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New platinum(II) and palladium(II) quinoline-imine-pyridine, quinoline-imine-thiazole and quinoline-imine-imidazole complexes by metal-assisted condensation reactions

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ABSTRACT

Pt(II) and Pd(II) methyl- and chloro-complexes with the tridentate N-donor ligands ((pyridin-2-yl)methylene)quinolin-8-amine (NNPy), ((pyridin-2-yl)ethylidene)quinolin-8-yl-amine (NNMePy), (phenyl(pyridin-2-yl)methylene)quinolin-8-yl-amine (NNPhPy), ((thiazol-2-yl)methylene)quinolin-8-amine (NNTh) and ((imidazol-4-yl)methylene)quinolin-8-amine (NNImH) were prepared by metal-assisted condensation of 8-aminoquinoline and an *ortho*-substituted aldehydo- or keto- N-heterocycle. Preliminary reactivity studies involving the coordinated tridentate N-donors, the chloro-ligand and the M-CH_3 bond were carried out, leading to the synthesis of several new complexes. During these studies, the formation of a novel five-coordinate Pt(II) carbonyl-complex was observed.

1. Introduction

Transition metal complexes with pyridine-based polydentate ligands such as 2,2′:6′,2″-terpyridine (terpy) are a deeply investigated field of research in coordination chemistry [1]. Terpy forms stable complexes with d^8 transition metal centres such as platinum(II) and palladium(II), which have been applied in the last years in the fields of bioinorganic chemistry [2], analytical chemistry [3] and supramolecular chemistry [4]. Among all, the chloro and methyl terpy-derivatives of the type $[ML(terpy)]^+$ {L = CH_3, Cl; M = Pd, Pt} are useful precursors for the synthesis of a wide range of other complexes [5,6].

Besides terpy, other polydentate N-donor ligands acting as tridentate towards a d^8 metal centre and having a delocalised π-system have been studied in the last years. Some examples of these ligands are the 2,3,5,6-tetrakis(2-pyridinyl)pyrazine [7] and the isomers of 2,6-di(pyrazolyl)-pyridine [8].

Other ligands having electronic and steric features similar to terpy are imine ligands derived from the condensation of 8-aminoquinoline and *ortho*-substituted aldehydo- or keto-pyridines. The synthesis and reactivity of complexes with this kind of chelates and similar ligands have been reported with various metal centres, such as iron(II), cobalt(II), cobalt(III), nickel(II) and platinum(IV) [9]. Chloro-complexes of Pd(II) and Pt(II) and methyl-complexes of Pd(II) with [N,N,N]-donor ligands formed by metal-assisted condensation of 8-aminoquinoline with pyridine-2-carboxaldehyde, 2-acetyl-pyridine and 2-benzoyl-pyridine were prepared some years ago by our research group [10].

In the present work we extended the metal-assisted approach to the synthesis of new platinum(II) cationic methyl-complexes. Moreover, pyridine-2-carboxaldehyde was replaced with other N-heterocycle aldehydes, such as thiazole-2-carboxaldehyde and imidazole-4-carboxaldehyde, to give insight into the effects of different heterocycles on the reactivity of the corresponding palladium and platinum complexes. The reaction of the methyl-complexes with CO allowed highlighting the effects induced by the different heterocycles on the electronic structure of the complexes.

2. Experimental section

2.1. Materials

The nitrogen heterocycles, 1,5-cyclooctadiene (COD), dimethylsulfide, tetramethyltin, palladium chloride and the inorganic

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salts were purchased from Aldrich and used without further purifications. Carbon monoxide was purchased form SIAD. $K_2[PtCl_4]$ was prepared from metallic platinum (Chimet) using a two-steps procedure: (1) the oxidation of metallic platinum to $[PtCl_6]^{2-}$ with *aqua regia* and the isolation of the Pt(IV) complex as potassium salt; (2) the slow reduction of $[PtCl_6]^{2-}$ to $[PtCl_4]^{2-}$ by dropwise addition of a hydrazine hydrochloride solution.

The organic solvents and the triethylamine were purified following common procedures [11]. Deuterated solvents were Euriso-Top products, with the exception of deuterated nitromethane (Aldrich).

Cis/trans-$PtCl_2(SMe_2)_2$ [12], $PtCl_2$(COD) [13], PtClMe(COD) [14], $PdCl_2$(COD) [15], and PdClMe(COD) [16] were synthesized on the basis of reported procedures. The synthesis of the palladium methyl-complex $[PdMe(NNPy)](SO_3CF_3)$ ($\mathbf{2^{Py}}$) was reported in a previous paper [10].

Safety notes: Nitromethane is a potentially explosive solvent and must be handled with care. Perchlorate salts of transition metal complexes with organic ligands are also potentially explosive, but in the experimental conditions described all the products were stable both in solution and in the solid state.

2.2. Instruments

Elemental analyses (C, H, N, Cl) were carried out at the "Istituto di Chimica Inorganica e delle Superfici", C.N.R., Padua. The purification of the stable products before the elemental analyses was carried out by slowly cooling (from +30 °C to −25 °C during a week) clear solutions of the complexes dissolved in mixtures of solvents such as dimethylformamide, nitromethane and diethylether. The vials or glass tubes containing the solutions were cooled in a jacketed glass vessel connected to a programmable Thermo Scientific C25P cryostat having a Phoenix II controlling unit.

IR spectra were recorded in the range 4000 cm^{-1}–450 cm^{-1} on a Perkin–Elmer Spectrum One spectrophotometer. Solid samples were dispersed in nujol or KBr. IR spectra in solution were recorded in the range 2350 cm^{-1}–1650 cm^{-1} on 10^{-2} M solutions of the complexes in nitromethane, using cells with KBr windows.

GC–MS experiments were carried out with a Finnegan Trace GC–MS. The assignments were done by comparison between theoretical and experimental isotopic clusters.

NMR spectra were recorded on a Bruker AC 200 and Bruker Avance 300 spectrometers. The NMR spectra of the complexes were collected at temperatures ranging from 298 K to 370 K, using CD_3NO_2 and/or $(CD_3)_2SO$ as solvents. The spectra of mixtures of 8-aminoquinoline with N-heterocycle aldehydes or ketones were recorded at 298 K in CD_3OD. ^1H and ^{13}C chemical shift values were attributed using tetramethylsilane as internal reference. COSY, NOESY, HSQC and HMBC experiments were carried out using their standard programs. NMR spectra were elaborated with the MestRe-C software package [17].

Conductivity measurements were carried out at 298 K on 10^{-3} M solutions of the complexes in dimethylformamide or nitromethane, using a Radiometer Copenhagen CDM 83 instrument. Molar conductivity values were compared with data reported in the literature [18].

2.3. Ligands

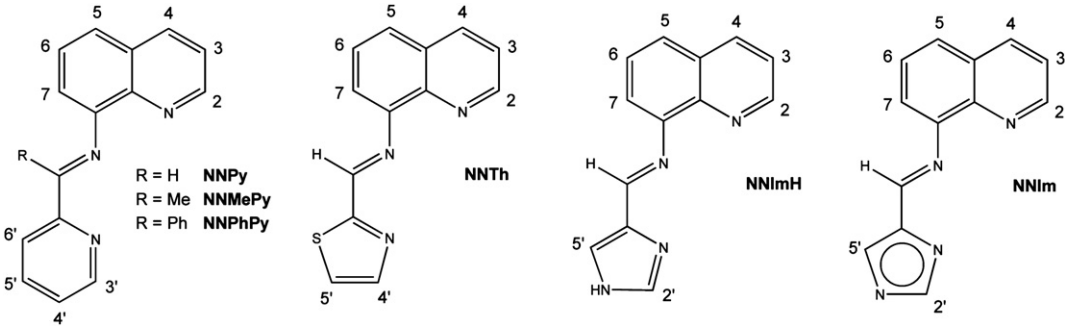
The polydentate ligands coordinated to the metal centres in the complexes described in this paper are sketched in Scheme 1. NNPy = ((pyridin-2-yl)methylene)quinolin-8-amine; NNMePy = ((pyridin-2-yl)ethylidene)quinolin-8-yl-amine; NNPhPy = (phenyl(pyridin-2-yl)methylene)quinolin-8-yl-amine; NNTh = ((thiazol-2-yl)methylene)quinolin-8-amine; NNImH = ((imidazol-4-yl) methylene)quinolin-8-amine; NNIm = ((imidazolate-4-yl)methylene)quinolin-8-amine. Heterocycle rings were numbered following common conventions.

2.4. Synthesis of $[PtMe(NNPy)](ClO_4)$ (1^{NNPy}), $[PtMe(NNMePy)]X$ ($X = ClO_4$ or SO_3CF_3) (1^{NNMePy}), $[PtMe(NNPhPy)](ClO_4)$ (1^{NNPhPy}), $[PtMe(NNTh)]X$ ($X = ClO_4$ or SO_3CF_3) (1^{NNTh}) and $[PtMe(NNImH)](ClO_4)$ (1^{NNImH})

A suspension of PtClMe(COD) (0.202 g, 0.57 mmol) in 30 mL of methanol was heated to 50 °C until the complete dissolution of the complex. Keeping the temperature constant, a solution containing 8-aminoquinoline (0.082 g, 0.57 mmol) and an equimolar amount of the proper aldehyde or ketone in 10 mL of methanol was added dropwise (pyridine-2-carboxaldehyde, 54 μL, for $\mathbf{1^{NNPy}}$; 2-acetylpyridine, 63 μL, for $\mathbf{1^{NNMePy}}$; 2-benzoyl-pyridine, 0.104 g, for $\mathbf{1^{NNPhPy}}$; thiazol-2-carboxaldehyde, 50 μL, for $\mathbf{1^{NNTh}}$; imidazol-4-carboxaldehyde, 0.054 g, for $\mathbf{1^{NNImH}}$). The resulting solution was stirred at room temperature for 3 h. Subsequently, a 5:1 excess of lithium triflate (0.455 g, 2.85 mmol) or lithium perchlorate (0.303 g, 2.85 mmol) was added. A yellow or red solid started to precipitate slowly. After keeping the reaction mixture at −25 °C for one night, the product was filtered, washed with 5 mL of methanol and 10 mL of diethylether. Slow diffusion of diethylether into dimethylformamide/nitromethane solutions purified all the complexes as microcrystalline solids. The yields were all >85% for the perchlorate salts and >60% for the triflate salts.

2.4.1. Characterization of 1^{NNPy}

Elemental analysis for $C_{16}H_{14}ClN_3O_4Pt$: calcd. C 35.4, H 2.60, N 7.74, Cl 6.53; found C 35.3, H 2.61, N 7.71, Cl 6.50. Λ_M (dmf, 298 K) = 71 Ω^{-1} mol^{-1} cm^2. No melting or decomposition at $T \leq 260$ °C. ^1H NMR {DMSO-d_6, 346 K, ppm}: 10.06 (s, 1H,



Scheme 1. Polydentate ligands considered in this paper.

$^3J_{PtH}$ = 38 Hz, *imine-CH*); 8.96 (d, 1H, $^3J_{HH}$ = 4.9 Hz, $^3J_{PtH}$ = 56 Hz, *quinoline-H$_2$*); 8.83 (d, 1H, $^3J_{HH}$ = 8.1 Hz, *quinoline-H$_4$*); 8.74 (d, 1H, $^3J_{HH}$ = 4.9 Hz, $^3J_{PtH}$ = 50 Hz, *pyridine-H$_{6'}$*); 8.48 (d, 1H, $^3J_{HH}$ = 7.5 Hz, *quinoline-H$_7$*); 8.35 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *pyridine-H$_{4'}$*); 8.22 (d, 1H, $^3J_{HH}$ = 7.5 Hz, *quinoline-H$_5$*); 8.09 (d, 1H, $^3J_{HH}$ = 7.5 Hz, *pyridine-H$_{3'}$*); 7.97–7.77 (m, 2H, *quinoline-H$_6$*, *pyridine-H$_{5'}$*); 7.68 (dd, 1H, $^3J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 8.1 Hz, *quinoline-H$_3$*); 1.10 (s, 3H, $^2J_{PtH}$ = 75 Hz, *Pt-CH$_3$*). ^{13}C {^{1}H} NMR {DMSO-d$_6$, 298 K, HSQC projection, ppm}: 156.8 *imine-C*, 151.2 *pyridine-C$_{6'}$*, 150.4 *quinoline-C$_2$*, 141.2 *pyridine-C$_{4'}$*, 139.0 *quinoline-C$_4$*, 131.1 *quinoline-C$_5$*, 130.7 *pyridine-C$_{3'}$*, 130.1 *pyridine-C$_{5'}$*, 129.3 *quinoline-C$_6$*, 124.5 *quinoline-C$_3$*, 121.1 *quinoline-C$_7$*, -7.70 *Pt-CH$_3$*.

2.4.2. Characterization of 1^{NNMePy}

Elemental analysis for $C_{18}H_{16}F_3N_3O_3PtS$: calcd. C 35.7, H 2.66, N 6.93; found C 35.6, H 2.67, N 6.91. Λ_M (dmf, 298 K) = 68 Ω^{-1} mol^{-1} cm^2. No melting or decomposition at $T \leq 260$ °C. ^{1}H NMR {DMSO-d$_6$, 298 K, ppm: 8.59 (d, 1H, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 1.0 Hz, *quinoline-H$_2$*); 8.55 (d, 1H, $^3J_{HH}$ = 8.5 Hz, *quinoline-H$_4$*); 8.34 (d, 1H, $^3J_{HH}$ = 5.7 Hz, *pyridine-H$_{6'}$*); 8.21–8.12 (m, 2H, *quinoline-H$_7$* and *pyridine-H$_{4'}$*); 8.05 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H$_{3'}$*); 7.92 (d, 1H, $^3J_{HH}$ = 8.2 Hz, *quinoline-H$_5$*); 7.64–7.53 (m, 2H, *quinoline-H$_6$* and *pyridine-H$_{5'}$*); 7.42 (dd, 1H, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 8.5 Hz, *quinoline-H$_3$*); 2.50 (s, 3H, *imine-CH$_3$*); 0.57 (s, 3H, $^2J_{PtH}$ = 72 Hz, *Pt-CH$_3$*). ^{13}C {^{1}H} NMR {DMSO-d$_6$, 298 K, ppm}: 149.5 *pyridine-C$_{6'}$*, 148.9 *quinoline-C$_2$*, 140.3 *pyridine-C$_{4'}$*, 138.6 *quinoline-C$_4$*, 130.8, 130.2, 130.1, 129.8 *quinoline-C$_5$*, *pyridine-C$_{3'}$*, *quinoline-C$_6$*, *pyridine-C$_{5'}$*, 126.3 *quinoline-C$_7$*, 124.0 *quinoline-C$_3$*, 19.5 *imine-CH$_3$*, -6.6 *Pt-CH$_3$* ($^1J_{PtC}$ = 805 Hz), 168.3, 162.5, 151.8, 139.3, 129.0 *ancillary ligand not H-bonded carbons*.

2.4.3. Characterization of 1^{NNPhPy}

Elemental analysis for $C_{22}H_{18}ClN_3O_4Pt$: calcd. C 42.7, H 2.93, N 6.79, Cl 5.73; found C 42.6, H 2.94, N 6.77, Cl 5.72. Λ_M (dmf, 298 K) = 61 Ω^{-1} mol^{-1} cm^2. No melting or decomposition at $T \leq 260$ °C. ^{1}H NMR {DMSO-d$_6$, 298 K, ppm}: 9.12 (d, 1H, $^3J_{HH}$ = 5.3 Hz, $^3J_{PtH}$ = 53 Hz, *quinoline-H$_2$*); 9.00 (d, 1H, $^3J_{HH}$ = 5.3 Hz, *pyridine-H$_{6'}$*); 8.90 (d, 1H, $^3J_{HH}$ = 8.2 Hz, *quinoline-H$_4$*); 8.30 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H$_{4'}$*); 8.21 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_7$*); 7.92 (m, 1H, *pyridine-H$_{5'}$*); 7.88–7.77 (m, 5H, *imine-phenyl*); 7.75 (dd, 1H, $^3J_{HH}$ = 5.3 Hz, $^3J_{HH}$ = 8.2 Hz, *quinoline-H$_3$*); 7.56 (t, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_6$*); 7.34 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H$_{3'}$*); 6.94 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_5$*); 1.21 (s, 3H, $^2J_{PtH}$ = 74 Hz, *Pt-CH$_3$*). ^{13}C {^{1}H} NMR {DMSO-d$_6$, 298 K, ppm}: 167.2 *imine-C*, 163.4–124.1 *ancillary ligand carbons*, −6.2 *Pt-CH$_3$*.

2.4.4. Characterization of 1^{NNTh}

Elemental analysis for $C_{15}H_{12}F_3N_3O_3PtS_2$: calcd. C 30.1, H 2.02, N 7.02; found C 30.0, H 2.02, N 7.00. Λ_M (nitromethane, 298 K) = 71 Ω^{-1} mol^{-1} cm^2. No melting or decomposition at $T \leq 260$ °C. ^{1}H NMR {CD_3NO_2, 298 K, ppm}: 9.77 (s, 1H, $^3J_{PtH}$ = 37 Hz, *imine-CH*); 8.78 (d, 1H, $^3J_{HH}$ = 5.0 Hz, $^3J_{PtH}$ = 59 Hz, *quinoline-H$_2$*); 8.66 (d, 1H, $^3J_{HH}$ = 8.5 Hz, *quinoline-H$_4$*); 8.31 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_7$*); 8.29 (d, 1H, $^3J_{HH}$ = 3.2 Hz, *thiazole-H$_{5'}$*); 8.12 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_5$*); 7.99 (d, 1H, $^3J_{HH}$ = 3.2 Hz, $^3J_{PtH}$ = 20 Hz, *thiazole-H$_{4'}$*); 7.74 (t, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_6$*); 7.56 (dd, 1H, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 8.5 Hz, *quinoline-H$_3$*); 1.22 (s, 3H, $^2J_{PtH}$ = 77 Hz, *Pt-CH$_3$*). ^{13}C {^{1}H} NMR {CD_3NO_2, 298 K, HSQC projection, ppm}: 150.6 *quinoline-C$_2$*, 148.6 *imine-C*, 143.4 *thiazole-C$_{4'}$*, 139.9 *quinoline-C$_4$*, 132.8 *quinoline-C$_5$*, 131.8 *thiazole-C$_{5'}$*, 131.0 *quinoline-C$_6$*, 126.0 *quinoline-C$_3$*, 122.1 *quinoline-C$_7$*, -11.1 *Pt-CH$_3$*.

2.4.5. Characterization of 1^{NNImH}

Elemental analysis for $C_{14}H_{13}ClN_4O_4Pt$: calcd. C 31.6, H 2.46, N 10.5, Cl 6.67; found C 31.5, H 2.45, N 10.5, Cl 6.65. Λ_M (dmf, 298 K) = 63 Ω^{-1} mol^{-1} cm^2. No melting or decomposition at $T \leq 260$ °C. ^{1}H NMR {DMSO-d$_6$, 298 K, ppm}: 13.81 (s, br, 1H, *imidazole-NH*); 9.53 (s, 1H, $^3J_{PtH}$ = 32 Hz, *imine-CH*); 8.75 (d, 1H, $^3J_{PtH}$ = 57 Hz, $^3J_{HH}$ = 5.1 Hz, *quinoline-H$_2$*); 8.69 (d, 1H, $^3J_{HH}$ = 8.3 Hz, *quinoline-H$_4$*); 8.28 (s, 1H, *imidazole-H$_{2'}$*); 8.25 (d, 1H, $^3J_{HH}$ = 8.1 Hz, *quinoline-H$_7$*); 8.24 (s, 1H, *imidazole-H$_{5'}$*); 7.98 (d, ^{1}H, $^3J_{HH}$ = 8.1 Hz, *quinoline-H$_5$*); 7.68 (t, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_6$*); 7.53 (dd, 1H, $^3J_{HH}$ = 5.1 Hz, $^3J_{HH}$ = 8.3 Hz, *quinoline-H$_3$*); 0.82 (s, 3H, $^2J_{PtH}$ = 75 Hz, *Pt-CH$_3$*). ^{13}C {^{1}H} NMR {DMSO-d$_6$, 298 K, ppm}: 148.9 *quinoline-C$_2$*, 148.7 *imine-C*, 139.2 *imidazole-C$_{2'}$*, 137.8 *quinoline-C$_4$*, 129.0 *quinoline-C$_5$*, 128.6 *quinoline-C$_6$*, 126.9 *imidazole-C$_{5'}$*, 123.9 *quinoline-C$_3$*, 119.8 *quinoline-C$_7$*, -16.7 ($^1J_{PtC}$ = 760 Hz) *Pt-CH$_3$*, 150.4, 147.0, 139.7, 130.8 *ancillary ligand not H-bonded carbons*.

2.5. Synthesis of [PdMe(NNTh)](X) (X = SO_3CF_3 or ClO_4) (2^{NNTh}) and [PdMe(NNImH)](ClO_4) (2^{NNImH})

The synthetic procedure for the preparation of **2^{NNTh}** and **2^{NNImH}** was the same as previously described for the Pt(II) complexes **1^{NNTh}** and **1^{NNImH}**, using PdClMe(COD) (0.151 g, 0.57 mmol) as starting reagent. The yields were >90% for all the perchlorate salts and >65% for the triflate salt.

2.5.1. Characterization of 2^{NNTh}

Elemental analysis of $C_{15}H_{12}F_3N_3O_3PdS_2$: calcd. C 35.3, H 2.37, N 8.24; found C 35.2, H 2.36, N 8.21. Λ_M (nitromethane, 298 K) = 84 Ω^{-1} mol^{-1} cm^2. Decomposition at $T > 240$ °C. ^{1}H NMR {CD_3NO_2, 336 K, ppm}: 9.30 (s, 1H, *imine-CH*); 8.74 (dd, 1H, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 1.3 Hz, *quinoline-H$_2$*); 8.65 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.3 Hz, *quinoline-H$_4$*); 8.33 (d, 1H, $^3J_{HH}$ = 7.9 Hz, *quinoline-H$_7$*); 8.28 (d, 1H, $^3J_{HH}$ = 3.2 Hz, *thiazole-H$_{5'}$*); 8.20 (d, 1H, $^3J_{HH}$ = 7.9 Hz, *quinoline-H$_5$*); 8.06 (d, 1H, $^3J_{HH}$ = 3.2 Hz, *thiazole-H$_{4'}$*); 7.87 (t, 1H, $^3J_{HH}$ = 7.9 Hz, *quinoline-H$_6$*); 7.74 (dd, 1H, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 8.4 Hz, *quinoline-H$_3$*); 1.08 (s, 3H, *Pd-CH$_3$*). ^{13}C {^{1}H} NMR {CD_3NO_2, 336 K, ppm}: 153.1, 148.1, 144.2, 141.3, 133.6, 130.7, 130.2, 125.2, 122.3 *ancillary ligand CH carbons*; 170.4, 151.5, 139.1, 132.9 *ancillary ligand not H-bonded carbons*; 1.9 *Pd-CH$_3$*.

2.5.2. Characterization of 2^{NNImH}

Elemental analysis of $C_{14}H_{13}ClN_4O_4Pd$: calcd. C 37.9, H 2.96, N 12.6, Cl 8.00; found C 37.7, H 2.97, N 12.5, Cl 7.97. Λ_M (dmf, 298 K) = 77 Ω^{-1} mol^{-1} cm^2. Decomposition at $T > 240$ °C. ^{1}H NMR {DMSO-d$_6$, 298 K, ppm}: 13.71 (s, very br, 1H, *imidazole-NH*); 9.12 (s, 1H, *imine-CH*); 8.61 (d, 1H, $^3J_{HH}$ = 8.3 Hz, *quinoline-H$_4$*); 8.53 (d, 1H, $^3J_{HH}$ = 5.0 Hz, *quinoline-H$_2$*); 8.23 (s, 1H, *imidazole-H$_{2'}$*); 8.20 (d, 1H, $^3J_{HH}$ = 7.7 Hz, *quinoline-H$_7$*); 8.14 (s, 1H, *imidazole-H$_{5'}$*); 8.00 (d, 1H, $^3J_{HH}$ = 7.7 Hz, *quinoline-H$_5$*); 7.72 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *quinoline-H$_6$*); 7.63 (dd, 1H, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 8.3 Hz, *quinoline-H$_3$*); 0.62 (s, 3H, *Pd-CH$_3$*). ^{13}C {^{1}H} NMR {DMSO-d$_6$, 298 K, ppm}: 151.0 *quinoline-C$_2$*, 149.3 *imine-C*, 139.4 *imidazole-C$_{2'}$*, 139.2 *quinoline-C$_4$*, 129.2 *quinoline-C$_5$*, 128.1 *quinoline-C$_6$*, 125.7 *imidazole-C$_{5'}$*, 123.3 *quinoline-C$_3$*, 119.5 *quinoline-C$_7$*, -3.7 *Pd-CH$_3$*, 148.2, 144.9, 138.1, 130.3 *ancillary ligand not H-bonded carbons*.

2.6. Synthesis of [PtCl(NNTh)](SO_3CF_3) (3^{NNTh}) and [PtCl(NNImH)](X) (X = SO_3CF_3 or ClO_4) (3^{NNImH})

The synthetic procedure for the preparation of chloro-complexes **3^{NNTh}** and **3^{NNImH}** was the same previously described for the methyl-complexes **1^{NNTh}** and **1^{NNImH}**, starting from 0.222 g (0.57 mmol) of *cis/trans*-$PtCl_2(SMe_2)_2$. The yields were >80% for the perchlorate salt and >70% for the triflate salts. Slow cooling of dimethylformamide/nitromethane/diethylether solutions purified all the complexes as microcrystalline solids.

2.6.1. Characterization of 3^{NNTh}

Elemental analysis for $C_{14}H_9ClF_3N_3O_3PtS_2$: calcd. C 27.2, H 1.47, N 6.79, Cl 5.73; found C 27.1, H 1.47, N 6.76, Cl 5.71. Λ_M (nitromethane, 298 K) = 74 Ω^{-1} mol^{-1} cm^2. No melting or decomposition at $T \leq 260$ °C. ^{1}H NMR {CD_3NO_2, 298 K, ppm}: 9.77 (s, ^{1}H, $^3J_{PtH}$ = 98 Hz, *imine-CH*); 9.0 (d, ^{1}H, $^3J_{HH}$ = 5.0 Hz, $^3J_{PtH}$ = 42 Hz, *quinoline-H$_2$*); 8.76 (d, 1H, $^3J_{HH}$ = 8.3 Hz, *quinoline-H$_4$*); 8.54 (d, ^{1}H, $^3J_{HH}$ = 3.2 Hz, *thiazole-H$_{5'}$*); 8.50 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_7$*); 8.25 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_5$*); 8.07 (d, 1H, $^3J_{HH}$ = 3.2 Hz, *thiazole-H$_{4'}$*); 7.88 (t, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_6$*); 7.69 (dd, ^{1}H, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 8.3 Hz, *quinoline-H$_3$*). ^{13}C {^{1}H} NMR {CD_3NO_2, 298 K, HSQC projection, ppm}: 153.7 *imine-C*, 151.4 *quinoline-C$_2$*, 144.0 *thiazole-C$_4$*, 141.5 *quinoline-C$_4$*, 133.5 *quinoline-C$_5$*, 133.0 *thiazole-C$_{5'}$*, 131.2 *quinoline-C$_6$*, 125.9 *quinoline-C$_3$*, 122.5 *quinoline-C$_7$*.

2.6.2. Characterization of 3^{NNImH}

Elemental analysis for $C_{13}H_{10}Cl_2N_4O_4Pt$: calcd. C 28.3, H 1.83, N 10.2, Cl 12.8; found C 28.2, H 1.82, N 10.1, Cl 12.79. Λ_M (dmf, 298 K) = 54 Ω^{-1} mol^{-1} cm^2. No melting or decomposition at $T \leq 260$ °C. ^{1}H NMR {DMSO-d$_6$, 298 K, ppm}: 14.5 (s, very br, 1H, *imidazole-NH*); 9.74 (s, 1H, $^3J_{PtH}$ = 96 Hz, *imine-CH*); 9.21 (d, 1H, $^3J_{HH}$ = 5.0 Hz, *quinoline-H$_2$*); 8.97 (d, 1H, $^3J_{HH}$ = 8.5 Hz, *quinoline-H$_4$*); 8.65 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_7$*); 8.62 (s, 1H, *imidazole*); 8.52 (s, 1H, *imidazole*); 8.25 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_5$*); 7.94 (t, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H$_6$*); 7.88 (dd, 1H, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 8.5 Hz, *quinoline-H$_3$*). ^{13}C {^{1}H} NMR {DMSO-d$_6$, 298 K, HSQC projection, ppm}: 155.6 *imine-C*, 150.9 *quinoline-C$_2$*, 141.9 *imidazole*, 140.9 *quinoline-C$_4$*, 130.5 *imidazole*, 130.4 *quinoline-C$_5$*, 130.1 *quinoline-C$_6$*, 125.0 *quinoline-C$_3$*, 121.4 *quinoline-C$_7$*.

2.7. Synthesis of [PdCl(NNTh)](SO_3CF_3) (4^{NNTh}) and [PdCl(NNImH)](SO_3CF_3) (4^{NNImH})

The synthetic procedure for the preparation of **4^{NNTh}** and **4^{NNImH}** was the same as previously described for the Pt(II) chloro-complexes **3^{NNTh}** and **3^{NNImH}**, using $PdCl_2$(COD) (0.163 g, 0.57 mmol) as starting reagent. The yield was >70% for both the complexes.

2.7.1. Characterization of 4^{NNTh}

Elemental analysis for $C_{14}H_9ClF_3N_3O_3PdS_2$: calcd. C 31.7, H 1.71, N 7.92, Cl 6.69; found C 31.6, H 1.70, N 7.89, Cl 6.67. Λ_M (nitromethane, 298 K) = 59 Ω^{-1} mol^{-1} cm^2. Decomposition at $T > 220$ °C. ^{1}H NMR {CD_3NO_2, 298 K, ppm}: 9.24 (s, 1H, *imine-CH*); 8.93 (d, 1H, $^3J_{HH}$ = 5.3 Hz, *quinoline-H$_2$*); 8.74 (d, 1H, $^3J_{HH}$ = 8.4 Hz, *quinoline-H$_4$*); 8.45 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H$_7$*); 8.42 (d, 1H, $^3J_{HH}$ = 3.3 Hz, *thiazole-H$_{5'}$*); 8.27 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H$_5$*); 8.13 (d, 1H, $^3J_{HH}$ = 3.3 Hz, *thiazole-H$_{4'}$*); 7.94 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H$_6$*); 7.79 (dd, 1H, $^3J_{HH}$ = 5.3 Hz, $^3J_{HH}$ = 8.4 Hz, *quinoline-H$_3$*). ^{13}C {^{1}H} NMR {CD_3NO_2, 298 K, HSQC projection, ppm}: 154.3 *quinoline-C$_2$*, 153.9 *imine-C*, 145.1 *thiazole-C$_4$*, 142.5 *quinoline-C$_4$*, 134.1 *quinoline-C$_5$*, 132.2 *thiazole-C$_{5'}$*, 130.7 *quinoline-C$_6$*, 125.5 *quinoline-H$_3$*, 122.8 *quinoline-C$_7$*.

2.7.2. Characterization of 4^{NNImH}

Elemental analysis for $C_{14}H_{10}ClF_3N_4O_3PdS$: calcd. C 32.8, H 1.96, N 10.9, Cl 6.91; found C 32.7, H 1.95, N 10.9, Cl 6.89. Λ_M (dmf, 298 K) = 57 Ω^{-1} mol^{-1} cm^2. Decomposition at $T > 220$ °C. ^{1}H NMR {DMSO-d$_6$, 298 K, ppm}: 14.22 (s, very br, 1H, *imidazole-NH*); 9.34 (s, 1H, *imine-CH*); 8.93 (d, 1H, $^3J_{HH}$ = 5.2 Hz, *quinoline-H$_2$*); 8.88 (d, 1H, $^3J_{HH}$ = 8.2 Hz, *quinoline-H$_4$*); 8.56 (d, 1H, $^3J_{HH}$ = 7.9 Hz, *quinoline-H$_7$*); 8.51 (s, 1H, *imidazole-H$_{2'}$*); 8.43 (s, 1H, *imidazole-H$_{5'}$*); 8.22 (d, 1H, $^3J_{HH}$ = 7.9 Hz, *quinoline-H$_5$*); 7.93 (t, 1H, $^3J_{HH}$ = 7.9 Hz, *quinoline-H$_6$*); 7.87 (dd, 1H, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 8.2 Hz, *quinoline-H$_3$*). ^{13}C {^{1}H} NMR {DMSO-d$_6$, 298 K, HSQC projection, ppm}: 155.5 *imine-C*, 151.9 *quinoline-C$_2$*, 140.7 *imidazole-C$_{5'}$*, 140.4 *quinoline-C$_4$*, 129.5 *quinoline-C$_5$*, 128.7 *quinoline-C$_6$*, 128.1 *imidazole-C$_{2'}$*, 123.8 *quinoline-C$_3$*, 120.5 *quinoline-C$_7$*.

2.8. Synthesis of [Pt(OSO_2CH_3)(NNImH)](SO_3CF_3) (5^{NNImH})

To a solution of **3^{NNImH}** (triflate salt, 0.162 g, 0.27 mmol) in 20 mL of nitromethane a stoichiometric amount of silver methanesulfonate (0.055 g, 0.27 mmol) was added. The reaction mixture was left overnight under stirring in the dark at room temperature. The AgCl formed was then removed by filtration and the solution was concentrated under reduced pressure to about 3 mL. Diethylether was then added drop by drop until a dark yellow solid started to separate. After one night at −25 °C the product was collected by filtration, washed with diethylether (20 mL) and dried at reduced pressure. Yield > 75%.

2.8.1. Characterization of 5^{NNImH}

Elemental analysis for $C_{15}H_{13}F_3N_4O_6PtS_2$: calcd. C 27.2, H 1.98, N 8.47; found C 27.3, H 2.00, N 8.44. Λ_M (nitromethane, 298 K) = 54 Ω^{-1} mol^{-1} cm^2; Λ_M (DMSO, 298 K) = 32 Ω^{-1} mol^{-1} cm^2. No melting or decomposition at $T \leq 260$ °C. ^{1}H NMR {DMSO-d$_6$, 298 K, ppm}: 9.76 (s, 1H, *imine-CH*); 9.50 (s, br, 1H, *imidazole-NH*); 9.05 (d, 1H, $^3J_{HH}$ = 8.6 Hz, *quinoline-H$_4$*); 8.91 (s, 1H, *imidazole-H$_{2'}$*); 8.84 (s, 1H, *imidazole-H$_{5'}$*); 8.74 (d, 1H, $^3J_{HH}$ = 8.2 Hz, *quinoline-H$_7$*); 8.65 (d, 1H, $^3J_{HH}$ = 5.3 Hz, *quinoline-H$_2$*); 8.31 (d, 1H, $^3J_{HH}$ = 8.2 Hz, *quinoline-H$_5$*); 8.01 (t, 1H, $^3J_{HH}$ = 8.2 Hz, *quinoline-H$_6$*); 7.87 (dd, 1H, $^3J_{HH}$ = 5.3 Hz, $^3J_{HH}$ = 8.6 Hz, *quinoline-H$_3$*); 2.35 (s, 3H, *CH_3SO_3*). ^{13}C {^{1}H} NMR {DMSO-d$_6$, 298 K, ppm}: 155.9 *imine-CH*, 151.2 *quinoline-C$_2$*, 149.6 *imidazole-C$_{2'}$*, 141.4 *quinoline-C$_4$*, 141.2 *imidazole-C$_{5'}$*, 130.5 *quinoline-C$_7$*, 130.2 *quinoline-C$_6$*, 125.2 *quinoline-C$_3$*, 121.1 *quinoline-C$_5$*, 148.5, 146.1, 141.5, 130.8 *ancillary ligand not H-bonded carbons*, 40.6 *CH_3SO_3* (HSQC projection).

2.9. Synthesis of [Pd(OSO_2CH_3)(NNImH)](SO_3CF_3) (6^{NNImH})

The synthetic procedure for the preparation of **6** was the same previously described for the Pt(II) complexes **5^{NNImH}**, using **4^{NNImH}** (0.139 g, 0.27 mmol) as starting reagent. Yield > 75%.

2.9.1. Characterization of 6^{NNImH}

Elemental analysis for $C_{15}H_{13}F_3N_4O_6PdS_2$: calcd. C 31.5, H 2.29, N 9.78; found C 31.4, H 2.28, N 9.75. Λ_M (nitromethane, 298 K) = 57 Ω^{-1} mol^{-1} cm^2; Λ_M (DMSO, 298 K) = 32 Ω^{-1} mol^{-1} cm^2. Decomposition at $T > 220$ °C. ^{1}H NMR {CD_3NO_2, 336 K, ppm}: 9.04 (s, 1H, *imine-CH*); 8.75 (d, 1H, $^3J_{HH}$ = 8.3 Hz, *quinoline-H$_4$*); 8.47 (s, 1H, *imidazole-H$_{2'}$*); 8.42 (d, 1H, $^3J_{HH}$ = 5.2 Hz, *quinoline-H$_2$*); 8.38 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H$_7$*); 8.31 (s, 1H, *imidazole-H$_{5'}$*); 8.11 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H$_5$*); 7.89 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H$_6$*); 7.78 (dd, 1H, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 8.3 Hz, *quinoline-H$_3$*); 2.10 (s, 3H, *CH_3SO_3*). ^{1}H NMR {DMSO-d$_6$, 298 K, ppm}: 9.46 (s, 1H, *imine-CH*); 9.44 (s, br, 1H, *imidazole-NH*); 8.96 (d, 1H, $^3J_{HH}$ = 8.4 Hz, *quinoline-H$_4$*); 8.70 (s, 1H, *imidazole-H$_{2'}$*); 8.65 (s, 1H, *imidazole-H$_{5'}$*); 8.63 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H$_7$*); 8.37 (d, 1H, $^3J_{HH}$ = 5.2 Hz, *quinoline-H$_2$*); 8.26 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H$_5$*); 8.00 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H$_6$*); 7.87 (dd, 1H, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 8.4 Hz, *quinoline-H$_3$*); 2.37 (s, 3H, *CH_3SO_3*). ^{13}C {^{1}H} NMR {CD_3NO_2, 317 K, ppm}: 155.9–120.6 *ancillary ligand CH carbons*, 40.2 *CH_3SO_3*. ^{13}C {^{1}H} NMR {DMSO-d$_6$, 298 K, ppm}: 156.0, 152.6, 148.9, 147.1, 144.2, 141.1, 140.7, 139.0, 130.5, 129.2, 128.9, 123.9, 119.8 *ancillary ligand carbons*.

2.10. Synthesis of [PtMe(NNIm)] (7^{NNIm})

In an NMR tube **1^{NNImH}** (38 mg, 71 μmol) was dissolved in 1 mL of DMSO-d_6. An equimolar amount of triethylamine (10 μL, 71 μL) was then added with a microsyringe and the ^{1}H NMR spectrum was recorded. After the addition of the base the ^{1}H NMR spectrum showed only signals attributable to the products formed. The complex was separated from the by-product [$NHEt_3$](ClO_4) by slow addition of diethylether followed by fractional crystallization. The complex was then washed several times with diethylether to remove the traces of DMSO and dried under vacuum.

2.10.1. Characterization of 7^{NNIm}

Elemental analysis for $C_{14}H_{12}N_4Pt$: calcd. C 39.0, H 2.80, N 13.0; found C 39.2, H 2.81, N 13.1. ^{1}H NMR {DMSO-d_6, 298 K, ppm}: 9.38 (s, 1H, $^3J_{PtH}$ = 36 Hz, *imine-CH*); 8.99 (d, 1H, $^3J_{HH}$ = 4.9 Hz, $^3J_{PtH}$ = 52 Hz, *quinoline-H_2*); 8.77 (d, 1H, $^3J_{HH}$ = 8.4 Hz, *quinoline-H_4*); 8.27 (d, 1H, $^3J_{HH}$ = 7.5 Hz, *quinoline-H_7*); 7.95 (d, 1H, $^3J_{HH}$ = 7.5 Hz, *quinoline-H_5*); 7.91 (s, 1H, *imidazolate*); 7.72 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *quinoline-H_6*); 7.57 (dd, 1H, $^3J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 8.4 Hz, *quinoline-H_3*); 7.54 (s, 1H, *imidazolate*); 0.99 (s, 3H, $^2J_{PtH}$ = 78 Hz, *Pt-CH_3*).

2.11. Synthesis of [PtMe(CO)(NNTh)](SO_3CF_3) (8^{NNTh})

A solution of **1^{NNTh}** (0.148 g, 0.25 mmol) in 25 mL of nitromethane was kept under stirring at room temperature under CO atmosphere. The evolution of the reaction was followed by IR spectroscopy. The reaction ends after about 9 h. The product can be isolated by addition of diethylether to the reaction mixture, but the final complex slowly loses CO with the formation of **1^{NNTh}**. A solution of pure complex for NMR characterization was prepared by carrying out the same reaction in 1 mL of deuterated nitromethane, using 15 mg (0.025 mmol) of **1^{NNTh}** as reactant.

2.11.1. Characterization of 8^{NNTh}

Λ_M (nitromethane, 298 K) = 80 Ω^{-1} mol^{-1} cm^2. IR (KBr): ν = 2095 cm^{-1} [ν(CO)], IR (nitromethane): ν = 2106 cm^{-1} [ν(^{12}CO)], ν = 2060 cm^{-1} [ν(^{13}CO)]. ^{1}H NMR {CD_3NO_2, 298 K, ppm}: 9.79 (s, ^{1}H, $^3J_{PtH}$ = 43 Hz, *imine-CH*); 9.22 (d, 1H, $^3J_{HH}$ = 4.7 Hz, $^3J_{PtH}$ = 46 Hz, *quinoline-H_2*); 8.91 (d, 1H, $^3J_{HH}$ = 8.1 Hz, *quinoline-H_4*); 8.46 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H_7*); 8.35 (d, 1H, $^3J_{HH}$ = 3.1 Hz, *thiazole-$H_{5'}$*); 8.27 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *quinoline-H_5*); 8.15–7.92 (m, 2H, *quinoline-H_6 and thiazole-$H_{4'}$*); 7.84 (dd, 1H, $^3J_{HH}$ = 4.7 Hz, $^3J_{HH}$ = 8.1 Hz, *quinoline-H_3*); 1.42 (s, 3H, $^2J_{PtH}$ = 71 Hz, *Pt-CH_3*).

2.12. Synthesis of [Pd(COMe)(NNTh)](SO_3CF_3) (9^{NNTh}), [Pd(COMe)(NNPy)](SO_3CF_3) (9^{NNpy}) and [Pd(COMe)(NNImH)](ClO_4) (9^{NNImH})

A solution of **2^{NNTh}** (0.102 g, 0.20 mmol), **2^{NNPy}** (triflate salt, 0.101 g, 0.20 mmol) or **2^{NNImH}** (0.089 g, 0.20 mmol) in 20 mL of nitromethane was put under a CO atm and allowed to stir at room temperature. The evolution of the reaction was followed by IR spectroscopy. After a variable time (48 h using **2^{NNTh}**, 8 h using **2^{NNPy}**, 2.5 h using **2^{NNImH}**) the solution was concentrated at reduced pressure to about 5 mL. Slow addition of diethylether caused the separation of a dark yellow solid, which was filtered, washed with diethylether (20 mL) and dried under vacuum. Yields >95% in all the cases.

2.12.1. Characterization of 9^{NNTh}

Elemental analysis for $C_{16}H_{12}F_3N_3O_4PdS_2$: calcd. C 35.7, H 2.25, N 7.81; found C 35.6, H 2.24, N 7.78. Λ_M (nitromethane, 298 K) = 60 Ω^{-1} mol^{-1} cm^2. Decomposition at T > 210 °C. IR (nujol): ν = 1689 cm^{-1} [ν(CO)]. ^{1}H NMR {CD_3NO_2, 298 K, ppm}: 9.16 (s, 1H, *imine-CH*); 8.55 (d, 1H, $^3J_{HH}$ = 8.3 Hz, *quinoline-H_4*); 8.53 (d, 1H, $^3J_{HH}$ = 5.0 Hz, *quinoline-H_2*); 8.26 (d, 1H, $^3J_{HH}$ = 3.3 Hz, *thiazole-$H_{5'}$*); 8.19 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H_7*); 8.11 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H_5*); 7.99 (d, 1H, $^3J_{HH}$ = 3.3 Hz, *thiazole-$H_{4'}$*); 7.79 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H_6*); 7.67 (dd, 1H, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 8.3 Hz, *quinoline-H_3*); 2.67 (s, 3H, *Pd-$COCH_3$*). ^{13}C {^{1}H} NMR {CD_3NO_2, 298 K, ppm}: 229.9 *Pd-$COCH_3$*, 169.0, 153.0, 137.9, 132.4 *ancillary ligand not H-bonded carbons*, 154.16 *quinoline-C_2*, 149.2 *imine-C*, 146.2 *quinoline-C_4*, 141.6 *thiazole-$C_{4'}$*, 133.6 *quinoline-C_5*, 130.6 *thiazole-$C_{5'}$*, 129.9 *quinoline-C_6*, 125.0 *quinoline-C_3*, 121.6 *quinoline-C_7*, 32.9 *Pd-$COCH_3$*.

2.12.2. Characterization of 9^{NNPy}

Elemental analysis for $C_{18}H_{14}F_3N_3O_4PdS$: calcd. C 40.7, H 2.65, N 7.90; found C 40.5, H 2.64, N 7.88. Λ_M (nitromethane, 298 K) = 81 Ω^{-1} mol^{-1} cm^2. Decomposition at T > 220 °C. IR (KBr): ν = 1677 cm^{-1} [ν(CO)]. ^{1}H NMR {CD_3NO_2, 298 K, ppm}: 9.16 (s, 1H, *imine-CH*); 8.59 (dd, 1H, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.5 Hz, *quinoline-H_4*); 8.53 (dd, 1H, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.5 Hz, *quinoline-H_2*); 8.30–7.72 (m, 7H, *aromatic protons*); 7.70 (d, 1H, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 4.8 Hz, *quinoline-H_3*); 2.67 (s, 3H, *Pd-$COCH_3$*). ^{13}C {^{1}H} NMR {CD_3NO_2, 298 K, ppm}: 235.9 *Pd-$COCH_3$*, 157.0 *imine-C*, 155.2 *quinoline-C_2*, 141.7 *quinoline-C_4*, 125.1 *quinoline-C_3*, 154.1, 142.6, 133.4, 131.5, 131.3, 129.9, 121.6 *aromatic rings CH carbons*, 158.4, 148.9, 138.0, 122.1 *aromatic rings not H-bonded carbons*, 32.8 *Pd-$COCH_3$*.

2.12.3. Characterization of 9^{NNImH}

Elemental analysis for $C_{15}H_{13}ClN_4O_5Pd$: calcd. C 38.2, H 2.74, N 11.9, Cl 7.52; found C 38.1, H 2.73, N 11.9, Cl 7.50. Λ_M (dmf, 298 K) = 66 Ω^{-1} mol^{-1} cm^2. Decomposition at T > 210 °C. IR (nujol): ν = 1666 cm^{-1} [ν(CO)]. ^{1}H NMR {CD_3NO_2, 298 K, ppm}: 11.21 (s, very br, 1H, *imidazole-NH*); 8.85 (s, 1H, *imine-CH*); 8.65 (dd, 1H, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.5 Hz, *quinoline-H_2*); 8.52 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.5 Hz, *quinoline-H_4*); 8.08 (s, 1H, *imidazole-$H_{2'}$*); 8.04 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H_7*); 7.98 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H_5*); 7.96 (s, 1H, *imidazole-$H_{5'}$*); 7.73 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *quinoline-H_6*); 7.67 (dd, 1H, $^3J_{HH}$ = 5.1 Hz, $^3J_{HH}$ = 8.4 Hz, *quinoline-H_3*); 2.60 (s, 3H, *Pd-$COCH_3$*). ^{13}C {^{1}H} NMR {CD_3NO_2, 298 K, ppm}: 229.4 *Pd-$COCH_3$*, 153.5, 150.3, 142.3, 141.3, 131.3, 129.5, 126.5, 124.4, 119.3 *ancillary ligand CH carbons*, 148.4, 145.3, 138.7, 132.2 *ancillary ligand not H-bonded carbons*, 34.9 *Pd-$COCH_3$*.

2.13. Theoretical calculations

Restricted DFT calculations were applied for the geometry optimisation of the Pt(II) and Pd(II) methyl-complexes and their adducts with CO. The calculations were carried out using the EDF2 and M06 hybrid functionals [19] in combination with the LACVP** basis set [20]. The stationary points were characterized as true minima by IR simulation. The energy differences between reactants and products were corrected for the zero-point vibrational energy and the basis set superposition error. Charge distributions were derived from Mulliken population analysis [21]. All the calculations were performed with an Intel Core I7-based x86-64 workstation using the Spartan '08 software package [22].

3. Results and discussion

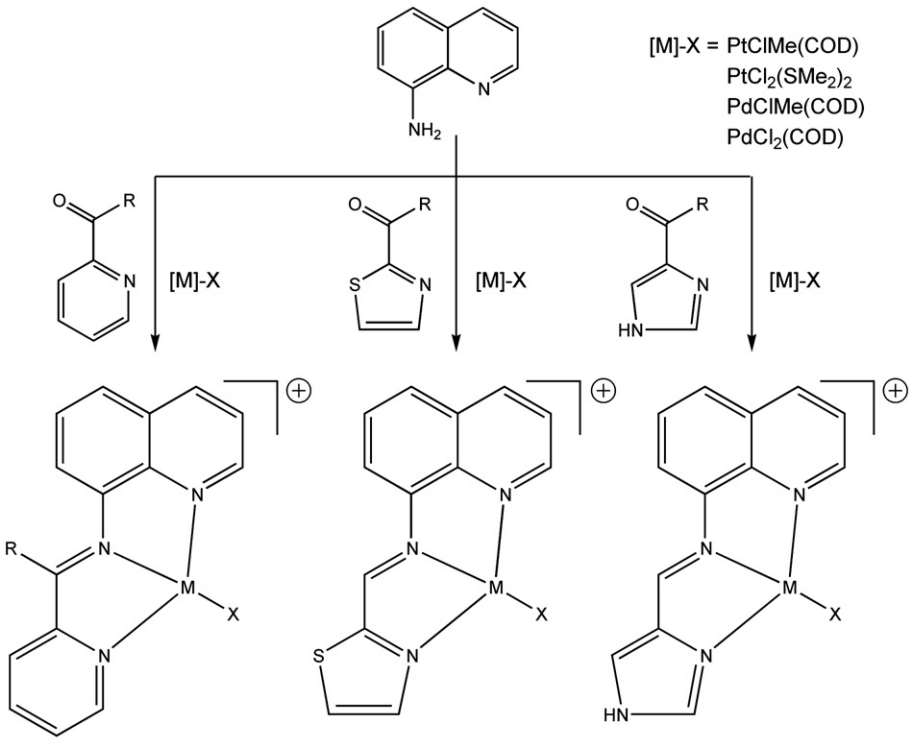
3.1. Metal-assisted synthesis of Pd(II) and Pt(II) complexes

The metal-assisted condensation between pyridine-2-carboxaldehyde or 2-keto-pyridines and 8-aminoquinoline, affording the formation of quinoline-imine-pyridine complexes

having d^8 metal centres, was already reported in the literature [9,10]. In particular, we published the synthesis and characterization of [PtCl(NNPy)](OTf), [PdCl(NNPy)](OTf), [PdMe(NNPy)](OTf) ($\mathbf{2}^{\mathbf{NNPy}}$), [PdMe(NNMePy)](OTf) and [PdMe(NNPhPy)](OTf).

The reaction of the starting precursor PtClMe(COD) with stoichiometic amounts of 8-aminoquinoline and aldehydes such as pyridine-2-carboxaldehyde, thiazole-2-carboxaldehyde and imidazole-4-carboxaldehyde leads to the formation of the new cationic Pt(II) methyl-complexes $[PtMe(NNPy)]^+$ ($\mathbf{1}^{\mathbf{NNPy}}$), $PtMe(NNTh)]^+$ ($\mathbf{1}^{\mathbf{NNTh}}$) and $[PtMe(NNImH)]^+$ ($\mathbf{1}^{\mathbf{NNImH}}$). The replacement of the aldehydes with ketones such as 2-acetyl-pyridine and 2-benzoyl-pyridine leads to the metal-assisted condensation products $[PtMe(NNMePy)]^+$ ($\mathbf{1}^{\mathbf{NNMepy}}$) and $[PtMe(NNPhPy)]^+$ ($\mathbf{1}^{\mathbf{NNPhPy}}$) (see Scheme 2). All these compounds have been isolated as triflate and/or perchlorate salts and characterized. Triflate salts are slightly more soluble in methanol than the corresponding perchlorates. The elemental analyses of the Pt(II) methyl-complexes are in agreement with the proposed formulations. Conductivity data show that these complexes behave as 1:1 electrolytes in nitromethane or dimethylformamide solutions. IR spectra do not show any signal attributable to the C=O stretching. In the ^{1}H NMR spectra of the aldehyde derivatives $\mathbf{1}^{\mathbf{NNPy}}$, $\mathbf{1}^{\mathbf{NNTh}}$ and $\mathbf{1}^{\mathbf{NNImH}}$ a sharp singlet is observable in the high-frequency region, attributable to the imine proton. Experiments at variable temperature (298–346 K) carried out on $\mathbf{1}^{\mathbf{NNPy}}$ have highlighted no meaningful influence of temperature on the ^{1}H NMR spectrum. The $^3J_{PtH}$ coupling constants are in the range 32–38 Hz. In the case of $\mathbf{1}^{\mathbf{NNMePy}}$ the methyl substituent on the imine group corresponds to a singlet at 2.50 ppm. The coordinated methyl ligand is observable in all the complexes as singlet in the low-frequency region with a $^2J_{PtH}$ coupling constant ranging from 73 to 77 Hz. The signals corresponding to the aromatic protons of the N-heterocycles have been assigned on the basis of COSY and NOESY spectra. In the case of complex $\mathbf{1}^{\mathbf{NNImH}}$ a broad signal at 13.81 ppm indicates the presence of the NH proton and the NOESY spectrum highlights its chemical exchange with water traces on the NMR timescale. ^{13}C {^{1}H} NMR spectra are in agreement with the proposed formulations and the carbon atoms have been correlated to their bonded hydrogen atoms on the basis of HSQC spectra. Imine carbon atoms give ^{13}C NMR signals in the range 167.2–148.6 ppm, while the coordinated methyl groups are observable between −16.7 and −6.2 ppm.

The methyl-complexes of palladium(II) $[PdMe(NNTh)]^+$ ($\mathbf{2}^{\mathbf{NNTh}}$) and $[PdMe(NNImH)]^+$ ($\mathbf{2}^{\mathbf{NNImH}}$) have been obtained on the basis of the same procedure described for $\mathbf{1}^{\mathbf{NNTh}}$ and $\mathbf{1}^{\mathbf{NNImH}}$, using PdClMe(COD) as precursor (see Scheme 2). The complex [PdMe(NNPy)](OTf) ($\mathbf{2}^{\mathbf{NNPy}}$), already described in a previous paper [10], has been synthesized again to compare its reactivity with that of $\mathbf{2}^{\mathbf{NNTh}}$ and $\mathbf{2}^{\mathbf{NNImH}}$. The formulations proposed for $\mathbf{2}^{\mathbf{NNTh}}$ and $\mathbf{2}^{\mathbf{NNImH}}$, isolated as perchlorate or triflate salts, are in agreement with the elemental analyses and the conductivity data. The solubility of $\mathbf{2}^{\mathbf{NNTh}}$ is lower using perchlorate as counter-anion. As for the Pt(II) complexes, the ^{1}H NMR spectra of $\mathbf{2}^{\mathbf{NNTh}}$ and $\mathbf{2}^{\mathbf{NNImH}}$ show singlets at 9.30 ppm ($\mathbf{2}^{\mathbf{NNTh}}$) and 9.12 ($\mathbf{2}^{\mathbf{NNImH}}$) attributable to the imine protons, while the coordinated CH_3 resonates at 1.08 ppm ($\mathbf{2}^{\mathbf{NNTh}}$) and 0.62 ppm ($\mathbf{2}^{\mathbf{NNImH}}$). Experiments at variable temperature (298–336 K) carried out on $\mathbf{2}^{\mathbf{NNTh}}$ have shown no meaningful change on the ^{1}H NMR spectrum. As for $\mathbf{1}^{\mathbf{NNImH}}$, also in the NOESY spectrum of $\mathbf{2}^{\mathbf{NNImH}}$ cross-peaks attributable to the chemical



Scheme 2. Synthesis of complexes **1**–**4**.

exchange between the NH (13.71 ppm) and water traces are observable. The aromatic regions of the ^{1}H NMR spectra are comparable with those of the corresponding Pt(II) derivatives, with the obvious absence of the ^{195}Pt satellites. Also the ^{13}C $\{^{1}H\}$ NMR spectra of $\mathbf{2}^{\mathbf{NNTh}}$ and $\mathbf{2}^{\mathbf{NNImH}}$ are strictly similar to those of the Pt(II) derivatives.

Chloro-complexes of Pt(II) and Pd(II), indicated as $[PtCl(NNTh)]^{+}$ ($\mathbf{3}^{\mathbf{NNTh}}$), $[PtCl(NNImH)]^{+}$ ($\mathbf{3}^{\mathbf{NNImH}}$), $[PdCl(NNTh)]^{+}$ ($\mathbf{4}^{\mathbf{NNTh}}$) and $[PdCl(NNImH)]^{+}$ ($\mathbf{4}^{\mathbf{NNImH}}$) have been obtained as perchlorate and/or triflate salts by metal-assisted condensation of thiazole-2-carboxaldehyde or imidazole-4-carboxaldehyde with 8-aminoquinoline, using as precursors *cis/trans*-$PtCl_2(SMe_2)_2$ and $PdCl_2(COD)$ (see Scheme 2). Chloro-complexes of Pt(II) and Pd(II) containing a pyridine ring in the tridentate ligand have been already prepared on the basis of the same synthetic approach [10]. Preliminary studies have shown that the complex $PtCl_2(COD)$ is not a suitable precursor for the metal-assisted condensations considered in this work, having a lower reactivity as compared to *cis/trans*-$PtCl_2(SMe_2)_2$ [23]. The formation of tridentate cationic complexes has been confirmed by their elemental analyses (C, H, N, Cl), the conductivity of their solutions in polar solvents and their NMR spectra. The high-frequency regions of the ^{1}H NMR and ^{13}C $\{^{1}H\}$ spectra are similar to those of the already described methyl-complexes. The $^{3}J_{PtH}$ coupling constant between the metal centre and the imine CH proton in $\mathbf{3}^{\mathbf{NNTh}}$ and $\mathbf{3}^{\mathbf{NNImH}}$ is around 96–98 Hz, meaningfully higher than those observed for the corresponding methyl-complexes, 32–37 Hz. This result highlights the greater *trans*-influence of the methyl ligand with respect to the chloro-ligand and the consequent elongation of the Pt-N(imine) bond [24].

The methyl- and chloro-complexes **1**–**4** have been obtained in very pure form by slow diffusion of diethylether in concentrated dimethylformamide or dimethylformamide/nitromethane solution of the complexes. Small crystals of these products have been also isolated by slowly cooling (from +30 °C to −25 °C during a week) clear solutions of these complexes in mixtures of dimethylformamide, nitromethane and diethylether. Other solvents, such as dimethylsulfoxide, dichloromethane, methanol and 2,2,2-trifluoroethanol have been used in various proportions, but we have never obtained crystals of the products using these last solvents. Even if several small crystals obtained were apparently suitable for X-Ray diffraction, all the measurements carried out using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation haven't led to any resolved structure, because all the crystals displayed high mosaicity and very poor diffraction figures.

3.2. Factors influencing the reaction mechanism

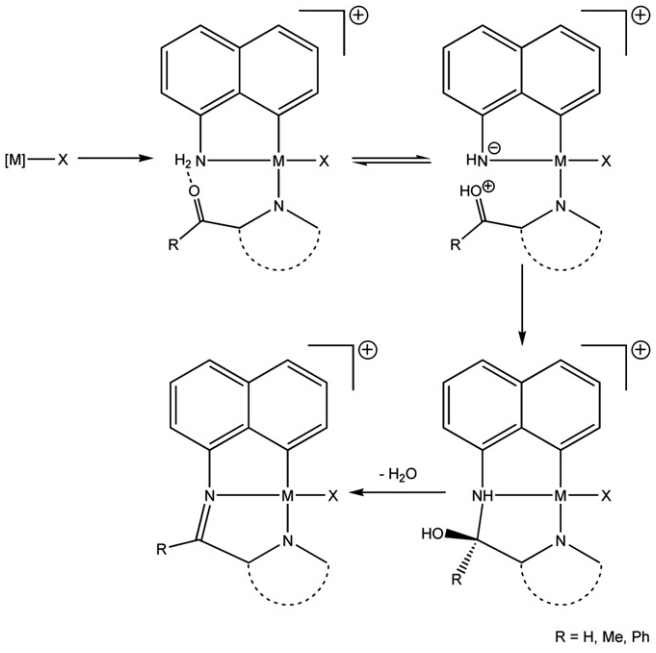
The reaction between 8-aminoquinoline and the various aldehydes and ketones considered in this paper has been studied by NMR spectroscopy in CD_3OD at room temperature. 8-aminoquinoline readily reacts with pyridine-2-carboxaldehyde with the formation of the corresponding emiaminal [10]. GS-MS measurements on a freshly prepared solution of 8-aminoquinoline and pyridine-2-carboxaldehyde in methanol showed a signal attributable to the imine-ligand NNPy ($m/z = 233$), but the elimination of a water molecule from the corresponding emiaminal is attributable to the temperature required for this experiment, above 100 °C. No reaction has been observed by NMR spectroscopy between 8-aminoquinoline and 2-acetyl-pyridine, 2-benzoyl-pyridine and imidazole-4-carboxaldehyde in the same experimental conditions used for the metal-assisted condensations, even if the formation of condensation products is possible in the presence of catalysts or using harsh conditions [9,25]. Finally, the reaction between 8-aminoquinoline and thiazole-2-carboxaldehyde leads to the presence in solution of a complex mixture of different species.

In the presence of an appropriate transition metal precursor we have observed in all the cases the formation of the condensation products coordinated to the metal centre. These results allow supposing that the reaction pathway leading to the final complexes is scarcely dependent upon possible equilibrium reactions between the organic ligands. The ability of the transition metal precursor to coordinate the 8-aminoquinoline and the other N-heterocycle is, instead, of primary importance. The metal-assisted condensation does not happen, for example, using $PtCl_2(COD)$, which is less reactive than *cis/trans*-$PtCl_2(SMe)_2$ [23]. Moreover, in our previous studies we have observed in some cases that the metal-assisted condensation happens only by removing a coordinated chloro-ligand from the transition metal precursor using a silver salt [10].

Probably, the key step of the metal-assisted condensation reactions is the formation of an intermediate species where both the 8-aminoquinolne and the other N-heterocycle are coordinated with a suitable geometry. This intermediate could be stabilized by an intramolecular hydrogen bond between the 8-aminoquinoline NH_2 group and the carbonyl oxygen atom. An increase of acidity of the NH protons caused by coordination is expectable, and a proton transfer from NH_2 to the carbonyl oxygen atom probably happens before the electrophilic attack of the carbonyl C atom on the coordinated sp^3 N atom of 8-aminoquinoline. After the formation of the hydroxy-amine species, the successive elimination of water should be favoured by the formation a π-extended system. The supposed reaction mechanism is depicted in Scheme 3.

3.3. Preliminary reactivity studies: reactions with silver salts and bases

The preliminary reactivity studies have been focused on the new imidazole-based complexes. The chloro-complexes $\mathbf{3}^{\mathbf{NNImH}}$ and $\mathbf{4}^{\mathbf{NNImH}}$ have been used as precursors for the preparation of Pt(II) and Pd(II) square-planar complexes having weak O-donor ligands in their coordination sphere [26]. In our previous work we obtained $[Pd(\eta^1\text{–}OSO_2CH_3)(NNMePy)](OTf)$ by reacting $[PdCl(NNMePy)](OTf)$ with a stoichiometric amount of $AgCH_3SO_3$ in



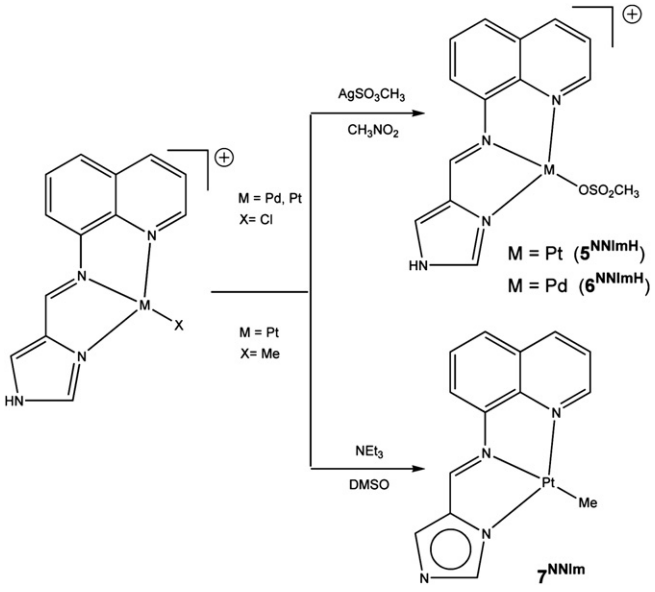
Scheme 3. Proposed reaction mechanism for the metal-assisted condensation.

nitromethane at room temperature [10]. The same reaction, carried out on the chloro-complexes $\mathbf{3}^{\mathbf{NNImH}}$ and $\mathbf{4}^{\mathbf{NNImH}}$, leads to the formation of the η^1-methanesulphonato-complexes [Pt(O-SO_2CH_3)(NNImH)](SO_3CF_3) ($\mathbf{5}^{\mathbf{NNImH}}$) and [Pt(O-$SO_2CH_3$)(NNImH)]($SO_3CF_3$) ($\mathbf{6}^{\mathbf{NNImH}}$), as depicted in Scheme 4.

The elemental analyses are in agreement with the proposed formulations. The complexes $\mathbf{5}^{\mathbf{NNImH}}$ and $\mathbf{6}^{\mathbf{NNImH}}$ behave as 1:1 electrolytes both in nitromethane solution and in dimethylsulfoxide solution. This last result allows concluding that the weak methanesulfonato ligand is not easily displaced by the soft ligand DMSO at room temperature either in the Pt(II) or in the Pd(II) complex. ^{1}H and ^{13}C {^{1}H} NMR spectra are comparable with those of the other imidazole-based complexes described in this work. The most important signals are the singlets corresponding to the methanesulfonato-ligand, which fall around 2.3–2.4 ppm in the ^{1}H NMR spectra and around 40–41 ppm in the ^{13}C{^{1}H} NMR spectra.

The presence of NH protons in the imidazole-based complexes, which resonate in the high-frequency region and give chemical exchange with water traces on the NMR timescale, has prompted us to study the deprotonation of the coordinated NNImH ligand. This reaction has been carried out in an NMR tube using DMSO-d_6 as solvent and triethylamine as base. The addition of a stoichiometric amount of NEt_3 to the methyl-complex $\mathbf{1}^{\mathbf{NNImH}}$ causes the immediate formation of the neutral complex PtMe(NNIm) ($\mathbf{7}^{\mathbf{NNIm}}$). The elemental analysis on the isolated product agrees with the formulation and solutions of compound $\mathbf{7}^{\mathbf{NNIm}}$ in DMSO are not conductive. The same reaction carried out on $\mathbf{2}^{\mathbf{NNImH}}$ or on the chloro-complexes $\mathbf{3}^{\mathbf{NNImH}}$ and $\mathbf{4}^{\mathbf{NNImH}}$ leads instead to the progressive formation of mixtures of products in solution, probably because of the higher reactivity of Pd(II) as compared to Pt(II) and the displacement of chloride by DMSO.

Complex $\mathbf{7}^{\mathbf{NNIm}}$ is scarcely soluble in most of the common organic solvents, with the exception of dimethylsulfoxide. The ^{1}H NMR spectrum shows a singlet for the coordinated methyl group at 0.99 ppm, with a $^2J_{PtH}$ coupling constant of 78 Hz. Besides the aromatic protons, in the high-frequency region a singlet for the imine CH at 9.38 ppm is observable, with a $^3J_{PtH}$ coupling constant of 36 Hz. The $^3J_{PtH}$ coupling constant between Pt(II) and the quinoline-H_2 is 52 Hz. In the charged precursor $\mathbf{1}^{\mathbf{NNImH}}$ the $^2J_{PtH}$ coupling constant corresponding to the Pt-CH_3 bond is 75 Hz, while the $^3J_{PtH}$ coupling constants between Pt(II) and the imine proton and the quinoline-H_2 are 32 Hz and 57 Hz, respectively. These values are compared in Table 1 for clarity.



Scheme 4. Synthesis of $\mathbf{5}^{\mathbf{NNImH}}$, $\mathbf{6}^{\mathbf{NNImH}}$ and $\mathbf{7}^{\mathbf{NNIm}}$.

Table 1
Selected coupling constants in $\mathbf{1}^{\mathbf{NNImH}}$ and $\mathbf{7}^{\mathbf{NNIm}}$.

Coupling constant	Fragment	$\mathbf{1}^{\mathbf{NNImH}}$ (Hz)	$\mathbf{7}^{\mathbf{NNIm}}$ (Hz)
$^2J_{PtH}$	Pt-CH_3	75	78
$^3J_{PtH}$	Pt-imine	36	32
$^3J_{PtH}$	Pt-quinoline	52	57

The comparison of the coupling constants between $\mathbf{7}^{\mathbf{NNIm}}$ and $\mathbf{1}^{\mathbf{NNImH}}$ shows that the removal of the positive charge from complex $\mathbf{1}^{\mathbf{NNImH}}$ causes a very limited variation of the bonds between the metal centre and the ligands, a result in agreement with the expected capability of charge delocalising of the polydentate ligands considered in this work. The reaction leading to the formation of $\mathbf{7}^{\mathbf{NNIm}}$ is sketched in Scheme 4.

3.4. Reactivity with CO

The preliminary reactivity studies have been prosecuted on the Pt(II) and Pd(II) methyl-complexes, using carbon monoxide as reactant. The reaction with CO at 1 atm in nitromethane at room temperature with the platinum derivatives $\mathbf{1}^{\mathbf{NNTh}}$, $\mathbf{1}^{\mathbf{NNPy}}$ and $\mathbf{1}^{\mathbf{NNImH}}$ has been followed by IR spectroscopy. In these experimental conditions the only complex that reacts with CO is the thiazole-derivative [PtMe(NNTh)]$^+$ ($\mathbf{1}^{\mathbf{NNTh}}$), leading to the carbonyl-complex $\mathbf{8}^{\mathbf{NNTh}}$. During about 9 h the progressive appearing of an IR signal at 2106 cm^{-1} has been observed, which has been attributed to the ^{12}CO carbonyl stretching. A weak signal at 2060 cm^{-1} corresponds to the isotopic band $\nu(^{13}CO)$, as observable in Fig. 1. The experimental $\nu(^{12}CO)/\nu(^{13}CO)$ ratio is 1.022, which agrees with the theoretical value for a single carbonyl-complex using the harmonic approximation.

In nitromethane solution complex $\mathbf{8}^{\mathbf{NNTh}}$ behaves as 1:1 electrolyte. This species can be isolated as solid, but a partial lose of CO during the work-up has been always observed, leading to the formation of the reactant $\mathbf{1}^{\mathbf{NNTh}}$. The ^{1}H NMR spectrum of a pure sample of $\mathbf{8}^{\mathbf{NNTh}}$ has been obtained by carrying out the reaction between $\mathbf{1}^{\mathbf{NNTh}}$ and CO in deuterated nitromethane. The ^{1}H NMR spectrum shows in the high-frequency region the signals of the NNTh ligand, whose pattern is similar to that observed in the ^{1}H NMR spectrum of $\mathbf{1}^{\mathbf{NNTh}}$. The coupling of the quinoline-H_2 and imine-CH protons with ^{195}Pt are clearly observable. In the low-frequency region a singlet at 1.42 ppm attributable to the

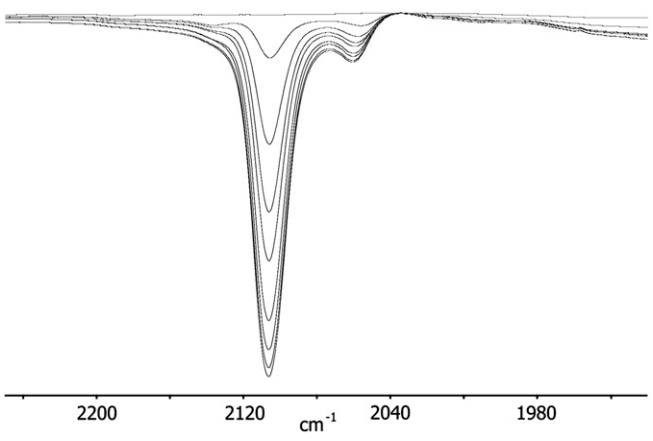


Fig. 1. IR spectra (nitromethane solution) of the reaction between 1^{NNTh} and CO taken at different times.

Table 2
Selected coupling constants in $\mathbf{1}^{\mathbf{NNTh}}$ and $\mathbf{8}^{\mathbf{NNTh}}$.

Coupling constant	Fragment	$\mathbf{1}^{\mathbf{NNTh}}$ (Hz)	$\mathbf{8}^{\mathbf{NNTh}}$ (Hz)
$^{2}J_{PtH}$	Pt-CH_3	77	71
$^{3}J_{PtH}$	Pt-imine	37	43
$^{3}J_{PtH}$	Pt-quinoline	59	46

coordinated methyl ligand is detectable, which couples with the Pt(II) centre with a $^{2}J_{PtH}$ coupling constant of 71 Hz. This coupling constant strongly supports the presence of a CH_3 ligand coordinated to the platinum centre. Selected coupling constants of $\mathbf{8}^{\mathbf{NNTh}}$ are compared with those of the precursor $\mathbf{1}^{\mathbf{NNTh}}$ in Table 2.

All the spectroscopic data for $\mathbf{8}^{\mathbf{NNTh}}$ are in agreement with the simple coordination of CO to $\mathbf{1}^{\mathbf{NNTh}}$ and the formation of a five-coordinate Pt(II) complex having formula [PtMe(CO)(NNTh)](OTf). Complexes of platinum(II) with a CO, an alkyl (or aryl) ligand and a tridentate N-donor ligand in the coordination sphere are not common and the most studied species are probably neutral scorpionate-based complexes having general formula Pt(R)(Tp)(CO) [27].

The formation of a five-coordinate species only in the presence of the thiazole-based ligand NNTh is quite interesting. The geometry of $\mathbf{8}^{\mathbf{NNTh}}$ has been elucidated using DFT methods and is reported in Fig. 2. Compound $\mathbf{8}^{\mathbf{NNTh}}$ is referable neither to a square pyramid nor to a trigonal bipyramid. The three coordinating N atoms and the Pt atom lie on the same plane and the N(thiazole)-Pt-N(imine) and N(imine)-Pt-N(quinoline) angles are around 76–77°. The CH_3 ligand is almost perpendicular to this plane and the C(methyl)-Pt-N(angle) angle is around 84–85°. The C atom of the methyl ligand is instead on the same plane of the Pt and N atoms in $\mathbf{1}^{\mathbf{NNTh}}$, giving a classical square-planar geometry distorted by the coordination of tridentate ligand, which imposes the N(thiazole)-Pt-N(imine) and N(imine)-Pt-N(quinoline) angles lower than 90°. The coordinated CO in $\mathbf{8}^{\mathbf{NNTh}}$ lies on the other side of the plane defined by the tridentate ligand, respect to CH_3. The C(methyl)-Pt-C(CO) angle is 158°. This coordination mode can be explained of considering that the π-acceptor CO probably tends to be in *trans* position to the methyl ligand, which is a strong σ-donor group. A selection of computed bond lengths and angles is reported in Table 3.

The coordination of CO in the Pt(II) methyl-complexes happens only using NNTh as ancillary ligand, *i.e.* that having the lower basicity. DFT calculations on all the Pt(II) methyl-complexes predict the formation of a weak Pt-CO bond only in the case of the NNTh ligand, in agreement with the experimental results. In the case of NNPy or NNImH the Pt(II) complexes keep their square-planar geometry by addition of CO, and the calculated Pt-CO distances are higher than 3.3 Å. The calculated energy for the reaction between the square-planar Pt(II) methyl complex and CO is 13 kcal/mol in the case of NNTh, while is around 2 kcal/mol for the NNPy and NNTh ligands.

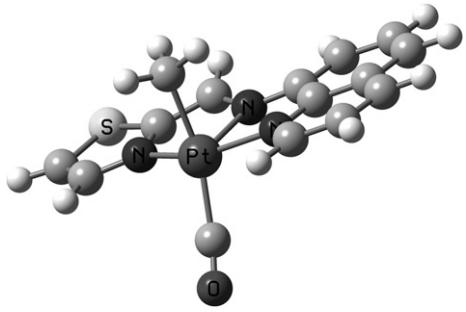


Fig. 2. DFT-optimised geometry (M06 functional) of complex 8^{NNTh}.

Table 3
Selected bond lengths (Å) and angles (°) calculated for complex $\mathbf{8}^{\mathbf{NNTh}}$ with the M06 and EDF2 DFT functionals.

	M06	EDF2		M06	EDF2
Pt-C(methyl)	2.098	2.102	C(CO)-Pt-C(methyl)	158.5	158.3
Pt-C(CO)	1.965	1.962	N(thiazole)-Pt-N(imine)	76.0	76.1
Pt-N(thiazole)	2.092	2.090	N(imine)-Pt-N(quinoline)	77.0	77.2
Pt-N(imine)	2.374	2.364	C(methyl)-Pt-N(imine)	84.9	83.8
Pt-N(quinoline)	2.084	2.084	C(CO)-Pt-N(imine)	116.5	117.9

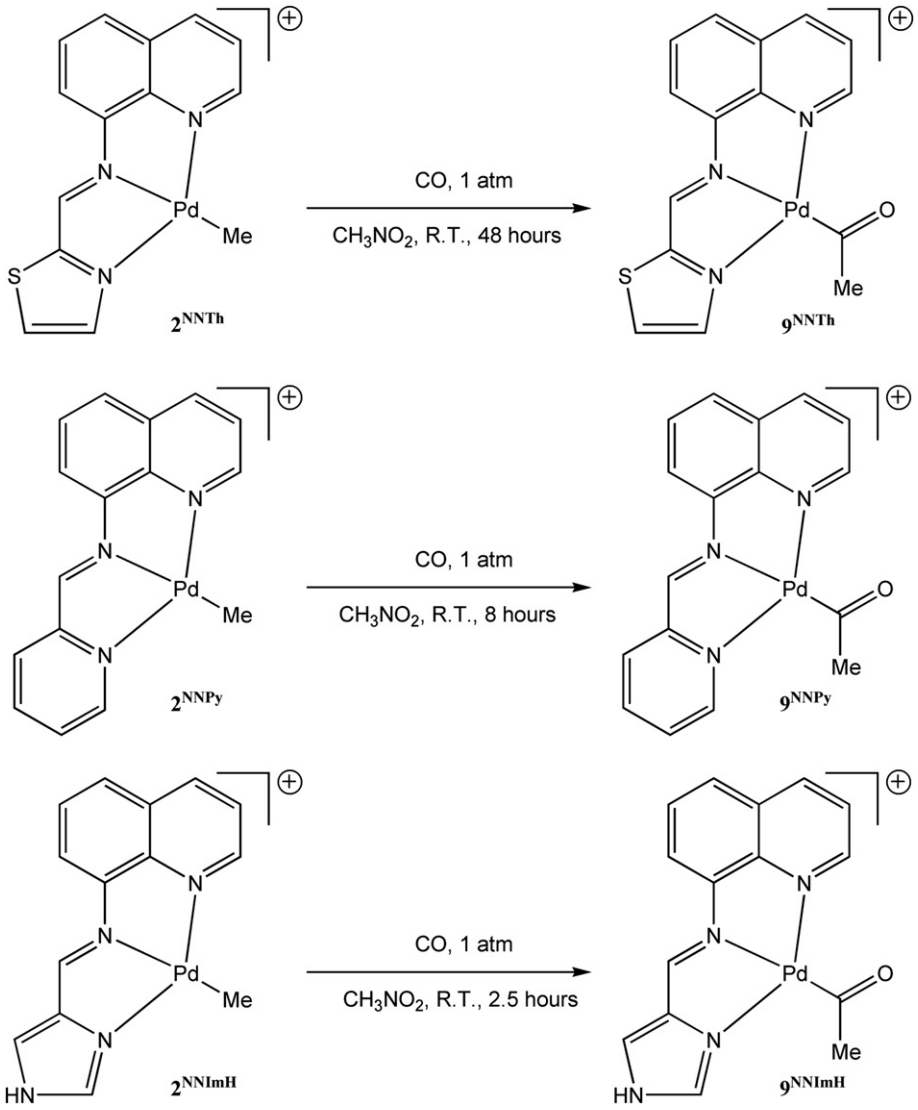
The CO frequency of $\mathbf{8}^{\mathbf{NNTh}}$, 2106 cm^{-1}, indicates that carbon monoxide coordinates Pt(II) mainly through σ-interaction. The lowest-energy unoccupied molecular orbital in the Pt(II) methyl-complexes able to interact with an additional ligand is that having Pt-6 p_z character and its relative energy grows on replacing the thiazole ring with pyridine or imidazole, as observable in Table 4. The influence of the N-ligands on the energy of this metal-centred unoccupied orbital is probably the reason of the coordination of CO only in the case of the thiazole derivative.

The reactivity studies on the new complexes have been prosecuted by reacting the Pd(II) methyl-complexes with CO. The palladium derivatives $\mathbf{2}^{\mathbf{NNTh}}$, $\mathbf{2}^{\mathbf{NNPy}}$ and $\mathbf{2}^{\mathbf{NNImH}}$ react with CO at 1 atm in nitromethane with the formation of the corresponding acyl-complexes $[Pd(COMe)(NNTh)]^+$ ($\mathbf{9}^{\mathbf{NNTh}}$), $[Pd(COMe)(NNPy)]^+$ ($\mathbf{9}^{\mathbf{NNPy}}$) and $[Pd(COMe)(NNImH)]^+$ ($\mathbf{9}^{\mathbf{NNImH}}$) (see Scheme 5). The C═O stretching, falling in the range 1689–1666 cm^{-1}, has been used to follow the reactions by IR spectroscopy. During our experiments we have never observed signals attributable to intermediate carbonyl-complexes. Besides the IR spectra, the formation of these acyl-complexes, isolated as triflate or perchlorate salts, has been confirmed by their elemental analyses, conductivity measurements and NMR spectroscopy. Unfortunately, we did not obtain crystals suitable for X-Ray diffraction because of the lack of stability of these complexes in solution for long time. Besides the characteristic signals of the tridentate N-donor ligands, in the ^{1}H NMR spectra the singlets attributable to the acyl ligands around 2.6–2.7 ppm are observable. Their ^{13}C NMR signals have been assigned on the basis of HSQC and HMBC experiments. The methyl carbon of C(═O)CH_3 resonates between 34.9 and 32.8, while the carbonyl carbon is observable in the range 235.9–229.4 ppm. This carbon atom gives a strong HMBC cross-peak not only with the protons of the acyl ligand but, interestingly, also with the hydrogen atom of the imine group, this confirming the presence of the C(═O)CH_3 ligand coordinated to the Pd(NNPy), Pd(NNTh) and Pd(NNImH) fragments.

The rate of formation of the acyl-complex depends upon the basicity of the N-donor ligand. The formation of the acyl complex is in fact faster using $[PdMe(NNImH)]^+$ ($\mathbf{2}^{\mathbf{NNImH}}$) as reactant, while the reaction is slower for $[PdMe(NNPy)]^+$ ($\mathbf{2}^{\mathbf{NNPy}}$) and it is still slower for $[PdMe(NNTh)]^+$ ($\mathbf{2}^{\mathbf{NNTh}}$). It is to be remembered that the basicity of the heterocycles follows the order imidazole ($pK_a = 6.95$) > pyridine ($pK_a = 5.25$) > thiazole ($pK_a = 2.44$) [28] and that the basicity of these N-donor heterocycles is usually a quite good parameter to estimate their relative σ-donor behaviour towards d^8 metal centres [29]. Interestingly, ground-state DFT calculations carried out on the

Table 4
Energy of the lowest-energy unoccupied molecular orbital having Pt-6 p_z character in $\mathbf{1}^{\mathbf{NNTh}}$, $\mathbf{1}^{\mathbf{NNPy}}$ and $\mathbf{1}^{\mathbf{NNImH}}$ (EDF2 functional).

Complex	Orbital	Energy (eV)
$\mathbf{1}^{\mathbf{NNTh}}$	LUMO+8	−2.099
$\mathbf{1}^{\mathbf{NNPy}}$	LUMO+7	−2.062
$\mathbf{1}^{\mathbf{NNImH}}$	LUMO+7	−1.951



Scheme 5. Synthesis of the complexes $\mathbf{9}^{\mathbf{NNTh}}$, $\mathbf{9}^{\mathbf{NNPy}}$ and $\mathbf{9}^{\mathbf{NNImH}}$.

Pd(II) methyl-complexes show a very poor influence of the N-ligands on the Pd-CH_3 bond. Moreover, these calculations predict a behaviour of the Pd(II) methyl-complexes towards CO coordination which is about the same previously described for the analogous Pt(II) complexes (see data reported in Table 5). This allows concluding that the influence of the N-donor ligands on the rate of CO insertion can not be explained on the basis of the ground-state electronic properties of these complexes. The N-ligands probably influence the transition state of the insertion reaction, which is positively charged and contains a strong π-acceptor ligand, CO. A more σ-donor N-ligand can lead to the relative stabilization of the five-coordinate transition state, making the insertion reaction faster. These considerations can explain the reactivity order NNTh < NNPy < NNImH experimentally observed for the CO insertion in the Pd-CH_3 bond.

Table 5
Selected ground-state properties of the Pd(II) methyl-complexes $\mathbf{2}^{\mathbf{NNTh}}$, $\mathbf{2}^{\mathbf{NNPy}}$, $\mathbf{2}^{\mathbf{NNImH}}$ and their adducts with CO (EDF2 functional).

Complex	Pd-CH_3 (Å)	CH_3 Mulliken Charge (a.u.)	Pd Mulliken Charge (a.u.)	E Pd-5 p_z MO (eV)	Pd-CO (Å)
$\mathbf{2}^{\mathbf{NNTh}}$	2.026	−0.059	0.481	−2.049	2.040
$\mathbf{2}^{\mathbf{NNPy}}$	2.029	−0.073	0.485	−2.021	> 3.1
$\mathbf{2}^{\mathbf{NNImH}}$	2.029	−0.072	0.475	−1.928	> 3.1

4. Conclusions

In this paper we have highlighted how the metal-assisted approach could be applied for the synthesis of new Pd(II) and Pt(II) complexes with several tridentate N-donor ligands containing different heterocycles. We have observed that the reactivity of both the palladium(II) and the platinum(II) methyl-complexes with CO is strongly dependent upon the electronic features of the heterocycles and this allows a fine-tune of the reactivity that could be of interest in different application fields.

Acknowledgements

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