Note

Cyclometallated platinum(II) complexes containing the chiral ligand [2-(diphenyl-phosphanyl)-benzylidene]-(1-phenyl-ethyl)-amine: Synthesis and molecular structures of the compounds [PtCl(Me){κ^2-(R)-Ph$_2$P(C$_6$H$_4$)CH=NCH(Ph)Me-P,N}] and [Pt{κ^3-(S)-Ph$_2$P(C$_6$H$_4$)CH=NCH(C$_6$H$_4$)Me-P,N,C}Py]BF$_4$

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Abstract

Diastoreoisomeric mixtures of the complex [PtIMe$_3${κ^2-Ph$_2$P(C$_6$H$_4$)CH=NCH(Ph)Me-P,N}] (Rc-1) react with AgBF$_4$ and SMePh to give a mixture of complexes [PtMe(SMePh){κ^2-Ph$_2$P(C$_6$H$_4$)CH=NCH(Ph)Me-P,N}]BF$_4$ (2) and [Pt{κ^3-Ph$_2$P(C$_6$H$_4$)CH=NCH(C$_6$H$_4$)-Me-P,N,C}(PhSMe)]BF$_4$ (3) which subsequently render the corresponding chloride compounds [PtClMe{κ^2-(R)-Ph$_2$P(C$_6$H$_4$)CH=NCH(Ph)Me-P,N}] (4) and [PtCl{κ^3-(R)-Ph$_2$P(C$_6$H$_4$)CH=NCH(C$_6$H$_4$)Me-P,N,C}] (5), by elution with CH$_2$Cl$_2$ on a aluminium oxide chromatography column. Refluxing of [PtIMe$_3${κ^2-Ph$_2$P(C$_6$H$_4$)CH=NC*H(Ph)Me-P,N}] (Sc-1) with AgBF$_4$ in a 1:1, CH$_2$Cl$_2$:Me$_2$CO mixture followed by the addition of SMePh, NCMe or pyridine (Py) affords the corresponding cyclometallated compounds [Pt{κ^3-(S)-Ph$_2$P(C$_6$H$_4$)CH=NCH(C$_6$H$_4$)Me-P,N,C}(L)]BF$_4$ [L = SMePh (3), NCMe (9), Py (10)]. These compounds have been characterised by analytical and spectroscopic means and by the molecular structure determination of complexes 4 and 10.
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1. Introduction

In the last decades the chemistry of cyclometallated transition metal complexes has attracted much interest [1]. In particular, cyclometallated complexes of Group 10 elements have been extensively studied due to their behaviour as versatile starting materials for organic synthesis [2–4], photochemistry [5,6], homogeneous catalysis [7], liquid crystal [8], asymmetric synthesis [9] and optical resolution [10,11] purposes.

Diarylplatinum(II) complexes containing labile dialkyl-sulfide ligands, of the type {PtR$_2$(μ-SMe$_2$)}$_2$ are suitable materials for preparing cyclometallated platinum(II) compounds. Thus, their reaction with iminic ligands, derived from halobenzylamines [12], N,N′-dimethylethylendiamine [13] or (S)-α-methylbenzylamine [14] and a variety of aldehydes, affords cyclometallated compounds through C–X (X = H, Cl, Br, I) bond activation. Moreover, taking advantage of the presence of Pt–N and Pt–C donor bonds, related cyclometallated Pt(IV) derivatives can be easily obtained from them by oxidative addition of alkyl halides [15]. In addition, cycloplatination of these type of ligands can be promoted by other platinum(II) substrates such as

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cis-[PtCl$_2$(DMSO)$_2$] [16] or [Pt(dba)$_2$] (dba = dibenzylideneacetone) [17].

Recently, we reported that the reaction of diastereoisomeric mixtures of the complex [PtIMe$_3${κ^2-Ph$_2$P(C$_6$H$_4$)-CH=NCH(Ph)Me-*P,N*}] with AgBF$_4$ in the presence of PPh$_3$ renders the cyclometallated complex [Pt{κ^3-Ph$_2$P-(C$_6$H$_4$)CH=NCH(C$_6$H$_4$)Me-*P,N,C*}(PPh$_3$)][BF$_4$] *via* consecutive reductive elimination and orthometallation processes. However, when pyridine (Py) was used instead of PPh$_3$ only the reductive elimination step occurred and [PtMe(Py){κ^2-Ph$_2$P(C$_6$H$_4$)CH= NCH(Ph)Me-*P,N*}][BF$_4$] was the product obtained [18].

Following our interest in the synthesis and reactivity of orthometallated Pt(II) complexes, in this note we report a more direct method for the synthesis of cyclometallated compounds of formula [Pt{κ^3-Ph$_2$P(C$_6$H$_4$)CH=NCH-(C$_6$H$_4$)Me-*P,N,C*}(L)][BF$_4$]. The molecular structures of complexes [PtClMe{κ^2-(*R*)-Ph$_2$P(C$_6$H$_4$)CH=NCH(Ph)-Me-*P,N*}] and [Pt{κ^3-(*S*)-Ph$_2$P(C$_6$H$_4$)H=NCH(C$_6$H$_4$)Me-*P,N,C*}Py]BF$_4$ are also reported.

2. Experimental

2.1. General

All reactions were carried out by standard Schlenk techniques under a dry nitrogen atmosphere. Reagent grade solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting complex [PtIMe$_3$]$_4$ [19], the ligands (*S*)- and (*R*)-Ph$_2$PC$_6$H$_4$CH=NCH(Ph)Me [20] and diastereomeric mixtures of the complex [PtIMe$_3${κ^2-Ph$_2$P(C$_6$H$_4$)CH=NCH(Ph)Me-*P,N*}] (**1**) [18] were synthesized according to literature procedures. ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-200P and Avance-400 spectrometers. Chemical shifts are reported in ppm relative to SiMe$_4$ (^{1}H,^{13}C) and 85% H$_3$PO$_4$ in D$_2$O (^{31}P) (positive shifts downfield) as internal and external standards, respectively. Elemental analyses (C, H, N, S) were carried out with a Fisons EA-118 microanalyser.

2.2. Synthesis of the complexes

2.2.1. [PtClMe{κ^2-(R)-Ph$_2$P(C$_6$H$_4$)CH=NCH(Ph)-Me-P,N}] (4) and [PtCl{κ^3-(R)-Ph$_2$P(C$_6$H$_4$)CH=NCH(C$_6$H$_4$)Me-P,N,C}] (5)

Complex (*Rc*-**1**, 150.6 mg, 0.198 mmol) in a mixture dichloromethane-acetone (1:1, 20 mL) was treated with AgBF$_4$ (40.9 mg, 0.210 mmol). After stirring the mixture for **1** h at room temperature, the AgI formed was removed by filtration. The filtrate was vacuum-evaporated to dryness and the solid residue was dissolved in dichloromethane (25 mL). To the resulting solution thioanisole (23.3 μL, 0.198 mmol) was added. The mixture was stirred under reflux for 1 h. After cooling, the resulting solution was vacuum-concentrated. Addition of diethyl ether gave a yellow solid (125.8 mg), which was characterized by ^{1}H and

^{31}P{^{1}H} NMR spectroscopy as a mixture of [PtMe{κ^2-(*R*)-Ph$_2$P(C$_6$H$_4$)CH=NCH(Ph)Me-*P,N*}(SMePh)][BF$_4$] [**2**; 101.9 mg (81%); ^{1}H NMR (CDCl$_3$)δ 8.51 (s, $^3J_{HPt}$ = 43.3 Hz, 1H, CH=N), 5.45 (q, $^3J_{HH}$ = 6.8 Hz, 1H, C*H), 2,77 (s, $^3J_{HPt}$ = 29.8 Hz, 3H, MeS), 1.52 (d, 3H, C*Me), 0.26 (d, $^3J_{HP}$ = 3.3 Hz, $^2J_{HPt}$ = 69.1 Hz, 3H, PtMe). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 17.26 (s, $^1J_{PPt}$ = 1812.2 Hz)] and [Pt{κ^3-(*R*)-Ph$_2$P(C$_6$H$_4$)CH=NCH- (C$_6$H$_4$)Me-*P,N,C*}-(SMePh)][BF$_4$] [**3**; 23.9 mg (19%); NMR: see Section 2.2.2]. The solid residue was dissolved in dichloromethane and chromatographed on neutral aluminium oxide in diethyl ether. A yellow band, eluted in dichloromethane, was collected. This solution was vacuum-evaporated to dryness giving complex **4** as a pale yellow solid. A second yellow band, eluted in ethanol, was collected and vacuum-evaporated to dryness to give complex **5** as a yellow solid.

Compound **4**. Yield: 50.3 mg (61.8%). Anal. Calc. for C$_{28}$H$_{27}$ClNPPt: C, 52.6; H, 4.3; N, 2.2. Found: C, 52.2; H, 4.1; N, 2.1%. ^{1}H NMR (CDCl$_3$): δ 8.10 (s, $^3J_{HPt}$ = 39.0 Hz, 1H, CH=N), 6.89 (q, $^3J_{HH}$ = 6.8 Hz, 1H, C*H), 1.53 (d, 3H, C*Me), 0.63 (d, $^3J_{HP}$ = 3.5 Hz, $^2J_{HPt}$ = 72.2 Hz, 3H, PtMe). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 15.31 (s, $^1J_{PPt}$ = 4712.2 Hz).

Compound **5**. Yield: 16.3 mg (85.9%). Anal. Calc. for C$_{27}$H$_{23}$ClNPPt: C, 52.1; H, 3.7; N, 2.3. Found: C, 51.9; H, 3.5; N, 2.1%. ^{1}H NMR (CDCl$_3$): δ 8.51 (s, $^3J_{HPt}$ = 119.3 Hz, 1H, CH=N), δ 5.25 (q, $^3J_{HH}$ = 6.7 Hz, $^3J_{HPt}$ = 49.1 Hz, 1H, C*H), 1.54 (d, $^3J_{HH}$ = 6.7 Hz, 3H, C*Me). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 17.30 (d, $^1J_{PPt}$ = 1883.2 Hz).

2.2.2. [Pt{κ^3-(S)-Ph$_2$P(C$_6$H$_4$)CH=NCH(C$_6$H$_4$)Me-C,N,P}(L)]BF$_4$ {L = SMePh (3), NCMe (9), Py (10)}

Complex (*Sc*-**1**, 150.6 mg, 0.198 mmol) and AgBF$_4$ (40.9 mg, 0.210 mmol) were stirred under reflux for 4 h in dichloromethane:acetone (30 mL, 1:1). The AgI formed was removed by filtration. The filtrate was vacuum-evaporated to dryness and the residue dissolved in dichloromethane. To the solution the corresponding L was added (L = SMePh (23.3 μL, 0.198 mmol), NCMe (21.1 μL, 0.400 mmol), Py (16.1 μL, 0.200 mmol). The mixture was stirred under reflux for 2 h and the resulting solution vacuum-concentrated. Addition of diethyl ether gave a pale yellow solid. Compound **10** was recrystallised from dichloromethane:diethyl ether.

Compound **3**. Yield: 71.3 mg (48.8%). Anal. Calc. for C$_{34}$H$_{31}$NPPtSBF$_4$: C, 51.1; H, 3.9; N, 1.8; S, 4.0. Found: C, 50.9; H, 4.3; N, 1.6; S, 3.8%. ^{1}H NMR (CDCl$_3$): δ 9.05 (s, $^3J_{HPt}$ = 114.1 Hz, 1H, CH=N), 5.73 (q, $^3J_{HH}$ = 6.5 Hz, $^3J_{HPt}$ = 50.7 Hz, 1H, C*H), 2,85 (s, $^3J_{HPt}$ = 55.2 Hz, 3H, MeS), 1.68 (d, 3H, C*Me). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 17.81(s, $^1J_{PPt}$ = 1808.4 Hz).

Compound **9**. Yield: 53.4 mg (40.8%). Anal. Calc. for C$_{29}$H$_{26}$N$_2$PPtBF$_4$: C, 48.7; H, 3.7; N, 3.9. Found: C, 49.1; H, 3.9; N, 3.6%. ^{1}H NMR (CDCl$_3$): δ 8.80 (s, $^3J_{HPt}$ = 124.2 Hz, 1H, CH=N), 5.55 (q, $^3J_{HH}$ = 6.6 Hz, $^3J_{HPt}$ = 48.9 Hz, 1H, C*H), 2.25 (d, $^5J_{HP}$ = 1.5 Hz,

$^3J_{HPt} = 15.4$ Hz, 3H, NCMe), 1.51 (d, 3 H, C*Me). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 17.33 (s, $^1J_{PPt} = 1772.6$ Hz).

Compound **10**. Yield: 78% (95 mg). Anal. Calc. for C$_{32}$H$_{28}$N$_2$PPtBF$_4$: C, 51.01; H, 3.74; N, 3.72. Found: C, 50.86; H, 3.58; N, 3.70%. Atom numbering for compound **10** is as follows:
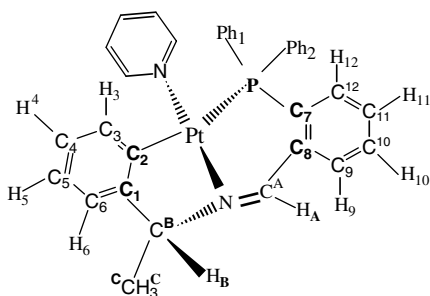
^1H NMR (CDCl$_3$, room temperature): δ 8.97 (s, 1H, H$_A$, $^3J_{HPt} = 104$ Hz), δ 8.16 (m, 1H, H$_9$), δ 7.79 {t, 1H, (Py: H$_p$)^3 $J_{HH} = 6.9$ Hz}, δ 7.71 (m, 3H, H$_{10}$ + H$_{11}$ + H$_{12}$), δ 7.26 [m, 4H, {H$_6$ + (Py: 2H$_m$ + 1H$_o$)}], δ 7.17 (t, 1H, H$_5$, $^3J_{HH} = 7.4$ Hz), δ 6.95 (t, 1H, H$_4$, $^3J_{HH} = 7.4$ Hz), δ 6.13 (st, 1H, H$_3$, $^3J_{HH} = 6.4$ Hz, $^4J_{HP} = 6.2$ Hz, $^3J_{HPt} = 34.7$ Hz); δ 5.66 (c, 1H, H$_B$, $^3J_{HBHC} = 6.6$ Hz, $^3J_{HPt} = 44.8$ Hz), δ 1.77 (d, 3H, H$_C$, $^3J_{HCHB} = 6.6$ Hz,); Ph1: δ 7.87 (d, 1H, H$_2$, $^3J_{H2H3} = 11$ Hz), δ 7.88 (d, 1H, H$_6$, $^3J_{H6H5} = 11$ Hz), δ 7.53 {(m, 4H, H$_3$ + H$_4$ + H$_5$ + (Py: 1H$_o$)}; Ph2: δ 7.06 (d, 1H, H$_2$, $^3J_{H2H3} = 11$ Hz), δ 7.07 (d, 1H, H$_6$, $^3J_{H6H5} = 11$ Hz), δ 7.39 (st, 1H, H$_4$, $^3J_{H4H3} = {}^3J_{H4H5} = 6$ Hz), δ 7.26 (m, 2H, H$_3$ + H$_5$). $^{13}C\{^1H\}$ NMR (CDCl$_3$, room temperature): δ 165.8 (d, 1C, C$_A$, $^3J_{CP} = 5.9$ Hz), δ 85.3 (s, 1C, C$_B$), δ 29.3 (s, 1C, C$_C$), δ 157.2 (d, 1C, C$_2$, $^2J_{CP} = 109$ Hz), δ 150.2 (s, 1C, C$_1$), δ 130.9 (s, 1C, C$_3$,), δ 126.8 (s, 1C, C$_5$), δ 125.8 (d, 1C, C$_4$, $^4J_{CP} = 7$ Hz), δ 120.4 (d, 1C, C$_6$, $^3J_{CP} = 5$ Hz), δ 124.0 (d, 1C, C$_7$, $^1J_{CP} = 44$ Hz), δ 130.9 (d, 1C, C$_8$, $^2J_{CP} = 18$ Hz), δ 139.2 (d, 1C, C$_9$, $^3J_{CP} = 9$ Hz), δ 133.5 (s, 1C, C$_{10}$), δ 133.1 (d, 1C, C$_{11}$, $^3J_{CP} = 2$ Hz), δ 134.2 (d, 1C, C$_{12}$, $^3J_{CP} = 6$ Hz), {Py: δ 152.4 (s, 2C, 2C$_0$), δ 138.9 (s, 1C, C$_p$), δ 127.1 (s, 2C; 2C$_m$)}; Ph$_1$: δ 130.1 (d, 1C, C$_1$, $^1J_{CP} = 48$ Hz) δ 134.38 (d, 2C, C$_2$ + C$_6$, $^2J_{C2P} = {}^2J_{C6P} = 14$ Hz), δ 132.56 (s, 1C, C$_4$), δ 129.88 (d, 2C, C$_3$ + C$_5$, $^3J_{C3P} = {}^3J_{C3P} = 11$ Hz)]; Ph$_2$: δ 126.5 (d, 1C, C$_1$, $^1J_{CP} = 51$ Hz) δ 132.0 (d, 2C, C$_2$ + C$_6$, $^2J_{C2P} = {}^2J_{C6P} = 11$ Hz), δ 131.27 (s, 1C, C$_4$), δ 129.31 (d, 2C, C$_3$ + C$_5$, $^3J_{C3P} = {}^3J_{C3P} = 10$ Hz)], $^{31}P\{^1H\}$ NMR (CDCl$_3$, room temperature): δ 18.67 (s, $^1J_{PPt} = 1844$ Hz, 1P, P–Pt), $^{19}F\{^1H\}$ NMR (CDCl$_3$, room temperature): δ −79 ppm.

2.3. Crystal structure determination of complexes 4 and 10

Suitable crystals for X-ray diffraction were grown by slow diffusion of *n*-pentane into THF (**4**) or toluene (**10**) solutions of the complexes. Intensity data were collected for both compounds at low temperature (100(2) K) on a Bruker SMART APEX area detector diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and using ω narrow frames (0.3°). The SMART software package was used for data collection [21a]. Lorentz, polarisation and absorption corrections were applied on raw frame data with SAINT [21b] and SAD-ABS [21c] programmes. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the SHELXTL suite of programmes [21d]. All non-hydrogen atoms were refined with isotropic and subsequent anisotropic displacement parameters. All hydrogen atoms (except those of the two methyl groups) were included in **4** from observed positions and refined as free isotropic atoms; those of the methyl groups were obtained from geometric considerations and refined riding on carbon atoms. In the case of **10**, all hydrogens were included from calculated positions and refined with thermal and positional riding parameters. The absolute configuration of the two molecules was estimated from the refinement of the absolute structure Flack parameter (x) [21e]. A summary of crystal data and refinement parameters is reported in Table 1.

3. Results and discussion

3.1. Synthesis and characterization of the complexes

Treatment of diastereomeric mixtures of [PtIMe$_3$\{κ^2-Ph$_2$P(C$_6$H$_4$)CH=NCH(Ph)Me-*P,N*\}] (Sc-**1**) [18] with silver tetrafluoroborate followed by addition of thioanisol gives rise to a mixture of complexes **2** and **3** (Scheme 1). Formation of compounds **2** and **3** from Sc-**1** implies a common step involving the reductive elimination of ethane and iodide abstraction but, while complex **2** retains the remaining Me–Pt group ($\delta_{Me} = 0.26$ ppm, $^2J_{HPt} = 69.1$ Hz, $^3J_{HP} = 3.3$ Hz), complex **3** can be described as the result of a further elimination of methane accompanied by an orthometallation reaction. Complex **3** was isolated as a pure sample by a direct preparative route (see below). Therefore, the mixture was characterized and quantified by ^1H NMR spectroscopy. Attempts to separate this mixture by column chromatography on aluminium oxide were unsuccessful. Instead, and the new chloride complexes, **4** and **5**, were obtained. The formation of these complexes is probably due to the presence of traces of hydrochloric acid originated from the dichloromethane used as eluent in the chromatography column.

We recently reported the preparation of the related complexes **7** and **8**, following a similar route, but using pyridine **7** or triphenylphosphine **8** as ancillary ligands (Scheme 2) [18]. It has been proposed the solvate **6** as a common intermediate for the formation of both types of products [18]. It seems that triphenylphosphine promotes the elimination of methane from **6** whereas other donor ligands such as pyridine stabilise this intermediate avoiding further reaction steps. The mixture of compounds **2** and **3** obtained by using thioanisol indicates that this ligand would occupy an intermediate position in this reaction pattern.

Table 1
Crystallographic data and structure refinement for compounds **4** and **10**

Compound	**4**	**10**
Empirical formula	$C_{28}H_{27}ClNPPt$	$C_{32}H_{28}BF_4N_2PPt$
Formula weight	639.02	753.43
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Unit cell dimensions		
a (Å)	8.6976(6)	9.3557(7)
b (Å)	14.4583(10)	19.8924(15)
c (Å)	10.5402(7)	15.0843(11)
β (°)	108.2050(10)	90.7580(10)
V (Å^3)	1259.11(15)	2807.1(4)
Z	2	4
D_{calc} (Mg m^{-3})	1.685	1.783
Absorption coefficient (mm^{-1})	5.757	5.108
$F(000)$	624	1472
Crystal size (mm)	$0.28 \times 0.26 \times 0.11$	$0.27 \times 0.17 \times 0.02$
θ Range data collection (°)	2.03–28.44	1.35–28.54
Index ranges	$-11 \leqslant h \leqslant 11$, $-19 \leqslant k \leqslant 19$, $-13 \leqslant l \leqslant 14$	$-12 \leqslant h \leqslant 12$, $-26 \leqslant k \leqslant 26$, $-20 \leqslant l \leqslant 20$
Reflections collected	14,792	34,085
Independent reflections	5808($R_{int} = 0.0199$)	13005($R_{int} = 0.0461$)
Data/restraints/parameters	5808/1/353	13005/1/741
Goodness-of-fit	1.043	1.002
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0167$, $wR_2 = 0.0399$	$R_1 = 0.0357$, $wR_2 = 0.0723$
R indices (all data)	$R_1 = 0.0174$, $wR_2 = 0.0402$	$R_1 = 0.0435$, $wR_2 = 0.0752$
Absolute structure parameter	$-0.014(4)$	$-0.005(5)$
Largest difference peak and hole (e Å^{-3})	0.615 and -0.471	1.332 and -1.509

At this point, searching for a general route to orthometallated compounds, we envisaged the possibility of forcing methane elimination from intermediate **6** in the absence of any additional donor ligand. Bearing this goal in mind, the metathetic reaction of Sc-**1** with silver tetrafluoroborate was carried out in a refluxing 1:1, dichloromethane:acetone mixture, for four hours. After separation by filtration of the silver iodide formed, addition of thioanisole, acetonitrile or pyridine afforded the corresponding orthometallated complexes (Scheme 3).

The new complexes **2–5**, **9** and **10**, were characterised by analytical and spectroscopic means and by the molecular structure determination of complexes **4** and **10**. The most noticeable features of their ^{1}H NMR spectra are a low field singlet in the 8.10–9.05 ppm region assigned to the amine proton and a quartet at 5.25–6.90 ppm and a doublet at 1.51–1.77 ppm corresponding to the HC*Me protons. Notably, while in complexes **2** and **4**, the $^3J_{PtH}$ coupling constant for the amine proton is around 40 Hz, it takes a value on the range 104–124 Hz in the orthometallated complexes **3**, **5**, **9**, and **10** [22,23]. Most probably, the low value of the $^3J_{HPt}$ coupling constant of complexes **2** and **4** is due to the presence of a methyl group in a *trans* disposition to the HC=N fragment; the change of the coordination mode of the chelate phosphino-amine ligand from bidentate to orthometallated tridentate accounts for this significant difference. Resonances corresponding to the ancillary ligand are also present. Thus, one doublet at 0.26 ppm, $^2J_{HPt} = 69.1$ Hz (complex **2**) and at 0.63 ppm, $^2J_{HPt} = 72.2$ Hz (complex **4**) is assigned to the Me–Pt protons. The MeS protons resonate as a singlet at 2.85 ppm, $^3J_{HPt} = 55.2$ Hz (complex **3**) and a doublet at 2.25 ppm, $^5J_{HP} = 1.5$ Hz, is attributed to the methyl acetonitrile protons of complex **9**. The ^{31}P{^{1}H} NMR spectra consist in a singlet at ca. 17.5 ppm. The $^1J_{PPt}$ coupling constants are characteristic for Pt(II) compounds with a carbon atom *trans* to a phosphorus (from 1773 to 1881 Hz) [24] or to a chloride (4713.0 Hz) [22,25] atom.

The ^{13}C{^{1}H} NMR spectra of compounds show a very complex pattern. For complex **10** the signals were assigned
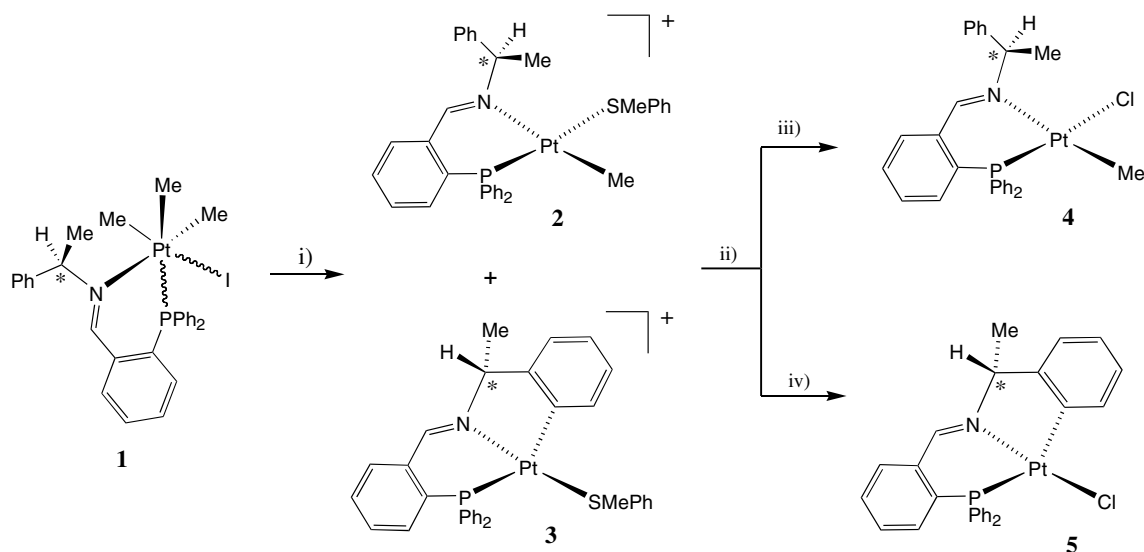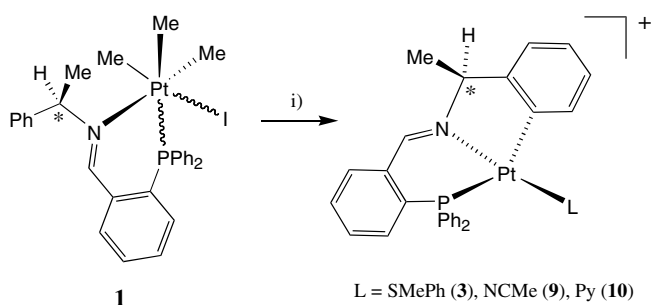

Scheme 1. Preparative route to complexes **4** and **5**. Only the R_C isomers are shown. (i) 1. AgBF$_4$, 1 h, r.t.; 2.SMePh, reflux, 1 h; CH$_2$Cl$_2$/(CH$_3$)$_2$CO. (ii) Al$_2$O$_3$ (column). (iii) CH$_2$Cl$_2$. (iv) CH$_3$CH$_2$OH.
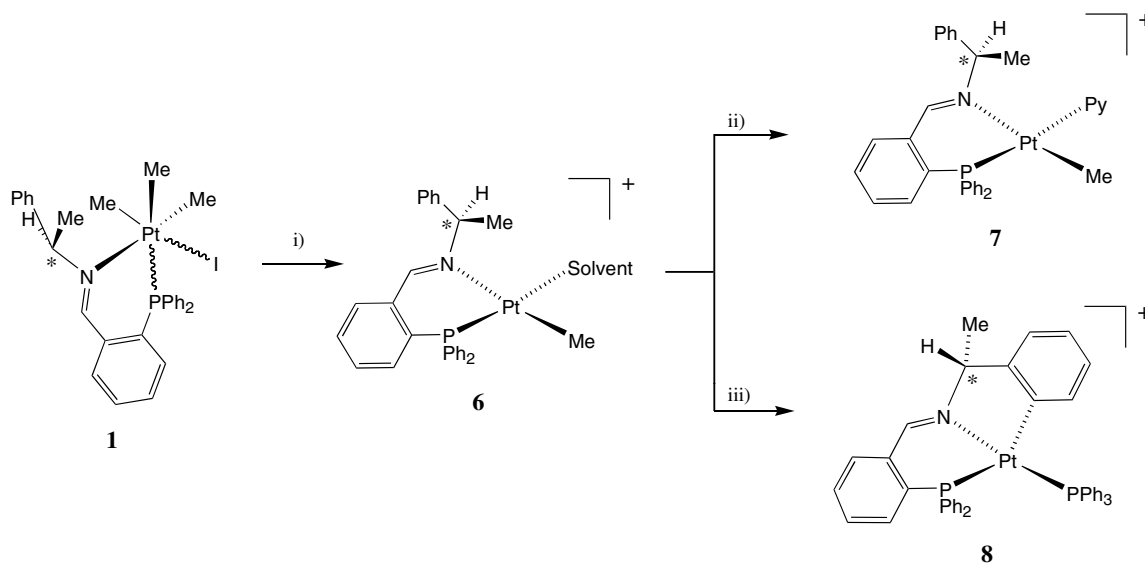
Scheme 2. Preparation of complexes **7** and **8** according to Ref. 18. (i) AgBF₄, 1 h, r.t., CH₂Cl₂/(CH₃)₂CO or CH₂Cl₂/THF (–AgI, –CH₃CH₃). (ii) Py, CH₂Cl₂, reflux, 2 h. (iii) PPh₃, CH₂Cl₂, reflux, 2 h (–CH₄).

Scheme 3. Preparation of the cyclometallated complexes **3**, **9**, and **10**. (i) 1. – AgBF₄, CH₂Cl₂/(CH₃)₂CO, reflux, 4 h (– AgI, –CH₃–CH₃, –CH₄). 2. – L, CH₂Cl₂, reflux, 2 h.

with the aid of ^{2}D experiments (^{31}P-HMQC, HMQC, HMBC and NOESY). The ^{13}C{^{1}H} NMR data show that the phenyl groups bonded to the phosphorus atom are not equivalent, and the satellites signals due to ^{13}C–^{195}Pt coupling are not observed.
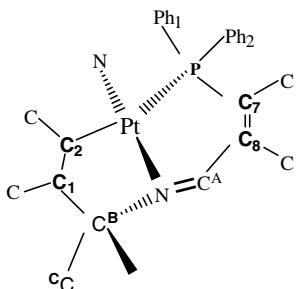
The ^{13}C{^{1}H} NMR spectrum shows a singlet and three doublet signals corresponding to the quaternary carbon atoms C_1, C_2, C_8 and C_7, which appear at δ 150.2, 157.2 [$^2J_{CP} = 109$ Hz], 130.9 [$^2J_{CP} = 18$ Hz] and 124.0 ppm

[$^1J_{CP} = 44$ Hz], respectively. The high value of the carbon-phosphorus coupling observed for the carbon atom bonded to the metal centre (C_2) is attributed to the *trans* influence of the phosphorus atom [22,24a,26]. Moreover, two doublet signals at δ 130.1 [$^1J_{CP} = 48$ Hz] and 126.5 ppm [$^1J_{CP} = 51$ Hz] are assigned to the phenyl carbon atoms (Ph₁ y Ph₂) bonded to the phosphorus atom, respectively. Finally, the ^{13}C NMR spectrum shows a doublet signal corresponding to the iminic carbon (C_A) at δ 165.8 ppm [$^3J_{CP} = 5.9$ Hz].

3.2. X-ray molecular structures of compounds 4 and 10

A perspective view of the molecular structure of complex **4** is shown in Fig. 1, while that of the cation of complex **10** is shown in Fig. 2. Relevant bond distances and bond angles are given in Table 2.
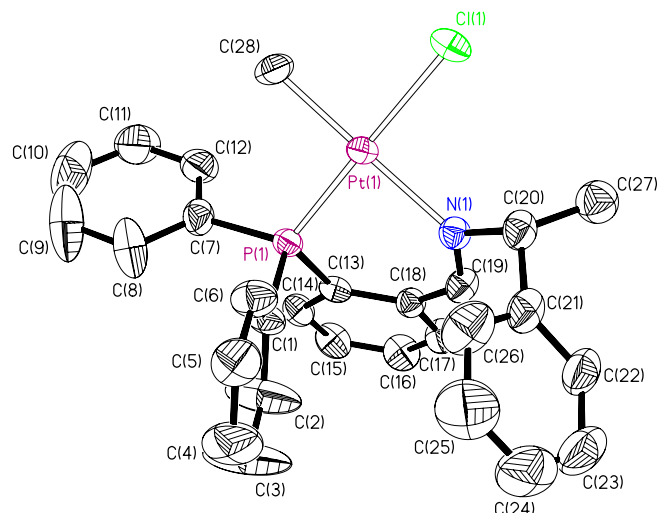

Fig. 1. Molecular structure of complex **4** with the labelling scheme used.
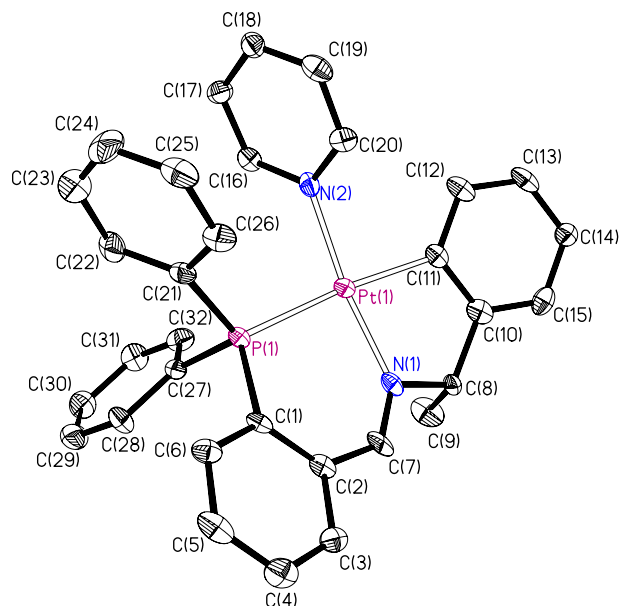
Fig. 2. Molecular structure of the cationic complex **10** with the labelling scheme used.

In both complexes the platinum atom shows a distorted square-planar environment. In complex **4** the (*R*)-ligand [2-(diphenylphosphine)benzylidene]-(1-phenyl-ethyl)-amine is bonded to the metal centre through the nitrogen and the phosphorus donor atoms; a chlorine atom and a methyl group complete the metal coordination sphere. Complex **10** consists of a fused (6,6,5,6) tetracycle system containing five and six-membered metallacycles, with the platinum atom coordinated in an analogous manner to that observed in **4** – to the nitrogen and phosphorus atoms of the phos-phine-amine chelate ligand – but also bonded to an *ortho*-methallated phenyl group of the corresponding (*S*)-phenyl-ethyl-amine moiety. A nitrogen atom of a pyridine group completes the square-planar coordination of the metal.

The metal coordination bond distances show the high *trans* influence of the alkyl (**4**) and aryl (**10**) ligands. Thus, the Pt–P bond length is 2.1791(7) Å in **4** when the phospho-rus is *trans* to a chloride ligand, but 2.2900(12) Å when it is *trans* to the phenyl group (**10**); the Pt–N bond distance is 1.996(5) Å in **10** where the amine group is *trans* to the pyr-idine ligand and 2.138(3) Å when the nitrogen atom is situated *trans* to the methyl group (**4**). Nevertheless, the Pt–C bond distances are identical in both structures (mean 2.043(3) Å) and similar to the values reported for analo-gous platinum (II) complexes [12,13,16,27].

The bite angle of the bidentate ligand P–Pt–N(1) ranges from 87.48(7) in **4** to 92.08(16) in one of the independent

Table 2
Selected bond distances and angles for **4** and **10**

Complex **4**		Complex **10**[a]		
Bond distances (Å)				
Pt–Cl	2.3693(8)	Pt–N(2)	2.026(5)	2.010(5)
Pt–P	2.1791(7)	Pt–P(1)	2.2922 (17)	2.2879(16)
Pt–N(1)	2.138(3)	Pt–N(1)	2.000(6)	1.991(6)
Pt–C(28)	2.047(3)	Pt–C(11)	2.035(6)	2.047(6)
P(1)–C(1)	1.821(3)	P(1)–C(1)	1.820(6)	1.817(6)
N(1)–C(7)	1.276(4)	N(1)–C(7)	1.273(8)	1.287(9)
N(1)–C(8)	1.512(4)	N(1)–C(8)	1.499(8)	1.494(8)
C(1)–C(2)	1.409(4)	C(1)–C(2)	1.394(9)	1.402(8)
C(2)–C(7)	1.468(5)	C(2)–C(7)	1.474(9)	1.482(9)
C(8)–C(9)	1.520(5)	C(8)–C(9)	1.509(9)	1.526(9)
C(8)–C(10)	1.506(5)	C(8)–C(10)	1.498(10)	1.507(9)
C(10)–C(11)	1.390(6)	C(10)–C(11)	1.406(9)	1.386(9)
Bond angles (°)				
Cl–Pt–P	176.51(3)	N(2)–Pt–P(1)	92.47(16)	92.64(15)
Cl–Pt–N(1)	91.55(7)	N(2)–Pt–N(1)	170.7(2)	176.7(2)
Cl–Pt–C(28)	87.09(10)	N(2)–Pt–C(11)	93.2(2)	97.1(2)
P–Pt–N(1)	87.48(7)	P(1)–Pt–N(1)	92.08(16)	89.17(16)
P–Pt–C(28)	94.03(10)	P(1)–Pt–C(11)	174.35(19)	170.18(19)
N(1)–Pt–C(28)	177.08(13)	N(1)–Pt–C(11)	82.3(2)	81.0(2)
Pt–P–C(1)	108.64(10)	Pt(1)–P(1)–C(1)	110.2(2)	105.5(2)
Pt–N(1)–C(7)	126.8(2)	Pt(1)–N(1)–C(7)	128.9(5)	129.2(5)
Pt(1)–N(1)–C(8)	117.5(2)	Pt(1)–N(1)–C(8)	114.4(4)	112.3(4)
C(7)–N(1)–C(8)	115.7(3)	C(7)–N(1)–C(8)	116.5(6)	118.1(6)
P–C(1)–C(2)	120.0(2)	P(1)–C(1)–C(2)	120.2(5)	119.2(5)
C(1)–C(2)–C(7)	124.9(3)	C(1)–C(2)–C(7)	126.6(6)	126.4(6)
N(1)–C(7)–C(2)	127.5(3)	N(1)–C(7)–C(2)	132.0(7)	126.6(6)
N(1)–C(8)–C(9)	110.0(3)	N(1)–C(8)–C(9)	110.0(5)	108.7(5)
N(1)–C(8)–C(10)	110.8(3)	N(1)–C(8)–C(10)	108.1(5)	105.7(5)
C(8)–C(10)–C(11)	118.5(4)	C(8)–C(10)–C(11)	117.5(6)	117.7(6)
		Pt(1)–C(11)–C(10)	113.2(5)	112.0(5)

[a] Two crystallographic independent molecules were observed in the asymmetric unit of **10**.

molecules of **10**; these values compare well with those of the closely related palladium complex [PClMe{Ph$_2$-P(C$_6$H$_4$)CH=NR*-*P,N*}] (R* = 1-mesitylethyl) (86.4(2)°) [27] and are common for structurally related phosphino-amine metal complexes containing the same *P,N*-bidentate fragment Ph$_2$P(C$_6$H$_4$)CR=NR′ (range 85.7(3)–90.0(5)°) [27–29]. These values indicate the reduced flexibility of this ligand and also its adequacy to orthogonal chelate coordination.

The six-membered metalacycles Pt–P–C(1)–C(2)–C(7)–N(1) are not planar but twisted with significant puckering amplitudes. In the case of **4** a screw-boat $^1S_2$ conformation is observed ($Q = 0.702(2)$ Å, $\theta = 62.7(3)$, $\phi = 25.2(3)°$) with the –C$_6$H$_4$CH= unit above the metal coordination plane (Fig. 1). For the two independent molecules in **10** analogous half-chair $^4H_5$ conformations are observed ($Q = 0.438(3)$ Å, $\theta = 124.5(4)$, $\phi = 214.3(5)°$ and $Q = 0.693(4)$ Å, $\theta = 118.4(5)$, $\phi = 210.1(6)°$) with the carbon atoms C(1), C(2) and C7 below the metal coordination plane (Fig. 2) [30].

If we compare the phosphine–amine conformation in **4** with that observed in **10**, the major geometrical alterations affect the torsion angles around the N(1)–C(8) and C(8)–C(10) single bonds, which are modified to allow approximation of C(11) atom to bonding distances of the Pt metal (C(7)–N(1)–C(8)–C(10) −58.3(4)° in **4**, −151.5(8)° in **10**; N(1)–C(8)–C(10)–C(11) −79.9(5)° in **4**, −18.6 (9)° in **10**). The five-membered metallacycle formed in **10** after ortho-metallation at C(11) adopt a slightly puckered envelope conformation with the nitrogen atom out of the ring plane ($Q = 0.224(4)$ Å, $\phi = 43.7(6)°$ and $Q = 0.361(3)$ Å, $\phi = 34.4(3)°$) [30].

An additional noteworthy feature detected in **10** is the π–π interaction between the co-ordinated pyridine ligand and one of the free phosphine phenyl groups (C(21)–C(26)). These aromatic rings show a typical π–π interaction with a nearly parallel disposition of their planes (mean dihedral angle 16.4(2)°) and with a short interplanar separation (centroid–centroid 3.603(3) Å) [31].

Acknowledgement

Appendix A. Supplementary material

CCDC 647957 and 647958 contain the supplementary crystallographic data for **4** and **10**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Crystallographic data for the two structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 647957 and 647958 for compounds **4** and **10**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccd.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.10.032.

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