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Synthesis, Characterization and Single-Crystal X-ray Analysis, biological targeting of Nickel(II) and Palladium(II) Complexes of Tetradentate Amidate NHC Ligands-Selective Formation of aNHC or nNHC Complexes

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Synthesis, Characterization and Single-Crystal X-ray Analysis, biological targeting of Nickel(II) and Palladium(II) Complexes of Tetradentate Amidate NHC Ligands-Selective Formation of aNHC or nNHC Complexes

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1. Abstract

A set of of Nickel (II) and Palladium (II) compounds of both tetradentate and bidentate amidate standard n-hetero-cyclic carbene (NHC) ligands have been synthesize and characterize. These compounds show the coordination of both amidate nitrogen atoms and NHC groups to the metal center yielding neutral molecules. A mixture of cis and trans isomeric geometry of Pd(II) compounds of bidentate ligands were form, while a set of intrinsic Isomers: a shapes of Pd(II) Tetradentate derivative ligands were acquired, with these isomers displaying a combination of normal (nNHC) or aberrant (aNHC) NHC modalities of

coordination. Redesign of the ligand systems resulted in the selective formation of only one isomeric form of Ni(II) and Pd(II) tetra-dentate amidate NHC ligands for each synthetic reaction, with these complexes displayed either bis-(aNHC) or bis-(nNHC) coordination to the metal center,

Keywords: n-hetero-cyclic carbene (NHC) ligands, Nickel (II) and Palladium (II) compounds of both tetradentate and bidentate amidate, Ni(II) and Pd(II) tetra-dentate amidate NHC ligands, bis-(aNHC) or bis-(nNHC) coordination to the metal center, Crystal Refinement Data, biological targeting, N-heterocyclic carbene (NHC) donors.

2. Introduction

Despite the promising properties of a NHCs and a growing curiosity in the potential uses of catalysis of their complexes of metals, the number of reported a NHC−metal complexes continues to be somewhat small compared to their n NHC analogues.[1-2] Previously, the synthesis of an $Au^{(I)}$−aNHC complex was described where the imidazolium salt was first deprotonated and then the free aNHC ligand was reacted with the gold source.[3] However this synthetic approach for forming aNHC complexes is often not suitable as to the significantly reduced acidity of C5−*H* relative to C2−*H*, resulting in the selective deprotonation of the C5−*H* being difficult to achieve.[1,3-4] Early studies by Crabtree *et. al.* show a sequence of $Ir^{(III)}$−aNHC Complex might be as separate as air and complex that are stable in dampness without the necessity of separating the free aNHC before metalation.[5-7] When heated in solution, such complexes (such as 3.I and 3.II, Figure 3.1) do not experience ligand translocation to create C2 bound isomers, indicating that they are stable and selectively generated due to steric constriction at the Ir(III) center.[5,7] Additionally, some researchers have shown that aNHC−metal complexes can develop when highly sterically stringent substitutes are added to the end of NHC groups.[8-12] Another commonly employed approach to induce aNHC binding entails deactivating the C2 location by combining a protecting / banning group on this website. Several studies by Albrecht *et. al.* demonstrated that substitution of C2−*H* by a CH_3 or an aryl group afforded only aNHC−metal complexes in presence of a weak base (e.g. **3.III** and **3.IV**).[13-15] However, because of the potential for oxidative breakage of $C(sp^2)$-$C(sp^3)$

bond, which could lead to synthesis of nNHC−metal structures following trans metalation, some safeguarding groups, such as n-alkyl or benzyl substitutes, might not be appropriate for trans metalation reactions with a simple precursor of Ag (such as Ag_2O).[16] The oxidant addition of a zero valent metal predecessor to an imidazolium based salt, where C5 position is replaced with a halogen, is a lesser often used method for creating aNHC-metal compounds..[1,17] This technique has made it possible to effectively create $Pd^{(II)}$– and $Pt^{(II)}$–aNHC complexes under mild reaction conditions, however synthesis of aNHC−metal componds with other transition metals via this approach is yet to be explored.

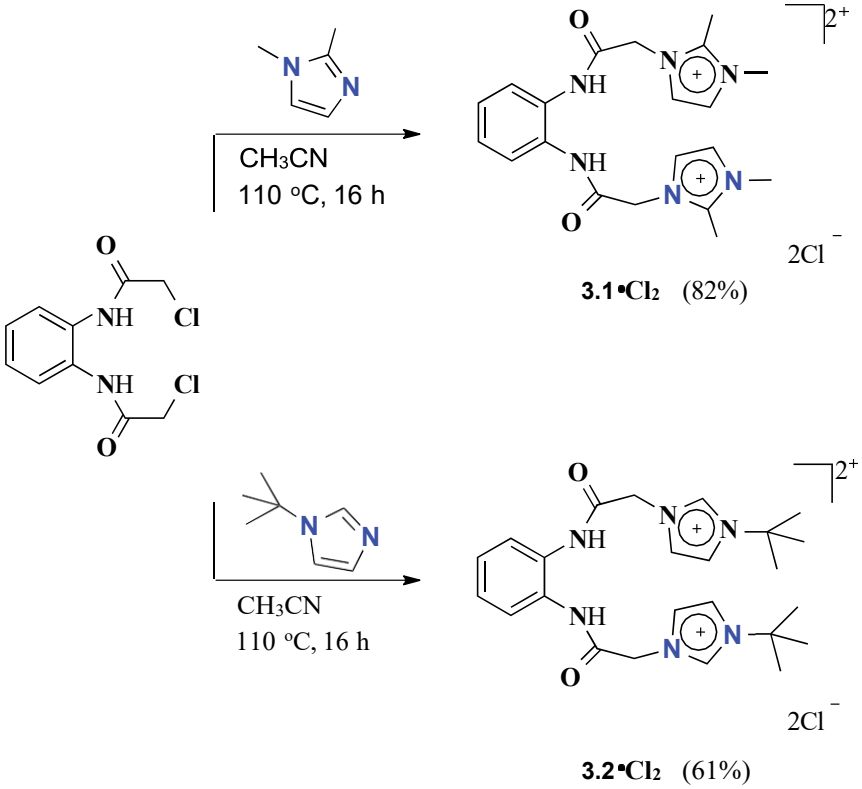
A number of Ni(II) and Pd(II) compounds with aberrant bis-(NHC/amidate) ligands were synthesized and characterized. A series of imidazolium salt, tetradentate NHC ligand forerunners have been prepared and metalated with either $Ni^{(II)}$ or $Pd^{(II)}$, where both NHC units were bound to these metals as either *bis*-aNHCs or *bis*-nNHCs. Through the use of C2 blocking groups or bulky substituents on the NHC units,

complex was achieved. This is in contrast to the formation of different geometrical varieties of isomers of the $Pd^{(II)}$ substances described.

3. Results & Discussion

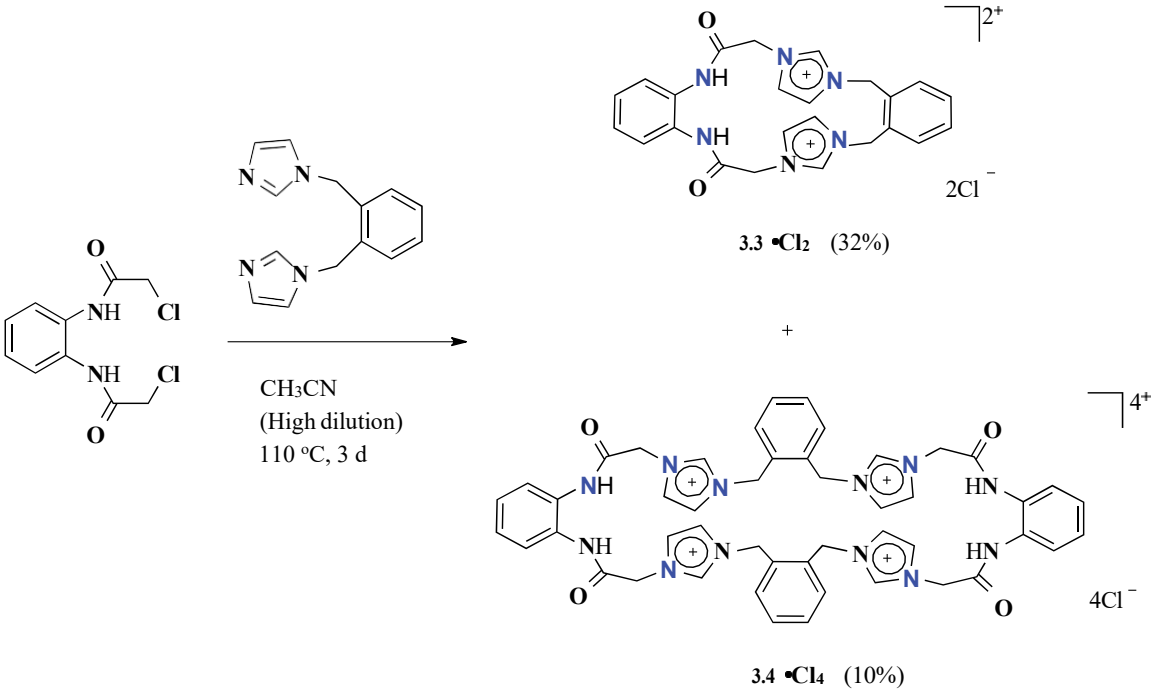
3.1 Preparation of Tetradentate Ligands Designed to Induce aNHC Binding

Three classes of tetradentate proligands that incorporated Imidazolium and amide groups were produced. Those ligands differed in that both contained C2 preventing atoms or structurally challenging groups on the typical wingtip of the imidazolium units, or were macrocyclic in nature. The proligand **3.1·Cl₂** was prepared with a CH_3 preventing group on C2 carbon of each of imidazolium unit, while imidazolium groups of **3.2·Cl₂** were substitute with structurally challenging tert-butyl (*t*-Bu) groups. In the case of imidazolium salt **3.3·Cl₂**, a macrocyclic, NHC ligand cursor was created by joining the two imidazolium-based subunits via o-xylene. Both the **3.1·Cl₂** and **3.2·Cl₂** were produced similarly as *N*,*N*'-*bis*(2-chloroacetyl)-1,2-phenylenediamine and suitable imidazole substitutes, 1,2-dimethylimidazole or 1-*t*-butylimidazole (Scheme 3.1).



Scheme 3.1: Imidazolium salt synthesis **3.1·Cl2** and **3.2·Cl2** through the appropriate derivative imidazole's alkylation with *N*,*N*'-*bis*(2-chloroacetyl)-1,2-phenylenediamine.

In both cases, a synthesize symmetrical imidazolium salts **3.1·Cl2** and **3.2·Cl2**provided straightforward 1H NMR spectra, with the deshelled amide N-H protons distinctive downfield resonances resonating at 10.72 and 10.69 ppm for **3.1·Cl2** and **3.2·Cl2**, respectively. Additionally, the deshelled pro-carbonic proton was noted at 9.62 ppm for **3.2·Cl2**. The macrocyclic proligand **3.3·Cl2** was created using equimolar mixtures of *N*,*N*'-*bis*(2-chloroacetyl)-1,2-phenylenediamine & 1,2-*bis*(imidazolylmethyl)benzene in heated acetonitrile at high dilute levels (Scheme 3.2). This reaction produced a crude product with a complex ^{1}H NMR, which was consistent with form of both larger macrocyclic tetra-imidazolium salt **3.4·Cl4** and the desired macrocycle **3.3·Cl2**. The main product of the reaction was the bis-imidazolium **3.3·Cl2**. By altering the reaction conditions, such as low reaction temperature, or using less diluted conditions, several attempts were prepare to suppress form of tetra-imidazolium **3.4·Cl4**. Although **3.4·Cl4** was still produce under these reaction conditions, these changes led to significantly lower yields of **3.3·Cl2** and recover of starting materials. The final tetra-cation is separate as a $[PF_6]^-$ salt through a metathesis reaction between crude product **3.4·Cl4** and KPF6.

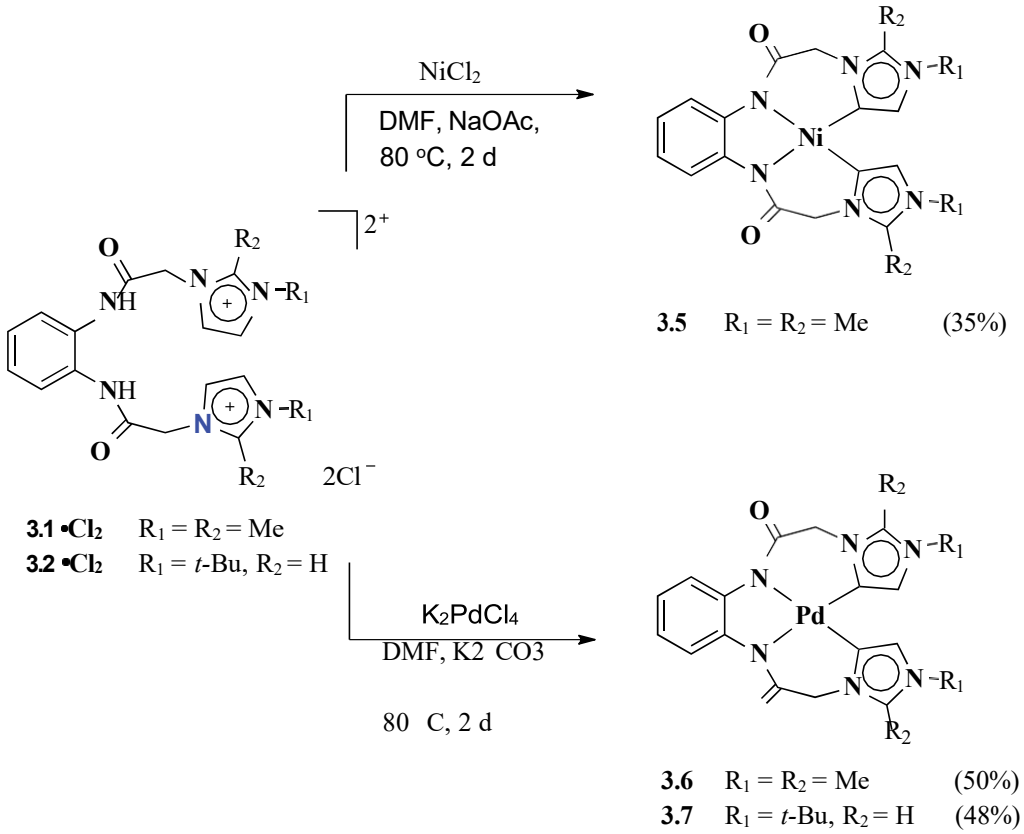


Scheme 3.2: Preparation of macrocyclic *bis*-imidazolium salt **3.3·Cl2** and **3.4·Cl4** tetra-imidazolium at high dilution.

The quantity of signs found in ^{13}C and ^{1}H NMR signals for both macrocycles **3.3·Cl2** and **3.4·(PF6)4** are consistent with symmetry molecules having two internal reflecting surfaces for **3.4 (PF6)** or a mirror plane of symmetrical that passes through both phenylenediamine & o-xylene link atoms for **3.3·Cl2**. The character downfield resonances are observe for pro-carbonic and amide N–*H* protons, with these resonances are happening at 8.96 and 10.39 ppm, 9.18 and 9.97 ppm for these protons of **3.3·Cl2** and **3.4·(PF6)4**, respectively. In both cases, the region of 5.13–5.68 ppm is where methylene protons resonate as singlet signals.

3.2 Preparation of Ni(II) and Pd(II) Compounds with tetra-dentate ligands

The $Ni^{(II)}$ compound **3.5** was synthesis by heat the 1:1 combination of pro-ligand **3.1·Cl2** and metal source $NiCl_2$ with mild base NaOAc in anhydrous dimethylformamide at 80 °C for two days. Despite several attempts $Ni^{(II)}$ compounds of pro-ligand **3.2·Cl2** could not be prepared. The $Pd^{(II)}$ compound **3.6** and **3.7** were also made similarly by heating the selected imidazolium salts (**3.1·Cl2** or **3.2·Cl2**) and the metal source K_2PdCl_4 in 1:1 ratio with mild base K_2CO_3 in anhydrous dimethylformamide (Scheme 3.3). All compounds were acquired in mediocre yield (35−50%) and were stable in presence of humidity and air.

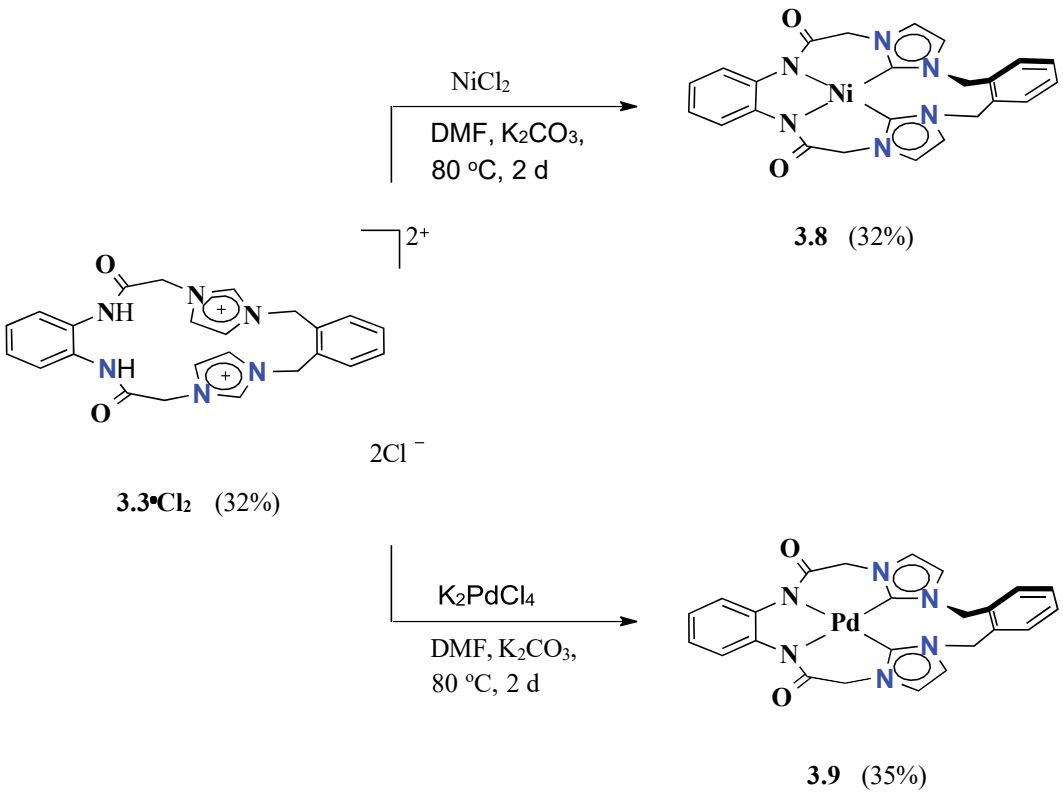


Scheme 3.3: Preparation of $Ni^{(II)}$ compound **3.5** and $Pd^{(II)}$ compounds **3.6** and **3.7** from C2 blocked imidazolium salt **3.1·Cl2** or the *t*-Bu substituted imidazolium salt **3.2·Cl2**.

Analysis of ^{1}H NMR spectra of crude products of $Ni^{(II)}$ and $Pd^{(II)}$ complexes **3.5**−**3.7** shown that in each instance, just one NHC–metal complex was produced. This is consistent with the formation of only one isomer of each complex with the same coordination mode for both of the NHC groups. Blocking of the C2 carbon with a CH_3 group or incorporation of bulky *t*-Bu substituents on the wingtips of the NHC units resulted in only the aNHC coordination mode. The no of signal observe in ^{1}H & ^{13}C NMR signals for compounds (**3.5**, **3.6** and **3.7**) are in line with an internal mirror plane of symmetry that passes through metal core (Ni(II) or Pd(II)) and phenylenediamine bridge band, the $Ni^{(II)}$ compound **3.5** and $Pd^{(II)}$ compound **3.6**, signals for C5−*H* and amide N−*H* proton were absent, suggesting that these groupings were deprotonated and synchronized with metal core to give neutral molecules. In case of $Pd^{(II)}$ complex **3.7**, the ^{1}H NMR spectrum show, disappearance of both C5−*H* & amide N−*H* signals, while C2−*H* (pro-carbonic proton) signal resonated as a de-shielded singlet at 8.98 ppm, suggesting that both NHC groups are bound to metal center as aNHCs. In all case, methylene protons resonated as singlet signals within, range of 4.51−4.63 ppm, indicating fluxional molecules for *endo* and *exo* proton air of these groups are exchange rapid with respect to NMR time scale. The reaction of $NiCl_2$ with the proligand **3.2·Cl₂** did not result in formation of a $Ni^{(II)}$ compound, regardless of reaction conditions used. For example, different bases (e.g. K_2CO_3, NaOAc and AgOAc), reaction times (8−96 hours) and temperatures (60−120°C) were investigated but no $Ni^{(II)}$ compound of this ligand could be isolated. Analysis of ^{1}H NMR of crude product show only form of decomposition products and unreacted starting materials in all cases. A possible explanation for inability to form

$Ni^{(II)}$ compound of this ligand (**3.2·Cl₂**) may be associated with steric interactions between bulky *t*-Bu groups of NHC units that preclude, *bis*-nNHC complex forming. In addition, the aNHC coordination mode was also not observed possibly due to $Ni^{(II)}$ metal ion being low active in C−H bond activation process than $Pd^{(II)}$, hence, formation of $Ni^{(II)}$–aNHC complex of **3.2·Cl₂** does not occur.

The $Ni^{(II)}$ compound **3.8** and $Pd^{(II)}$ compound **3.9** formed from macrocyclic imidazolium salt **3.3·Cl₂** were prepared by heating 1:1 mixture of chosen metal source (either $NiCl_2$ or K_2PdCl_4) and pro-ligand **3.3·Cl₂** with K_2CO_3 in anhydrous dimethylformamide (Scheme 3.4).



3.3•Cl₂ (32%)

3.8 (32%)

3.9 (35%)

Scheme 3.4: Preparation of $Ni^{(II)}$ compound **3.8** and $Pd^{(II)}$ compound **3.9** from macrocyclic imidazolium salt **3.3·Cl$_2$**.

In contrast to complex **3.7**, analysis of ^{1}H NMR spectra for **3.8** and **3.9** show the disappearance of distinctive resonances downfield for both pro-carbonic and amide N–*H* protons, implying that both amidate nitrogen atoms and C2 carbon of NHC groups (nNHC) were coordinate to metal center. The methylene protons show up as distinct, split AX sequences.

3.3 X-Ray Structural Studies

X-ray-suitable single crystallography was obtained for following compounds: **3.2·(PF$_6$)$_2$**, **3.3·(NTf)$_2$**, **3.5**, **3.7** and **3.8**. The crystallographic information for these structures are provided in Appendix 1 and Table A2. Specific bond lengths (Å) & bond angles (°) of imidazolium salts (**3.2·(PF$_6$)$_2$** and **3.3·(NTf)$_2$**) and complexes (**3.5**, **3.7** and **3.8**) are given in Table **3.1** and Table **3.2**, in that order.

Table 3.1: Specific bond lengths (Å) and bond angle (°) information for imidazolium salts **3.2·(PF$_6$)$_2$** and **3.3·(NTf)$_2$**.

	3.2·(PF$_6$)$_2$	**3.3·(NTf)$_2$**
C1−N1	1.327(2)	1.333(3)
C1−N2	1.321(2)	1.324(3)
C1−N1	1.325(2)	1.328(3)
C1−N2	1.330(2)	1.330(3)
N1−C1−N2	109.4(2)	108.4(2)
N1−C1−N2	108.2(2)	108.7(2)

Table 3.2: Specific bond lengths (Å) & bond angle (°) data for $Ni^{(II)}$ and $Pd^{(II)}$ compounds of **3.5**, **3.7** and **3.8**.

	3.5	**3.7**	**3.8**
	$Ni^{(II)}$	$Pd^{(II)}$	$Pd^{(II)}$
M−C1			1.872(2)
M−C2	1.864(2)	1.974(2)	
M−C1			1.863(3)
M−C2	1.861(2)	1.973(2)	
M−N3	1.925(2)	2.051(2)	1.928(2)
M−N3	1.915(2)	2.044(2)	1.916(2)
C_{NHC}−M−C'_{NHC}	90.7(1)	95.3(1)	96.1(1)
N3−M−N3	85.1(1)	80.6(1)	84.8(1)

The crystal structures of **3.2·(PF$_6$)$_2$** and **3.3·(NTf)$_2$** are shown in Figure 3.2. For compound **3.2·(PF$_6$)$_2$**, a brief interaction between hydrogen bonds of 2.632(9) Å is observe between proton of phenylenediamine group (C7−*H*) and a fluorine atom (F1) of the PF_6^- counterion. Similarly for **3.3·(NTf)$_2$**, a hydrogen bond interaction of 2.172 Å is observe between amide proton (N3'−*H*) and one of the carbonyl oxygen atom (O2) of the *bis*-triflimide counterion. Each of the imidazolium groups are oriented parallel to one another with both pro-carbenic protons oriented away from the phenyl ring of *o*-xylene group.

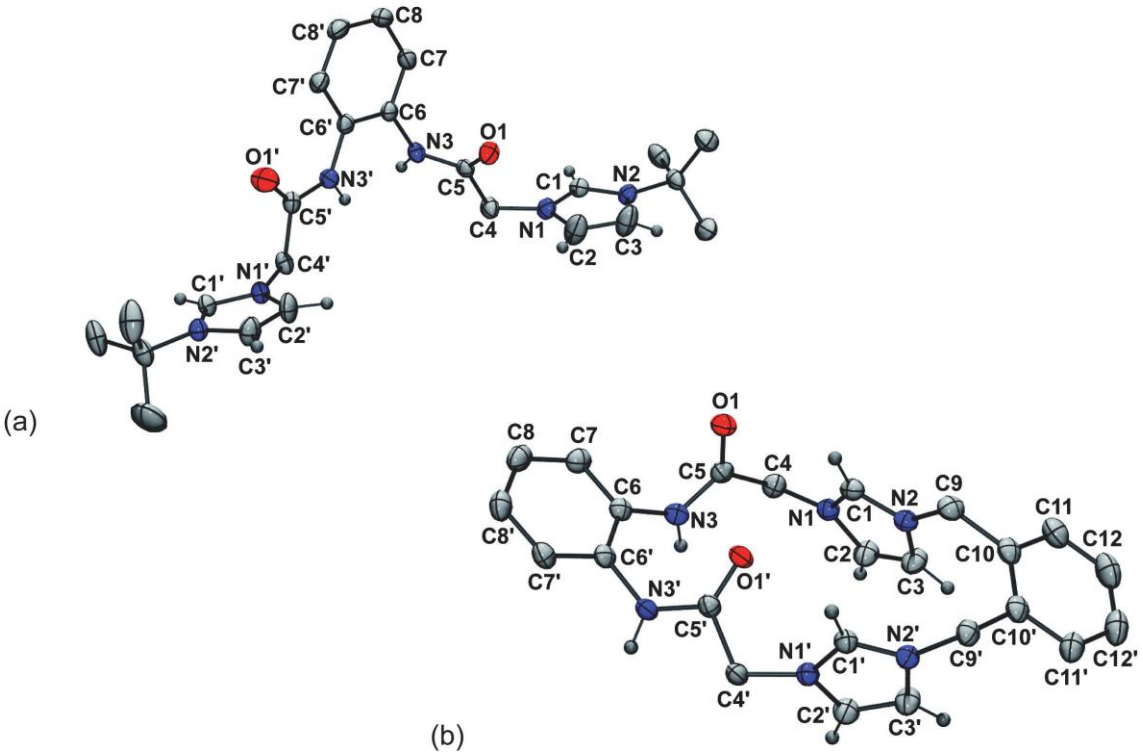


Figure 3.2: ORTEP[18] illustrations of crystal formations in X-rays of (a) **3.2·(PF$_6$)$_2$** and (b) **3.3·(NTf)$_2$**. Counterions (PF_6^-, **3$_6$2·(PF$_6$)$_2$**) and NTf^-, (**3.3·(NTf)$_2$**) and hydrogen atoms (except those on the amide groups and imidazolyl units) are omitted for clarity. Ellipsoid shapes representing atomic mobility are displayed at 50% confidence level.

The $Ni^{(II)}$ complex **3.5** and $Pd^{(II)}$ complex **3.7** adopt comparatively unaltered square-planar shapes concerning the metal centers (Figure 3.3a and b), with two NHC groups worked together as aNHCs in addition to the amidate nitrogen atoms. The *bis*-aNHC coordination paradigm produces a structure devoid of strain brought on by steric interactions among a NHC R (Me or *t*-Bu) groups. In contrast, the complex **3.8** displays the *bis*-nNHC coordination mode with $Ni^{(II)}$ metal center adopting a square-planar shape that is deformed (Figure 3.3c). This outcome is in line with a number of previous research, which has shown that aNHC cooperation occurs preferentially when C2 coordination site of NHC ligand has been blocked[14-15] or to alleviate the blockage brought on by steric interaction between NHC R groups.[6-8] For complexes **3.5** and **3.7**, each of

NHC units are twist out of metal coordination plane by 15° and 45°, and 33° and 28°, respectively. Significant ligand curvature is also shown for **3.7**, where methylene carbon atoms (C4 and C4') are displace by 1.233 and 1.321 Å, off the optimum plane formed by C2, C2', N3, and N3'. The capacity for *o*-xylene linker group to twist out of plane is like to be for both NHC group to bind as nNHCs. The crystal structure of **3.5**, **3.7** and **3.8** are shown in Figure 3.3.

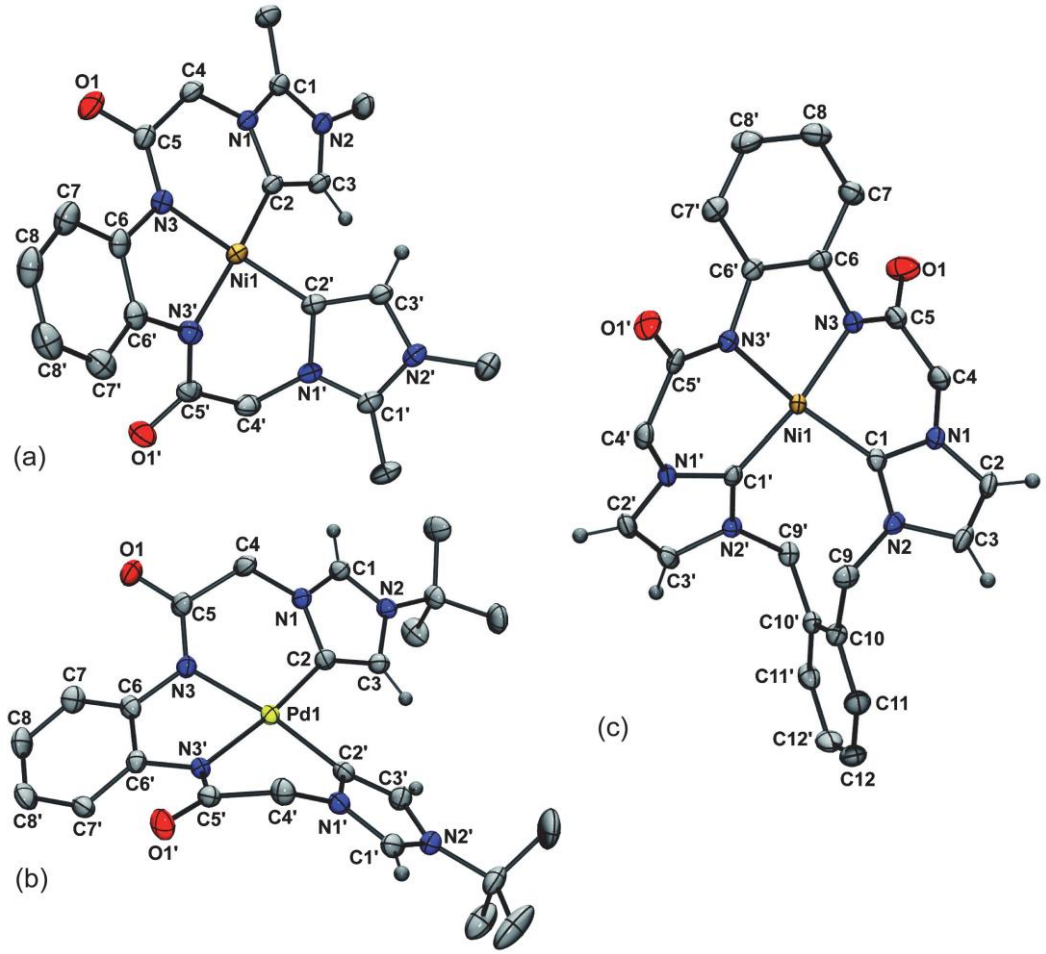


Figure 3.3: ORTEP[18] illustrations of X-ray crystal structure of (a) **3.5**, (b) **3.7** and (c) **3.8**. Co-crystallized molecules of methanol (**3.5**), water (**3.7**), dimethylformamide (**3.8**) and hydrogen atoms (except those on imidazolyl units) are omit for clarity. Ellipsoid shapes representing atomic mobility are displayed at 50% confidence level.

NHC contributors are renowned for having potent σ-donating capabilities, with the *trans* effect being by NHC being especially crucial for catalytic processes.[19] Analysis of $Ni^{(II)}$ compounds **3.5** and **3.8** and $Pd^{(II)}$ complex **3.7** showed minimal proof of a NHC *Transgender impact*, with average Ni−$N_{amidate}$ bond distance being 1.920(2) and 1.922(2) Å for **3.5** and **3.8**, respectively, while average Pd−$N_{amidate}$ bond distance is 2.048(2) Å for **3.7** (Table 3.2), there appears to be little or no difference of *trans* influence exerted by aNHC units in compound **3.5** in comparison to the nNHC units in complex **3.8**. It is also noted that the kinetic *trans* influence in these systems has not been investigated and the absence of evident structural influence does not preclude the kinetic effects Additionally, the average Ni−C bond distance in the 'abnormal' form (**3.5**) is identical to the 'normal'

complex **3.8**. There is also little difference observed between the metal−ligand bond lengths of **3.5**.

3.4 Concluding Remarks

A set of $Ni^{(II)}$ and $Pd^{(II)}$ compounds of tetra-dentate ligands incorporating amidate and NHC donor groups have been prepared and characterized. These complexes were neutral and displayed the coordination of the amidate nitrogen atoms in combination with NHC groups, where both NHC units coordinated to metal as either aNHCs or nNHCs. Incorporation of CH_3 preventing groupings on C2 carbon of each NHC unit result in selective formation of $Ni^{(II)}$ and $Pd^{(II)}$–aNHC compounds (**3.5** and **3.6**, respectively). The emergence of sterically challenging *t*-Bu groups on NHC wingtips also resulted in formation of only one isomeric form of $Pd^{(II)}$ complex **3.7**, with both NHC groups coordinated as aNHCs. In contrast, the desired $Ni^{(II)}$–aNHC complex of the proligand **3.2·Cl$_2$** could not be prepared. The inhabit to form a $Ni^{(II)}$ compound of **3.2·Cl$_2$** is like to result from steric interactions between *t*-Bu groups on each NHC units, precluding nNHC coordination mode. The lack of aNHC coordination mode, both $Ni^{(II)}$ (**3.8**) and $Pd^{(II)}$ (**3.9**) complexes of macrocyclic proligand

3.3·Cl$_2$ were prepared and these complexes displayed the *bis*-nNHC coordination mode.

Analysis of X-ray crystal structure of $Ni^{(II)}$ complex **3.8** showed that ligand is flexible and able to accommodate nNHC binding mode.

3.5 Experimental Evaluation

3.5.1 Synthesis of 1-*t*-butylimidazole

This chemical was made using a method described in the published works.[20] To a solution of tert-butylamine (1.05 mL, 0.01 mol) in CH_3OH (50 mL) was add 40% aqueous glyoxal (4.2 mL, 0.029 mol) and resulting mixture are agitated at RT for 16 h. NH_4Cl (10.7 g, 0.2 mol), 37% aqueous CH_2O (16 mL, 0.2 mol) and methanol (400 mL) are added sequential and combination experienced reflux for 1 h. The result mixture is added concentrate H_3PO_4 (14 mL, 85%) and refluxed for 2 d, after cool to RT, at lower pressure, the solvent are extract, and residue was add cold H_2O (300 mL), follow by 40% KOH solution was add to raise pH to 9. The solution was then extract with diethyl ether (5 × 100 mL), combined, drier over $MgSO_4$ and solvent was removed under reduce pressure. The resulting residue was subjected to column chromatography purification (4:1 hexane:ethyl acetate) to give product as a yellow. Yield = 6.21 g (50%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.51 (s, 9H, C−(C*H*$_3$)$_3$), 6.99 (s, 1H, *H*$_{imi}$), 7.01 (s, 1H, *H*$_{imi}$), 7.58 (s, 1H, NC*H*N) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 30.8 (C−(*C*H$_3$)$_3$), 54.9 (*C*−(CH$_3$)$_3$), 116.5 (*C*$_{imi}$), 129.1 (*C*$_{imi}$), 134.5 (N*C*N) ppm. The NMR data was consistent with the reported values.

1,2-*bis*(imidazolylmethyl)benzene

This chemical was made using a method described in the published works.[21] a solution of imidazole (20.3 g, 0.298 mol) and α,α'-dibromo-*o*-xylene (5 g, 0.0190 mol) in methanol (200 mL) was heated at 80 °C for 2 d. The solvent is remove under reduce pressure and residue was dissolve in an aqueous solution of K_2CO_3 (1.5 M, 200 mL). The solution was

stored in a fridge overnight and the precipitated white solid was collect, wash with diethyl ether to the product as white powder.

Yield = 4.53 g (44%). ^{1}H NMR (400.13 MHz, *d*$_6$−DMSO): δ 5.30 (s, 4H, C*H*$_2$), 6.93 (s, 2H, *H*$_{imi}$), 6.93−6.95 (m, 2H, Ar−*H*), 7.07 (s, 2H, *H*$_{imi}$), 7.26−7.30 (m, 2H, Ar−*H*), 7.68 (s, 2H, NC*H*N) ppm. ^{13}C NMR (100.61 MHz, *d*$_6$−DMSO): δ 46.9 (*C*H$_2$), 120.3 (*C*$_{imi}$), 128.5 (*C*$_{imi}$), 128.7 (*C*$_{aryl}$), 129.2 (*C*$_{aryl}$), 135.7 (*C*$_q$), 138.2 (N*C*N) ppm. The NMR information was consistent with the report values.

3.1.Cl$_2$

A solution of *N*,*N*'-*bis*(2-chloroacetyl)-1,2-phenylenediamine (0.475 g, 1.82 mmol) and 1,2-dimethylimidazole (0.35 g, 3.64 mmol) in CH$_3$CN (30 mL) are heat at 100 °C for 16 h. A white precipitate form, which are collect while hot, and wash with diethyl ether (3 × 5 mL) to afford **3.1·Cl$_2$** as a white powder.

Yield = 0.677 g (82%). ^{1}H NMR (400.13 MHz, *d*$_6$−DMSO): δ 2.63 (s, 6H, C−C*H*$_3$), 3.81 (s, 6H, N−C*H*$_3$), 5.46 (s, 4H, C*H*$_2$), 7.14−7.16 (m, 2H, Ar−*H*), 7.58−7.60 (m, 2H, Ar−*H*), 7.67 (s, 2H, *H*$_{imi}$), 7.81 (s, 2H, *H*$_{imi}$), 10.72 (s, 2H, N−*H*) ppm. ^{13}C NMR (100.61 MHz, *d*$_6$−DMSO): δ 9.5 (C−*C*H$_3$), 34.8 (N−*C*H$_3$), 50.5 (*C*H$_2$), 122.0 (*C*$_{imi}$), 122.3 (*C*$_{imi}$), 124.7 (*C*$_{aryl}$), 125.1 (*C*$_{aryl}$), 129.7 (*C*$_q$), 145.8 (N*C*N), 164.1 (*C*=O) ppm.

3.2.Cl$_2$

This complex was prepare from *N*,*N*'-*bis*(2-chloroacetyl)-1,2-phenylenediamine (0.605 g, 2.32 mmol) and 1-*t*-butylimidazole (0.576 g, 4.64 mmol) using method describe for **3.1·Cl$_2$**, except reaction was conducted in CH$_3$CN (20 mL), to afford product **3.2·Cl$_2$**

as white solid.

Yield = 0.721 g (61%). ^{1}H NMR (400.13 MHz, *d*$_6$−DMSO): δ 1.61 (s, 18H, C−(C*H*$_3$)$_3$), 5.44 (s, 4H, C*H*$_2$), 7.16−7.18 (m, 2H, Ar−*H*), 7.61−7.64 (m, 2H, Ar−*H*), 7.92 (s, 2H, *H*$_{imi}$), 8.04 (s, 2H, *H*$_{imi}$), 9.62 (s, 2H, NC*H*N), 10.69 (s, 2H, N−*H*) ppm. ^{13}C NMR (100.61 MHz, *d*$_6$−DMSO): δ 29.0 (C−(*C*H$_3$)$_3$), 51.4 (*C*−(CH$_3$)$_3$), 59.6 (*C*H$_2$), 119.6 (*C*$_{imi}$), 124.1 (*C*$_{imi}$), 124.8 (*C*$_{aryl}$), 125.2 (*C*$_{aryl}$), 129.8 (*C*$_q$), 135.9 (N*C*N), 164.3 (*C*=O) ppm.

To obtain suitable for X-ray crystallography, a metathesis reaction was carried out on **3.2·Cl$_2$** as following: To a solution of **3.2·Cl$_2$** (0.01 g, 0.0196 mmol) in water (2 mL) was add a solution of KPF$_6$ (0.0108 g, 0.0588 mmol) in water (2 mL). After stirring for 1 h a white precipitation was form, which was collect and wash with diethyl ether (3 × 3 mL) to **3.2·(PF$_6$)$_2$** quantitatively as a white solid. Further analysis and characterization of this compound was not undertaken.

3.3. Cl$_2$

To a solution of *N*,*N*'-*bis*(2-chloroacetyl)-1,2-phenylenediamine (0.224 g, 0.858 mmol) in anhydrous CH$_3$CN (200 mL) was add a solution of 1,2-*bis*(imidazolylmethyl)benzene (0.204 g, 0.858 mmol) in anhydrous CH$_3$CN (200 mL) beneath an air of N$_2$. The resulting solution are heat to 110 °C for 3 d. A pink precipitate was form, which was collected from the hot solution. The remaining filtrate was remove under reduce pressure to afford a pink residue. The residue are triturate with ethyl acetate (3 × 10 mL) follow by diethyl ether (3 × 10 mL). The crude product was recrystallize four times with ethanol to afford **3.3·Cl$_2$** as white solid.

Yield = 0.137 g (32%). ^{1}H NMR (500.14 MHz, *d*$_6$−DMSO): δ 5.29 (s, 4H, C−C*H*$_2$), 5.68 (s, 4H, C*H*$_2$), 7.20−7.22 (m, 2H, Ar−*H*), 7.37−7.38 (m, 2H, Ar−*H*), 7.57−7.59 (m, 2H, Ar−*H*), 7.71−7.73 (m, 2H, Ar−*H*), 7.78 (s, 2H, *H*$_{imi}$), 7.83 (s, 2H, *H*$_{imi}$), 8.96 (s, 2H, NC*H*N), 10.39 (s, 2H, N−*H*) ppm. ^{13}C NMR (125.77 MHz, *d*$_6$−DMSO): δ 49.8 (C−*C*H$_2$),

52.2 (*C*H_2), 122.6 (*C*imi), 124.6 (*C*imi), 126.0 (*C*aryl), 126.2 (*C*aryl), 130.9 (*C*aryl), 131.0 (2 × *C*q), 133.0 (*C*aryl), 137.1 (N*C*N), 164.3 (*C*=O) ppm.

To get single crystals that are appropriate for X-ray crystallography, a metathesis reaction was carried out on **3.3·Cl$_2$** as following: To a solution of **3.3·Cl$_2$** (0.01 g, 0.02 mmol) in water (2 mL) are add a solution of Li(NTf)$_2$ (0.0172 g, 0.06 mmol) in water (2 mL). After stirring for 1 h a white precipitate was form, was collect and wash with diethyl ether (3 × 3 mL) to **3.3·(NTf)$_2$** quantitatively as a white solid. Further analysis and characterization of this compound was not undertaken.

3.4·(PF$_6$)$_4$

The pale pink precipitate (collected from the hot CH_3CN solution in the synthesis of **3.3·Cl$_2$**) was wash with ethyl acetate (3 × 10 mL) follow by diethyl ether (3 × 10 mL) to afford **3.4·Cl$_4$** as a hygroscopic solid (calculated yield = 0.0857 g, 10%). The crude product are dissolve in H_2O (3 mL) and a solution of KPF_6 (0.158 g, 0.858 mmol) in water (3 mL) was add. After stirring for 1 h, a precipitate are form and collect, and crude product are recrystallize from a combination of CH_3CN / diethyl ether to afford **3.4·(PF$_6$)$_4$** as white powder.

Yield = 0.0863 g (70%). ^{1}H NMR (500.14 MHz, *d*$_6$−DMSO): δ 5.13 (s, 8H, C*H*$_2$), 5.61 (s, 8H, C−C*H*$_2$), 7.23−7.25 (m, 4H, *H*aryl), 7.26−7.28 (m, 4H, *H*aryl), 7.47−7.50 (m, 8H, 2 × *H*aryl), 7.70 (s, 4H, *H*imi), 7.73 (s, 4H, *H*imi), 9.18 (s, 4H, NC*H*N), 9.97 (s, 4H, N−*H*) ppm. ^{13}C NMR (125.77 MHz, *d*$_6$−DMSO): δ 49.1 (C−*C*H$_2$), 51.4 (*C*H$_2$), 122.2 (*C*imi), 124.5 (*C*imi), 125.0 (*C*aryl), 126.0 (*C*aryl), 129.4 (*C*aryl), 129.7(*C*aryl), 130.2 (*C*q), 132.8 (*C*q), 137.9 (N*C*N), 163.9 (*C*=O) ppm.

3.5

To a solution of **3.1·Cl2** (0.052 g, 0.115 mmol) in anhydrous DMF (5 mL) are add NaOAc (0.0472 g, 0.575 mmol) and a solution of $NiCl_2$ (0.0149 g, 0.115 mmol) in anhydrous DMF (3 mL). The result mixture is heat to 80 °C for 2 d, and it was cool to RT, the mixture are filter and solvent was remove under reduced pressure. The crude product are triturate with ethyl acetate (3 × 5 mL) followed by diethyl ether (3× 5 mL). The crude product was recrystallized four times from a mixture of methanol / diethyl ether to give **3.5** as a brown powder.

Yield = 0.0178 g (35%). ^{1}H NMR (500.14 MHz, *d*6−DMSO): δ 2.47 (s, 6H, C−C*H*3), 3.58 (s, 6H, N−C*H*3), 4.51 (s, 4H, C*H*2), 6.52 (s, 2H, *H*imi), 6.53−6.55 (m, 2H, Ar−*H*), 8.12−8.14 (m, 2H, Ar−*H*) ppm. ^{13}C NMR (125.77 MHz, *d*6−DMSO): δ 9.1 (C−*C*H3), 33.3 (N−*C*H3), 52.8 (*C*H2), 119.0 (*C*imi), 121.4 (*C*aryl), 125.5 (*C*aryl), 139.9 (N*C*N), 141.6 (Ni−*C*), 144.6 (*C*q), 165.9 (*C*=O) ppm.

3.6

This compound are prepare from a solution of **3.1·Cl2** (0.107 g, 0.236 mmol), K_2CO_3 (0.163 g, 1.18 mmol) and K_2PdCl_4 (0.077 g, 0.236 mmol) by using method describe for **3.5**. The crude product are recrystallize thrice from a combination methanol / diethyl ether to give **3.6** as brown solid.

Yield = 0.0572 g (50%). ^{1}H NMR (500.14 MHz, *d*6−DMSO): δ 2.54 (s, 6H, C−C*H*3), 3.66 (s, 6H, N−C*H*3), 4.53 (s, 4H, C*H*2), 6.58−6.60 (m, 2H, Ar−*H*), 6.92 (s, 2H, *H*imi), 8.16−8.18 (m, 2H, Ar−*H*) ppm. ^{13}C NMR (125.77 MHz, *d*6−DMSO): δ 9.7 (C−*C*H3), 33.7 (N−*C*H3), 55.6 (*C*H2), 119.8 (*C*aryl), 122.3 (*C*aryl), 123.1 (*C*imi), 140.8 (N*C*N), 141.6 (Pd−*C*), 144.9 (*C*q), 164.7 (*C*=O) ppm.

3.7

To a solution of **3.2·Cl2** (0.109 g, 0.214 mmol) in anhydrous DMF (3 mL) was add K_2CO_3 (0.148 g, 1.070 mmol) and a solution of K_2PdCl_4 (0.0698 g, 0.214 mmol) in anhydrous DMF (3 mL). The result mixture are heat to 80 °C for 2 d, and it was cool to RT, the mixture are filter and solvent was remove under reduce pressure. The crude product are triturate with diethyl ether (3 × 5 mL) and resulting residue is crystal from CH_3CN to give **3.7** as a light brown solid.

Yield = 0.0557 g (48%). ^{1}H NMR (500.14 MHz, *d*6−DMSO): δ 1.59 (s, 18H, C−(C*H*3)3), 4.63 (s, 4H, C*H*2), 6.58−6.61 (m, 2H, Ar−*H*), 7.22 (d, 2H, $^4J_{HH}$ = 1.5 Hz, *H*imi), 8.06−8.09 (m, 2H, Ar−*H*), 8.98 (d, 2H, $^4J_{HH}$ = 1.5 Hz, NC*H*N) ppm. ^{13}C NMR (125.77 MHz, *d*6−DMSO): δ 29.4 (C−(*C*H3)3), 56.9 (*C*−(CH3)3), 57.2 (*C*H2), 120.0 (*C*aryl), 120.5 (*C*imi), 122.2 (*C*aryl), 132.0 (N*C*N), 143.9 (Pd−*C*), 144.9 (*C*q), 164.7 (*C*=O) ppm.

3.8

This compound are prepare from a solution of **3.3·Cl2** (0.111 g, 0.222 mmol), K_2CO_3 (0.152 g, 1.11 mmol) and $NiCl_2$ (0.0288 g, 0.222 mmol) by using method describe for **3.7**. The crude product are crystal from a mixture of DMF / ethyl acetate to give **3.8** as a yellow powder.

Yield = 0.0344 g (32%). ^{1}H NMR (400.13 MHz, *d*6−DMSO): δ 4.71 (br s, 4H, C−C*H*2 and C*H*2), 4.97 (br s, 4H, C−C*H*2 and C*H*2), 6.61−6.64 (m, 2H, Ar−*H*), 7.05 (d, 2H, $^3J_{HH}$ = 1.6 Hz, *H*imi), 7.32−7.36 (m, 2H, Ar−*H*), 7.39 (d, 2H, $^3J_{HH}$ = 1.6 Hz, *H*imi), 7.42−7.46 (m, 2H, Ar−*H*), 8.25−8.29 (m, 2H, Ar−*H*) ppm. ^{13}C NMR (100.61 MHz, *d*6−DMSO): δ 51.3 (*C*H2), 53.9 (C−*C*H2), 119.8 (*C*aryl), 121.9 (*C*imi), 123.1 (*C*imi), 123.2 (*C*aryl), 128.7 (*C*aryl), 131.1 (*C*aryl), 136.4 (*C*q), 143.4 (*C*q), 160.5 (Ni−*C*), 167.1 (*C*=O) ppm.

3.9

This compound are prepare from a solution of **3.3·Cl2** (0.082 g, 0.164 mmol), K_2CO_3 (0.113 g, 0.82 mmol) and K_2PdCl_4 (0.0535 g, 0.164 mmol) by using method describe for **3.7**. The crude product are crystal from a mixture of DMF / diethyl ether to give **3.9** as beige powder.

Yield = 0.0305 g (35%). ^{1}H NMR (500.14 MHz, d_6−DMSO): δ 4.75 (d, 2H, $^2J_{HH}$ = 16.5 Hz, C−CH_2), 4.96 (d, 2H, $^2J_{HH}$ = 16.5 Hz, C−CH_2), 4.99 (d, 2H, $^2J_{HH}$ = 14.5 Hz, CH_2), 5.19 (d, 2H, $^2J_{HH}$ = 14.5 Hz, CH_2), 6.69−6.73 (m, 2H, Ar−*H*), 7.19 (d, 2H, $^3J_{HH}$ = 2 Hz, H_{imi}), 7.40−7.44 (m, 2H, Ar−*H*), 7.49 (d, 2H, $^3J_{HH}$ = 2 Hz, H_{imi}), 7.55−7.57 (m, 2H, Ar−*H*), 8.37−8.40 (m, 2H, Ar−*H*) ppm. ^{13}C NMR (125.77 MHz, d_6−DMSO): δ 51.6 (*C*H$_2$), 55.8 (C−*C*H$_2$), 120.3 (C_{aryl}), 121.3 (C_{imi}), 123.1 (C_{imi} and C_{aryl}), 129.0 (C_{aryl}), 131.5 (C_{aryl}), 135.6 (C_q), 143.6 (C_q), 162.5 (Pd−*C*), 165.8 (*C*=O) ppm.

5.6. biological Activity

A framework of rising curiosity for catalysis and biological targeting, N-heterocyclic carbene (NHC) donors joined with amidate arms generate stiff, electron-rich tetradentate pockets that securely bind Ni(II) and Pd(II) in stable square-planar geometries. Pd(II) analogs frequently exhibit improved kinetic stability influencing selectivity, DNA binding via intercalation/groove interaction, probed by UV-vis and fluorescence titration, possible inhibition of enzymes and protein targets through the electrophilic metal center, reported antimicrobial action against Gram-positive and Gram-negative strains, cytotoxic/anticancer activity linked to ROS generation and apoptosis induction. Well-established antibacterial and anticancer drugs with labile ligand release-driven action may have broad but less adjustable selectivity and poor stability in vivo.

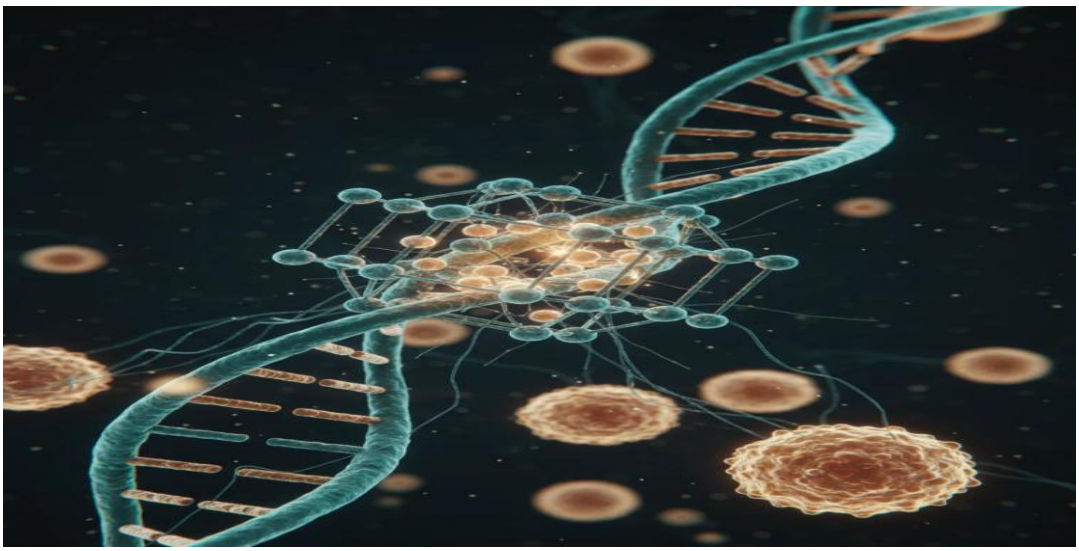


Figure 3.4: Schematic representation of DNA interaction with a metal complex.

5.7. Conclusions

The synthesis of a set of tetradentate ligands incorporating amidate and NHC donor groups, for which only one isomeric form of Ni(II) and Pd(II) compounds were obtained, which is in contrast to the mixed aNHC / nNHC geometrical isomers described. Despite the growing interest in aNHCs due to their stronger σ-donating properties as compared to nNHCs, the factors that induce the aNHC bindings 166 are generally poorly understood. Incorporation of a CH_3 blocking group on C2 carbon of NHC units resulted in the formation of only aNHC complexes for both Ni(II) and Pd(II), with the Ni(II)–aNHC compound representing one of the very few example of an aNHC bound to this metal reported to date. Similarly, introduction of highly sterically challenging t-Bu groups on NHC wingtips also gave rise to only the Pd(II)–aNHC complex, however the Ni(II) compond of this ligand could not be prepared. The inability to prepare the Ni(II) compound is likely to be due to the bulky t-Bu groups on NHC units that precludes the formation of nNHC complex. In contrast, both Ni(II) and Pd(II) componds of a macrocyclic ligand displayed only nNHC coordination mode. This result is explained by X-ray crystal structure of Ni(II) compound, which shows that the flexibility of the macrocyclic ligand allows only the nNHC binding mode.

5.8. Suggestion for further work

Future studies may focus on developing new amidate-NHC ligand architectures to control the selective formation of normal and abnormal NHC coordination modes. Detailed catalytic, electronic, and computational investigations could further clarify the structure–property relationships and explore potential applications of these Ni(II) and Pd(II) complexes in homogeneous catalysis.

Disclosure statement

Regarding publishing of this work, the authors affirm that they have no conflicts of conflict.

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AUTHOR CONTRIBUTIONS

Konda Santosh Kumar: Conceptualization, methodology, synthesis and characterization of the ligand and metal complexes, investigation, data collection, and manuscript preparation.
Nalamada Kotilingaiah: Supervision, project administration, conceptualization, interpretation of results, critical revision of manuscript, and overall guidance.
Jagadish Tota: Experimental investigation, spectroscopic characterization, data analysis, and manuscript review.
Gundu Mallikarjun: Synthesis and characterization, interpretation of spectroscopic data, and validation of the experimental results.
P Jyothi: X-ray diffraction analysis, crystallographic data interpretation, and validation.
Saritha Keerthi: Biological activity studies, data analysis, interpretation of biological results, and manuscript review.
All authors contribute to discussion and interpretation of results, review the manuscript critical, and approve final version for publication.

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