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Stereoselective oxidative addition of methyl iodide to chiral cyclometallated platinum(II) compounds derived from (*R*)-(+)-1-(1-naphthylethylamine). Crystal structure of [PtMe{3-(*R*)-($C_{10}H_7$)CHMeNCHC$_4$H$_2$S}PPh$_3$]

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Abstract

The reaction of 3-(*R*)-($C_{10}H_7$)CHMeNCHC$_4$H$_3$S (**2a**) with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] in acetone gave the new chiral cyclometallated platinum(II) compound [PtMe{3-(*R*)-($C_{10}H_7$)CHMeNCHC$_4$H$_2$S}SMe$_2$] (**3a**). Addition of PPh$_3$ produced compound [PtMe{3-(*R*)-($C_{10}H_7$)CHMeNCHC$_4$H$_2$S}PPh$_3$] (**4a**) which was characterized by X-ray diffraction methods. While oxidative addition of methyl iodide to **3a** gave two pairs of diastereomers, the analogous reaction for **4a** produced only one diastereomer of the platinum(IV) compound [PtMe$_2$I{3-(*R*)-($C_{10}H_7$)CHMeNCHC$_4$H$_2$S}PPh$_3$] (**7a**). Subsequent isomerization of the resulting platinum(IV) compound gave a new pair of diastereomers in relative amounts 90 and 10%. Analogous proportions of final diastereomers were obtained for the oxidative addition of methyl iodide to the new chiral compounds [PtMe{3-(*R*)-($C_{10}H_7$)CHMeNCHAr}PPh$_3$] (Ar = C_6H_4 (**4b**), 2-FC_6H_3 (**4c**), 2-CF$_3$C$_6$H$_3$ (**4d**)). The reaction of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] with imines (*R*)-($C_{10}H_7$)CHMeNCH(2-BrC$_6H_4$) (**2e**) and (*R*)-($C_{10}H_7$)CHMeNCH(2,6-Cl$_2C_6H_3$) (**2f**) produced intramolecular oxidative addition to yield platinum(IV) compounds with some degree of stereoselectivity.

Keywords: Platinum; Cyclometallation; Oxidative addition; Stereoselectivity

1. Introduction

Oxidative addition reactions involving transition metals are fundamental steps in stoichiometric and catalytic processes. Recently, attention has been focused on the stereoselectivity of oxidative addition of alkyl halides to chiral square–planar platinum(II) complexes [1–3]. Following our previous results for the oxidative addition of methyl iodide to platinum(II) complexes with chiral imines derived from (*S*)-phenylethylamine [4–6] we decided to undertake a similar study for analogous compounds with ligands derived from the more sterically demanding (1-naphthyl)ethylamine. Naphthalenyl cyclopalladated complexes are frequently superior to benzyl analogues as resolving agents of phosphines or arsines [7–9], which has been related to the increased conformational rigidity of the naphthylethylamine derivatives [10,11]. Recently, optically active palladacycles containing imines derived from 1-(1-naphthyl)ethylamine have been used to resolve P-chiral ligands [12]. In view of these results, a high degree of stereoselectivity for the oxidative addition reaction to platinum(II) complexes containing chiral imines derived from naphthylethylamine could be anticipated, even if metallation at the naphthyl ring is not expected.

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2. Results and discussion

Ligands (R)-($C_{10}H_7$)CHMeNCHAr (**2**) were prepared by reaction of (R)-(+)-1-(1-naphthyl)ethylamine with the equimolar amount of the corresponding aldehyde in refluxing ethanol and characterized by ^1H- and ^{13}C-NMR spectroscopies.

*2.1. Oxidative addition of methyl iodide to chiral cyclometallated platinum(II) compounds [PtMe{3-(R)-($C_{10}H_7$)CHMeNCHC_4H_2S}L] (L = SMe_2 (**3a**), PPh_3 (**4a**))*

The reaction of 3-(R)-($C_{10}H_7$)CHMeNCHC_4H_3S (**2a**) with [Pt_2Me_4(μ-SMe_2)$_2$] in acetone gave [PtMe{3-(R)-($C_{10}H_7$)CHMeNCHC_4H_2S}SMe_2] (**3a**), which was characterized by ^1H- and ^{13}C-NMR spectroscopies and elemental analysis. Data are consistent with the proposed formula in which the imine acts as a [C,N] donor ligand and the coordination sphere of the platinum(II) is completed with a methyl group and a SMe_2 ligand. As reported for related ligands PhCH_2NCHC_4H_3S [13] and PhCHMeNCHC_4H_3S [6], metallation took place, along with methane formation, at the thiophene ring to yield an *endo*-metallacycle (containing the imine functionality) and not at the naphthyl group which would give an *exo*-metallacycle containing the chiral carbon.

Addition of PPh_3 to **3a** in acetone produced the cyclometallated compound [PtMe{3-(R)-($C_{10}H_7$)-CHMeNCHC_4H_2S}PPh_3] (**4a**), in which the phosphine ligand replaced the dimethylsulfide. This compound was characterized by ^1H- and ^{31}P-NMR spectroscopies, elemental analysis, mass spectroscopy and crystallography. The relatively high value for the coupling constant J(P–Pt) indicates that the PPh_3 ligand is *trans* to the thienyl group [13]. Manipulation with molecular models indicates that free rotation around the N–CHMe($C_{10}H_7$) bond is inhibited by the presence of the bulky PPh_3 in a *cis* position to the N–Pt bond. As only one set of signals was obtained in the ^1H- and ^{31}P-NMR spectra, the compound seems to be locked in one rotamer. It is most likely that the preferred conformation in solution is the same as the one which was determined by X-ray diffraction methods (Fig. 1).

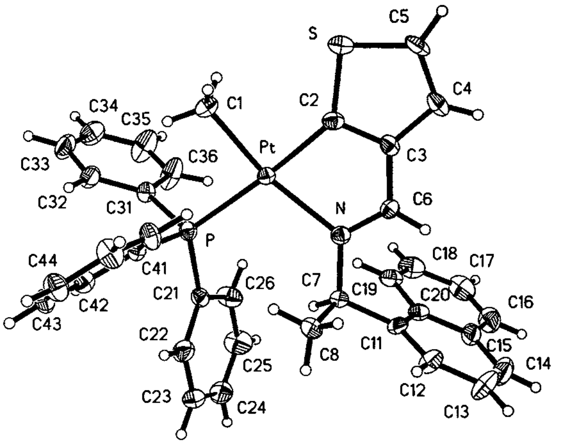

Fig. 1. View of compound [PtMe{3-(R)-($C_{10}H_7$)CHMeNCHC_4H_2S}PPh_3] (**4a**) with the thermal ellipsoids represented at the 30% probability level.

Suitable crystals of **4a** were obtained as yellow plates from a dichloromethane solution, which was layered with hexane. The crystal structure is shown in Fig. 1, and confirms the expected geometry. No hydrogen bonds are expected in this type of structure. The molecules are held together in the crystal only by van der Waals forces. The methyl ligand is in *trans* position to the nitrogen atom, the C=N group is *endo* to the cycle and the stereochemistry of the asymmetric carbon is R. The imine adopts an (E)-configuration, the torsion angle C(7)–N–C(6)–C(3) being − 175.1(4)°. The platinum atom displays a slightly tetrahedral distorted planar coordination and the following displacements (Å) are observed from the least-squares plane of the coordination sphere: Pt, 0.009(2); P, 0.054(2); N, − 0.067(3); C(1), − 0.073(3); C(2), 0.077(3). The metallacycle is approximately planar (mean deviation 0.011(3) Å) and the largest deviation from the mean plane determined by the five atoms is 0.017(3) Å for C(3). It is nearly coplanar with the coordination plane, the dihedral angle being 3.5(3)°. The bond distances and angles are listed in Table 1. These values are in the usual range for analogous compounds [6,13,14]. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 77.5(2)–106.0(1)°, the smallest angle corresponding to the metallacycle and the largest to the N–Pt–P angle. The latter is much larger (106.0(1)°) than for the analogous compound [PtMe{3-(PhCH_2NCH)-C_4H_2S}PPh_3] (98.0(2)°) [13], which indicates a much more congested molecule due to the presence of the bulky naphthyl group. In order to minimize the steric hindrance in the coordination sphere of platinum, the naphthyl lies away from the triphenylphosphine ligand.

Oxidative addition of methyl iodide to chiral platinum(II) compound **3a** was monitored by ^1H-NMR in acetone. Four isomers of the expected cyclometallated platinum(IV) compound were detected in the NMR from the early stages of the reaction and their ratio remained constant over several days in solution.

The reaction was also carried out in a preparative scale and gave a light yellow solid for which the elemental analysis was consistent with the formulation [$PtMe_2$I{3-(R)-($C_{10}H_7$)CHMeNCHC_4H_2S}SMe_2]. The ^1H-NMR spectra showed the presence of the four isomers in the same relative amounts as in the NMR experiment.

From the $^2J(^1H-^{195}Pt)$ coupling constants for the methyl groups, a *fac*-PtC_3 structure is assigned to all isomers. In agreement with previous studies, the reso-

Table 1
Selected bond lengths (Å) and angles (°)

Bond lengths			
Pt–C(2)	2.008(5)	Pt–C(1)	2.078(6)
Pt–N	2.197(4)	Pt–P	2.2949(13)
P–C(41)	1.828(4)	P–C(21)	1.831(6)
P–C(31)	1.838(6)	S–C(2)	1.703(6)
S–C(5)	1.714(6)	N–C(6)	1.293(6)
N–C(7)	1.476(6)	C(2)–C(3)	1.392(8)
C(3)–C(4)	1.418(7)	C(3)–C(6)	1.454(7)
C(4)–C(5)	1.380(9)	C(7)–C(8)	1.531(7)
C(7)–C(11)	1.539(7)	C(11)–C(12)	1.361(8)
C(11)–C(20)	1.431(8)	C(12)–C(13)	1.412(10)
C(13)–C(14)	1.344(10)	C(14)–C(15)	1.417(10)
C(15)–C(16)	1.414(9)	C(15)–C(20)	1.434(8)
C(16)–C(17)	1.339(12)	C(17)–C(18)	1.429(11)
C(18)–C(19)	1.364(9)	C(19)–C(20)	1.419(8)
Bond angles			
C(2)–Pt–C(1)	90.4(3)	C(2)–Pt–N	77.5(2)
C(1)–Pt–N	167.0(2)	C(2)–Pt–P	175.4(2)
C(1)–Pt–P	86.3(2)	N–Pt–P	105.99(11)
C(41)–P–C(21)	103.8(2)	C(41)–P–C(31)	105.4(3)
C(21)–P–C(31)	102.4(2)	C(41)–P–Pt	112.5(2)
C(21)–P–Pt	120.2(2)	C(31)–P–Pt	111.1(2)
C(2)–S–C(5)	95.1(3)	C(6)–N–C(7)	119.9(4)
C(6)–N–Pt	112.5(3)	C(7)–N–Pt	127.3(3)
C(3)–C(2)–S	107.3(4)	C(3)–C(2)–Pt	117.6(4)
S–C(2)–Pt	134.7(4)	C(2)–C(3)–C(4)	116.3(5)
C(2)–C(3)–C(6)	113.8(4)	C(4)–C(3)–C(6)	129.8(5)
C(5)–C(4)–C(3)	110.7(6)	C(4)–C(5)–S	110.6(4)
N–C(6)–C(3)	118.5(5)	N–C(7)–C(8)	107.7(4)
N–C(7)–C(11)	114.3(4)	C(8)–C(7)–C(11)	112.9(5)

nances at lower δ correspond to axial methyl groups *trans* to iodide and were assigned to a pair of diastereomers (C_{Pt}, R_C) and (A_{Pt}, R_C) (**5a** in Chart 1) arising from *trans* oxidative addition of methyl iodide to the platinum(II) centre. Their relative amounts (16.4 and 5.5%) could be deduced from averaged integration of the identified signals in NMR, although specific resonances could not be assigned individually to each diastereomer. The two more abundant isomers (39.9 and 38.2%) consist of a new pair of diastereomers (A_{Pt}, R_C) and (C_{Pt}, R_C) (**6a** in Chart 1) apparently arising from *cis* oxidative addition.

The reaction of racemic [PtMe{3-(±)-($C_{10}H_7$)-CHMeNCHC$_4$H$_2$S}SMe$_2$] (**3a**′) with methyl iodide was also monitored by ^{1}H-NMR. Again, four sets of resonances in the same ratio as for chiral compound **3a** were observed and assigned to the two pairs of diastereoisomers, each with its enantiomer.

It is generally accepted that the oxidative addition of alkyl halides to platinum(II) compounds gives *trans* stereochemistry and compounds with *cis* stereochemistry may be formed in a subsequent isomerization process [15,16]. A comparison with the results obtained for the analogous compound [PtMe{3-(*S*)-(PhCH-MeNCH)C$_4$H$_2$S}SMe$_2$] indicates for the more sterically demanding naphthyl group: (i) a higher degree of stereoselectivity in the initial *trans* oxidative addition—although subsequent isomerization yields nearly equal amounts of diastereomers **6a**—and (ii) a higher degree of the isomerization from **5a** to **6a**.

Oxidative addition of methyl iodide to chiral cyclometallated compound **4a** was monitored by ^{1}H- and ^{31}P-NMR in acetone and the products are depicted in Chart 1. In the early stages of the reaction only one isomer was detected (**7a**; 100% stereoselectivity). NMR parameters are consistent with the cyclometallated platinum(IV) compound [PtMe$_2$I{3-(*R*)-($C_{10}H_7$)CHMe-NCHC$_4$H$_2$S}PPh$_3$] (**7a**) in which the axial methyl group is *trans* to iodine and the PPh$_3$ ligand is *trans* to the thienyl group (J(PPt) = 1577 Hz). This consists of one single diastereomer but it is not possible to assign the absolute stereochemistry (C or A) at the octahedral platinum centre. As the reaction proceeded, new signals appeared and fully replaced the former ones within 18 h. The ^{31}P-NMR spectra reveals clearly the presence of a major resonance at $\delta = -12.08$ ppm (J(P–Pt) = 970 Hz) together with a much lower intensity signal (less than 15%) at $\delta = -6.05$ ppm (J(P–Pt) = 985 Hz). These were assigned according to the J(P–Pt) values to a pair of diastereomers (A_{Pt}, R_C) and (C_{Pt}, R_C) with the stereochemistry depicted in Chart 1 for **8a**. In the ^{1}H-NMR spectrum, only the resonances due to the major diastereomer of **8a** (ca. 90%) could be unambiguously assigned and the reduced coupling constant of the axial methyl to platinum (^2J(H–Pt) = 60 Hz) confirm a *trans* arrangement of the axial methyl with the PPh$_3$.

The reaction was also carried out in a preparative scale and gave a light yellow solid for which the elemental analysis was consistent with the formulation [PtMe$_2$I{3-(*R*)-($C_{10}H_7$)CHMeNCHC$_4$H$_2$S}PPh$_3$] and the ^{1}H- and ^{31}P-NMR spectra showed the presence of the two diastereoisomers of compound **8a** in relative amounts ca. 90 and 10%.

The reaction of racemic [PtMe{3-((±)-($C_{10}H_7$)-CHMeNCHC$_4$H$_2$S}PPh$_3$] (**4a**′) with methyl iodide was also studied by NMR and results were identical to those obtained for chiral compound **4a**.

*2.2. Oxidative addition of methyl iodide to chiral cyclometallated platinum(II) compounds [PtMe{3-(R)-($C_{10}H_7$)CHMeNCHAr}PPh$_3$] (Ar = C_6H_4 (**4b**), 2-FC_6H_3 (**4c**), 2-CF$_3$C$_6$H$_3$ (**4d**))*

In order to compare the results obtained for the thienyl system with those for other aromatic systems as well as to study the effect of substituents in the aryl ring, we prepared new chiral cyclometallated platinum(II) derived from the imines (*R*)-($C_{10}H_7$)-CHMeNCHC$_6$H$_5$ (**2b**), (*R*)-($C_{10}H_7$)CHMeNCH(2-FC$_6$H$_4$) (**2c**) and (*R*)-($C_{10}H_7$)CHMeNCH(2-CF$_3$C$_6$H$_4$) (**2d**).

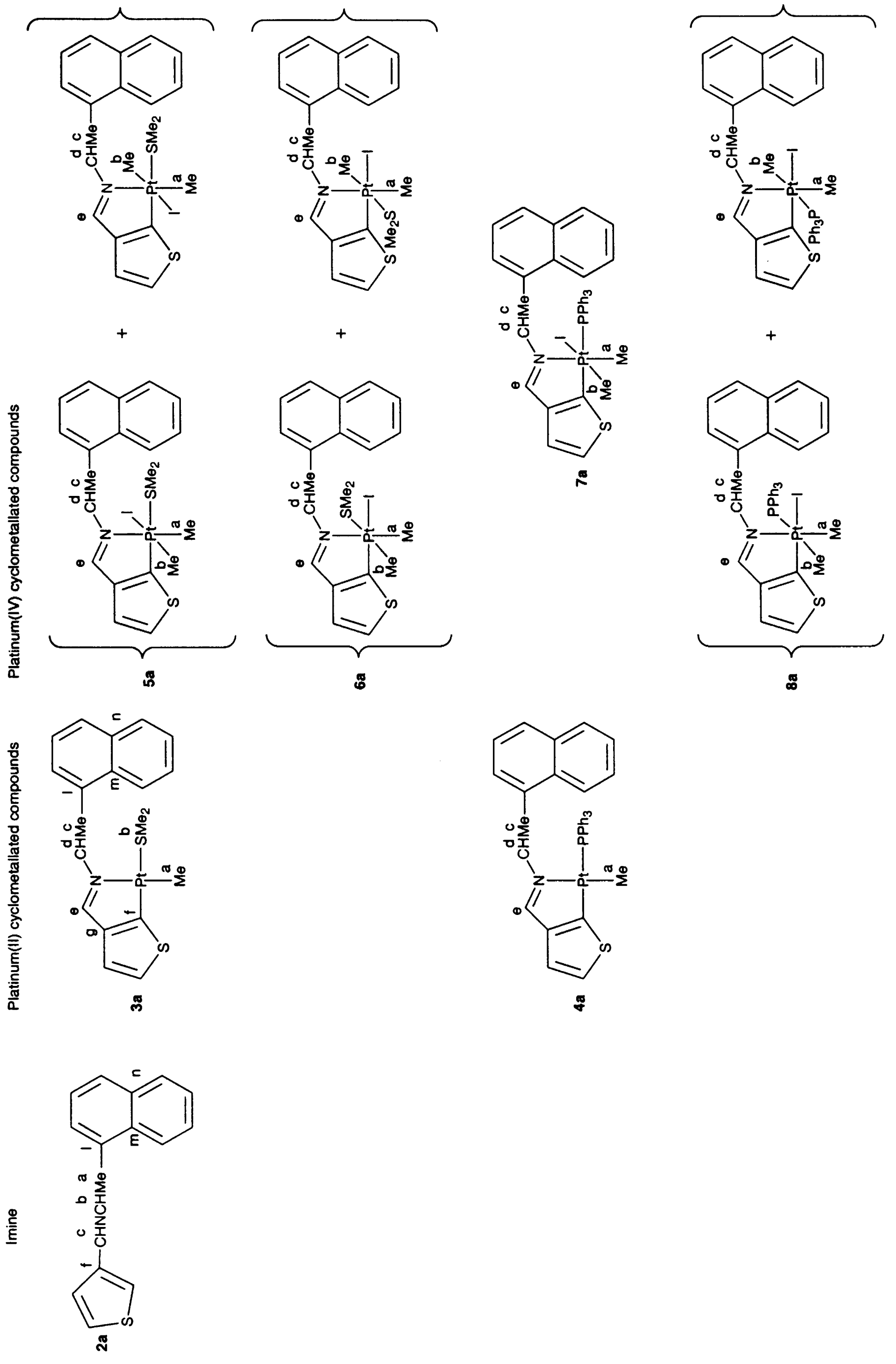
Imine
Platinum(II) cyclometallated compounds
Platinum(IV) cyclometallated compounds
2a
3a
4a
5a
6a
7a
8a

Chart 1.

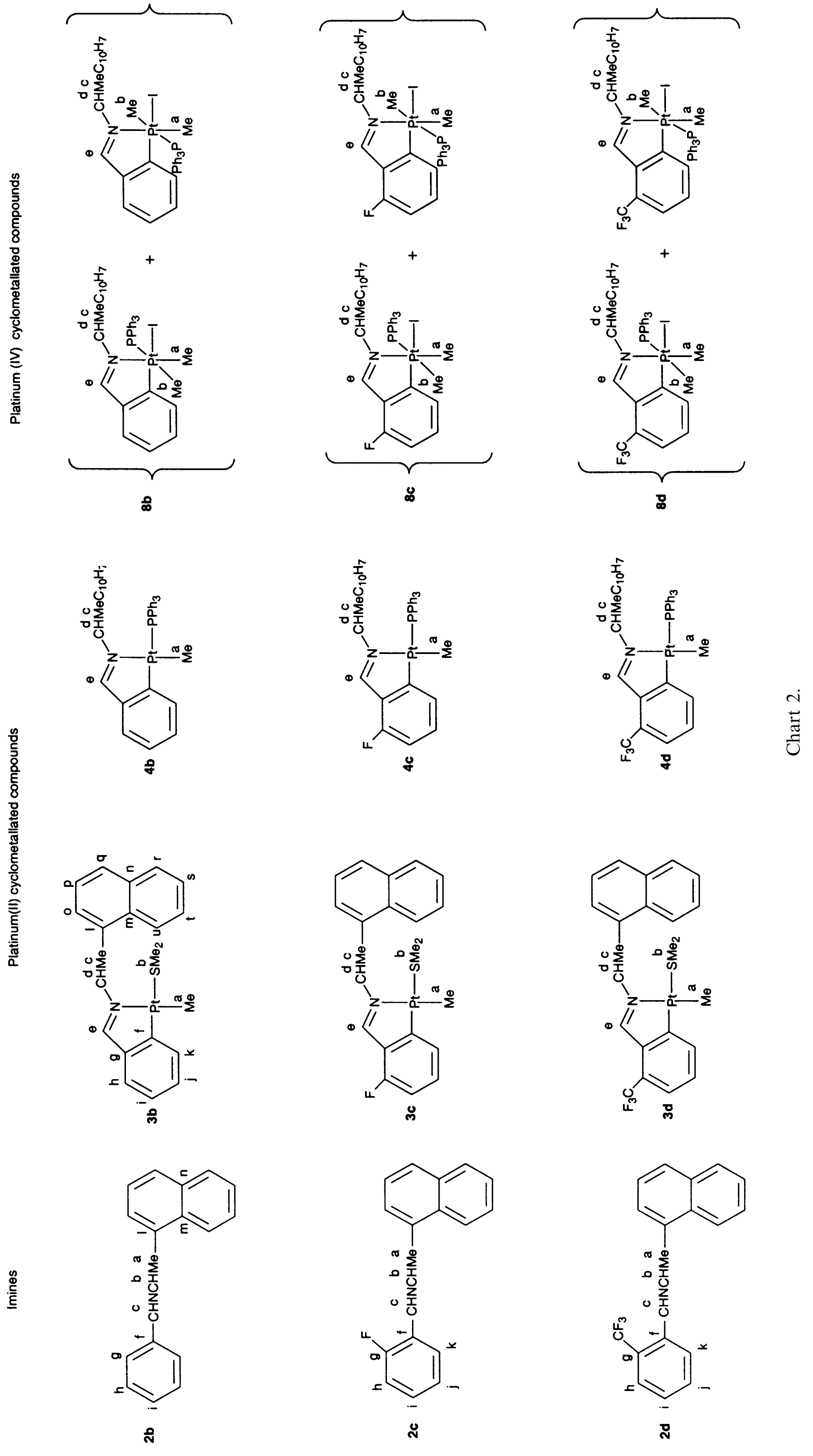
Imines
Platinum(II) cyclometallated compounds
Platinum (IV) cyclometallated compounds
2b
2c
2d
3b
3c
3d
4b
4c
4d
8b
8c
8d
CHNCHMe
CHMe
SMe2
PPh3
CHMeC10H7
Ph3P
Pt
Me
I
F
CF3
F3C

Chart 2.

The reactions of **2a**–**2d** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ were carried out in acetone. As reported for analogous ligands [17,18], activation of a C(Ar)–H bond at the phenyl ring followed by methane elimination gave chiral cyclometallated platinum(II) compounds $[PtMe\{3\text{-}(R)\text{-}(C_{10}H_7)CHMeNCHAr\}SMe_2]$ ($Ar = C_6H_4$ (**3b**), $2\text{-}FC_6H_3$ (**3c**), $2\text{-}CF_3C_6H_3$ (**3d**)) containing a dangling naphthalenyl group. Addition of PPh_3 to compounds **3b**–**3d** in acetone produced the corresponding cyclometallated compounds $[PtMe\{3\text{-}(R)\text{-}(C_{10}H_7)\text{-}CHMeNCHAr\}PPh_3]$ ($Ar = C_6H_4$ (**4b**), $2\text{-}FC_6H_3$ (**4c**), $2\text{-}CF_3C_6H_3$ (**4d**)). Compounds **3** and **4** were characterized by NMR spectroscopies and elemental analysis. Data are consistent with the proposed formulae shown in Chart 2 in which the imine acts as a [C,N] donor ligand and the coordination sphere of the platinum(II) is completed with a methyl group and either a SMe_2 (compounds **3**) or a PPh_3 (compounds **4**) ligand.

Oxidative addition of methyl iodide to chiral compounds **4b**–**4d** was carried out in acetone and the obtained products **8b**–**8d** are depicted in Chart 2. When the reactions were monitored by ^1H- and ^{31}P-NMR spectroscopies, the presence of two platinum(IV) diastereomers, formally arising from *cis*-oxidative addition of the methyl iodide was observed from the early stages of the reaction. Their relative amounts (85 and 15%) remained constant. According to previous studies [6,13], it might be assumed that the oxidative addition gives *trans* stereochemistry and is followed by a very fast isomerization process. Since the final proportion of isomers is similar to that obtained for **4a** we might suggest that the initial *trans* oxidative addition should also be highly stereoselective for the phenyl systems.

The oxidative addition of methyl iodide to **4c** and **4d** took place along with formation of a small (**4c**) to fair (**4d**) amount of $[PPh_3Me]I$, which could be easily detected by NMR [19] and prevents the possibility of obtaining good elemental analyses for **8d**. Due to the electron-withdrawing ability of fluoro- or trifluoromethyl groups, the oxidative addition to the platinum(II) centre is less favoured, which leads to some degree of decomposition, which includes formation of phosphonium salt and metallic platinum. Nevertheless, the same ratio of the isomers was obtained for all the groups under study, which can be related to the fact that the substituents of the aryl ring lie in the plane of the metallacycle and are not sterically significant.

From their relative integrated intensities, each set of signals in the NMR spectra could be assigned to an individual isomer although it is not possible to assign the absolute configurations. Both ^2J(H–Pt) for the axial methyl and J(P–Pt) values are consistent with a *trans* arrangement of the axial methyl with the PPh_3 ligand. As shown in Table 2, for all compounds under study both the axial methyl group (Me^b) and the methyl group bound to the chiral carbon atom (Me^c) are shifted upfield for the major diastereoisomer when compared to the minor diastereoisomer. An increase in J(PPt) value is also observed for the minor isomer in all cases. The consistency of NMR data suggest that the major and minor isomer adopt the same conformation for all the compounds.

2.3. Intramolecular oxidative addition of C(aryl)–X bonds of chiral imines

In order to compare the stereochemistry of intra-versus intermolecular oxidative addition reactions we extended our studies to chiral imines $(R)\text{-}(C_{10}H_7)\text{-}CHMeNCH(2\text{-}BrC_6H_4)$ (**2e**) and $(R)\text{-}(C_{10}H_7)\text{-}CHMeNCH(2,6\text{-}Cl_2C_6H_3)$ (**2f**). There have been several reports of the intramolecular oxidative addition of aryl–halogen bonds to a platinum substrate, and recently the stereochemistry of such reactions has been addressed [20].

Table 2
Selected ^1H- and ^{31}P-NMR data for compounds **8** [a]

	$\delta(Me^a)$ $[^2J(HPt)]$	$\delta(Me^b)$ $[^2J(HPt)]$	δ (Me)	δ(CHN) $[^3J(HPt)]$	δ(P) $[J(PPt)]$
8a major	1.65 (69)	1.10 (60)	0.91	8.23 (46)	−12.08 (970)
8a minor [b]					−6.05 (985)
8b major	1.44 (71)	0.99 (62)	0.99	8.97 (49)	−9.39 (982)
8b minor	1.40 (70)	1.42 (60)	1.90	8.86 (49)	−3.95 (1011)
8c major	1.46 (70)	1.00 (61)	1.10	9.06 (48)	−9.85 (984)
8c minor	1.44 (70)	1.42 (60)	1.97	8.87 (48)	−4.11 (1007)
8d major	1.49 (70)	0.97 (61)	1.11	9.01(49)	−11.13 (982)
8d minor	1.48 (70)	1.40 (60)	1.71	8.82 (48)	−4.63 (1013)
8e major	1.30 (70)	0.76 (60)	1.00	8.95 (49)	−6.53 (976)
8e minor	1.34 (70)	1.21 (60)	2.02	8.50 (48)	−2.55 (1006)
8f major	1.25 (69)	0.64 (60)	1.14	9.13 (50)	−5.25 (926)
8f minor	1.35 (70)	1.12 (60)	2.22	9.08 (50)	−1.36 (975)

[a] δ in parts per million, J in Hertz, in acetone-d_6.

[b] ^1H-NMR data not assigned for the minor isomer.

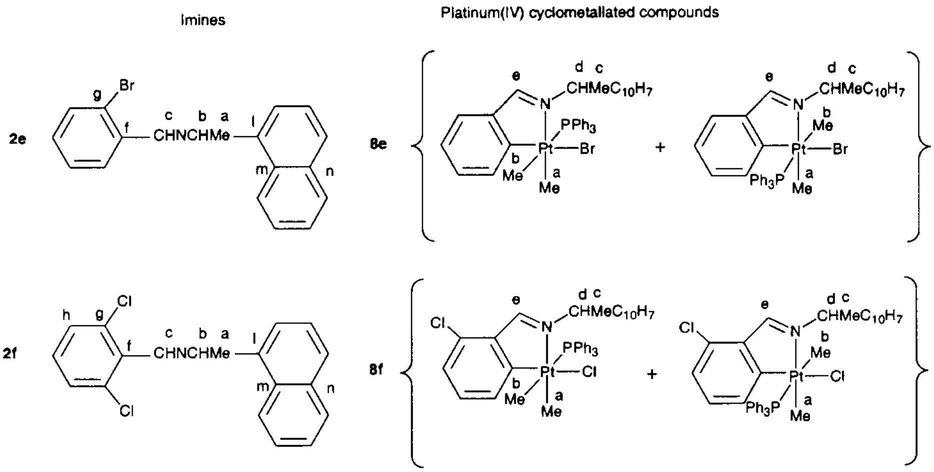

Chart 3.

In agreement with previous results [17,18], the reaction of ligands **2e** and **2f** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ is expected to produce intramolecular oxidative addition of C–Br and C–Cl bonds, respectively, to yield platinum(IV) compounds containing a chelate [C,N] ligand. The reactions were carried out in acetone and subsequent addition of PPh_3 produced platinum(IV) compounds $[PtMe_2Br\{3\text{-}(R)\text{-}(C_{10}H_7)CHMeNCHC_6H_4\}PPh_3]$ (**8e**) and $[PtMe_2Cl\{3\text{-}(R)\text{-}(C_{10}H_7)CHMeNCH(C_6H_3Cl\}PPh_3]$ (**8f**), which were characterized by NMR spectroscopies and elemental analyses.

A pair of diastereomers (A_{Pt}, R_C) and (C_{Pt}, R_C) with a *fac*-PtC_3 geometry are possible and as evidenced from NMR, the relative amounts of the two diastereomers are 85 and 15% for **8e** and 60 and 40% for **8f**. The NMR data are fully consistent with those obtained for compounds **8a**–**8d** and upfield shifts of the axial methyl–platinum (Me^b) and the methyl substituent of the chiral carbon (Me^c) are observed for the major isomer. Therefore, the stereochemistries depicted in Chart 3 formally arising from *trans* oxidative addition of the C(aryl)–halogen bond can be assigned to **8e** and **8f**. It is not evident however if *trans* intramolecular oxidative addition takes place or if *cis* addition is followed by isomerization of either the resulting platinum(IV) compounds or the triphenylphosphine derivatives.

The bromo derivative proportions of the final diastereomers are similar to those observed for the intermolecular oxidative addition. It seems likely that the smaller size of the chlorine atom when compared to bromine or iodine atoms is responsible for the lower stereoselectivity observed in the formation of **8f**.

3. Conclusions

A high degree of stereoselectivity has previously been reported in the oxidative addition of alkyl halides to $[PtMe\{1\text{-}(N{=}CHC_6H_4)\text{-}2\text{-}(N{=}CHC_6H_5)C_6H_{10}\}]$ in which a locked conformation results from the presence of a [N,N,C] donor tridentate system [2]. For compound **4a**, containing a bidentate [C,N] chelate system and a chiral carbon in a dangling group, 100% stereoselectivity has been observed in the initial *trans* oxidative addition of methyl iodide. This result can be related to the locked conformation resulting from steric hindrance between the bulky PPh_3 ligand and the naphthyl group, which hinders the approach of CH_3I to one side of the platinum(II) substrate. Subsequent isomerization of the resulting platinum(IV) compound places the triphenylphosphine in an axial position in order to minimize steric effects, thus some loss of diastereoselectivity occurs, along with the reduction of steric congestion at the metal centre. This yields a pair of diastereomers in relative amounts 90 and 10%. Since similar proportions (85 and 15%) of final diastereomers were obtained for the phenyl derivatives **4b**–**4d**, the oxidative addition of methyl iodide to these systems probably follows the same path. The lower *trans* influence of the thienyl when compared to the phenyl group [13] slows down the isomerization step and a clearer picture of the intermolecular oxidative addition is obtained for **4a**. The close relationship of the stereoselectivity with the relative steric hindrance of the studied systems is evidenced by the lower stereoselectivity obtained when smaller ligands such as SMe_2 (**5a**/**6a**) or chlorine (**8f**) are present in the platinum(IV) coordination sphere.

4. Experimental

4.1. Instrumentation

^{1}H-, ^{13}C-{^{1}H}-, ^{31}P-{^{1}H}- and ^{19}F-NMR spectra were recorded using Varian Gemini 200 (^{1}H, 200 MHz; ^{13}C, 50.28), Varian Unity 300 (^{13}C, 75.43 MHz; ^{19}F, 282.26), Varian 500 (^{1}H, 500 MHz) and Bruker 250 (^{31}P, 101.25 MHz) spectrometers, and referenced to $SiMe_4$ (^{1}H, ^{13}C), H_3PO_4 (^{31}P) and CF_3COOH (^{19}F). δ Values are given in ppm and J values in Hz. Microanalyses and FABMS were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona.

4.2. Preparation of compounds

Compound $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (**1**) was prepared as reported [21].

4.2.1. Synthetic procedure for compounds 2

The compounds (*R*)-($C_{10}H_7$)CHMeNCHAr (**2**) were prepared by the reaction of 0.5 g (2.92 mmol) of (*R*)-(+)-1-(1-naphthyl)ethylamine with the equimolar amount of the corresponding aldehyde (**2a**, 0.327 g; **2b**, 0.310 g; **2c**, 0.362 g; **2d**, 0.508 g; **2e**, 0.540 g; **2f**, 0.511 g) in refluxing EtOH (20 ml). After 4 h, the solvent was removed in a rotary evaporator to yield white solids. Racemic ($C_{10}H_7$)CHMeNCHC_4H_3S (**2a′**) was prepared by an analogous procedure from (±)-1-(1-naphthyl)ethylamine. **2a**: Ar = C_4H_3S. Yield 0.65 g (84%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.73$ [d, $J(H^aH^b) = 6.8$, H^a]; 5.30 [q, $J(H^a-H^b) = 6.8$, H^b]; {7.31 [dd, $J(H-H) = 5; 3$, 2H]; 7.44–7.65 [m, 4H]; 7.74–7.90 [m, 3H]; 8.20 [d, $J(H-H) = 8$, 1H], aromatics}; 8.41 [s, H^c]. ^{13}C-NMR (50.28, $CDCl_3$): $\delta = 24.43$ [C^b]; 65.33 [C^a]; {123.55, 123.96, 125.25, 125.60, 125.74, 125.93, 126.19, 127.28, 128.28, 128.85, [130.59, 133.90, 140.73, 140.93, $C^{f,l,m,n}$]; aromatics}; 153.92[C^c].

2b: Ar = C_6H_5. Yield 0.6 g (79%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.74$ [d, $J(H^a-H^b) = 6.6$, H^a]; 5.36 [q, $J(H^a-H^b) = 6.6$, H^b]; {7.15–7.29 [m, 3H]; 7.39–7.54 [m, 4H]; 7.74–7.89[m, 4H]; 8.25 [d, $J(H-H) = 8$, 1H], aromatics}; 8.42 [s, H^c]. ^{13}C-NMR (50.28, $CDCl_3$): $\delta = 24.55$ [C^b]; 65.54 [C^a]; {123.52, 123.94, 125.23, 125.60, 125.72, 127.24, 128.14, [128.19, 128.46, $C^{g,h}$], 128.85, 130.52, [128.96, 133.88, 136.37, 141.03, $C^{f,l,m,n}$], aromatics}; 159.55 [C^c]. **2c**: Ar = 2-FC_6H_4. Yield 0.7 g (86%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.74$ [d, $J(H^a-H^b) = 7$, H^a]; 5.39 [q, $J(H^a-H^b) = 7$, H^b]; {7.01–7.23 [m, 2H]; 7.34–7.58 [m, 4H]; 7.74–7.90 [m, 3H]; 8.15 [m, 1H]; 8.26[d, $J(H-H) = 8$, 1H], aromatics}; 8.77 [s, H^c]. ^{13}C-NMR (50.28, $CDCl_3$): $\delta = 24.62$ [C^b]; 66.11 [C^a]; {115.60 [d, $J(CF) = 21$, C^h]; 123.45, 123.86, 124.21 [d, $J(HF) = 4$, C^i], 125.26, 125.59, 125.76, 127.31, 127.85 [d, $J(CF) = 3$, C^j], 128.85, 130.47, 132.06, 133.90, 140.88, aromatics}; 152.91 [C^c]. ^{19}F-NMR (282.26 MHz, $CDCl_3$): $\delta = -166.72$ [m]. **2d**: Ar = 2-$CF_3C_6H_4$. Yield 0.7 g (76%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.75$ [d, $J(H^a-H^b) = 7$, H^a]; 5.42 [q, $J(H^a-H^b) = 7$, H^b]; {7.22 [m, 2H]; 7.44–7.64 [m, 5H]; 7.82 [m, 2H]; 8.25 [d, $J(H-H) = 7$, 1H]; 8.34 [d, $J(H-H) = 7$, 1H], aromatics}; 8.83 [d, $J(H-H) = 2$, H^c]. **2e**: Ar = 2-BrC_6H_4. Yield 0.8 g (81%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.75$ [d, $J(H^a-H^b) = 6.6$, H^a]; 5.42 [q, $J(H^a-H^b) = 6.6$, H^b]; {7.20–7.57 [m, 6H]; 7.75–7.90 [m, 3H]; 8.17 [dd, $J(HH) = 8;2$, 1H]; 8.27 [d, $J(HH) = 8$, 1H], aromatics}; 8.83 [s, H^c]. ^{13}C-NMR (50.28, $CDCl_3$): $\delta = 24.64$ [C^b]; 65.83 [C^a]; {123.45, 123.82, 125.29, 125.60, 125.79, 127.34, 127.51, 128.88, 128.98, 131.67, 132.88, [125.03, 127.60, 130.49, 133.91, 134.72, $C^{f,l,m,n}$], aromatics}; 158.71 [C^c].

2f: Ar = 2,6-$C_6H_3Cl_2$. Yield 0.75 g (78%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.80$ [d, $J(H^aH^b) = 7$, H^a]; 5.51 [q, $J(H^aH^b) = 7$, H^b]; {7.19–7.35 [m, 3H]; 7.45–7.57 [m, 3H]; 7.62–7.91 [m, 3H]; 8.22 [d, $J(HH) = 7$, 1H], aromatics}; 8.56 [s, H^c]. ^{13}C-NMR (50.28, $CDCl_3$): $\delta = 24.21$ [C^b]; 66.19 [C^a]; {123.55, 124.17, 125.31, 125.61, 125.81, 127.49, 128.51[C^h], 128.85, 130.14, [130.58, 133.16, 133.87, 134.60, 139.68, $C^{f,g,j,k,l}$], aromatics}; 155.85 [C^c].

4.2.2. Synthetic procedure for the compounds 3a–3d

Compounds [PtMe{(*R*)-($C_{10}H_7$)CHMeNCHR}SMe_2] (**3**) were obtained by adding a solution of 3.5×10^{-4} mol of the corresponding imine (**2a**, 93 mg; **2b**, 91 mg; **2c**, 97 mg; **2d**, 114 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 3 h (**3a**) or 16 h (**3b**–**3d**) at room temperature (r.t.) and the acetone was removed in a rotary evaporator. The residue was washed with hexane and dried in vacuum to yield orange (**3a**) or yellow (**3b**–**3d**) solids. Racemic [PtMe{($C_{10}H_7$)CHMeNCHC_4H_2S}SMe_2] (**3a′**) was prepared in an analogous way from racemic **2a′**. **3a**: R = C_4H_2S. Yield 140 mg (75%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 1.12$ [s, $^2J(Pt-H) = 78$, Me^a]; 1.79 [d, $J(H^c-H^d) = 7$, H^c]; 1.95 [s, $^3J(H^b-Pt) = 30$, H^b]; 6.02 [q, $J(H^c-H^d) = 7$, H^d]; {7.19 [m, 2H]; 7.49 [m, 4H], 7.85 [m, 2H], 8.06 [d, $J(H-H) = 8$, 1H], aromatics}; 8.39 [s, $^3J(Pt-H^e) = 54$, H^e]. ^{13}C-NMR (75.43, $CDCl_3$): $\delta = -21.25$ [$J(CPt) = 888$, C^a]; 18.91 [C^b]; 20.02 [C^c]; 58.53 [C^d]; {129.16, 130.97, 134.06, 138.44, 148.47, $C^{f,g,l,m,n}$}; {123.21, 123.83, 124.07, 125.14, 125.39, 125.57, 126.32, 127.96, 128.67, aromatics}; 163.57 [$J(CPt) = 71$, C^e]. Anal. Found: C, 44.6; H, 4.4; N, 2.6. Calc. for $C_{20}H_{23}NPtS_2$: C, 44.77; H, 4.32; N, 2.61%. **3b**: R = C_6H_4. Yield 140 mg (76%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 0.91$ [s, $^2J(Pt-H) = 83$, Me^a]; 1.80 [d, $J(H^c-H^d) = 7$, H^c]; 2.04 [s, $^3J(H^b-Pt) = 26$, H^b]; 6.21 [q, $J(H^c-H^d) = 7$, H^d]; {6.92 [td, $J(H-H) = 6;1$, 1H]; 7.14 [td, $J(H-H) = 8;1$, 1H], 7.29–7.32 [m, 1H], 7.44–7.62 [m, 4H], 7.86–7.96 [m, 3H], 8.19 [d, $J(H-H) = 9$, 1H], aromatics}; 8.62 [s, ^{3}J(Pt–H^{e}) = 57, H^{e}]. ^{13}C-NMR (75.43, acetone-d_6): $\delta = -14.65$ [C^{a}]; 18.67 [C^{b}]; 19.95 [C^{c}]; 58.76 [J(CPt) = 21, C^{d}]; 127.82 [J(CPt) = 38, C^{i}]; 122.51 [C^{h}]; 130.01 [J(CPt) = 72, C^{j}]; 131.43 [J(CPt) = 100, C^{k}]; {134.11, 138.05, C^{f,g}}; {123.85, 124.24, 125.14, 125.62, 126.36, 128.12, 128.69, C^{o,p,q,r,s,t,u}}; {148.86, 156.10, C^{l,m,n}}; 171.91 [J(CPt) = 83, C^{e}]. Anal. Found: C, 49.7; H, 4.8; N, 2.6. Calc. for $C_{22}H_{25}NPtS$: C, 49.80; H, 4.75; N, 2.64%. **3c**: R = 2-FC_6H_3. Yield 150 mg (78%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 0.95$ [s, ^{2}J(Pt–H) = 83, Me^{a}]; 1.84 [d, J(H^{c}–H^{d}) = 7, H^{c}]; 2.08 [s, ^{3}J(H^{b}–Pt) = 28, H^{b}]; 6.29 [q, J(H^{c}–H^{d}) = 7, H^{d}]; {6.64 [dd, J(H–F) = 10; J(H–H) = 8, 1H]; 7.21–7.42 [m, 3H], 7.51–7.63 [m, 3H], 7.93 [m, 2H], 8.18 [d, J(H–H) = 8, 1H], aromatics}; 8.85 [s, ^{3}J(Pt–H^{e}) = 58, H^{e}]. ^{19}F-NMR (282.26 MHz, $CDCl_3$): $\delta = -157.23$ [dd, J(F–Pt) = 59.3, J(F–H) = 11; 6]. FABMS (NBA): 533 [M − CH_3], 470 [M − CH_3–SMe_2]. Anal. Found: C, 48.6; H, 4.5; N, 2.5. Calc. for $C_{22}H_{24}FNPtS$: C, 48.17; H, 4.41; N, 2.55%. **3d**: R = 2-$CF_3C_6H_3$. Yield 160 mg (77%). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.01$ [s, ^{2}J(Pt–H) = 80, Me^{a}]; 1.83 [d, J(H^{c}–H^{d}) = 6, H^{c}]; 1.88 [s, ^{3}J(H^{b}–Pt) = 24, H^{b}]; 6.15 [q, J(H^{c}–H^{d}) = 6, H^{d}]; {7.35 [m, 3H]; 7.45 [t, J(H–H) = 8, 1H]; 7.55 [td, J(H–H) = 8; 2, 3H]; 7.81 [d, J(H–H) = 8, 1H]; 7.89 [d, J(H–H) = 10, 1H]; 7.98 [m, 1H]; 8.08 [d, J(H–H) = 8, 1H], aromatics}; 8.85 [s, ^{3}J(Pt–H^{e}) = 58, H^{e}]. Anal. Found: C, 46.2; H, 4.1; N, 2.3. Calc. for $C_{23}H_{24}F_3NPtS$: C, 46.15; H, 4.04; N, 2.34%.

*4.2.3. Synthetic procedure for the compounds **4a**–**4d***

Compounds [PtMe{($C_{10}H_7$)CHMeNCHR}PPh_3] (**4**) were obtained by the reaction of 50 mg (**3a**: 0.93×10^{-4} mol; **3b**: 0.94×10^{-4} mol; **3c**: 0.91×10^{-4} mol; **3d**: 0.83×10^{-4} mol) of the corresponding compound **3** with 25 mg (0.95×10^{-4} mol) of PPh_3 in acetone (20 ml). After continuous stirring at r.t. during 3 h, the solvent was removed in a rotary evaporator and the resulting yellow solid was filtered, washed with hexane and Et_2O and dried in vacuum. Racemic [PtMe{($C_{10}H_7$)CHMeNCHC_4H_2S}PPh_3] (**4a′**) was prepared in an analogous way from racemic **3a′**. **4a**: R = C_4H_2S. Yield 48 mg (70%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 0.93$ [d, ^{3}J(P–H) = 8, ^{2}J(Pt–H) = 80, Me^{a}]; 1.29 [d, J(H^{c}–H^{d}) = 7, H^{c}]; 4.75 [q, J(H^{c}–H^{d}) = 7, H^{d}]; {7.09–7.20 [m, 1H]; 7.35–7.45 [m, 15H], 7.70–7.86 [m, 8H], aromatics}; 8.14 [s, ^{3}J(Pt–H^{e}) = 55, H^{e}]. ^{31}P-NMR (101.25 MHz, acetone-d_6): $\delta = 30.01$ [s, ^{1}J(P–Pt) = 2589]. FABMS (NBA): 737 [M], 721 [M − CH_3]. Anal. Found: C, 58.6; H, 4.4; N, 1.9. Calc. for $C_{36}H_{32}NPPtS$: C, 58.69; H, 4.38; N, 1.90%. **4b**: R = C_6H_4. Yield 50 mg (73%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 0.70$ [d, ^{3}J(P–H) = 8, ^{2}J(Pt–H) = 83, Me^{a}]; 1.31 [d, J(H^{c}–H^{d}) = 7, H^{c}]; 4.86 [q, J(H^{c}–H^{d}) = 7, H^{d}]; {6.93 [t, J(H–H) = 9, 1H]; 7.19 [m, 1H], 7.39–7.47 [m, 15H], 7.88–7.92 [m, 9H], aromatics}; 8.32 [s, ^{3}J(Pt–H^{e}) = 59, H^{e}]. ^{31}P-NMR (101.25 MHz, acetone-d_6): $\delta = 33.50$ [s, ^{1}J(P–Pt) = 2149]. Anal. Found: C, 62.5; H, 4.6; N, 1.8. Calc. for $C_{38}H_{34}NPPt$: C, 62.46; H, 4.69; N, 1.92%. **4c**: R = 2-FC_6H_3. Yield 52 mg (76%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 0.73$ [d, ^{3}J(P–H) = 7, ^{2}J(Pt–H) = 82, Me^{a}]; 1.34 [d, J(H^{c}–H^{d}) = 7, H^{c}]; 4.89 [q, J(H^{c}–H^{d}) = 7, H^{d}]; {6.62 [dd, J(H–F) = 10; J(H–H) = 9, 1H]; 7.35–7.49 [m, 15H], 7.83–7.98 [m, 9H], aromatics}; 8.56 [s, ^{3}J(Pt–H^{e}) = 59, H^{e}]. ^{19}F-NMR (282.26 MHz, $CDCl_3$): $\delta = -157.55$ [dt, J(F–Pt) = 46, J(F–P) = 8, J(F–H) = 8; 6]. ^{31}P-NMR (101.25 MHz, acetone-d_6): $\delta = 32.95$ [d, J(P–F) = 8, ^{1}J(P–Pt) = 2213]. Anal. Found: C, 61.3; H, 4.6; N, 1.9. Calc. for $C_{38}H_{33}FNPPt$: C, 60.96; H, 4.44; N, 1.87%. **4d**: R = 2-$CF_3C_6H_3$. Yield 53 mg (80%). ^{1}H-NMR (200 MHz, acetone-d_6): $\delta = 0.75$ [d, ^{3}J(P–H) = 7, ^{2}J(Pt–H) = 82, Me^{a}]; 1.35 [d, J(H^{c}–H^{d}) = 7, H^{c}]; 4.95 [q, J(H^{c}–H^{d}) = 7, H^{d}]; {7.26 [d, J = 7; 4; 1, 1H]; 7.35–7.50 [m, 15H], 7.83–7.97 [m, 9H], aromatics}; 8.62 [s, ^{3}J(Pt–H^{e}) = 59, H^{e}]. ^{31}P-NMR (101.25 MHz, acetone-d_6): $\delta = 32.66$ [s, ^{1}J(P–Pt) = 2214]. Anal. Found: C, 58.5; H, 4.0; N, 1.5. Calc. for $C_{39}H_{33}F_3NPPt$: C, 58.64; H, 4.16; N, 1.75%.

4.2.4. Synthetic procedure for the intermolecular oxidative addition reactions

Compounds **5a**/**6a** were obtained from the reaction of 50 mg (0.93×10^{-4} mol) of **3a** with an excess of methyl iodide (0.1 ml) in acetone (10 ml). The mixture was stirred for 4 h at r.t., and the solvent was removed under vacuum to yield a light yellow solid. [$PtMe_2I${($C_{10}H_7$)CHMeNCHC_4H_2S}SMe_2] (**5a**/**6a**). Yield 48 mg (76%). ^{1}H-NMR (500 MHz, acetone-d_6): **5a**: Major isomer: $\delta = 0.71$ [s, ^{2}J(Pt–H) = 68, Me^{b}]; 1.41 [s, ^{2}J(Pt–H) = 68, Me^{a}]; 1.88 [d, J(H–H) = 7, H^{c}]; 6.59 [q, J(H–H) = 7, H^{d}]; 8.74 [s, ^{3}J(Pt–H) = 40, H^{e}]. Minor isomer: $\delta = 0.87$ [s, ^{2}J(Pt–H) = 68, Me^{b}]; 1.63 [s, ^{2}J(Pt–H) = 68, Me^{a}]. **6a**: Major isomer: $\delta = 1.44$ [s, ^{2}J(Pt–H) = 70, Me^{b}]; 1.68 [s, ^{2}J(Pt–H) = 68, Me^{a}]; 1.93 [d, J(H–H) = 6.5, H^{c}]; 6.79 [q, J(H–H) = 7, H^{d}]; 8.16 [s, ^{3}J(Pt–H) = 45, H^{e}]. Minor isomer: $\delta = 1.40$ [s, ^{2}J(Pt–H) = 70, Me^{b}]; 1.68 [s, ^{2}J(Pt–H) = 68, Me^{a}]; 1.93 [d, J(H–H) = 6.5, H^{c}]; 6.94 [q, J(H–H) = 7, H^{d}]; 8.05 [s, ^{3}J(Pt–H) = 43, H^{e}]. Anal. Found: C, 37.3; H, 3.9; N, 1.9. Calc. for $C_{21}H_{26}INPtS_2$: C, 37.17; H, 3.86; N, 2.06%.

Compounds [$PtMe_2I${($C_{10}H_7$)CHMeNCHR}PPh_3] (**8**) were obtained in an analogous way from compounds **4**. **8c** and **8d** were washed with tiny amounts of water prior to be dried under vacuum. **8a**: R = C_4H_2S. Yield 45 mg (75%). ^{1}H-NMR (500 MHz, acetone-d_6): Major isomer: $\delta = 0.91$ [d, J(H–H) = 7, H^{c}]; 1.10 [d, ^{3}J(H–P) = 7.6, ^{2}J(Pt–H) = 60, Me^{b}]; 1.65 [d, ^{3}J(H–P) = 7.6, ^{2}J(Pt–H) = 69, Me^{a}]; 6.61 [q, J(H–H) = 7, H^{d}]; 8.33 [s, ^{3}J(Pt–H) = 46, H^{e}]. ^{31}P-NMR (101.26

MHz, acetone-d_6): Major isomer: $\delta = -12.08$ [s, J(Pt–P) = 970]. Minor isomer: $\delta = -6.05$ [s, J(Pt–P) = 985]. FABMS (NBA): 847 [M − 2Me], 734 [M − I–CH$_3$], 720 [M − I]. Anal. Found: C, 50.4; H, 4.2; N, 1.5. Calc. for $C_{37}H_{35}INPPtS$: C, 50.57; H, 4.01; N, 1.59%. **8b**: R = C_6H_4. Yield 45 mg (75%).^{1}H-NMR (500 MHz, acetone-d_6): Major isomer: $\delta = 0.99$ [d, ^3J(HP) = 7.5, ^2J(Pt–H) = 62, Me^b]; 0.99 [d, J(H–H) = 7, H^c]; 1.44 [d, ^3J(H–P) = 7.5, ^2J(Pt–H) = 71, Me^a]; 6.85 [m, H^d]; {6.45 [d, J(H–H) = 8, J(H–Pt) = 42, 1H], 8.24 [d, J(H–H) = 8, 1H], aromatics}; 8.97 [s, ^3J(Pt–H) = 49, H^e]. Minor isomer: $\delta = 1.40$ [d, ^3J(H–P) = 8, ^2J(Pt–H) = 70, Me^a]; 1.42 [d, ^3J(HP) = 7.5, ^2J(Pt–H) = 60, Me^b]; 1.90 [d, J(H–H) = 7, H^c]; 6.78 [m, H^d]; 8.36 [d, J(H–H) = 7, 1H aromatic]; 8.86 [s, ^3J(Pt–H) = 49, H^e]. ^{31}P-NMR (101.26 MHz, acetone-d_6): Major isomer: $\delta = -9.39$ [s, J(Pt–P) = 982]. Minor isomer: $\delta = -3.95$ [s, J(Pt–P) = 1011]. Anal. Found: C, 53.9; H, 4.4; N, 1.5. Calc. for $C_{39}H_{37}INPPt$: C, 53.68; H, 4.27; N, 1.60%. **8c**: R = 2-FC$_6$H$_3$. Yield 47 mg (79%). ^{1}H-NMR (500 MHz, acetone-d_6): Major isomer: $\delta = 1.00$ [d, ^3J(H–P) = 7.5, ^2J(Pt–H) = 61, Me^b]; 1.10 [d, J(H–H) = 7, H^c]; 1.46 [d, ^3J(H–P) = 8, ^2J(Pt–H) = 70, Me^a]; 6.52 [m, H^d]; {6.31 [d, J(H–H) = 7.5, J(H–Pt) = 41.5, 1H], 8.58 [m, 1H], aromatics}; 9.06 [s, ^3J(Pt–H) = 48, H^e]. Minor isomer: $\delta = 1.42$ [d, ^3J(HP) = 7.5, ^2J(Pt–H) = 60, Me^b]; 1.44 [d, ^3J(HP) = 8, ^2J(Pt–H) = 70, Me^a]; 1.97 [d, J(H–H) = 7, H^c]; 6.50 [m, H^d]; 8.87 [s, J(H–Pt) = 48, 1H aromatic]; 9.20 [s, H^e]. ^{31}P-NMR (101.26 MHz, acetone-d_6): Major isomer: $\delta = -9.85$ [s, J(Pt–P) = 984]. Minor isomer: $\delta = -4.11$ [s, J(Pt–P) = 1007]. ^{19}F-NMR (282.26 MHz, CDCl$_3$): Major isomer: $\delta = -158.39$ [dd, J(F–Pt) = 39, J(F–H) = 11; 6]. Minor isomer: $\delta = -158.06$ [dd, J(F–Pt) = 38, J(F–H) = 11; 6]. FABMS (NBA): 748 [M − Me–I]. Anal. Found: C, 52.3; H, 4.2; N, 1.5. Calc. for $C_{39}H_{36}FINPPt$: C, 52.59; H, 4.07; N, 1.57%. **8d**: R = 2-CF$_3$C$_6$H$_3$. Yield 46 mg (78%). ^{1}H-NMR (500 MHz, acetone-d_6): Major isomer: $\delta = 0.97$ [d, ^3J(H–P) = 7.5, ^2J(Pt–H) = 61, Me^b]; 1.11 [d, J(H–H) = 7, H^c]; 1.49 [d, ^3J(H–P) = 8.5, ^2J(Pt–H) = 70, Me^a]; 6.87 [m, H^d]; 9.01 [s, ^3J(Pt–H) = 49, H^e]. Minor isomer: $\delta = 1.40$ [d, ^3J(H–P) = 7.5, ^2J(Pt–H) = 60, Me^b]; 1.48 [d, ^3J(H–P) = 8, ^2J(Pt–H) = 70, Me^a]; 1.71 [d, J(H–H) = 6.5, H^c]; 8.82 [s, ^3J(Pt–H) = 48, H^e]. ^{31}P-NMR (101.26 MHz, acetone-d_6): Major isomer: $\delta = -11.13$ [s, J(Pt–P) = 982]. Minor isomer: $\delta = -4.63$ [s, J(Pt–P) = 1013].

The reactions of compound **4a** with methyl iodide were monitored by NMR in the following way, 10 μl of methyl iodide were added to 20 mg of the platinum(II) compound dissolved in 0.6 ml of acetone-d_6 in a 5mm NMR tube and ^{1}H- and ^{31}P-NMR spectra were taken, which allowed spectral characterization of **7a**. **7a**: R = C$_4$H$_2$S. ^{1}H-NMR (500 MHz, acetone-d_6): $\delta = 0.24$ [d, ^3J(H–P) = 6.6, ^2J(Pt–H) = 68, Me^b]; 1.52 [d, ^3J(H–P) = 7.6, ^2J(Pt–H) = 67, Me^a]; 1.75 [d, J(H–H) = 7, H^c]; 6.28 [q, J(H–H) = 7, H^d]; {6.42 [d, J(H–H) = 9, 1H], 7.01–7.89 [23H], aromatics}; 8.62 [s, ^3J(Pt–H) = 45, H^e]. ^{31}P-NMR (101.26 MHz, acetone-d_6): $\delta = -4.18$ [s, J(Pt–P) = 1577].

4.2.5. Synthetic procedure for the intramolecular oxidative addition reactions

Compounds **8e** and **8f** were prepared by the reaction of 100 mg (1.74×10^{-4} mol) of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (**1**) with 3.50×10^{-4} mol of the corresponding imine (**2e**: 118 mg; **2f**: 114 mg) in acetone (10 ml). The mixture was stirred for 5 h and 90 mg (3.50×10^{-4} mol) of PPh$_3$ were added. After 1 h, hexane (10 ml) was added and the resulting precipitate was collected by filtration, washed with hexane, and dried in vacuo. **8e**: R = 2-BrC$_6$H$_3$. Yield 150 mg (52%). ^{1}H-NMR (500 MHz, acetone-d_6): Major isomer: $\delta = 0.76$ [d, ^3J(HP) = 7.5, ^2J(Pt–H) = 60, Me^b]; 1.00 [d, J(H–H) = 7.5, H^c]; 1.30 [d, ^3J(H–P) = 8, ^2J(Pt–H) = 70, Me^a]; 6.84 [qd, J(H–H) = 7.5; 1.5, H^d]; {6.50 [d, J(H–H) = 8, J(H–Pt) = 42.5, 1H], 7.76 [d, J(H–H) = 8.5, 1H], 7.88 [d, J(H–H) = 8.5, 1H], 8.30 [d, J(H–H) = 8.5, 1H], aromatics}; 8.95 [s, ^3J(Pt–H) = 49, H^e]. Minor isomer: $\delta = 1.21$ [d, ^3J(H–P) = 7.5, ^2J(Pt–H) = 60, Me^b]; 1.34 [d, ^3J(HP) = 8, ^2J(Pt–H) = 70, Me^a]; 2.02 [d, J(H–H) = 7, H^c]; 6.95 [m, H^d]; 8.50 [s, ^3J(Pt–H) = 48, H^e]. ^{31}P-NMR (101.26 MHz, acetone-d_6): Major isomer: $\delta = -6.53$ [s, J(Pt–P) = 976]. Minor isomer: $\delta = -2.55$ [s, J(Pt–P) = 1006]. FABMS (NBA): 795 [M − 2Me], 730 [M − Me–Br], 715 [M − 2Me–Br]. Anal. Found: C, 56.6; H, 4.5; N, 1.7. Calc. for $C_{39}H_{37}BrNPPt$: C, 56.73; H, 4.52; N, 1.70%. **8f**: R = 2,6-Cl$_2$C$_6$H$_2$. Yield 155 mg (56%). ^{1}H-NMR (500 MHz, acetone-d_6): Major isomer: $\delta = 0.64$ [d, ^3J(HP) = 7.5, ^2J(Pt–H) = 60, Me^b]; 1.14 [d, J(H–H) = 7, H^c]; 1.25 [d, ^3J(H–P) = 8, ^2J(Pt–H) = 69, Me^a]; {6.58 [d, J(H–H) = 8, J(Pt–H) = 43, 1H], 6.63 [t, J(H–H) = 8, 1H], 6.68 [t, J(H–H) = 8, 1H], 7.81 [d, J(H–H) = 8.5, 1H], 8.39 [d, J(H–H) = 8.5, 1H], aromatics}; 9.13 [s, ^3J(Pt–H) = 50, H^e]. Minor isomer: $\delta = 1.12$ [d, ^3J(H–P) = 7.5, ^2J(Pt–H) = 60, Me^b]; 1.35 [d, ^3J(HP) = 8.5, ^2J(Pt–H) = 70, Me^a]; 2.22 [d, J(H–H) = 7, H^c]; 6.54 [d, J(H–H) = 8, J(Pt–H) = 45, H^d]; 9.08 [s, ^3J(Pt–H) = 50, H^e]. ^{31}P-NMR (101.26 MHz, acetone-d_6): Major isomer: $\delta = -5.25$ [s, J(Pt–P) = 926]. Minor isomer: $\delta = -1.36$ [s, J(Pt–P) = 975]. Anal. Found: C, 57.3; H, 4.6; N, 1.7. Calc. for $C_{39}H_{36}Cl_2NPPt$: C, 57.42; H, 4.45; N, 1.72%.

4.3. X-ray structure analysis

A yellow rectangular plate ($0.48 \times 0.21 \times 0.10$ mm) was selected. The crystallographic measurements were done on a Siemens P4 diffractometer using graphite-monochromatized Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation.

Table 3
Crystallographic data and structure refinement parameters

Empirical formula	$C_{36}H_{32}NPPtS$
Formula weight	736.75
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	10.684(2)
b (Å)	16.412(3)
c (Å)	17.089(3)
V (Å^3)	2996.2(9)
Z	4
D_{calc} (Mg m^{-3})	1.633
Absorption coefficient (mm^{-1})	4.832
F(000)	1456
Reflections collected	18 284
Independent reflections	8734 (0.0607)
Reflections observed	6965
Data/restraints/parameters	8734/0/362
Goodness-of-fit on F^2	1.037
$R_1(I>2\sigma(I))$	0.0394
wR_2 (all data)	0.0661
Largest difference peak and hole (e Å^{-3})	0.964, −0.613

The cell dimensions were determined at r.t., from a least-squares refinement of the angles 2θ, ω and χ obtained for 31 well-centred reflections. The data collection (half sphere) was made by the $2\theta/\omega$ scan technique ($2\theta_{max} = 60°$) using the XSCANS program [22]. The background time to scan time ratio was 0.5. The coordinates of the Pt atom were determined by direct methods and all the other non-hydrogen atoms were found by the usual Fourier methods. The refinement of the structure was done on F^2 by full-matrix least-squares analysis. The hydrogen atom positions were fixed in their calculated positions with $U_{eq} = 1.2U_{eq}$ (or 1.5 for methyl groups) of the carbon to which they are bonded. Corrections were made for absorption (semi-empirical from psi-scans), Lorentz and polarization effects. The residual peaks were located in the close environment of the platinum atom. The calculations were done using the Siemens SHELXTL system [22]. The refinement of the scale factor, coordinates and anisotropic temperature factors of all the non-hydrogen atoms converged to $R_1 = 0.0394$ (6965 observed reflection with $I > 2\sigma(I)$) and $wR_2 = 0.0661$ (all data). The absolute structure parameter was $-0.015(7)$. Further crystallographic details are provided in Table 3.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 161706 for compound **4a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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