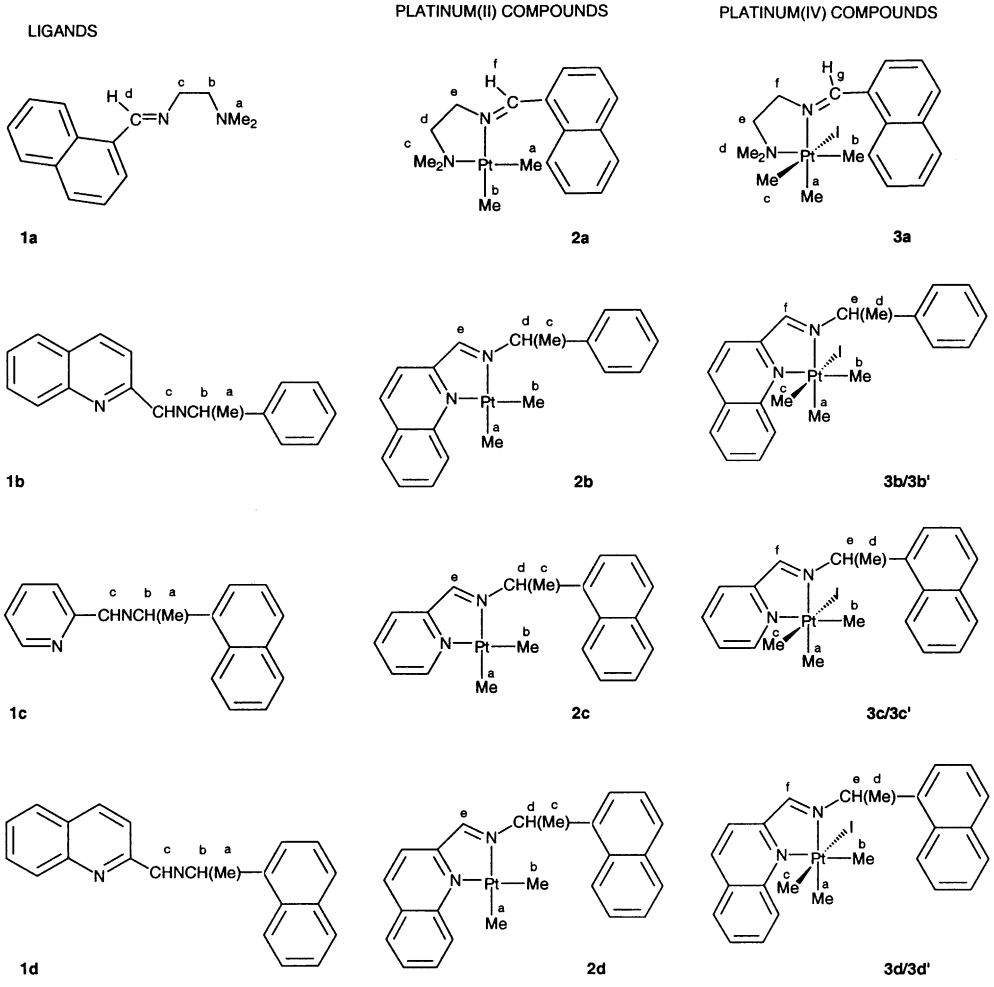

Chart 1.

different rotamers, both with the imine in an E form, where the naphthyl group points either towards the iodide or the axial methyl ligands. Molecular models suggest that rotation about the C–C bond of the pendant part of the ligand is likely to be restricted due to steric hindrance between the bulky naphthyl group and the equatorial methyl *cis* to the imine. Exchange cross-peak signals between the corresponding methyl groups of each rotamer, that is (Me^{a}, $Me^{a'}$), (Me^{b}, $Me^{b'}$), (Me^{c}, $Me^{c'}$), were observed in the 2D-NOESY spectra. A variable temperature ^{1}H NMR study in $CHCl_3$ in the range 25–50 °C was performed, however, no exchange broadening of any signals was observed. In addition to the sharp signals observed for both rotamers, formation of a third isomer (**3a**″) was observed at 35 °C along with some decomposition processes evidenced by the appearance of a new signal in the aldehyde region and other minor resonances. The abundance of the new isomer, which was assigned to a Z isomer based on the reduced coupling of the imine proton to platinum (J(H–Pt) = 20 Hz), increases up to about 10% of the final mixture at 50 °C.

Table 1
Selected bond lengths (Å) and angles (°) for compound **3a** with estimated standard deviations

Bond lengths			
Pt–C(18)	2.013(10)	N(1)–C(11)	1.249(10)
Pt–C(17)	2.031(9)	N(1)–C(12)	1.484(10)
Pt–C(16)	2.085(9)	N(2)–C(13)	1.455(11)
Pt–N(1)	2.236(7)	C(12)–C(13)	1.488(12)
Pt–N(2)	2.284(7)	C(10)–C(11)	1.488(12)
Pt–I	2.8090(10)		
Bond angles			
C(18)–Pt–C(17)	85.6(4)	N(1)–Pt–N(2)	81.1(3)
C(18)–Pt–C(16)	87.8(4)	C(18)–Pt–I	92.8(3)
C(17)–Pt–C(16)	85.8(4)	C(17)–Pt–I	89.7(3)
C(16)–Pt–N(1)	88.7(3)	N(1)–Pt–I	91.15(17)
C(18)–Pt–N(2)	93.1(4)	N(2)–Pt–I	90.66(19)
C(16)–Pt–N(2)	93.9(3)		

2.2. Crystal structure of **3a**

Suitable crystals of isomer **3a** were grown from acetone solution. The crystal structure is composed of discrete molecules separated by van der Waals interactions. Selected bond lengths and angles are given in Table 1 and the molecular structure is shown in Fig. 1. The study confirms the octahedral co-ordination for the platinum atom with the facial arrangement of the three methyl groups. The imine adopts the E conformation, the torsion angle C(12)–N(1)–C(11)–C(10) being 174.2(9) Å. The dangling naphthyl group points towards the axial methyl ligand and forms a dihedral angle of 64.55(5)° with the co-ordination plane Pt–C(17)–C(18)–N(1)–N(2). The chelate ring Pt–N(2)–C(13)–C(12)–N(1) has an envelope conformation on C(13) and is nearly coplanar with the aforementioned co-ordination plane, the dihedral angle being 6.39(5)°. The Pt–N distances are unequal with the bond to the amine nitrogen being slightly longer than that to the imine nitrogen, which is consistent with the relatively weak ligating ability of tertiary amines for platinum. The Pt–C and Pt–I distances are within the range of expected values for reported *fac*-$PtMe_3I$ complexes [8–10] and the Pt–C bonds follow the trend that the equatorial bonds (*trans* to N) are somewhat shorter than the axial bonds (*trans* to I). The octahedron around platinum is as expected somewhat distorted, the main distortion being due to the small N(1)–Pt–N(2) "bite angle" of 81.1(3)°.

2.3. Oxidative addition of methyl iodide to chiral platinum (II) compounds **2b**, **2c** and **2d**

Some recent studies on intermolecular oxidative addition to chiral platinum (II) compounds involve cyclometallated compounds [2,5,6,11]. Our previous work on both inter- and intramolecular oxidative addition processes leading to cyclometallated platinum (IV)

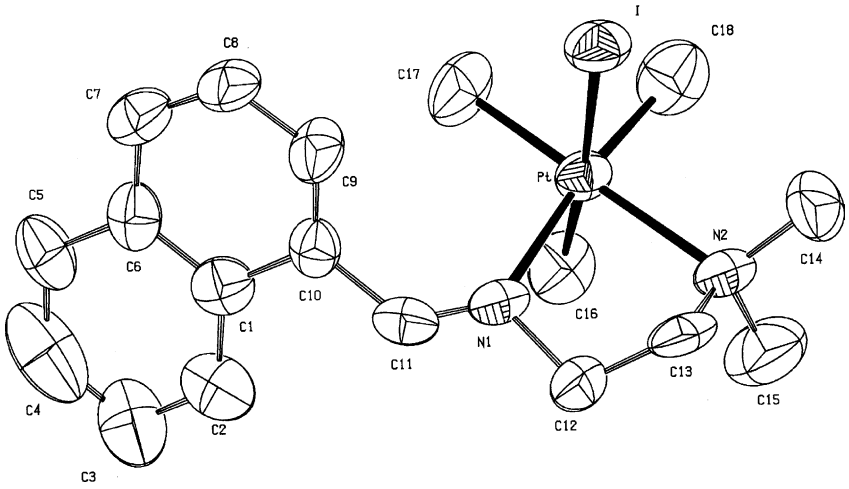

Fig. 1. Molecular structure of compound **3a**.

compounds indicate a close relationship of the stereoselectivity with the steric hindrance which is evidenced by the lower stereoselectivity obtained when smaller ligands (SMe_2 versus PPh_3 or Cl versus I) are present in the co-ordination sphere of the platinum [12]. Moreover, a higher degree of stereoselectivity is obtained for chiral ligands derived from the more sterically demanding (*R*)-(+)-1-(1-naphthyl)ethylamine [12] than for those derived from (*S*)-methylbenzylamine [13,14]. Optically active naphthyl-derived complexes have proved to be superior over closely related benzyl analogues in most reported applications such as resolving agents for chiral ligands [15–18].

Dimethylplatinum (II) compounds containing bidentate dinitrogen chiral ligands are also suitable substrates to study the stereoselectivity of the oxidative addition reaction since the platinum centre is expected to have a high electronic density and the *fac*-$PtMe_3$ geometry resulting from reaction with methyl iodide renders the octahedrally coordinated platinum a chiral centre. Additional interest in the preparation of new optically active transition metal complexes, in particular those containing nitrogen ligands [20,21], is due to their potential applications in catalysis [22].

We have previously reported that the *trans* oxidative addition of methyl iodide to [$PtMe_2$\{(*S*)-PhCHMeN CHC_5H_4N\}] containing a chiral [*N*,*N*′] ligand gave two diastereomers in nearly equal amounts [19]. The aim of the present study is to examine the effect of bulkier groups on the stereoselectivity of the oxidative addition. Thus, ligands **1b**–**1d** were prepared from condensation reactions of 2-pyridinecarboxaldehyde or 2-quinolylcarboxaldehyde and chiral imines (*S*)-methylbenzylamine or (*R*)-1-naphthylamine and new co-ordination chiral platinum (II) compounds were obtained from reaction of these ligands with platinum substrate [$Pt_2Me_4(\mu\text{-}SMe_2)_2$]. Chiral platinum (II) compounds **2b**, **2c** and **2d** were obtained as red or purple solids, which were characterised by elemental analysis, FAB-MS and ^1H and ^{13}C NMR (**2d**) spectroscopies. As reported for analogous platinum compounds, the intense colour is due to the presence of a metal-to-ligand charge transfer band in the visible region of the spectrum [23]. The data are consistent with the proposed formulae shown in Chart 1 in which the chiral ligand is coordinated to platinum through both nitrogen atoms. Three distinct resonances appeared in the methyl region, two of them corresponding to the methyl groups bound to platinum [^2J(Pt–H) = 84–90 Hz] and the third assigned to the methyl substituent at the asymmetric carbon of the ligand. The value of the coupling of the imine hydrogen to platinum is in the expected range.

Oxidative addition of methyl iodide to chiral platinum (II) compounds produced in each case a mixture of two diastereomers of the corresponding compounds **3**, which were characterised by elemental analyses and ^1H and ^{13}C (**3d/3d′**) NMR spectroscopies. Assuming a *trans* addition, two diastereomers (C,S) and (A,S) for compounds derived from (*S*)-benzylamine and (C,R) and (A,R) for compounds derived from (*R*)-1-naphthylamine, in which C/A represents the absolute stereochemistry at the platinum, are in principle possible. According to ^1H NMR spectra taken at 200 and 500 MHz, the relative amounts of the two diastereomers are nearly equal within experimental error (ca. 55% and 45%) in all cases. Formation of rotamers as reported for **3a** is not observed. Each diastereomer presents three resonances corresponding to the three non-equivalent methyl-platinum and the values of the coupling constants to platinum are consistent with a *fac*-Pt (IV)Me_3 arrangement. In each case, the NMR data are very similar for the two diastereomers, and the largest differences in chemical shifts involve the imine proton (H^f) and the methyl bound to the asymmetric carbon (Me^d). A 2D-NOESY NMR spectrum was also taken for **3b/3b′** and in this case cross-peak signals were observed within each isomer but no exchange cross-peaks were observed. In particular, for both isomers the equatorial methyl *trans* to the quinolyl group shows a cross-peak with methylene proton H^e but not with Me^d. This is consistent with Me^d pointing away from the platinum centre in order to minimise unfavourable steric effects between Me^d and methyl ligands bound to platinum.

The reactions of **2b** and **2d** with methyl iodide were monitored by ^1H NMR at room temperature in $CDCl_3$. In both cases, in the early stages of the reaction one diastereomer (**3b** or **3d**) is present in larger amount (ca 5:1). After a short time (ca. 10 min) both isomers (**3b/3b′** or **3d/3d′**) are present in nearly equal amounts as reported above for the experiments carried out under preparative conditions. No further interconversion of the isomers was observed and their ratio remained constant over several days in solution. As previously reported for analogous systems [5], we might assume that the attack of methyl iodide occurs initially on the less hindered side of the chiral square-planar platinum (II) reagent to yield one diastereoisomer. However, loss of iodide gives the cationic intermediate, which can undergo methyl migration to yield finally a mixture of two diastereomers in nearly equal amounts. Exchange of Pt–Me groups is a well-known feature of *fac*- [$PtMe_3X$(L–L)] compounds [24] and facilitates the easy epimerisation process observed for these compounds.

In conclusion, for the co-ordination platinum (II) compounds under study, oxidative addition of methyl iodide is not inhibited by the presence of bulky groups. The increased size of the ligands does not seem to be sterically significant, either because it just involves in-plane crowding (quinoline versus pyridine) or is minimised by rotation of the bulky group away from the

co-ordination sphere of the platinum. Processes such as C–C restricted rotation of the pendant part of the ligand, or E–Z isomerisation of the imine (possibly aimed at reducing steric crowding at the co-ordination sphere of platinum) have been detected for the resulting $[PtMe_3I(N–N)]$ compounds by NMR studies in solution. When chiral ligands are used, two diastereomers in nearly equal amounts are obtained and the lack of diastereoselectivity might be related to the easy interconversion of the diastereomers.

3. Experimental

3.1. General

^1H, ^{13}C and ^{195}Pt NMR spectra were recorded by using Varian Gemini 200 (^1H, 200 MHz; ^{13}C, 50 MHz), Varian 300 (^1H–^1H NOESY, 300 MHz (**1a**, **2a**), ^{13}C, 75 MHz), Bruker 250 (^{195}Pt, 54 MHz) and Varian Inova (^1H–^1H COSY, ^1H–^1H NOESY (**3a**, **3b/3b′**) and variable temperature ^1H (**3a**), 500 MHz) spectrometers, and referenced to $SiMe_4$ (^1H and ^{13}C) and H_2PtCl_6 in D_2O (^{195}Pt). δ values are given in ppm and J values in Hz. Microanalyses and mass spectra (FAB, 3-nitrobenzyl alcohol matrix) were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona.

Compounds $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ [25] and **2a** [7] were prepared as reported.

3.2. Synthesis of the compounds

3.2.1. Synthesis of ligands

Compounds **1** were prepared by the reaction of 2.5 mmol of the corresponding aldehyde (**1b** and **1d**: 0.39 g of 2-quinolylcarboxaldehyde, **1c**: 0.27 g of 2-pyridinecarboxaldehyde) with an equimolar amount of the corresponding amine (**1b**: 0.30 g of (*S*)-methylbenzylamine and **1d** and **1c**: 0.43 g of (*R*)-1-naphthylamine) in refluxing ethanol (20 ml). The mixture was stirred under reflux for 2 h. The solvent was removed in a rotary evaporator to yield yellow–brown oils (**1b** and **1d**) or a yellow solid (**1c**). **2-((*S*)-CHNCH(Me)C_6H_5)C_9H_6N (1b)**. Yield 0.5 g (77%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.65$ [d, ^3J(H0-Me) = 7, Me^a], 4.72 [q, ^3J(H–Me) = 7, H^b], {7.26–7.61 [m, 6H], 7.74 [m, 1H], 7.84 [dd, J(H–H) = 8, J(H–H) = 1, 1H], 8.12 [d, J(H–H = 8, 1H], 8.18 [d, J(H–H) = 8, 1H], 8.27 [d, J(H–H) = 8, 1H], aromatics}; 8.64 [s, H^c]. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 24.64$ [s, C^a], 69.63 [C^b], {126.65, 126.96, 127.29, 127.64, 128.44, 129.45, 129.67, 131.32, 136.37, 143.88, 145.91, aromatics}; 160.81 [s, C^c]. **2-((*R*)-CHNCH(Me)$C_{10}H_7$)C_5H_4N (1c)**. Yield 0.55 g (81%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.77$ [d, ^3J(H–Me) = 7, Me^a], 5.48 [q, ^3J(H–Me) = 7, H^b], {7.29–7.34 [m, 1H], 7.48–7.58 [m, 2H], 7.71 [m, 1H], 7.75–7.89 [m, 3H], 8.15 [dd, J(H–H) = 8, J(H–H) = 1, 1H], 8.24 [d, J(H–H) = 8, 1H], 8.63 [m, 1H], aromatics}, 8.52 [s, H^c]. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 24.18$ [s, C^a], 65.17 [C^b], {121.39, 123.45, 125.54, 125.84, 127.47, 128.86, 130.61, 133.92, 136.45, 140.24, 140.26, 154.70, aromatics}, 160.58 [s, C^c]. **2-((*R*)-CHNCH(Me)$C_{10}H_7$)C_9H_6N (1d)**. Yield 0.6 g (77%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.80$ [d, ^3J(H–Me) = 7, Me^a], 5.55 [q, ^3J(H–Me) = 7, H^b], {7.47–7.61 [m, 4H], 7.72 [m, 2H], 7.78–7.91 [m, 3H], 8.11 [d, J(H–H) = 8, 1H], 8.20 [d, J(H–H) = 8, 1H], 8.25 [s, 1H], 8.32 [d, J(H–H) = 8, 1H], aromatics}, 8.70 [s, H^c]. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 24.18$ [s, C^a], 65.25 [C^b], {123.50, 124.03, 125.32, 125.87, 127.53, 127.64, 128.71, 128.56, 129.44, 129.68, 136.39, aromatics}, 161.07 [s, C^c].

3.2.2. Synthesis of compounds 2

Compounds **2** were obtained by adding a solution of 3.9×10^{-4} mol of the imine (**1b** and **1c**: 101 mg; **1d**: 121 mg) in acetone (10 ml) to a solution of 100 mg (1.74×10^{-4} mol) of compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in acetone (10 ml). The mixture was stirred for 20 min at room temperature and acetone was removed in a rotary evaporator. The residue was treated with hexane to yield red (**2b**) or purple (**2c** and **2d**) solids which were filtered, washed with hexane (3×2 ml) and dried in vacuum. **[$PtMe_2${2-((*S*)-CHNCH(Me)C_6H_5)C_9H_6N}] (2b)**. Yield 135 mg (79%). ^1H NMR (200 MHz, CD_3COCD_3): $\delta = 1.30$ [s, ^2J(Pt–H) = 90, Me^a], 1.52 [s, ^2J(Pt–H) = 85, Me^b], 1.83 [d, ^3J(H–H) = 7, Me^c], 5.80 [q, ^3J(H–H) = 7, H^d], {7.23–7.35 [m, 5H], 7.64 [m, 1H], 7.77–7.83 [m, 2H], 7.97 [d, J(H–H) = 8, 1H], 8.85 [d, J(H–H) = 8, 1H], 9.02 [d, J(H–H) = 8, 1H], aromatics}, 9.74 [s, ^3J(Pt–H) = 35, H^e]. FAB(+)-MS, m/z: 485 [M], 455 [M-2Me]. *Anal.* Found: C, 47.6; H, 4.6; N, 5.5. Calc. for $C_{20}H_{22}N_2Pt \cdot H_2O$: C, 47.71; H, 4.80; N, 5.56%. **[$PtMe_2${2-((*R*)-CHNCH(Me)$C_{10}H_7$)C_5H_4N}] (2c)**. Yield 132 mg (78%). ^1H NMR (200 MHz, CD_3COCD_3): $\delta = 1.27$ [s, ^2J(Pt–H) = 88, Me^a], 1.22 [s, ^2J(Pt–H) = 85, Me^b], 1.94 [d, ^3J(H–H) = 7, Me^c], 6.52 [q, ^2J(H–H) = 7, H^d], {7.48–7.81 [m, 6H], 7.92–7.97 [m, 2H], 8.15 [t, J(H–H) = 8, 1H], 8.28–8.33 [m, 1H], 9.22 [d, J(H–H) = 5, 1H], aromatics}, 9.07 [s, ^3J(Pt–H) = 36, H^e]. ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = -15.73$ [Me^a], −17.27 [Me^b], 21.42 [C^c], 59.30 [C^d], {124.79, 125.49, 126.14, 126.24, 127.42, 127.74, 128.51, 129.35, 134.07, 136.39, 147.11, aromatics}, 161.44 [C^e]. FAB(+)-MS, m/z: 455 [M-2Me]. *Anal.* Found: C, 47.7; H, 4.7; N, 5.5. Calc. for $C_{20}H_{22}N_2Pt \cdot H_2O$: C, 47.71; H, 4.80; N, 5.56%. **[$PtMe_2${2-((*R*)-CHNCH(Me)$C_{10}H_7$)C_9H_6N}] (2d)**. Yield 127 mg (68%). ^1H NMR (200 MHz, CD_3COCD_3): $\delta = 1.52$ [s, ^2J(Pt–H) = 90, Me^a], 1.64 [s, ^2J(Pt–H) = 84, Me^b], 1.98 [d, ^3J(H–H) = 7, Me^c], 6.45 [q, ^2J(H–H) = 7, H^d], {7.49 [m, 2H], 7.64 [t, J(H–H) = 8, 2H], 7.79 [t, J(H–H) = 7, 2H], 7.92–8.00 [m, 4H], 8.35 [m, 1H], 8.70 [d, J(H–H) = 8, 1H], 9.10 [d, J(H–H) = 8, 1H], aromatics}, 9.42 [s, ^3J(Pt–H) = 35, H^e]. FAB(+)-MS, m/z: 505 [M-2Me]. *Anal.* Found: C, 52.2; H, 4.5; N, 5.1. Calc. for $C_{24}H_{24}N_2Pt \cdot H_2O$: C, 52.07; H, 4.73; N, 5.1%.

3.2.3. Synthesis of compounds **3**

Compounds **3** were obtained by adding 0.1 ml of methyl iodide to a solution of 50 mg of the corresponding compound **2** in acetone (20 ml). The mixture was stirred for 2 h at room temperature and acetone was removed in a rotary evaporator. The residue was treated with ether (**3a**) or hexane (**3b**–**3d**) to yield yellow solids which were filtered, washed (3 × 2 ml) with ether (**3a**) or hexane (**3b**–**3d**) and dried in vacuum. **[PtMe$_3$I{Me$_2$NCH$_2$CH$_2$NCH(1-C$_7$H$_{10}$)}]** (**3a**). Yield 50 mg (76%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.60$ [s, ^2J(Pt–H) = 73, Me^c], 0.77 [s, ^2J(Pt–H) = 71, Me^a], 1.15 [s, ^2J(Pt–H) = 72, Me^b], {2.49 [s, ^3J(H–Pt) = 14, 3H], 3.23 [s, ^3J(H–Pt) = 11, 3H], Me^d}, {2.78 [m, 1H], 3.53 [m, 1H], 4.05 [m, 1H], 4.30 [m, 1H], H^{e,f}}, {7.55 [m, 4H], 7.92 [m, 2H], 8.13 [d, J(H–H) = 7, 1H], aromatics}, 9.41 [s, ^3J(Pt–H) = 33, H^g]. ^{13}C NMR (75 MHz, $CDCl_3$): δ = {−11.30, −11.18, −5.28, Me^{a,b,c}}, {41.26, 48.87, Me^d}, {57.57, 57.95, C^{e,f}}; {118.40, 119.65, 121.20, 121.86, 122.42, 123.68, 125.66, aromatics}; 164.41[C^g]. ^{195}Pt NMR (54 MHz, $CDCl_3$): −2552 ppm. ^{1}H NMR (500 MHz, $CDCl_3$): isomer **3a**: $\delta = 0.58$ [s, ^2J(Pt–H) = 73, Me^c], 0.77 [s, ^2J(Pt–H) = 71, Me^a], 1.13 [s, ^2J(Pt–H) = 72, Me^b], {2.49 [s, ^3J(H–Pt) = 14, 3H], 3.23 [s, ^3J(H–Pt) = 10, 3H], Me^d}, {2.78 [ddd, J(H–H) = 12; 6; 3, 1H], 3.53 [m, 1H], 4.05 [tt, J(H–H) = 12; 2; 1H], 4.30 [m, 1H], H^{e,f}}, {7.74 [t, J(H–H) = 7, 2H], 7.90 [d, J(H–H) = 7, 2H], 8.09 [d, J(H–H) = 7, 1H], aromatics}, 9.41 [s, ^3J(Pt–H) = 34, H^g]. isomer **3a′**: $\delta = 0.39$ [s, ^2J(Pt–H) = 72, Me$^{c'}$], 0.54 [s, ^2J(Pt–H) = 73, Me$^{a'}$], 0.91 [s, ^2J(Pt–H) = 72, Me$^{b'}$], {2.49 [s, ^3J(H–Pt) = 14, 3H], 2.97 [s, ^3J(H–Pt) = 10, 3H], Me$^{d'}$}, {2.69 [dt, J(H–H) = 12; 4, 1H], 3.50 [m, 1H], 4.10 [m, 2H], H$^{e',f'}$}, {7.93 [d, J(H–H) = 9, 2H], 8.30 [d, J(H–H) = 7, 1H], aromatics}, 9.43 [s, ^3J(Pt–H) = 32, H$^{g'}$], aromatic region: 7.52–7.57 [m, 2H **3a** + 4H **3a′**]. ^{1}H NMR (500 MHz, 50 °C, $CDCl_3$): isomer **3a″**: $\delta = 0.98$ [s, ^2J(Pt–H) = 72, Me$^{c''}$], 1.23 [s, ^2J(Pt–H) = 70, Me$^{a''}$], 1.57 [s, ^2J(Pt–H) = 71, Me$^{b''}$], {2.37 [s, ^3J(H–Pt) = 15, 3H], 3.20 [s, ^3J(H–Pt) = 11, 3H], Me$^{d''}$}, {3.25–3.30 [m, 1H], 3.62–3.69 [m, 2H], 3.95–3.97 [m, 1H], 4.30 [m, 1H], H$^{e'',f''}$}, 9.28 [s, ^3J(Pt–H) = 20, H$^{g''}$]. FAB(+)-MS, m/z: 578 [M-Me], 563 [M-2Me], 466 [M-I], 419 [M-I-3Me]. *Anal.* Found: C, 36.8; H, 5.0; N, 4.8. Calc. for $C_{18}H_{27}IN_2Pt$: C, 36.43; H, 4.59; N, 4.72%. **[PtMe$_3$I{2-((*S*)-CHNCH(Me)C$_6$H$_5$)C$_9$H$_6$N}]** (**3b/3b′**). Yield 53 mg (82%). ^{1}H NMR (500 MHz, CD_3COCD_3): isomer **3b**: $\delta = 0.50$ [s, ^2J(Pt–H) = 70, Me^c], 1.61 [s, ^2J(Pt–H) = 74, Me^a], 1.75 [s, ^2J(Pt–H) = 73, Me^b], 1.95 [d, ^3J(H–H) = 7, Me^d], 5.85 [q, ^3J(H–H) = 7, H^e], {8.30 [d, J(H–H) = 8, 1H], 8.80 [d, J(H–H) = 8, 1H], 8.88 [d, J(H–H) = 8, 1H], aromatics}, 9.54 [s, ^3J(Pt–H) = 31, H^f]; isomer **3b′**: $\delta = 0.68$ [s, ^2J(Pt–H) = 70, Me$^{c'}$], 1.70 [s, ^2J(Pt–H) = 71, Me$^{a'}$], 1.72 [s, ^2J(Pt–H) = 70, Me$^{b'}$], 1.85 [d, ^3J(H–H) = 7, Me$^{d'}$], 6.00 [q, ^3J(H–H) = 7, H$^{e'}$], {8.13 [d, J(H–H) = 8, 1H], 8.73 [d, J(H–H) = 8, 1H], 8.89 [d, J(H–H) = 9, 1H], aromatics}, 9.12 [s, ^3J(Pt–H) = 30, H$^{f'}$]; aromatic region: 7.37–7.56 [m, 8H], 7.79–7.87 [m, 4H], 7.97–8.01 [m, 2H], 8.16–8.19 [m, 2H]. ^{1}H NMR (500 MHz, $CDCl_3$): isomer **3b**: $\delta = 0.59$ [s, ^2J(Pt–H) = 71, Me^c], 1.74 [s, ^2J(Pt–H) = 73, Me^a], 1.81 [s, ^2J(Pt–H) = 71, Me^b], 2.02 [d, ^3J(H–H) = 7, Me^d], 5.71 [q, ^3J(H–H) = 7, H^e], {8.39 [d, J(H–H) = 8, 1H], 8.95 [d, J(H–H) = 8, 1H], aromatics}, 8.73 [s, ^3J(Pt–H) = 29, H^f]; isomer **3b′**: $\delta = 0.71$ [s, ^2J(Pt–H) = 71, Me$^{c'}$], 1.78 [d, ^3J(H–H) = 7, Me$^{d'}$], 1.79 [s, ^2J(Pt–H) = 70, Me$^{a'}$], 1.82 [s, ^2J(Pt–H) = 73, Me$^{b'}$], 6.07 [q, ^3J(H–H) = 7, H$^{e'}$], {7.61 [d, J(H–H) = 8, 1H], 8.35 [d, J(H–H) = 8, 1H], 8.90 [d, J(H–H) = 9, 1H], aromatics}; 8.60 [s, ^3J(Pt–H) = 29, H$^{f'}$]; aromatic region: 7.36–7.46 [m, 7H], 7.68–7.71 [m, 5H], 7.85–7.90 [m, 5H]. *Anal.* Found: C, 40.0; H, 4.0; N, 4.4. Calc. for $C_{21}H_{25}IN_2Pt$: C, 40.20; H, 4.02; N, 4.46%. **[PtMe$_3$I{2-((*R*)-CHNCH(Me)C$_{10}$H$_7$)C$_5$H$_4$N}]** (**3c/3c′**). Yield 55 mg (85%). ^{1}H NMR (500 MHz, $CDCl_3$): isomer **3c**: $\delta = 0.75$ [s, ^2J(Pt–H) = 73, Me^c], 1.57 [s, ^2J(Pt–H) = 70, Me^a], 1.60 [s, ^2J(Pt–H) = 71, Me^b], 1.93 [d, ^3J(H–H) = 7, Me^d], 6.44 [q, ^3J(H–H) = 7, H^e], 8.11 [s, ^3J(Pt–H) = 29, H^f]; isomer **3c′**: $\delta = 0.81$ [s, ^2J(Pt–H) = 73, Me$^{c'}$], 1.57 [s, ^2J(Pt–H) = 71, Me$^{a'}$], 1.77 [s, ^2J(Pt–H) = 71, Me$^{b'}$], 2.18 [d, ^2J(H–H) = 7, Me$^{d'}$], 6.38 [q, ^3J(H–H) = 6, H$^{e'}$], 8.36 [s, ^3J(Pt–H) = 28, H$^{f'}$]; aromatic region: 7.48–7.63 [m, 12H], 7.70 [d, J(H–H) = 7, 1H], 7.85 [d, J(H–H) = 8, 1H], 7.90–7.94 [m, 5H], 8.02 [d, J(H–H) = 9, 1H], 8.87 [d, J(H–H) = 8, 1H], 8.92 [d, J(H–H) = 6, 1H]. ^{13}C NMR (62.5 MHz, $CDCl_3$): isomer **3c** or **3c′**: $\delta = -7.73$ [Me^c], −4.75 [Me^a], 7.94 [Me^b]; 20.09 [C^d], 60.52 [C^e], 162.99 [C^f]; isomer **3c** or **3c′**: $\delta = -7.07$ [Me^c], −4.40 [Me^a], 8.20 [Me^b], 22.93 [C^d], 60.96 [C^e], 162.67 [C^f], aromatics: 124.61, 125.05, 125.80, 126.05, 126.20, 126.67, 126.93, 127.32, 127.39, 127.58, 128.15, 128.58, 129.03, 129.51, 129.89, 133.99, 138.42, 147.50. *Anal.* Found: C, 40.3; H, 4.2; N, 4.4. Calc. for $C_{21}H_{25}IN_2Pt$: C, 40.20; H, 4.02; N, 4.46%. **[PtMe$_3$I{2-((*R*)-CHNCH(Me)C$_{10}$H$_7$)C$_9$H$_6$N}]** (**3d/3d′**). Yield 40 mg (63%). ^{1}H NMR (500 MHz, $CDCl_3$): isomer **3d**: $\delta = 0.74$ [s, ^2J(Pt–H) = 70, Me$^{c'}$], 1.82 [s, ^2J(Pt–H) = 73, Me$^{a'}$], 1.99 [s, ^2J(Pt–H) = 72, Me$^{b'}$], 2.23 [d, ^3J(H–H) = 7, Me$^{d'}$], 6.56 [q, ^3J(H–H) = 7, H$^{e'}$], 8.67 [s, ^3J(Pt–H) = 28, H$^{f'}$]; isomer **3d′**: $\delta = 0.78$ [s, ^2J(Pt–H) = 70, Me^c], 1.86 [s, ^2J(Pt–H) = 71, Me^a], 1.87 [s, ^2J(Pt–H) = 71, Me^b], 1.95 [d, ^3J(H–H) = 7, Me^d], 6.49 [q, ^3J(H–H) = 6, H^e], 8.53 [s, ^3J(Pt–H) = 28, H^f]; aromatic region: 7.43 [d, J(H–H) = 8, 1H], 7.47 [t, J(H–H) = 8, 1H], 7.52–7.59 [m, 7H], 7.63–7.70 [m, 2H], 7.76 [d, J(H–H) = 7, 1H], 7.82–7.89 [m, 7H], 7.93 [d, J(H–H) = 8, 2H], 8.05 [d, J(H–H) = 9, 1H], 8.26 [d, J(H–H) = 9, 1H], 8.33 [d, J(H–H) = 8, 1H], 8.95 [d, J(H–H) = 9, 1H], 8.96 [d, J(H–H) = 9, 1H]. *Anal.* Found: C, 44.1; H, 4.2; N, 4.0. Calc. for $C_{25}H_{27}IN_2Pt$: C, 44.32; H, 4.02; N, 4.13%.

3.3. X-ray structure analysis

3.3.1. Data collection

Prismatic crystals were selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit cell

Table 2
Crystallographic and refinement data for compound **3a**

Formula	$C_{18}H_{27}IN_2Pt$
Formula weight	593.41
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	13.397(3)
b (Å)	7.747(4)
c (Å)	20.308(6)
β (°)	108.54(2)
V (Å^3)	1998.3(13)
Z	4
d (calculated) (Mg/m^3)	1.972
Absorption coefficient (mm^{-1})	8.566
F (0 0 0)	1120
Number of reflections collected/unique	5945/5804 [R(int) = 0.0272]
Data/restraints/parameters	5804/0/199
GOF on F^2	0.846
$R_1(I > 2\sigma(I))$	0.0420
wR_2 (all data)	0.1106
Peak and hole (e Å^{-3})	0.548 and −0.695

parameters were determined from automatic centering of 25 reflections ($12° < \theta < 21°$) and refined by least-squares method. Intensities were collected with graphite monochromatised Mo Kα radiation, using $\omega/2\theta$ scan-technique. 5945 reflections were measured in the range $2.12° < \theta < 29.95°$ and 2487 were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control, significant intensity decay was not observed. Lorentz polarisation and absorption corrections were made. Further details are given in Table 2.

3.3.2. Structure solution and refinement

The structures were solved by direct methods, using SHELXS computer program [26], and refined by the full-matrix least-squares method, with the SHELX97 computer program [26] using 5804 reflections (very negative intensities were not assumed). The function minimised was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0420P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from International Tables of X-Ray Crystallography [27]. All hydrogen atoms were computed and refined, using a riding model, with an isotropic factor equal to 1.2 times the equivalent temperature factor of the atom to which they are linked. Further details are given in Table 2.

4. Supplementary material

Supplementary data are available from the CCDC. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on request, quoting the deposition No. CCDC 210609.

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References

[1] L.M. Rendina, R.J. Puddephatt, Chem. Rev. 97 (1997) 1735.
[2] A. von Zelewsky, A.P. Suckling, H. Stoeckli-Evans, Inorg. Chem. 32 (1993) 4585.
[3] V. De Felice, B. Giovannitti, A. De Renzi, D. Tesauro, A. Panunzi, J. Organomet. Chem. 593 (2000) 445.
[4] C.R. Baar, G.S. Hill, J.J. Vittal, R.J. Puddephatt, Organometallics 17 (1998) 32.
[5] C.R. Baar, H.A. Jenkins, J.J. Vittal, G.P.A. Yap, R.J. Puddephatt, Organometallics 17 (1998) 2805.
[6] C.R. Baar, L.P. Carbray, M.C. Jennings, R.J. Puddephatt, Organometallics 19 (2000) 2482.
[7] M. Crespo, M. Font-Bardía, S. Pérez, X. Solans, J. Organomet. Chem. 642 (2002) 171.
[8] E.W. Abel, P.J. Heard, K.G. Orrell, M.B. Hursthouse, M.A. Mazid, J. Chem. Soc., Dalton Trans. (1993) 3795.
[9] K.G. Orrell, A.G. Osborne, V. Sik, M. Webba da Silva, M.B. Hursthouse, D.E. Hibbs, K.M. Abdul Malik, N.G. Vassilev, J. Organomet. Chem. 555 (1998) 35.
[10] M.L. Creber, K.G. Orrell, A.G. Osborne, V. Sik, S.J. Coles, D.E. Hibbs, M.B. Hursthouse, Inorg. Chim. Acta 299 (2000) 209.
[11] M. Gianini, A. Forster, P. Haag, A. Von Zelewsky, H. Stoeckli-Evans, Inorg. Chem. 35 (1996) 4889.
[12] C. Anderson, M. Crespo, F.D. Rochon, J. Organomet. Chem. 631 (2001) 164.
[13] C. Anderson, M. Crespo, M. Font-Bardía, X. Solans, J. Organomet. Chem. 604 (2000) 178.
[14] M. Crespo, M. Font-Bardía, X. Solans, Polyhedron 17 (1998) 3927.
[15] S.B. Wild, Coord. Chem. Rev. 166 (1997) 291.
[16] J. Albert, J.M. Cadena, J. Granell, G. Muller, J.I. Ordinas, D. Panyella, C. Puerta, C. Sañudo, P. Valerga, Organometallics 18 (1999) 3623.
[17] J. Albert, J.M. Cadena, J. Granell, G. Muller, D. Panyella, C. Sañudo, Eur. J. Inorg. Chem. (2000) 1283.
[18] G.S. He, K.F. Mok, P.H. Leung, Organometallics 18 (1999) 4027.
[19] M. Crespo, Polyhedron 15 (1996) 1981.
[20] A. Togni, L.M. Venanzi, Angew. Chem. Int. Ed. Engl. 33 (1994) 497.
[21] H. Brunner, Angew. Chem. Int. Ed. Engl. 38 (1999) 1194.
[22] A. von Zelewsky, O. Mamula, J. Chem. Soc., Dalton Trans. (2000) 219.
[23] P.K. Monaghan, R.J. Puddephatt, Organometallics 3 (1984) 444.
[24] E.W. Abel, S.K. Bhargava, K.G. Orrell, Prog. Inorg. Chem. 32 (1984) 1.
[25] G.S. Hill, M.J. Irwin, L.M. Rendina, R.J. Puddephatt, Inorg. Synth. 32 (1998) 149.
[26] G.M. Sheldrick, SHELXS97. A Computer Program for Crystal Structure Determination, University of Göttingen, Germany, 1997.
[27] International Tables of X-Ray Crystallography, vol. IV, Kynoch Press, Birmingham, UK, 149 (1974) pp. 99–100.