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Novel platinum(II) compounds with *N*-benzylidenebenzylamines: Synthesis, crystal structures and the effect of *cis* or *trans* geometry on cycloplatination

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Dedicated to the memory of Xavier Solans; he will always be with us

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ABSTRACT

Coordination compounds with a *trans*-stereochemistry were prepared for ligands $(4-\text{ClC}_6\text{H}_4)\text{CH}=$ NCH₂(4'-ClC₆H₄) (**L**_a), (2,4,6-Me₃C₆H₂)CH=NCH₂(4'-ClC₆H₄) (**L**_b) and (2,6-Cl₂C₆H₃)CH=NCH₂(4'-ClC₆H₄) (**L**_c) and were shown to be precursors of the corresponding cyclometallated compounds. The reactions between *cis*-[PtCl₂(dmso)₂] and ligands ArCH=NCH₂(4'-ClC₆H₄) (Ar = 2-BrC₆H₄ (**L**_d); 2-ClC₆H₄ (**L**_c); C₆F₅ (**L**_f); 2,6-F₂C₆H₃ (**L**_g)) under previously described conditions for cycloplatination of *N*-benzylidenebenzyl-amines gave a cyclometallated compound only for imine **L**_f; the other imines produced coordination compounds with a *cis* arrangement from which cyclometallation could not be achieved. Formation of either *cis* or *trans* coordination compounds [PtCl₂(**L**)dmso] (**L** = *N*-benzylidenebenzylamine) can be related to steric effects and to the *E*/*Z* configuration of the C=N bond. All compounds were fully characterized including structure determinations for *trans*-[PtCl₂(4-ClC₆H₄)CH=NCH₂(4'-ClC₆H₄)]SOMe₂] (**2**c) and the amine derivative *trans*-[PtCl₂(4-ClC₆H₄)CH=NCH₂(4'-ClC₆H₄)]SOMe₂] (**2**) obtained as a by-product.

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1. Introduction

Cyclometallation of N-donor ligands by platinum and palladium has remained as one of the major topics in organometallic chemistry [1]. Recently *cis*-[PtCl₂(dmso)₂] has become an useful substrate for direct cycloplatination, and numerous examples have been reported including tridentate [C,N,X] (X = N [2], S [3] and O[4]) as well as bidentate [C,N] systems derived from imines [5], oximes [6], pyridines[7] or even tertiary amines leading to either mono [8] or dinuclear [9] compounds.

Coordination compounds [PtCl₂(**L**)dmso] (**L** = nitrogen donor ligand) with a *trans* geometry have been postulated as precursors to the cyclometallated derivatives [5c,10] and crystal structures of these compounds confirm the proposed *trans* arrangement [5c,8c,10,11]. However, these results do not address specifically whether only *trans* isomer of the precursor or also *cis* isomer may lead to successful cyclometallation.

In view of these facts, the synthesis of novel coordination compounds [PtCl₂(**L**)dmso] (**L** = nitrogen donor ligand) was envisaged in this work in order to ascertain whether their *cis* or *trans* arrangement is decisive for a successful cyclometallation process. We have recently reported the reactions of *cis*-[PtCl₂(dmso)₂] with bifunctional *N*-benzylidenebenzylamines of general formula ArCH- $NCH_2(4'-ClC_6H_4)$ leading to either *endo* (containing the imine functionality) or *exo* cyclometallated platinum compounds [12]. These ligands along with similar ones with *ortho* substituents of different bulk were selected for this study.

2. Results and discussion

2.1. Coordination compounds as precursors to cycloplatinated derivatives

Initial work was carried out for imines $(4-ClC_6H_4)CH=NCH_2(4'-ClC_6H_4)$ (L_a), $(2,4,6-Me_3C_6H_2)CH=NCH_2(4'-ClC_6H_4)$ (L_b) and $(2,6-Cl_2C_6H_3)CH=NCH_2(4'-ClC_6H_4)$ (L_c) for which cyclometallated derivatives **3a**, **3b** and **3c** (see Chart 1) have been previously prepared in a "one-pot" synthesis using *cis*-[PtCl_2(dmso)_2] as metallating agent [12]. The aim of isolating the corresponding coordination compounds is (i) to determine the *cis* or *trans* arrangement and (ii) to confirm that these compounds are intermediates in the cycloplatination process.

The reaction of the imine $4-\text{ClC}_6\text{H}_4\text{CH}=\text{NCH}_2(4'-\text{ClC}_6\text{H}_4)$ with $cis-[\text{PtCl}_2(\text{dmso})_2]$ in refluxing methanol for 4 h produced the corresponding aldehyde and the amine derivative $trans-[\text{PtCl}_2(4-\text{ClC}_6\text{H}_4\text{CH}_2\text{NH}_2)\text{SOMe}_2]$ (2) which was characterized crystallographically. This result suggests hydrolysis of the imine with adventitious water in the solvent, a process that has been reported for palladium or platinum compounds under metallation



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conditions [2a]. When the reaction was carried out in refluxing dry toluene, hydrolysis was avoided and a mixture of *trans* and *cis*-[PtCl₂((4-ClC₆H₄)CH=NCH₂(4'-ClC₆H₄))SOMe₂] (**2a** and **2a**' shown in Chart 1) was produced. Suitable crystals for structure resolution of the *trans* isomer were obtained. The ¹H NMR spectra of the *cis* and *trans* isomers display distinct features. For the *cis* isomer, both the methylene hydrogen atoms and the methyl groups of the dimethylsulfoxide ligand appear as non-equivalent which suggest a low symmetry, and the imine hydrogen displays a large *J*(H–Pt) value (117.4 Hz) which is consistent with the presence of a chloro

ligand in a *trans* position and with an *E* conformation¹ of the imine as confirmed by a 2D-NOESY experiment. Conversely, for the *trans* isomer both the methylene hydrogen atoms and the methyl groups of the dimethylsulfoxide ligand appear as equivalent and the J(H-Pt) for the imine hydrogen is reduced (84.5 Hz) compared to the *cis* isomer which is consistent with the presence of a dimethylsulfoxide li-

 $^{^{1}}$ Z/E conformation has been assigned as for the free imine (not taking into account the platinum coordination to the nitrogen).

gand in a *trans* position to the nitrogen atom. The presence of a cross-peak signal between the imine and the methylene protons in a 2D-NOESY NMR spectrum supports an E conformation across the C=N bond.

The reactions of imines \mathbf{L}_{b} and \mathbf{L}_{c} with cis-[PtCl₂(dmso)₂] were also studied in refluxing toluene and produced the corresponding compounds *trans*-[PtCl₂{(2,4,6-Me₃C₆H₂)CHNCH₂(4'-ClC₆H₄)}SOMe₂] (**2b**) and *trans*-[PtCl₂{(2,6-Cl₂C₆H₃)CHNCH₂(4'-ClC₆H₄)}SOMe₂] (**2c**). For these compounds, both the methylene hydrogen atoms and the methyl groups of the dimethylsulfoxide ligand appear as equivalent as expected for a *trans* stereochemistry. The *J*(H–Pt) values for the imine hydrogen of **2b** and **2c** are consistent with a *Z* conformation across the C=N bond [13] since it is reduced (37.2 and 42.6 Hz, respectively) compared to that of **2a** (84.5 Hz).

In order to confirm that *trans*-[PtCl₂(4-ClC₆H₄CH=NCH₂(4'-ClC₆H₄))SOMe₂] (**2a**) is a precursor to the cyclometallated compound **3a**, the coordination compound was dissolved in toluene and treated with an equimolar amount of sodium acetate dissolved in methanol. Refluxing the mixture for 48 h produced quantitative formation of the cyclometallated compound **3a**, thus confirming that the coordination compound is an intermediate in the cyclometallation process which requires the presence of added base. Analogous reactions carried out for *trans*-[PtCl₂{(2,4,6-Me₃-C₆H₂)CHNCH₂(4'-ClC₆H₄)}SOMe₂] (**2b**) in refluxing toluene and for *trans*-[PtCl₂{(2,6-Cl₂C₆H₃)CHNCH₂(4'-ClC₆H₄)}SOMe₂] (**2c**) in refluxing methanol lead to the corresponding *exo*-metallacycles **3b** and **3c**.

However, an analogous experiment carried out with a mixture of *trans* and *cis*-[PtCl₂(4-ClC₆H₄CH=NCH₂(4'-ClC₆H₄))SOMe₂] (**2a**/ **2a**') gave a mixture of the cyclometallated compound **3a** and the *cis* coordination compound **2a**' which was recovered unchanged. This result suggests that only the *trans* isomer may lead to cyclometallation.

2.2. Crystal structures of trans- $[PtCl_2(4-ClC_6H_4CH_2NH_2)SOMe_2]$ (2), trans- $[PtCl_2{(4-ClC_6H_4)CH=NCH_2(4'-ClC_6H_4)}SOMe_2]$ (2a) and trans- $[PtCl_2{(2,6-Cl_2 C_6H_3)CHNCH_2(4'-ClC_6H_4)}SOMe_2]$ (2c)

Crystals of compounds **2**, **2a** and **2c** were grown from dichloromethane–methanol. The crystal structures are composed of discrete molecules separated by van der Waals interactions. The structures of **2** and **2c** consist of the packing in the asymmetric unit of four and two independent molecules, respectively, in both cases with bond parameters equal within experimental error $[3\sigma]$. The structures are shown in Figs. 1–3 and selected molecular dimensions are listed in Table 1. The molecular structures confirm the geometries predicted from spectroscopic data. The coordination sphere of platinum is square-planar with two mutually *trans*



Fig. 2. Molecular structure of 2a.

chloro ligands, a S-bound dimethylsulfoxide and the N-donor ligand completing the coordination sphere. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 85.9–95.36° (**2**), 88.40–93.77° (**2a**) and 87.67–94.16° (**2c**). Pt–Cl, Pt–N and Pt–S bond lengths are well within the range of values obtained for similar complexes of platinum [8c,10,11].

For **2a**, the configuration at the C=N moiety is *E* which is the adequate arrangement for formation of an *endo*-metallacycle through activation of a C-H bond at the benzal ring. The Pt \cdots H(14)–C(14) distance is only 2.651 Å, a smaller value than the one observed for the *ortho* hydrogen atoms of the benzylamine (3.161 Å) which suggest that formation of an *endo*-cycle from **2a** is more favoured than that of an *exo* derivative, as experimentally observed [12]. For **2c**, the configuration at the C=N moiety is *Z*, a form that allows formation of an *exo*-cycle [12] and the shortest distance between platinum and the *ortho* hydrogen atoms is 3.289 Å for Pt \cdots H(110)–C(110). For **2a** and **2c**, the distances between platinum



Fig. 1. Molecular structure of 2 (molecule 1).



Fig. 3. Molecular structure of 2c (molecule 1).

Table 1
Selected bond lengths (Å) and angles (°) with estimated standard deviations

Compound 2 (molecule 1)		Compound 2a		Compound 2c (molecule 1)	Compound 2c (molecule 1)	
Pt(1)–N(1)	2.079(10)	Pt-N(1)	2.050(8)	Pt(1)-N(11)	2.070(6)	
Pt(1)-S(1)	2.214(2)	Pt–S	2.222(3)	Pt(1)-S(11)	2.2202(19)	
Pt(1)-Cl(13)	2.280(2)	Pt-Cl(3)	2.301(4)	Pt(1)-Cl(11)	2.288(3)	
Pt(1)-Cl(12)	2.287(3)	Pt-Cl(2)	2.303(3)	Pt(1)-Cl(12)	2.305(3)	
N(1)-C(17)	1.443(16)	N(1)-C(8)	1.304(12)	N(11)-C(17)	1.276(8)	
C(16)-C(17)	1.523(17)	N(1)-C(7)	1.514(13)	N(11)-C(18)	1.482(10)	
N(1)-Pt(1)-Cl(13)	85.9(3)	N(1)-Pt-Cl(3)	88.6(3)	N(11)-Pt(1)-Cl(11)	89.4(2)	
S(1)-Pt(1)-Cl(13)	89.01(9)	S-Pt-Cl(3)	88.40(14)	S(11)-Pt(1)-Cl(11)	87.67(8)	
N(1)-Pt(1)-Cl(12)	90.0(3)	N(1)-Pt-Cl(2)	89.5(3)	N(11)-Pt(1)-Cl(12)	88.7(2)	
S(1)-Pt(1)-Cl(12)	95.36(10)	S-Pt-Cl(2)	93.77(14)	S(11)-Pt(1)-Cl(12)	94.16(9)	
C(17) - N(1) - Pt(1)	118.2(8)	C(6)-C(7)-N(1)	111.1(9)	N(11)-C(18)-C(19)	109.5(7)	
N(1)-C(17)-C(16)	113.7(10)	C(7)-N(1)-C(8)	117.0(8)	C(17)-N(11)-C(18)	122.0(6)	
		N(1)-C(8)-C(9)	129.4(9)	N(11)-C(17)-C(16)	124.9(7)	

and *ortho* C–H bonds are in the range reported for an analogous compound with a coordinated aryl oxime (3.153 Å), described as an intermediate in the cyclometallation process [10]. The distances between platinum and *ortho* hydrogen atoms observed for the 4-chlorobenzylamine derivative **2** are considerably greater (4.668 Å is the shortest distance for molecule 1) and, consistently, the cyclometallation of 4-chlorobenzylamine did not occurred so readily as for the benzylidenebenzylamine **L**_a [12].

2.3. Reactions of cis-[PtCl₂(dmso)₂] with ligands ArCH=NCH₂(4'-ClC₆H₄) (Ar = 2-BrC₆H₄ (L_d); 2-ClC₆H₄ (L_e); C₆F₅ (L_f); 2,6-F₂C₆H₃ (L_g))

In order to complete this study, the reactions of *cis*-[PtCl₂-(dmso)₂] with ligands L_d-L_g which had not been tested so far towards cycloplatination, were also studied. The *N*-benzylidenebenzylamine ligands L_d-L_g were prepared by a condensation reaction of 4-chlorobenzylamine with the corresponding aldehyde.

They were formed as single isomers and the expected *E* configuration of the C=N bond was confirmed by a cross-peak between the imine and the methylene protons in the 2D-NOESY NMR spectra taken for L_d and L_f (see Chart 2).

Ligands L_d and L_e might in principle lead to either *endo* (containing the imine functionality) or *exo* five-membered metallacycles. Ligands L_f and L_g contain fluoro substituents in the *ortho* positions of the benzal ring and, although intramolecular C–F bond activation for analogous ligands has been reported at electron rich platinum(II) substrates [14], this process is not expected in principle for an electrophilic substrate such as *cis*-[PtCl₂(dmso)₂]; therefore, formation of an *exo*-metallacycle through C–H activation in the benzylamine ring is more likely. As shown in Chart 3, both *endo-* and *exo*-cycles can be formed from the *E* form, while only *exo*-cycles are possible for the *Z* form.

Initially, the reactions of imines L_d - L_g were carried out using *cis*-[PtCl₂(dmso)₂], the imine and CH₃CO₂Na in a 1:1:2 ratio and heat-







2

ing the obtained mixture in refluxing methanol during 48 h. According to the NMR spectra of the crude products, only one platinum compound was detected in each reaction, along with formation of metallic platinum and the corresponding aldehyde. Due to decomposition processes of the platinum compounds as well as to hydrolysis of the imines, low yields were obtained. After work-up of the reaction mixtures, a cyclometallated compound was obtained in extremely low yield for imine $C_6F_5CHNCH_2(4-C_6H_4Cl)$ (L_f) while the other imines produced coordination compounds with a *cis* arrangement. The proposed structures are shown in Chart 2. For imine L_e , the reaction time was increased up to six days, however the *cis* coordination compound was again the only product and no evidence of formation of the corresponding cyclometallated compound was observed.

With the aim of achieving the syntheses of cyclometallated derivatives, the reactions of imines L_d and L_e were tested under more drastic conditions. A molar ratio [Pt]:[L]:[acetate] = 1:1:1 was used; sodium acetate was dissolved in a small amount of methanol and added to a solution of imine and *cis*-[PtCl₂(dmso)₂] in toluene and the mixture was refluxed for 48 h under nitrogen. Since a higher concentration of the base could favour the cyclometallation process, a molar ratio [Pt]:[L]:[acetate] = 1:1:2 was also tested for both reactions. In all cases, the coordination compounds described above were obtained with similar yields to those obtained when methanol was used as a solvent.

Attempts to obtain the corresponding cyclometallated compound were also carried out using the coordination compound 2e' as starting material. In one experiment, compound 2e' was dissolved in toluene, sodium acetate dissolved in methanol was added and the mixture was heated under reflux for 48 h; in another experiment, coordination compound 2e' in the solid state was heated at 145 °C in an oven for three days following a literature procedure for cycloplatination of a benzophenone imine [11]. In both cases, the coordination compound was recovered and longer reaction times lead only to partial decomposition with no evidence of cyclometallation.

The obtained compounds were characterized by ¹H, ¹³C (**2e**'), ¹⁹F (**3f** and **2g**'), COSY ¹H–¹H (**2d**'), NOESY ¹H–¹H (**2e**', **3f** and **2g**') and gHSQC ¹H–¹³C (**2e**', **3f** and **2g**') NMR spectra, mass spectrometry

and elemental analyses (except for **3f** due to its low stability). For compound **3f**, the presence of only three crossing peaks in the aromatic region of the ${}^{1}H^{-13}C$ -heterocorrelation spectra can be taken as evidence of cyclometallation leading to an exo-metallacycle and the presence of a cross-peak signal between the imine and the methylene protons in a 2D-NOESY NMR spectrum supports an *E* conformation across the C=N bond ¹. Coordination compounds 2d', 2e' and 2g' display analogous NMR spectral features to those described in the previous section for compound 2a'. In addition, the presence of 6 (2e') or 4 (2g') crossing peaks in the aromatic region of the ${^{1}H-^{13}C}$ -heterocorrelation spectra confirms that intramolecular C-H activation did not occur in these reactions. A cis arrangement of these coordination compounds is consistent with all the spectral data. In addition, the NOESY NMR spectrum of 2e' indicates that each methyl of the dimethylsulfoxide ligand is close to one of the aromatic rings of the imine.

The very low yield obtained for cyclometallated compound **3f** was not totally unexpected taking into account the low stability of *exo*-metallacycles as previously observed for ligand 2,4,6-Me₃C₆H₂CHNCH₂(4'-ClC₆H₄) [12]. More striking is the failure to obtain cyclometallated derivatives for ligands **L**_d, **L**_e and **L**_g which are analogous to the *N*-benzylidenebenzylamines previously studied (**L**_a-**L**_c) for which cyclometallation was successful. This result could be related to the *cis* arrangement of the coordination compounds derived from **L**_d, **L**_e and **L**_g versus the *trans* geometry of **L**_a, **L**_b and **L**_c derivatives.

In an attempt to obtain the corresponding *trans* isomer, the reaction of imine L_e with *cis*-[PtCl₂(dmso)₂] was studied under the conditions used for imines L_a , L_b and L_c , which consist in refluxing the mixture in toluene for 4 h. In contrast to the results obtained for the latter imines, the reaction of L_e produced exclusively the *cis* isomer of the coordination compound **2e**' without traces of the *trans* isomer. In an analogous procedure for imine L_f no reaction was observed and the starting materials were recovered; this suggests that the low basicity of the imine bearing an electron-withdrawing group such as C_6F_5 inhibits the coordination to platinum.

3. Conclusions

In agreement with previously suggested mechanism for the cyclometallation process [5c,8c,10], the results here obtained show that cycloplatination is successful for those ligands leading to a trans isomer of the coordination compound $(L_a, L_b \text{ and } L_c)$, while the cyclometallation process is inhibited for those ligands leading to a *cis* isomer of the coordination compound (L_d, L_e and L_g). Crystal structures for trans complexes 2a and 2c indicate a suitable arrangement of these compounds as precursors of endo (3a) and exo (3c) metallacycles, respectively. Unfortunately, suitable crystals for structure determination of the cis coordination compounds could not be obtained. It is expected, however, that steric effects are important due to the mutual proximity of dimethylsulfoxide and imine ligands in an E conformation. In order to minimize the steric effects, it is likely that both aryl rings of the imine ligand would be tilted away from the coordination plane in an arrangement which is not suitable for cyclometallation. In addition, for the cis isomer there is only one Pt-Cl cis to the N-donor ligand and available for cyclometallation.

It has been reported in the literature that the reaction between cis-[PtCl₂(dmso)₂] and nitrogen donor ligands lead to formation of trans-[PtCl₂(**L**)dmso] [15] in a substitution process that takes place with stereo-chemical change as shown in Eq. (1).

$$cis$$
-[PtCl₂(dmso)₂] + L \rightarrow trans-[PtCl₂(L)dmso] + dmso (1)

In addition, slow *trans* to *cis* isomerization might be observed since complexes having the *cis* configuration are usually more stable than

the *trans* compounds [16]. Further studies indicated that if there is a high steric hindrance due to *ortho* substituents in the ligand, direct formation of the *cis* isomer takes place [15]. These results are related to the position of the entering ligand in the five-coordinate intermediate or transition state: axial for non-bulky ligands and equatorial for bulky ligands.

The results here reported can be rationalized on steric grounds taking into account that upon coordination to metal centres, Nbenzylidenebenzylamines of considerable size might reduce the steric hindrance through E to Z isomerization around the imine bond [13,17]. Therefore, three distinct types of coordination compounds [PtCl₂(L)dmso] have been obtained: (i) The less bulky ligand L_a produced a *trans* isomer with an *E* conformation of the imine which in the absence of added base isomerizes partially to the cis isomer **2a**', but in the presence of CH₃CO₂Na gives the corresponding cyclometallated compound **3a**: (ii) Ligands L_d . L_p and L_q containing, respectively, one bromo, one chloro or two fluoro substituents in the ortho positions of the benzal ring are sterically more demanding than ligand L_a and direct formation of the cis isomers 2d', 2e' and 2g' takes place; therefore, cyclometallation is inhibited; (iii) The bulkier ligands \mathbf{L}_{b} and \mathbf{L}_{c} adopt a Z conformation of the imine to reduce the steric hindrance upon coordination and this allows formation of *trans* isomers **2b** and **2c** which are precursors of cyclometallated compounds **3b** and **3c**. In conclusion, the combined effect of steric hindrance due to ortho substituents and of the *E* or *Z* configuration of the C=N bond seems decisive on the formation of either cis or trans coordination compounds of Nbenzylidenebenzylamines and, consequently, on the success of the cyclometallation process.

4. Experimental

4.1. General

Toluene (ACS) and methanol (ACS; max. $0.005 H_2O$) were used as received from commercial sources.

Microanalyses were performed at Serveis Cientifico-tècnics (Universitat de Barcelona) and at Servei de Recursos Científics i Tècnics (Universitat Rovira i Virgili, Tarragona).

Mass spectra were performed at Servei d'Espectrometria de Masses (Universitat de Barcelona). Electrospray mass spectra were carried out in a LC/MSD-TOF spectrometer using H₂O–CH₃CN 1:1 to introduce the sample. CI mass spectra were carried out in a HP-5988A spectrometer using NH₃. NMR spectra were performed at Unitat de RMN d'Alt Camp (Universitat de Barcelona). ¹H, ¹³C and ¹⁹F spectra were recorded by using Varian Unity 300 (¹H, 300 MHz; ¹⁹F, 282.2 MHz), Mercury-400 (¹H, 400 MHz; ¹³C, 100.6 MHz; ¹⁹F, 376.5 MHz) and Varian Inova DMX-500 (¹H, 500 MHz; ¹H–¹H-COSY; ¹H–¹H-NOESY, ¹H–¹³C-gHSQC) spectrometers, and referenced to SiMe₄ (¹H, ¹³C), and CFCl₃ (¹⁹F). δ values are given in ppm and *J* values in Hz. Abbreviations used: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad; NMR labelling as shown in Charts 1 and 3.

4.2. Preparation of the compounds

4-Chlorobenzylamine was used as received from commercial sources. cis-[PtCl₂(dmso)₂] [18] and ligands L_a , L_b and L_c [12] were prepared using reported procedures.

4.2.1. Preparation of the ligands

Compounds L_d – L_g were prepared from the reaction of 0.507 g (2.7 mmol) of 2-bromobenzaldehyde (L_d), 0.509 g (3.6 mmol) of 2-chlorobenzaldehyde (L_e), 0.503 g (2.6 mmol) of pentafluorobenzaldehyde (L_f) or 0.506 g (3.6 mmol) of 2,6-difluorobenzaldehyde

 (L_g) with an equimolar amount (0.396 g (L_d) , 0.511 g (L_e) , 0.371 g (L_f) , 0.511 g (L_g)) of 4-chlorobenzylamine in dichloromethane (20 mL) with an excess of Na₂SO₄. The mixture was stirred under reflux for 2 h and filtered. The solvent was removed in a rotary evaporator to yield white (L_d, L_e) or yellow (L_f, L_g) solids. (2-BrC₆H₄)CHNCH₂(4'-ClC₆H₄) (L_d): Yield 708 mg (85%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.77$ [s, 1H, H⁵], 8.06 [dd, ³J(H-H) = 7.8, ${}^{4}J(H-H) = 1.8, 1H, H^{4}], 7.58 [dd, {}^{3}J(H-H) = 8.0, {}^{4}J(H-H) = 1.2, 1H,$ H¹], 7.36–7.24 [m, 6H, H^{2,3,7,8}], 4.82 [s, 2H, H⁶]. CI-MS (NH₃) *m/z*: 308.2 $[M]^+$. (2-ClC₆H₄)CHNCH₂(4'-ClC₆H₄) (L_e): Yield 818 mg (86%). ¹H NMR (400 MHz, CDCl₃): δ = 8.84 [s, 1H, H⁵], 8.08 [dd, ${}^{3}J(H-H) = 7.8, {}^{4}J(H-H) = 1.8, 1H, H^{4}], 7.38-7.26 [m, 6H, H^{1,2,3,7,8}],$ 4.82 [s, 2H, H⁶]. (C₆F₅)CHNCH₂(4-ClC₆H₄) (L_f): Yield 648 mg (78%). ¹H NMR (400 MHz, CDCl₃): δ = 8.50 [s, 1H, H¹], 7.36–7.25 [m, 4H, H^{3,4}], 4.86 [s, 2H, H²]. ¹⁹F NMR (376.5 MHz, CDCl₃): $\delta = -138.67$ [dd, 2F, J(F-F) = 24.4; 8.0, F^{ortho}], -146.68 [t, 1F, J(F-F) = 21.8, F^{para} , -157.83 [td, 2F, J(F-F) = 21.8; 8.0, F^{meta}]. CI-MS (NH₃) m/z: 320.3 [M+H]⁺. (2,6-F₂C₆H₃)CHNCH₂(4'-ClC₆H₄) (L_{σ}): Yield 746 mg (78%). ¹H NMR (400 MHz, CDCl₃): δ = 8.60 [s, 1H, H³], 7.39–7.23 [m, 5H], 7.00–6.92 [m, 2H], 4.85 [s, 2H, H⁴]. ¹⁹F NMR (282.2 MHz, CDCl₃): δ = -113.67 [t, ³J(F–H) = 7.0, 2F]. CI-MS (NH₃) *m*/*z*: 266.7 [M+H]⁺.

4.2.2. Preparation of platinum compounds

 $[PtCl_2{(4-ClC_6H_4)CHNCH_2(4'-ClC_6H_4)}SOMe_2]$ (2a/2a') was obtained from 0.322 g (0.76 mmol) of cis-[PtCl₂(dmso)₂] and 0.200 g (0.76 mmol) of the imine L_a which were allowed to react in dry toluene (50 mL) at 100 °C for 4 h. Unreacted cis-[PtCl₂(dmso)₂] was removed by filtration of the reaction mixture, the solvent was removed in a rotary evaporator and the residue was re-crystallized in dichloromethane-methanol, yielding a first crop of orange-yellow crystals of 2a (yield 66 mg; 14.3%) followed by pale-yellow solid which was a mixture of 2a and 2a' (yield 115 mg; 24.7%) and a final crop of **2a**' (yield 45 mg; 9.8%). Total yield 226 mg (48.8%). **2a**: ¹H NMR (500 MHz, CDCl₃): δ = 8.62 [d, ${}^{3}J(H^{1}-H^{2}) = 8.6, 2H, H^{1}], 8.28 [t, {}^{3}J({}^{195}Pt-H^{3}) = 84.5, {}^{4}J(H^{4}-H^{3}) = 84.5, 4J(H^{4}-H^{3}) = 84.5, 4J(H^{4}-H^{$ H^{3}) = 1.5, 1H, H^{3}], 7.51 [d, ${}^{3}/(H^{1}-H^{2})$ = 8.6, 2H, H^{2}], 7.45–7.40 [m, 4H, $H^{5,6}$], 5.21 [d, 4 /(H^{4} – H^{3}) = 1.5, 2H, H^{4}], 3.34 [s, 6H, H^{7}]. gHSQC $(500 \text{ MHz}): \delta = 168.2 \text{ [C}^3\text{]}, 132.1 \text{ [C}^1\text{]}, 132.0 \text{ [C}^5\text{]}, 129.1 \text{ [C}^6\text{]}, 128.9$ [C²], 66.6 [C⁴], 43.4 [C⁷]. Compound **2a**': ¹H NMR (300 MHz, $CDCl_3$): 8.65 [s, ${}^{3}I(Pt-H^3) = 117.4$, 1H, H³], 8.65 [d, ${}^{3}I(H^1-H^2) = 8.4$, 2H, H¹], 7.68 [d, ${}^{3}/({}^{H^{0}}-{}^{H^{7}}) = 8.5, 2H, H^{6}$], 7.58 [d, ${}^{3}/({}^{H^{1}}-{}^{H^{2}}) = 8.4,$ 2H, H^2], 7.46 [d, ${}^{3}J(H^6-H^7) = 8.5$, 2H, H^7], 5.52 [dd, ${}^{2}J(H^4-H^7) = 8.5$, 2H, H^7], 5.52 [dd, ${}^{2}J(H^4-H^7) = 8.5$, 2H, H^7], 5.52 [dd, ${}^{2}J(H^4-H^7) = 8.5$, 2H, H^7], 5.52 [dd, ${}^{2}J(H^4-H^7) = 8.5$, 2H, H^7], 5.52 [dd, ${}^{2}J(H^4-H^7) = 8.5$, 2H, H^7], 5.52 [dd, ${}^{2}J(H^4-H^7) = 8.5$, 2H, H^7], 5.52 [dd, ${}^{2}J(H^4-H^7) = 8.5$, 2H, H^7], 5.52 [dd, ${}^{2}J(H^4-H^7) = 8.5$, 2H, H^7], 5.52 [dd, ${}^{2}J(H^4-H^7) = 8.5$, 2H, H^7], 5.52 [dd, ${}^{2}J(H^4-H^7) = 8.5$, 2H, ${}^{2}H^7 = 8.5$, H^{5}) = 13.5, ${}^{4}/(H^{3}-H^{4})$ = 1.9, 1H, H^{4}], 4.94 [d, ${}^{2}/(H^{4}-H^{5})$ = 13.6, 3 /(Pt-H⁵) = 54.4, 1H, H⁵], 2.67 [s, br, 3H, H⁸], 2.65 [s, br, 3H, H⁹]. Anal. Calc. for C₁₆H₁₇Cl₄NOPtS: C, 31.59; H, 2.82; N, 2.30; S, 5.27. Found: C, 31.9; H, 3.0; N, 2.4; S, 5.2%.

[PtCl₂(4-ClC₆H₄CH₂NH₂)SOMe₂] (**2**) was obtained as a by-product in the reaction of equimolar amounts of *cis*-[PtCl₂(dmso)₂] and imine **L**_a (see above) carried out in refluxing methanol. The solvent was removed in a rotary evaporator and the residue was re-crystallized in dichloromethane–methanol at low temperature. Orange-yellow crystals of **4** were obtained. ¹H NMR (300 MHz, CDCl₃): δ = 7.34 [d, ³*J*(H¹–H²) = 8.6, 2H, H²], 7.28 [d, ³*J*(H¹–H²) = 8.7, 2H, H¹], 4.61 [s, 2H, H⁴], 4.02 [m, 2H, H³], 3.41 [s, ³*J*(1⁹⁵Pt–H⁵) = 23.7, 6H, H⁵]. ESI-MS, *m/z*: 502.99 [M+NH₄]⁺; 485.96 [M]⁺; 449.98 [M–Cl]⁺; 414.01[M–2Cl]⁺. *Anal.* Calc. for C₉H₁₄Cl₃NOPtS: C, 22.25; H, 2.90; N, 2.89; S, 6.60. Found: C, 22.5; H, 3.0; N, 2.9; S, 6.6%.

 $[PtCl_2\{(2,4,6-Me_3C_6H_2)CHNCH_2(4'-ClC_6H_4)\}SOMe_2] ~ (2b) was obtained from 0.079 g (0.187 mmol) of$ *cis* $-[PtCl_2(dmso)_2] and 0.051 g (0.184 mmol) of the imine$ **L** $_b which were allowed to react in toluene under reflux for 4 h. The solvent was removed in a rotary evaporator and the residue was dried in vacuo. Upon addition of diethylether a yellow solid was obtained, filtered and dried in vacuo (yield 73.5 mg; 64.9%). ¹H NMR (400 MHz, CDCl_3): 9.05 [s,$

³*J*(Pt-H⁴) = 37.2, 1H, H⁴], {7.33 [d, ³*J*(H¹-H²) = 8.8, 2H], 7.29 [d, ³*J*(H¹-H²) = 8.8, 2H], H^{1.2}}, 6.94 [s, 2H, H⁶], 4.78 [d, ³*J*(H³-H⁴) = 1.6, 2H, H³], 3.30 [s, 6H, H⁸], 2.32 [s, 3H, H⁷]; 2.27 [s, 6H, H⁵], gHSQC (400 MHz): δ = 169.7 [C⁴], 131.9 [C²], 129.3 [C⁶], 129.0 [C¹], 57.9 [C³], 43.8 [C⁸], 21.1 [C⁷], 19.2 [C⁵]. ESI-MS, *m/z*:

129.0 [C¹], 57.9 [C³], 43.8 [C⁸], 21.1 [C⁷], 19.2 [C⁵]. ESI-MS, m/z: 580.06 [M–Cl]⁺; 616.04 [M+H]⁺; 633.06 [M+NH₄]⁺. Anal. Calc. for C₁₉H₂₄Cl₃NOPtS · H₂O: C, 36.0; H, 4.1; N, 2.2; S: 5.1. Found: C, 36.04; H, 3.98; N, 2.25; S, 5.55%. [PtCl₂{(2,6-Cl₂C₆H₃)CHNCH₂(4'-ClC₆H₄)}SOMe₂] (**2c**) was ob-

[PtCl₂{(2,0-Cl₂C₆H₃)CHNCH₂(4-ClC₆H₄)]SOM2₂] (2C) was obtained from 142 mg (0.34 mmol) of *cis*-[PtCl₂(dmso)₂] and 100 mg (0.34 mmol) of the imine L_c which were allowed to react in refluxing toluene (50 mL) at 100 °C for 4 h. The solvent was removed in a rotary evaporator and the residue was re-crystallized in dichloromethane–methanol, yielding **2c** (yield 140 mg; 64%). ¹H NMR (400 MHz, CDCl₃): 8.92 [t, ³*J*(H³–H⁴) = 1.5, ³*J*(Pt–H⁴) = 42.6, 1H, H⁴], 7.43 [s, 3H, H^{5,6,7}], {7.36 [d, ³*J*(H¹–H²) = 8.0, 2H], 7.33 [d, ³*J*(H¹–H²) = 8.0, 2H], H^{1,2}}, 4.92 [d, ³*J*(H³–H⁴) = 1.5, ³*J*(Pt–H³) = 27.6, 2H, H³], 3.30 [s, ³*J*(Pt–H⁸) = 16.8, 6H, H⁸]. ESI-MS, *m/z*: 640.91 [M+H]⁺, 604.93 [M–Cl], 568.96 [M–2Cl]. *Anal.* Calc. for C₁₆H₁₆Cl₃NOPtS: C, 29.90; H, 2.51; N, 2.18; S, 4.99. Found: C, 29.8; H, 2.6; N, 2.3; S, 4.9%.

 $[PtCl_2{(2-BrC_6H_4)CHNCH_2(4'-ClC_6H_4)}SOMe_2]$ (2d') was obtained from 0.207 g (0.49 mmol) of *cis*-[PtCl₂(dmso)₂], 0.151 g (0.489 mmol) of imine L_d and 80 mg (0.975 mmol) which were allowed to react in refluxing methanol (30 mL) for 48 h. The reaction mixture was filtered, the solvent was removed in a rotary evaporator and the residue was re-crystallized in dichloromethane-methanol, yielding a light yellow solid which was filtered in vacuo. Yield 81.2 mg (25.4%). ¹H NMR (400 MHz, CDCl₃): $\delta = 9.35$ [dd, ³J(H³- H^4) = 7.7, ${}^4J(H^2-H^4)$ = 1.6, 1H, H^4], 8.87 [s, ${}^3J(Pt-H^5)$ = 115.0, ${}^{4}J(H^{5}-H^{6}) = 1.9, 1H, H^{5}], 7.69-7.63 [m, 2H, H^{1,3}], 7.67 [d, {}^{3}J(H^{8} H^9$ = 8.3, 2H, H^8], 7.51 [td, ${}^{3}J(H^2-H^{1,3}) = 7.7, {}^{4}J(H^2-H^4) = 1.7, 1H,$ H^{2}], 7.47 [d, ${}^{3}J(H^{8}-H^{9}) = 8.4$, 2H, H^{9}], 5.6 [dd, ${}^{2}J(H^{6}-H^{7}) = 13.4$, ${}^{4}J(H^{5}-H^{6}) = 1.9, 1H, H^{6}], 4.94 \text{ [d, } {}^{2}J(H^{6}-H^{7}) = 13.4, 1H, H^{7}], 2.63 \text{ [s,}$ br, 3H, H¹⁰], 2.48 [s, br, 3H, H¹¹]. Anal. Calc. for C₁₆H₁₇BrCl₃NOPtS: C, 29.44; H, 2.63; N, 2.15; S, 4.91. Found: C, 30.0; H, 2.8; N, 2.3; S, 4.6%.

 $[PtCl_2{(2-ClC_6H_4)CHNCH_2(4'-ClC_6H_4)}SOMe_2]$ (2e') was obtained from 0.242 g (0.573 mmol) of *cis*-[PtCl₂(dmso)₂], 0.151 g (0.572 mmol) of imine L_e and 93 mg (1.134 mmol) of sodium acetate, using the procedure reported for 2d'. Yield 166.2 mg (47.7%). ¹H NMR (500 MHz, CDCl₃): $\delta = 9.36 \text{ [dd, } {}^{3}\text{[(H^{3}-H^{4})]} = 5.7, {}^{4}\text{[(H^{2}-H^{4})]} = 5.7, {}^{4}\text{[(H^$ H^4) = 3.6, 1H, H^4], 8.95 [s, 3 /(Pt- H^5) = 120.2, 1H, H^5], 7.67 [d, ${}^{3}I(H^{8}-H^{9}) = 8.4, 2H, H^{8}], 7.60 [d, {}^{3}I(H^{3}-H^{4}) = 5.9, {}^{4}I(H^{2}-H^{4}) = 3.4,$ 2H, H^{2,3}], 7.51–7.50 [m, 1H, H¹], 7.47 [d, ³J(H⁸–H⁹) = 8.4, 2H, H⁹], H^7) = 13.3, ${}^{3}J(Pt-H^7)$ = 56.3, 1H, H^7], 2.62 [s, ${}^{3}J(Pt-H^{10})$ = 22.8, 3H, H^{10}], 2.48 [s, ³J(Pt-H¹¹) = 22.8, 3H, H^{11}]. ¹³C NMR (100.6 MHz, $CDCl_3$): $\delta = 161.05 [1C, C^7], 136.00 [1C, C^6], 135.24 [1C, C^9],$ 133.66 [1C, C³], 132.97 [1C, C¹], 132.84 [2C, C¹⁰], 132.69 [1C, C¹²], 130.20 [1C, C⁵], 129.89 [1C, C²], 129.17 [2C, C¹¹], 126.77 [1C, C⁴], 69.78 [1C, C⁸], 43.66 [1C, C¹³], 43.44 [1C, C¹⁴]. ESI-MS, *m*/*z*: 626.98 [M+NH₄]⁺. Anal. Calc. for C₁₆H₁₇Cl₄NOPtS: C, 31.59; H, 2.82; N, 2.30; S, 5.27. Found: C, 31.6; H, 3.2; N, 2.3; S, 6.2%.

[PtCl{C₆F₅CHNCH₂(4-ClC₆H₃)}SOMe₂] (**3f**) was obtained from 0.203 g (0.480 mmol) of *cis*-[PtCl₂(dmso)₂], 0.154 g (0.481 mmol) of imine **L**_f and 79 mg (0.963 mmol) of sodium acetate, using the procedure reported for **2d**'. Yield 20 mg (6.6%). ¹H NMR (500 MHz, CDCl₃): $\delta = 8.69$ [d, ³*J*(Pt-H¹) = 82.9, ⁴*J*(H¹-H²) = 1.4, 1H, H¹], 8.01 [d, ³*J*(Pt-H⁵) = 50.9, ⁴*J*(H⁵-H^{3.4}) = 1.7, 1H, H⁵], 7.08 [t, *J*(Pt-H^{3.4}) = 20.2, *J*(H⁵-H^{3.4}) = 2.0, 2H, H^{3.4}], 5.05 [s, ³*J*(Pt-H²) = 25.2, 2H, H²], 3.47 [s, 6H, H⁶]. ¹⁹F NMR (376.5 MHz, CDCl₃): $\delta = -150.93$ [t, *J*(F-F) = 20.8, 1F, F^{para}], -163.83 [dd, *J*(F-F) = 20.5; 5.7, 2F, F^{ortho}], -169.48 [td, *J*(F-F) = 18.4; 2.1, 2F, F^{meta}]. gHSQC (500 MHz) $\delta = 154.0$ [C¹], 133.6 [C⁵], {120.5, 124.5 [C³, C⁴]}, 68.5 [C²], 44.5 [C⁶]. ESI-MS, *m/z*: 663.46 [M+2H₂0]⁺.

[PtCl₂{(2,6-F₂C₆H₃)CHNCH₂(4'-ClC₆H₄)}SOMe₂] (**2g**') was obtained from 0.242 g (0.573 mmol) of *cis*-[PtCl₂(dmso)₂], 0.151 g (0.572 mmol) of imine **L**_g and 93 mg (1.134 mmol) of sodium acetate, using the procedure reported for **2d**'. Yield 36.5 mg (10.0%). ¹H NMR (500 MHz, CDCl₃): δ = 8.80 [s, ³*J*(Pt-H³) = 120.2, 1H, H³], 7.64 [d, ³*J*(H⁶-H⁷) = 8.4, 2H, H⁶], 7.61-7.58 [m, 1H, H²], 7.47 [d, ³*J*(H⁶-H⁷) = 8.4, 2H, H⁶], 7.61-7.58 [m, 1H, H²], 7.47 [d, ³*J*(H⁶-H⁷) = 8.4, 2H, H⁷], 7.11 [t, ³*J*(H¹-H²) = 8.2, ³*J*(H¹-F) = 8.2, 2H, H¹], 5.71 [dd, ²*J*(H⁴-H⁵) = 13.5, ⁴*J*(H³-H⁴) = 1.8, 1H, H⁴], 5.05 [d, ²*J*(H⁴-H⁵) = 13.5, 1H, H⁵], 2.75 [s, br, 3H, H⁸], 2.64 [s, br, 3H, H⁹]. ¹⁹F NMR (376.5 MHz, CDCl₃): δ = -104.00 [t, ³*J*(F-H¹) = 7.0]. gHSQC (500 MHz) δ = 162.9 [C³]; 134.0 [C²]; 132.6 [C⁶]; 128.9 [C⁷], 112.0 [C¹]; 69.8 [C⁴]; 42.0 [C⁸]. ESI-MS, *m/z*: 1237.95 [2M+H₂0]⁺; 1182.95 [2M-Cl]⁺; 626.99 [M+H₂0]⁺; 573.99 [M-Cl]⁺; 538.02 [M-2Cl]⁺. *Anal.* Calc. for C₁₆H₁₆Cl₃F₂NOPtS: C, 31.51; H, 2.64; N, 2.30; S, 5.26. Found: C, 31.9; H, 2.9; N, 2.4; S, 5.3%.

4.3. X-ray structure analysis for 2, 2a and 2c

Prismatic crystals were selected and mounted on a MAR 345 diffractometer. Unit cell parameters were determined from 6776 (2), 309 (2a) and 7029 (2c) reflections ($3^{\circ} < \theta < 31^{\circ}$) and refined by least-squares methods. Intensities were collected with graphite mono-chromatized Mo K α radiation. 28622 (2), 9983 (2a) and 9836 (2c) reflections were measured in the range 2.60° < $\theta < 30.00^{\circ}$ (2), $3.06^{\circ} < \theta < 30.00^{\circ}$ (2a) or $2.73^{\circ} < \theta < 32.34^{\circ}$ (2c). 12272 (2), 5345 (2a) and 7929 (2c) reflections were assumed as observed applying the condition I > 2 σ (I). Lorentz polarization and absorption corrections were made for 2 and 2c.

The structures were solved by direct methods using SHELXS program [19], and refined by full-matrix least-squares method with

Table 2

Crystallographic and refinement data

	Compound 2	Compound 2a	Compound 2c
Empirical formula	C9H14Cl3NOPtS	C ₁₆ H ₁₇ Cl ₄ NOPtS	C ₁₆ H ₁₆ Cl ₅ NOPtS
Molecular weight	485.71	608.26	642.70
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	triclinic, <i>P</i> 1	monoclinic, P2 ₁	monoclinic, P2 ₁ /c
Unit cell dimensions			
a (Å)	13.603(7)	11.126(6)	9.890(6)
b (Å)	14.699(5)	7.842(3)	32.240(15)
<i>c</i> (Å)	16.323(6)	12.127(4)	13.289(5)
α (°)	67.60(2)	90	90
β (°)	89.04(3)	109.93(2)	97.76(3)
γ (°)	77.35(2)	90	90
Volume (Å ³)	2936(2)	994.7(7)	4198(4)
Z; D_{calc} (Mg m ⁻³)	8; 2.198	2; 2.031	8; 2.034
Absorption coefficient (mm ⁻¹)	10.225	7.699	7.425
F(000)	1824	580	2448
Crystal size (mm)	$0.1 \times 0.1 \times 0.2$	$0.09 \times 0.05 \times 0.05$	$0.2\times0.1\times0.1$
θ Range for data collection (°)	2.60-30	3.06-30	2.73-32.34
Reflections collected/	28622/14588	9983/5596	9836/9836
unique (R _{int})	(0.0947)	(0.0714)	(0.0370)
Completeness to θ	85.1 (<i>θ</i> = 30.00)	98.2 (<i>θ</i> = 30.00)	78.1 (<i>θ</i> = 25.00)
Refinement method	full-matrix	full-matrix least-	full-matrix
	least-squares on F ²	squares on F^2	least-squares on F ²
Data/restraints/ parameters	14588/5/578	5596/1/218	9836/8/457
Goodness-of-fit on F ²	1.087	1.118	1.146
Final R indices	$R_1 = 0.0547$,	$R_1 = 0.0593$,	$R_1 = 0.0452$,
$[I > 2\sigma(I)]$	$wR_2 = 0.1449$	$wR_2 = 0.1568$	$wR_2 = 0.1392$
R indices (all data)	$R_1 = 0.0612,$ $wR_2 = 0.1511$	$R_1 = 0.0624,$ $wR_2 = 0.1630$	$R_1 = 0.0547,$ $wR_2 = 0.1450$
Largest difference in peak and hole (e Å ⁻³)	0.916 and -0.763	0.970 and -0.922	0.883 and -0.916

SHELXL97 computer program using 28622 (2), 9983 (2a) and 9836 (2c) reflections. The function minimized was $\sum w||F_0|^2 - |F_c|^2|^2$, where $w = [\sigma^2(l) + (0.0501P)^2 + 11.8165P]^{-1}$ (2), $[\sigma^2(l) + (0.0986P)^2 + 3.6436P]^{-1}$ (2a) or $[\sigma^2(l) + (0.0734P)^2 + 4.1280P]^{-1}$ (2c) and $P = (|F_0|^2 + 2|F_c|^2)/3$. *f*, *f* and *f'* were taken from International Tables of X-ray Crystallography [20]. All hydrogen atoms were computed and refined using a riding model with an isotropic temperature 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.

5. Supplementary data

CCDC 68025, 68026 and 68027 contain the supplementary crystallographic data for **2**, **2a** and **2c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

- [1] (a) A.D. Ryabov, Synthesis (1985) 233;
- (b) V.V. Dunina, O.A. Zalevskaya, V.M. Potapov, Russ. Chem. Rev. 57 (1988) 434;
- (c) A.D. Ryabov, Chem. Rev. 90 (1990) 403;
- (d) P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, Coord. Chem. Rev. 117 (1992) 215:
- (e) C. Navarro-Ranninger, I. López-Solera, J.M. Pérez, J.R. Masaguer, C. Alonso, Appl. Organomet. Chem. 7 (1993) 57;
- (f) M. Albrecht, M. Lutz, A.L. Spek, G. van Koten, Nature (2000) 406;
- (g) M. Albrecht, G. van Koten, Angew. Chem., Int. Ed. 40 (2001) 3750;
- (h) J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917;
- (i) I. Omae, Coord. Chem. Rev. 248 (2004) 995;
- (j) J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 252.
- [2] (a) J. Bravo, C. Cativiela, R. Navarro, E.P. Urriolabeitia, J. Organomet. Chem. 650 (2002) 157;
 - (b) S. Pérez, C. López, A. Caubet, X. Solans, M. Font-Bardía, New J. Chem. 27 (2003) 975;
 - (c) M. Crespo, M. Font-Bardía, J. Granell, M. Martínez, X. Solans, Dalton Trans. (2003) 3763;
 - (d) A. Capapé, M. Crespo, J. Granell, M. Font-Bardía, X. Solans, J. Organomet. Chem. 690 (2005) 4309.
- [3] (a) X. Riera, A. Caubet, C. López, V. Moreno, X. Solans, M. Font-Bardía, Organometallics 19 (2000) 1384;
 (b) X. Riera, C. López, A. Caubet, V. Moreno, X. Solans, M. Font-Bardía, Eur. J.
- Inorg. Chem. (2001) 2135. [4] C. López, A. Caubet, S. Pérez, X. Solans, M. Font-Bardía, E. Molins, Eur. J. Inorg.
- Chem. (2006) 3974. [5] (a) L. Ding, D.P. Zou, Y.J. Wu, Polyhedron 17 (15) (1998) 2511;
- (b) C. López, A. Caubet, S. Pérez, X. Solans, M. Font-Bardía, Chem. Commun. (2004) 540;

(c) Y.J. Wu, L. Ding, H.X. Wang, Y.H. Liu, H.Z. Yuan, X.A. Mao, J. Organomet. Chem. 535 (1997) 49.

[6] (a) L. Alexandrova, O.G. D'yachenko, G.M. Kazankov, V.A. Polyakov, P.V. Samuleev, E. Sansores, A.D. Ryabov, J. Am. Chem. Soc. 122 (2000) 5189;
(b) A.D. Ryabov, G.M. Kazankov, I.M. Panyashkina, O.V. Grozovsky, O.G. Dyachenko, V.A. Polyakov, L.M. Kuz'mina, J. Chem. Soc., Dalton Trans. (1997) 4385;
(c) A.D. Ryabov, S. Otto, P.V. Samuleev, V.A. Polyakov, L. Alexandrova, G.M. Kazankov, S. Shova, M. Bavanco, L. Linkowski, M.H. Johansson, Jaorg. Chem. 41

Kazankov, S. Shova, M. Revenco, J. Lipkowski, M.H. Johansson, Inorg. Chem. 41 (16) (2002) 4286.

[7] (a) A.D. Ryabov, I.M. Panyashkina, V.A. Polyakov, A. Fischer, Organometallics 21 (2002) 1633;

(b) S. Tollari, S. Cenini, A. Penoni, G. Granata, G. Palmisano, F.J. Demartin, J. Organomet. Chem. 608 (2000) 34.

 [8] (a) R. Annunziata, S. Cenini, F. Demartin, G. Palmisano, S. Tollari, J. Organomet. Chem. 496 (1995) C1;
 (b) D. Meijer, C. de Welf, M. Lutz, A.L. Stell, C.D.M. user Klink, C. user Keter, J.

(b) M.D. Meijer, E. de Wolf, M. Lutz, A.L. Spek, G.P.M. van Klink, G. van Koten, Organometallics 20 (2001) 4198;

(c) P.R.R. Ranatunge-Bandarage, B.H. Robinson, J. Simpson, Organometallics 13 (1994) 500;

(d) A.D. Ryabov, I.M. Panyashkina, A.V. Polyakov, J.A.K. Howard, L.G. Kuz'mina, M.S. Datt, C. Sacht, Organometallics 17 (1998) 3615.

- [9] (a) C.E.L. Headford, R. Mason, P.R. Ranatunge-Bandarage, B.H. Robinson, J. Simpson, J. Chem. Soc., Chem. Commun. (1990) 601;
 - (b) M.D. Meijer, A.W. Kleij, M. Lutz, A.L. Spek, G. van Koten, J. Organomet. Chem. 640 (2001) 166;
 - (c) M.D. Meijer, A.W. Kleij, B.S. Williams, D. Ellis, M. Lutz, A.L. Spek, G.P.M. van Klink, G. van Koten, Organometallics 21 (2002) 264;
 - (d) P.R.R. Ranatunge-Bandarage, N.W. Duffy, S.M. Johnston, B.H. Robinson, J. Simpson, Organometallics 13 (1994) 511.
- [10] S. Otto, A. Chanda, P.V. Samuleev, A.D. Ryabov, Eur. J. Inorg. Chem. (2006) 2561.
- [11] Y.Y. Scaffidi-Domianello, A.A. Nazarov, M. Haukka, M. Galanski, B. Keppler, J. Schneider, P. Du, R. Eisenberg, V.Y. Kukuskin, Inorg. Chem. 46 (11) (2007) 4469.
- [12] (a) A. Capapé, M. Crespo, J. Granell, A. Vizcarro, J. Zafrilla, M. Font-Bardía, X. Solans, Chem. Commun. (2006) 4128;

(b) A. Capapé, M. Crespo, J. Granell, M. Font-Bardía, X. Solans, Dalton Trans. (2007) 2030.

- [13] M. Crespo, M. Font-Bardía, X. Solans, J. Organomet. Chem. 691 (2006) 1897.
- [14] (a) C.M. Anderson, M. Crespo, G. Ferguson, A.J. Lough, R.J. Puddephatt,
 - Organometallics 11 (1992) 1177; (b) O. López, M. Crespo, M. Font-Bardía, X. Solans, Organometallics 16 (1997) 1233.
- [15] G. Annibale, M. Bonivento, L. Cattalini, M.L. Tobe, J. Chem. Soc., Dalton Trans. (1992) 3433.
- [16] (a) F.D. Rochon, J.R.L. Priqueler, Can. J. Chem. 82 (2004) 649;
- (b) N. Nédélec, F.D. Rochon, Inorg. Chim. Acta 319 (2001) 95.
- [17] R. Bosque, M. Crespo, E. Evangelio, M. Font-Bardía, X. Solans, J. Organomet. Chem. 690 (2005) 2062.
- [18] (a) J.H. Price, A.N. Williamson, R.F. Schramm, B.B. Wayland, Inorg. Chem. 11 (6) (1972) 1280;
 (b) V.Y. Kukushkin, A.J. L Pombeiro, C.M.P. Ferreira, L.I. Elding, Inorg. Synth. 33
- (2002) 189.[19] G.M. Sheldrick, SHELXS97, A Computer Program for Crystal Structure Determination, University of Göttingen, Germany, 1997.
- [20] International Tables of X-ray Crystallography, vol. IV, Kynoch Press, Birmingham, UK, 1974. p. 99, 149.