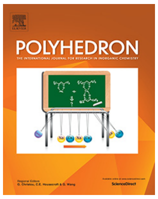
Polyhedron 173 (2019) 114123

Contents lists available at ScienceDirect

Polyhedron

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



Trinuclear Cu(I)–NHC as NHC transfer agent: Synthesis of mono- and di-nuclear palladium and mercury complexes

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ARTICLE INFO

Article history:
Received 7 June 2019
Accepted 17 August 2019
Available online 26 August 2019

Keywords:
Trinuclear Cu–NHC
Transmetallation
Trans influence
Pd–NHC
Double transmetallation

ABSTRACT

Mono and dinuclear palladium–NHC complexes of 1,3-bis(2-pyridyl)imidazolin-2-ylidene (py_2im) ligand, such as $[Pd(py_2im)_2](PF_6)_2$ (**2**) $[Pd_2Cl_2(py_2im)_2](PF_6)_2$ (**3**), and $[PdCl_2(py_2im)]$ (**4**) were synthesized by carbene transfer method using trinuclear Cu(I)–NHC complex, $[Cu_3(py_2im)_3](PF_6)_3$ (**1**). Also addition of PPh_3 to the solution of **3** or in the reaction medium of **1** with $PdCl_2$ resulted in a mononuclear bisphosphine complex $[PdCl(PPh_3)_2(py_2im)](PF_6)$ (**5**) which can also be prepared using *trans*-$[PdCl_2(PPh_3)_2]$ (**6**) and $[Cu(PPh_3)_2(py_2im)](PF_6)$ (**7**) as precursors. In addition a mono nuclear complex $[Hg(py_2im)_2](PF_6)_2$ (**8**) was synthesized through carbene transfer from **1**.

1. Introduction

Since the isolation of *N*-heterocyclic carbene (NHC) by Arduengo an impetuous effort has been given for the synthesis of metal complexes containing NHCs [1]. Among them the late transition metal NHCs complexes have been widely studied due to their potential applications in catalysis [2–17]. In particular the C–C bond coupling reactions are of interest and they are carried out using NHC stabilized palladium dihalide as catalyst. As it is observed that mixed donor ligands in palladium complexes, such as phosphine and pyridine groups, have a tremendous influence on their catalytic activity, it has been extended to palladium complexes containing functionalized NHC ligands [18–23,67]. Indeed the presence of additional tethering in NHCs, with aromatic heterocycles or pendent amino/ether/thioether moiety as hemilabile units, show strong influence in the catalytic activity, especially in C–C bond coupling reactions [24–35].

In general, NHC stabilized metal complexes are prepared by (a) direct reaction of isolated or *in situ* generated NHC with metal precursors, (b) deprotonation of imidazolium salt with basic metal precursors, and (c) carbene transfer method. Out of these, the carbene transfer route using silver–NHC complexes is preferred. This is due to its facile carbene transfer to other metals even in the presence of air or moisture and functional group tolerance. Thus a large number of metal–NHCs, containing functional or non-functional substitutions on the nitrogen centers, have been prepared. However, there were a few drawbacks in this method such as, (a) reaction needs to be performed in the absence of light (b) presence of silver ions in the product and (c) unsuccessful carbene transfer in some cases [36–41]. Recently, an interesting reverse carbene-transfer from nickel to silver has been described by Huynh and co-workers [42]. Therefore, gold- or copper–NHC complexes were chosen as carbene transfer agents alternatively [43–46]. Among them the transfer of NHCs from copper would be preferred, from an economical point of view, because of the availability and the cost effectiveness of copper precursors.

Albrecht and coworkers reported the first example of NHC transfer from copper(I)–NHC to ruthenium(II) complexes [44]. Later, Furst and Cazin synthesized the palladium and gold complexes of non-functionalized NHCs by carbene transfer route from copper(I) complexes [45]. Although a number of palladium complexes 1,3-bis(2-pyridyl)imidazolin-2-ylidene containing functionalized NHCs were successfully synthesized using the corresponding silver carbene complexes, this method could not be applied for the preparation of mononuclear palladium dihalide of (py_2im). Therefore, it is of our interest to synthesize the palladium complexes of pyridyl functionalized NHCs, here with py_2im, starting from the corresponding copper complex.

Similarly, compared to other transition metal–NHC complexes less attention has been given for the synthesis of Hg–NHC complexes. The first mercury–NHC complex was synthesized by Wanzlick and Schönherr in 1968 [47–52]. Since then a number of mercury(II)–NHC complexes have been synthesized by direct metallation using imidazolium salts and Hg-precursors. Recently, mercury–NHCs have been used as transmetallating agents for the synthesis of other transition metal–NHC complexes [48,49]. It is

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https://doi.org/10.1016/j.poly.2019.114123
0277-5387/

noteworthy that the carbene ligand transfer from group 11 to group 12 metals is not known so far.

We have prepared a known trinuclear copper(I) complex (**1**) containing the hemilabile ligand py$_2$im through a simple and cost effective method starting from copper(II) acetate monohydrate and py$_2$imH·PF$_6$ [53–54]. The copper–NHC complex **1** possesses three units of py$_2$im, where the carbene carbon atom is bridged between two copper ions in a constrained environment. Thus it may be easier to transfer py$_2$im from copper centre to other metal ions. With this assumption the reactions of **1** with palladium precursors and mercury salts were carried out by varying the stoichiometry, solvents and by using additional coordinating reagents like PPh$_3$. Herein, we report the synthesis of palladium (**2**–**5**) and mercury (**8**) complexes, obtained through carbene transfer route starting from **1**, and the structural characterizations of **3**–**5**. In addition we also report various synthetic routes to obtain [PdCl(PPh$_3$)$_2$(py$_2$im)](PF$_6$) (**5**) using *trans*-[PdCl$_2$(PPh$_3$)$_2$] (**6**) and [Cu(PPh$_3$)$_2$(py$_2$im)](PF$_6$) (**7**) as precursors.

2. Experimental

2.1. Material and methods

All the carbene transfer reactions were performed using dry solvent under nitrogen atmosphere. Dry CH$_3$OH was prepared by refluxing single distilled methanol over Mg/I$_2$ mixture in methanol and followed by distillation. Acetonitrile was dried over CaH$_2$ and distilled under nitrogen atmosphere [56,57]. Cu(OAc)$_2$·H$_2$O, Hg(OAc)$_2$, HgCl$_2$ and PPh$_3$ were procured from sdfine-chem limited (SDFCL). KPF$_6$, 2-chloropyridine, 2-bromopyridine, N-methylimidazole, PdCl$_2$, and Pd(OAc)$_2$ were obtained from Sigma Aldrich. The ligand 1,3-bis(2-pyridyl) imidazolium hexaflurophosphate (py$_2$imH•PF$_6$) was synthesized according to literature procedure [54,55,61,69]. *Trans*-[PdCl$_2$(PPh$_3$)$_2$] (**6**) was synthesized according to the literature procedure using PdCl$_2$ and PPh$_3$ in DMF [58]. Synthesis of compound **7** has been described in SI.

2.2. Physical measurements

Melting point was measured in a glass capillary under air using a JSGW melting point apparatus. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT-IR spectrometer operating at 4000–400 cm^{-1}. Elemental analyses of the compounds were obtained from thermoquest CE instruments CHNS-O, EA/1110 model and Perkin Elmer Series-II 2400 Elemental Analyzers. ESI-MS) spectra were recorded on a Waters Q-TOF Premier mass spectrometer.^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500FT and JEOL ECS-400 instrument using DMSO-d_6 and CD$_3$CN with TMS as internal standard and all the ^{31}P NMR was recorded in JEOL ECS-400 instrument using DMSO-d_6.

2.3. X-ray crystallographic study

Single crystals suitable for X-ray crystallographic analyses were obtained by the slow evaporation of solvent from the reaction solution. Single crystal X-ray data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART APEX CCD diffractometer at 140 K. The linear absorption coefficients, scattering factors for the atoms and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography. The program SMART was used for collecting frames of data, indexing reflections, and determining lattice parameters. The data integration and reduction were processed with SAINT software. An empirical absorption correction was applied to the collected reflections with SADABS using XPREP. All the structures were solved by the direct method using the program SHELXS-97 [59–60] and refined by full-matrix least squares on F^2, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c, are the observed and calculated structure amplitudes, and the weight $w = 1$. All non-hydrogen atoms were refined with anisotropic displacement parameters in all the structure. The hydrogen atom positions or thermal parameters were not refined but were included in the structure factor calculations.

2.4. Synthesis

2.4.1. Synthesis of [Pd(py$_2$im)$_2$](PF$_6$)$_2$ (**2**)

Method (A). A mixture of [Cu$_3$(py$_2$im)$_3$](PF$_6$)$_3$ (0.13 g, 0.1 mmol) and Pd(OAc)$_2$ (0.02 g, 0.1 mmol) in CH$_3$OH (12 mL) was stirred at room temperature for 24 h. Light green precipitate was obtained which was filtered and dried under vacuum. This solid was washed by ethanol followed by diethyl ether. The solid was dissolved in CH$_3$CN. Colorless crystalline solid of **2** was obtained by slow evaporation at room temperature. Yield: 0.07 g (87% based on Pd(OAc)$_2$). *Method (B)*: A similar procedure was used except that a methanolic solution (20 mL) of **1** (0.39 g, 0.3 mmol) was added PdCl$_2$ (0.05 g, 0.3 mmol) as solid. The solution mixture was stirred at room temperature for 24 h. *Artichoke* green precipitate was obtained which was filtered. The volatiles were removed from the filtrate under vacuum and the residue was washed with diethyl ether. The product was dissolved in CH$_3$CN/CH$_3$OH (2:1) and kept for slow evaporation at room temperature. Colorless crystals of **2** were obtained within two days. Yield of **2**: 0.11 g (44% based on PdCl$_2$). **2**: Mp: 226–228 °C, ^{1}H NMR (CD$_3$CN, 500 MHz): δ 8.47 (d, 4H, ^3J = 4.10 Hz, CH$_{py}$), 8.04 (m, 4H, CH$_{py}$), 7.82 (d, 4H, ^3J = 7.75 Hz, CH$_{py}$), 7.70 (s, 4H, CH$_{im}$), 7.52 (m, 4H, CH$_{py}$). ^{13}C NMR (CD$_3$CN, 125 MHz): δ 155.3 (Pd-C), 150.4, 150.2, 141.8, 125.9, 122.9, 117.2. IR (KBr pellet, cm^{-1}) 3159(m), 2372(m), 1618(s), 1451(vs), 1334(m), 1289(m), 1155(w), 1101(w), 1000(w), 959(w), 839(vs), 736(s), 556(s). ESI-MS: calculated for [C$_{26}$H$_{20}$N$_8$Pd]$^{2+}$, 275.0423, Found: 275.0375. *Anal.* Calc. for C$_{26}$H$_{20}$F$_{12}$N$_8$P$_2$Pd: C, 37.14; H, 2.40; N, 13.33, Found: C, 37.12; H, 2.34; N, 13.06.

2.4.2. Synthesis of [Pd$_2$Cl$_2$(py$_2$im)$_2$](PF$_6$)$_2$ (**3**)

A mixture of **1** (0.39 g, 0.3 mmol) and PdCl$_2$ (0.16 g, 0.9 mmol) in CH$_3$OH (60 mL) was stirred at room temperature for 24 h. A grayish turbid solution was obtained. The solvent was evaporated under vacuum to obtain the *artichoke* green colored residue. The residue was dissolved in CH$_3$CN and CH$_3$OH (1:1) mixture and kept for crystallization. Pale yellow colored hexagonal shaped single crystals suitable for X-ray studies were obtained. Yield: 0.30 g (66% based on PdCl$_2$). **3**: Mp: 222–224 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.86 (d, 1H, ^3J = 5.5 Hz, CH$_{py}$), 8.84 (d, 1H, ^3J = 1.9 Hz, CH$_{im}$), 8.79 (d, 1H, ^3J = 5.3 Hz, CH$_{py}$), 8.47 (m, 1H, CH$_{py}$), 8.38 (d, 1H, ^3J = 8.4 Hz, CH$_{py}$), 8.26 (m, 1H, CH$_{py}$), 8.21 (d, 1H, ^3J = 2.3 Hz, CH$_{im}$), 7.92 (d, 1H, ^3J = 8 Hz, CH$_{py}$), 7.64 (m, 1H, CH$_{py}$), 7.48 (m, 1H, CH$_{py}$); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 154.5 (Pd-C), 153.5, 151.3, 150.7, 148.9, 144.6, 143.6, 127.8, 126.1, 117.9, 113.7, 124.5, 124.3. FT-IR (KBr pellet, cm^{-1}) 3129(w), 2924(w), 1609(s), 1574(w), 1484(s), 1454(s), 1367(w), 1324(m), 1282(w), 1145(w), 1094(w), 1038(w), 957(w), 841(vs), 781(s), 735(s), 557(s). ESI-MS: calcd m/z for [C$_{26}$H$_{20}$Cl$_2$F$_6$N$_8$PPd$_2$]$^+$ 872.8941. Found: 872.8950. *Anal.* Calc. for C$_{26}$H$_{20}$Cl$_2$F$_{12}$N$_8$P$_2$Pd$_2$: C, 30.67; H, 1.98; N, 11.01. Found: C, 30.52; H, 1.97; N, 10.60.

2.4.3. Synthesis of [PdCl$_2$(py$_2$im)] (**4**)

A mixture of **1** (0.39 g, 0.3 mmol) and PdCl$_2$ (0.16 g, 0.9 mmol) in CH$_3$OH or CH$_3$CN (100 mL) was stirred at room temperature for 24 h. Greenish turbid solution was obtained. The solution was filtered. The residue was dissolved in CH$_3$CN/CH$_3$OH (6:1) mixture (100 mL) and the volume was reduced under vacuum to half of the solution. During this process, a yellow block shaped crystalline solid of **4** was obtained. Yield of **4**: 0.06 g, (50%). The latter yellow colored solid was filtered and the filtrate was kept for crystallization to afford pale yellow colored hexagonal shaped crystals of **3**. Yield of **3**: 0.06 g, (20%) **4**: ^{1}H NMR (DMSO-d_6, 500 MHz): δ 9.15 (br), 8.55 (br), 8.38 (br), 8.23 (br), 7.94 (br), 7.69 (br), 7.59 (br). ESI-MS: calcd *m*/*z* for $[C_{13}H_{10}ClN_4Pd]^+$ 364.9626. Found: 364.9628. *Anal.* Calc. for $C_{13}H_{10}Cl_2N_4Pd$: C, 39.08; H, 2.52; N, 14.02. Found: C, 38.95; H, 2.54; N, 13.63.

2.4.4. Synthesis of trans-$[PdCl(PPh_3)_2(py_2im)](PF_6)$ (**5**)

Method (A): A mixture of **3** (0.05 g, 0.05 mmol) and PPh_3 (0.05 g, 0.2 mmol) was taken in CH_3CN (20 mL) and stirred for 7 h. Pale yellow colored precipitate of **5** was obtained which was filtered. Yellow colored crystals of **5** were obtained either from the filtrate at 5 °C or CH_3CN/DCM (1:2) mixture at room temperature. Collective yield is 0.08 g (77%). *Method (B):* To a methanolic solution (30 mL) of **1** (0.13 g, 0.1 mmol), $PdCl_2$ (0.05 g, 0.3 mmol) was added as solid and stirred for 10 min. To this solution PPh_3 (0.16 g, 0.6 mmol) was added as solid. The reaction mixture was stirred for additional 10 h. *Artichoke* green colored precipitate was obtained and the solution was filtered. The residue was washed by CH_3OH and crystallized in CH_3CN. Yield: 0.26 g (88%). *Method (C):* A mixture of **1** (0.13 g, 0.1 mmol) and *trans*-$[PdCl_2(PPh_3)_2]$ (0.21 g, 0.3 mmol) was taken in CH_3OH (30 mL) and stirred for 10 h. Pale yellow precipitate was obtained. The solution was filtered and washed by CH_3OH. Yield: 0.26 g (82%). *Method (D):* A mixture of **1** (0.10 g, 0.1 mmol) and $PdCl_2$ (0.02 g, 0.1 mmol) was taken in CH_3OH (10 mL) and stirred for 10 h. *Artichoke* green precipitate was obtained. The solution was filtered and the precipitate was collected and washed by CH_3OH. Crystals of **5** were obtained in CH_3CN through slow evaporation at room temperature. Yield: 0.073 g (71%). **5**: Mp: 222 °C, ^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.48(d, 1H, $^3J = 4.6$ Hz, CH_{py}), 8.04(d, 2H, $^3J = 8$ Hz, CH_{py}), 7.89(m, 2H, CH_{py}), 7.64(s, 2H, CH_{im}), 7.57(m, 2H, CH_{py}), 7.44 (broad, 6H, CH_{ph}), 7.34(broad, 12H, CH_{ph}). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 163.8 (Pd-$C_{carbene}$), 149.2, 148.8, 140.4, 134.2 (broad), 131.4, 130.5, 129.2, 128.9, 125.4, 123.6, 118.3, 117.2. ^{31}P NMR (DMSO-d_6, 160 MHz): δ 18.65 (s, PPh_3), −143.57 (sept, PF_6). FT-IR (KBr pellet, cm^{-1}): 3059(w), 1592(w), 1574(w), 1482(w), 1471 (w), 1437(s), 1412(w), 1323(w), 1282(w), 1097(m), 996(w), 841 (vs), 782(w), 748(w), 698(m), 558(m), 518(m), 497(w). ESI-MS: calcd *m*/*z* for $[M-PF_6]^+$ 887.1452, Found: 887.1451. *Anal.* Calc. for $C_{49}H_{40}ClF_6N_4P_3Pd$: C, 56.94; H, 3.90; N, 5.42. Found: C, 55.17; H, 3.90; N, 5.16.

2.4.5. Synthesis of $[Hg(py_2im)_2](PF_6)_2$ (**8**)

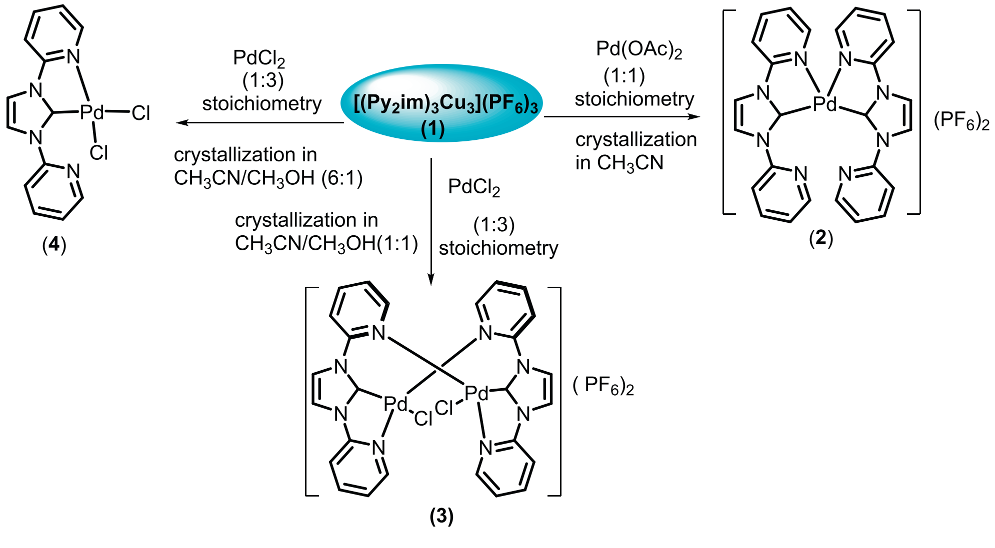
Method (A): A mixture of **1** (0.13 g, 0.1 mmol) and $Hg(OAc)_2$ (0.1 g, 0.3 mmol) was added CH_3OH (15 mL) and stirred at room temperature for 13 h. Gray colored turbid solution was obtained. The solution was filtered and the residue was washed by DCM and CH_3OH. The colorless powder of **9** was obtained. Yield: 0.12 g (85%). *Method B:* A mixture of **1** (0.13 g, 0.1 mmol) and $HgCl_2$ (0.08 g, 0.3 mmol) was taken in CH_3OH (10 mL) and stirred at room temperature for 8 h. Colorless precipitate was obtained. The solution was filtered and the residue was washed by DCM. The colorless powder of **8** was obtained. Yield: 0.11 g (81%). ^{1}H NMR (CD_3CN, 500 MHz): δ 8.35 (s, 1H, CH_{im}), 8.13 (td, 1H, $^3J = 8$ Hz, $^4J = 1.7$ Hz , CH_{im}), 7.98 (d, 1H, $^3J = 4$ Hz, CH_{py}), 7.94 (d, 1H, $^3J = 8$ Hz, CH_{py}), 7.44 (td, 1H, $^3J = 7.2$ Hz, $^4J = 2.3$ Hz, CH_{py}) ^{13}C NMR (CD_3CN, 125 MHz): δ 170.9 (Hg-C), 148.6, 147.3, 141.2, 125.7, 122.3, 114.6. FT-IR (KBr pellet, cm^{-1}) 3183(w), 3155(w), 1600(s), 1579(m), 1477(m), 1447(s), 1347(s), 1272(s), 1167(w), 1136(w), 1052(w), 1000(w), 960(w), 892(m), 836(vs), 781(s), 729 (m), 624(w), 556(s), 403(w). *Anal.* Calc. for $C_{26}H_{20}F_{12}HgN_8P_2$: C, 33.40; H, 2.16; N, 11.98. Found: C, 33.02; H, 2.14; N, 11.74 ESI-MS: calcd *m*/*z*: 791.1159, Found: 791.1156 for $\{[M-PF_6]^+\}$.

3. Results and discussion

3.1. Carbene transfer from **1** to palladium(II) centre

Trinuclear Cu(I)–NHC complex (**1**) was synthesized in multigram scale by simple and facile route starting from the less expensive $Cu(OAc)_2 \cdot H_2O$ and $py_2imH \cdot PF_6$, in the presence of L-ascorbic acid as reducing agent, in CH_3OH under aerobic conditions [54]. The carbene transfer reactions were carried out using **1** and the palladium precursors in different stoichiometric ratios.

The reaction of **1** with one equivalent of $Pd(OAc)_2$ affords the complex **2** quantitatively (Scheme 1). The ^{1}H NMR spectrum in CD_3CN shows five distinguished sharp peaks for pyridine and imidazolin-2-ylidene protons with the same integral values. This indicates the symmetrical arrangement of py_2im around the metal center in solution. Further, the ESI-MS reveals the formation of $[Pd(py_2im)_2]^{2+}$ ion (*m*/*z* 275.0375) in **2**. To confirm the structure of **2**, the single crystals were subjected to X-ray diffraction study



Scheme 1. Synthetic scheme of mono and binuclear Pd–NHC complexes (**2**–**4**) from **1**.

and it replicates the structural data of $[Pd(pyimypy)_2][PF_6]_2$ reported earlier by Chen and Lin [61]. In contrast, the reaction of **1** with one equivalent of $PdCl_2$ resulted in **2** only in a moderate yield. The ^1H NMR spectrum of the crude product from this reaction showed broad peaks in the region of 7.0–9.0 ppm. In addition, the ESI-MS indicates that the presence of additional products, such as $[PdCl(py_2im)]^+$ (364.9686) and $[PdCl(py_2im)_2]^+$ (587.0534), apart from the major product **2**.

The reactions of **1** with $PdCl_2$ in 1:3 molar ratios in dry CH_3OH or acetonitrile were carried out (Scheme 1). The products **3** and **4** were isolated by varying the solvent of crystallization, such as methanol and acetonitrile mixture. Resulted products were thoroughly characterized by spectroscopic, analytical and single crystal X-ray diffraction methods. The ^1H NMR spectra of **3** exhibit ten distinct peaks indicating unsymmetrical coordination of two pyridine rings around the metal ion (Fig. S3). In case of **4**, the ^1H NMR spectrum recorded in DMSO-d_6 shows six broad peaks (Fig. S6). In ^{13}C NMR spectrum, the resonances for carbene carbon atom in **3** are observed at 154.5 ppm and 155.9 ppm respectively, which are similar to that of known Pd–NHC complexes [62–64]. Further, the ESI-MS shows the masses corresponding to different types of species present such as, dinuclear $\{[Pd_2Cl_2(py_2im)_2](PF_6)\}^+$ (m/z 872.8950) in (**3**) and mononuclear $[PdCl(py_2im)]^+$ (m/z 364.9628) (**3** and **4**) complexes. To understand better the structures of **3** and **4**, the single crystals obtained from these reactions were subjected to X-ray diffraction analysis.

The formation of **3** and **4** indicates that the reaction might have proceeded in a sequential manner. Earlier, it was reported that the presence of a mixture of anions in the starting materials resulted in anion exchanged products and this exchange depends on the thermodynamic stability of the final products [61]. For example, the reaction between $[PdCl_2(dppf)]$ and $AgBF_4$ yielded the dinuclear palladium complex $[Pd_2Cl_2(dppf)_2](BF_4)_2$ and AgCl [65]. Comparing to this reaction, in the present case the products **3** and **4** could have formed through an intermediate product $[PdCl(py_2im)]^+$ (Eqs. (1)–(3)). Further chloride ions present in the medium is a determining factor of product due to the favorable formation of CuCl as a major driving force [66].

$$\underset{\mathbf{1}}{[Cu_3(py_2im)_2](PF_6)_3} + 3PdCl_2 \rightarrow 3\underset{\mathbf{4}}{[PdCl_2(py_2im)]} + 3Cu(PF_6) \tag{1}$$

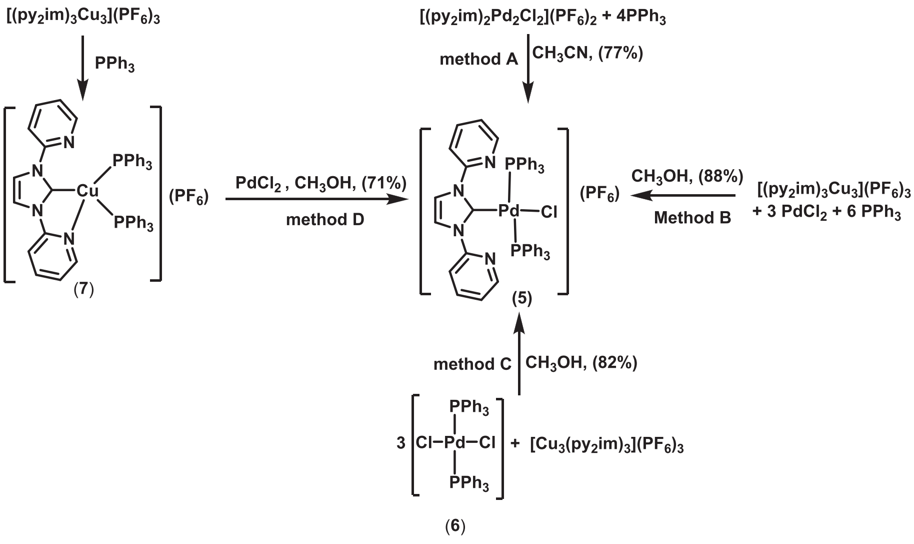
$$\underset{\mathbf{4}}{[PdCl_2(py_2im)]} + Cu(PF_6) \rightarrow [PdCl(py_2im)](PF_6) + CuCl \tag{2}$$

$$2[PdCl(py_2im)](PF_6) \rightarrow [Pd_2Cl_2(py_2im)_2(PF_6)_2] \tag{3}$$

The reactivity of **3** with PPh_3 was carried out. In this regard reaction of **3** with four equivalents of PPh_3 was performed which results yellow colored complex of *trans*-$[PdCl(PPh_3)_2(py_2im)](PF_6)$ and interestingly the same product was obtained from the reaction between **1** and $PdCl_2$ in the presence of six equivalents of PPh_3 (Scheme 2; method A and B). ^1H NMR spectrum of **5** recorded in DMSO-d_6 showed five distinct peaks of protons in py_2im ligand along with two broad merged peaks for phenyl protons of PPh_3. This indicates the symmetrical arrangement of both pyridyl rings of py_2im and also suggests 1:2 compositions of py_2im and PPh_3 in **5**. Here the preference for phosphines to coordinate cis to NHC is due to the transphobia effect [66]. In **5** both the bulky phosphine are cis to the NHC due to this effect. In fact a *trans* configuration is only observed for bulky NHCs [67]. ESI-MS analysis of **5** shows the presence of a peak at m/z 887.1383 which corresponds to $[M\text{-}PF_6]^+$. Moreover, the ^{31}P NMR exhibits a single sharp peak at 18.65 ppm for coordinated phosphines, suggesting the magnetic equivalence of two phosphine units, and a septet for the presence of $(PF_6)^-$ ion in **5**. Elemental analysis also supports the formation of complex **5**. For further confirmation multifaceted yellow colored crystals of **5** obtained in CH_3CN and DCM (1:2) mixture, was subjected to single crystal X-ray diffraction study.

The isolation of **5** led to the evaluation of other possible synthetic routes for **5** starting from **1** (Scheme 2, method C and D; see experimental section). The starting material $[Cu(PPh_3)_2(py_2im)](PF_6)$ (**7**) for method D was obtained by the addition of six equivalents of PPh_3 to **1** in CH_3OH/DCM mixture. **7** was characterized thoroughly by spectroscopic, spectrometric and analytical methods. The ^1H NMR spectrum of **7** shows five distinct peaks of protons for py_2im, along with the phenyl protons of PPh_3 in 1:2 compositions. A peak is observed at 188.5 ppm in ^{13}C NMR spectrum indicating the Cu–$C_{carbene}$ bond. Further, a single sharp peak at 4.73 ppm in the ^{31}P NMR spectrum suggests the symmetrical arrangements of coordinated phosphines in **7**. Moreover, the ESI-MS [m/z 809.2026, $(M\text{-}PF_6)^+$] and the elemental analysis support the composition of **7**. In addition, the single crystal X-ray diffraction study was carried out to authenticate the structure of **7**.

Reactions of [*trans*-$PdCl_2(PPh_3)_2$] (**6**) with **1** (method C) or **7** with $PdCl_2$ (method D) led to the isolation of **5** in very good yield. It should be noted that in method C only carbene was transferred from Cu to Pd center but in the case of method D both carbene



Scheme 2. Preparation of **5** by different synthetic routes.

as well as PPh_3 was transferred from Cu to Pd center. The latter method describes the double transfer of ligands such as phosphine and py$_2$im from copper to palladium center. To the best of our knowledge this is one of the first examples of double transmetallation reactions where both phosphine and carbene are transferred from one metal center to the other.

3.2. Carbene transfer from **1** to mercury(II) ion

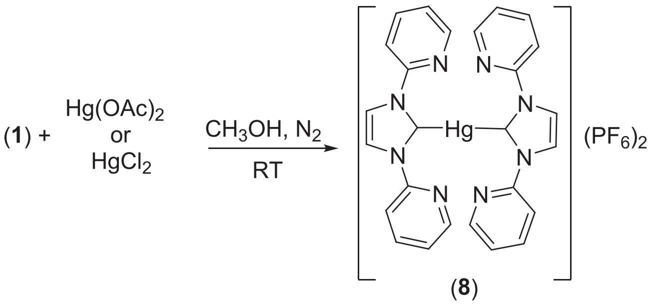
Finally the NHC transfer from Cu to group 12 metal ions is also evaluated to understand the strength of py$_2$im coordination in **1**. As an initiative to this direction the carbene transfer from **1** to mercury(II) salts was studied. Thus the reactions of **1** with $Hg(OAc)_2$ or $HgCl_2$ in methanol (Scheme 3) with 1:3 stoichiometric ratio was carried out. The product **8** was isolated in 85% yield. ^{1}H NMR shows five distinct peaks indicating the symmetrical arrangement of ligands around mercury(II) ion centre. The ^{13}C NMR spectrum shows a peak at 170.9 ppm which stands for carbene carbon bound to mercury. ESI-MS analysis shows the presence of $[(M\text{-}PF_6)]^+$ ion (*m*/*z* 791.1036) corresponding to $[Hg(py_2im)_2](PF_6)_2$ complex. The structure of **8** was also confirmed by single crystal X-ray diffraction study. However, Lin and coworkers reported this complex by direct metallation using mercury acetate [68].

3.3. X-ray crystallography

3.3.1. Structure of **3**

Pale yellow colored hexagonal shaped crystals of **3** obtained in CH_3CN/CH_3OH (1:1) mixture was subjected to single crystal X-ray diffraction studies. It reveals that **3** crystallized in monoclinic space group $P2_1/c$. Crystallographic and structural parameters are given in Table 1. The selected bond distances and angles are given in the legend of Fig. 1. Molecular structure of **3** shows a dinuclear palladium complex in which both palladium ions are coordinated by a carbene carbon atom, two pyridyl nitrogen atoms of py$_2$im and a chlorido ligand adopting square planar geometry. The chlorido ligand ions occupy *trans* position to the carbene carbon. Interestingly, each py$_2$im ligand is involved in C^N chelation as well as N^C^N bridging mode with the palladium ions to build an overall 'V' shaped structure (Fig. 1). The charge of the dicationic complex is balanced with two $(PF_6)^-$ ions.

The Pd-N bond distances in **3** are in the range of 2.029(4) Å–2.046(4) Å. However, these Pd–N bond distances are shorter than that of the analogous mononuclear palladium complexes



Scheme 3. Synthetic diagram of Hg–NHC (**8**).

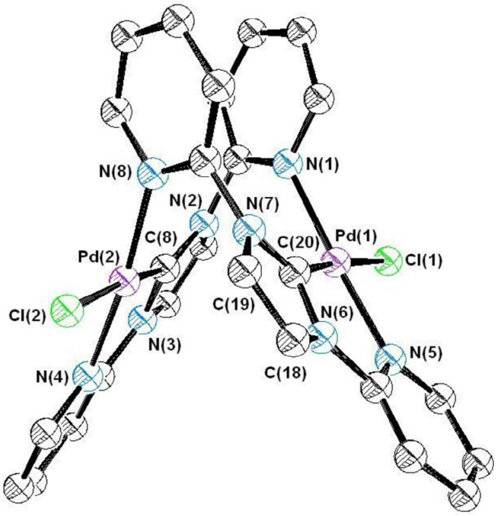


Fig. 1. ORTEP diagram of **3** (50% probability), where counter anions are omitted for clarity. Selected bond distances (Å) and angles (deg): C(20)–Pd(1), 1.972(5); C(8)–Pd(2), 1.961(4); N(1)–Pd(1), 2.046(4); N(4)–Pd(2), 2.029(4); N(5)–Pd(1), 2.033(3); N(8)–Pd(2), 2.038(3); Cl(1)–Pd(1), 2.345 (1); Cl(2)–Pd(2), 2.3179(12); C(20)–Pd(1)–N(5), 79.04(16); C(20)–Pd(1)–N(1), 98.97(17); N(5)–Pd(1)–N(1), 175.52(14); C(20)–Pd(1)–Cl(1), 174.40(13); N(5)–Pd(1)–Cl(1), 86.48(12); C(8)–Pd(2)–N(4), 79.69(17); C(8)–Pd(2)–N(8), 97.87(16).

Table 1
Crystallographic data of X-ray diffraction **3**–**5**.

Complexes	**3**	**4**	**5**
CCDC No.	1024344	1024346	1024347
Formula	$C_{26}H_{20}Cl_2F_{12}N_8P_2Pd_2$	$C_{26}H_{20}Cl_4N_8Pd_2$	$C_{50}H_{42}Cl_3F_6N_4P_3Pd$
Fw	1018.14	799.10	1118.54
Crystal system space group	monoclinic $P2_1/c$	tetragonal $P4_32_12$	orthorhombic $P2_12_12_1$
a (Å)	21.071(5)	9.3557(4)	14.7780(19)
b (Å)	15.185(4)	9.3557(4)	16.243(2)
c (Å)	10.556(3)	32.501(3)	19.840(3)
α (°)	90	90	90
β (°)	103.719(4)	90	90
γ (°)	90	90	90
V (Å^3)	3281.2(1)	2844.7(3)	4762.4(1)
Z	4	4	4
ρ(calc), g/cm^3	2.080	1.866	1.560
μ(mm^{-1})	1.461	1.673	0.723
θ (°)	1.99 to 26.00	2.51 to 25.99	1.86 to 26.00
Data/restraints/parameters	6366/12/514	2801/0/181	9356 /0/604
GOOF on F^2	1.058	1.113	1.022
Final R indices $[(I > 2\sigma(I)]$[a]	0.0426	0.0244	0.0434
$wR2$	0.0984	0.0563	0.0909
R indices (all data)	0.0539	0.0255	0.0533
$wR2$	0.1073	0.0569	0.0973

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{[\Sigma w(|F_o|^2\ |F_c|^2)^2/\Sigma\ w(|F_o|^2)^2]\}^{1/2}$.

reported by Chen and Lin [61]. However, the average Pd–C, (1.967 (5) Å) and Pd–Cl, (2.332(1) Å) bond distances are similar to that of the reported $[Pd(CH_3im(CH_3\text{-}py))_2Cl](PF_6)$ complex [69]. The imidazolin-2-ylidene and one of the pyridine rings of py$_2$im are present in the square plane. The other pyridine is twisted (dihedral angle 74.44°) and coordinated to the second palladium ion (torsional angles are C(6)–N(2)–C(5)–C(4), 53.60° and C(19)–N(7)–C (21)–C(22), 66.45). The two twisted pyridine rings of both py$_2$im units are nearly parallel to each other and show π–π stacking interaction (3.459 Å).

3.3.2. Structure of 4

Pale yellow colored crystals of **4** obtained in CH_3CN/CH_3OH mixture was subjected to single crystal X-ray diffraction method. **4** crystallized in tetragonal chiral space group $P4_32_12$. Crystallographic and structural parameters are given in Table 1. The selected bond distances and angles are given in the legend of Fig. 2. Molecular structure of **4** shows that palladium ion is coordinated by carbene carbon and one pyridyl nitrogen atoms of py$_2$im in C^N chelating mode, and the two chlorido ligand ions present in *cis* position to form square planar geometry (Fig. 2). Imidazolin-2-ylidene and the coordinated pyridine rings of py$_2$im are remained in the same plane as that of palladium ion. The Pd–C (C(1)–Pd(1), 1.958(3) Å) and Pd–N (N(3)–Pd(1), 2.039(3)Å) bond distances are almost similar to the reported palldium–NHC complexes [59–61]. The two Pd–Cl bond distances are 2.289(7)Å (Cl(1)–Pd(1)) and 2.343 (8)Å (Cl(2)–Pd(1)) and a longer Cl(2)–Pd(1) bond distance is attribute to the *trans* influence of carbene [66,70].

3.3.3. Structure of 5

Compound **5** crystallized in orthorhombic, $P2_12_12_1$ chiral space group. Crystallographic and structural parameters are given in Table 1 and selected bond distances and angles are given in the legend of Fig. 3. As analyzed through spectroscopic methods, palladium is surrounded by carbene carbon of py$_2$im, one chlorido ligand ion and two PPh_3 molecules to form a square planar geometry. In **5**, carbene carbon is *trans* to chlorido ligand and the two phosphines are *trans* to each other which are responsible for single peak in ^{31}P NMR. The Pd-C and Pd-Cl bond distances are comparable to **3** and **4** as well as reported values in the literature [61–62]. The average Pd-P bond distance is 2.336 (11) Å.

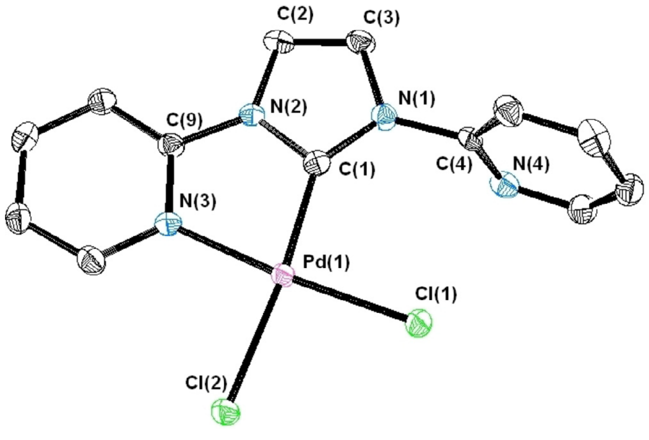


Fig. 2. Ortep diagram of **4** (50% probability). Selected bond distances (Å) and angles (deg): C(1)–Pd(1), 1.958(3); N(3)–Pd(1), 2.039(3); Cl(1)–Pd(1), 2.2886(7); Cl(2)–Pd (1), 2.3432(8); C(1)–Pd(1)–N(3), 79.99(11); C(1)–Pd(1)–Cl(1), 96.08(9); N(3)–Pd (1)–Cl(1), 175.24(7); C(1)–Pd(1)–Cl(2),171.86(9); N(3)–Pd(1)–Cl(2), 93.27(7); Cl (1)–Pd(1)–Cl(2), 90.86(3).

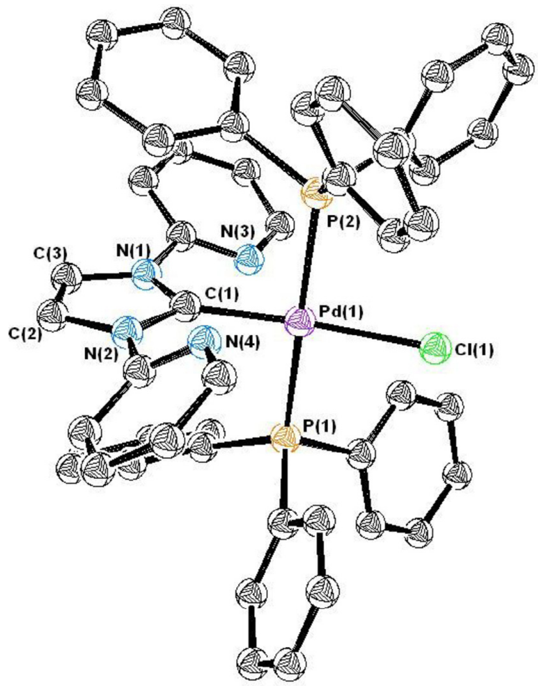


Fig. 3. ORTEP diagram of **5** (50% probability). Solvent and counter anion have been omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)–Pd(1), 1.978 (4); P(1)–Pd(1), 2.3298(11); P(2)–Pd(1), 2.3421(11); Pd(1)–Cl(1), 2.3438(10); C(1)–Pd(1)–P(1), 88.26(12); C(1)–Pd(1)–P(2), 91.84(12); P(1)–Pd(1)–P(2), 174.37(4); C (1)–Pd(1)–Cl(1), 174.97(12); P(1)–Pd(1)–Cl(1), 90.09(4); P(2)–Pd(1)–Cl(1), 90.27(4).

4. Conclusions

Mononuclear (**2** and **4**) and dinuclear **3** palladium(II)–NHC as well as mononuclear Hg–NHC (**8**) complexes were synthesized by carbene transfer method starting from trinuclear Cu(I)–NHC complex (**1**). All the other complexes (**3**–**5**) except **2** and **8** were newly prepared using this procedure and characterized by X-ray crystallography. **3** shows a 'V' shaped structure. Like silver complexes, the transmetallation from **1** to Pd was found to be sensitive to the variation of the stoichiometry of the reactants and also to the solvents. **5** was isolated as one of the most thermodynamically stable product obtained by carbene transfer from **1** in presence of PPh_3. The complex **5** was also synthesized from various other routes. Among them a double transmetallation of py$_2$im and PPh_3 was observed from compound **7** and this is the first time, to the best of our knowledge such transmetallation route is reported. Moreover we have showed for the first time that the NHC transfer from Cu(I)–NHC (**1**) to mercury(II) salts to form thermodynamically favored $\{[Hg(py_2im)_2](PF_6)_2\}$ complex (**8**). Biological and catalytic applications of these complexes are under progress.

Acknowledgement

BS thank the Indian Institute of Technology, Kanpur for infrastructure and financial support.

Appendix A. Supplementary data

CCDC 1024344, 1024346, and 1024347 contains the supplementary crystallographic data for this paper. 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 to this article can be found online at https://doi.org/10.1016/j.poly.2019.114123.

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