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Cyclometallated platinum(II) compounds with imine ligands derived from amino acids: Synthesis and oxidative addition reactions

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ABSTRACT

The reactions of $[PtMe_2(\mu\text{-}SMe_2)]_2$ with imines 4-$ClC_6H_4CH{=}NCHRCO_2Me$ (R = H (**1a**), Me (**1b**), ^{i}Pr (**1c**), $CH_2C_6H_4$(4'-OH) (**1d**), C_6H_5 (**1e**), $CH_2C_6H_5$(**1f**)) derived from natural amino acids produced under mild conditions cyclometallated platinum(II) compounds $[PtMe\{\kappa^2\text{-}(C,N)\text{-}4\text{-}ClC_6H_3CH{=}NCHRCO_2Me\}(SMe_2)]$ (**2a–2f**). These compounds gave the corresponding phosphine derivatives $[PtMe\{\kappa^2\text{-}(C,N)\text{-}4\text{-}ClC_6H_3CH{=}NCHRCO_2Me\}(PPh_3)]$ (**3a–3f**). The corresponding cyclometallated platinum(IV) compounds $[PtMe_2I\{\kappa^2\text{-}(C,N)\text{-}4\text{-}ClC_6H_3CH{=}NCHRCO_2Me\}(PPh_3)]$ (**4**) arising from intermolecular oxidative addition of methyl iodide were obtained with a high degree of stereo selectivity. Analogous results were obtained for imine 2,6-$Cl_2C_6H_3CH{=}NCH(CH_2C_6H_5)CO_2Me$ (**1g**) in a process involving intramolecular oxidative addition of a C–Cl bond. The obtained compounds were fully characterized including structure determinations for compounds **3f**, **4d** and **4f**.

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1. Introduction

There is growing interest in the synthesis, reactivity and applications of organometallic complexes with biologically important ligands, in particular α-amino acids and their derivatives are highly versatile ligands in this field. Several examples of cyclopalladated compounds with ligands derived from amino acids have been reported [1] while platinum analogues have been less explored [2]. In addition, compared to the reported examples of platinum(II) complexes with amino acid derivatives as ligands, there are much fewer examples of platinum(IV) complexes in spite of the biological activity of the latter [3].

On the other hand, studies concerning oxidative addition of alkyl halides to chiral-at-ligand platinum(II) planar complexes have been reported [4] and the potential stereo selectivity of this process is relevant in asymmetric catalysis.

The aim of this work is to prepare cyclometallated platinum(II) compounds with imine ligands derived from methyl esters of natural amino acids and to study the oxidative addition of methyl iodide to such compounds in order to obtain the corresponding platinum(IV) derivatives.

2. Results and discussion

Imines **1a**–**1d** were prepared following an analogous procedure to that reported in the literature [5] while imines **1e**–**1g** were prepared as reported [1a] (see Table 1). As shown in Scheme 1, the cycloplatination reaction of imines **1a**–**1f** was carried out using $[PtMe_2(\mu\text{-}SMe_2)]_2$ as precursor and the conditions reported in the literature [6]. The process involves activation of a C–H bond followed by methane elimination and leads to formation of platinum(II) compounds **2a**–**2f** in high yields. Compounds **2** were characterized by elemental analyses, mass spectrometry and ^{1}H and ^{195}Pt NMR spectroscopy. All data are consistent with the structures proposed in Scheme 1 for compounds **2** in which the imine acts as a bidentate [C,N] ligand and the coordination sphere of platinum is completed with a methyl and a dimethylsulfide ligands [6]. These are coupled to platinum and the observed *J*(H-Pt) values are in the expected ranges, which are *ca.* 80 Hz for the methyl ligand and 25–30 Hz for the dimethylsulfide ligand. In addition, both the imine proton and the aromatic proton adjacent to the metallated carbon (H_1) are coupled to platinum with *J*(H–Pt) values in the range 50–55 and 66–68 Hz, respectively. In the ^{195}Pt NMR spectra, a single peak is observed in each case and the chemical shift is consistent with a platinum(II) coordinated to a [C,C,N,S] donor atoms set [7]. In all cases, the most intense peak in the mass spectra corresponds to the loss of a methyl ligand.

The reaction of compounds **2** with 1 equiv. of triphenylphosphine produced the corresponding compounds **3** in a substitution

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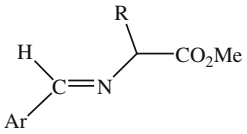
Table 1
Imines studied in this work

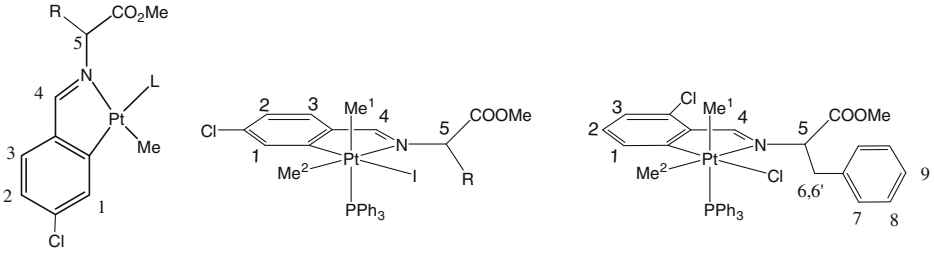
General formula:



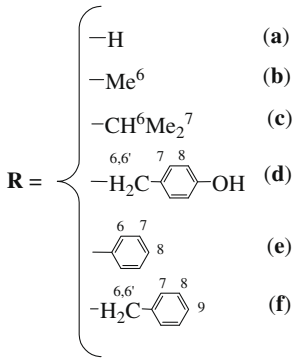
	Ar	R	Related amino acid
1a	4-ClC_6H_4	H	*Glycine*
1b	4-ClC_6H_4	Me	*Alanine*
1c	4-ClC_6H_4	$CHMe_2$	*Valine*
1d	4-ClC_6H_4	$CH_2C_6H_4$(4'-OH)	*Tyrosine*
1e	4-ClC_6H_4	C_6H_5	*Phenylglycine*
1f	4-ClC_6H_4	$CH_2C_6H_5$	*Phenylalanine*
1g	2,6-$Cl_2C_6H_3$	$CH_2C_6H_5$	*Phenylalanine*

process of the sulfide for the phosphine ligand carried out in acetone. The lower yields obtained for **3a** and **3b** might be related to the higher solubility of these compounds in diethyl ether used to isolate the products. The compounds were characterized by elemental analyses, mass spectrometry, ^1H, ^{31}P and ^{195}Pt NMR spectroscopy, and the crystal structure of **3f** was solved. The obtained data indicate that the [C,N] metallacycle is preserved in the substitution process and the coordination of the platinum(II) atom is completed with a methyl and a triphenylphosphine ligands. In the ^1H NMR spectra, in addition to signals corresponding to the coordinated PPh_3, a high field shift of the protons of both the methyl ligand and the amino ester moiety compared to compounds **2** is observed. The latter observation suggests that the aromatic rings of the phosphine ligand are close to these groups. In addition, the measured *J*(H–Pt) values for the methyl ligand and the imine proton are in the same range than those observed for compounds **2**, while the coupling to platinum decreases from 66–68 to 52–54 Hz for the aromatic proton adjacent to the metallated position. These results suggest that the triphenylphosphine is *trans* to the metallated aryl which is confirmed by the *J*(P–Pt) values in the range 2260–2290 Hz observed in both the ^{31}P and the ^{195}Pt NMR spectra [8]. The $\delta(^{195}Pt)$ values are high-field shifted upon replacement of SMe_2 for PPh_3 ligand in *ca.* 200 ppm in agreement with previous data for analogous compounds [7]. The crystal structure obtained for compound **3f** reveals total racemization of the imine ligand since it consists of a racemate. This suggests that the asymmetric carbon in the amino acid fragment is more prone to racemization than those in analogous ligands derived from *S*-α-methylbenzylamine or *R*-1-(1-naphthyl)ethylamine for which analogous platinum(II) derivatives have been obtained without evidence of racemization [9]. The higher acidity of the hydrogen bonded to the asymmetric carbon in the amino acid derivatives favours the racemization process [10] as previously observed for analogous palladium derivatives [1a].

Formation of the corresponding platinum(IV) compounds was initially attempted by intermolecular oxidative addition reaction of methyl iodide to compounds **3** (method **A** in Scheme 1). Analogous processes have been studied and shown to produce initial *trans* oxidative addition [11] followed by isomerization in such a way that the bulky triphenylphosphine is placed in a less hindered position which is perpendicular to the metallacycle plane [9]. Following this procedure platinum(IV) compounds **4a**, **4e** and **4f**, shown in Scheme 1, were obtained with high yields while the corresponding reactions for the remaining compounds led to decomposition processes. In view of these results, a "one-pot" procedure (method **B** in Scheme 1) was attempted from imines **1b**, **1c** and **1d**. This procedure gave platinum(IV) compounds **4c** and **4d** in fair yields, while formation of compound **4b** remained elusive. The only compound that could be isolated for imine **1b** following methods **A** or **B** was characterized by NMR spectra as *trans*-[PtMeI(PPh_3)$_2$] [12]. This compound was also produced from imines **1c** and **1d** using method **A**. Finally, for ligand **1g** derived from phenylalanine and containing two chloro substituents in the *ortho* positions of the aryl ring, an intramolecular oxidative addition of a C–Cl bond [13], followed by reaction with triphenylphosphine (method **C** in Scheme 1) allowed the preparation of platinum(IV) compound **4g**.



L = SMe_2 (**2**); PPh_3 (**3**) (**4**) (**4g**)



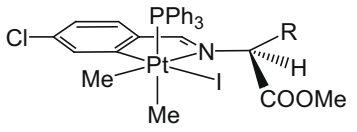
R = –H (**a**); –Me^6 (**b**); –CH^{6}Me$_2$^{7} (**c**); –H$_2$C–C$_6$H$_4$–OH (**d**); –C$_6$H$_5$ (**e**); –H$_2$C–C$_6$H$_5$ (**f**)

Scheme 1.

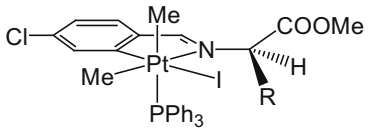
The isomers of octahedral platinum(IV) compounds **4** are restricted from the strong preference for the facial coordination of the three carbon donor atoms [4,6,11], the bidentate [C,N] coordination of the imine and the favoured *cis* to the chelate position of the bulky triphenylphosphine ligand [9]. For compounds **4b**–**4g** derived from chiral ligands, two diastereomers (C_{Pt}, S_C) and (A_{Pt}, S_C) – in which *C* and *A* describe the stereochemistry clockwise or anticlockwise of the octahedral platinum [14] and *S* the chirality of the asymmetric carbon atom – are possible. Since the expected racemization of the asymmetric carbon [10,15] was confirmed by the crystal structures of **3f**, **4d** and **4f** (see below), the two proposed diastereomers of compounds **4** should consist of two pairs of enantiomers (C_{Pt}, S_C)/(A_{Pt}, R_C) and (A_{Pt}, S_C)/(C_{Pt}, R_C). In the ^{31}P NMR spectra of the compounds **4c**, **4e**, **4f** and **4g**, obtained as soon as possible after isolation of the compounds to avoid further isomerization, two sets of resonances indicate the presence of the two diastereomers (see Table 2). In most cases, the low abundance of the minor isomer did not allow the assignment of the corresponding resonances in the ^{195}Pt or in the ^{1}H NMR spectra. Compound **4a** containing an achiral ligand and compound **4d** were obtained as

Table 2
Obtained yields and diastereomeric ratios for compound **4**.

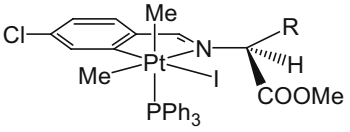
	Method	Yield (%)	(C_{Pt},S_C)/(A_{Pt},R_C): (A_{Pt},S_C)/(C_{Pt},R_C)
4c	B	46	7: 1
4d	B	49	(C_{Pt},S_C)/(A_{Pt},R_C) exclusively
4e	A	97	3: 1
4f	A	96	7: 1
4g	C	47	11: 1



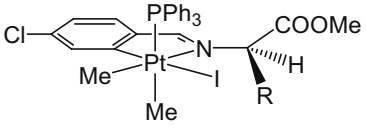
(C_{Pt}, S_C)



(A_{Pt}, R_C)



(A_{Pt}, S_C)



(C_{Pt}, R_C)

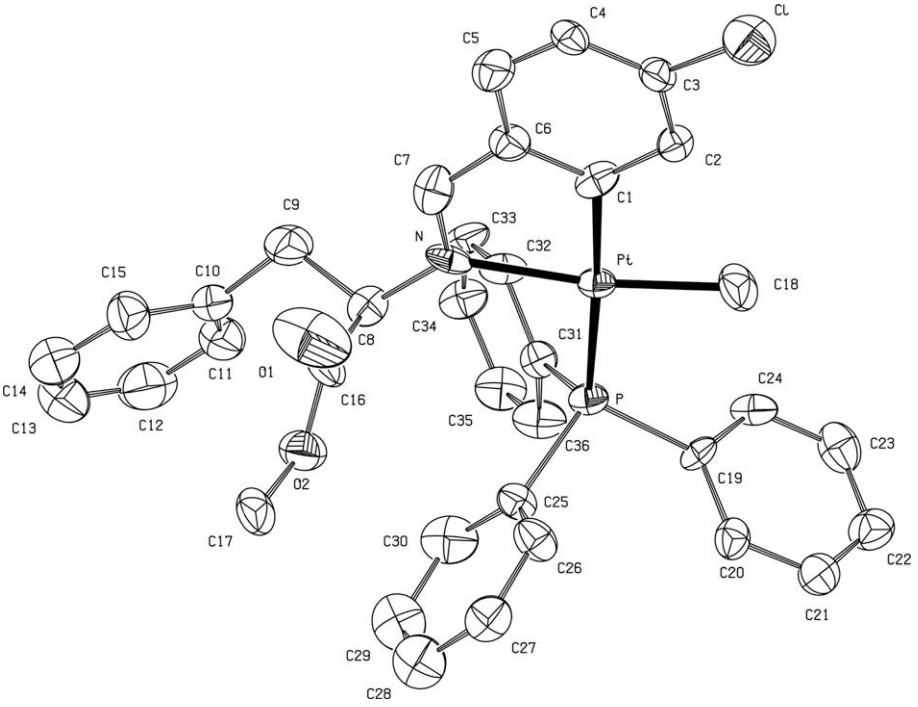


Fig. 1. Molecular structure of compound **3f**.

single isomers. The diastereomeric ratios shown in Table 2 indicate a high degree of stereoselectivity for the oxidative addition process ranging from exclusive formation of one diastereomer (**4d**), consisting of a pair of enantiomers, to formation of two diastereomers, each consisting of a pair of enantiomers, in a 3:1 ratio (**4e**). When method **A** was used to prepare the platinum(IV) compounds high yields were obtained (96–97%), however yields are lower for methods **B** and **C** and, in these cases (**4c**, **4d** and **4g**), the observed stereoselectivities might not be fully reliable. Compounds **4** were characterized by mass spectrometry, ^{1}H, ^{31}P and ^{195}Pt NMR spectroscopy, and the crystal structures of **4d** and **4f** were solved. The molecular structures of **4d** and **4f** correspond to the pair of enantiomers (C_{Pt}, S_C)/(A_{Pt}, R_C) and this is the relative stereochemistry assigned to the major diastereomer, while the minor diastereomer

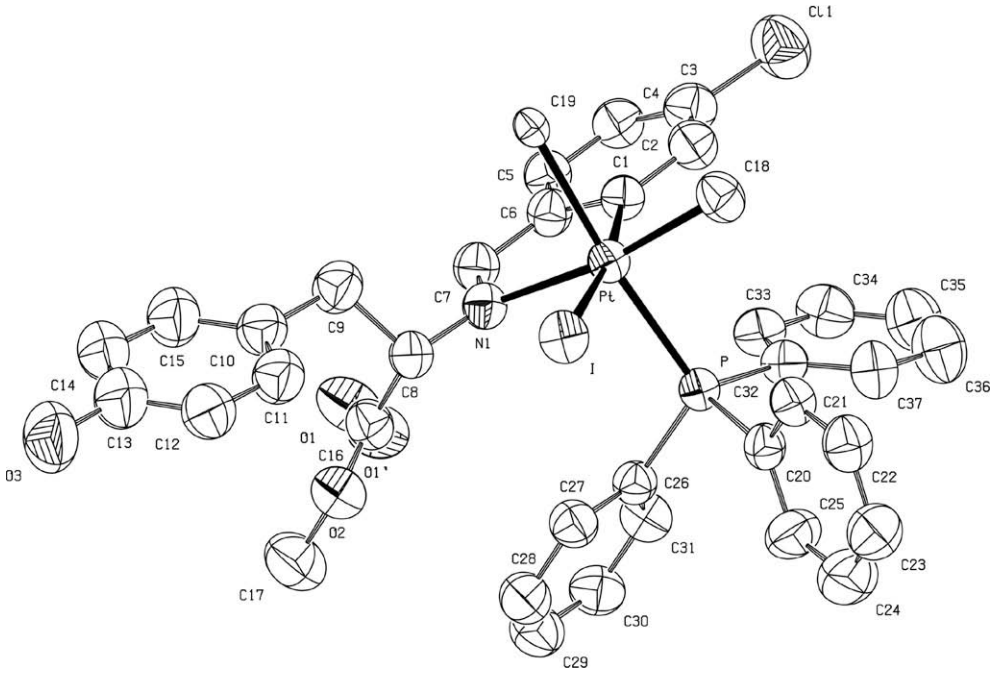


Fig. 2. Molecular structure of compound **4d**.

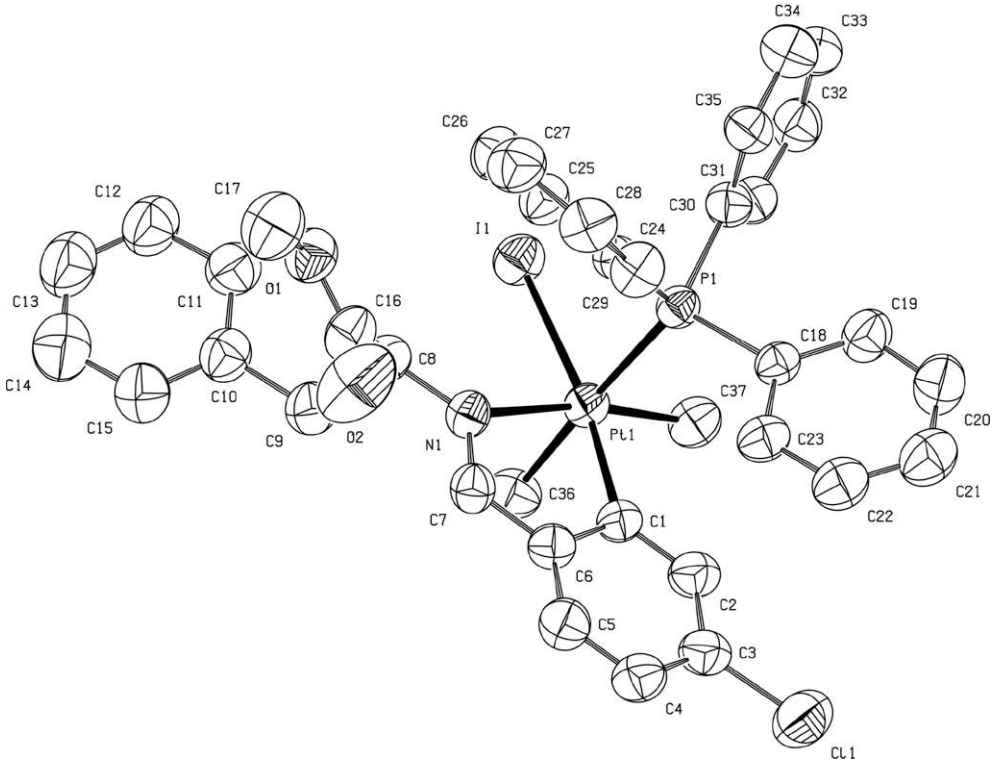


Fig. 3. Molecular structure of compound **4f**.

Table 3
Selected bond lengths (Å) and angles (°) for compounds **3f**, **4d** and **4f** with estimated standard deviations.

Compound **3f**		Compound **4d**		Compound **4f**	
Pt–C(18)	2.003(10)	Pt–C(1)	2.042(4)	Pt–C(1)	2.027(4)
Pt–C(1)	2.072(12)	Pt–C(18)	2.079(4)	Pt–C(37)	2.068(5)
Pt–N	2.131(9)	Pt–C(19)	2.409(3)	Pt–C(36)	2.139(5)
Pt–P	2.308(3)	Pt–N(1)	2.208(3)	Pt–N(1)	2.220(4)
N(1)–C(7)	1.292(14)	Pt–P	2.4347(10)	Pt–P(1)	2.4482(12)
		Pt–I	2.7583(13)	Pt–I(1)	2.7589(8)
		N(1)–C(7)	1.286(5)	N(1)–C(7)	1.284(6)
C(18)–Pt–C(1)	91.3(4)	C(1)–Pt–C(18)	91.95(17)	C(1)–Pt–C(37)	91.55(19)
C(1)–Pt–N	79.9(4)	C(1)–Pt–N(1)	80.05(14)	C(1)–Pt–C(36)	85.21(19)
C(18)–Pt–P	91.4(3)	C(1)–Pt–C(19)	85.13(12)	C(37)–Pt–C(36)	85.4(2)
N–Pt–P	97.4(2)	C(18)–Pt–C(19)	85.13(12)	C(1)–Pt–N(1)	80.36(16)
		N(1)–Pt–C(19)	88.90(11)	C(36)–Pt–N(1)	87.42(18)
		C(1)–Pt–P	94.22(10)	C(1)–Pt–P(1)	94.20(13)
		C(18)–Pt–P	90.97(14)	C(37)–Pt–P(1)	91.41(16)
		N(1)–Pt–P	95.96(9)	N(1)–Pt–P(1)	95.64(10)
		C(18)–Pt–I	93.08(14)	C(37)–Pt–I(1)	92.56(15)
		N(1)–Pt–I	94.12(9)	C(36)–Pt–I(1)	88.25(15)
		C(19)–Pt–I	88.42(7)	N(1)–Pt–I(1)	94.73(10)
		P–Pt–I	92.70(3)	P(1)–Pt–I(1)	92.59(3)

observed for **4c**, **4e**, **4f** and **4g** should correspond to the pair of enantiomers (A_{Pt}, S_C)/(C_{Pt}, R_C).

In the ^{1}H NMR of compounds **4**, two methyl-platinum resonances are observed both coupled to ^{195}Pt and to ^{31}P nucleus. In each case, *J*(H–Pt) values are lower than those observed for platinum(II) compounds and the lowest value corresponds to the methyl *trans* to phosphorous which is consistent with the higher *trans* influence of the PPh_3 [16]. In addition, both the imine proton and the aromatic proton adjacent to the metallated carbon (H_1) are coupled to platinum with *J*(H–Pt) values smaller than those observed for compounds **2** and **3**, which is consistent with the higher oxidation state of the platinum. The *J*(P–Pt) coupling constants are also reduced compared to platinum(II) compounds with values in the range 1000–1040 Hz for the major diastereomer and 970–1000 Hz for the minor diastereomer. The observed chemical shifts for ^{31}P and ^{195}Pt in the ranges −4.8 to −9.8 ppm and −2900 to −3340 ppm are also consistent with formation of platinum(IV) compounds.

Suitable crystals of **3f**, **4d** and **4f** were obtained from dichloromethane–methanol (1:1) solutions at room temperature (**3f** and **4f**) or at low temperature (**4d**). Although crystals of **4f** were of poor quality they were just good enough to allow structure solution. Compound **4d** crystallizes as a dichloromethane solvate **4d**·0.5 CH_2Cl_2 and compound **4f** as the hydrate **4f**·1.5 H_2O. The molecules are held together in the crystal by van der Waals interactions. The molecular structures are shown in Figs. 1–3, and confirm the expected geometries. The bond distances and angles are listed in Table 3. These values are in the usual range for analogous compounds [9]. As previously observed [17], differences in the Pt–N and Pt–C bond lengths between platinum(II) and platinum(IV) compounds are not significant. For compound **3f**, the platinum atom displays a planar coordination, the methyl ligand is in a *trans* position to the nitrogen atom and the C=N group is *endo* to the cycle. The sum of internal angles of the five-membered *endo*-metallacycle is 539.1°, which suggest a planar arrangement [18]. The angles between adjacent atoms in the coordination sphere of platinum lie in the range 79.9(4)–97.4(2)° the smallest angle corresponding to the "bite" angle of the metallacycle and the largest to the N–Pt–P angle. For compounds **4d** and **4f**, the platinum atom displays an octahedral coordination with a *fac*-PtC_3 arrangement and the bulky triphenylphosphine in the less hindered position which is *trans* to a methyl group. In both cases, the metallacycles which contain the imine functionality are planar with the sum of internal angles being 539.55° (**4d**) and 539.76° (**4f**). The smallest angle in the coordination sphere of platinum corresponds to the "bite" angle of the metallacycle (80.05(14)° for **4d** and 80.36(16)° for **4f**). In all cases, the spatial groups are centrosymmetric and the compounds consist of racemates, either the mixture of enantiomers (S_C) and (R_C) for **3f**, or the enantiomeric pair (C_{Pt}, S_C)/(A_{Pt}, R_C) for **4d** and **4f**.

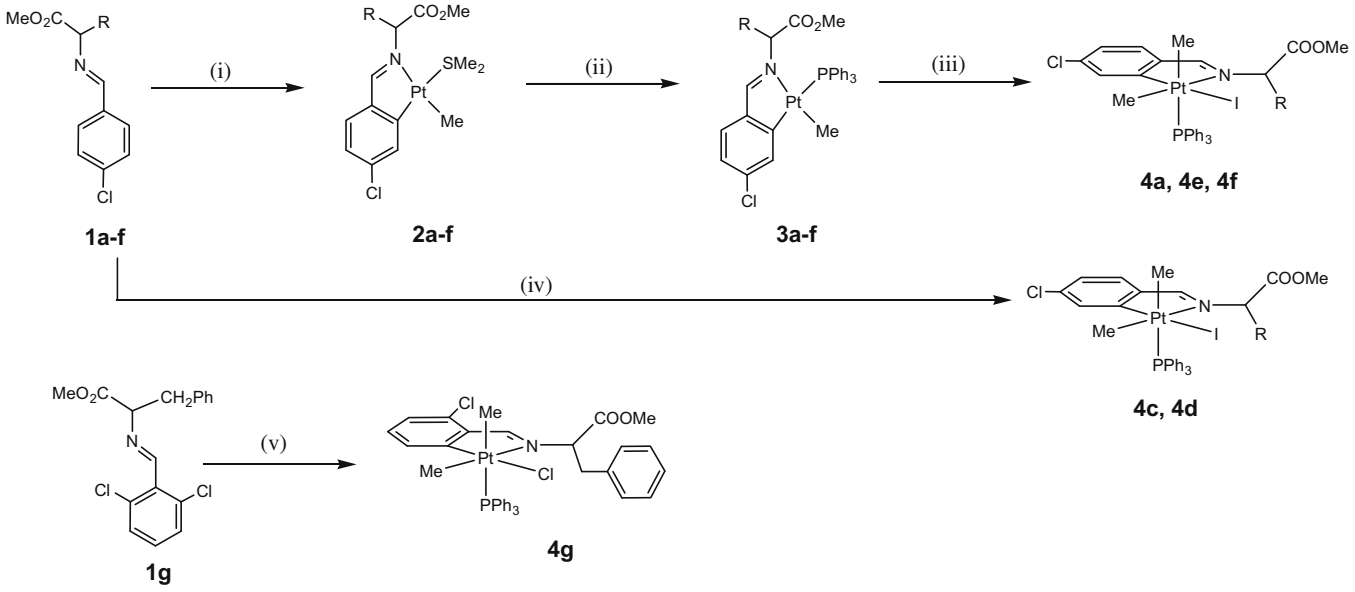
3. Conclusions

The results obtained in this work indicate easy racemization of the chiral imine ligands derived from methyl ester of amino acids as evidenced in the crystal structure of **3f**. In spite of the observed racemization of the coordinated imine ligand, a high degree of stereoselectivity has been observed in the oxidative addition of methyl iodide. As shown in Table 2, in this process, formation of one of the possible diastereomers is favoured. This result can be related to the steric hindrance created by the combined effect of the methyl ester and the R substituent of the chiral carbon along with the bulky PPh_3 ligand, which hinders the approach of MeI to one side of the platinum(II) substrate. Subsequent isomerization of the resulting platinum(IV) compound places the triphenylphosphine in a position that minimizes steric effects. As a result, exclusive formation of the enantiomeric pair (C_{Pt}, S_C)/(A_{Pt},R_C) is observed for **4d**, and this is assumed to be the major isomer obtained for **4c**, **4e** and **4f**. Analogous results were obtained when the process involves intramolecular oxidative addition of a C–Cl bond as for **4g**.

4. Experimental

4.1. General

^{1}H NMR spectra were registered on Varian Gemini 200, Varian Unity 300 and Varian Mercury 400 instruments. ^{31}P–{^{1}H} NMR spectra were recorded on Bruker DRX 250 and Varian Unity 300 spectrometers, operating at 101.2 and 121.4 MHz respectively. ^{195}Pt spectra were recorded on Bruker DRX 250 and Mercury 400 spectrometers, operating at 53.8 and 86.1 MHz, respectively. NMR experiments were carried out at 298 K using $CDCl_3$ as solvent, chemical shifts δ (in ppm) were measured relative to $SiMe_4$ for ^{1}H, to 85% H_3PO_4 for ^{31}P and to H_2PtCl_6 in D_2O for ^{195}Pt, and coupling constants *J* were measured in Hz. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; NMR labelling as shown in Chart 1. Microanalyses were performed by the *Ser-*



(i): + $[PtMe_2(\mu\text{-}SMe_2)]_2$ in acetone or diethylether at r.t. for 16h.
(ii): + PPh_3 in acetone at r.t. for 2 h.
(iii): + MeI in acetone at r.t. for 2 h. (**method A**)
(iv): + $[PtMe_2(\mu\text{-}SMe_2)]_2$ in ether at r.t. for 16h; + PPh_3 at r.t. for 2 h;+MeI at r.t. for 2h. (**method B**)
(v): + $[PtMe_2(\mu\text{-}SMe_2)]_2$ in ether at r.t. for 16h; + PPh_3 at r.t. for 2 h.(**method C**)

Chart 1.

vei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili (Tarragona) and by the *Serveis Científico-Tècnics de la Universitat de Barcelona*. Infrared spectra were recorded as KBr disks on a FTIR Nicolet 5700 spectrometer. MALDI TOF(+) mass spectra were recorded on a VOYAGER-DE-RP spectrometer (with a dithranol or a 2,5-dihydroxybenzoic acid matrix), electrospray ESI(+) mass spectra were carried out in a LC/MSD-TOF spectrometer using H_2O–CH_3CN 1:1 to introduce the sample and CI mass spectra were recorded on a ThermoFinnigan TRACE DSQ spectrometer, using NH_3 as reactive gas.

4.2. Preparation of the compounds

All starting materials were purchased from commercial sources and used as received. All solvents were dried and degassed by standard methods. Compound $[PtMe_2(\mu\text{-}SMe_2)]_2$ [19], and imines **1e**–**1g** [1a] were prepared according to the literature methods.

*[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH$_2$CO$_2$Me}(SMe$_2$)] (**2a**).* A mixture of imine **1a** (0.348 mmol, 74 mg) and $[PtMe_2(\mu\text{-}SMe_2)]_2$ (0.174 mmol, 100 mg) in 20 mL of acetone was stirred a room temperature for 16 h. The resulting suspension was filtered through celite and the filtrate was concentrated to dryness on a rotatory evaporator to give an orange solid, after addition of diethyl ether. The solid was washed with diethyl ether and dried to obtain **2a**. Yield: 161 mg (96%). ^{1}H NMR (200 MHz), δ: 8.53 (s, 1H, ^3J(Pt–H) = 52.4, H_4), 7.67 (d, 1H, ^3J(Pt–H) = 67.6, ^4J(H–H) = 1.9, H_1), 7.33 (d, 1H, ^3J(H–H) = 8.0, H_3), 7.04 (dd, 1H, ^3J(H–H) = 7.9, ^4J(H–H) = 2.0, H_2), 4.67 (s, 2H, ^3J(Pt–H) = 14.0, H_5), 3.77 (s, 3H, CO_2Me), 2.40 (s, 6H, ^3J(Pt–H) = 28.0, SMe_2), 1.06 (s, 3H, ^2J(Pt–H) = 82.2, Me). ^{195}Pt NMR (53.8 MHz) δ: −4034.3 (s). IR (KBr), ν (cm^{-1}): υ(C=O) = 1734, υ(C=N) = 1616. MS–MALDI TOF(+) *m*/*z*: $[M+H]^+$ = 482.0, $[M-Me]^+$ = 468.0, $[M-Me\text{-}SMe_2]^+$ = 406.1. Anal. Calc. for $C_{13}H_{18}ClNO_2PtS$: C, 32.33; H, 3.76%; N, 2.90; S, 6.64. Found: C, 32.4; H, 3.9; N, 2.9; S, 6.7%.

*[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH(Me)CO$_2$Me}(SMe$_2$)] (**2b**).*Compound **2b** was obtained using the same procedure than that described above from 79 mg (0.348 mmol) of imine **1b**. Yield: 161 mg (96%). ^{1}H NMR (400 MHz), δ: 8.63 (s, 1H, ^3J(Pt–H) = 52.8, H_4), 7.66 (d, 1H, ^3J(Pt–H) = 67.0, ^4J(H–H) = 2.0, H_1), 7.33 (d, 1H, ^3J(H–H) = 8.0, H_3), 7.05 (dd, 1H, ^3J(H–H) = 7.9, ^4J(H–H) = 1.9, H_2), 4.86 (q, 1H, ^3J(H–H) = 7.0, H_5), 3.75 (s, 3H, CO_2Me), 2.41 (s, 6H, ^3J(Pt–H) = 27.8, SMe_2), 1.64 (d, 3H, ^3J(H–H) = 7.0, H_6), 1.06 (s, 3H, ^2J(Pt–H) = 82.6, Me). ^{195}Pt NMR (53.8 MHz) δ: −4031.2 (s). IR (KBr), ν (cm^{-1}): υ(C=O) = 1729, υ(C=N) = 1605. MS-MALDI TOF (+) *m*/*z*: $[M+H]^+$ = 496.2, $[M-Me]^+$ = 482.2, $[M-Me\text{-}SMe_2]^+$ = 420.3. Anal. Calc. for $C_{14}H_{20}ClNO_2PtS$: C, 33.84; H, 4.06; N, 2.82; S, 6.64. Found: C, 33.8; H, 4.2; N, 2.8; S, 6.7%.

*[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH(^{i}Pr)CO$_2$Me}(SMe$_2$)] (**2c**). Compound* **2c** was obtained using the same procedure than that described above from 88 mg (0.348 mmol) of imine **1c**. Yield: 166 mg (91%). ^{1}H NMR (400 MHz), δ: 8.86 (s, 1H, ^3J(Pt–H) = 54.9, H_4), 7.65 (d, 1H, ^3J(Pt–H) = 66.7, ^4J(H–H) = 2.0, H_1), 7.35 (d, 1H, ^3J(H–H) = 8.0, H_3), 7.05 (dd, 1H, ^3J(H–H) = 8.0, ^4J(H–H) = 1.9, H_2), 4.58 (d, 2H, ^3J(Pt–H) = 11.7, ^3J(H–H) = 9.7, H_5), 3.72 (s, 3H, CO_2Me), 2.43 (s, 7H, ^3J*(Pt–H)* = 24.3, SMe_2, H_6 overlapped), 1.05 (s, 3H, ^2J(Pt–H) = 82.1, Me), 1.04 (d, 3H, ^3J(H–H) = 5.7, H_7), 1.01 (d, 3H, ^3J(H–H) = 7.0, $H_{7'}$), ^{195}Pt NMR (53.8 MHz) δ: −4045.0 (s). IR (KBr), ν (cm^{-1}): υ(C=O) = 1735, υ(C=N) = 1598. MS-MALDI TOF (+) *m*/*z*: $[M-Me]^+$ = 509.0. Anal. Calc. for $C_{16}H_{24}ClNO_2PtS$: C, 36.61; H, 4.90; N, 2.87; S, 6.11. Found: C, 37.0; H, 5.0; N, 2.9; S, 6.3%.

*[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH(CH$_2$C$_6$H$_4$-(4'-OH))CO$_2$Me}(SMe$_2$)] (**2d**).* Compound **2d** was obtained using the same procedure than that described above from 111 mg (0.348 mmol) of imine **1d**. Yield: 199 mg (97%). ^{1}H NMR (400 MHz), δ: 8.39 (s, 1H, ^3J(Pt–H) = 53.2, H_4), 7.67 (d, 1H, ^3J(Pt–H) = 67.4, ^4J(H–H) = 1.8, H_1), 7.26 (m, H_3 overlapped with $CHCl_3$), 7.02 (dd, 1H, ^3J(H–H) = 7.9, ^4J(H–H) = 1.9, H_2), 7.09 (d, 2H, ^3J(H–H) = 8.4, H_7), 6.71 (d, 2H, ^3J(H–H) = 8.5, H_8), 4.94 (br s, 1H, OH), 4.82 (t, 1H, ^3J(H–H) = 7.0, H_5), 3.71 (s, 3H, CO_2Me), 3.36 (dd, 1H, ^2J(H–H) = 13.9, ^3J(H–H) = 6.5, H_6), 3.18 (dd, 1H, ^2J(H–H) = 13.7, ^3J(H–H) = 7.1, $H_{6'}$), 2.43 (s, 6H, ^3J(Pt–H) = 27.8, SMe_2), 1.08 (s, 3H, ^2J(Pt–H) = 82.4, Me). ^{195}Pt NMR (53.8 MHz) δ: −4044.0 (s). IR (KBr), ν (cm^{-1}): υ

(C=O) = 1735, δ(C=N) = 1607. MS-MALDI TOF (+) *m/z*: $[M+H]^+$ = 590.0, $[M-Me]^+$ = 574.0, $[M-Me\text{-}SMe_2]^+$ = 512.0. Anal. Calc. for $C_{20}H_{24}ClNO_2PtS$: C, 40.78; H, 4.11; N, 2.38; S, 5.44%. Found: C, 40.9; H, 4.3; N, 2.4; S, 5.7%.

[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH(C$_6$H$_5$)CO$_2$Me}(SMe$_2$)] (***2e***). Compound **2e** was obtained using an analogous procedure than that described above using 203 mg (0.35 mmol) of $[PtMe_2(\mu\text{-}SMe_2)]_2$ and 200 mg (0.70 mmol) of imine **1e** and anhydrous diethyl ether as solvent. The mixture was stirred at room temperature for 16 h and after filtration, the solvent was removed on a rotatory evaporator to yield an orange solid. Yield: 322 mg (89%). ^{1}H NMR (400 MHz), δ: 8.54 (s, 1H, ^3J(Pt–H) = 53.3, H_4), 7.76 (d, 1H, ^4J(H–H) = 2, J(Pt–H) = 66.3, H_1), 7.34–7.43 (m, 5H, H_6, H_7 and H_8), 7.28 (d, 1H, ^3J(H–H^7) = 8, H_3), 7.03 (dd, 1H, ^4J(H–H) = 2, ^3J(H–H) = 8, H_2), 6.08 (s, 1H, H_5), 3.80 (s, 3H, CO_2Me), 2.24 (s, 6H, ^3J(Pt–H) = 27.6, SMe_2), 1.04 (s, 3H, ^2J(Pt–H) = 82.6, Me). ^{195}Pt NMR (53.8 MHz) δ: −4017.3 (s). ESI-MS {H_2O:CH_3CN (1:1)}, *m/z* (%): $[M-Cl]^+$ = 522.06. Anal. Calc. for $C_{19}H_{22}ClNO_2PtS$: C, 40.82; H, 3.97; N, 2.51; S, 5.74%. Found: C, 40.8; H, 4.0; N, 2.5; S, 5.3%.

[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH(CH$_2$C$_6$H$_5$)CO$_2$Me}(SMe$_2$)] (***2f***). Compound **2f** was obtained using the same procedure than that described for **2e** using 202 mg (0.35 mmol) of $[PtMe_2(\mu\text{-}SMe_2)]_2$ and 212 mg (0.71 mmol) of imine **1f**. Yield: 377 mg (94%). ^{1}H NMR (300 MHz) δ: 8.35 (s, 1H, ^3J(Pt–H) = 53.2, H_4), 7.60 (d, 1H, J(Pt–H) = 67.6, H_1), 7.16–7.21 (m, 6H, H_3, H_7, H_8 and H_9), 6.95 (dd, 1H, ^4J(H–H) = 1.7, ^3J(H–H) = 7.9, H_2), 4.92 (t, 1H, ^3J(H–H) = 7.0, H_5), 3.63 (s, 6H, CO_2Me), 3.34 (dd, 1H, ^2J(H–H) = 15,3; ^3J(H–H) = 6.7, H_6), 3.19 (dd, 1H, ^2J(H–H) = 13.6; ^3J(H–H) = 7.2, $H_{6'}$), 2.35 (s, 3H, ^3J(Pt–H) = 27.7, SMe_2), 1.01 (s, 3H, ^2J(Pt–H) = 81.5, Me). ^{195}Pt NMR (53.8 MHz) δ: −4025.3 (s). ESI-MS {H_2O:CH_3CN (1:1)}, *m/z* (%): $[M-CH_3]^+$ = 557.07. Anal. Calc. for $C_{19}H_{22}ClNO_2PtS$: C, 41.92; H, 4.22; N, 2.44; S, 5.60. Found: C, 42.0; H, 4.3; N, 2.5; S, 5.4%.

[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH$_2$CO$_2$Me}(PPh$_3$)] (***3a***). A mixture of **2a** (0.150 mmol, 72 mg) and PPh_3 (0.150 mmol, 39 mg) in 20 mL of acetone was stirred at room temperature for 2 h. The resulting suspension was filtered through celite and the filtrate was concentrated to dryness on a rotatory evaporator to give an orange solid, after addition of diethyl ether. The solid was washed with diethyl ether and dried to obtain **3a**. Yield: 46 mg (45%). ^{1}H NMR (400 MHz), δ: 8.56 (s, 1H, ^3J(Pt–H) = 50.8, H_4), 7.80 (dd, 1H, ^3J(Pt–H) = 54.0, ^4J(P–H) = 5.8, ^4J(H–H) = 1.9, H_1), 7.6–7.75 (m, 6H, PPh_3 *ortho*), 7.35–7.50 (m, 10H, H_3, PPh_3 *meta, para*), 7.11 (dd, 1H, ^3J(H–H) = 8.0, ^4J(H–H) = 2.0, H_2), 3.93 (s, 2H, ^3J(Pt–H) = 11.6, H_5), 3.36 (s, 3H, CO_2Me), 0.77 (d, 3H, ^2J(Pt–H) = 83.0, ^3J(P–H) = 7.5, Me). ^{31}P{^{1}H} NMR (121.4 MHz) δ: 29.68 (s, ^1J(Pt–P) = 2288.7). ^{195}Pt NMR (53.8 MHz) δ: −4288.8 (d, ^1J(Pt–P) = 2276.5). IR (KBr), *ν* (cm^{-1}): υ(C=O) = 1748, υ(C=N) = 1623, PPh_3 (q-X sensitive) = 1096. MS-MALDI TOF (+) *m/z*: $[M+H]^+$ = 681.0, $[M-Me]^+$ = 668.0. Anal. Calc. for $C_{29}H_{27}ClNO_2PPt$: C, 50.59; H, 3.98; N, 2.02. Found: C, 50.7; H, 4.2; N, 2.1%.

[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH(Me)CO$_2$Me}(PPh$_3$)] (***3b***). Compound **3b** was obtained using the same procedure than that described above from 75 mg (0.150 mmol) of **2b**. Yield: 37 mg (35%). ^{1}H NMR (400 MHz), δ: 8.78 (s, 1H, ^3J(Pt–H) = 53.2, H_4), 7.66 (dd, 1H, ^3J(Pt–H) = 53.8, J(P–H) = 5.8, ^4J(H–H) = 2.0, H_1), 7.65–7.75 (m, 6H, PPh_3 *ortho*), 7.35–7.50 (m, 10H, H_3, PPh_3 *meta* and *para*), 7.11 (dd, 1H, ^3J(H–H) = 8.0, ^4J(H–H) = 1.9, H_2), 4.07 (q, 1H, ^3J(H–H) = 7.2, H_5), 3.43 (s, 3H, CO_2Me), 0.94 (d, 3H, ^3J(H–H) = 7.2, H_6), 0.78 (d, 3H, ^2J(Pt–H) = 82.4, J(P–H) = 7.5, Me). ^{31}P{^{1}H} NMR (121.4 MHz) δ: 30.34 (s, ^1J(Pt–P) = 2268.4). ^{195}Pt NMR (53.8 MHz) δ: −4234.3 (d, ^1J(Pt–P) = 2284.8). IR (KBr), *ν* (cm^{-1}): υ(C=O) = 1737, υ(C=N) = 1622, PPh_3 (q-X sensitive) = 1096. MS-MALDI TOF (+) *m/z*: $[M+H]^+$ = 695.8, $[M-Me]^+$ = 681.8. Anal. Calc. for $C_{30}H_{29}ClNO_2PPt$: C, 51.69; H, 4.19; N, 2.01. Found: C, 51.8; H, 4.4; N, 2.0%.

[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH(^{i}Pr)CO$_2$Me}(PPh$_3$)] (***3c***). Compound **3c** was obtained using the same procedure than that described above from 79 mg (0.150 mmol) of **2c**. Yield: 78 mg (72%). ^{1}H NMR (400 MHz), δ: 8.99 (s, 1H, ^3J(Pt–H) = 55.9, H_4), 7.77 (dd, 1H, ^3J(Pt–H) = 53.6, ^4J(P–H) = 5.8, J(H–H) = 2.0, H_1), 7.65–7.75 (m, 6H, PPh_3 *ortho*), 7.35–7.5 (m, 10H, H_3, PPh_3 *meta* and *para*), 7.10 (dd, 1H, ^3J(H–H) = 8.0, ^4J(H–H) = 2.0, H_2), 3.70 (d, 1H, ^3J(Pt–H) = 11.6, ^3J(H–H) = 9.6, H_5), 3.41 (s, 3H, CO_2Me), 1.92 (m, 1H, H_6), 0.76 (d, 3H, ^2J(Pt–H) = 82.3, J(P–H) = 7.4, Me), 0.47 (d, 3H, ^3J(H–H) = 6.7, H_7), 0.44 (d, 3H, ^3J(H–H) = 6.6, $H_{7'}$). ^{31}P{^{1}H} NMR (121.4 MHz) δ: 30.74 (s, ^1J(Pt–P) = 2258.3). ^{195}Pt NMR (53.8 MHz) δ: −4254.3 (d, ^1J(Pt–P) = 2258.8). IR (KBr), *ν* (cm^{-1}): υ(C=O) = 1742, υ(C=N) = 1619, PPh_3 (q-X sensitive) = 1095. MS-MALDI TOF (+) *m/z*: $[M+H]^+$ = 723.9, $[M-Me]^+$ = 708.9. Anal. Calc. for $C_{32}H_{33}ClNO_2PPt$: C, 53.00; H, 4.59; N, 1.93. Found: C, 52.4; H, 4.2; N, 1.9%.

[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH(CH$_2$C$_6$H$_4$-(4'-OH))CO$_2$Me}(PPh$_3$)] (***3d***). Compound **3d** was obtained using the same procedure than that described above from 88 mg (0.150 mmol) of **2d**. Yield: 77 mg (65%). ^{1}H NMR (400 MHz), δ: 8.50 (s, 1H, ^3J(Pt–H) = 53.8, H_4), 7.79 (dd, 1H, ^3J(Pt–H) = 52.3, ^4J(P–H) = 5.7, ^4J(H–H) = 1.9, H_1), 7.68–7.76 (m, 6H, PPh_3 *ortho*), 7.35–7.5 (m, 10H, H_3, PPh_3 *meta* and *para*), 7.01 (dd, 1H, ^3J(H–H) = 8.0, ^4J(H–H) = 2.0, H_2), 6.53 (d, 2H, ^3J(H–H) = 8.5, H_7), 6.37 (d, 2H, ^3J(H–H) = 8.5, H_8), 4.81 (br s, 1H, OH), 4.31 (dd, 1H, ^3J(H–H) = 8.3, ^4J(H–H) = 4.4, H_5), 3.29 (s, 3H, CO_2Me), 2.72 (dd, 1H, ^2J(H–H) = 13.7, ^3J(H–H) = 4.4, H_6), 2.44 (dd, 1H, ^2J(H–H) = 13.7, ^3J(H–H) = 8.4, $H_{6'}$), 1.08 (d, 3H, ^2J(Pt–H) = 82.8, J(P–H) = 7.6, Me). ^{31}P{^{1}H} NMR (121.4 MHz) δ: 30.85 (s, ^1J(Pt–P) = 2276.9). IR (KBr), *ν* (cm^{-1}): υ(C=O) = 1734, υ(C=N) = 1612, PPh_3 (q-X sensitive) = 1096. MS-MALDI TOF (+) *m/z*: $[M+H]^+$ = 788.2, $[M-Me]^+$ = 774.2. Anal. Calc. for $C_{36}H_{33}ClNO_3PPt$: C, 54.79%; H, 4.21%, N, 1.77%. Found: C, 55.0; H, 4.5; N, 1.8%.

[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH(C$_6$H$_5$)CO$_2$Me}(PPh$_3$)] (***3e***). Compound **3e** was obtained using the same procedure than that described above from 273 mg (0.52 mmol) of **2e**. Yield: 376 mg (95%). ^{1}H NMR (300 MHz), δ: 8.65 (s, 1H, J(Pt–H) = 52.9, H_4), 7.69–7.80 (m, 6H, PPh_3 *ortho*), 7.41–7.04 (m, 16H, H_{arom}), 6.62 (d, 1H, ^3J(H–H) = 7, H_3), 5.31 (s, 1H, H_5); 3.39 (s, 3H, CO_2Me), 0.81 (d, 3H, J(Pt–H) = 83.1, ^3J(Me–P) = 7.6, Me). ^{31}P{^{1}H} NMR (121.4 MHz, $CHCl_3$) δ: 31.92 (s, J(Pt–P) = 2262.1). ^{195}Pt NMR (53.8 MHz), δ: −4266.5 (d, ^1J(Pt–P) = 2264.3). ESI-MS {H_2O:CH_3CN (1:1)}, *m/z* (%): $[M+H]^+$=759.16; $[2\,M+Na]^+$ = 1539.30. Anal. Calc. for $C_{35}H_{31}ClNO_2PPt$: C, 55.38; H, 4.12; N, 1.85. Found: C, 56.0; H, 4.1; N, 1.9%.

[PtMe{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH(CH$_2$C$_6$H$_5$)CO$_2$Me}(PPh$_3$)] (***3f***). Compound **3f** was obtained using the same procedure than that described above from 286 mg (0.50 mmol) of **2f**. Yield: 376 mg (98%). ^{1}H NMR (300 MHz), δ: 8.53 (s, 1H, ^4J(Pt–H) = 53.8, H_4), 7.69–7.85 (m, 6H, PPh_3 *ortho*), 7.45–7.05 (m, 16H, H_{arom}), 6.50 (dd, 1H, ^3J(H–H) = 7.9, ^4J(H–H) = 1.3, H_2), 4.36 (dd, 1H, ^3J(H–H) = 8.7, ^3J(H–H) = 4.4, H_5), 3.27 (s, 3H, CO_2Me), 2.80 (dd, 1H, ^2J(H–H) = 13.7; ^3J(H–H) = 4.4, H_6), 2.53 (dd, 1H, ^2J(H–H) = 13.5; ^3J(H–H) = 8.7, $H_{6'}$), 0,79 (d, 3H, J(Pt–H) = 82.6, ^3J(P–H) = 7.6, Me). ^{31}P{^{1}H} NMR (121.4 MHz) δ: 32.86 (s, ^1J(Pt–P) = 2269.1). ^{195}Pt NMR (86.1 MHz), δ: −4241.6 (d, ^1J(Pt–P) = 2270.4). ESI-MS {H_2O:CH_3CN (1:1)}, *m*/z (%): $[M+H]^+$ = 774.17. Anal. Calc. for $C_{36}H_{33}ClNO_2PPt$: C, 55.92; H, 4.30; N, 1.81. Found: C, 56.3; H, 4.4; N, 1.9%.

[PtMe$_2$I{κ²-(C,N)-4-ClC$_6$H$_3$CH=NCH$_2$CO$_2$Me}(PPh$_3$)] (***4a***)**.** An excess (0.15 mL, 2.4 mmol) of methyl iodide was added to a solution of **3a** (75 mg, 0.11 mmol) in acetone. The solution was stirred at room temperature for 2 h and the solvent was concentrated to dryness on a rotatory evaporator. After addition of diethyl ether to the residue a white solid was obtained. The solid was washed with diethyl ether and dried to obtain **4a**. Yield: 68 mg (76%). ^{1}H NMR

(400 MHz), δ: 8.33 (s, 1H, ^3J(Pt–H) = 46.2, H_4), 7.20–7.50 (m, 16H, H_3, PPh_3), 7.01 (dd, 1H, ^3J(H–H) = 8.1, ^4J(H–H) = 0.9, H_2), 6.45 (s, 1H, ^3J(Pt–H) = 48.6, H_1), 5.17 (d, 1H, ^2J(H–H) = 17.5, H_5), 4.55 (s, 1H, ^2J(H–H) = 17.5, ^3J(Pt–H) = 12.0, $H_{5'}$), 3.69 (s, 3H, CO_2Me), 1.55 (d, 3H, ^2J(Pt–H) = 70.8, ^3J(P–H) = 7.8, Me_2), 1.20 (d, 3H, ^2J(Pt–H) = 59.8, ^3J(P–H) = 7.5, Me_1). $^{31}P\{^1H\}$ NMR (121.4 MHz) δ: −9.77 (s, ^1J(Pt–P) = 1006.2). IR (KBr), ν (cm^{-1}): υ(C=O) = 1747, υ(C=N) = 1623. MS-MALDI TOF (+) m/z: $[M-2Me-I]^+$ = 668.0, $[M-Me-I]^+$ = 682.0. Anal. Calc. for $C_{30}H_{30}ClINO_2PPt$: C, 43.68; H, 3.66; N, 1.70. Found: C, 43.8; H, 3.8; N, 1.9%.

*[$PtMe_2I\{\kappa^2$-(C,N)-4-ClC_6H_3CH=NCH(^iPr)$CO_2Me\}(PPh_3)$] (**4c**).* *Compound* **4c** was obtained from $[PtMe_2(\mu\text{-}SMe_2)]_2$ (156 mg, 0.27 mmol) and imine **1c** (135 mg, 0.53 mmol) which were allowed to react at room temperature in 20 mL of anhydrous diethyl ether for 16 h. Triphenylphosphine (138 mg, 0.53 mmol) was added to the obtained yellow solution and the mixture was stirred for 2 h. Finally an excess of methyl iodide (0.1 mL) was added with continuous stirring for 2 h. The solvent was removed on a rotary evaporator and the residue was recrystallized in dichloromethane–methanol at room temperature to produce yellow crystals. Yield 217 mg (46%). ^1H NMR (300 MHz), δ: 8.91 (s, 1H, ^3J(Pt–H) = 48.3, H_4), 7.12–7.50 (m, 16H, H_3, PPh_3), 6.97 (dd, 1H, ^3J(H–H) = 8.0, ^4J(H–H) = 1.1, H_2), 6.29 (s, 1H, ^3J(Pt–H) = 47.6, H_1), 5.72 (d, 1H, ^3J(H–H) = 3.1, H_5), 3.51 (s, 3H, CO_2Me), 2.46 (m, 1H, ^3J(H–H) = 3.5, H_6), 1.52 (d, 3H, ^2J(Pt–H) = 70.3, ^3J(P–H) = 7.9, Me_2), 1.23 (d, 3H, ^2J(Pt–H) = 59.2, ^3J(P–H) = 7.3, Me_1), 1.19 (d, 3H, ^3J(H–H) = 7.3, $Me_{7'}$), 0.86 (d, 3H, ^3J(H–H) = 6.9, $Me_{7'}$). $^{31}P\{^1H\}$ NMR (121.4 MHz) δ: −9.03 (s, ^1J(Pt–P) = 1011.5, *major isomer*), −9.49 (s, ^1J(Pt–P) = 997.3, *minor isomer*). ^{195}Pt NMR (86.1 MHz), δ: −3318.7 (d, ^1J(Pt–P) = 1012.9, *major isomer*). ESI-MS (+) m/z: $[M-I]^+$ = 739.18. Anal. Calc. for $C_{33}H_{36}ClINO_2PPt$: C, 45.71; H, 4.18; N, 1.62. Found: C, 45.4; H, 4.2; N 1.6%.

*[$PtMe_2I\{\kappa^2$-(C,N)-4-ClC_6H_3CH=NCH($CH_2C_6H_4$-(4'-OH))$CO_2Me\}(PPh_3)$] (**4d**).* *Compound* **4d** was obtained as yellow crystals using the procedure indicated above for **4c** from 166 mg of imine **1d** (0.52 mmol). Yield 237 mg (49%). ^1H NMR (400 MHz), δ: 7.77 (d, 1H, ^3J(Pt–H) = 48.3, J(H–H) = 1.6, H_4), 7.47–7.55 (m, 6H, PPh_3 *ortho*), 7.28–7.15 (m, 11H, H_2, H_3, PPh_3 *meta* and *para*), 6.92 (d, 2H, ^3J(H–H) = 8.5, H_7), 6.69 (d, 2H, ^3J(H–H) = 8.5, H_8), 6.24 (s, 1H, ^3J(Pt–H) = 48.5, H_1), 3.56 (dd, 1H, ^2J(H–H) = 13.9, ^3J(H–H) = 4.2, H_6), 3.47 (s, 3H, CO_2Me), 2.99 (dd, 1H, ^2J(H–H) = 14.0, ^3J(H–H) = 6.5, $H_{6'}$), 1.52 (d, 3H, ^2J(Pt–H) = 68.5, ^3J(P–H) = 7.8, Me_2), 1.36 (d, 3H, ^2J(Pt–H) = 58.0, ^3J(P–H) = 7.3, Me_1). $^{31}P\{^1H\}$ NMR (121.4 MHz) δ: −9.14 (s, ^1J(Pt–P) = 1036.9). ^{195}Pt NMR (86.1 MHz), δ: −3331.9 (d, ^1J(Pt–P) = 1035.4). ESI-MS (+) m/z: $[M-I]^+$ = 803.18. Anal. Calc. for $C_{37}H_{36}ClINO_3PPt$: C, 47.73; H, 3.90; N, 1.50. Found: C, 47.3; H, 3.7; N, 1.2%.

*[$PtMe_2I\{\kappa^2$-(C,N)-4-ClC_6H_3CH=NCH(C_6H_5)$CO_2Me\}(PPh_3)$] (**4e**).* *Compound* **4e** was obtained as a yellow solid using the procedure indicated above for **4a** from 149 mg of compound **3e** (0.20 mmol). Yield 171 mg (97%). ^1H NMR (400 MHz), δ: 8.66 (s, 1H, ^3J(Pt–H) = 47.8, H_4), 7.91 (s, 1H, ^3J(Pt–H) = 44.1, H_1), 7.91–7.83 (m, 6H, PPh_3 *ortho*), 7.41–7.20 (m, 20H), 7.14 (d, 1H, ^3J(H–H) = 8.0, H_2 or H_3), 6.62 (d, 1H, ^3J(H–H) = 8.0, H_2 or H_3), 5.31 (s, 1H, H_5), 3.83 (s, 3H, CO_2Me), 1.51 (d, 3H, ^2J(Pt–H) = 70.9, ^3J(P–H) = 7.9, Me_2), 0.98 (d, 3H, ^2J(Pt–H) = 59.3, ^3J(P–H) = 7.6, Me_1). $^{31}P\{^1H\}$ NMR (121.4 MHz) δ: −7.63 (s, ^1J(Pt–P) = 1016.5, *major isomer*), −8.98 (s, ^1J(Pt–P) = 977.4, *minor isomer*). ^{195}Pt NMR (53.8 MHz), δ: −3333.8 (d, ^1J(Pt–P) = 1023.4, *major isomer*). ESI-MS (+) m/z: $[M-I]^+$ = 773.17. Anal. Calc. for $C_{36}H_{34}ClINO_2PPt$: C, 47.99, H, 3.80, N, 1.55. Found: C, 47.8; H, 3.9; N, 1.6%.

*[$PtMe_2I\{\kappa^2$-(C,N)-4-ClC_6H_3CH=NCH($CH_2C_6H_5$)$CO_2Me\}(PPh_3)$] (**4f**).* *Compound* **4f** was obtained as a yellow solid using the procedure indicated above for **4a** from 328 mg of compound **3f** (0.42 mmol). Yield 372 mg (96%). ^1H NMR (400 MHz), δ: 8.57 (s, 1H, ^3J(Pt–H) = 46.4, H_4), 7.75–7.68 (m, 6H, PPh_3 *ortho*), 7.53–7.35 (m, 9H, PPh_3 *meta* and *para*), 7.32–7.03 (m, 5H, H_7, H_8, H_9), 4.36 (dd, 1H, ^3J(H–H) = 8.6, 4.5, H_5), 3.27 (s, 3H, CO_2Me), 2.80 (dd, 1H, ^2J(H–H) = 13.5, ^3J(H–H) = 4.4, H_6), 2.53 (dd, 1H, ^2J(H–H) = 13.5, ^3J(H–H) = 8.7, $H_{6'}$), 1.52 (d, 3H, ^2J(Pt–H) = 70.4, ^3J(P–H) = 8.0, Me_2), 1.38 (d, 3H, ^2J(Pt–H) = 59.2, ^3J(P–H) = 7.2, Me_1). $^{31}P\{^1H\}$ NMR (121.4 MHz) δ: −8.10 (s, ^1J(Pt–P) = 1034.2, *major isomer*), −7.16 (s, ^1J(Pt–P) = 992.2, *minor isomer*). ^{195}Pt NMR (53.8 MHz), δ: −3332.6 (d, ^1J(Pt–P) = 1035.1, *major isomer*), δ: −3313.9 (d, ^1J(Pt–P) = 990.5, *minor isomer*). ESI-MS (+) m/z: $[M-I-Me]^+$ = 771.15, $[M-I]^+$ = 787.17. Anal. Calc. for $C_{37}H_{36}ClINO_2PPt$: C 48.56%, H 3.97%, N 1.53%. Found: C 48.7%, H 4.0%, N 1.6%.

*[$PtMe_2Cl\{\kappa^2$-(C,N)-2-ClC_6H_3CH=NCH($CH_2C_6H_5$)$CO_2Me\}(PPh_3)$] (**4g**).* *Compound* **4g** was obtained from $[PtMe_2(\mu\text{-}SMe_2)]_2$ (201 mg, 0.35 mmol) and imine **1g** (234 mg, 0.70 mmol) which were allowed to react at room temperature in 20 mL of diethyl ether for 16 h. Triphenylphosphine (183 mg, 0.36 mmol) was added to the obtained yellow solution and the mixture was stirred for 2 h. The

Table 4
Crystallographic and refinement data for compounds **3f**, **4d** and **4f**.

	Compound **3f**	Compound **4d**	Compound **4f**
Formula	$C_{36}H_{33}ClNO_2PPt$	$2(C_{37}H_{36}ClINO_3PPt),CH_2Cl_2$	$2(C_{37}H_{36}ClINO_2PPt),3(H_2O)$
Fw	773.14	1947.08	1884.20
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.019(3)	10.717(5)	10.726(3)
b (Å)	11.898(7)	13.317(4)	13.363(3)
c (Å)	24.121(7)	15.345(4)	14.864(3)
α (°)	90	114.41(2)	113.38(2)
β (°)	90.24(2)	107.68(2)	106.74(2)
γ (°)	90	90.53(3)	92.02(2)
V (Å^3); Z	3162(2)	1877.0(12)	1845.4(8); 1
D_{calc} (Mg/m^3)	1.624	1.723	1.695
Absolute coefficient (mm^{-1})	4.605	4.781	4.790
F(0 0 0)	1528	946	918
Reflections collected/unique	9377/9189	19 042/9809	18 028/9622
Data/restraint/parameters	9189/1/373	9809/7/435	9622/3/424
GOF on F^2	0.814	1.119	1.085
$R_1(I > 2\sigma(I))$	0.0489	0.0319	0.0396
wR_2 (all data)	0.1226	0.0938	0.1081
Peak and hole (e Å^{-3})	0.959 and −0.556	1.393 and −1.466	0.988 and −0.873

solvent was removed on a rotary evaporator and the residue was recrystallized in dichloromethane–methanol at low temperature to produce yellow crystals. Yield 102 mg (47%). ^{1}H NMR (300 MHz), δ: 8.16 (d, 1H, ^3J(Pt–H) = 50.8, ^4J(H–H) = 1.9, H_4), 7.48–7.58 (m, 6H, PPh_3 *ortho*), 7.07–7.23 (m, 9H, PPh_3 *meta* and *para*), 7.04–6.68 (m, 5H, H_7, H_8, H_9), 6.70 (d, 1H, ^3J(H–H) = 7.9, H_3), 6.54 (t, 1H, ^3J(H–H) = 7.9, H_2), 6.41 (d, 1H, ^3J(H–H) = 7.9, H_1), 5.99 (dd, 1H, ^3J(H–H) = 6.7, 4.0, H_5), 3.61 (dd, 1H, ^2J(H–H) = 13.8, ^3J(H–H) = 4.2, H_6), 3.35 (s, 3H, CO_2Me), 3.00 (dd, 1H, ^2J(H–H) = 13.8, ^3J(H–H) = 6.6, H_6), 1.28 (d, 3H, ^2J(Pt–H) = 68.6, ^3J(P–H) = 8.2, Me_2), 1.03 (d, 3H, ^2J(Pt–H) = 58.3, ^3J(P–H) = 7.6, Me_1). ^{31}P{^{1}H} NMR (121.4 MHz) δ: −5.56 (s, ^1J(Pt–P) = 1015.7, *major isomer*), −4.83 (s, ^1J(Pt–P) = 972.4, *minor isomer*). ^{195}Pt NMR (53.8 MHz), δ: −2946.7 (d, ^1J(Pt–P) = 1015.6, *major isomer*). ESI-MS (+) *m*/*z*: $[M-PPh_3\text{-}Cl-2Me]^+$ = 496.86, $[M-2Me]^+$ = 790.08. Anal. Calc. for $C_{37}H_{36}Cl_2NO_2PPt$: C, 53.95; H, 4.40; N, 1.70. Found: C, 55.1; H, 4.4; N, 1.5%.

4.3. X-ray structure analysis

Prismatic crystals were selected and mounted on an Enraf-Nonius CAD4 four-circle (**3f**) or on a MAR345 (**4d** and **4f**) diffractometer with an image plate detector. Intensities were collected with graphite monochromatized Mo Kα radiation. The structures were solved by direct methods using SHELXS computer program [20] and refined by the full-matrix least-squares method, with the SHELXL97 computer program [20] using 9377 (**3f**), 19042 (**4d**) and 18028 (**4f**) reflections (very negative intensities were not assumed). The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0294P)^2]^{-1}$ (**3f**), $w = [\sigma^2(I) + (0.0456P)^2 + 1.0625P]^{-1}$ (**4d**), $w = [\sigma^2(I) + (0.0544P)^2 + 1.4112P]^{-1}$ (**4f**) and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from International Tables of X-ray Crystallography [21]. 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 4.

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Appendix A. Supplementary data

CCDC 723579, 723580 and 723581 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.04.019.

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