A comparative study of the structures and reactivity of cyclometallated platinum compounds of *N*-benzylidenebenzylamines and cycloplatination of a primary amine

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The reaction of *cis*-[$PtCl_2(dmso)_2$] with ligands 4-$ClC_6H_4CHNCH_2C_6H_5$ (**1a**) and 4-ClC_6H_4-$CHNCH_2$(4-ClC_6H_4) (**1b**) in the presence of sodium acetate and using either methanol or toluene as solvent produced the corresponding five-membered *endo*-metallacycles [PtCl{(4-ClC_6H_3)$CHNCH_2$-C_6H_5}{$SOMe_2$}] (**2a**) and [PtCl{(4-ClC_6H_3)$CHNCH_2$(4′-ClC_6H_4)}{$SOMe_2$}] (**2b**). An analogous reaction for ligands 2,6-$Cl_2C_6H_3CHNCH_2C_6H_5$ (**1c**) and 2,6-$Cl_2C_6H_3CHNCH_2$(4-ClC_6H_4) (**1d**) produced five-membered *exo*-metallacycles [PtCl{(2,6-$Cl_2C_6H_3$)$CHNCH_2C_6H_4$}{$SOMe_2$}] (**2c**) and [PtCl{(2,6-$Cl_2C_6H_3$)$CHNCH_2$(4′-ClC_6H_3)}{$SOMe_2$}] (**2d**) when the reaction was carried out in methanol and seven-membered *endo*-platinacycles [PtCl{(MeC_6H_3)$ClC_6H_3CHNCH_2C_6H_4$}{$SOMe_2$}] (**3c**) and [PtCl{(MeC_6H_3)$ClC_6H_3CHNCH_2$(4′-ClC_6H_3)}{$SOMe_2$}] (**3d**) when toluene was used as a solvent. The reaction of 2,4,6-$(CH_3)_3C_6H_2CHNCH_2$(4-ClC_6H_4) (**1e**) produced in both solvents an *exo*-platinacycle [PtCl{(2,4,6-$(CH_3)_3C_6H_2$)$CHNCH_2$(4′-ClC_6H_3)}{$SO(CH_3)_2$}] (**2e**). Cyclometallation of 4-chlorobenzylamine was also achieved to produce compound [PtCl{(4-ClC_6H_3)CH_2NH_2}-{$SOMe_2$}] (**2g**). The reactions of *endo*- and *exo*-metallacycles with phosphines evidenced the higher lability of the Pt–N bond in *exo*-metallacycles while a comparative analysis of the crystal structures points out a certain degree of aromaticity in the *endo*-metallacycle.

Introduction

Cyclometallation of N-donor ligands by platinum and palladium has remained as one of the major topics in organometallic chemistry for nearly four decades.[1] Although cyclometallated platinum group metal complexes containing nitrogen ligands have been extensively studied, the factors that control the regioselectivity of the process are not fully understood. Cyclometallation of *N*-benzylidenebenzylamines could in principle produce two different five-membered metallacycles, one in which the cycle contains the imine functionality (*endo*) and one in which it does not (*exo*).[2] The tendency to give *endo*-cycles is so strong that it allows activation of an aliphatic C–H bond with formation of a six-membered palladacycle in preference to the activation of an aromatic C–H bond with formation of a five-membered *exo*-palladacycle.[3] Aromaticity of the resulting metallacycle involving the two conjugated bonds C=C and C=N and the filled palladium d orbitals of appropriate symmetry has been proposed to explain the greater stability of *endo*-cycles.[4] Analogous results have been obtained when the platinum compound [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] was used as metallation substrate,[5] but activation of a C–H bond in *exo* was not successful for this system.

Recently, *cis*-[$PtCl_2(dmso)_2$] has become an useful substrate for direct cycloplatination, and numerous examples have been reported including tridentate [C,N,X] (X = N[6] or S[7]) as well as bidentate [C,N] systems derived from imines,[8] oximes,[9] pyridines[10] or even tertiary amines leading to either mono[11] or dinuclear[12] compounds. In all the reported examples leading to bidentate [C,N] imines or oximes the obtained metallacycle contains the C=N functionality. In order to explore the synthetic ability of the platinum(II) sulfoxide complex in the preparation of *exo*-platinacycles, as well as to gain more insight into the factors responsible for the higher stability of *endo*- *versus* *exo*-metallacycles, the reactions of *cis*-[$PtCl_2(dmso)_2$] with bifunctional *N*-benzylidenebenzylamines of general formula $R_xC_6H_{5-x}CHNCH_2(R_yC_6H_{5-y})$ was planned. In particular, the crystallographic data should provide valuable information regarding the so-called *endo effect*, which is considered to play a major role in the regioselectivity of the cyclometallation reaction. A preliminary account of part of this work has been already published.[13] The present study is focused on two issues: (1) an evaluation of the versatility of *cis*-[$PtCl_2(dmso)_2$] as metallating agent in the synthesis of several types of platinacycles, (2) a comparative analysis of the reactivity and structure of *endo*- *versus* *exo*-platinacycles. Further work aimed at analyzing the extent and mechanism of the formation of compounds **3** is currently in progress.

Results and discussion

Synthesis and characterization of cyclometallated compounds

The *N*-benzylidenebenzylamine ligands **1a–1e** were prepared by a condensation reaction of the corresponding amine with the corresponding aldehyde.[5] They were formed as single isomers which are assumed to have the more stable *E* stereochemistry

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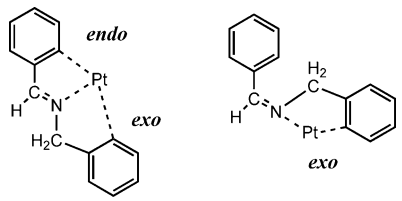


E-form Z-form

Chart 1

about the C=N bond. As shown in Chart 1, from the *E* form both *endo*- and *exo*-cycles can be formed, while only *exo*-cycles are possible for the *Z* form.

As reported in the literature,[6b–d,8] the most widely used conditions to prepare cyclometallated compounds using *cis*-$[PtCl_2(dmso)_2]$ as starting material are refluxing an equimolar mixture of the platinum substrate and the required ligand in a donor solvent such as methanol for long periods of time, in some cases in the presence of an external base such as sodium acetate. Initially, the reactions of imines 4-$ClC_6H_4CHNCH_2C_6H_5$ (**1a**) and 4-$ClC_6H_4CHNCH_2$(4-ClC_6H_4) (**1b**) were carried out using *cis*-$[PtCl_2(dmso)_2]$, the imine and $Na(CH_3CO_2)$ in a 1 : 1 : 1 ratio and heating the obtained mixture in refluxing methanol for 48 h. Under these conditions, the formation of metallic platinum is observed. In order to keep the reduction of platinum to a minimum the temperature should be carefully controlled to avoid overheating of the reaction mixture. Reaction times longer than 48 h should also be avoided since decomposition increases with time. Work-up of the reaction mixture includes filtration of metallic platinum and insoluble residues, followed by crystallization of the desired compounds **2a** and **2b**.

Following a method indicated in the literature[8] a slight modification was introduced in order to obtain higher yields. The reactions were carried out under nitrogen using dry toluene as solvent, and only a small amount of methanol was used to dissolve the sodium acetate. The reaction mixture was heated at 90 °C for 48 h and smaller amounts of metallic platinum were formed despite the higher reaction temperature. Compounds **2a** and **2b** were obtained in moderate yield and characterized by elemental analyses, FAB mass spectra, IR and NMR spectroscopies and **2b** was also characterized crystallographically. As expected from the higher stability of *endo- versus exo*-metallacycles, for both compounds activation of the C–H bond took place at the benzal ring leading to five-membered *endo*-metallacycles, as shown in Scheme 1. In the ^1H NMR spectra, the imine and the methylene protons are coupled to platinum (J(H–Pt) *ca.* 114–117 Hz and J(H–Pt) *ca.* 13–20 Hz, respectively), as well as the aromatic hydrogen adjacent to the metallation site (J(H–Pt) *ca.* 48 Hz) which confirms the formation of a bidentate [C,N] chelate system. Both methyl groups of the dimethylsulfoxide are equivalent and coupled to platinum. 2D-NOESY NMR spectra indicate that the dimethylsulfoxide is close to the metallated ring, that is *trans* to the nitrogen atom. ^{195}Pt NMR was also taken for **2b**, and the chemical shift is in the expected range for platinum(II) coordinated to a [C,N,S,Cl] donor atoms set.[14] FAB mass spectra are consistent with the proposed formulae.

With the aim of obtaining cycloplatinated compounds containing an *exo*-metallacycle, the reactions of *cis*-$[PtCl_2(dmso)_2]$ with ligands 2,6-$Cl_2C_6H_3CHNCH_2C_6H_5$ (**1c**), 2,6-$Cl_2C_6H_3CHNCH_2$(4-ClC_6H_4) (**1d**) and 2,4,6-$(CH_3)_3C_6H_2CHNCH_2$(4-ClC_6H_4) (**1e**) were also tested. Ligands **1c** and **1d** contain chloro substituents in the *ortho* positions of the benzal ring, although intramolecular C–Cl bond activation for analogous ligands has been reported at electron rich platinum(II) substrates,[5] this process is not expected in principle for an electrophilic substrate such as *cis*-$[PtCl_2(dmso)_2]$, and therefore formation of an *exo*-metallacycle would be forced. Ligand **1e** derives from mesitylaldehyde and activation of an aliphatic C–H bond to yield a six-membered *endo*-metallacycle, as reported for palladium systems[3] could compete with formation of a five-membered *exo*-metallacycle. Additionally, formation of *exo*-metallacycles in which the imine bond is not included in the metallacycle may lead to two different conformers with either *E* or *Z* arrangement around the C=N bond.

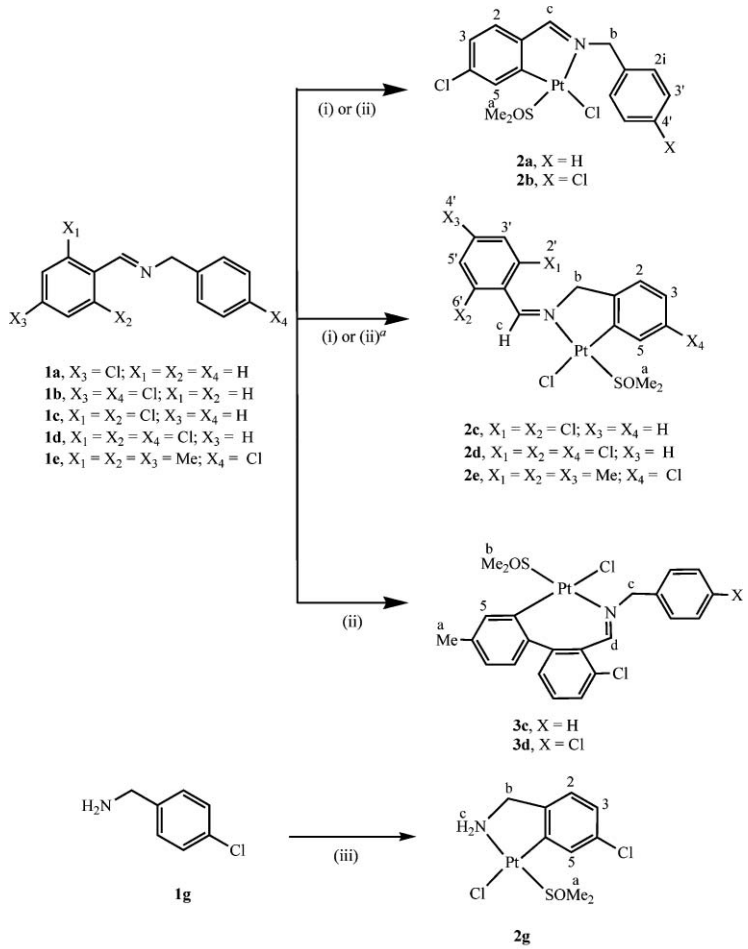
The reactions of ligands **1c–e** with *cis*-$[PtCl_2(dmso)_2]$ in the presence of $Na(CH_3CO_2)$ in a 1 : 1 : 1 ratio were carried out in refluxing methanol over 48 h and produced, in all cases, the expected *exo*-metallacycles **2c–e** although yields were extremely low. Formation of large amounts of metallic platinum indicates decomposition processes.

In order to improve the obtained yields, the reactions of **1c**, **1d** and **1e** were also carried out using toluene–methanol mixtures according to the method described above. For **1c** and **1d**, this slight modification of the method gave striking differences in the obtained compounds which were identified as compounds **3c** and **3d**, shown in Scheme 1. Compound **3d** was crystallized in dichloromethane–methanol from the crude product while **3c** was crystallized after purifying the crude product by column chromatography (silica, ethyl acetate : hexane = 100 : 20). The new compounds arise from a novel process leading to seven-membered platinacycles *via* insertion of a solvent toluene molecule.[13]

Analogous seven-membered metallacycles have been obtained in the reactions of *cis*-$[PtPh_2(SMe)_2]$ with imines 2-$BrC_6H_4CH{=}NCH_2Ph$ or $RCH{=}NCH_2CH_2NMe_2$ (R = 2,6-$C_6Cl_2H_3$; 2-ClC_6H_4)[15] as a result of formal insertion of a phenyl ligand in the cyclometallated Pt–C bond, previously formed *via* C–Br or C–Cl bond activation, and elimination of a C_6H_6 molecule. The process here reported is more complex since it requires both intramolecular C–Cl activation of the coordinated imine to produce a [C,N]-metallacycle and intermolecular C–H bond activation of the toluene molecule[16] presumably to form a σ-bond Pt–C_{aryl} with elimination of HCl, as previous steps to undergo the formal insertion of toluene in the metallacycle with elimination of another HCl molecule. Both the presence of sodium acetate which facilitates HCl elimination and the lability of $SOMe_2$[9] in the plausible platinum(IV) intermediates, arising from intramolecular activation of C–Cl bonds, enable this unprecedented process at platinum. As discussed below, NMR data for compounds **3c** and **3d** indicate the presence of two isomers both with an *E* conformation of the imine.

For **1e**, a ligand containing two methyl groups in the *ortho* positions of the benzal ring, no significant changes were observed when the reaction was carried out in toluene–methanol mixtures. This fact suggests that intramolecular C–Cl bond activation and concomitant platinum(II) to platinum(IV) formal oxidation could play a decisive role in the toluene insertion process described above for **1c** and **1d**.

Compound **2e** arising from C–H activation in the benzylamine ring was obtained with a low yield which is possibly associated



[a] method (ii) for **1e** only; for **1c** and **1d**, see text.
(i): + $[PtCl_2(dmso)_2]$ + $Na(CH_3CO_2)$ (1:1:1) in MeOH, 65°C, 48h;
(ii): + $[PtCl_2(dmso)_2]$ + $Na(CH_3CO_2)$/ MeOH (1 mL) (1:1:1) in toluene, 90°C, 48h;
(iii): + $[PtCl_2(dmso)_2]$ + $Na(CH_3CO_2)$/ MeOH (1 mL) (1:1:1) in toluene, 80°C, 5 days.

Scheme 1

with the low stability of *exo*-metallacycles. A *Z* conformation around the imine bond is obtained from both synthetic strategies, a result that can be related to the bulk of the mesityl group which should favor a conformation in which the aryl group is pointing away from the platinum centre. Despite the low yield obtained for **2e**, formation of a six-membered *endo*-metallacycle arising from activation of an aliphatic C–H bond was not detected, which indicates that for this system activation of an aromatic C–H bond leading to a five-membered *exo*-metallacycle is preferred. In order to attempt activation of an aliphatic C–H bond at platinum, an analogous reaction was studied for the imine 2,4,6-$(CH_3)_3C_6H_2CHN(4\text{-}OMeC_6H_4)$ (**1f**) for which formation of a four-membered *exo*-metallacycle is precluded. However, work-up of the reaction mixture indicated only the presence of metallic platinum and free ligand.

Compounds **2c**, **2d**, **3c**, **3d** and **2e** were characterized by elemental analyses, FAB mass spectra, IR and NMR spectroscopies and **2e** and **3c** were also characterized crystallographically.

The proposed structures are shown in Scheme 1 and, as expected, compounds **2c**, **2d** and **2e** contain an *exo*-metallacycle. In the ^{1}H NMR spectra of these compounds, the imine resonance is downfield shifted and display a lower *J*(H–Pt) value (*ca.* 50 Hz) compared to the data for *endo*-cycles which suggests a *Z* conformation around the C=N bond. The methylene hydrogens and the aromatic hydrogen adjacent to the metallation site in the benzylamine ring are also coupled to platinum (*J*(H–Pt) *ca.* 32–33 and 44–52 Hz, respectively) which confirms the formation of a bidentate [C,N] chelate system. Consistently, 5 crossing peaks are observed in the aromatic region of the {^{1}H-^{13}C}-heterocorrelation NMR spectrum taken for **2d**. Both methyl groups of the dimethylsulfoxide are equivalent and coupled to platinum.

In the ^{1}H NMR spectra of compounds **3c** and **3d**, the imine hydrogen is coupled to platinum and both the methylene hydrogen atoms and the methyl groups of the dimethylsulfoxide ligand appear as non-equivalent, as a result of the lack of planarity of the seven-membered metallacycle. The presence of the methyl substituent in the tolyl group is confirmed by the corresponding signal in the ^{1}H NMR spectra. In addition to the set of signals described above, resonances due to a minor isomer (abundance

ca. 20% (**3c**) and 30% (**3d**)) with the same spectral pattern were observed. Studies concerning activation of aromatic C–H bonds of toluene[16] indicate a selectivity order C–H (*meta*) > C–H (*para*) > C–H (*ortho*); therefore, the major isomer could be assigned to that with a *meta* arrangement between the Pt–C bond and the methyl substituent (as in the crystal structure of **3c**) and the minor isomer could correspond to the *para* isomer. A singlet resonance coupled to platinum at 6.63 (**3c**) or 6.56 ppm (**3d**) corresponding to the major isomer is assigned to the aromatic proton adjacent to the Pt–C bond.

The successful formation of *exo*-cyclometallated compounds such as **2c–e** indicates that the presence of a C=N bond included in the platinacycle is not essential for metallacycle formation. Therefore, and in order to extend the reported synthetic strategy to the cyclometallation of other nitrogen ligands, the reaction with a primary amine was also tested. The reaction was carried out using *cis*-[$PtCl_2(dmso)_2$], 4-chlorobenzylamine and $Na(CH_3CO_2)$ in a 1 : 1 : 1 ratio in toluene–methanol mixtures and heating the obtained mixture at 80 °C for 5 days. Under these conditions, cycloplatination of the primary amine was achieved leading to compound **2g** shown in Scheme 1. Compound **2g**, obtained in low yield, was characterized by ^{1}H NMR spectroscopy, elemental analyses and mass spectra. The amino group, which appears as a broad signal, the methylene protons and the aromatic hydrogen adjacent to the metallated position are coupled to platinum, thus confirming the formation of a [C,N] platinacycle. Both methyl groups of the dimethylsulfoxide are equivalent and coupled to platinum as observed for analogous compounds **2a–e** derived from imines.

It is interesting to point out that, in spite of initial difficulties[17] well established methods[18] have now been developed for the cyclopalladation of primary amines, however, the preparation of platinum analogues still remains uncommon.[19]

Crystal structures of 2b, 2e and 3c

Crystals of compounds **2b**, **2e** and **3c** were grown from acetone (**2b** and **2e**) or methanol (**3c**). The crystals of **2e** were of poor quality but good enough to allow for structure resolution. The crystal structures are composed of discrete molecules separated by van der Waals distances. The structures are shown in Fig. 1–3 and selected molecular dimensions are listed in Table 1. The molecular structures confirm the geometries predicted from spectroscopic data.

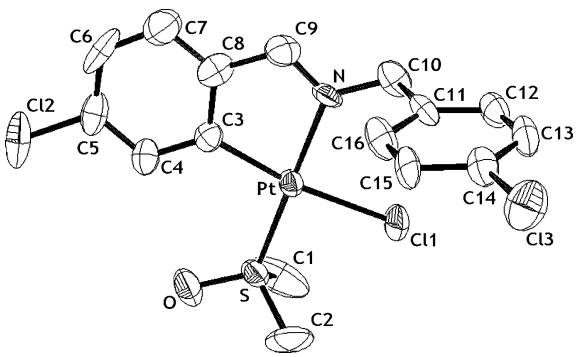


Fig. 1 Molecular structure of compound **2b** with thermal ellipsoids at 50% probability.

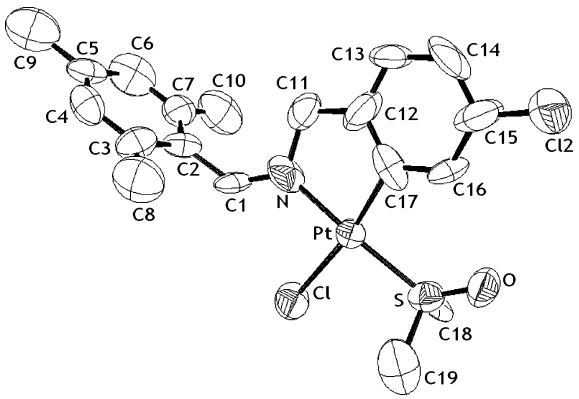


Fig. 2 Molecular structure of compound **2e** with thermal ellipsoids at 50% probability.

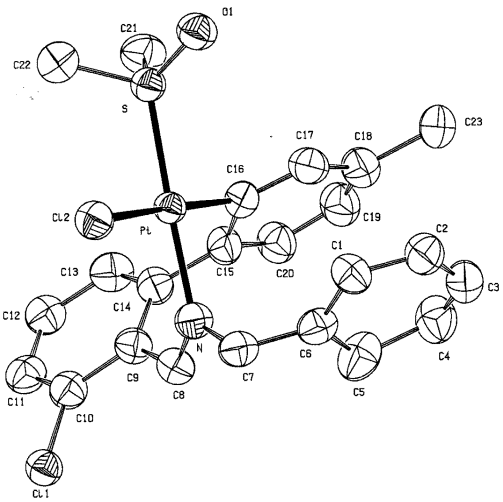


Fig. 3 Molecular structure of compound **3** with thermal ellipsoids at 50% probability.

Compounds **2b** and **2e** consist of a fused [5, 6] bicyclical system containing a five-membered metallacycle and the *ortho*-metallated phenyl group. The molecular structures provide decisive evidence of the fact that in **2b** the imine bond is included in the metallacycle leading to an *endo* system, while in **2e** an *exo* structure is adopted with a *Z* conformation around the imine bond. The molecular structure of compound **3c** was previously reported[13] and contains a seven-membered non-planar *endo*-metallacycle in which the two phenyl rings of the metallated biphenyl are tilted 57.6(3)° from each other. In all cases, the square-planar coordination environment of the metal is completed by a dimethylsulfoxide ligand coordinated through the sulfur atom *trans* to the imine nitrogen and a chloro ligand.

As shown in Table 1, bond lengths and angles are well within the range of values obtained for analogous compounds.[6,9,15,20] Most bond angles at platinum are close to the ideal value of 90°, and the smallest angles correspond to the metallacycle (80.9(3)° (**2b**) 79.8(7)° (**2e**), 87.3(2)° (**3c**)).

The data obtained for **2b** and **2e** allow for a comparison between these two types (*endo* or *exo*) of five-membered metallacycles. The

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

2b		**2e**		**3c**	
Pt–N	2.066(6)	Pt–N	1.98(2)	Pt–N	2.030(4)
Pt–C(3)	1.990(8)	Pt–C(17)	2.029(12)	Pt–C(16)	2.082(7)
Pt–S	2.200(2)	Pt–S	2.209(6)	Pt–S	2.2092(14)
Pt–Cl(1)	2.421(4)	Pt–Cl	2.405(5)	Pt–Cl(2)	2.3978(19)
N–C(9)	1.315(15)	N–C(1)	1.23(2)	N–C(8)	1.270(6)
C(3)–C(8)	1.433(16)	N–C(11)	1.48(2)	C(8)–C(9)	1.478(7)
C(8)–C(9)	1.464(19)	C(11)–C(12)	1.67(2)	C(9)–C(14)	1.427(7)
		C(12)–C(17)	1.39(0)	C(14)–C(15)	1.447(7)
				C(15)–C(16)	1.395(8)
C(3)–Pt–N	80.9(3)	N–Pt–C(17)	79.8(7)	N–Pt–C(16)	87.3(2)
C(3)–Pt–S	99.6(3)	C(17)–Pt–S	97.8(6)	C(16)–Pt–S	88.21(15)
N–Pt–Cl(1)	91.2(2)	N–Pt–Cl	91.5(5)	N–Pt–Cl(2)	90.78(14)
S–Pt–Cl(1)	88.21(10)	S–Pt–Cl	90.9(2)	S–Pt–Cl(2)	93.79(5)
C(9)–N–Pt	114.9(7)	C(12)–C(17)–Pt	113.2(12)	C(8)–N–Pt	123.3(4)
N–C(9)–C(8)	115.9(10)	C(17)–C(12)–C(11)	116.2(15)	N–C(8)–C(9)	114.0(3)
C(3)–C(8)–C(9)	114.2(11)	N–C(11)–C(12)	98.3(15)	C(8)–C(9)–C(14)	125.7(5)
C(8)–C(3)–Pt	113.7(8)	C(11)–N–Pt	116.2(15)	C(9)–C(14)–C(15)	118.5(5)
				C(16)–C(15)–C(14)	128.2(6)
				C(15)–C(16)–Pt	115.9(4)

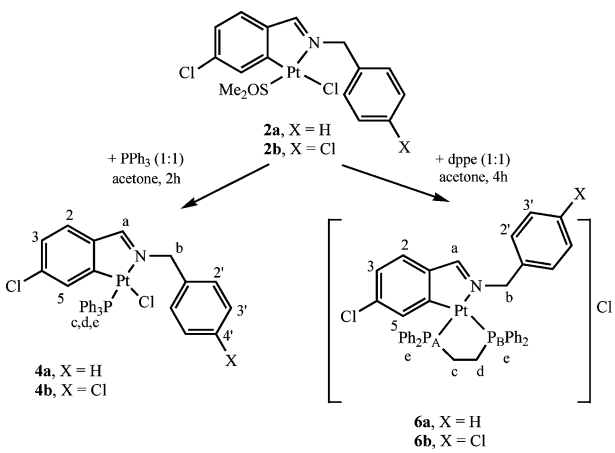
sum of internal angles of the five-membered metallacycles are 539.6° (**2b**) and 523.7° (**2e**), which suggest a planar arrangement for the *endo*-metallacycle in **2b** (angle close to 540°) and a deviation from planarity for the *exo*-metallacycle in **2e**.[21] The dihedral angles between the mean planes of the metallacycle and the coordination plane are 11.09° (**2b**) and 25.81° (**2e**). A certain degree of aromaticity in the *endo*-metallacycle involving the imine bond, one C=C bond of the phenyl ring and a filled d orbital of the platinum as previously suggested for five-membered metallacycles[4] is consistent with the greater C=N bond length observed for **2b** (1.315(15) Å) than for **2e** (1.23(2) Å). Since no significant differences in C=N bond lengths have been observed for *exo* and *endo*-cyclic five-membered cyclopalladated derivatives,[2,22] we might suggest that the more external 5d orbital of platinum is more likely to be involved in aromaticity than the 4d orbital of palladium. However, due to the poor resolution of **2e** and the different stereo-electronic features of imines **1b** and **1e**, the results obtained are not conclusive.

In both compounds an intramolecular interaction C–H···O between the oxygen atom of the dmso and one aryl carbon is observed (d(C···O) = 2.993(14) Å (**2b**) and 2.880(19) Å (**2e**)); these interactions produce the equivalence of both methyl groups as previously reported for analogous compounds.[9] In **2e**, the bulky mesityl group is pointing away from the platinum centre, thus minimising the steric crowding, and the imine proton is involved in an interaction with the chloro ligand C–H···Cl (d(C···Cl) = 3.20 (2) Å). In relation to intermolecular interactions, a *ca.* 3.7 Å distance was observed between the aromatic rings of **2b**. That might suggest π–π interactions within the aromatic moieties, as reported previously for platinum cyclometallated compounds.[23]

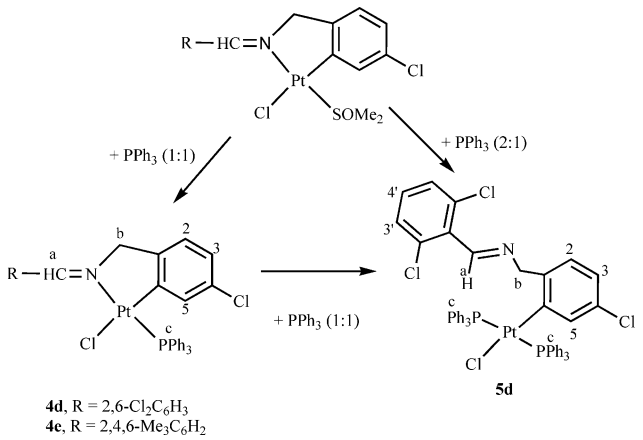
Reactions with phosphines

The tendency of cyclometallated palladium and platinum compounds to cleave the metal–nitrogen bond upon reaction with phosphines has been taken as a metallacycle stability criterion.[2,24] Therefore, a comparative analysis of the analogous *endo*- and *exo*-platinacycles was planned. Coordination of a monodentate phosphine in the coordination sphere of platinum should produce the displacement of the more labile dimethylsulfoxide ligand, while the reaction with an excess of a monodentate phosphine or with bidentate phosphines may produce either cleavage of the metallacycle leading to monodentate [C] systems or extrusion of the chloride ligand giving an ionic derivative.

The reactions of triphenylphosphine with cyclometallated platinum compounds **2a**, **2b**, **2d** and **2e** were studied and the resulting compounds are depicted in Schemes 2 and 3. In compounds **4a**, **4b**, and **4d** the imine behaves as a [C,N] bidentate ligand and the square-planar coordination of platinum (II) is completed with a phosphine and a chloro ligand. The *trans* arrangement of the triphenylphosphine and the imine is expected according to the transphobia effect,[25] and experimental evidence is obtained from the value of J(P–Pt) in the range 4050–4300 Hz and from the observed coupling of the imine to the phosphorus in a *trans* position. The coupling of the imine proton to platinum is considerably reduced for the *exo*-derivative when compared to the *endo*-analogues as a result of the mutual *Z* arrangement of the proton and the platinum around the C=N bond. According to the ^{1}H and ^{31}P NMR spectra, the attempted synthesis of compound **4e**



Scheme 2



4d, R = 2,6-$Cl_2C_6H_3$
4e, R = 2,4,6-$Me_3C_6H_2$

Scheme 3

using the same procedure as above took place along with formation of free ligand and $[PtCl_2(PPh_3)_2]$. Attempts to obtain **4e** in a pure form were unsuccessful due to the low stability of this compound.

While **4a** and **4b** did not react further with triphenylphosphine, the reaction of **4d** with one equivalent of PPh_3—or the reaction of **2d** with a 2 : 1 excess of PPh_3—produced compound **5d**. In this compound the imine behaves as a monodentate [C] ligand, and the coordination of platinum is completed with a chloro and two mutually *trans* PPh_3 ligands, as evidenced by the absence of platinum satellites for the imine resonance and the observed J(P–Pt) of 3035 Hz. The reaction of **2e** with a twofold excess of phosphine yielded $[PtCl_2(PPh_3)_2]$ and free ligand as the only identified products. Such processes as cleavage of the metallacycle (**2d**) or complete decoordination of the nitrogen ligand (**2e**) upon reaction with an excess of triphenylphosphine point to a higher lability of the Pt–N bond for *exo*- than for *endo*-platinacycles.

In order to study the stability of *endo*-platinacycles, the reactions of **2a** and **2b** with bidentate 1,2-bis(diphenylphosphine)ethane (dppe) were also carried out. In the resulting compounds **6a** and **6b** both the imine and the diphosphine behave as bidentate ligands leading to rather unstable ionic compounds which were characterized spectroscopically. The ^{31}P NMR spectra of compounds **6** show two sets of resonances due to two non-equivalent phosphorus atoms, both coupled to platinum. The mass spectra are also consistent with the proposed ionic formulae, showing in each case the peak assigned to the corresponding cation. The formation of compounds **6a and 6b** clearly shows the high stability of the *endo*-metallacycles, which are resistant to cleavage even when reacted with chelating diphosphine.

Conclusions

The preparation of five-membered *endo* and *exo* cyclometallated platinum compounds has been achieved using *cis*-$[PtCl_2(dmso)_2]$ as metallating agent and allows for a comparative study of their structures and reactivity. The crystal structure of **2b** indicates a certain degree of aromaticity of the planar *endo*-platinacycles, which are reluctant to cleave upon reaction with mono or bidentate phosphines. In contrast, the Pt–N bond of the *exo*-metallacycles is more labile and easily cleaved upon reaction with triphenylphosphine. In addition, other types of cycloplatinated compounds such as **3c** and **3d** containing a seven-membered metallacycle or compound **2g** with a metallated amine have been prepared following analogous strategies. Compounds **3c** and **3d** are obtained in a novel process involving intermolecular C–H bond activation of a toluene molecule[13] and cycloplatination of a primary amine is still rather uncommon. Therefore the synthetic procedure developed here might be considered a method with wide scope for the preparation of several classes of interesting cycloplatinated compounds.

Experimental

General

The solvents were purified and distilled by standard methods. Methanol (dry, max. 0.005% H_2O) was purchased from Panreac.

Mass spectra were performed by the Servei d'Espectrometria de Masses de la Universitat de Barcelona. NMR spectra were performed at the Unitat de NMR d'Alt Camp de la Universitat de Barcelona. Microanalyses were performed by the Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili de Tarragona.

IR spectra were recorded using Nicolet 520, Thermo-Nicolet 5700 and Thermo-Nicolet Avatar 330 spectrophotometers, using KBr pellets for solid samples and NaCl support for liquid samples.

FAB mass spectra were carried out with VG-Quattro (with a 3-nitrobenzyl alcohol matrix) and MALDI mass spectra using a Voyager DE–RP (with a dithranol matrix) spectrometer. ^1H, ^{31}P and ^{195}Pt NMR spectra were recorded by using Varian Gemini-200 (^1H, 200 MHz), Bruker DRX-250 (^1H, 250 MHz, ^{31}P, 101 MHz, ^{195}Pt, 54 MHz), Mercury-400 (^1H, 400 MHz, ^1H-^1H NOESY, ^1H-^{13}C gHSQC) and Bruker DMX-500 (^1H, 500 MHz, ^1H-^1H COSY) spectrometers, and referenced to $SiMe_4$ (^1H), $P(OMe)_3$ in $(CD_3)_2CO$ (^{31}P) and H_2PtCl_6 in D_2O (^{195}Pt). δ values are given in ppm and J values in Hz. Abbreviations used: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad, NMR labelling as shown in Schemes 1–3.

Preparation of the compounds

$[PtCl_2(dmso)_2]$[26] and ligands **1a-1f**[5] were prepared as reported elsewhere.

Preparation of cyclometallated compounds

$[PtCl\{(4\text{-}ClC_6H_3)CHNCH_2C_6H_5\}\{SOMe_2\}]$ (2a). **2a** was obtained from 0.187 g (0.44 mmol) of *cis*-$[PtCl_2(dmso)_2]$, 0.102 g (0.44 mmol) of imine **1a** and 36 mg (0.44 mmol) of sodium acetate (in 1 mL methanol) which were allowed to react in dry toluene (30 mL) at 90 °C for 48 h. The reaction mixture was filtered, the solvent was removed in a rotary evaporator and the residue was recrystallized in dichloromethane–methanol, yielding a deep yellow solid which was isolated by filtration *in vacuo*.. Yield 125 mg (53%). IR: ν(CH=N) = 1608.5 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 8.25 [d, ^4J(H–H) = 1.8, ^3J(Pt–H) = 48.5, 1 H, H^5], 7.79 [s, 1 H, ^3J(Pt–H) = 116.8, 1 H, H^c], 7.50–7.30 [m, 5 H, $H^{2',3',4'}$], 7.15 [d, ^3J(H–H) = 8.0, 1 H, H^2], 7.08 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.8, H^3], 5.18 [s, ^3J(Pt–H) = 20.0, 2 H, H^b], 3.57 [s, ^3J(Pt–H) = 23.78, 6 H, H^a]. FAB-MS, m/z: 502.3 $[M–Cl]^+$, 461.2 $[M–Cl–dmso]^+$, 423.28 $[M–2Cl–dmso]^+$. Anal. Found (calc. for $C_{16}H_{17}Cl_2NOPtS$): C: 35.4 (35.76); H: 3.0 (3.19); N: 2.7 (2.60); S: 5.7 (5.97).

[PtCl{(4-ClC$_6$H$_3$)CHNCH$_2$(4′-ClC$_6$H$_4$)}{SOMe$_2$}] (2b). **2b** was obtained from 0.160 g (0.38 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.100 g (0.38 mmol) of imine **1b** and 31 mg (0.38 mmol) of sodium acetate, using the procedure reported for **2a**. Yield 119 mg (55%). IR: ν(CH=N) = 1624.6 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 8.24 [d, ^4J(H–H) = 2.0, ^3J(Pt–H) = 48.3, 1 H, H^5], 7.86 [s, ^3J(Pt–H) = 114.0, 1 H, H^c], 7.36 [d, ^3J(H–H) = 8.6, 2 H, H$^{2'}$], 7.30 [d, ^3J(H–H) = 8.6, 2 H, H$^{3'}$], 7.19 [s, ^3J(H–H) = 8.0, 1 H, H^2], 7.11 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.7, 1 H, H^3], 5.15 [s, ^3J(Pt–H) = 13.0, 2 H, H^b], 3.55 [s, ^4J(Pt–H) = 24.0, 6 H, H^a]. ^{195}Pt NMR (54 MHz, CDCl$_3$): δ = −3833.96 [s]. FAB–MS, *m*/*z*: 536.3 [M–Cl]$^+$, 459.3 [M–Cl–dmso]$^+$. Anal. Found (calc. for C$_{16}$H$_{16}$Cl$_3$NOPtS): C: 34.0 (33.61); H: 3.2 (2.82); N: 2.4 (2.45); S: 5.6 (5.61).

[PtCl{(2,6-Cl$_2$C$_6$H$_3$)CHNCH$_2$C$_6$H$_4$}{SOMe$_2$}] (2c). **2c** was obtained from 0.215 g (0.51 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.134 g (0.51 mmol) of imine **1c** and 42 mg (0.51 mmol) of sodium acetate 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 recrystallized in dichloromethane–methanol, yielding a solid which was isolated by filtration *in vacuo*.. Yield 44 mg (15%). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 9.64 [t, ^4J(H–H) = 2.4, ^3J(Pt–H) = 51.5, 1H, H^c], 8.14 [m, ^3J (Pt–H) = 44.0, 1H, H^5], 7.44 [m, 3H], 7.09 [m, 2H], 6.97 [m, 1H], 4.70 [d, ^4J(H–H) = 2.4, 2H, ^3J(Pt–H) = 32.6, H^b], 3.63 [s, ^3J(Pt–H) = 24.2, 6H, H^a]. FAB-MS, *m*/*z*: 686.85 [M + Cl + dmso]$^+$, 650.90 [M + dmso]$^+$. Anal. Found (calc. for C$_{16}$H$_{16}$Cl$_3$NOPtS): C: 34.0 (33.61); H: 2.9 (2.82); N: 2.5 (2.45); S: 5.9 (5.61).

[PtCl{(2,6-Cl$_2$C$_6$H$_3$)CHNCH$_2$(4′-ClC$_6$H$_3$)}{SOMe$_2$}] (2d). **2d** was obtained as a white solid from 0.218 g (0.52 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.150 g (0.52 mmol) of imine **1d** and 42 mg (0.52 mmol) of sodium acetate using the procedure reported for **2c**. Yield 57 mg (18%). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 9.59 [t, ^4J(H–H) = 2.2, ^3J(Pt–H) = 50.0, 1H, H^c], 8.15 [d, ^4J(H–H) = 2.1, ^3J(Pt–H) = 51.8, 1H, H^5], 7.5–7.3 [m, 3H], 7.07 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 2.1, 1H], 6.88 [d, ^3J(H–H) = 8.0, 1H], 4.66 [d, ^4J(H–H) = 2.2, ^3J(Pt–H) = 32.8, 2H, H^b], 3.63 [s, ^3J(Pt–H) = 24.5, 6H, H^a]. ^{195}Pt NMR (54 MHz, CDCl$_3$): δ = −3584.54. FAB–MS, *m*/*z*: 607.05 [M$^+$], 570.03 [M–Cl]$^+$. Anal. Found (calc. for C$_{16}$H$_{15}$Cl$_4$NOPtS): C: 32.1 (31.70); H: 2.2 (2.49); N: 2.4 (2.31); S: 4.8 (5.29).

[PtCl{(2,4,6-(CH$_3$)$_3$C$_6$H$_2$)CHNCH$_2$(4′-ClC$_6$H$_3$)}{SO(CH$_3$)$_2$}] (2e). **2e** was obtained as a pale brown solid from 0.160 g (0.38 mmol) of [PtCl$_2$(dmso)$_2$], 0.100 g (0. 38 mmol) of imine **1e** and 0.031 g (0.38 mmol) of sodium acetate using either the procedure reported for **2a** or for **2c**. Yield 33 mg (15%). IR: ν(CH=N) = 1634.9 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 9.61 [s, ^3J(Pt–H) = 52.7, 1H, H^c], 8.13 [d, ^4J(H–H) = 1.7, ^3J(Pt–H) = 51.4, 1H, H^5], 7.04 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.7, 1H, H^3], 6.93 [s, 2H, H$^{3',5'}$], 6.85 [d, ^3J(H–H) = 8.0, 1H, H^2], 4.50 [s, ^3J(Pt–H) = 33.4, 2H, H^b], 3.61 [s, ^3J(Pt–H) = 23.4, 6H, H^a], 2.33 [s, 3H, H$^{4'}$], 2.17 [s, 6H, H$^{2',6'}$]. FAB–MS, *m*/*z*: 578.93 [M]$^+$, 543.95 [M–Cl]$^+$, 462.95 [M–Cl–dmso]$^+$. Anal. Found (calc. for C$_{19}$H$_{23}$Cl$_2$NOPtS): C: 39.0 (39.38); H: 4.2 (4.00); N: 2.4 (2.42); S: 6.5 (5.53).

[PtCl{(MeC$_6$H$_3$)ClC$_6$H$_3$CHNCH$_2$C$_6$H$_4$}{SOMe$_2$}] (3c). **3c** was obtained from 0.243 g (0.57 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.152 g (0.57 mmol) of imine **1c** and 47 mg (0.57 mmol) of sodium acetate (dissolved in 1 mL methanol) which were allowed to react in dry toluene (30 ml) at 90 °C for 48 h. The mixture was filtered, the solvent was removed under vacuum and the residue was eluted in a silica column chromatography using ethyl acetate : hexane = 100 : 20 as eluent. The first fractions collected contain aldehyde and **2c**; **3c** was obtained from a further fraction and crystallized in dichloromethane–methanol. Yield 54 mg (15%). ^{1}H NMR (250 MHz, CDCl$_3$): major isomer δ = 8.53 [s, ^3J(Pt–H) = 112.8, 1H, H^d], 7.47–7.31 [m, 4H], 7.27 [d, ^3J(H–H) = 7.2, 2H], 7.18 [d, ^3J(H–H) = 7.2, 2H], 6.85 [d, ^3J(H–H) = 7.8, 1H], 6.76 [d, ^3J(H–H) = 7.8, 1H], 6.63 [s, ^3J(Pt–H) = 52.4, 1H, H^5], 5.43 [d, ^2J(H–H) = 13.2, 1H, H^c], 5.04 [d, ^2J(H–H) = 13.2, 1H, H^c], 3.30 [s, ^3J(Pt–H) = 20.4, 3H, H^b], 2.83 [s, ^3J(Pt–H) = 31.2, 3H, H^b], 2.14 [s, 3H, Me^a], minor isomer δ = 8.47 [s, ^3J(Pt–H) = 109.6, 1H, H^d], 6.73 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 2.0, 1H], 5.35 [dd, ^2J(H–H) = 14.2, ^4J(H–H) = 2.0, 1H, H^c], 5.15 [d, ^2J(H–H) = 14.2, 1H, H^c], 3.31 [s, 3H, H^b], 2.86 [s, 3H, H^b], 2.24 [s, 3H, Me^a]. ES-MS, *m*/*z*: 592 [M–Cl]$^+$, 514 [M–Cl–dmso]$^+$. Anal. Found (calc. for C$_{23}$H$_{23}$Cl$_2$NOPtS): C: 43.7 (44.02); H: 4.0 (3.69); N: 2.3 (2.23); S: 5.0 (5.11)

[PtCl{(MeC$_6$H$_3$)ClC$_6$H$_3$CHNCH$_2$(4′-ClC$_6$H$_3$)}{SOMe$_2$}] (3d). **3d** was obtained from 0.142 g (0.34 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.100 g (0.34 mmol) of imine **1d** and 28 mg (0.34 mmol) of sodium acetate (dissolved in 1 mL methanol) which were allowed to react in dry toluene (30 ml) at 90 °C for 48 h. The mixture was filtered, the solvent was removed under vacuum and the residue was recrystallized in dichloromethane–methanol, yielding a light yellow solid which was isolated by filtration *in vacuo*.. Yield 67.5 mg (30%). ^{1}H NMR (250 MHz, CDCl$_3$): major isomer δ = 8.59 [s, ^3J(Pt–H) = 116.0, 1H, H^d], 7.46–7.34 [m, 3H], 7.24 [d, ^3J(H–H) = 8.0, 2H], 7.12 [d, ^3J(H–H) = 8.0, 2H], 6.84 [d, ^3J(H–H) = 7.6, 1H], 6.77 [d, ^3J(H–H) = 7.0, 1H], 6.56 [s, ^3J(Pt–H) = 48.0, 1H, H^5], 5.48 [dd, ^2J(H–H) = 13.0, ^4J(H–H) = 1.6, 1H, H^c], 4.90 [d, ^2J(H–H) = 13.0, ^3J(Pt–H) = 50.0, 1H, H^c], 3.29 [s, ^3J(Pt–H) = 21.6, 3H, H^b], 2.82 [s, ^3J(Pt–H) = 30.0, 3H, H^b], 2.17 [s, 3H, Me^a], minor isomer δ = 8.52 [s, ^3J(Pt–H) = 104.0, 1H, H^d], 7.24 [d, ^3J(H–H) = 8.0, 2H], 7.13 [d, ^3J(H–H) = 8.0, 2H], 5.40 [dd, ^2J(H–H) = 13.6, ^4J(H–H) = 1.7, 1H, H^c], 5.03 [d, ^2J(H–H) = 14.2, 1H, H^c], 3.30 [s, 3H, H^b], 2.85 [s, ^3J(Pt–H) = 30.0, 3H, H^b], 2.24 [s, 3H, Me^a]. ^{195}Pt NMR (54 MHz, CDCl$_3$): δ = −3802.06 (major isomer). FAB-MS, *m*/*z*: 626 [M–Cl]$^+$, 548 [M–Cl–dmso]$^+$, 510 [M–2Cl–dmso]$^+$. Anal. Found (calc. for C$_{23}$H$_{22}$Cl$_3$NOPtS): C: 42.0 (41.73); H: 3.2 (3.35); N: 2.1 (2.12); S: 5.0 (4.84).

[PtCl{(4-ClC$_6$H$_3$)CH$_2$NH$_2$}{SOMe$_2$}] (2g). **2g** was obtained from 0.273 g (0.65 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.092 g (0.65 mmol) of 4-chlorobenzylamine and 53 mg (0.65 mmol) of sodium acetate—dissolved in 1 mL of methanol—which were allowed to react in toluene (30 ml) at 80 °C for 5 days. The reaction mixture was filtered and the solvent was removed in a rotary evaporator. The residue was recrystallized in dichloromethane–methanol, yielding a solid which was isolated by filtration *in vacuo*.. Yield 29 mg (10%). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 7.91[d, ^4J(H–H) = 2.0, ^3J(Pt–H) = 51.7, 1H, H^5], 7.00 [dd, ^3J(H–H) = 7.5, ^4J(H–H) = 2.0, 1H, H^3], 6.90 [d, ^3J(H–H) = 7.5, 1H, H^2], 4.66 [s, br, ^3J(Pt–H) = 64.2, 2H, H^c], 4.14 [t, ^3J(H–H) = 6.0, ^3J(Pt–H) = 41.8, 2H, H^b], 3.49 [s, ^3J(Pt–H) = 24.0, 6H, H^a]. MALDI-MS, *m*/*z*: 450.3 [M]$^+$, 414.2 [M–Cl]$^+$. Anal. Found (calc.

for $C_9H_{13}Cl_2NOPtS{\cdot}2CH_2Cl_2$): C: 20.9 (21.33); H: 2.4 (2.76); N: 2.4 (2.26); S: 5.9 (5.17).

Preparation of phosphine derivatives

[PtCl{(4-ClC$_6$H$_3$)CHNCH$_2$C$_6$H$_5$}PPh$_3$] (4a). **4a** was obtained from 0.030 g (0.056 mmol) of compound **2a** and 0.014 g (0.053 mmol) of triphenylphosphine which were allowed to react in acetone at room temperature for 2 h. The solvent was removed in a rotary evaporator and the residue was treated with dichloromethane–methanol, yielding a bright yellow solid which was dried *in vacuo.*. Yield 30 mg (75%). IR: ν(CH=N) = 1620.2 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 [d, ^4J(H–P) = 8.8, ^3J(Pt–H) = 92.0, 1H, H^a], 7.74 [d, ^3J(H–H) = 7.2, ^3J(P–H) = 12.0, ^4J(H–H) = 1.2, 6H, H^c], 7.5–7.3 [m, 14H, H$^{d,e,2',3',4'}$], 7.07 [d, ^3J(H–H) = 8.0, 1H, H^2], 6.84 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.8, 1H, H^3], 6.39 [t, ^4J(H–H) = 1.8, ^3J(Pt–H) = 55.0, 1H, H^5], 5.35 [s, b, 2H, H^b]. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 20.09 [s, ^1J(P–Pt) = 4050.2]. MALDI-MS, *m*/*z*: 686.4 [M–Cl]$^+$. Anal. Found (calc. for $C_{32}H_{26}Cl_2NPPt$): C: 53.6 (53.27); H: 3.9 (3.63); N: 2.0 (1.94).

[PtCl{(4-ClC$_6$H$_3$)CHNCH$_2$(4′-ClC$_6$H$_4$)}PPh$_3$] (4b). **4b** was obtained as bright yellow crystals from 0.045 g (0.079 mmol) of compound **2b** and 0.020 g (0.076 mmol) of triphenylphosphine using the procedure reported for **4a**. Yield 35 mg (59%). IR: ν(CH=N) = 1622.2 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.10 [d, ^4J(H–P) = 9.2, ^3J(Pt–H) = 90.0, 1H, H^a], 7.73 [d, ^3J(H–H) = 8.0, ^3J (P–H) = 12.0, ^4J(H–H) = 1.5, 6H, H^c], 7.5–7.3 [m, 11H, H^{d,e,2,3}], 7.11 [d, ^3J(H–H) = 7.8, 2H, H$^{3'}$], 6.87 [d, ^3J(H–H) = 7.8, ^4J(H–H) = 1.8, 2H, H$^{2'}$], 6.39 [t, ^3J(H–H) = 1.8, ^3J(Pt–H) = 54.8, 1H, H^5], 5.32–5.30 [2H, H^b]. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 20.00 [s, ^1J(P–Pt) = 4143.1]. MALDI-MS, *m*/*z*: 719.95 [M–Cl]$^+$; Anal. Found (calc. for $C_{32}H_{25}Cl_3NPPt$): C: 51.2 (50.84); H: 4.0 (3.33); N: 1.9 (1.85).

[PtCl{(2,6-Cl$_2$C$_6$H$_3$)CHNCH$_2$(4′-ClC$_6$H$_3$)}PPh$_3$] (4d). **4d** was obtained as a yellow solid from 0.012 g (0.020 mmol) of compound **2d** and 0.005 g (0.019 mmol) of triphenylphosphine using the procedure reported for **4a**. Yield 10 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.80 [dt, ^4J(H–P) = 5.6, J(H–H) = 2.0, ^3J(Pt–H) = 22.4, 1H, H^a], 7.82–7.77 [m, 5H, H^c], 7.51–7.39 [m, 10H, H^c], 7.32 [t, J(H–H) = 7.4, 1H, H$^{4'}$], 7.17 [m, J(H–H) = 7.4, 2H, H$^{3'}$], 6.82 [m, 2H, H^{2,3}], 6.44 [s, ^3J (H–Pt) = 60.8, 1H, H^5], 4.77 [s, br, 2H, H^b]. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 21.55 [s, ^1J(P–Pt) = 4315.8]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ = −3956.00 [d, ^1J(P–Pt) = 4315.8]. FAB-MS, *m*/*z*: 753.6 [M–Cl]$^+$, 717.8 [M–2Cl]$^+$. Anal. Found (calc. for $C_{32}H_{24}Cl_4NPPt$): C: 49.7 (48.62); H: 3.3 (3.06); N: 1.5 (1.77).

[PtCl{(2,4,6-(CH$_3$)$_3$C$_6$H$_2$)CHNCH$_2$(4′-ClC$_6$H$_3$)}PPh$_3$] (4e). **4e** was prepared from 0.040 g (0.069 mmol) of compound **2e** and 0.018 g (0.069 mmol) of triphenylphosphine using the procedure reported for **4a**. The obtained product was contaminated with [$PtCl_2(PPh_3)_2$], but attempts to obtain **4e** in a pure form lead to further decomposition. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.82 [d, ^4J(H–P) = 6.0, ^3J(Pt–H) = 38.8, 1H, H^a], 6.42 [t, J(H–H) = 2.4, ^3J(Pt–H) = 59.1, 1H, H^5], 4.62 [t, J(H–H) = 2.4, ^3J(Pt–H) = 20.8, 2H, CH_2], 2.32 [s, 3H, H$^{4'}$], 2.20 [s, 6H, H$^{2,6'}$]. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 24.44 [s, ^1J(P–Pt) = 3169.4].

[PtCl{(2,6-Cl$_2$C$_6$H$_3$)CHNCH$_2$(4′-ClC$_6$H$_3$)}(PPh$_3$)$_2$] (5d). **5d** was obtained as a white solid from 0.012 g (0.020 mmol) of compound **2d** and 0.010 g (0.038 mmol) of triphenylphosphine using the procedure reported for **4a**. Yield 10 mg (47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 [s, 1H, H^a], 7.69–7.64 [m, 2H], 7.58–7.23 [m, 31 H], 6.64 [d, J(H–H) = 2.0, 1H], 6.48 [d, J(H–H) = 8.4, 1H], 6.39 [dd, J(H–H) = 8.4, 2.0, 1H], 4.73 [s, 2H, H^b]. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 22.66 [s, ^1J(P–Pt) = 3035.0].

[Pt{(4-ClC$_6$H$_3$)CHNCH$_2$C$_6$H$_5$}Ph$_2$P(CH$_2$)$_2$PPh$_2$]Cl (6a). **6a** was obtained from 0.050 g (0.093 mmol) of compound **2a** and 0.037 g (0.09 mmol) of bis(diphenylphosphino)ethane (dppe) which were allowed to react in acetone at room temperature for 4 h. The solvent was removed in a rotary evaporator, yielding a yellow oil. Yield 58 mg (75%). IR: ν(CH=N) = 1681.6 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 [d, ^4J(H–P) = 9.0, ^3J(Pt–H) = 88.4, 1H, H^a], 7.86 [dd, ^3J(P–H) = 12.3, ^3J(H–H) = 7.3, 4H, H^e], 7.74 [dd, ^3J(P–H) = 11.3, ^3J(H–H) = 7.3, 4H, H^e], 7.6–7.3 [m, 16H], 7.03 [dd, ^3J(H–H) = 8.0, ^4J(H–H) = 1.7, 1H, H$^{2'\text{ or }3'}$], 6.83 [d, ^3J(H–H) = 6.4, 2H, H$^{2'\text{ or }3'}$], 6.75 [dt, ^3J(P–H) = 6.8, ^4J(H–H) = 1.7, ^3J(Pt–H) = 44.0, 1H, H^5], 4.59 [s, b, 2H, H^b], 2.62 [m, 4H, H^{c,d}]. ^{31}P NMR (101 MHz, $CDCl_3$): δ = 48.35 [s, ^1J(Pt–P_B)= 1944.3, P_B], 40.93 [s, ^1J(Pt–P_A)= 3584.5, P_A]. MALDI-MS, *m*/*z*: 821.07 [M]$^+$, 787.13 [M–Cl]$^+$.

[Pt{(4-ClC$_6$H$_4$)CHNCH$_2$(4′-ClC$_6$H$_4$)}(Ph$_2$P(CH$_2$)$_2$PPh$_2$)]Cl (6b). **6b** was obtained as a dark oil from 0.050 g (0.087 mmol) of compound **2b** and 0.037 g (0.09 mmol) of bis(diphenylphosphino)ethane (dppe) using the procedure reported for **4a**. Yield 39 mg (50%). IR: ν(CH=N) = 1655.3 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 [d, ^4J(P–H) = 7.6, ^3J(Pt–H) = 85.0, 1H, H^a], 4.70 [s, b, 2H, H^b], 2.61 [s, 4H, H^{c,d}]. ^{31}P NMR (101 MHz, $CDCl_3$): δ 46.89 [s, ^1J(P_B–Pt)= 1940.0, P_B], 40.00 [s, ^1J(P_A–Pt)= 3586.4, P_a]. FAB-MS, *m*/*z*: 856.18 [M]$^+$, 732.12 [M–2Cl–C_7H_6]$^+$.

X-Ray structure analysis for 2b, 2e and 3c

Prismatic crystals were selected and mounted on an Enraf-Nonius CAD4 four circle (**2b** and **2e**) or a MAR 345 (**3c**) diffractometers. Unit cell parameters were determined from automatic centering of 25 reflections (12° < θ < 21°) (**2b** and **2e**) or from 245 reflections (3° < θ < 31°) for **3c** and refined by least-squares methods. Intensities were collected with graphite monochromatized Mo Kα radiation. 2786 (**2b**), 6183 (**2e**) and 18 892 (**3c**) reflections were measured in the range 2.22° < θ < 29.99° (**2b**), 2.21° < θ < 29.96° (**2e**) or 3.42° < θ < 31.34° (**3c**). 2625 (**2b**), 1019 (**2e**) and 5735 (**3c**) reflections were observed applying the condition $I > 2\sigma(I)$. Lorentz polarization and absorption corrections were made.

The structures were solved by using the SHELXS program,[27] and refined by full-matrix least-squares method with the SHELXL97 computer program using 2786 (**2b**), 6183 (**2e**) and 5735 (**3c**) reflections. The function minimized was $\Sigma w||Fo|^2 - |Fc|^2|^2$, where $w = [\sigma 2(I) + (0.0640P)^2]^{-1}$ (**2b**), $w = [\sigma 2(I)]^{-1}$ (**2e**) or $w = [\sigma 2(I) + (0.0355P)^2]^{-1}$ (**3c**) and $P = (|Fo|^2 + 2|Fc|^2)/3$. f, $f'$and f'' were taken from the International Tables of X-Ray Crystallography.[28] 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. CCDC reference numbers 630802, 630803 and 640014.

Table 2 Crystallographic and refinement data

	Compound **2b**	Compound **2e**	Compound **3c**
Empirical formula	$C_{16}H_{16}Cl_3NOPtS$	$C_{19}H_{23}Cl_2NOPtS$	$C_{23}H_{23}Cl_2NOPtS$
Molecular weight	571.8	579.43	627.47
Temperature/K	293(2)	293(2)	293(2)
Wavelength/Å	0.71073	0.71069	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*Cc*	$P2_1/n$	$P2_1/a$
Unit cell dimensions			
a/Å	16.222(8)	6.230(3)	10.301(5)
b/Å	13.120(6)	27.614(9)	22.018(9)
c/Å	10.932(9)	12.442(3)	10.850(4)
β/°	127.88(6)	96.60(3)	109.34(3)
Volume/Å^3	1836(2)	2126.3(13)	2322.0(17)
Z	4	4	4
Calculated density/Mg m^{-3}	2.068	1.810	1.795
Absorption coefficient/mm^{-1}	8.192	6.955	6.377
F(000)	1088	1120	1216
Crystal size/mm	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
Theta range for data collection	2.22–29.99°	2.21–29.96°	3.42–31.34°
Reflections collected/unique	2786/2786 [*R*(int) = 0.0430]	6183/6183 [*R*(int) = 0.0335]	18892/5735 [*R*(int) = 0.0605]
Completeness to theta (%)	99.5 (*θ* = 29.99)	100.0 (*θ* = 29.96)	75.3 (*θ* = 31.34)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2786/2/209	6183/0/202	5735/0/262
Goodness-of-fit on F^2	1.100	0.725	1.191
Final *R* indices [$I > 2\sigma(I)$]			
*R*1	0.0342	0.0424	0.0281
w*R*2	0.0811	0.0715	0.0724
R indices (all data)			
*R*1	0.0369	0.0614	0.0410
w*R*2	0.0822	0.1339	0.0921
Largest diff. peak and hole/e Å^{-3}	0.732 and −0.865	0.958 and – 0.952	1.063 and −1.281

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618128g.

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References

1 (*a*) A. D. Ryabov, *Synthesis*, 1985, 233; (*b*) V. V. Dunina, O. A. Zalevskaya and V. M. Potapov, *Russ. Chem. Rev. (Engl. Transl.)*, 1988, **57**, 434; (*c*) A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403; (*d*) P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano and E. Sola, *Coord. Chem. Rev.*, 1992, **117**, 215; (*e*) C. Navarro-Ranninger, I. López-Solera, J. M. Pérez, J. R. Masaguer and C. Alonso, *Appl. Organomet. Chem.*, 1993, **7**, 57; (*f*) M. Albrecht, M. Lutz, A. L. Spek and G. van Koten, *Nature*, 2000, 406; (*g*) M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750; (*h*) J. Dupont, M. Pfeffer and J. Spencer, *Eur. J. Inorg. Chem.*, 2001, 1917; (*i*) I. Omae, *Coord. Chem. Rev.*, 2004, **248**, 995; (*j*) J. Dupont, C. S. Consorti and J. Spencer, *Chem. Rev.*, 2005, **105**, 2527.

2 (*a*) J. Albert, M. Gómez, J. Granell, J. Sales and X. Solans, *Organometallics*, 1990, **9**, 1405; (*b*) J. Albert, J. Granell, J. Sales, M. Font-Bardía and X. Solans, *Organometallics*, 1995, **14**, 1393.

3 (*a*) J. Albert, J. Granell, J. Sales, X. Solans and M. Font-Altaba, *Organometallics*, 1986, **5**, 2567; (*b*) J. Albert, R. M. Ceder, M. Gomez, J. Granell and J. Sales, *Organometallics*, 1992, **11**, 1536.

4 (*a*) A. Crispini and M. Ghedini, *J. Chem. Soc., Dalton Trans.*, 1997, 75; (*b*) C. Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J. Rodriguez-Ramos, J. R. Masaguer, J. L. García-Ruano and X. Solans, *Organometallics*, 1993, **12**, 4104.

5 (*a*) C. M. Anderson, M. Crespo, M. C. Jenninngs, A. J. Lough, G. Ferguson and R. J. Puddephatt, *Organometallics*, 1991, **10**, 2672; (*b*) M. Crespo, M. Martinez, J. Sales, X. Solans and M. Font-Bardía, *Organometallics*, 1992, **11**, 1288; (*c*) M. Crespo, C. Grande and A. Klein, *J. Chem. Soc., Dalton Trans.*, 1999, 1629.

6 (*a*) J. Bravo, C. Cativiela, R. Navarro and E. P. Urriolabeitia, *J. Organomet. Chem.*, 2002, **650**, 157; (*b*) S. Pérez, C. López, A. Caubet, X. Solans and M. Font-Bardía, *New J. Chem.*, 2003, **27**, 975; (*c*) M. Crespo, M. Font-Bardía, J. Granell, M. Martínez and X. Solans, *Dalton Trans.*, 2003, 3763; (*d*) A. Capapé, M. Crespo, J. Granell, M. Font-Bardía and X. Solans, *J. Organomet. Chem.*, 2005, **690**, 4309.

7 (*a*) X. Riera, A. Caubet, C. López, V. Moreno, X. Solans and M. Font-Bardía, *Organometallics*, 2000, **19**, 1384; (*b*) X. Riera, C. López, A. Caubet, V. Moreno, X. Solans and M. Font-Bardía, *Eur. J. Inorg. Chem.*, 2001, 2135.

8 (*a*) L. Ding, D. P. Zou and Y. J. Wu, *Polyhedron*, 1998, **17**(15), 2511; (*b*) C. López, A. Caubet, S. Pérez, X. Solans and M. Font-Bardía, *Chem. Commun.*, 2004, 540; (*c*) Y. J. Wu, L. Ding, H. X. Wang, Y. H. Liu, H. Z. Yuan and X. A. Mao, *J. Organomet. Chem.*, 1997, **535**, 49.

9 (*a*) L. Alexandrova, O. G. D'yachenko, G. M. Kazankov, V. A. Polyakov, P. V. Samuleev, E. Sansores and A. D. Ryabov, *J. Am. Chem. Soc.*, 2000, **122**, 5189; (*b*) A. D. Ryabov, G. M. Kazankov, I. M. Panyashkina, O. V. Grozovsky, O. G. Dyachenko, V. A. Polyakov and L. M. Kuźemina, *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. Revenco, J. Lipkowski and M. H. Johansson, *Inorg. Chem.*, 2002, **41**(16), 4286.

10 (*a*) A. D. Ryabov, I. M. Panyashkina, V. A. Polyakov and A. Fischer, *Organometallics*, 2002, **21**, 1633; (*b*) S. Tollari, S. Cenini, A. Penoni, G. Granata, G. Palmisano and F. J. Demartin, *J. Organomet. Chem.*, 2000, **608**, 34.

11 (*a*) R. Annunziata, S. Cenini, F. Demartin, G. Palmisano and S. Tollari, *J. Organomet. Chem.*, 1995, **496**, C1; (*b*) M. D. Meijer, E. de Wolf, M. Lutz, A. L. Spek, G. P. M. van Klink and G. van Koten, *Organometallics*, 2001, **20**, 4198; (*c*) P. R. R. Ranatunge-Bandarage, B. H. Robinson and J. Simpson, *Organometallics*, 1994, **13**, 500; (*d*) A. D. Ryabov, I. M. Panyashkina, A. V. Polyakov, J. A. K. Howard, L. G. Kuz'mina, M. S. Datt and C. Sacht, *Organometallics*, 1998, **17**, 3615.

12 (*a*) C. E. L. Headford, R. Mason, P. R. Ranatunge-Bandarage, B. H. Robinson and J. Simpson, *J. Chem. Soc., Chem. Commun.*, 1990, 601; (*b*) M. D. Meijer, A. W. Kleij, M. Lutz, A. L. Spek and G. van Koten, *J. Organomet. Chem.*, 2001, **640**, 166; (*c*) M. D. Meijer, A. W. Kleij, B. S. Williams, D. Ellis, M. Lutz, A. L. Spek, G. P. M. van Klink and G. van Koten, *Organometallics*, 2002, **21**, 264; (*d*) P. R. R. Ranatunge-Bandarage, N. W. Duffy, S. M. Johnston, B. H. Robinson and J. Simpson, *Organometallics*, 1994, **13**, 511.

13 A. Capapé, M. Crespo, J. Granell, A. Vizcarro, J. Zafrilla, M. Font-Bardía and X. Solans, *Chem. Commun.*, 2006, 4128.

14 P. S. Pregosin, *Coord. Chem. Rev.*, 1982, **44**, 247.

15 (*a*) M. Font-Bardía, C. Gallego, M. Martínez and X. Solans, *Organometallics*, 2002, **21**, 3305; (*b*) M. Crespo, M. Font-Bardía and X. Solans, *Organometallics*, 2004, **23**, 1708.

16 (*a*) S. Reinartz, S. White, M. Brookhart and J. L. Templeton, *Organometallics*, 2001, **20**, 1709; (*b*) L. Johansson, O. B. Ryan, C. Romming and M. Tilset, *J. Am. Chem. Soc.*, 2001, **123**, 6579; (*c*) A. F. Heyduk, T. G. Driver, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2004, **126**, 15034; (*d*) F. Zhang, C. W. Kirby, D. W. Hairsine, M. C. Jennings and R. J. Puddephatt, *J. Am. Chem. Soc.*, 2005, **127**, 14196; (*e*) T. G. Driver, M. W. Day, J. A. Labinger and J. E. Bercaw, *Organometallics*, 2005, **24**, 3644; (*f*) S. B. Zhao, D. Song, W. L. Jia and S. Wang, *Organometallics*, 2005, **24**, 3290.

17 A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909.

18 (*a*) J. Vicente, I. Saura-Llamas, M. Palin, P. G. Jones and M. C. Ramírez de Arellano, *Organometallics*, 1997, **16**, 826; (*b*) J. Vicente, I. Saura-Llamas, J. Cuadrado and M. C. Ramírez de Arellano, *Organometallics*, 2003, **22**, 5513; (*c*) Y. Fuchita, K. Yoshinaga, T. Hanaki, H. Kawano and J. Kinoshita-Nagaoka, *J. Organomet. Chem.*, 1999, **580**, 273; (*d*) Y. Fuchita, K. Yoshinaga, Y. Ikeda and J. Kinoshita-Kawashima, *J. Chem. Soc., Dalton Trans.*, 1997, 2495; (*e*) J. Albert, J. Granell, J. Zafrilla, M. Font-Bardía and X. Solans, *J. Organomet. Chem.*, 2005, **690**, 422.

19 (*a*) N. W. Alcock, A. Avshu, R. D. O'Sullivan, A. W. Parkins and R. M. Countryman, *J. Chem. Soc., Dalton Trans.*, 1983, 1619; (*b*) P. J. Bednarski, E. Ehrensperger, H. Shönenberger and T. Burgemeister, *Inorg. Chem.*, 1990, **30**, 3015; (*c*) R. Annunziata, S. Cenini, F. Demartin, G. Palmisano and S. Tollari, *J. Organomet. Chem.*, 1995, **496**, C1.

20 (*a*) B. Teijido, A. Fernández, M. López Torres, S. Castro-Ruiz, A. Suárez, J. M. Ortigueira, J. M. Vila and J. J. Fernández, *J. Organomet. Chem.*, 2000, **598**, 71; (*b*) D. Vázquez-García, A. Fernández, J. J. Fernández, M. López-Torres, A. Suárez, J. M. Ortigueira, J. M. Vila and H. Adams, *J. Organomet. Chem.*, 2000, **595**, 199; (*c*) J. M. Vila, M. T. Pereira, J. M. Ortigueira, D. Lata, M. López Torres, J. J. Fernández, A. Fernández and H. Adams, *J. Organomet. Chem.*, 1998, **566**, 93.

21 H. F. Klein, S. Camadanli, R. Beck, D. Leukel and U. Flörke, *Angew. Chem., Int. Ed.*, 2005, **44**, 975.

22 (*a*) J. Albert, J. Granell, R. Moragas, M. Font-Bardía and X. Solans, *J. Organomet. Chem.*, 1996, **522**, 59; (*b*) J. Albert, R. M. Ceder, J. Granell and J. Sales, *Organometallics*, 1992, **11**, 1536; (*c*) P. W. Clark, S. F. Dyke, G. Smith and C. H. L. Kennard, *J. Organomet. Chem.*, 1987, **330**, 447.

23 W. Lu, C. W. Chan, K. K. Cheung and C. M. Che, *Organometallics*, 2001, **20**, 2477.

24 (*a*) M. Crespo, X. Solans and M. Font-Bardía, *Organometallics*, 1995, **14**, 355; (*b*) M. Crespo, J. Granell, X. Solans and M. Font-Bardía, *J. Organomet. Chem.*, 2003, **681**, 143.

25 J. Vicente, J. A. Arcas, E. Martínez-Viviente and P. G. Jones, *Organometallics*, 2002, **21**, 4454.

26 (*a*) J. H. Price, A. N. Williamson, R. F. Schramm and B. B. Wayland, *Inorg. Chem.*, 1972, **11(6)**, 1280; (*b*) V. Y. Kukushkin, A. J. L. Pombeiro, C. M. P. Ferreira and L. I. Elding, *Inorg. Synth.*, 2002, **33**, 189.

27 G. M. Sheldrick, *SHELXS97, A Computer Program for Crystal Structure Determination*, University of Göttingen, Germany, 1997.

28 *International Tables of X-Ray Crystallography*, Kynoch Press, Birmingham, UK, 1974, vol. IV, pp. 99–100, 149.