Polyhedron 37 (2012) 66–76

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterization of novel pyridine–isourea complexes of Pd(II)

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ARTICLE INFO

Article history:
Received 25 January 2012
Accepted 13 February 2012
Available online 21 February 2012

Keywords:
Palladium
Isourea
Pyridine
N-donor ligands
Seven-membered rings

ABSTRACT

New neutral palladium(II) complexes having formula $PdCl_2(pyiu^{Pr})$, $PdCl_2(pyiu^{Cy})$, $Pd(OCOCH_3)_2(pyiu^{Pr})$, $Pd(OCOCH_3)_2(pyiu^{Cy})$, $Pd(CH_3)Cl(pyiu^{Pr})$ and $Pd(CH_3)_2(pyiu^{Pr})$, where $pyiu^{Pr}$ and $pyiu^{Cy}$ are the novel ligands 1,3-diisopropyl-2-((pyridin-2-yl)methyl)isourea and 1,3-dicyclohexyl-2-((pyridin-2-yl)methyl) isourea, were synthesized and characterized. These neutral ligands act as bidentate and coordinate the palladium center through the pyridine N-atom and one of the nitrogen atoms of the isourea dent, as deducted by variable-temperature NMR experiments and DFT calculations and observed by X-ray diffraction experiments on the complex $PdCl_2(pyiu^{Cy})$.

1. Introduction

Amidines and amidinate ions are well-known ligands in coordination and organometallic chemistry. These N-ligands are characterized by several different possible coordination modes and usually bind one or two metal centers. Their electronic and steric features can be tuned on changing the groups bonded to the nitrogen atoms and to the carbon atom between the two nitrogen atoms [1]. Moreover, ligands containing more than one amidinate group have been synthesized [2] and polydentate ligands have been obtained also through the introduction of suitable substituents on the amidine C or N atoms [3].

Isoureas can be considered species analogous to amidines, where an alkoxy group formally replaces the alkyl group or the hydrogen atom bonded to the amidine carbon. Despite of this similarity, the coordination chemistry of isoureas has been scarcely investigated. Palladium(II) complexes with two coordinated alkyl-substituted isourea molecules have been obtained from the reaction of methanol with Pd-coordinated carbodiimides or by reacting Na_2PdCl_4 with two isourea equivalents. X-ray diffraction studies have shown that the coordination of the N-donor ligands in these complexes occurs through the imine nitrogen atom [4]. A Pd(II) isourea complex bonded through the imine N-atom and a C-atom of a phenyl ring has been reported by Vicente et al. This species has been obtained by reacting dicyclohexylcarbodiimide with a palladium precursor containing a C-bonded phenol in the coordination sphere [5]. Finally, several complexes of late transition metals with isourea ligands having coordinating groups bonded to one of the nitrogen atoms have been published. Examples of these additional coordinating fragments are the benzoyl, the ethoxycarbonyl and the carbamimidoyl groups [6].

The few data actually reported in the literature do not allow a comparison of the electronic and steric features of alkyl-substituted isourea ligands with respect to other, more common N-donor ligands. Our research group is currently interested in the synthesis, characterization and reactivity of palladium(II) complexes with polydentate nitrogen-donor ligands [7]. To the best of our knowledge, isourea groups with alkyl substituents on the nitrogen atoms have not yet considered as potential dents for the preparation of new chelating ancillary ligands. Square-planar palladium(II) complexes containing novel bidentate N-donor ligands are of paramount interest in several fields of applied coordination chemistry, as an example as catalytic precursors for olefin polymerization and co-polymerization [8]. In this paper we report the synthesis of the pyridine–isourea ligands 1,3-dicyclohexyl-2-((pyridin-2-yl)methyl)isourea (**$pyiu^{Cy}$**) and 1,3-diisopropyl-2-((pyridin-2-yl) methyl)isourea (**$pyiu^{Pr}$**). The coordination chemistry of these N-donor ligands towards the Pd(II) metal center has been investigated by NMR and X-ray diffraction techniques.

2. Experimental

2.1. Materials and methods

All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques. The reagents 2-pyridinemethanol, *N,N′*-dicyclohexylcarbodiimide, *N,N′*-diisopropylcarbodiimide,

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doi:10.1016/j.poly.2012.02.014

1,5-cyclooctadiene (COD), tetramethyltin, potassium *tert*-butoxide, methanesulfonic acid, palladium(II) chloride and palladium(II) acetate were purchased from Aldrich and used without further purifications. Copper(I) iodide was an Acros product. Solvents were purified following common procedures [9]. The NMR solvents were purchased from Euriso-Top, with the exception of deuterated nitromethane (Aldrich). The complexes *cis*-$PdCl_2(NCCH_3)_2$, $PdCl_2$(COD) and $Pd(CH_3)Cl$(COD) were synthesized following reported procedures [10].

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 to −25 °C during a week) clear solutions of the ligands and the complexes dissolved in mixtures of solvents such as dimethylformamide, nitromethane, acetone, dichloromethane 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 of solid samples dispersed in KBr were recorded from 4000 to 450 cm^{-1} on a Perkin-Elmer Spectrum One spectrophotometer. IR spectra in solution were recorded in the range 2200–1500 cm^{-1} on 10^{-2} M solutions of the complexes in dichloromethane, using cells with KBr windows. ^1H NMR, homodecoupled ^1H NMR, ^{13}C {^1H} NMR, COSY, NOESY, HSQC and HMBC spectra were recorded on a Bruker AC 200 and Bruker Avance 300 spectrometers. The NMR spectra of the complexes were collected at variable temperature using $CDCl_3$, CD_2Cl_2, CD_3NO_2 and $(CD_3)_2CO$ as solvents. ^1H and ^{13}C chemical shifts (ppm) were referenced internally to undeuterated solvent resonances and are quoted relative to tetramethylsilane (δ = 0 ppm). The numbering of pyridine hydrogen and carbon atoms used for NMR assignments is reported in Schemes 1 and 2 for clarity. Conductivity measurements were carried out at 298 K on 10^{-3} M dimethylformamide solutions using a Radiometer Copenhagen CDM 83 instrument and the molar conductivity values were compared with literature data [11].

2.2. Synthesis of 1,3-dicyclohexyl-2-((pyridin-2-yl)methyl)isourea (**pyiu^{Cy}**) ($C_{19}H_{29}N_3O$, MW = 315.45 g mol^{-1}) and 1,3-diisopropyl-2-((pyridin-2-yl)methyl)isourea (**pyiu^{Pr}**) ($C_{13}H_{21}N_3O$, MW = 235.33 g mol^{-1})

To a solution containing 2-pyridinemethanol (1.131 g, 10.36 mmol) and an equimolar amount of the proper carbodiimide (2.138 g of dicyclohexylcarbodiimide for **pyiu^{Cy}**; 1.6 mL of diisopropylcarbodiimide for **pyiu^{Pr}**) in 100 mL of dichloromethane a catalytic amount of copper(I) iodide (0.141 g, 0.74 mmol) was added and the resulting reaction mixture was kept under vigorous stirring at room temperature for 24 h. The solvent was then removed by evaporation under reduced pressure, obtaining a dark brown oil which was purified by chromatography on silica gel, using ethyl acetate as eluent. After elimination of the solvent by evaporation under reduced pressure, pentane (20 mL) was added and the resulting solution was filtered. Removing the solvent under vacuum isolated the final product. These purification operations must be carried out quickly to avoid the formation of decomposition products and the products must be stored at low temperature. The products start decomposing after few days also if stored at −20 °C under inert atmosphere. Yield (**pyiu^{Cy}**) = 59% (1.928 g). Yield (**pyiu^{Pr}**) = 51% (1.243 g).

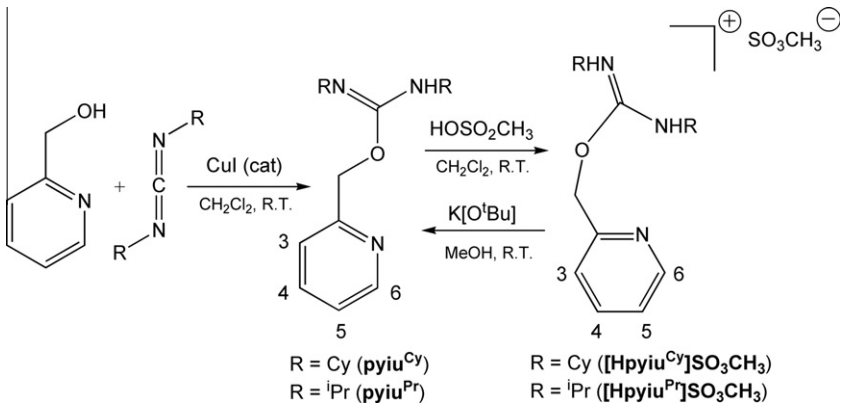
The same products can be obtained in nearby quantitative yield by reacting their conjugated acids **[Hpyiu^{Cy}]SO_3CH_3** and **[Hpyiu^{Pr}]SO_3CH_3** (see below) with a stoichiometric amount of potassium *tert*-butoxide in methanol at room temperature. In a typical preparation, to a solution containing 1.00 mmol of **[Hpyiu^{Cy}]SO_3CH_3** (0.412 g) or **[Hpyiu^{Pr}]SO_3CH_3** (0.331 g) in 30 mL of methanol 1.00 mmol (0.112 g) of solid K[O^{t}Bu] were added. The solvent was then removed by evaporation at reduced pressure and diethylether (30 mL) was then added. The desired product was finally obtained after filtration of the resulting solution and evaporation of the solvent.

2.3. Characterization of **pyiu^{Cy}**

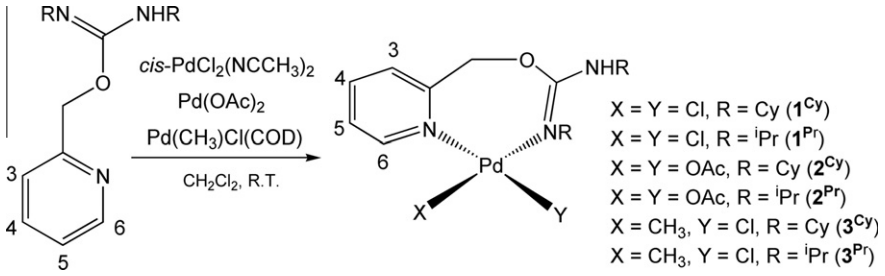
Elemental *Anal.* Calc. for $C_{19}H_{29}N_3O$: C, 72.3; H, 9.27; N, 13.3. Found: C, 72.2; H, 9.25; N, 13.2%. IR (KBr): 1669 cm^{-1} $\nu_{C=N}$. ^1H NMR ($CDCl_3$, 240 K): 8.52 (d, 1H, $^3J_{HH}$ = 4.9 Hz, *pyridine-H*$_6$); 7.68 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_4$); 7.36 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_3$); 7.18 (dd, 1H, $^3J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_5$); 5.19 (s, 2H, *CH*$_2$*-O*); 3.60 (d, 1H, $^3J_{HH}$ = 7.0 Hz, *NH*); 3.44 (s, br, *CH-N*$_{amine}$); 2.74 (s, br, *CH-N*$_{imine}$); 2.20–0.90 (m, 20H, *cyclohexyl groups*). ^{13}C {^1H} NMR ($CDCl_3$, 298 K): 158.4 *pyridine-C*$_2$; 150.4 *isourea-C*; 148.9 *pyridine-C*$_6$; 136.2 *pyridine-C*$_4$; 122.0 *pyridine-C*$_5$; 121.4 *pyridine-C*$_3$; 67.2 *CH*$_2$*-O*; 54.5 *CH-N*$_{imine}$; 48.9 *CH-N*$_{amine}$; 35.0–24.0 *cyclohexyl groups*.

2.4. Characterization of **pyiu^{Pr}**

Elemental *Anal.* Calc. for $C_{13}H_{21}N_3O$: C, 66.4; H, 8.99; N, 17.9. Found: C, 66.2; H, 8.97; N, 17.8%. IR (KBr): 1658 cm^{-1} $\nu_{C=N}$. ^1H NMR ($CDCl_3$, 240 K): 8.54 (d, 1H, $^3J_{HH}$ = 5.1 Hz, *pyridine-H*$_6$); 7.67 (t, 1H, $^3J_{HH}$ = 7.9 Hz, *pyridine-H*$_4$); 7.40 (d, 1H, $^3J_{HH}$ = 7.9 Hz, *pyridine-H*$_3$); 7.19 (dd, 1H, $^3J_{HH}$ = 5.1 Hz, $^3J_{HH}$ = 7.9 Hz, *pyridine-H*$_5$); 5.19 (s, 2H, *CH*$_2$*-O*); 3.83 (m, slightly br, 1H, $(CH_3)_2\underline{CH}$-*N*$_{amine}$); 3.56 (s, br, 1H, *NH*); 3.18 (sept, slightly br, $^3J_{HH}$ = 6.5 Hz, $(CH_3)_2$*CH-N*$_{imine}$); 1.12 (d, 6H, $^3J_{HH}$ = 6.0 Hz, $(\underline{CH_3})_2$*CH-N*$_{amine}$); 1.07



Scheme 1. Synthesis of **pyiu^{Cy}** and **pyiu^{Pr}** and of their conjugated acids **[Hpyiu^{Cy}]SO_3CH_3** and **[Hpyiu^{Pr}]SO_3CH_3**.



Scheme 2. Synthesis of the palladium(II) complexes $\mathbf{1^{Cy}}$, $\mathbf{1^{Pr}}$, $\mathbf{2^{Cy}}$, $\mathbf{2^{Pr}}$, $\mathbf{3^{Cy}}$ and $\mathbf{3^{Pr}}$.

(d, 6H, $^3J_{HH}$ = 6.5 Hz, ($C\underline{H}_3$)$_2$*CH-N*$_{imine}$). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K): 158.0 *pyridine-C*$_2$; 150.9 *isourea-C*; 148.9 *pyridine-C*$_6$; 136.3 *pyridine-C*$_4$; 122.1 *pyridine-C*$_5$; 121.6 *pyridine-C*$_3$; 67.5 *CH*$_2$*-O*; 46.1 *CH-N*$_{imine}$; 43.5 *CH-N*$_{amine}$; 24.0, 23.4 ($\underline{C}H_3$)$_2$*CH*.

2.5. Synthesis of $\mathbf{[Hpyiu^{Cy}]SO_3CH_3}$ ($C_{20}H_{33}N_3O_4S$, MW = 411.56 g mol^{-1}) and $\mathbf{[Hpyiu^{Pr}]SO_3CH_3}$ ($C_{14}H_{25}N_3O_4S$, MW = 331.43 g mol^{-1})

To a solution containing 4.75 mmol of $\mathbf{pyiu^{Cy}}$ (1.498 g) or $\mathbf{pyiu^{Pr}}$ (1.118 g) in dichloromethane (30 mL) methanesulfonic acid (290 μL, 4.50 mmol) was added with a microsyringe at room temperature. The solution was stirred at room temperature for 30 min and subsequently the solvent was removed by evaporation under reduced pressure. Diethylether (30 mL) was then added and the resulting mixture was left under vigorous stirring overnight. In the case of the cyclohexyl-substituted product a white solid separated out, which was filtered, washed with about 10 mL of diethylether and dried under vacuum. Yield = 1.779 g, 91%. The isopropyl-derivative was instead a yellowish oil, which was washed three times with about 20 mL of diethylether and dried under vacuum. Yield = 1.401 g, 89%. Both the products resulted stable for many months if stored at −20 °C. The slow cooling of dichloromethane/diethyl ether solutions of $\mathbf{[Hpyiu^{Cy}]SO_3CH_3}$ afforded crystals suitable for X-ray analysis.

2.6. Characterization of $\mathbf{[Hpyiu^{Cy}]SO_3CH_3}$

Elemental *Anal.* Calc. for $C_{20}H_{33}N_3O_4S$: C, 58.4; H, 8.08; N, 10.2. Found: C, 58.2; H, 8.05; N, 10.2%. IR (KBr): 3422 cm^{-1}, 3327 cm^{-1} ν_{N-H}; 1644 cm^{-1} $\nu_{C=N}$. Λ_M (dimethylformamide, 298 K) = 51 ohm^{-1} mol^{-1} cm^2. ^{1}H NMR ($CDCl_3$, 298 K): 9.24 (s, br, 2H, *NH*); 8.57 (d, 1H, $^3J_{HH}$ = 5.1 Hz, *pyridine-H*$_6$); 7.82 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_4$); 7.54 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_3$); 7.38 (dd, 1H, $^3J_{HH}$ = 5.1 Hz, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_5$); 5.44 (s, 2H, *CH*$_2$*-O*); 3.72 (s, br, 2H, *CH-N*); 2.72 (s, 3H, *CH*$_3$*SO*$_3$); 1.95–1.00 (m, 20H, *cyclohexyl groups*). ^{1}H NMR ($CDCl_3$, 253 K): 9.80 (s, br, 1H, *NH*); 8.87 (d, slightly br, 1H, $^3J_{HH}$ = 7.3 Hz, *NH*); 8.55 (d, 1H, $^3J_{HH}$ = 5.1 Hz, *pyridine-H*$_6$); 7.85 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_4$); 7.56 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_3$); 7.41 (dd, 1H, $^3J_{HH}$ = 5.1 Hz, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_5$); 5.41 (s, 2H, *CH*$_2$*-O*); 4.13–3.26 (m, br, 2H, *CH-N*); 2.73 (s, 3H, *CH*$_3$*SO*$_3$); 2.10–0.95 (m, 20H, *cyclohexyl groups*). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K): 152.5 *pyridine-C*$_2$; 157.8 *isourea-C*; 148.9 *pyridine-C*$_6$; 138.1 *pyridine-C*$_4$; 124.5 *pyridine-C*$_5$; 124.4 *pyridine-C*$_3$; 74.0 *CH*$_2$*-O*; 52.1 *CH-N* (br); 39.7 *CH*$_3$*SO*$_3$; 32.2–23.8 *cyclohexyl rings*.

2.7. Characterization of $\mathbf{[Hpyiu^{Pr}]SO_3CH_3}$

Elemental *Anal.* Calc. for $C_{14}H_{25}N_3O_4S$: C, 50.7; H, 7.60; N, 12.7. Found: C, 50.5; H, 7.60; N, 12.6%. IR (KBr): 3422 cm^{-1}, 3327 cm^{-1} ν_{N-H}; 1647 cm^{-1} $\nu_{C=N}$. Λ_M (dimethylformamide, 298 K) = 52 ohm^{-1} mol^{-1} cm^2. ^{1}H NMR ($CDCl_3$, 328 K): 8.89 (s, br, 2H, *NH*); 8.66 (s, br, 1H, *pyridine-H*$_6$); 7.89 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_4$); 7.66 (d, slightly br, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_3$); 7.44 (dd, slightly br, 1H, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_5$); 5.58 (s, 2H, *CH*$_2$*-O*); 4.08 (s, br, *CH-N*); 2.72 (s, 3H, *CH*$_3$*SO*$_3$); 1.26 (d, 12H, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 7.7 Hz, ($C\underline{H}_3$)$_2$*CH-N*). ^{1}H NMR ($CDCl_3$, 258 K): 9.33 (s, br, 1H, *NH*); 8.80–8.45 (m, br, 2H, *NH* and *pyridine-H*$_6$); 7.93 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_4$); 7.66 (d, slightly br, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_3$); 7.48 (m, slightly br, 1H, *pyridine-H*$_5$); 5.52 (s, 2H, *CH*$_2$*-O*); 4.25–3.84 (m, br, 2H, *CH-N*); 2.72 (s, 3H, *CH*$_3$*SO*$_3$); 1.23 (m, br, 12H, ($C\underline{H}_3$)$_2$*CH-N*). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K): 157.3 *isourea-C*; 152.1 *pyridine-C*$_2$; 148.7 *pyridine-C*$_6$; 138.1 *pyridine-C*$_4$; 124.4 *pyridine-C*$_5$; 124.1 *pyridine-C*$_3$; 73.4 *CH*$_2$*-O*; 45.2 *CH-N*; 39.4 *CH*$_3$*SO*$_3$; 32.2–21.9 ($\underline{C}H_3$)$_2$*CH*.

2.8. Synthesis of $\mathbf{PdCl_2(pyiu^{Cy})}$ ($\mathbf{1^{Cy}}$) ($C_{19}H_{29}Cl_2N_3OPd$, MW = 492.78 g mol^{-1}) and $\mathbf{PdCl_2(pyiu^{Pr})}$ ($\mathbf{1^{Pr}}$) ($C_{13}H_{21}Cl_2N_3OPd$, MW = 412.65 g mol^{-1})

To a solution of *cis*-$PdCl_2(CH_3CN)_2$ (1.00 mmol, 0.259 g) in 20 mL of CH_2Cl_2 a solution containing 1.00 mmol of freshly prepared $\mathbf{pyiu^{Cy}}$ or $\mathbf{pyiu^{Pr}}$ in 10 mL of CH_2Cl_2 was slowly added. The resulting reaction mixture was left under stirring at room temperature for 3 h, then the solution was concentrated to about 5 mL by evaporation under reduced pressure and diethylether (10 mL) was slowly added. The yellow solid obtained was collected by filtration. The product was purified by dissolving it in dimethylformamide (3 mL). The DMF solution was then filtered and diethylether was added until a yellow solid separated out, which was collected by filtration, washed with diethylether and dried under vacuum. Yield ($\mathbf{1^{Cy}}$) = 86%, 0.424 g. Yield ($\mathbf{1^{Pr}}$) = 80%, 0.330 g. The slow cooling of acetone/nitromethane/diethyl ether solutions of $\mathbf{1^{Cy}}$ afforded crystals suitable for X-ray analysis.

2.9. Characterization of $\mathbf{1^{Cy}}$

Elemental *Anal.* Calc. for $C_{19}H_{29}Cl_2N_3OPd$: C, 46.3; H, 5.93; Cl, 14.4; N, 8.53. Found: C, 46.2; H, 5.90; Cl, 14.4; N, 8.50%. IR (KBr): 1612 cm^{-1} $\nu_{C=N}$. ^{1}H NMR (acetone-d_6, 241 K): 8.79 (d, 1H, $^3J_{HH}$ = 5.6 Hz, *pyridine-H*$_6$); 8.19 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_4$); 7.96 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_3$); 7.91 (d, 1H, $^2J_{HH}$ = 12.7 Hz, *CH*$_2$*-O*); 7.74 (dd, 1H, $^3J_{HH}$ = 5.6 Hz, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_5$); 5.98 (d, 1H, $^3J_{HH}$ = 7.5 Hz, *NH*); 5.82 (d, 1H, $^2J_{HH}$ = 12.7 Hz, *CH*$_2$*-O*); 3.61 (m, br, 1H, *CH-N*$_{amine}$); 3.11 (m, br, 1H, *CH-N*$_{imine}$); 2.00–0.80 (m, 20H, *cyclohexyl groups*). ^{1}H NMR (acetone-d_6, 311 K): 8.81 (d, 1H, $^3J_{HH}$ = 5.6 Hz, *pyridine-H*$_6$); 8.11 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_4$); 7.97 (s, very br, *CH*$_2$*-O*); 7.85 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_3$); 7.68 (dd, 1H, $^3J_{HH}$ = 5.6 Hz, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_5$); 5.74 (s, very br, 1H, *CH*$_2$*-O*); 5.50 (d, slightly br, 1H, $^3J_{HH}$ = 7.5 Hz, *NH*); 3.63 (m, slightly br, 1H, *CH-N*$_{amine}$); 2.85 (m, slightly br, 1H, *CH-N*$_{imine}$); 2.00–0.80 (m, 20H, *cyclohexyl groups*). ^{1}H NMR (CD_3NO_2, 298 K): 8.75 (d, 1H, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 1.5 Hz, *pyridine-H*$_6$); 8.05 (td, 1H, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, *pyridine-H*$_4$); 7.89 (d, 1H, $^2J_{HH}$ = 13.0 Hz, *CH*$_2$*-O*); 7.73 (d, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_3$);

7.61 (dd, 1H, $^3J_{HH}$ = 5.6 Hz, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_5$); 5.67 (d, 1H, $^2J_{HH}$ = 13.0 Hz, *CH*$_2$*-O*); 4.78 (d, 1H, $^3J_{HH}$ = 7.6 Hz, *NH*); 3.64 (m, 1H, *CH-N*$_{amine}$); 2.86 (m, 1H, *CH-N*$_{imine}$); 2.50–1.00 (m, 20H, *cyclohexyl groups*). ^{13}C {^{1}H} NMR (CD_3NO_2, 248 K): 155.3, 154.9 *not H-bonded carbon atoms*; 154.0, 141.6, 128.3, 128.1 *pyridine-CH*; 72.0 *CH-O*; 54.0–25.0 *cyclohexyl rings*.

2.10. Characterization of $\mathbf{1^{Pr}}$

Elemental *Anal.* Calc. for $C_{13}H_{21}Cl_2N_3OPd$: C, 37.8; H, 5.13; Cl, 17.2; N, 10.2. Found: C, 37.8; H, 5.10; Cl, 17.1; N, 10.1%. IR (KBr): 1613 cm^{-1} $\nu_{C=N}$. ^{1}H NMR (acetone-d_6, 270 K): 8.80 (d, 1H, $^3J_{HH}$ = 5.5 Hz, *pyridine-H*$_6$); 8.18 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_4$); 8.07 (d, 1H, $^2J_{HH}$ = 12.7 Hz, *CH*$_2$*-O*); 7.96 (d, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_3$); 7.74 (dd, 1H, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_5$); 5.83 (d, 1H, $^2J_{HH}$ = 12.7 Hz, *CH*$_2$*-O*); 5.81 (d, 1H, $^3J_{HH}$ = 6.5 Hz, *NH*); 3.99 (m, 1H, *CH-N*$_{amine}$); 3.22 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, *CH-N*$_{imine}$); 1.81 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{imine}$); 1.30 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{imine}$); 1.19 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{amine}$); 1.05 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{amine}$). ^{1}H NMR (acetone-d_6, 318 K): 8.81 (d, 1H, $^3J_{HH}$ = 5.5 Hz, *pyridine-H*$_6$); 8.13 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_4$); 7.88 (d, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_3$); 7.69 (dd, 1H, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_5$); 5.51 (d, 1H, $^3J_{HH}$ = 6.5 Hz, *NH*); 4.01 (m, 1H, *CH-N*$_{amine}$); 3.28 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, *CH-N*$_{imine}$); 1.57 (s, br, 6H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{imine}$); 1.16 (d, 6H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{amine}$). ^{1}H NMR (CD_3NO_2, 298 K): 8.74 (d, 1H, $^3J_{HH}$ = 5.7 Hz, *pyridine-H*$_6$); 8.06 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_4$); 8.01 (d, 1H, $^2J_{HH}$ = 12.9 Hz, *CH*$_2$*-O*); 7.75 (d, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_3$); 7.63 (dd, 1H, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_5$); 5.69 (d, 1H, $^2J_{HH}$ = 12.9 Hz, *CH*$_2$*-O*); 4.78 (d, 1H, $^3J_{HH}$ = 7.5 Hz, *NH*); 3.97 (m, 1H, *CH-N*$_{amine}$); 3.14 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, *CH-N*$_{imine}$); 1.81 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$ *CH-N*$_{imine}$); 1.30 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{imine}$); 1.19 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{amine}$); 1.05 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (*CH*$_3$)$_2$ *CH-N*$_{amine}$). ^{13}C {^{1}H} NMR (CD_3NO_2, 298 K): 155.8, 155.5 *not H-bonded carbon atoms*; 154.2, 141.7, 128.3, 128.1 *pyridine-CH*; 72.3 *CH*$_2$*-O*; 53.4, 46.8 *CH-N*; 26.2, 23.7, 23.3, 22.6 (C$\underline{H}_3$)$_2$*CH-N*.

2.11. Synthesis of $\mathbf{Pd(OCOCH_3)_2(pyiu^{Cy})}$ ($\mathbf{2^{Cy}}$) ($C_{23}H_{35}N_3O_5Pd$, MW = 539.96 g mol^{-1}) and $\mathbf{Pd(OCOCH_3)_2(pyiu^{Pr})}$ ($\mathbf{2^{Pr}}$) ($C_{17}H_{27}N_3O_5Pd$, MW = 459.83 g mol^{-1})

To a solution of palladium(II) acetate (1.00 mmol, 0.225 g) in 20 mL of CH_2Cl_2 a solution containing 1.00 mmol of freshly prepared **pyiu^{Cy}** or **pyiu^{Pr}** in 10 mL of CH_2Cl_2 was slowly added. The resulting reaction mixture was left under stirring at room temperature for 4 h, then the solvent was removed by evaporation under reduced pressure and diethylether (10 mL) was added. The solid which separated out was filtered, washed with diethylether (10 mL) and dried under vacuum. Yield (**2^{Cy}**) = 90%, 0.486 g. Yield (**2^{Pr}**) = 88%, 0.407 g.

2.12. Characterization of $\mathbf{2^{Cy}}$

Elemental *Anal.* Calc. for $C_{23}H_{35}N_3O_5Pd$: C, 51.2; H, 6.53; N, 7.78. Found: C, 51.3; H, 6.55; N, 7.80%. IR (KBr): 1610 cm^{-1} (broad signal) $\nu_{C=N}$ and $\nu_{C=O}$. IR (CH_2Cl_2): 1630 cm^{-1} (shoulder), 1609 cm^{-1} $\nu_{C=N}$ and $\nu_{C=O}$. ^{1}H NMR ($CDCl_3$, 242 K): 9.64 (d, 1H, $^2J_{HH}$ = 13.4 Hz, *CH*$_2$*-O*); 8.68 (d, 1H, $^3J_{HH}$ = 5.4 Hz, *pyridine-H*$_6$); 7.87 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_4$); 7.52 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_3$); 7.40 (dd, 1H, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_5$); 5.51 (d, 1H, $^2J_{HH}$ = 13.4 Hz, *CH*$_2$*-O*); 4.03–3.15 (m, 3H, *NH* and *CH-N*$_{amine}$ and *CH-N*$_{imine}$); 1.92 (s, 3H, *CH*$_3$*COO*); 1.83 (s, 3H, *CH*$_3$*COO*); 2.50–0.80 (m, 20H, *cyclohexyl groups*). ^{1}H NMR ($CDCl_3$, 271 K): 9.64 (s, br, 1H, *CH*$_2$*-O*); 8.71 (d, 1H, $^3J_{HH}$ = 5.4 Hz, *pyridine-H*$_6$); 7.85 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_4$); 7.51 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_3$); 7.39 (dd, 1H, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 7.8 Hz, *pyridine-H*$_5$); 5.49 (s, br, 1H, *CH*$_2$*-O*); 3.93 (d, 1H, $^3J_{HH}$ = 7.1 Hz, *NH*); 3.42 (s, br, 1H, *CH-N*$_{amine}$); 3.00 (s, br, 1H, *CH-N*$_{imine}$); 1.91 (s, 3H, *CH*$_3$*COO*); 1.83 (s, 3H, *CH*$_3$*COO*); 2.50–0.80 (m, 20H, *cyclohexyl groups*).

2.13. Characterization of $\mathbf{2^{Pr}}$

Elemental *Anal.* Calc. for $C_{17}H_{27}N_3O_5Pd$: C, 44.4; H, 5.92; N, 9.14. Found: C, 44.5; H, 5.95; N, 9.15%. IR (KBr): 1625 cm^{-1} (broad signal) $\nu_{C=N}$ and $\nu_{C=O}$. IR (CH_2Cl_2): 1630 cm^{-1} (shoulder), 1616 cm^{-1} $\nu_{C=N}$ and $\nu_{C=O}$. ^{1}H NMR ($CDCl_3$, 239 K): 9.58 (d, 1H, $^2J_{HH}$ = 13.0 Hz, *CH*$_2$*-O*); 8.67 (d, 1H, $^3J_{HH}$ = 5.5 Hz, *pyridine-H*$_6$); 7.87 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *pyridine-H*$_4$); 7.51 (d, 1H, $^3J_{HH}$ = 7.6 Hz, *pyridine-H*$_3$); 7.41 (dd, 1H, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 7.6 Hz, *pyridine-H*$_5$); 5.50 (d, 1H, $^2J_{HH}$ = 13.0 Hz, *CH*$_2$*-O*); 4.12 (d, 1H, $^3J_{HH}$ = 6.6 Hz, *NH*); 3.77 (m, 1H, *CH-N*$_{amine}$); 2.87 (m, 1H, *CH-N*$_{imine}$); 1.89 (s, 3H, *CH*$_3$*COO*); 1.81 (s, 3H, *CH*$_3$*COO*); 2.30–0.80 (m, 12H, (C$\underline{H}_3$)$_2$*CH*). ^{1}H NMR ($CDCl_3$, 317 K): 8.76 (d, 1H, $^3J_{HH}$ = 5.5 Hz, *pyridine-H*$_6$); 7.83 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_4$); 7.48 (d, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_3$); 7.37 (dd, 1H, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 7.6 Hz, *pyridine-H*$_5$); 4.00 (d, 1H, $^3J_{HH}$ = 6.9 Hz, *NH*); 3.81 (m, 1H, *CH-N*$_{amine}$); 2.96 (sept, 1H, $^3J_{HH}$ = 6.6 Hz, *CH-N*$_{imine}$); 1.89 (s, 3H, *CH*$_3$*COO*); 1.81 (s, 3H, *CH*$_3$*COO*); 1.62 (d, br, 6H, $^3J_{HH}$ = 6.6 Hz, (*CH*$_3$)$_2$*CH-N*$_{imine}$); 1.05 (d, 6H, $^3J_{HH}$ = 6.3 Hz, (*CH*$_3$)$_2$*CH-N*$_{amine}$).

2.14. Synthesis of $\mathbf{Pd(CH_3)Cl(pyiu^{Cy})}$ ($\mathbf{3^{Cy}}$) ($C_{20}H_{32}ClN_3OPd$, MW = 472.36 g mol^{-1}) and $\mathbf{Pd(CH_3)Cl(pyiu^{Pr})}$ ($\mathbf{3^{Pr}}$) ($C_{14}H_{24}ClN_3OPd$, MW = 392.23 g mol^{-1})

To a solution of Pd(CH_3)Cl(COD) (1.00 mmol, 0.265 g) in 20 mL of CH_2Cl_2 a solution containing 1.00 mmol of freshly prepared **pyiu^{Cy}** or **pyiu^{Pr}** in 10 mL of CH_2Cl_2 was slowly added. The resulting reaction mixture was left under stirring at room temperature for 4 h, then the solvent was removed by evaporation under reduced pressure and diethylether (10 mL) was added. The solid which separated out was filtered, washed with diethylether (10 mL) and dried under vacuum. The products were purified by slowly cooling saturated dichloromethane/diethylether solutions from room temperature to −25 °C. Yield (**3^{Cy}**) = 75%, 0.354 g. Yield (**3^{Pr}**) = 76%, 0.298 g.

2.15. Characterization of $\mathbf{3^{Cy}}$

Elemental *Anal.* Calc. for $C_{20}H_{32}ClN_3OPd$: C, 50.9; H, 6.83; Cl, 7.51; N, 8.90. Found: C, 50.8; H, 6.80; Cl, 7.50; N, 8.90%. IR (KBr): 1630 cm^{-1} $\nu_{C=N}$. ^{1}H NMR ($CDCl_3$, 225 K): 8.54 (d, 1H, $^3J_{HH}$ = 5.5 Hz, *pyridine-H*$_6$); 8.02 (d, 1H, $^2J_{HH}$ = 12.5 Hz, *CH*$_2$*-O*); 7.93 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_4$); 7.62 (d, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_3$); 7.49 (dd, 1H, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_5$); 5.32 (d, 1H, $^2J_{HH}$ = 12.5 Hz, *CH*$_2$*-O*); 3.60 (d, 1H, $^3J_{HH}$ = 6.4 Hz, *NH*); 3.24 (m, 1H, *CH-N*$_{amine}$); 2.57 (m, 1H, *CH-N*$_{imine}$); 2.30–0.90 (m, 20H, *cyclohexyl groups*); 0.78 (s, 3H, *Pd-CH*$_3$).

2.16. Characterization of $\mathbf{3^{Pr}}$

Elemental *Anal.* Calc. for $C_{14}H_{24}ClN_3OPd$: C, 42.9; H, 6.17; Cl, 9.04; N, 10.7. Found: C, 43.0; H, 6.20; Cl, 9.05; N, 10.7%. IR (KBr): 1629 cm^{-1} $\nu_{C=N}$. ^{1}H NMR (CD_2Cl_2, 241 K): 8.43 (d, 1H, $^3J_{HH}$ = 5.5 Hz, *pyridine-H*$_6$); 7.83 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_4$); 7.81 (d, 1H, $^2J_{HH}$ = 12.0 Hz, *CH*$_2$*-O*); 7.51 (d, 1H, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_3$); 7.39 (dd, 1H, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 7.7 Hz, *pyridine-H*$_5$); 5.25 (d, 1H, $^2J_{HH}$ = 12.0 Hz, *CH*$_2$*-O*); 3.80–3.52 (m, 2H, *NH* and *CH-N*$_{amine}$); 2.99 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, *CH-N*$_{imine}$); 1.67 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{imine}$); 1.10 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{imine}$); 1.02 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{amine}$); 0.89 (d, 3H, $^3J_{HH}$ = 6.4 Hz, (C$\underline{H}_3$)$_2$*CH-N*$_{amine}$); 0.57 (s, 3H, *Pd-CH*$_3$).

2.17. Crystal structure determinations

The crystal data of compounds **[Hpyiu^{Cy}]SO$_3$CH$_3$** and **1^{Cy}** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation. The data sets were integrated with the Denzo-SMN package [12] and corrected for Lorentz, polarization and absorption effects (SORTAV [13]). The structures were solved by direct methods (SIR97 [14]) and refined using full-matrix least-squares with all non-hydrogen atoms anisotropically. For structure **[Hpyiu^{Cy}]SO$_3$CH$_3$** the hydrogens were refined isotropically except those of the SO_3CH_3 anion which were included in the calculated positions. For structure **1^{Cy}** the hydrogens were included on calculated positions, riding on their carrier atoms, except the aminic hydrogen which was refined isotropically. All calculations were performed using SHELXL-97 [15] and PARST [16] implemented in WINGX [17] system of programs. The crystal data are given in Table 1.

2.18. Theoretical calculations

The computational geometry optimization of the complexes was carried out using the hybrid DFT B3PW91 method [18] without symmetry constrains in combination with a polarized triple-ζ quality basis set composed by the 6-311G(d,p) basis set on the light atoms and the LANL2TZ(f) basis set on the metal center [19]. Implicit solvation was added by using the C-PCM model for acetone ($\varepsilon = 20.7$) [20]. The "restricted" formalism was applied in all calculations. The geometries were initially refined *in vacuo* by using the M06 DFT method [21] in combination with the LACVP** [22] basis set and the stationary points were characterized as true minima by IR simulation. The software used for M06 calculations was the SPARTAN 08 [23], while GAUSSIAN 09 [24] was used for B3PW91 calculations. The simulations were performed on a local Intel-based x86-64 workstation and at CINECA (Centro Italiano di Supercalcolo, Bologna, Italy) using a IBM P6-575 workstation equipped with 64-bit IBM Power6 processors.

Table 1
Crystallographic data for **[Hpyiu^{Cy}]SO$_3$CH$_3$** and **1^{Cy}**.

Compound	[Hpyiu^{Cy}]SO$_3$CH$_3$	1^{Cy}
Formula	$C_{20}H_{33}N_3O_4S$	$C_{19}H_{29}Cl_2N_3Opd$
M	411.55	492.75
Space group	$P2_1/n$	$P2_1/c$
Crystal system	monoclinic	monoclinic
a (Å)	15.1881(3)	16.6464(4)
b (Å)	9.9542(2)	7.2914(2)
c (Å)	16.1021(3)	18.7464(6)
β (°)	112.863(1)	111.306(1)
U (Å^3)	2243.14(8)	2119.8(1)
Z	4	4
T (K)	295	295
D_{calc} (g cm^{-3})	1.219	1.544
F(000)	888	1008
μ(Mo Kα) (cm^{-1})	1.73	11.40
Measured reflections	9650	14449
Unique reflections	5367	5010
R_{int}	0.0214	0.0414
Observed reflections [$I \geqslant 2\sigma(I)$]	3943	3933
θ_{min}–θ_{max} (°)	3.56–28.00	3.64–27.91
hkl ranges	−20, 20; −12, 13; −21, 21	−21, 21; −9, 9; −24, 24
$R(F^2)$ (observed reflections)	0.0493	0.0367
$wR(F^2)$ (all reflections)	0.1457	0.0860
Number of variables	374	239
Goodness of fit	1.020	1.054
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	0.29; −0.37	0.51; −0.68
CCDC Deposition Number	CCDC 853518	CCDC 853519

3. Results and discussion

3.1. Synthesis and characterization of the ligands

The ligands **pyiu^{Cy}** and **pyiu^{Pr}** were obtained with yields higher than 50% by reacting 2-pyridinemethanol with an equimolar amount of dicyclohexylcarbodiimide or diisopropylcarbodiimide in dichloromethane at room temperature in the presence of a catalytic amount of copper(I) iodide, as sketched in Scheme 1. The yields of the reactions were not meaningfully improved on changing the reaction conditions. The reaction between a benzyl alcohol and a carbodiimide to obtain the corresponding isourea is reported in the literature [25]. The commonly used catalysts are copper(I) or copper(II) salts, but in the case of 2-pyridinemethanol as reactant preliminary experiments showed the complete inefficacy of Cu(II) salts as catalysts for such a reaction.

The elemental analyses of **pyiu^{Cy}** and **pyiu^{Pr}** are in agreement with the proposed formulations. The IR spectra show a quite strong band attributable to the C=N stretching, at 1669 cm^{-1} for **pyiu^{Cy}** and at 1658 cm^{-1} for **pyiu^{Pr}**.

The ^{1}H NMR spectra show in the high-frequency region four signals attributable to the pyridine ring. The O-bonded CH_2 group corresponds in both the ligands to a sharp singlet centered at 5.19 ppm. In the spectral region comprised between 4.0 and 2.5 ppm the signals corresponding to the NH and CH-N protons are observable. In both the compounds the CH bonded to N_{amine} resonates at higher frequency with respect to that bonded to N_{imine}. The ^{1}H NMR spectra were recorded at 240 K in order to distinguish these groups. In the low-frequency region the other signals of the cyclohexyl or isopropyl groups are observable.

The ^{13}C {^{1}H} NMR spectra show in the high-frequency region six signals, five attributable to the pyridine ring and one to the isourea group carbon atom, which falls around 150 ppm. The assignment was based on HSQC and HMBC spectra. The O-bonded CH_2 corresponds to a singlet around 67 ppm. In the range comprised between 50.0 and 40.0 ppm the CH-N groups are observable and, differently from the ^{1}H NMR resonances, the CH bonded to N_{imine} is more down-shifted with respect to the CH-N_{amine} group. Finally, the other signals corresponding to the cyclohexyl or isopropyl groups are present in the low-frequency region.

The compounds **pyiu^{Cy}** and **pyiu^{Pr}** are scarcely stable. Addition of a stoichiometric amount of methanesulfonic acid to these neutral compounds in dichloromethane caused the formation of the conjugated acids **[Hpyiu^{Cy}]SO$_3$CH$_3$** and **[Hpyiu^{Pr}]SO$_3$CH$_3$** (see Scheme 1), which are on the contrary stable for many months if stored at −25 °C.

[Hpyiu^{Cy}]SO$_3$CH$_3$ and **[Hpyiu^{Pr}]SO$_3$CH$_3$** behave as 1:1 electrolytes in DMF solution and their elemental analyses are in agreement with the proposed formulations. The IR spectra show bands attributable to the N–H stretching in the region comprised between 3450 and 3300 cm^{-1}. The C=N stretching corresponds to a band at 1644 cm^{-1} for **[Hpyiu^{Cy}]SO$_3$CH$_3$** and at 1647 cm^{-1} for **[Hpyiu^{Pr}]SO$_3$CH$_3$.**

The ^{1}H NMR spectra of these species in $CDCl_3$ at 298 K show in the high-frequency region, besides the signals of the pyridine ring, a broad singlet attributable to the NH protons. If the temperature is lowered below 260 K, this singlet separates in two signals, the first one above 9.3 ppm and quite broad, the second one below 8.8 ppm and more sharp. This fluxional behavior of **[Hpyiu^{Cy}]SO$_3$CH$_3$** and **[Hpyiu^{Pr}]SO$_3$CH$_3$** is attributable to proton exchange, which becomes slow on the NMR timescale at low temperature. The chemical shifts of the N-bonded hydrogen atoms are influenced by hydrogen bonding, as observed also by single-crystal X-ray diffraction (see below). In both the compounds the CH_2-O ^{1}H NMR signals are singlets around 5.5–5.4 ppm. In the aliphatic region the signals

of the N-bonded substituents and of the methanesulfonate counter-ion are observable.

The $^{13}C\{^1H\}$ NMR spectra of the two compounds show in the high-frequency region, besides the pyridine C-atoms, the isourea carbon around 158–157 ppm. The other signals present in the $^{13}C\{^1H\}$ NMR spectra are those of the O-bonded methylene and of the aliphatic substituents on the nitrogen atoms.

Crystals suitable for X-ray structure diffraction have been obtained for **[Hpyiu^{Cy}]SO$_3$CH$_3$**. ORTEP [26] view is shown in Fig. 1 and a selection of bond distances and angles is given in Table 2. The protonation of the neutral pyridine–isourea ligands by methanesulfonic acid occurs at the N_{imine} atom of the isourea dent. The similarity of C1–N2 and C1–N3 distances of 1.315(3) and 1.314(2) Å, respectively, reveals a significant delocalization of the positive charge as well as of the double bond on the N2–C1–N3 moiety. The crystal packing is characterized by chains of alternate [Hpyiu^{Cy}]$^+$ cations and $SO_3CH_3^-$ anions linked by strong intermolecular N2–H...O2 and N3–H...O3 hydrogen bonds (Table 3). Other short C–H...O interactions between cations and anions are involved in the reinforcement of the crystal packing (Table 3).

Reaction of **[Hpyiu^{Cy}]SO$_3$CH$_3$** and **[Hpyiu^{Pr}]SO$_3$CH$_3$** with potassium *tert*-butoxide in methanol at room temperature allows obtaining again with nearby quantitative yields the conjugated bases **pyiu^{Cy}** and **pyiu^{Pr}** (see Scheme 1).

Table 2
Selected geometrical parameters for **[Hpyiu^{Cy}]SO$_3$CH$_3$** (Å and °).

Distances		Angles	
C1–O1	1.329(2)	C1–O1–C2	120.0(1)
C2–O1	1.457(2)	O1–C1–N2	121.7(1)
C1–N2	1.315(3)	O1–C1–N3	114.6(1)
C1–N3	1.314(2)	N2–C1–N3	123.7(2)
C8–N2	1.474(2)	C1–N2–C8	124.2(1)
C14–N3	1.471(3)	C1–N3–C14	125.8(2)

Table 3
Hydrogen bond parameters for **[Hpyiu^{Cy}]SO$_3$CH$_3$**.

Hydrogen bonds	Symm. op.	D–H (Å)	D...A (Å)	H...A (Å)	D–H...A (°)
N2–H2N...O2		0.88(2)	2.880(2)	2.03(2)	165(2)
N3–H3N...O3	1/2 − *x*, 1/2 + *y*, 1/2 − *z*	0.86(2)	2.817(2)	1.98(2)	166(2)
C8–H8...O3	1/2 − *x*, 1/2 + *y*, 1/2 − *z*	0.99(2)	3.332(2)	2.62(2)	129(2)
C4–H4...O4	1 − *x*, −1 − *y*, 1 − *z*	0.94(3)	3.293(3)	2.42(3)	155(2)
C2–H2A...O2	1 − *x*, −1 − *y*, 1 − *z*	0.96(2)	3.443(2)	2.49(2)	173(2)

3.2. Coordination of the pyridine–isourea ligands to the Pd(II) center

The ligands **pyiu^{Cy}** and **pyiu^{Pr}** easily react with the precursors *cis*-$PdCl_2(NCCH_3)_2$, Pd(II) acetate and $Pd(CH_3)Cl(COD)$ in dichloromethane at room temperature to form the corresponding complexes **PdCl$_2$(pyiu^{Cy}) (1^{Cy})**, **PdCl$_2$(pyiu^{Pr}) (1^{Pr})**, **Pd(OAc)$_2$(pyiu^{Cy}) (2^{Cy})**, **Pd(OAc)$_2$(pyiu^{Pr}) (2^{Pr})**, **Pd(CH$_3$)Cl(pyiu^{Cy}) (3^{Cy})** and **Pd(CH$_3$)Cl(pyiu^{Pr}) (3^{Pr})**, as depicted in Scheme 2. The dichloro-complexes **1^{Cy}** and **1^{Pr}** are poorly soluble in dichloromethane and chloroform, while they are quite soluble in more polar solvents such as acetone and nitromethane and very soluble in dimethylformamide. The complexes **2^{Cy}**, **2^{Pr}**, **3^{Cy} and 3^{Pr}** are instead very soluble in all these solvents.

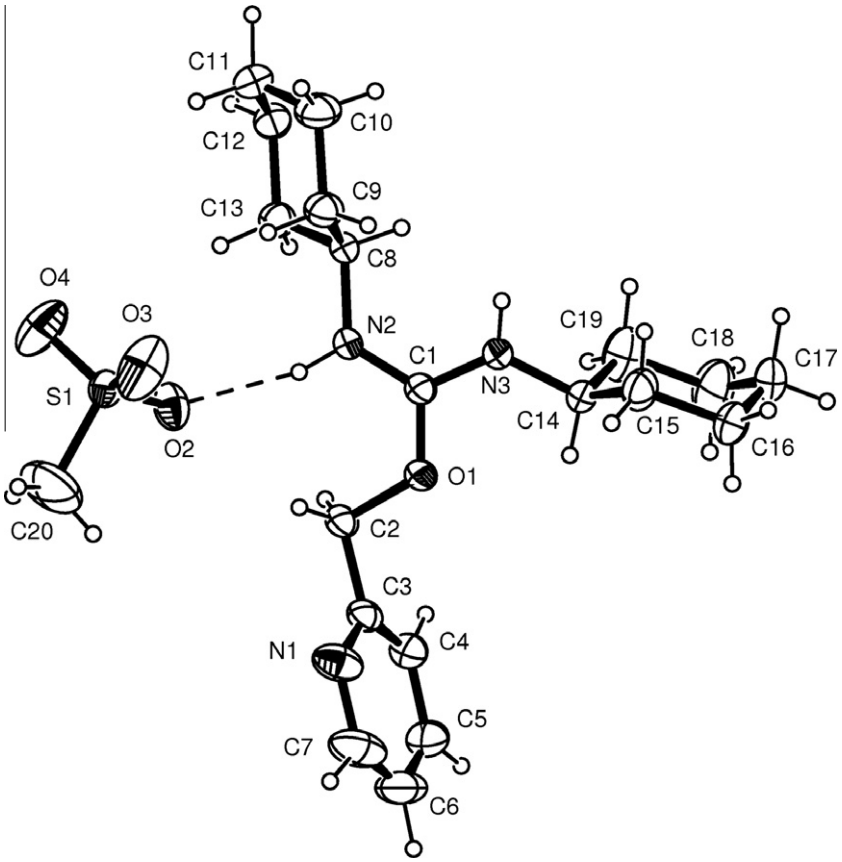


Fig. 1. ORTEP view of compound **[Hpyiu^{Cy}]SO$_3$CH$_3$** showing the thermal ellipsoids at 30% probability level.

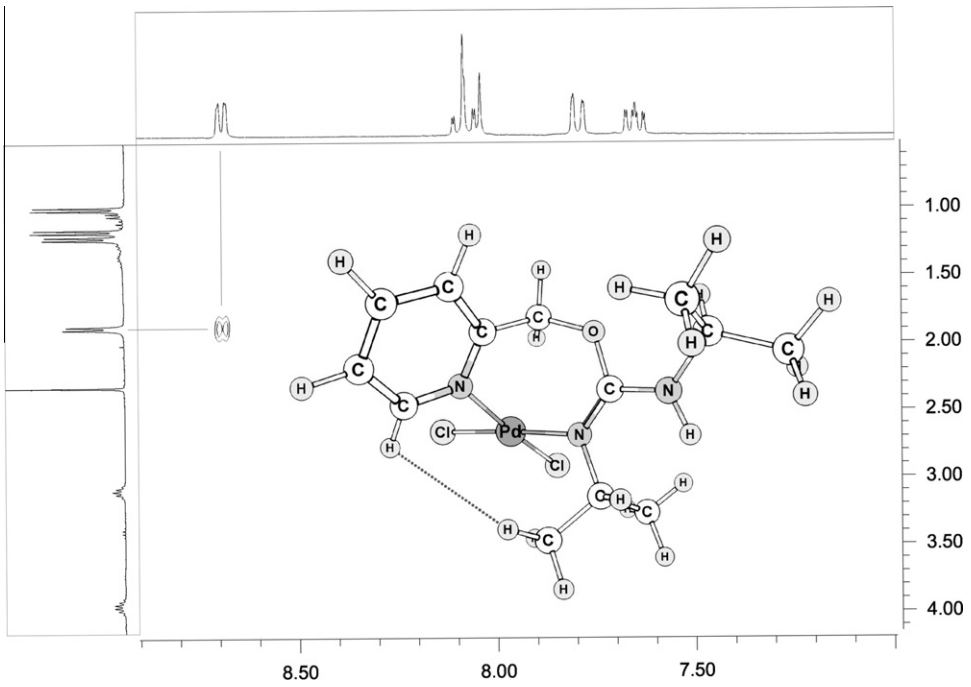


Fig. 2. Section of ^{1}H NOESY spectrum of $\mathbf{1^{Pr}}$ in CD_3NO_2 at 298 K.

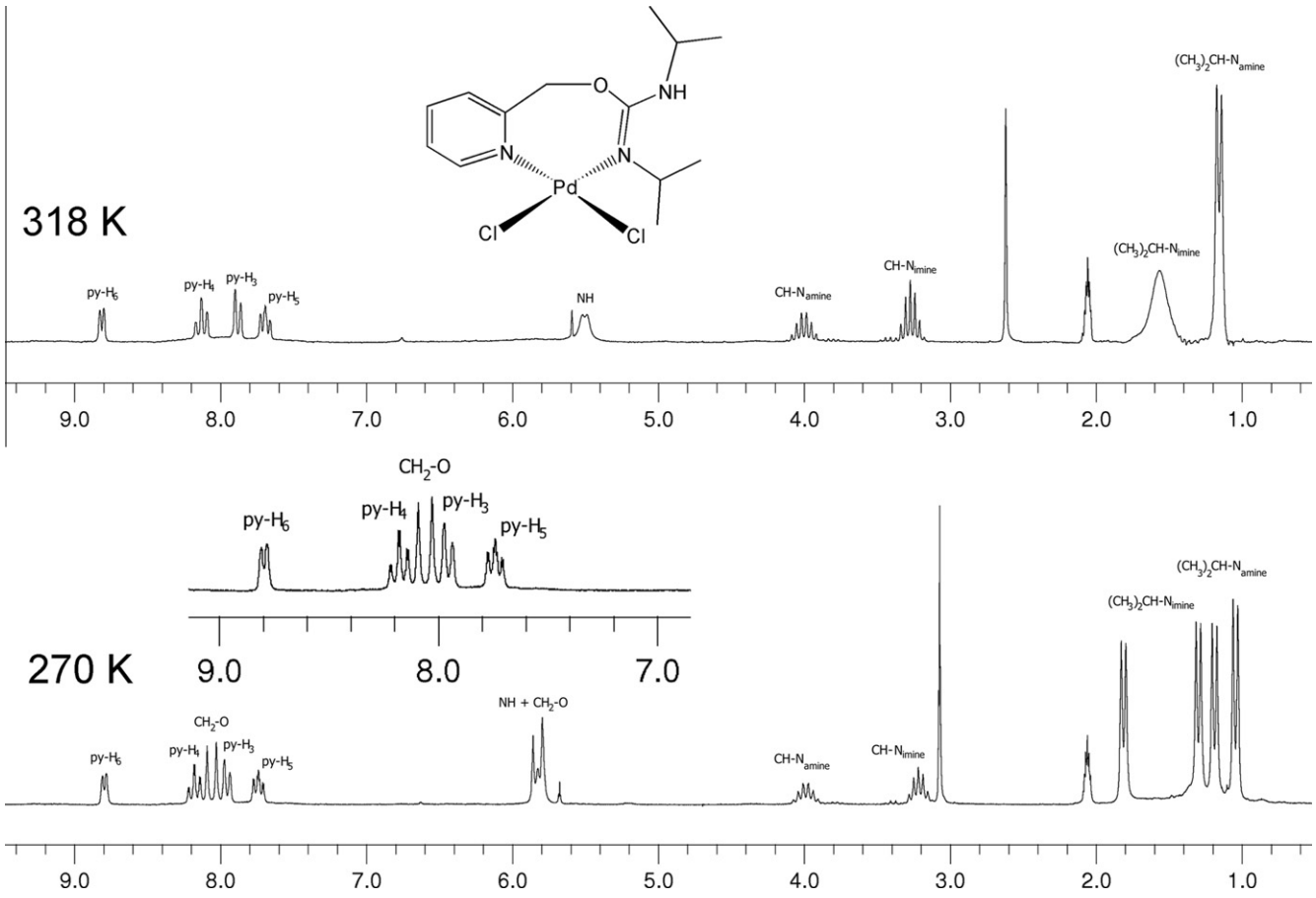


Fig. 3. ^{1}H NMR spectra in acetone-d_6 of $\mathbf{1^{Pr}}$ at 270 and 318 K.

All these complexes are not conductive in dimethylformamide solution and their elemental analyses agree with the proposed formulations. The IR spectra show bands attributable to the C=N stretching in the range 1630–1612 cm^{-1}. For all the complexes this

stretching falls at wavenumbers lower than those recorded for the corresponding free ligands. In the case of the diacetato-derivatives $\mathbf{2^{Cy}}$ and $\mathbf{2^{Pr}}$ the C=N stretching is superposed with those due to the C=O bonds and the resulting wide band cannot be completely resolved also by recording the IR spectra of the samples in CH_2Cl_2 solution.

The ^{1}H NMR spectra of all the complexes show in the high-frequency region the signals due to the pyridine ring. The isourea NH resonance strongly depends upon the solvent: in acetone and nitromethane the chemical shift value is comprised between 6.0 and 4.7 ppm, while the same signal falls between 4.1 and 3.5 ppm in chloroform or dichloromethane. On the basis of the scalar coupling with this NH group the ^{1}H NMR signals of the aliphatic groups bonded to N_{imine} and N_{amine} of the isourea dent have been attributed. The CH_2-O protons correspond in all the complexes to a AB spin system if the temperature is sufficiently low, with $^2J_{HH}$ coupling constant values comprised between 12.0 and 13.5 Hz. The coordinated ligands have however a fluxional behavior and the CH_2-O signals become broader or not detectable on rising the temperature.

These NMR signals agree with a coordination mode where the ligands act as bidentate and coordinate the metal fragments through the pyridine and the isourea groups. The coordinating nitrogen atom of the isourea dent has been identified on the basis of low-temperature NOESY experiments. The cross-peak between one of the N-bonded isopropyl fragments and the pyridine-H_6 in $\mathbf{1^{Pr}}$, $\mathbf{2^{Pr}}$ and $\mathbf{3^{Pr}}$ (see Fig. 2 as example) allows concluding that the isourea group coordinates the metal center through the imine nitrogen, as already observed for other Pd(II)–isourea complexes (see Scheme 2) [4].

The signals corresponding to the isopropyl fragments are strongly affected by the temperature. If the temperature is sufficiently low both the isopropyl fragments show two distinct methyl resonances, while on rising the temperature the two methyl of the same group give as single signal. This result can be attributed to a slow inversion at the N atom of the amine unit at low temperature, or to a slow inversion of the seven-membered ring. As an example, Fig. 3 reports the ^{1}H NMR spectra of $\mathbf{1^{Pr}}$ in acetone-d_6 at 270 and 318 K: the two CH_3 signals of the N_{amine}-bonded isopropyl group (1.19 and 1.05 ppm at 270 K) become a single sharp doublet at 1.16 ppm at 318 K, while the two CH_3 doublets of the N_{imine}-bonded isopropyl group (1.81 and 1.30 ppm at 270 K) coalesce in broad, unresolved peak centered at 1.57 ppm at 318 K. Another example of the same behavior is observable in the NMR spectra of $\mathbf{2^{Pr}}$ in $CDCl_3$ reported in Fig. 4. At 239 K four separate CH_3 signals are observable in the range comprised between 2.30 and 1.80 ppm, while a broad signal at 1.62 ppm and a sharp doublet at 1.05 ppm are present in the spectrum recorded at 317 K, corresponding to the N_{imine}- and N_{amine}-bonded isopropyl groups, respectively.

Other NMR signals observable in the aliphatic region of the ^{1}H NMR spectra are the two singlets corresponding to the two acetato-ligands in $\mathbf{2^{Cy}}$ and $\mathbf{2^{Py}}$ and the low-frequency singlet due to the Pd-CH_3 group in $\mathbf{3^{Cy}}$ and $\mathbf{3^{Pr}}$. The NOESY cross peak between this signal and that of pyridine-H_6 allows concluding that the Pd-bonded methyl group and the pyridine ring are mutually in *cis* position, as sketched in Scheme 2.

The coordination mode of the pyridine–isourea ligands towards palladium(II) proposed on the basis of NMR measurements has been confirmed by the X-ray structure determination of $\mathbf{1^{Cy}}$ and an ORTEP [26] view of the molecular structure of this complex is

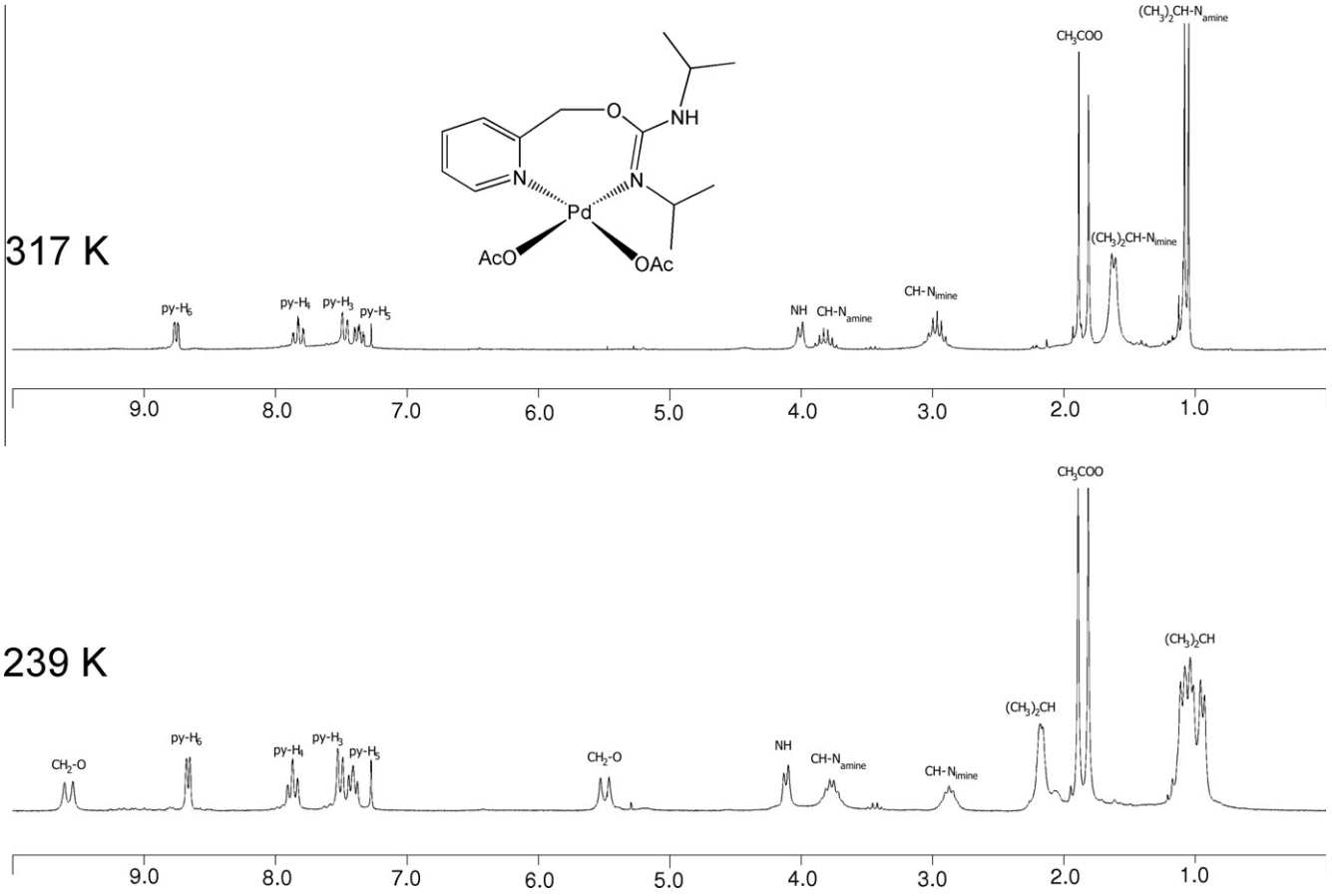


Fig. 4. ^{1}H NMR spectra in $CDCl_3$ of $\mathbf{2^{Pr}}$ at 239 and 317 K.

shown in Fig. 5. Selected bond distances and angles are listed in Table 4. The geometry around Pd(II) is a distorted square planar arrangement. The ligand is coordinated to the Pd central atom in a bidentate mode through the pyridine-N-atom and the N-imine of the isourea group with the formation of a seven-membered ring displaying a boat conformation. The two Cl anions are bonded to the Pd atom in the *cis* position. Similar coordination modes have been observed in other $PdCl_2$ complexes [27]. The Pd atom shows a deviation from the square-planar geometry of 0.0126(2) Å from the least squares plane defined by the four coordinated atoms. In the crystal packing the molecules are linked in chains by means of N3–H...Cl2 hydrogen bonds (Table 4). The Pd–N(pyridine) bond length is 0.02 Å shorter than that between the Pd center and the coordinating isourea N-atom. The difference between the two Pd–Cl bond lengths is below 0.01 Å, this indicating similar *trans*-influence of the two dents of the N-donor ligand.

The possible coordination modes of the pyridine–isourea ligands towards Pd(II) have been studied also from a computational point of view, by optimizing the geometries of three possible isomers of $\mathbf{1^{Pr}}$. In the first isomer the ligand interacts with the metal center through the pyridine N-atom and the N_{imine} of the isourea group, as suggested by the NMR data and shown by the X-ray structure of $\mathbf{1^{Cy}}$. In the second isomer the coordination happens through the pyridine N-atom and the amine nitrogen atom of the isourea group. Finally, in the last isomer the ligand is bonded to the metal center through the two nitrogen atoms of the isourea group and there is no bond between palladium and the pyridine ring. The first isomer resulted more stable of about 11 kcal mol^{-1} with respect to the second isomer and of more than 20 kcal mol^{-1} with respect to the last isomer considered.

The geometry in solution of the most stable isomer of $\mathbf{1^{Pr}}$ has been investigated also by means of DFT calculations in combination with an implicit solvation model for acetone and the resulting structure is depicted in Fig. 6. The computed Pd—H distance (2.500 Å) and Pd—H–C angle (103.8°) calculated for $\mathbf{1^{Pr}}$ are typical for a hydrogen-bonding interaction between a hydrogen atom of the methylene group and the metal center. This type of weak bond, which is typically associated with d^8 transition metals centers that are square planar prior to the interaction, is well known from a long time [28] and it is actually called "anagostic" [29]. In complexes containing an anagostic bond the interacting hydrogen is high-frequency shifted, contrary to "classic" agostic interactions. The great chemical shift difference between the two hydrogen atoms of the methylene bridge in compounds **1**–**3** and the presence of a strong ^{1}H NMR high frequency shift only for one of the two H atoms could therefore be explained on the basis on such an interaction. A partial confirmation of this hypothesis comes from the Mulliken charge distribution analysis [30]. The computed charges of the two methylene hydrogen atoms are in fact quite different, 0.216 a.u. for the H atom near the metal center and 0.172 a.u. for the other one. Also this result agrees with the picture of a weak pseudo hydrogen bond connecting the metal center and the methylene fragment, where the bridging H atom is more electron-poor than the other one. It is to be noted, however, that no trace of interaction between the palladium center and the methylene bridge is present in the X-ray structure of $\mathbf{1^{Cy}}$ depicted in Fig. 5.

Table 4
Selected geometrical parameters and hydrogen bond parameters for $\mathbf{1^{Cy}}$ (Å and °).

Distances			Angles		
Pd1–Cl1	2.3001(8)		Cl1–Pd1–Cl2		91.49(3)
Pd1–Cl2	2.3076(8)		Cl1–Pd1–N1		91.02(7)
Pd1–N1	2.026(2)		Cl1–Pd1–N2		175.28(7)
Pd1–N2	2.047(2)		Cl2–Pd1–N1		176.62(7)
C1–O1	1.356(5)		Cl2–Pd1–N2		93.17(7)
C2–O1	1.387(4)		N1–Pd1–N2		84.35(9)
C3–N1	1.352(5)		C1–O1–C2		122.2(3)
C1–N2	1.283(4)		Pd1–N1–C3		120.4(2)
C1–N3	1.319(4)		Pd1–N2–C1		119.1(2)
C2–C3	1.501(5)		O1–C1–N2		118.6(3)
			O1–C2–C3		119.1(3)
Hydrogen bond	Symm. op.	D–H (Å)	D...A (Å)	H...A (Å)	D–H...A (°)
N3–N3...Cl2	*x*, *y* + 1, *z*	0.78(4)	3.409(3)	2.66(4)	163(4)

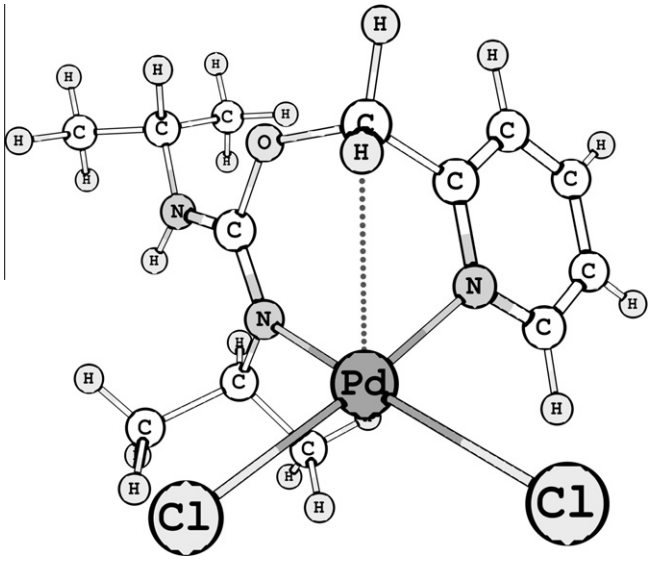


Fig. 6. DFT/C-PCM optimized model for complex $\mathbf{1^{Pr}}$ in acetone.

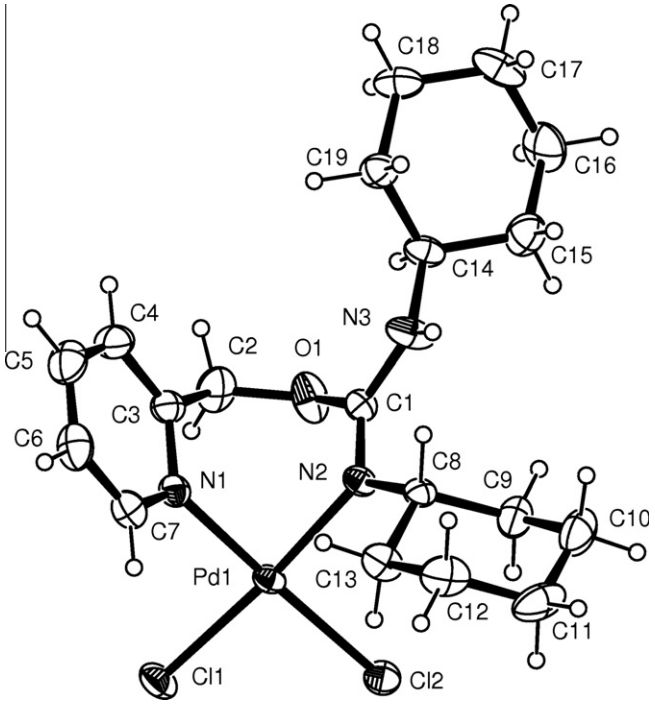


Fig. 5. ORTEP view of the complex $\mathbf{1^{Cy}}$ showing the thermal ellipsoids at 30% probability level.

4. Conclusions

To summarize, in this paper the synthesis of several new palladium(II) complexes with novel pyridine–isourea ligands has been

reported. The characterization data allowed establishing the coordination mode of these ligands, which act as bidentate towards the Pd(II) metal center, forming a seven-membered ring. This preliminary work will be prosecuted trying to coordinate these ligands to other transition metals, to ascertain if the coordination mode depends upon the electronic configuration of the metal center. Moreover, the reactivity of the coordinated pyridine–isourea ligands will be explored, in particular for what concerns their acid–base behavior.

Acknowledgments

Financial support was provided by the Ca' Foscari University of Venice (Ateneo Fund 2010). We acknowledge the CINECA Award N. HP10CRPVUO, 2011 for the availability of high performance computing resources and support.

Appendix A. Supplementary data

CCDC 853518 and 853519 contain the supplementary crystallographic data for compound **[Hpyiu^{Cy}]SO$_3$CH$_3$** and complex **PdCl$_2$(pyiu^{Cy})** (**1^{Cy}**), respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2012.02.014.

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