Synthesis and reactivity of new trimethylplatinum(IV) complexes containing chiral Schiff bases as ligands: Crystal structure of (OC-6-44-C)-[$PtIMe_3\{\kappa^2$-(*R*)-$Ph_2P(C_6H_4)CH{=}NC^*H(Ph)Me$-P,N}]

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Abstract

Reaction of the tetranuclear complex $[PtIMe_3]_4$ with the ligand (*S*)- and (*R*)-$Ph_2P(C_6H_4)CH{=}NC^*H(Ph)Me$ in a 1:4 molar ratio yields the mononuclear neutral complexes in diastereoisomeric mixtures [$PtIMe_3\{\kappa^2$-$Ph_2P(C_6H_4)CH{=}NC^*H(Ph)Me$-P,N}]. Iodide abstraction from mixture with $AgBF_4$ in the presence of pyridine (Py) induces a reductive elimination reaction with loss of ethane, leading to the cationic complex [PtMe(Py){κ^2-$Ph_2P(C_6H_4)CH{=}NC^*H(Ph)Me$-P,N}][$BF_4$] [C* = (*S*)-, **3**; (*R*)-, **4**]. When this reaction was carried out in the presence of PPh_3 a consecutive *ortho*metallation reaction with loss of methane is produced, forming the cationic complex [$Pt(PPh_3)\{\kappa^3$-$Ph_2P(C_6H_4)CH{=}NC^*H(C_6H_4)Me$-C,P,N}][$BF_4$], [(*S*)-, **5**; (*R*)-, **6**]. All species were characterised in solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, elemental analysis and mass spectrometry.

The crystal structure of the diastereoisomer (OC-6-44-C)-[$PtIMe_3\{\kappa^2$-(*R*)-$Ph_2P(C_6H_4)CH{=}NC^*H(Ph)Me$-P,N}] has been determined by single-crystal X-ray diffraction.

Keywords: Trimethylplatinum(IV) complexes; Optically active Schiff base complexes; Reductive elimination reaction; Cyclometallated platinum complexes

1. Introduction

A feature of interest in complexes containing the trimethylplatinum(IV) unit, in particular those containing phosphines and pyridines as ligands, is the fact that some of them undergo a reductive elimination reaction with the formation of platinum(II) complexes and ethane. The mechanism involved in this kind of reaction has been the object of several studies [1].

Another characteristic of trimethylplatinum complexes is that the *fac*-methyl groups in these compounds make the octahedrally coordinated metal a chiral centre whenever there are three different *trans* donor atoms or multidentate ligands which remove the planes of symmetry. Kite and co-workers [2] have reported complexes of trimethylplatinum(IV) halides with optically active Schiff base ligands of the type (*S*)-$C_5H_4NC(R){=}NC^*H(Ph)Me$, where R = H or Me. In both cases, the complexes were obtained in diastereoisomeric mixtures, where both the metal centre and the carbon atom were chiral. There are also few reports of complexes containing the trimethylplatinum(IV) fragment and achiral Schiff base as ligand [3].

Generally these type of complexes were prepared by reaction of the tetramer complex $[PtIMe_3]_4$ with the corresponding Schiff base. However, trimethylplatinum (IV)-Schiff base compounds can be synthesised through an oxidative addition reaction on Pt(II) complexes [4]. On the other hand, related neutral and cationic trimethylplatinum(IV) complexes containing analogous ligands with donors atoms such as P, N; P, S; N, N; N, S; N,O and O,O have also been reported [5].

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Recently, we reported the preparation of some new trimethylplatinum(IV) complexes of the type $[PtIMe_3(\kappa^2\text{-}L_2)]$ where $L_2 = Ph_2P(E)C_6H_4SMe$ [E = S (**1**) or Se (**2**)]. In the preparation of cationic complexes by iodide abstraction from this compounds with the $AgPF_6$, in the presence of a ligand L (PPh_3, Py), we have verified that using complex **2** and the ligand PPh_3, a reductive elimination reaction takes place yielding the described complex $[PtMe(\kappa^2\text{-}MeSC_6H_4PPh_2\text{-}P,S)(PPh_3)][PF_6]$ [6].

As an extension to our works on complexes containing the $PtIMe_3$ unit we have decided to prepare new neutral and cationic trimethylplatinum(IV) complexes containing optically active Schiff base ligands with a P,N-donor set, considering that the optically active diphosphines ligands are widely used in enantioselective catalysis [7]. In this paper, we report the preparation of new trimethylplatinum(IV) complexes containing the ligands (*S*)- and (*R*)-$Ph_2PC_6H_4CH{=}NC^*H(Ph)Me$, in order to modify the metal centre electronic density to achieve reductive elimination reactions. In some cases we were able to isolate a novel cyclometallated complex of platinum(II), where a new Pt–C σ-bond is formed and the Schiff base is acting as a tridentate ligand with a C,P,N-donor set. It is noteworthy that cyclometallated complexes have been thoroughly studied [8]; they have been utilised in organic synthesis [9], catalysis [10,11], asymmetric synthesis [12] and photochemistry [13].

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 $[PtIMe_3]_4$ [14] and the ligands (*S*)- and (*R*)-$Ph_2PC_6H_4CH{=}NC^*H(Me)Ph$ were synthesised according to the literature procedures [15]. Elemental analyses (C, H, N, S) were made with a Fisons EA-118 microanalyser. Mass spectra were measured on a VG Autospec double-focusing mass spectrometer using the FAB^+ operating mode; ions were produced with the standard Cs^+ gun at ca. 30 kV and 3-nitrobenzylalcohol (NBA) was used as the matrix. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-200P and Avance-400 spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ (^1H) and 85% H_3PO_4 [$^{31}P\{^1H\}$, positive shifts downfield] as internal and external standards, respectively.

2.2. Synthesis of complexes

2.2.1. *[PtIMe₃{κ²-(S)-Ph₂P(C₆H₄)CH=NC*H(Ph)-Me-P,N}] (**1**) and [PtIMe₃{κ²-(R)-Ph₂P(C₆H₄)-CH=NC*H(Ph)Me-P,N}] (**2**)*

To a solution of complex $[PtIMe_3]_4$ (200 mg; 5.45 mmol) in dichloromethane (30 mL), a 5% excess of the corresponding chiral Schiff base [L_1 and L_2 (225 mg)] was added. The resulting solution was refluxed for 4 h and then vacuum-evaporated to dryness. The solid was dissolved in chloroform and the addition on *n*-pentane gives a yellow solid, which was recrystallised from CH_2Cl_2/pentane. Compound **1**, yield 327 mg (80%) (molar ratio **1a**:**1b** = 59:41). Anal. Calc. for $C_{30}H_{33}INPPt$: C, 47.3; H, 4.4; N, 1.8. Found: C, 47.7; H, 4.3; N, 1.8%. MS (FAB+, *m*/*s*, %): 603, 40% [M − IMe_2], 587, 100% [M − (IMe_2 + CH_4)]. Isomer **1a**: ^1H NMR ($CDCl_3$): δ 8.15 [d, 1H, $^4J(HP) = 1.9$ Hz, $^3J(HPt) = 29.3$ Hz, HC=N], 5.50 [q, 1H, $^3J(HH) = 6.8$ Hz, HC*], 1.78 [d, 3H, $^3J(HH) = 6.8$ Hz, MeC*], 1.58 [d, 3H, $^3J(HP) = 7.4$ Hz, $^2J(HPt) = 57.9$ Hz, Me *trans* P], 1.29 [d, 3H, $^3J(HP) = 7.3$ Hz, $^2J(HPt) = 70.8$ Hz, Me *trans* N], 0.90 [d, 3H, $^3J(HP) = 6.9$ Hz, $^2J(HPt) = 69.7$ Hz, Me *trans* I]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.75 [s, $^1J(PPt) = 1204$ Hz]. Isomer **1b**: ^1H NMR ($CDCl_3$): δ 8.22 [d, 1H, $^4J(HP) = 2.0$ Hz, $^3J(HPt) = 29.3$ Hz, HC=N], 5.68 [q, 1H, $^3J(HH) = 6.8$ Hz, HC*], 1.39 [d, 3H, $^3J(HH) = 6.8$ Hz, MeC*], 1.50 [d, 3H, $^3J(HP) = 7.4$ Hz, $^2J(HPt) = 57.9$ Hz, Me *trans* P], 1.30 [d, 3H, $^3J(HP) = 7.2$ Hz, $^2J(HPt) = 71.2$ Hz, Me *trans* N], 0.94 [d, 3H, $^3J(HP) = 7.0$ Hz, $^2J(HPt) = 70.5$ Hz, Me *trans* I]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −1.02 [s, $^1J(PPt) = 1202$ Hz].

Compound **2**: Yield: 272 mg (66%) (molar ratio **2a**:**2b** = 60:40). Anal. Calc. for $C_{30}H_{33}INPPt$: C, 47.3; H, 4.4; N, 1.8. Found: C, 47.7; H, 4.3; N, 1.8%. MS (FAB+, *m*/*s*, %): 603, 40% [M − IMe_2], 587, 100% [M − (IMe_2 + CH_4)]. Isomer **2a**: ^1H NMR ($CDCl_3$): δ 8.09 [d, 1H, $^4J(HP) = 2.1$ Hz, $^3J(HPt) = 28.4$ Hz, HC=N], 5.45 [q, 1H, $^3J(HH) = 6.7$ Hz, HC*], 1.72 [d, 3H, $^3J(HH) = 6.8$ Hz, MeC*], 1.58 [d, 3H, $^3J(HP) = 7.4$ Hz, $^2J(HPt) = 57.8$ Hz, Me *trans* P], 1.29 [d, 3H, $^3J(HP) = 6.8$ Hz, $^2J(HPt) = 70.8$ Hz, Me *trans* N], 0.90 [d, 3H, $^3J(HP) = 6.9$ Hz, $^2J(HPt) = 69.7$ Hz, Me *trans* I]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.007 [s, $^1J(PPt) = 1204$ Hz]. Isomer **2b**: δ 8.16 [d, 1H, $^4J(HP) = 2.2$ Hz, $^3J(HPt) = 28.5$ Hz, HC=N], 5.63 [q, 1H, $^3J(HH) = 6.8$ Hz, HC*], 1.33 [d, 3H, $^3J(HH) = 6.8$ Hz, MeC*], 1.50 [d, 3H, $^3J(HP) = 7.4$ Hz, $^2J(HPt) = 57.9$ Hz, Me *trans* P], 1.30 [d, 3H, $^3J(HP) = 6.8$ Hz, $^2J(HPt) = 71.2$ Hz, Me *trans* N], 0.94 [d, 3H, $^3J(HP) = 6.9$ Hz, $^2J(HPt) = 70.5$ Hz, Me *trans* I]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.24 [s, $^1J(PPt) = 1196$ Hz].

2.2.2. *[PtMe(Py){κ²-(S)-Ph₂P(C₆H₄)CH=NC*H(Ph)-Me-P,N}][BF₄] (**3**) and [PtMe(Py){κ²-(R)-Ph₂P-(C₆H₄)CH=NC*H(Ph)Me-P,N}][BF₄] (**4**)*

2.2.2.1. *Method A.* A solution of complex [$PtIMe_3${κ²-(*S*)-$Ph_2P(C_6H_4)CH{=}NC^*H(Ph)Me$-P,N}] or [$PtIMe_3${κ²-(*R*)-$Ph_2P(C_6H_4)CH{=}NC^*H(Ph)Me$-P,N}] (200 mg; 0.263 mmol) in a mixture dichloromethane–acetone (1:1) was treated with $AgBF_4$ (54 mg, 0.277 mmol). After stirring the mixture for 1 h at room temperature, the AgI formed was removed by filtration. The filtered solution was vacuum-evaporated to dryness and the solid residue was dissolved in dichloromethane. To this solution pyridine (22.5 μL) was added. The mixture was stirred under reflux for 2 h. After cooling, the resulting solution was vacuum-concentrated. The addition of diethyl ether gave a pale-yellow solid. Compound **3**: yield 127 mg (63%). Anal. Calc. for $C_{33}H_{32}N_2PPtBF_4$: C, 51.5; H, 4.2; N, 3.6. Found: C, 51.9; H, 4.4; N, 3.3%. MS (FAB+, *m/s*, %): 666, 100% [M − (BF_4 + CH_4)]. ^{1}H NMR ($CDCl_3$): δ 0.29 [d, 3H, ^3J(HH) = 3.14 Hz, ^2J(HPt) = 71.2 Hz, Pt–Me], 1.46 [d, 3H, ^3J(HH) = 6.7 Hz, MeC*], 4.69 [q, 1H, ^3J(HH) = 6.7 Hz, HC*], 8.63 [s, 1H, ^3J(HPt) = 40.4 Hz, HC=N]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.95 [s, ^1J(PPt) = 4159 Hz]. Compound **4**: yield 131 mg (65%). Anal. Calc. for $C_{33}H_{32}N_2PPtBF_4$: C, 51.5; H, 4.2; N, 3.6. Found: C, 52.2; H, 4.3; N, 3.5%. MS (FAB+, *m/s*, %): 666, 20% [M − (CH_4 + BF_4)], 603, 67% [M − (BF_4 + Py)], 587, 100% [M − (BF_4 + Py + CH_4)]. ^{1}H NMR ($CDCl_3$): δ 0.29 [d, 3H, ^3J(HH) = 3.10 Hz, ^2J(HPt) = 68.5 Hz, Pt–Me], 1.46 [d, 3H, ^3J(HH) = 6.7 Hz, MeC*], 4.68 [c, 1H, ^3J(HH) = 6.7 Hz, HC*], 8.63 [s, 1H, ^3J(HPt) = 40.4 Hz, HC=N]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.95 [s, ^1J(PPt) = 4158 Hz].

2.2.2.2. Method B. A solution of complex $[PtIMe_3]_4$ (250 mg, 0.681 mmol) in a mixture dichloromethane–THF (1:1) was treated with $AgBF_4$ (139 mg, 0.714 mmol). After stirring the mixture for 1 h at room temperature, AgI formed was removed by filtration. The filtered solution was vacuum-evaporated to dryness and the residue was dissolved in dichloromethane. To this solution was added 281 mg (0.714 mmol) of the corresponding ligand. The mixture was stirred under reflux for 2 h. After cooling, 55 μL (0.714 mmol) of pyridine was added to the resulting solution. The mixture was stirred under reflux for 2 h and concentrated at reduced pressure. The addition of diethyl ether led to the precipitation of a solid, which was filtered off, washed with diethyl ether and dried under vacuum. Compound **3**: yield 306 mg (58%). Compound **4**: yield 205 mg (39%).

*2.2.3. Preparation of [Pt(PPh$_3$){κ^3-(S)-Ph$_2$P(C$_6$H$_4$)CH=NC*H(Ph)Me-C,P,N}][BF$_4$] (5) and [Pt(PPh$_3$){κ-(R)-Ph$_2$P(C$_6$H$_4$)CH=NC*H(Ph)Me-C,P,N}][BF$_4$] (6)*

2.2.3.1. Method A. A solution of the neutral complexes **1** or **2** (**1**: 200 mg; 0.263 mmol. Compound **2**: 80 mg; 0.105 mmol) in a mixture dichloromethane–THF (1:1) was treated with $AgBF_4$ (54 mg, 0.277 mmol and 21.5 mg, 0.110 mmol, respectively). After stirring the mixture for 1 h at room temperature, the AgI formed was removed by filtration. The filtered solution was then vacuum-evaporated until dryness and the residue was dissolved in dichloromethane. To this solution was added PPh_3 (69 mg, 0.263 mmol and 28.9 mg, 0.110 mmol, respectively). The mixture was stirred under reflux for 2 h and concentrated under reduced pressure. The addition of diethyl ether led to the precipitation of a yellow solid, which was filtered off and washed with diethyl ether. The solid was dissolved in the minimal volume of dichloromethane–diethyl ether 1:1 and chromatographed on neutral aluminium oxide. The complex was isolated by elution with ethanol. The solution was evaporated until dryness at reduced pressure. The solid residue was dissolved in the minimal volume of dichloromethane and the complex precipitated by the addition of diethyl ether. The solid was filtered, washed with diethyl ether and dried in vacuum. Compound **5**: yield 210 mg (85%). Anal. Calc. for $C_{33}H_{32}N_2PPtBF_4 \cdot 0.5CH_2Cl_2$: C, 55.5; H, 4.0; N, 1.4. Found: C, 55.9; H, 4.6; N, 1.9%. MS (FAB+, *m/s*, %): 849, 100% [M − BF_4], 587, 40% [M − (BF_4 + PPh_3)]. ^{1}H NMR ($CDCl_3$): δ 1.94 [d, 3H, ^3J(HH) = 6.4 Hz, MeC*], 5.79 [m, 1H, HC*], 9.01 [d, 1H, ^3J(HPt) = 77.3 Hz, ^4J(HP) = 13.2 Hz, HC=N]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.20 [d, ^1J(PPt) = 1795 Hz, ^2J(PP) = 15 Hz, P Schiff-base], 20.90 [d, ^1J(PPt) = 3958 Hz, ^2J(PP) = 15 Hz, PPh_3]. Compound **6**: yield 23 mg (23.4%). Anal. Calc. for $C_{33}H_{32}N_2PPtBF_4 \cdot 0.5CH_2Cl_2$: C, 55.5; H, 4.0; N, 1.4. Found: C, 55.6; H, 4.2; N, 1.6%. MS (FAB+, *m/s*, %): 849, 100% [M − BF_4], 586, 25% [M − (BF_4 + PPh_3)]. ^{1}H NMR ($CDCl_3$): δ 1.95 [d, 3H, ^3J(HH) = 6.2 Hz, MeC*], 6.05 [m, 1H, HC*], 9.99 [d, 1H, ^3J(HPt) = 78.8 Hz, ^4J(HP) = 12.6 Hz, HC=N]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.24 [d, ^1J(PPt) = 1798 Hz, ^2J(PP) = 15 Hz, P Schiff-base], 20.80 [d, ^1J(PPt) = 3936 Hz, ^2J(PP) = 15 Hz, PPh_3].

2.2.3.2. Method B. A solution of complex $[PtIMe_3]_4$ (250 mg; 0.681 mmol) in a mixture of dichloromethane–THF (1:1) was treated with $AgBF_4$ (139 mg; 0.714 mmol). After stirring the mixture for 1 h at room temperature, the AgI formed was removed by filtration. The filtered solution was vacuum-evaporated until dryness and the subsequent residue dissolved in dichloromethane. To this solution was added the corresponding chiral Schiff base ligand L_1 or L_2 (281 mg; 0.714 mmol). The mixture was stirred under reflux for 2 h. After cooling, PPh_3 (178 mg; 0.681 mmol) was added, the resulting solution was stirred under reflux for 2 h and concentrated under reduced pressure. The addition of diethyl ether led to the precipitation of a solid complex, which was filtered off and washed with diethyl ether. The solid was dissolved in the minimal volume of dichloromethane–diethyl ether 1:1 and chromatographed on neutral aluminium oxide using ethanol as eluent. The solution was evaporated until dryness at reduced pressure; the solid residue was dissolved in the minimal volume of chloroform and the complex precipitated by the addition of diethyl ether. The solid was filtered, washed with diethyl ether and vacuum dried. Compound **5**, yield 351 mg (55%). Compound **6**: yield 218 mg (34%).

*2.3. Crystal structure determination of (OC-6-44-C)-[PtIMe$_3${κ^2-(R)-Ph$_2$PC$_6$H$_4$CH=NC*H(Me)Ph}]*

Crystals for X-ray structure determination were obtained from a slow diffusion of diethyl ether into a solution of complex **2a** in dichloromethane. Intensity data were collected at room temperature on a Siemens R3m/V diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) in the θ–2θ scan mode. Empirical corrections were applied for absorption. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares calculations with SHELXL-97 [16]. A riding model was applied to H atoms, placed at calculated positions, with C–H = 0.96 Å and isotropic $U = U_{eq}$ of parents atoms. The absolute structure of the compound could be determined with Flack parameter equal to −0.008(9). Maximum peaks in the final Fourier difference map were found in the vicinity of the heavy atom. Interestingly, the crystal structure of this compound shows hydrofobic channels along the fourfold axis. This fact, together with the existence in this spatial region of several – but very weak (range 0.68–0.55 e/Å^3) – residual peaks, suggest the presence of disordered or partially occupied solvent molecules, most probably diethyl ether. Unfortunately, no clear model of solvent could be established from these weak peaks. Relevant crystal data and refinement parameters are summarised in Table 1.

Table 1
Crystal data and structure refinement for complex (OC-6-44)-[$PtMe_3I\{\kappa^2$-(*R*)-$Ph_2PC_6H_4CH$=NC*H(Ph)Me}]

Empirical formula	$C_{30}H_{33}INPPt$
Formula weight	760.53
T (K)	297(2)
λ (Å)	Mo Kα (0.71073)
Crystal system	Tetragonal
Space group	$P4_3$
Unit cell dimensions	
a (Å)	14.825(1)
b (Å)	14.825(1)
c (Å)	13.819(1)
V (Å$^{3)}$	3037.1(4)
Z	4
D_{calc} (Mg m^{-3})	1.663
Absorption coefficient (mm^{-1})	5.706
F(000)	1464
Crystal size (mm)	0.36 × 0.14 × 0.14
θ Range for data collection (°)	1.94–27.56
Index ranges	$-19 \leqslant h \leqslant 19$, $-19 \leqslant k \leqslant 19$, $-17 \leqslant l \leqslant 17$
Reflections collected	7628
Independent reflections	6861 (R_{int} = 0.0362)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6861/1/307
Goodness-of-fit on F^2	0.886
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0464$, $wR_2 = 0.1041$
R indices (all data)	$R_1 = 0.0791$, $wR_2 = 0.1141$
Absolute structure parameter	−0.008(9)
Largest difference in peak and hole (e Å$^{-3)}$	1.306 and −1.221

3. Results and discussion

3.1. Syntheses of ligands

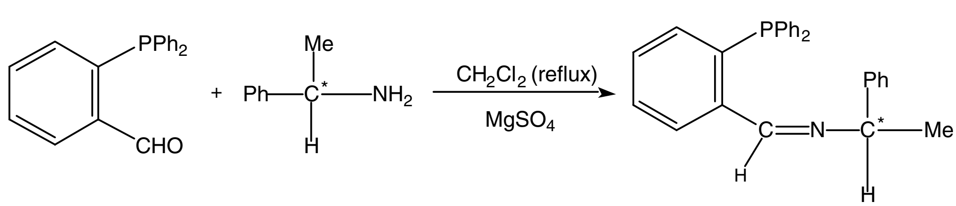
The chiral ligands (*S*)- and (*R*)-$Ph_2P(C_6H_4)CH$=NC*H(Ph)Me were synthesised by condensing 2-(diphenylphosphino)benzaldehyde with the respective chiral amine, according to the literature procedure [15]. The addition of a slight excess of magnesium sulphate as a dehydrating agent decreases the reflux time of the reaction (Scheme 1).

The ligands were characterised by NMR spectroscopy. The ^{1}H NMR spectra of the ligands L_1 and L_2 showed a doublet and quartet signals assigned to the proton methyl group and the proton bonded to the chiral carbon atom, respectively. Also, showed a doublet signal attributed to the iminic proton coupled with the phosphorus atom. The $^{31}P\{^1H\}$ NMR showed a singlet signal at −13.82 ppm assigned to the phosphorus atom.

3.2. Synthesis of complexes

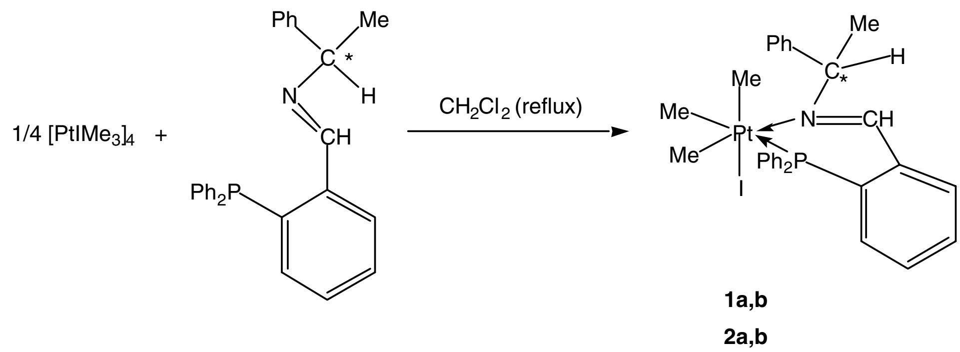
Complexes **1** and **2** (Scheme 2) were prepared by reaction of the tetranuclear complex $[PtIMe_3]_4$ with the ligands (*S*)- and (*R*)-$Ph_2P(C_6H_4)CH$=NC*H(Ph)Me in a 1:4 molar ratio, in dichloromethane solution. The reaction gave a mixture of two diastoreoisomers (*a*, *b*) due to the fact that both the platinum and the carbon atom of the Schiff base in the complexes were chiral. The molar ratio of the diastereoisomers in the mixture were found by ^{1}H NMR spectroscopy, **1a**:**1b** = 59:41 and **2a**:**2b** = 60:40. The reason to prepare the complexes using both types of isomer ligands (*R* and *S*) is to find a possible change in the molar ratio of diastereoisomer in the mixture.

The diastoreoisomers mixture of **1** and **2** reacted in THF–acetone with silver tetrafluoroborate to form silver iodide and a Pt(IV) solvated intermediate, which rapidly produced a reductive elimination reaction forming the Pt(II) solvated complex [$PtMe\{\kappa^2$-$Ph_2P(C_6H_4)CH$=



(S)- L_1
(R)- L_2

Scheme 1.



Scheme 2.

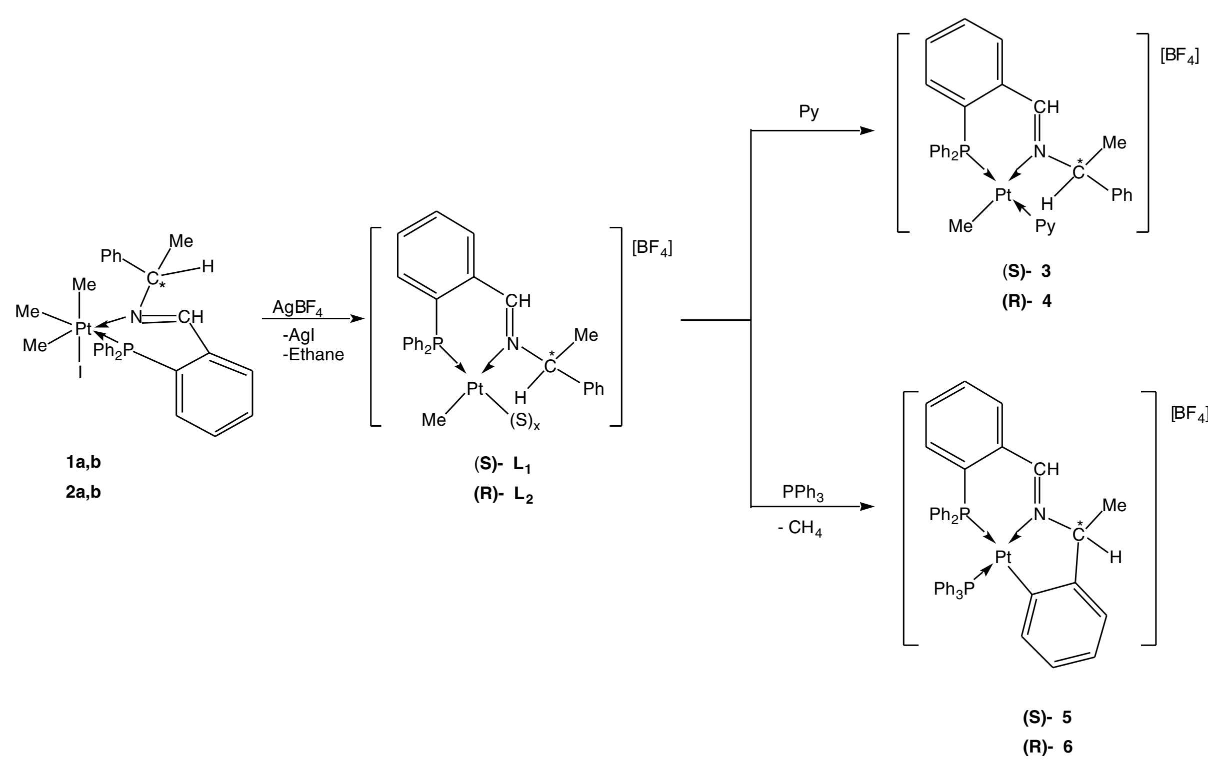
CH(Ph)Me-P,N}(solvent)]$^+$ and the elimination of ethane. This intermediate, which was characterised by ^{1}H NMR, further reacts with one equivalent of an ancillary ligand L to give cationic complexes. When L = Py, the reaction yield complexes of formula [PtMe(Py){κ^2-Ph$_2$P(C$_6$H$_4$)-CH=NC*H(Ph)Me-P,N}][BF$_4$] [C* = (*S*)-, **3;** (*R*)-, **4**]. However, when the reaction was carried out with L = PPh$_3$ a simultaneous cycloorthometallation reaction was produced with methane elimination and formation of the complex [Pt(PPh$_3$){κ^3-Ph$_2$P(C$_6$H$_4$)CH=NC*H(C$_6$H$_4$)-Me-C,P,N}][BF$_4$] [C* = (*S*)-, **5**; (*R*)-, **6**] (Scheme 3).

Generally, the *ortho*metallation reaction is carried out from palladium or platinum precursors in low oxidation state (0,II). This reaction occurs through an oxidative addition by activation of a C(sp^2)–H or C(sp^2)–X bond (X = halide) [17]. In our case, in the presence of triphenylphosphine, the *ortho*metallation reaction was produced onto a cationic complex, therefore the activation the C–H bond of the phenyl group bonded to the chiral carbon is probably due to a simultaneous interaction of the hydrogen to the methyl group to form methane and a nucleophilic attack of the carbon atom to the metal centre.

Complexes **1**–**6** were isolated as air stable solids and characterised by elemental analysis, mass spectrometry and NMR spectroscopy.

*3.3. Solution NMR studies of complexes **1**–**6***

The ^{1}H NMR spectrum of the complexes **1** and **2** shows the presence of two diastereoisomers, *a* and *b*, which were assigned according to their abundance: diastereoisomer *a* is



Scheme 3.

the most abundant, according to the integration of signals in the ^1H NMR spectra (Table 2).

The spectrum of each neutral complex shows a duplication of all signals, each one corresponding to a diastereoisomer. As expected, the isomers are present in different proportion. The diastereomeric ratio in both complexes was obtained from the ^1H NMR peak integration of the proton bonded to the chiral carbon atom. The relative proportions of the isomers are $a/b = 1.44$ and 1.50 for **1** and **2**, respectively. The spectra of both complexes show, in the region between 0.9 and 2.0 ppm, a number of signals corresponding to the methyl groups bonded to the platinum and chiral carbon atoms. At lower fields (δ 5.45–5.68 ppm) each isomer shows a quartet signal assigned to the proton bonded to the chiral carbon atom of the ligand. The chemical shift and the coupling constant, $^3J(HH) = 6.8$ and 6.7 Hz, are consistent with those observed for other similar compounds [2]. At low field two overlapped sets of signals appear in the range 8.0–8.22 ppm, assigned to the protons of the iminic group. The split of the signals are due to a long-range ^{31}P [$^4J(HP) = 1.9$–2.2 Hz] coupling. Also, is observed a ^{195}Pt [$^3J(HPt) = 28.4$–29.3 Hz] coupling. In spite of this, there is still not enough data in existence to assign the configuration of the diastereoisomers in the mixtures. The $^{31}P\{^1H\}$ NMR spectra of each mixture show two singlet signals corresponding to the phosphorus atom of the ligand in each diastereoisomer, which show a coupling to the ^{195}Pt (Table 3). These data are in agreement with those of similar compounds [6,18].

The ^1H NMR spectra of complexes **3** and **4** are practically identical, and quite simple compared to the spectra of the neutral precursors. The spectra show a doublet signal at δ 0.29 ppm, which was assigned to protons of the methyl group bonded to platinum [$^2J(HPt) = 71.2$ (**3**) and 68.5 (**4**) Hz; $^3J(HP) = 3.1$ Hz]. This result proves that the neutral complex react with $AgBF_4$ and the cationic platinum(IV) intermediate undergoes a reductive elimination reaction with loss of ethane. Both the chemical shift and coupling constant to ^{195}Pt are in agreement with a methyl group bonded to the metal centre *trans* to a nitrogen atom [18,19]. Moreover, the ^1H NMR spectra of the complexes show three other characteristic signals corresponding to the ligand. At high field (δ 1.46 ppm) the ^1H NMR spectrum shows a doublet signal assigned to the protons of the methyl group bonded to the chiral carbon atom [$^3J(HH) = 6.7$ Hz]. At lower field (δ 4.69 ppm) a quartet appears, assigned to a proton bonded to the chiral carbon atom [$^3J(HH) = 6.7$ Hz] and, a singlet signal (δ 8.63 ppm) assigned to the iminic proton coupled to ^{195}Pt [$^3J(HPt) = 40$ Hz].

The $^{31}P\{^1H\}$ NMR spectra of these complexes show a singlet signal assigned to the phosphorus atom of the chiral Schiff base ligand, along with the corresponding satellites due to ^{31}P–^{195}Pt coupling. In general, the ^{19}F NMR spectra of the cationic complexes show a signal corresponding to the tetrafluoroborate anion (BF_4^-) at δ −79.1 ppm.

The ^1H NMR spectra of complexes **5** and **6** do not show any signal at high field, which indicates that there are no methyl groups bonded to the platinum centre and confirm the methane elimination and the formation of a cyclometallated complex (Scheme 3). Furthermore, the spectra of these complexes show a doublet signal at δ 1.94 and 1.95 ppm for complexes **5** and **6**, respectively, corresponding to the methyl groups of the ligand. The signals assigned to HC* appear as multiplets at δ 5.79 and 6.05 ppm for complexes **5** and **6**, respectively. Moreover, in these complexes the ^1H NMR show a doublet signal at δ 9.01 [$^4J(HP) = 13.2$ Hz] and 9.99 [$^4J(HP) = 12.6$ Hz] ppm for **5** and **6** respectively, assigned to iminic proton of the ligand. These complexes also show a ^1H–^{195}Pt coupling [$^3J(HPt) = 77.3$ Hz and $^3J(HPt) = 78.8$ Hz, respectively].

The $^{31}P\{^1H\}$ NMR spectra of these complexes exhibit two doublets signals assigned to the P atoms of the $Ph_2P(C_6H_4)CH{=}NC^*H(Ph)Me$ (L) and the triphenylphosphine (L_2) ligands. Also, both signals show a coupling to ^{195}Pt (Table 3). The low value observed for the coupling constant, $^2J(P_L–P_{L2}) = 15$ Hz, confirms that the phosphorus atoms are in a *cis* position [20] and also is in agreement with the formation of a cyclometallated derivatives.

Table 2
^1H NMR chemical shifts (δ ppm) and coupling constants (Hz) of platinum complexes **1** and **2**[a]

Complex	Population (%)	N=C–H			HC*	
Isomer		δ	$^4J(PH)$	$^3J(HPt)$	δ	$^3J(HH)$
1a	59	8.15 (d)	1.9	29.3	5.50 (q)	6.8
1b	41	8.22 (d)	2.0	29.3	5.68 (q)	6.8
2a	60	8.09 (d)	2.1	28.4	5.45 (q)	6.7
2b	40	8.16 (d)	2.2	28.5	5.63 (q)	6.8

[a] Measured in $CDCl_3$ at room temperature. Chemical shifts relative to Me_4Si as internal standard. d, doublet; q, quartet. All complexes show multiplet in the region 6.80–7.60 ppm corresponding to the phenyl groups of the ligands.

Table 3
$^{31}P\{^1H\}$ NMR chemical shifts (δ ppm) and coupling constant (Hz) of platinum complexes[a]

Complex	δ_P	$^1J(PPt)$	$^2J(P_L–P_{L2})$[b]
1			
Isomer *a*	−0.75 (s)	1204	
Isomer *b*	−1.02 (s)	1202	
2			
Isomer *a*	0.007 (s)	1204	
Isomer *b*	−0.24 (s)	1196	
3	11.95 (s)	4159	
4	11.95 (s)	4158	
5	17.20 (d)[b]	1795	15
	20.90 (d)[c]	3958	15
6	17.24 (d)[b]	1798	15
	20.80 (d)[c]	3936	15

[a] Measured in $CDCl_3$ at room temperature. Chemical shifts relative to H_3PO_4 (85%) as standard. s, singlet; d, doublet.
[b] L correspond to the Schiff base ligand.
[c] L_2 correspond to the PPh_3 ligand.

3.4. Crystal structure determination of (OC-6-44-C)-[$PtIMe_3\{\kappa^2$-(R)-$Ph_2PC_6H_4CH{=}NC^*H(Ph)Me\}$] (**2a**)

A perspective ORTEP view of the structure of complex **2a** with the labelling of the atoms is shown in Fig. 1. Relevant bond distances and angles are given in Table 4. The platinum atom shows a distorted octahedral coordination and is bonded to three methyl carbon atoms in a facial arrangement, to a iodide atom and to a nitrogen and phosphorus atoms from the (2-diphenylphosphine)methylbenzylimine bidentate ligand.

The main distortion of the octahedral co-ordination of the platinum centre is due to the small N–Pt–P and C(6)–Pt–P angles of 83.5(2)° and 176.3(4)°, respectively.

The Pt–C(Me) bond distances of the carbon *trans* to N and I [2.05(1) and 2.10(1) Å] compares well with similar distances found in related "$PtIMe_3$" derivatives with N,N-donor ligands, such as [$PtIMe_3(\{8\text{-}(2\text{-}N{=}CHC_5H_4N)\}C_9H_6N)$] [3b], [$PtIMe_3\{1\text{-}(Me_2NCH_2CH_2NCH)C_{10}H_7\}$] [4] and [$PtIMe_3$(terpy)] [21]. Moreover, the Pt–N and Pt–I bond distances [P–N: 2.192(8) and Pt–I: 2.778(1) Å] are in the range to those found in the above complexes [P–N: average 2.1615(5) and Pt–I: 2.7919(6) Å] [3b], [P–N: average 2.260(7) and Pt–I: 2.8090(10) Å] [4], and [P–N: average 2.2064(8) and Pt–I: 2.798(4) Å] [3]. The Pt–C(6) bond length [C *trans* to P, 2.15(1) Å] is larger than the other C–Pt bonds of the $PtMe_3$ moiety, and slightly larger than the distance found in the related compound [$PtMe_3(bipy)PPh_3$][O_3SCF_3] [22]. The Pt–P bond distance [2.376(3) Å] compares well with those found in the above complex [Pt–P: 2.418(1) Å].

In the co-ordinated bidentate ligand, the bond angles involving the P and N atoms reflect a tetrahedral [average 109.1(4)°] and trigonal-plane [average 119.8(7)°] geometry, respectively. It is noteworthy that the C(1)–N–C(2) angle is smaller than those of Pt–P–C(1) and Pt–N–C(2).

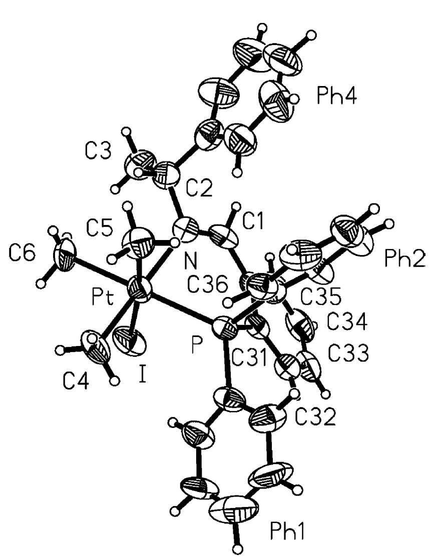


Fig. 1. Molecular structure of **2a**. Thermal ellipsoids are shown at the 50% probability level.

Table 4
Selected bond lengths (Å) and angles (°) for complex (OC-6-44)-[$PtMe_3I\{\kappa^2$-(*R*)-$Ph_2PC_6H_4CH{=}NC^*H(Ph)Me\}$]

Bond lengths (Å)	
Pt–C(4)	2.054(11)
Pt–C(6)	2.149(10)
Pt–P	2.376(3)
P–C(11)	1.837(10)
P–C(21)	1.855(10)
P–C(31)	1.832(10)
Pt–C(5)	2.103(11)
Pt–N	2.192(8)
Pt–I	2.7787(10)
N–C(1)	1.244(13)
N–C(2)	1.492(13)
Bond angles (°)	
C(4)–Pt–C(5)	87.2(5)
C(4)–Pt–C(6)	85.9(5)
C(5)–Pt–C(6)	88.4(5)
C(4)–Pt–P	95.9(4)
C(5)–Pt–P	94.9(3)
C(6)–Pt–P	176.3(4)
N–Pt–P	83.5(2)
N–Pt–I	90.1(2)
P–Pt–I	91.89(7)
C(31)–P–C(11)	103.9(4)
C(11)–P–C(21)	104.8(5)
C(11)–P–Pt	119.3(4)
C(4)–Pt–N	178.8(5)
C(5)–Pt–N	91.8(4)
C(6)–Pt–N	94.7(4)
C(4)–Pt–I	90.9(4)
C(5)–Pt–I	173.1(3)
C(6)–Pt–I	84.8(4)
C(1)–N–C(2)	112.7(9)
C(1)–N–Pt	127.7(7)
C(2)–N–Pt	119.1(6)
C(31)–P–C(21)	102.5(4)
C(31)–P–Pt	107.2(3)
C(21)–P–Pt	117.1(3)

3.5. Analysis of mass spectra of complexes **1**–**6**

Fast bombardment (FAB) mass spectrometry of complexes **1** and **2** shows the highest peak with *m*/*s* at 587 and 603 corresponding to the fragment $[M-(IMe_2+CH_4)]^+$ and $[M-IMe_2]^+$, respectively. The less intense peak with *m*/*s* 633 corresponds to fragment $[M-I]^+$. The low abundance of the cationic fragment $[M-I]^+$ indicates its low stability and agrees with the reductive elimination reaction observed in cationic complexes. The fragment $[M-(IMe_2+CH_4)]^+$ displays the highest abundance and corresponds to a cyclometallated species, which is in accordance with the experimental preparative method. This is because the fragment $[Pt\{\kappa^3\text{-}Ph_2P(C_6H_4)CH{=}NC^*H\text{-}(C_6H_4)\text{-}Me\text{-}C,P,N\}]^+$ should be a stable species in order to generate **5** and **6**. The mass spectra of complexes **5** and **6** have the highest peak at *m*/*s* 849, corresponding to the fragment $[M-BF_4]^+$. A less intense peak with *m*/*s* 587, indicates that the most probable fragmentation mechanism would involve the loss of the PPh_3 ligand from the cationic intermediate $[M-BF_4]^+$.

On the other hand, the mass spectra of complexes **3** and **4** show a less intense peak with *m/s* 682, corresponding to fragment $[M - BF_4]^+$. The mass spectra also show two peaks with *m/s* 666 (20%) and 603 (67%), which correspond to the loss of methane and pyridine from the cationic intermediate $[M - BF_4]^+$, respectively. The highest peak with *m/s* 587 corresponds to the loss of pyridine from the fragment with *m/s* 666 and/or the loss of methane from fragment *m/s* 603. The lowest abundance of the fragment with *m/s* 666 indicates that the most probable fragmentation mechanism for complexes **3** and **4** would involve the loss of the counter ion BF_4^-, followed by the loss of methane and the loss of pyridine.

4. Conclusions

We have found that the iodide abstraction from the diastereoisomeric mixture of the complexes $[PtIMe_3\{\kappa^2\text{-}Ph_2P(C_6H_4)CH{=}NC^*H(Ph)Me\text{-}P,N\}]$ (**1**, **2**) with $AgBF_4$ in the presence of an ancillary ligand, induces a reductive elimination reaction with loss of ethane. We have shown that using pyridine as ligand, cationic complexes of formula $[PtMe(Py)\{\kappa^2\text{-}Ph_2P(C_6H_4)CH{=}NC^*H(Ph)Me\text{-}P,N\}][BF_4]$ [C* = (*S*)-, **3**; (*R*)-, **4**] were obtained. However, the use of a higher π-aceptor ancillary ligand as PPh_3, caused an unexpected consecutive *ortho*metallation reaction with loss of methane, forming square-plane complexes with the ligand acting in its tridentate anionic form, $[Pt(PPh_3)\{\kappa^3\text{-}Ph_2P(C_6H_4)CH{=}NC^*H(C_6H_4)Me\text{-}C,P,N\}]$-$[BF_4]$, [(*S*), **5**; (*R*)-, **6**].

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 271651 for compound **2a**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccd.cam.ac.uk).

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References

[1] (a) K.L. Barlett, K.I. Goldberg, W. Thatcher, J. Am. Chem. Soc. 122 (2000) 1456;
(b) H.C. Clark, L.E. Manzer, Inorg. Chem. 12 (1973) 362;
(c) K.I. Goldberg, J. Yan, E. Winter, J. Am. Chem. Soc. 116 (1994) 1573;
(d) M.P. Brown, R.J. Puddephatt, C.E. Upton, J. Chem. Soc., Dalton Trans. (1974) 2457;
(e) K.I. Goldberg, J. Yan, E.M. Beitung, J. Am. Chem. Soc. 117 (1995) 6889.
[2] E.M. Abel, K. Kite, P.S. Perkins, Polyhedron 6 (1987) 319.
[3] (a) D.H. Goldsworthy, K. Kite, J. Organomet. Chem. 319 (1987) 257;
(b) M.L. Creber, K.G. Orrell, A.G. Osborne, V. Sik, S.J. Coles, D.E. Hibbs, M.B. Hursthouse, Inorg. Chim. Acta 299 (2000) 209;
(c) H. Junicke, D. Steinborn, Inorg. Chim. Acta 346 (2003) 129.
[4] M. Crespo, E. Evangelio, M. Font-Bardía, S. Pérez, X. Solans, Polyhedron 22 (2003) 3363.
[5] (a) T.G. Appleton, J.R. Hall, T.G. Jones, J.A. Sinkinson, Polyhedron 14 (1995) 2613;
(b) R. Contreras, M. Valderrama, C. Beroggi, D. Boys, Polyhedron 20 (2001) 3127;
(c) A. Gelling, K.G. Orrel, A.G. Osborne, V. Sik, M.B. Hursthouse, S.J. Coles, Polyhedron 15 (1996) 3203;
(d) R. Contreras, M. Valderrama, E.M. Orellana, D. Boys, D. Carmona, L.A. Oro, M.P. Lamata, J. Ferrer, J. Organomet. Chem. 606 (2000) 197.
[6] P. Romero, M. Valderrama, R. Contreras, D. Boys, J. Organomet. Chem. 673 (2003) 102.
[7] W. Tang, X. Zhang, Chem. Rev. 103 (2003) 3029.
[8] (a) A.D. Ryabov, Chem. Rev. 90 (1990) 403;
(b) E.C. Constable, Polyhedron 3 (1984) 1037;
(c) A.C. Cope, R.W. Siekman, J. Am. Chem. Soc. 87 (1965) 3272.
[9] (a) A.D. Ryabov, Synthesis (1985) 233;
(b) A.D. Ryabov, I.K. Sakodinskaya, A.K. Yatsimirsky, J. Chem. Soc., Perkin Trans. II (1983) 1511;
(c) Y. Yamamoto, H. Yamazaki, Inorg. Chim. Acta 41 (1980) 229.
[10] N.L. Lewis, J. Am. Chem. Soc. 108 (1986) 743.
[11] (a) D. Morales-Morales, R. Redón, C. Young, M.C. Jensen, Chem. Commun. (2000) 1619;
(b) M. Viciu, R.A. Kelly, E.D. Stevens, F. Naud, M. Studer, S. Nolan, Org. Lett. 5 (2003) 1479.
[12] V.I. Sokolov, Pure Appl. Chem. 55 (1983) 1837.
[13] (a) Y. Wakatsuki, H. Yamazaki, P.A. Grutsch, M.M. Southama, C. Kutal, J. Am. Chem. Soc. 107 (1985) 8153;
(b) C.A. Craig, R.J. Watts, Inorg. Chem. 28 (1989) 309.
[14] C. Baldwin, W.C. Kasha, Inorg. Chem. 14 (1975) 2020.
[15] H. Brunner, A.F.M.M. Rahman, Chem. Ber. 117 (1984) 710.
[16] G.M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen Göttingen, Germany, 1997.
[17] (a) C.M. Anderson, R.J. Pudeephatt, G. Ferguson, A.J. Lough, J. Chem. Soc., Chem. Commun. (1989) 1297;
(b) C.M. Anderson, M. Crespo, M.C. Jenning, A.J. Lough, G. Ferguson, R.J. Puddephatt, Organometallics 10 (1991) 2672;
(c) C.M. Anderson, M. Crespo, G. Ferguson, A.J. Lough, R.J. Puddephatt, Organometallics 11 (1992) 1177;
(d) O. López, M. Crespo, M. Font-Bardía, X. Solans, Organometallics 16 (1997) 1233;
(e) M. Crespo, C. Grande, A. Klein, M. Font-Bardía, X. Solans, J. Organomet. Chem. 563 (1998) 179;
(f) M. Crespo, J. Granell, X. Solans, M. Font-Bardía, Organometallics 21 (2002) 5140.
[18] (a) F.S.M. Hassan, D.M. McEwan, P.G. Pringle, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1985) 1501;
(b) M. Crespo, M. Font-Bardía, X. Solans, Polyhedron 21 (2002) 105.
[19] (a) N.C. Payne, D.W. Stephan, J. Organomet. Chem. 221 (1991) 203;
(b) M. Crespo, X. Solans, M. Font-Bardía, Polyhedron 17 (1998) 1651.
[20] (a) J.K. Jawad, R.J. Puddephatt, M.A. Stalteri, Inorg. Chem. 21 (1982) 332, and references therein;
(b) H.A. Ankersmit, B.H. Løken, H. Kooijman, A.L. Spek, K. Vrieze, G. van Koten, Inorg. Chim. Acta 252 (1996) 141.
[21] E.W. Abel, V.S. Dimitrov, N.J Long, K.G. Orrel, A.G. Osborne, V. Sik, M.B. Hursthouse, M.A. Mazid, J. Chem. Soc., Dalton Trans. (1993) 291.
[22] A. Bayler, A.J. Canty, B.W. Skelton, A.H. White, J. Organomet. Chem. 595 (2000) 296.