



## Structural variations in nickel, palladium, and platinum complexes containing pyrimidyl *N*-heterocyclic carbene ligand

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### ABSTRACT

Nickel(II), palladium(II), and platinum(II) complexes of 2-(3-mesitylimidazolylidene)pyrimidine (L), [Ni<sub>2</sub>(μ-Cl)<sub>2</sub>(L)<sub>4</sub>][Ag<sub>2</sub>Cl<sub>4</sub>] (**3**), [Ni<sub>2</sub>(μ-I)<sub>2</sub>(L)<sub>4</sub>][Ni(L)<sub>2</sub>(CH<sub>3</sub>CN)]<sub>2</sub>[Ag<sub>4</sub>I<sub>8</sub>] (**4**), [PdCl<sub>2</sub>(L)] (**5**), [PdI<sub>2</sub>(L)] (**6**), and [PtCl(L)<sub>2</sub>][AgCl<sub>2</sub>] (**7**) have been obtained from the carbene transfer reactions of [Ag(L)Cl] (**2**). These complexes have been fully characterized by spectroscopic methods and single-crystal X-ray structure analyses. The mono(carbene)palladium and bis(carbene)platinum complexes display normal square-planar structures. Nickel complexes **3** and **4** are rare examples of paramagnetic nickel(II) complexes of *N*-heterocyclic carbenes having octahedral geometry.

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## 1. Introduction

The first isolation of stable *N*-heterocyclic carbene (NHC) by Arduendo [1] inspired the development of organometallic and coordination chemistry of NHC ligands. Very new trends about carbodicarbenes have appeared from the Bertrand's group [2]. *N*-Heterocyclic carbenes have proved an alternative of tertiary phosphines in homogeneous catalysis since their strong σ-donating ability resembles that of phosphines [3]. Transition metal complexes of NHCs are suitable catalyst precursors that are more stable to air, moisture, and heat and are more tolerant toward oxidation than their phosphine counterparts. NHC complexes of transition metals have showed enhanced catalytic activity in many organic transformations such as polymerization [4], metathesis [5], hydrosilylation [6], and C–C coupling reactions [7]. A large number of nickel [8], palladium [9], and platinum [10] complexes of NHC ligands have been prepared and structurally characterized in the recent decade because of practical demands of non-phosphine catalyst systems. The heteroditopic ligands that incorporate strongly coordinating function of *N*-heterocyclic carbene along with a more labile heteroatoms such as N, O, P, and S moieties are quite promising. The combination of the carbene moiety with a pyridine [11], pyrazole [12], amine and imine [7c,13], ether and phenol [14], thioether [15], or

phosphine [10b,15a,16] groups allows a tuning of the metal coordination sphere. Complexes with donor-functionalized bidentate carbene ligands have been employed as catalysts for a number of catalytic transformations. The strongly bonded carbene donor function favors to the stabilization of metal complexes in different oxidation states, while the hemilabile behaviour of the heteroatom donor groups allow reversible dissociation from the metal center, thereby generating vacant coordination sites for substrate complexation in catalytic cycles.

Very recently we reported the synthesis and characterization of a few pyridine-functionalized bis(NHC) complexes of nickel which are good catalyst for Suzuki and Kumada reactions under mild conditions [7d,8i]. We found that pyridine-functionalized NHCs form square-planar nickel complexes, whereas the analogous pyrimidine-functionalized NHC ligand forms an unusual penta-coordinated palladium complex, which is also an efficient catalyst precursor for Heck coupling reaction [17]. To further explore the coordination behaviour of pyrimidine-functionalized NHC ligand, here in this paper we describe the synthesis and characterization of nickel, palladium, and platinum complexes of 2-(3-mesitylimidazolylidene)pyrimidine (L).

## 2. Results and discussion

Nickel(II), palladium(II), and platinum(II) complexes of NHCs are usually synthesized via three routes. Although the reaction of a free carbene with a metal salt is useful, the generation of free

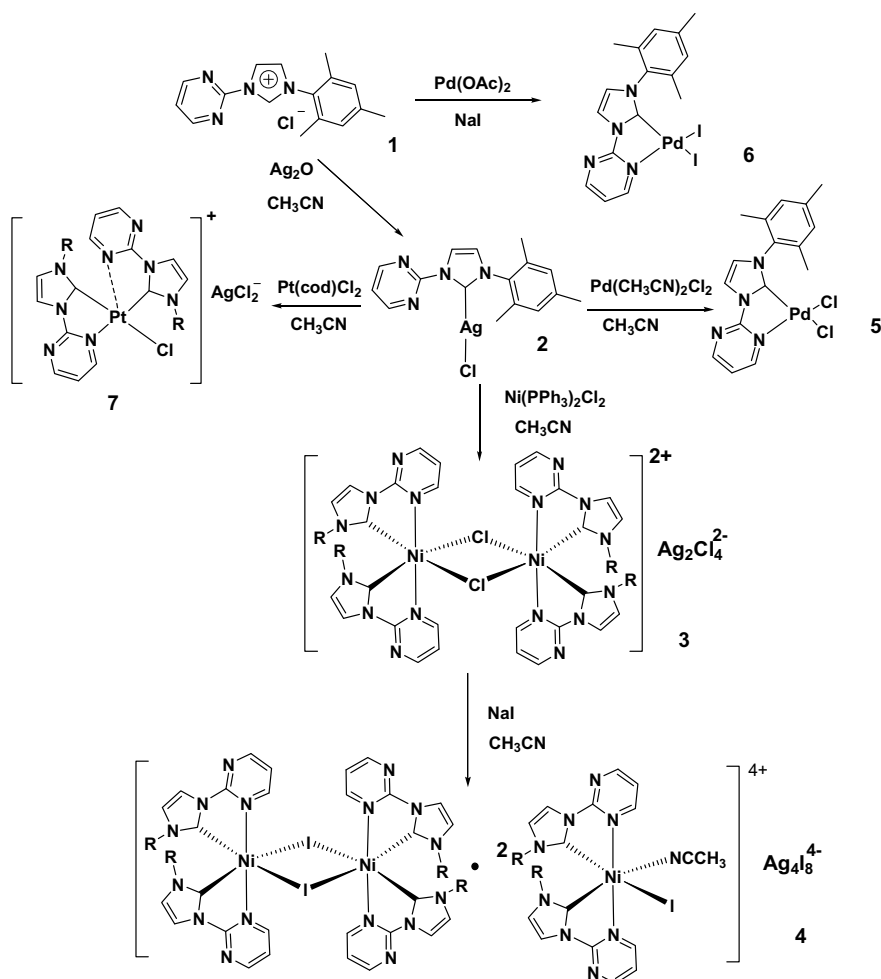
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carbenes often requires special bases and handling unstable free carbenes require harsh conditions. The direct reaction of an imidazolium salt and Pd(OAc)<sub>2</sub> has been shown to form Pd–NHC complexes, but this route is usually suitable for palladium, and there have been few reports of Ni- and Pt–NHC complexes generated by this procedure. Some platinum–NHC complexes can be prepared from 2-functionalized isocyanides [18]. A popular route for the preparation of Ni, Pd, and Pt complexes is the transmetalation of the NHC from a silver complex that can be synthesized by reacting Ag<sub>2</sub>O with the imidazolium salt, originally reported by Wang and Lin [19]. This transmetalation is especially useful for NHCs that are difficult to isolate or that are somewhat unstable as free carbenes. The nickel, palladium, and platinum complexes reported here are prepared using the corresponding silver–NHC as intermediate (see Scheme 1).

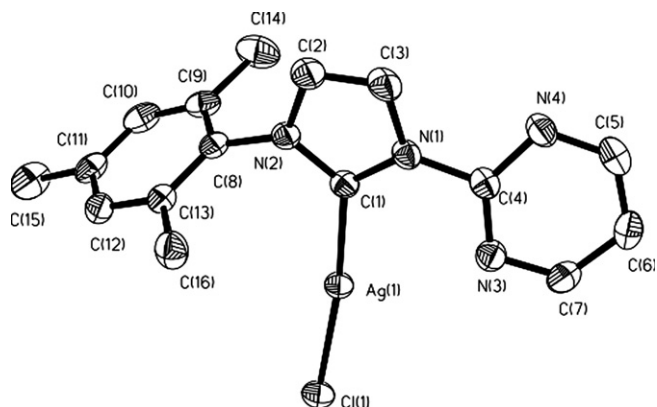
The imidazolium salt, 2-(3-mesitylimidazoliumyl)-pyrimidine chloride (**1**, L · HCl) was easily obtained by reacting *N*-mesitylimidazole and 2-chloropyrimidine in refluxing toluene. The formation of the imidazolium salt is identified by the observation of the downfield resonance signal at 10.40 ppm due to acidic NCHN proton in its <sup>1</sup>H NMR spectrum. The deprotonation of **1** with Ag<sub>2</sub>O in CH<sub>3</sub>CN afforded the expected silver–NHC complex [Ag(L)Cl] (**2**, L = 2-(3-mesitylimidazolylidene)pyrimidine) at room temperature. <sup>13</sup>C NMR spectrum reveals a singlet at 184.6 ppm characteristic of silver–NHC complexes. The ESI-MS spectrum of **2** in acetonitrile exhibits the most intense peak at 635.19 amu and a weak peak at 265.25 amu corresponding to bis(carbene)silver

[Ag(L)<sub>2</sub>]<sup>+</sup> and L<sup>+</sup>, respectively. No peak assignable to [Ag(L)Cl]<sup>+</sup> and [Ag(L)]<sup>+</sup> was observed. This observation demonstrates that [Ag(L)<sub>2</sub>][AgCl<sub>2</sub>] may exist as the major species in solution [20]. The molecular structure of **2** in the solid state was established by X-ray diffraction analysis, which is shown in Fig. 1. The central silver atom is bi-coordinated in linear geometry similar to many known silver complexes [21]. Both Ag–C and Ag–Cl bond distances are normal. The dihedral angle between the imidazolylidene and pyrimidine rings is 23.16°, whereas the dihedral angle between the imidazolylidene and mesitylene is 78.83°. The pyrimidine moiety is arranged with one of the nitrogen atom pointing toward the metal center. The Ag(1)–N(3) distance of 2.954 Å is relatively long illustrating that there is no significant interaction of the pyridimidine with the silver ion.

Addition of an acetonitrile solution of **2** to a half equivalent of [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] in the same solvent readily leads to the formation of the dinuclear nickel complex [Ni<sub>2</sub>(μ-Cl)<sub>2</sub>(L)<sub>4</sub>][Ag<sub>2</sub>Cl<sub>4</sub>] (**3**) due to a carbene transfer reaction. Using an excess of [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] the reaction still affords the same compound other than the expected [NiCl<sub>2</sub>(L)] compound. The compound was isolated as a paramagnetic brown solid that is stable to air in the solid and in solution. It is soluble in acetonitrile and methanol and slightly soluble in dichloromethane. ESI-MS spectrum of **3** in acetonitrile shows the most intense peak at 621.29 amu (100%) due to [Ni(L)<sub>2</sub>Cl]<sup>+</sup>, and the second largest peak at 1278.87 amu (47%) assigned to [Ni<sub>2</sub>(L)<sub>4</sub>Cl<sub>3</sub>]<sup>+</sup>, illustrating that both dimer and monomer exist in solution and in gas phase.

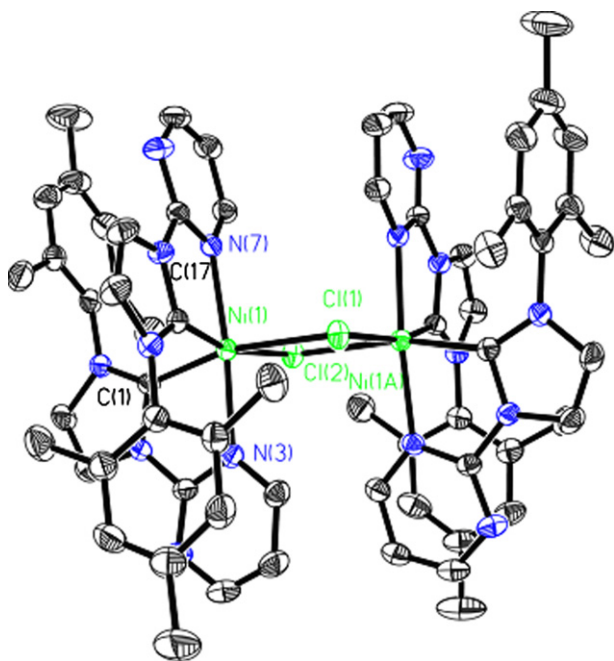


Scheme 1. Synthesis of Ni, Pd, Pt complexes 2–7.



**Fig. 1.** ORTEP drawing of complex **2** showing atomic numbering scheme at 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ag(1)–Cl(1) 2.073(4), Ag(1)–Cl(11) 2.318(1), C(1)–Ag(1)–Cl(1) 170.95(11).

Because of its paramagnetic nature, the characterization of compound **3** is based on X-ray diffraction analysis. The structure of **3** is depicted in Fig. 2 with selected bond lengths and angles listed in the caption. The complex consists of discrete  $[\text{Ni}_2(\mu\text{-Cl})_2(\text{L})_4]^{2+}$  and  $[\text{Ag}_2(\mu\text{-Cl})_2\text{Cl}_2]^{2-}$  in its lattice. Half of one molecule comprises the asymmetric unit of its structure, and the whole structure is generated through the inversion center lying at the center of the  $[\text{Ni}_2(\mu\text{-Cl})_2]$  core. In the cation, both nickel ions are hexa-coordinated in distorted octahedral geometry and each metal ion is surrounded by two chelating 2-(3-mesitylimidazolylidene)pyrimidine ligands two bridging chlorides. The two NHCs are *trans*-positioned to two chlorides at the equatorial plane, and two pyrimidines are mutually *trans*-arranged at the axial positions.



**Fig. 2.** ORTEP drawing of the cation of complex **3** showing atomic numbering scheme at 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ni(1)–C(1) 2.036(4), Ni(1)–C(17) 2.036(4), Ni(1)–N(3) 2.156(3), Ni(1)–N(7) 2.157(3), Ni(1)–Cl(1) 2.470(1), Ni(1)–Cl(2) 2.489(1), C(1)–Ni(1)–C(17) 99.24(15), C(1)–Ni(1)–N(3) 78.14(14), C(17)–Ni(1)–N(3) 98.32(14), C(1)–Ni(1)–N(7) 98.26(13), C(17)–Ni(1)–N(7) 78.23(14), N(3)–Ni(1)–N(7) 174.64(12), C(1)–Ni(1)–Cl(1) 165.34(11), C(17)–Ni(1)–Cl(1) 90.32(11), N(3)–Ni(1)–Cl(1) 89.55(9), N(7)–Ni(1)–Cl(1) 94.54(8), C(1)–Ni(1)–Cl(2) 90.16(11), C(17)–Ni(1)–Cl(2) 165.69(11), N(3)–Ni(1)–Cl(2) 94.15(8), N(7)–Ni(1)–Cl(2) 89.80(9), Cl(1)–Ni(1)–Cl(2) 82.75(4).

The Ni–C bond distances (2.036(4) Å) of the octahedral complex are significantly longer than those of the known Ni–NHC complexes having square planar geometry. The Ni–C bond distances for square-planar nickel(II)–NHC complexes are normally found to range from 1.83 to 1.92 Å [8]. The Ni–N distances (2.156(3) and 2.157(3) Å) are also significantly longer than those of nickel(II) complexes containing pyridine-functionalized NHC ligands [4b,8e,22]. So far most of the structurally characterized nickel(II)–NHC complexes are four-coordinate square-planar complexes which are normally diamagnetic. The tetrahedral complexes and hexa-coordinate octahedral nickel(II)–NHC complexes are quite rare. To the best of our knowledge, only one example of structurally characterized paramagnetic nickel complex  $[\text{Ni}(\mu\text{-Br})_2(\text{L})_2\text{NiBr}_2]$  containing an octahedral and a tetrahedral nickel centers has been reported [23].

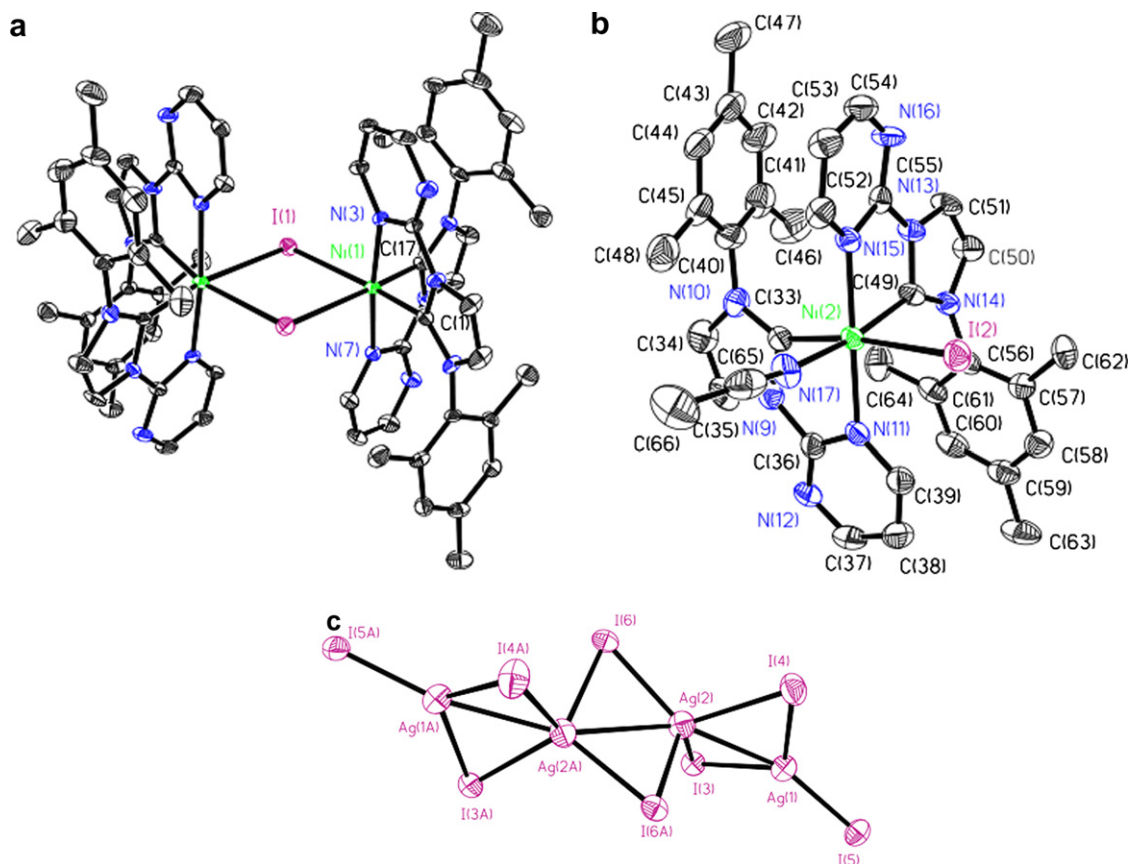
The anionic  $[\text{Ag}_2(\mu\text{-Cl})_2\text{Cl}_2]^{2-}$  has a nearly planar structure, in which two silver ions are bridged by two chlorides adopting triangular coordination geometry. The orthogonal Ag··Ag distance is 3.465 Å excluding argentophilic interaction. The Ag–Ag interaction in some silver–NHC complexes have been previously reported [24].

Treatment of complex **3** with an excess of NaI in acetonitrile yielded  $[\text{Ni}_2(\mu\text{-I})_2(\text{L})_4][\text{Ni}(\text{L})_2(\text{CH}_3\text{CN})_2][\text{Ag}_4\text{I}_8]$  (**4**) as a red solid. Similar to **3**, the compound is also paramagnetic, and its characterization is based on elemental analysis, ESI-MS, and X-ray diffraction studies. As shown in Fig. 3, the asymmetric unit contains two kinds of nickel cations,  $[\text{Ni}_2(\mu\text{-I})_2(\text{L})_4]^{2+}$  and  $[\text{Ni}(\text{L})_2(\text{CH}_3\text{CN})]^+$ , and anionic  $[\text{Ag}_4\text{I}_8]^{4-}$  chain. The dimeric cation,  $[\text{Ni}_2(\mu\text{-I})_2(\text{L})_4]^{2+}$  is isostructural to **3** containing two nickel centers with the same distorted octahedral geometry. Two NHCs *trans* to two iodide ions lie at the equatorial plane of nickel, whereas two pyrimidine moieties are mutually *trans* to each other at the axial positions. The Ni–C and Ni–N bond distances are comparable to those of **3**. The monomeric  $[\text{Ni}(\text{L})_2(\text{CH}_3\text{CN})]^+$  also has an octahedral nickel center but the nickel is surrounded by two chelating 2-(3-mesitylimidazolylidene)pyrimidine ligands, one iodide and one acetonitrile molecule. This cation can be viewed as a cleavage product of  $[\text{Ni}_2(\mu\text{-I})_2(\text{L})_4]^{2+}$  by an acetonitrile molecule. The bond parameters of the monomer do not show notable differences from the dinickel cation. The equatorial Pt–N<sub>acetonitrile</sub> distance is only slightly shorter than those of the axial Pt–N<sub>pyrimidine</sub> bonds.

In the ESI-MS spectrum of **4**, the peaks at 841.37 (100%) and 713.05 (58%) amu were observed ascribed to  $[\text{Ni}_2(\text{L})_2]^+$  and  $[\text{Ni}(\text{L})_2]^+$  fragments, respectively, whereas the peak due to the dimeric  $[\text{Ni}_2(\text{L})_4]^+$  was not seen. It implies that the monomers are the major species in the solution of **4**. However, recrystallization of **4** from its hot acetonitrile solution did not produce pure  $[\text{Ni}(\text{L})_2(\text{CH}_3\text{CN})]^+$  upon cooling.

Tetrameric  $\text{Ag}_4\text{I}_8^{4-}$  anion in **4** is composed of two edge-sharing  $\text{AgI}_4$  tetrahedra and two  $\text{AgI}_3$  planar triangles. Such anionic chain has been found in  $(\text{Pr}_4\text{N})_4\text{Ag}_4\text{I}_8$  [25a] and  $[\text{N-isopentylquinolinium}]_4\text{-Ag}_4\text{I}_8$  [25b].

The silver complex **2** was reacted with one equivalent of  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  in acetonitrile at room temperature yielding the neutral  $[\text{PdCl}_2(\text{L})]$  (**5**) as yellow crystalline solid in high yield, whereas the reaction of  $[\text{HL}]^+\text{Cl}^-$  and  $\text{Pd}(\text{OAc})_2$  in the presence of NaI afforded  $[\text{PdI}_2(\text{L})]$  (**6**) as a red solid. The formulation of the two complexes was confirmed by elemental analysis.  $^1\text{H}$  NMR spectrum of **5** in  $\text{DMSO-}d_6$  shows two not well-resolved doublets at 9.41 and 9.13 ppm assignable to 4- and 6-positioned protons of pyrimidine.  $^{13}\text{C}$  NMR spectrum of **5** also shows two different peaks due to 4- and 6-positioned carbon atoms. These results illustrate that the rotation of pyrimidine is prohibited upon complexation. The  $^{13}\text{C}$  resonance peak of the carbonyl carbon appears at 154.3 ppm, which is consistent with those of known palladium–NHC complexes. Different from **5**, the iodide gives a broad peak at 9.48 ppm due to 4- and 6-positioned protons of pyrimidine,

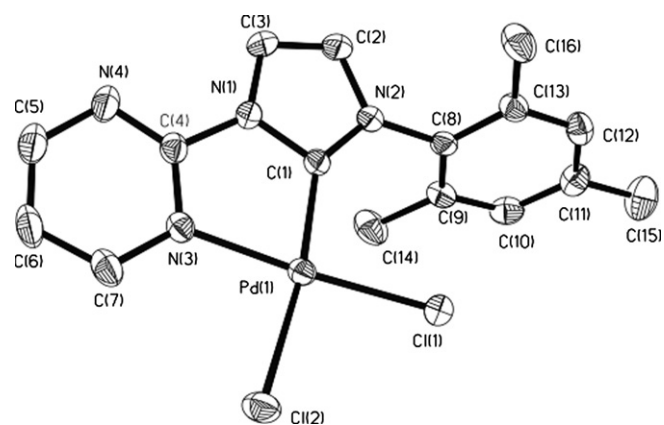


**Fig. 3.** ORTEP drawing of the discrete cations (a and b) and anion (c) of complex **4** showing atomic numbering scheme at 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ni(1)–C(17) 2.020(9), Ni(1)–C(1) 2.025(9), Ni(2)–C(49) 2.038(9), Ni(2)–C(33) 2.054(10), Ni(1)–N(7) 2.128(7), Ni(1)–N(3) 2.130(6), Ni(2)–N(15) 2.114(7), Ni(2)–N(11) 2.148(8), Ni(1)–I(1) 2.808(1), Ni(1)–I(1)#1 2.889(1), Ni(1)#1–I(1) 2.888(1), Ni(2)–I(2) 2.843(1), C(17)–Ni(1)–C(1) 102.8(3), C(17)–Ni(1)–N(7) 78.2(3), C(1)–Ni(1)–N(7) 97.5(3), C(17)–Ni(1)–N(3) 98.6(3), C(1)–Ni(1)–N(3) 78.7(3), N(7)–Ni(1)–N(3) 174.5(2), C(17)–Ni(1)–I(1) 89.6(2), C(1)–Ni(1)–I(1) 166.7(2), N(7)–Ni(1)–I(1) 89.53(17), N(3)–Ni(1)–I(1) 95.0(2), C(17)–Ni(1)–I(1)#1 170.5(2), C(1)–Ni(1)–I(1)#1 85.7(2), N(7)–Ni(1)–I(1)#1 96.6(2), N(3)–Ni(1)–I(1)#1 87.1(2), I(1)–Ni(1)–I(1)#1 82.3(1), C(49)–Ni(2)–C(33) 92.9(4), C(49)–Ni(2)–N(17) 170.3(4), C(33)–Ni(2)–N(17) 89.6(4), C(49)–Ni(2)–N(15) 78.8(3), C(33)–Ni(2)–N(15) 101.3(4), N(17)–Ni(2)–N(15) 91.5(3), C(49)–Ni(2)–N(11) 99.5(3), C(33)–Ni(2)–N(11) 77.9(4), N(17)–Ni(2)–N(11) 90.2(3), N(15)–Ni(2)–N(11) 178.1(3), C(49)–Ni(2)–I(2) 92.8(3), C(33)–Ni(2)–I(2) 172.3(3), N(17)–Ni(2)–I(2) 85.6(2), N(15)–Ni(2)–I(2) 84.9(2), N(11)–Ni(2)–I(2) 96.1(2). Symmetry code: #1  $-x + 1, y, -z + 1/2$ .

illustrating that two protons adjacent to two nitrogen atoms of pyrimidine are magnetically equal. The carbenic carbon resonance of **5** at 154.3 ppm, the normal position for palladium–NHC complexes [10]. The corresponding  $^{13}\text{C}$  signal of **6** due to carbenic carbon was not observed. Obviously, complex **6** is fluxional in solution.

Slow diffusion of diethyl ether into the acetonitrile solutions of **5** and **6** yielded suitable single crystals for X-ray diffraction studies. The structures of **5** and **6** are shown in Figs. 4 and 5, respectively. The structure determination showed that the two compounds are both square-planar. The asymmetric unit of **5** contains two independent molecules which are essentially the same, and thus only one is shown in Fig. 5. The Pd–C and Pd–X bond distances are normal and consistent with those of palladium(II) halide complexes containing NHC ligands. The bond distance of Pd–X trans to NHC ligand is longer than that of Pd–X trans to pyridine group for both **5** and **6** due to larger *trans* effect of the carbene ligand. The mesityl ring plane is twisted out of the coordination plane, and the dihedral angles between the coordination plane of palladium and the mesityl plane are 72.47° and 84.40° for **5** and **6**, respectively, while the imidazolylidene ring and the pyrimidyl ring are essentially coplanar. We have noted that the imidazolium salt and some related palladium complexes have been reported previously [7h,16k,26].

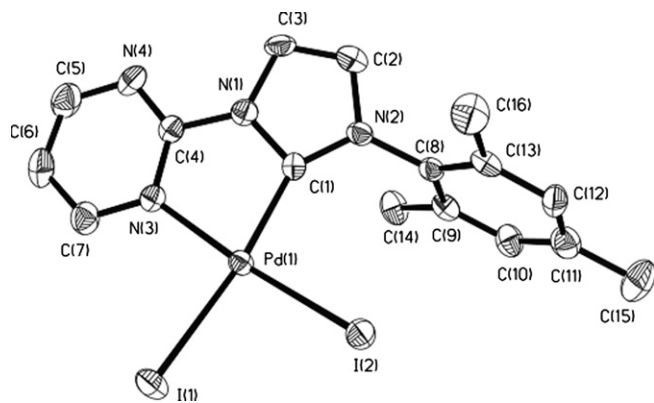
Treatment of **2** with one equivalent of  $\text{Pt}(\text{cod})\text{Cl}_2$  in acetonitrile did not yield the expected isostructural compound of **5**, instead,



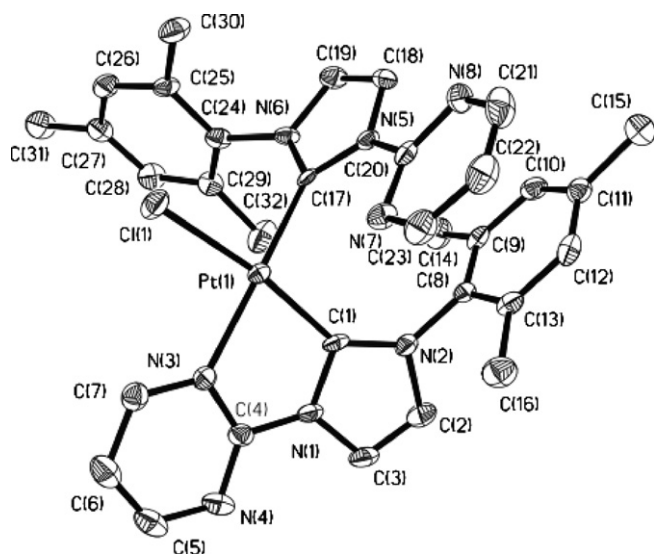
**Fig. 4.** ORTEP drawing of the cation of complex **5** showing atomic numbering scheme at 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.964(3), Pd(1)–N(3) 2.055(2), Pd(1)–Cl(1) 2.292(1), Pd(1)–Cl(2) 2.344(1), C(1)–Pd(1)–N(3) 79.66(10), C(1)–Pd(1)–Cl(1) 96.02(8), N(3)–Pd(1)–Cl(1) 175.59(7), C(1)–Pd(1)–Cl(2) 171.95(8), N(3)–Pd(1)–Cl(2) 92.43(7), Cl(1)–Pd(1)–Cl(2) 91.91(3).

$[\text{PtCl}(\text{L})_2][\text{AgCl}_2]$  (**7**) was obtained in high yield. Even an excess of  $\text{Pt}(\text{cod})\text{Cl}_2$  was employed, the bis(NHC) compound was still the sole product. The asymmetric unit of the complex consists of discrete  $[\text{PtCl}(\text{L})_2]^+$  and  $[\text{AgCl}_2]^-$  pair. An ORTEP drawing the cationic





**Fig. 5.** ORTEP drawing of the cation of complex 6 showing atomic numbering scheme at 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 2.009(8), Pd(1)–N(3) 2.106(7), Pd(1)–I(2) 2.574(1), Pd(1)–I(1) 2.632(1), C(1)–Pd(1)–N(3) 79.3(3), C(1)–Pd(1)–I(2) 96.4(2), N(3)–Pd(1)–I(2) 174.17(18), C(1)–Pd(1)–I(1) 172.5(2), N(3)–Pd(1)–I(1) 93.64(19), I(2)–Pd(1)–I(1) 90.56(3).



**Fig. 6.** ORTEP drawing of the cation of complex 7 showing atomic numbering scheme at 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): Pt(1)–C(17) 1.972(5), Pt(1)–C(1) 1.988(6), Pt(1)–N(3) 2.077(5), Pt(1)–Cl(1) 2.316(2), C(17)–Pt(1)–C(1) 99.8(2), C(17)–Pt(1)–N(3) 173.8(2), C(1)–Pt(1)–N(3) 78.7(2), C(17)–Pt(1)–Cl(1) 88.47(16), C(1)–Pt(1)–Cl(1) 171.75(17), N(3)–Pt(1)–Cl(1) 93.06(14).

section of **7** as well as selected bond angles and distances for complex **7** are given in Fig. 6. The central platinum atom is surrounded by a chloride ion and two 2-(3-mesitylimidazolylidene)pyrimidine ligands in a square-planar geometry. One 2-(3-mesitylimidazolylidene)pyrimidine is bound in a bidentate fashion and coplanar with the coordination plane. The Pt–C bond of the chelate NHC ligand *trans* to chloride is slightly longer than that of the sec-

ond NHC ligand *trans* to pyrimidine (Pt(1)–C(1) = 1.988(6) Å and Pt(1)–C(17) = 1.972(5) Å). One of the pyrimidine group lie up the coordination plane with one nitrogen atom directed toward Pt. The bond distance (3.027 Å) between Pt and N(7) is relatively long illustrating the second pyrimidine ring is not coordinated. The central metal atom is only deviated 0.048 Å from the C<sub>2</sub>NCl plane toward N(7). The pyrimidine and imidazolylidene rings are roughly co-planar for both 2-(3-mesitylimidazolylidene)pyrimidine ligands. In the crystal, the molecule adopts a conformation in which the mesityl of the chelate L and the uncoordinated pyrimidyl ring lie on the same side with respect to the coordination plane, and the rings are nearly parallel with a small dihedral angle of 4°. Because of the large interligand repulsion between the mesityl and the pyrimidyl groups, the two *cis*-arranged imidazolylidene rings are twisted with a dihedral angle of 72.76°. The dihedral angles between imidazolylidene ring and the mesityl ring of the bidentate (83.84°) and monodentate (77.16°) NHC ligand are not much different from each other. In addition, no Ag...Pt interaction is observed as evidenced by the long Ag...Pt distance of 5.547 Å. The dative Pt → Ag bonds have been reported recently for a number of heteronuclear platinum–silver complexes [27].

In both <sup>1</sup>H and <sup>13</sup>C spectra of the Pt–NHC complex only one set of resonance signals assigned to the two ligands has been observed, illustrating that the two inequivalent ligands in solid state (Fig. 6) become equal in solution because of fluxional behaviour depicted in Scheme 2. Three pyrimidine protons are observed at 9.75 and 9.15 ppm as doublet of doublet, and 7.76 ppm as a triplet. <sup>13</sup>C NMR spectrum display a singlet at 143.8 ppm due to two carbene carbon, but no <sup>195</sup>Pt–<sup>13</sup>C coupling was observed. The solid state structure implies the penta-coordinated intermediate in the association and dissociation equilibrium (Scheme 2).

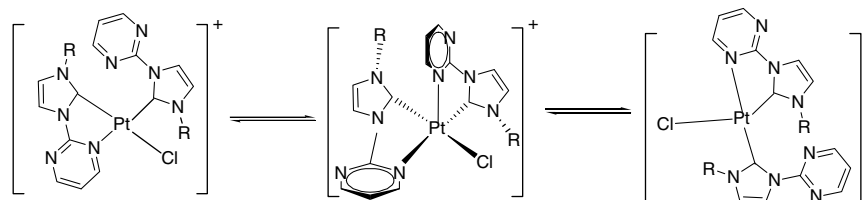
### 3. Conclusions

In summary, we have demonstrated that the transmetalation reactions between [Ag(L)Cl] and Ni(II), Pd(II), and Pt(II) dihalides can successfully afford metal–NHC complexes with different structural motifs. Palladium forms neutral mono(NHC) complex of the formulation [PdCl<sub>2</sub>(L)] and platinum yields bis(NHC) complex [PtCl(L)<sub>2</sub>]<sup>+</sup>. Both complexes have normal square-planar structures. In the case of nickel, unusual 6-coordinate dinuclear complexes were obtained. Variation of the central metals lead to a dramatical change of the coordination behaviour of the NHC ligand. The structural elucidation of 4- to 6-coordinate d<sup>8</sup> metal complexes may provide valuable clues for the study of mechanism of catalytic reactions they participate.

### 4. Experimental

#### 4.1. General procedures

All chemicals were of reagent grade quality obtained from commercial sources and used as received, unless stated otherwise. N-Mesitylbenzoimidazole was prepared according to the known



**Scheme 2.**

procedures [28].  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts ( $\delta$ ) are expressed in ppm downfield to TMS at  $\delta = 0$  ppm and coupling constants ( $J$ ) are expressed in hertz. ESI-mass spectral data were acquired using a Waters Micromass ZQ mass spectrometer (+ mode, ESI source).

#### 4.2. Synthesis of 2-(3-mesitylimidazolium)pyrimidine chloride, **1**

A solution of *N*-mesitylimidazole (1.0 g, 5.4 mmol) and 2-chloropyrimidine (0.7 g, 6.1 mmol) in toluene (20 mL) was refluxed overnight. The resulted white solid was filtered and washed with ether. Yield: 1.35 g, 83%. Anal. Calc. for  $\text{C}_{16}\text{H}_{17}\text{ClN}_4$ : C, 63.89; H, 5.70; N, 18.63. Found: C, 63.64; H, 5.72; N, 18.56%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 10.40 (s, NCHN, H), 9.00 (d,  $J = 4.8$  Hz, *o*- $\text{C}_4\text{H}_3\text{N}$ , 2H), 8.72 (s, imi-*H*, H), 8.13 (s, imi-*H*, H), 7.78 (t,  $J = 4.8$  Hz, *p*- $\text{C}_4\text{H}_3\text{N}$ , H), 7.04 (s,  $\text{CCH}_2\text{C}$ , 2H), 2.35 (s,  $\text{CCH}_3$ , 3H), 2.19 (s,  $\text{C}(\text{CH}_3)_2$ , 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 159.8, 151.8, 141.3, 135.5, 133.7, 130.3, 129.7, 126.2, 122.8, 120.2, 20.9, 17.6.

#### 4.3. Synthesis of $[\text{Ag}(\text{L})\text{Cl}]$ , **2**

A solution of **1** (120 mg, 0.4 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) was treated with  $\text{Ag}_2\text{O}$  (48 mg, 0.2 mmol). The mixture was stirred at room temperature for 30 min with exclusion of light. After filtration through a plug of Celite, the solvent was removed in vacuo and washed with ether. Complex **2** was obtained as a white power. Yield: 133 mg, 82%. Anal. Calc. for  $\text{C}_{16}\text{H}_{16}\text{AgClN}_4$ : C, 47.14; H, 3.96; N, 13.74. Found: C, 47.13; H, 3.94; N, 13.76%.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ): 8.90 (d,  $J = 4.8$  Hz, 4- and 6- $\text{C}_4\text{H}_3\text{N}_2$ , 2H), 8.47 (d,  $J = 2.4$  Hz, imi-*H*, 1H), 7.78 (d,  $J = 2.4$  Hz, imi-*H*, 1H), 7.65 (t,  $J = 4.8$  Hz, 5- $\text{C}_4\text{H}_3\text{N}_2$ , 2H), 7.09 (s, mesityl, 2H), 2.34 (s,  $\text{CH}_3$ , 3H), 1.95 (s,  $\text{CH}_3$ , 6H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ): 184.6 (Ag-C), 160.5, 156.0, 139.9, 137.1, 135.2, 130.1, 125.9, 122.6, 120.7, 21.7, 18.4.

#### 4.4. Synthesis of $[\text{Ni}_2(\mu\text{-Cl})_2(\text{L})_4][\text{Ag}_2\text{Cl}_4] \cdot 2\text{Et}_2\text{O}$ , **3**

A solution of **1** (120 mg, 0.4 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) was treated with  $\text{Ag}_2\text{O}$  (48 mg, 0.2 mmol). The mixture was stirred at room temperature for 2 h with exclusion of light. Then  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  (130 mg, 0.2 mmol) was added to the solution and stirred at room temperature for 2 h. The color of the solution changed to dark green. After filtration through a plug of Celite, the solvent was removed and the residue was washed with diethyl ether. The compound was obtained as a brown solid. Yield: 65 mg, 46.3%. Anal. Calc. for  $\text{C}_{72}\text{H}_{84}\text{Ag}_2\text{Cl}_6\text{N}_{16}\text{Ni}_2\text{O}_2 \cdot 3\text{CH}_3\text{CN}$ : C, 49.98; H, 5.00; N, 14.20. Found: C, 49.86; H, 4.76; N, 14.31%. Crystals suitable for X-ray diffraction were grown by slow diffusion of  $\text{Et}_2\text{O}$  into its  $\text{CH}_3\text{CN}$  solution.

#### 4.5. Synthesis of $[\text{Ni}_2(\mu\text{-I})_2(\text{L})_4][\text{Ni}(\text{L})_2(\text{CH}_3\text{CN})_2][\text{Ag}_4\text{I}_8] \cdot 4\text{CH}_3\text{CN}$ , **4**

A solution of **1** (120 mg, 0.4 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) was treated with  $\text{Ag}_2\text{O}$  (48 mg, 0.2 mmol). The mixture was stirred at room temperature for 2 h with exclusion of light.  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  (130 mg, 0.2 mmol) was added to the solution and stirred at room temperature for 2 h. Then an excess of NaI (300 mg, 2.0 mmol) was added to the solution giving a suspension, which turned to dark red. The suspension was stirred at room temperature overnight, and the solvent was removed in vacuo. The residue was redissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$  and filtered by passing through a plug of Celite. Yield: 78 mg, 29.8%. Anal. Calc. for  $\text{C}_{140}\text{H}_{146}\text{Ag}_4\text{I}_2\text{N}_{38}\text{Ni}_4 \cdot 10\text{CH}_2\text{Cl}_2$ : C, 33.04; H, 2.93; N, 10.10. Found: C, 33.37; H, 3.10; N, 9.86%. Crystals suitable for X-ray diffraction were grown by slow diffusion of  $\text{Et}_2\text{O}$  into its  $\text{CH}_2\text{Cl}_2$  solution.

#### 4.6. Synthesis of $[\text{PdCl}_2(\text{L})_2] \cdot \text{CH}_3\text{CN}$ , **5**

A solution of **1** (120 mg, 0.4 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) was treated with  $\text{Ag}_2\text{O}$  (48 mg, 0.2 mmol). The mixture was stirred at room temperature for 2 h with exclusion of light. Then the mixture was filtered and  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  (130 mg, 0.2 mmol) was added to the filtrate. The mixture was allowed to react 2 h at room temperature. After filtration through a plug of Celite, the solvent was removed in vacuo and the residue was washed with diethyl ether. Complex **5** was obtained as a yellow power. Yield: 129 mg, 67%. Anal. Calc. for  $\text{C}_{18}\text{H}_{19}\text{Cl}_2\text{N}_5\text{Pd}$ : C, 44.79; H, 3.97; N, 14.51. Found: C, 44.94; H, 3.97; N, 14.85%.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ): 9.40, 9.12 (both br, 4- and 6- $\text{C}_4\text{H}_3\text{N}_2$ , each 1H), 8.38, 7.60 (both d,  $J = 2.0$  Hz, imi-*H*, each 1H), 7.77 (t,  $J = 4.8$  Hz, 5- $\text{C}_4\text{H}_3\text{N}_2$ , 1H), 7.00 (s, mesityl, 2H), 2.30 (s,  $\text{CH}_3$ , 3H), 2.07 (s,  $\text{CH}_3$ , 6H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ): 161.6, 158.5, 156.9, 154.3 (Pd-C), 138.8, 135.1, 134.5, 128.8, 126.3, 120.8, 118.2, 21.1, 17.9. Crystals suitable for X-ray diffraction were grown by slow diffusion of  $\text{Et}_2\text{O}$  into its  $\text{CH}_3\text{CN}$  solution.

#### 4.7. Synthesis of $[\text{PdI}_2(\text{L})]$ , **6**

A mixture of  $\text{Pd}(\text{OAc})_2$  (50 mg, 0.22 mmol), **1** (66 mg, 0.22 mmol) and NaI (415 mg, 2.5 mmol) in 10 mL of THF was stirred at room temperature for 2 h. The solvent was removed in vacuo leaving a dark solid. The residue was dissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$ , and filtered through a plug of Celite. After removal of the solvent, the residue was washed with diethyl ether and dried. Yield: 112 mg, 44.9%. Anal. Calc. for  $\text{C}_{16}\text{H}_{16}\text{I}_2\text{N}_4\text{Pd}$ : C, 30.77; H, 2.58; N, 8.97. Found: C, 30.86; H, 2.60; N, 9.02%.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ): 9.49 (br s, 4- and 6- $\text{C}_4\text{H}_3\text{N}_2$ , 2H), 8.39, 7.62 (both d,  $J = 2.0$  Hz, imi-*H*, each 1H), 7.81 (t,  $J = 4.8$  Hz, 5- $\text{C}_4\text{H}_3\text{N}_2$ , 2H), 7.00 (s, mesityl, 2H), 2.32 (s,  $\text{CH}_3$ , 3H), 2.00 (s,  $\text{CH}_3$ , 6H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ): 161.2, 157.2, 139.4, 136.6, 135.0, 129.1, 125.7, 121.3, 118.9, 21.2, 18.4. The carbene  $^{13}\text{C}$  NMR resonance of carbenic carbon was not observed. Crystals suitable for X-ray diffraction were grown by slow diffusion of  $\text{Et}_2\text{O}$  into its  $\text{CH}_2\text{Cl}_2$  solution.

#### 4.8. Synthesis of $[\text{PtCl}(\text{L})_2][\text{AgCl}_2]$ , **7**

A solution of **1** (120 mg, 0.4 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) was treated with  $\text{Ag}_2\text{O}$  (48 mg, 0.2 mmol). The mixture was stirred at room temperature for 2 h with exclusion of light. Then  $\text{Pt}(\text{cod})\text{Cl}_2$  (130 mg, 0.2 mmol) was added to the solution and stirred at room temperature for 2 h. After filtration through a plug of Celite, the solvent was removed in vacuo and washed with diethyl ether. Complex **7** was obtained as a yellow solid. Yield: 104 mg, 55.6%. Anal. Calc. for  $\text{C}_{32}\text{H}_{32}\text{AgCl}_3\text{N}_8\text{Pt}$ : C, 40.98; H, 3.44; N, 11.95. Found: C, 41.12; H, 3.62; N, 12.18%.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ): 9.75, 9.15 (both dd,  $J = 2.0$ ,  $J = 4.8$  Hz, 4- and 6- $\text{C}_4\text{H}_3\text{N}_2$ , each 2H), 8.34, 7.61 (both d,  $J = 2.0$  Hz, imi-*H*, each 2H), 7.76 (t,  $J = 4.8$  Hz, 5- $\text{C}_4\text{H}_3\text{N}_2$ , 2H), 6.99 (s, mesityl, 4H), 2.30 (s,  $\text{CH}_3$ , 6H), 2.07 (s,  $\text{CH}_3$ , 12H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ): 160.9, 158.2, 157.0, 143.8 (Pt-C), 138.9, 135.0, 134.7, 129.0, 126.2, 120.4, 118.5, 117.8, 21.2, 17.9.

#### 4.9. X-ray diffraction analysis

Single-crystal X-ray diffraction data for the complexes were collected at 298(2) K on a Siemens SMART/CCD area-detector diffractometer with a Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) by using an  $\omega$ -2 $\theta$  scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software [29]. All structures were solved by direct methods and refined against  $F^2$  by the full-matrix least squares techniques [30]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their calculated

**Table 1**  
Summary of X-ray crystallographic data for complexes 2–7

	2	3	4	5	6	7
Formula	C <sub>16</sub> H <sub>16</sub> AgClN <sub>4</sub>	C <sub>72</sub> H <sub>84</sub> Ag <sub>2</sub> Cl <sub>6</sub> N <sub>16</sub> ·Ni <sub>2</sub> O <sub>2</sub>	C <sub>140</sub> H <sub>146</sub> Ag <sub>4</sub> I <sub>2</sub> ·N <sub>38</sub> Ni <sub>4</sub>	C <sub>18</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>5</sub> Pd	C <sub>16</sub> H <sub>16</sub> I <sub>2</sub> N <sub>4</sub> Pd	C <sub>32</sub> H <sub>32</sub> AgCl <sub>3</sub> N <sub>8</sub> Pt
Formula weight	407.65	1751.41	4550.07	482.68	624.55	937.97
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /c	C2/c	C2/c	P2 <sub>1</sub> /c	P2 <sub>1</sub>	P2 <sub>1</sub> /c
a (Å)	9.9780(8)	19.536(2)	39.269(4)	10.488(1)	7.932(1)	17.285(2)
b (Å)	13.018(2)	17.336(2)	16.904(1)	14.315(1)	16.130(2)	12.081(1)
c (Å)	14.385(1)	23.818(3)	25.328(3)	13.789(1)	14.986(2)	16.046(2)
β (°)	116.855(6)	100.397(2)	100.220(2)	105.691(2)	102.123(2)	99.439(2)
V (Å <sup>3</sup> )	1658.6(3)	7934.0(16)	16546(3)	1993.1(3)	1874.5(4)	3305.5(8)
Z	4	4	4	4	4	4
D (g cm <sup>-3</sup> )	1.633	1.466	1.827	1.609	2.213	1.885
Reflections collected	8251	20299	42649	9822	9527	16072
Independent reflections, R <sub>int</sub>	2962, 0.0314	6976, 0.0259	14569, 0.0753	3513, 0.0216	5014, 0.0239	5798, 0.0513
Goodness-of-fit on F <sup>2</sup>	1.028	1.038	0.922	1.144	1.091	1.050
R <sub>1</sub> , wR <sub>2</sub> [I > 2σ(I)]	0.0312, 0.0693	0.0416, 0.0896	0.0564, 0.1302	0.0247, 0.0563	0.0292, 0.0599	0.0322, 0.0700
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.0529, 0.0831	0.0754, 0.1126	0.1168, 0.1497	0.0360, 0.0659	0.0362, 0.0639	0.0579, 0.0823
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.412 and -0.392	1.208 and -1.409	1.491 and -1.369	0.491 and -0.335	0.535 and -0.872	1.151 and -1.440

positions. Details of the X-ray experiments and crystal data are summarized in Table 1.

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### Appendix A. Supplementary material

CCDC 689319–689324 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.07.026.

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