ORGANOMETALLICS

Nickel(II) and Palladium(II) Complexes with Chelating N-Heterocyclic Carbene Amidate Ligands: Interplay between Normal and Abnormal Coordination Modes

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Supporting Information

ABSTRACT: A series of six Ni(II) and Pd(II) complexes of two bidentate and two tetradentate N-heterocyclic carbene (NHC)/ amidate ligands have been prepared. The complexes are uncharged, with square-planar coordination geometries, and the ligands are bound via the NHC groups and the deprotonated amide nitrogen atoms. Pd(II) complexes were prepared for the bidentate ligands, and in each case, two chelating bidentate ligands were bound to the metal center, yielding *cis/trans* geometric isomeric forms. The Pd(II) complexes of the tetradentate ligands were obtained as a series of constitutional isomeric forms that were separable by fractional crystallization. The constitutional isomers differed in the coordination mode of the NHC groups, which were bound as either "normal" (nNHC) or "abnormal" (aNHC) carbenes. Density functional theory (DFT) studies show that the energies of the



isomeric forms increase in the order nNHC/nNHC < nNHC/aNHC < aNHC/aNHC and suggest that the "abnormal" NHC coordination mode occurs in kinetic rather than thermodynamic reaction products. The Ni(II) complexes of the tetradentate ligand showed only "normal" NHC coordination, suggesting that the mechanism by which aNHC binding occurs is metal dependent. The Ni(II) and Pd(II) complexes with nNHC donors displayed distorted-square-planar coordination geometries and axial chirality.

INTRODUCTION

N-heterocyclic carbenes (NHCs) are among the most important and widely studied ligand types in contemporary organometallic chemistry.¹ The main reason for this high level of interest is the outstanding activity of NHC–metal complexes in homogeneous catalysis.^{2–7} NHCs are particularly attractive, as they provide excellent framework flexibility and, in comparison to phosphines, NHC–metal complexes often show enhanced stability to air, moisture, and heat.⁸ The high stability and catalytic activity displayed by NHC–metal complexes can be attributed to the robust metal–carbene bond and the strong σ -donating properties of NHCs.^{7.9} New applications of NHCs in organometallic chemistry are constantly being developed.^{10–12}

Despite the very large number of known NHC complexes, the synthesis of NHCs with tunable electronic properties remains a challenge.^{11,13} In the vast majority of reported cases, the five-membered imidazole-based NHC coordinates to the metal via the C2 carbon. However, there has been growing interest in so-called "abnormal" NHCs (aNHCs), where coordination is via the C4 carbon.^{14–20} The abnormal bonding mode provides an $\alpha_{\beta}\beta'$ relationship for the heteroatoms relative to the metal-bound carbon, as opposed to the normal mode, where the heteroatoms are located in the α -positions.¹⁵ The abnormal binding mode for NHCs was first described by Crabtree and co-workers in 2001,²¹ and this initial report was followed by a series of further studies on the nature of aNHCs.^{22–24} It was demonstrated that aNHCs are stronger σ donors than their C2-bound counterparts and that metalation at the C4 position may occur via C–H bond activation.²³ Subsequently, both experimental¹⁶ and theoretical^{10,25,26} studies have shown that aNHCs are among the most basic of all known neutral donors. Recently, a metal-free aNHC was isolated and crystallographically characterized.¹⁹

Given the very strong σ -donating properties of aNHCs, there is growing interest in the potential catalytic application of these ligands. Pd^{II}—aNHC complexes have been evaluated in Suzuki—Miyaura and Heck^{27,28} and Sonogashira²⁹ coupling reactions. Ir^{III}—aNHC complexes have been shown to catalyze the cross-coupling of alcohols and amines³⁰ and the benzylation of arenes.³¹ Albrecht and co-workers have demonstrated in a

Received: January 13, 2013 Published: March 8, 2013 series of studies that for catalytic applications where an electron-rich metal center is advantageous, aNHCs produce more active systems than "normal" NHCs (nNHCs). For example, the Pd(II) aNHC complex i was shown to be an active catalyst in the hydrogenation of olefins, while the "normal" NHC analogue ii was inactive.^{16,32}



Chelating NHC-based ligands, functionalized with anionic donors (e.g., amide, alkoxide, and phenoxide) are useful, as they allow for the synthesis of NHC complexes of metals in high oxidation states.^{33–35} Of particular interest in our research is the combination of NHCs with deprotonated amide (amidate or amido) donors. Ligands of this type and their metal complexes have been the subject of a number of studies.^{36–42} In particular, Ghosh and co-workers have investigated both the potential catalytic and biomedical application of such ligands with a variety of metals.^{43–47} These researchers have described a series of dianionic amidate functionalized NHC ligands designed to form highly stable Ni(II) complexes (e.g., iii) as potential immunotolerance agents.^{45,47}

In this paper we report the synthesis and characterization of a series of Ni(II) and Pd(II) complexes of bidentate and tetradentate NHC/amidate ligands. For the Pd(II) complexes of the tetradentate ligands, a remarkable interplay is seen in the nature of the NHC coordination mode, where these groups are bound to the metal as either "normal" or "abnormal" NHCs. This series of metal complexes is significant, as it provides a potential avenue for a comparison of the influence that aNHC versus nNHC binding has on structural and electronic properties. Density functional theory (DFT) calculations provide insight into the structure, bonding, and properties of these aNHC and nNHC metal complexes.

RESULTS AND DISCUSSION

Two classes of amide-functionalized imidazolium salts (NHC ligand precursors) were prepared; the bidentate proligands [I]Cl, [II]Cl and the tetradentate proligands $[III]Cl_2$ and [IV]Cl₂. These salts were prepared in a similar manner from the α -chloroamide starting materials N-(2-chloroacetyl)aniline³⁷ and N,N'-bis(2-chloroacetyl)-1,2-phenylenediamine⁴⁸ and the substituted imidazoles 1-methylimidazole and 1phenylimidazole (Scheme 1). The methyl-substituted imidazolium salt [I]Cl and the Ni(II) complex of the NHC ligand derived from it have been described previously.³⁹ Similar ¹H NMR spectra were obtained for the imidazolium salts [I]·Cl, $[II] \cdot Cl_{2}$, $[III] \cdot Cl_{2}$, and $[IV] \cdot Cl_{2}$ in d_{6} -DMSO. In each case characteristic downfield resonances for the deshielded procarbenic and amide N-H protons were observed, with resonances occurring within the ranges of 9.19-10.18 and 10.75-11.15 ppm for these groups, respectively. For each of





^aConditions: CH₃CN, 100 °C, 16 h.

the proligands the methylene group proton resonances occurred as singlet signals within the range 5.27-5.57 ppm.

The square-planar Pd(II) complexes (1 and 2) of the bidentate NHC ligands were prepared by heating the chosen proligand ([I]Cl or [II]Cl) and K_2PdCl_4 in a 2/1 ratio with the mild base K_2CO_3 in anhydrous DMF at 110 °C (Scheme 2).





The complexes formed under these conditions were uncharged, with two chelating ligands coordinated to the Pd(II) center via the NHC group and the deprotonated amide nitrogen atom (amidate), as has been found previously for similar systems.³⁷

Analysis of the ¹H NMR spectra indicated that two geometric isomers were formed, with the *cis/trans* ratios being 0.66/0.34 and 0.63/0.37 for 1 and 2, respectively. The geometric isomers were separated by stirring a suspension of the crude product in methanol, with the *trans* isomers of 1 and 2 being less soluble and readily isolated. For compound 1, removal of the solvent from the filtrate and recrystallization of the residue from methanol afforded pure *cis*-1. However, the *cis* isomer of 2 could not be purified in this way. The Pd(II) complexes of a related series of bidentate ligands have been described previously, and the ratio of *cis* to *trans* isomers was found to be influenced by the polarity of the chosen reaction solvent.³⁷

The numbers of signals observed in the ¹H NMR spectra for trans-1, cis-1, and trans-2 are consistent with the ligand environments being magnetically equivalent. The equivalence arises from an inversion center relationship for trans-1 and *trans-2* (point group C_i), with the inversion center lying on the Pd(II) atom. In the case of *cis*-1 there is a 2-fold axis of rotation, which interconverts the ligand environments (point group C_2). The signal for the pro-carbenic proton was absent from the ¹H NMR spectra, and a characteristic downfield chemical shift was observed for the carbenic carbon atom, occurring at 171.4, 163.1, and 167.2 ppm for trans-1, cis-1, and trans-2, respectively. Additionally, no amide N-H was observed in the spectra of the complexes, which indicates that this group is deprotonated and bound to the Pd(II) center. Upon coordination of the NHC and amidate groups a six-membered chelate ring is formed, and in all cases the methylene protons appear as sharp, wellseparated AX patterns, implying that the structures are rigid in solution and the rate of interconversion of the endo and exo proton environments is slow with respect to the NMR time scale.

The Ni(II) complexes (3 and 4) and the Pd(II) complexes (5 and 6) formed from the tetradentate proligands [III]Cl₂ and [IV]Cl₂ were prepared by heating a 1/1 mixture of the metal source (anhydrous NiCl₂ or K₂PdCl₄) and the chosen proligand in DMF. Higher reaction temperatures (~110 °C) were required for formation of 3 and 4. In contrast, 70 °C was sufficient for the formation of 5 and 6, with higher temperatures leading to the formation of decomposition products. After recrystallization from dichloromethane and diethyl ether, the Ni(II) complexes were obtained as dark brown powders in low to moderate yields (Scheme 3).

Scheme 3. Synthesis of the Ni(II) Complexes 3 and 4^a



¹H NMR analysis of the crude products obtained in the synthesis of **5** and **6** showed that in each case a mixture of isomeric species was formed. With careful fractional crystallization, complex **5** (methyl substituents) could be separated into two structural (constitutional) isomers. These isomeric forms differed in the coordination mode of the NHC group, where either both of the NHC units are coordinated as "abnormal" carbenes (**5**_{a,a}) or as a combination of the "normal" and "abnormal" coordination modes (**5**_{n,a}). The ratio of isomers (**5**_{n,a}/**5**_{a,a}) formed in the reaction was 0.39/0.61, as estimated from the ¹H NMR spectrum of the crude product (before purification).

In the case of complex 6 (phenyl substituents), structural isomeric forms representing all three possible combinations of coordination modes were obtained $(6_{n,n}, 6_{n,a})$ and $6_{a,a}$, and these were also separated by fractional crystallization (Scheme 4). The ratio of isomers $(6_{n,n}/6_{n,a}/6_{a,a})$ formed in the reaction was 0.25/0.35/0.40. For both complexes 5 and 6, the crude

Scheme 4. Synthesis of the Geometric Isomeric forms of the Pd(II) Complexes 5 and 6^a



 $^{\prime\prime}n$ = normal NHC and a = abnormal NHC. Isolated yields are reported. Conditions: DMF, 70 °C, 16 h.

yield of each isomeric form (Scheme 4) shows the aNHC coordination mode to be favored over the nNHC coordination mode. The synthesis of complexes 5 and 6 at different temperatures (55-85 °C) had little effect on the ratio of isomers formed. However, higher temperatures (110-120 °C) resulted in the formation of decomposition products, which made metal complex isolation difficult. Previously, the synthesis and separation of a similar constitutional isomeric mixture (aNHC/nNHC and nNHC/nNHC) has been described for a Rh(III) complex of a trimethylene-bridged bis-NHC ligand.⁴⁹

Upon formation of the Ni(II) and Pd(II) complexes, signals for the pro-carbenic proton or the amide N-H were no longer present, indicating that these groups are deprotonated and coordinated to the metal center. The methylene protons occur as a well-separated AX pattern for 3 and an AB pattern for 4. For both 3 and 4 the signals for each pair of equivalent Ar-H protons on the phenylene diamine linker group are separated by ~ 2 ppm, with those closer to the carbonyl oxygen of the amide group being more strongly deshielded, probably as a result of an interaction with this group. The chemical shift difference for the signals attributed to the imidazolium group protons is small, indicating that these protons are in similar magnetic environments.

Significant variation was seen in the ¹H NMR spectra attributable to the different isomeric forms of 5 and 6. The ¹H NMR spectra for the three isomers of 6 (R = Ph; $6_{n,n'}$, $6_{n,a'}$, and $\boldsymbol{6}_{a.a})$ are shown in Figure 1. The spectrum for $\boldsymbol{6}_{n,n}$ is similar to that seen for the analogous Ni(II) complex 4, indicating that the NHC groups are bound in the normal manner for this isomeric form. The number of signals observed for $\mathbf{6}_{n,n}$ is consistent with an effective plane of symmetry passing through the phenylenediamine linker and the metal center. The same symmetry relationship is apparent for $5_{a,a}$ and $6_{a,a}$, with both NHC groups now bound as abnormal NHCs. In contrast to the case for $\mathbf{6}_{n,n}$, the methylene protons for $\mathbf{5}_{a,a}$ and $\mathbf{6}_{a,a}$ appear as a singlet signal, rather than an AB/AX pattern, indicating a fluxional molecule for which the endo and exo proton environments are exchanging. Also of note is the signal for the equivalent H1/H1' protons, which appear as a highly deshielded singlet at 9.54 ppm. The NMR data for the mixed coordination mode complex $5_{n,a}$ is consistent with a structure lacking the symmetry relationships seen for the bis-normal and



Figure 1. ¹H NMR spectra for the three geometric (constitutional) isomeric forms of the Pd(II) complex 6 ($6_{n,n}$, $6_{n,a}$, and $6_{a,a}$). The proton numbering scheme is shown in the chemical structures (Im = imidazolyl, Ar = aryl).

Table 1. Selected Bond Distance (Å) and Bond Angle (deg) Data for Complexes cis-1, trans-1, trans-2, 3, 4, 5_{n,a}, 5_{a,a}, 6_{n,n}, and 6_{a,a}

		$metal-C_{carbene}$			metal-N _{amide}		bond angle		
complex	metal	M1-C1	M1-C2	M1-C1'	M1-C2′	M1-N3	M1-N3′	C _{carb} -M- C _{carb}	N3-M-N3'
cis-1	Pd(II)	1.970(2)		1.962(2)		2.097(2)	2.094(2)	94.22(9)	93.80(7)
trans-1	Pd(II)	2.020(3)		2.014(3)		2.064(3)	2.061(3)	178.8(1)	178.9(1)
trans-2	Pd(II)	2.024(3)		2.024(3)		2.033(3)	2.033(3)	180.0	179.99(1)
3	Ni(II)	1.857(3)		1.851(3)		1.917(2)	1.906(2)	93.9(1)	86.01(9)
4	Ni(II)	1.860(2)		1.865(2)		1.908(2)	1.911(2)	92.5(1)	85.49(8)
5 _{n,a}	Pd(II)	1.977(3)			1.978(3)	2.052(2)	2.051(2)	95.6(1)	81.90(9)
5 _{a,a}	Pd(II)		1.993(2)		1.990(2)	2.056(2)	2.044(2)	98.7(1)	80.34(8)
6 _{n,n}	Pd(II)	1.958(2)		1.963(2)		2.031(2)	2.034(2)	95.4(1)	83.23(8)
6 _{a,a}	Pd(II)		1.985(3)		1.976(3)	2.060(3)	2.046(3)	94.6(1)	81.1(1)

bis-abnormal coordination modes. The methylene groups are nonequivalent and appear as two singlets, indicating conformational freedom similar to that seen for $5_{a,a}$ and $6_{a,a}$. The imidazolyl H3 proton for compound $6_{n,a}$ is shielded and resonates at 5.99 ppm (Figure 1). This upfield shift is likely to be due to shielding from the phenyl R group of the normally bound NHC unit, which may form a $\pi-\pi$ stacking interaction with the abnormally bound NHC unit (see Structural Studies).

Structural Studies. X-ray crystal structures were obtained for the following complexes: *trans*-1, *cis*-1, *trans*-2, 3, 4, $5_{a,a}$, $5_{n,a}$, $6_{n,n}$, and $6_{a,a}$. Selected bond distances and crystallographic refinement data for all of the structures solved are given in Table 1 and Table S1 (Supporting Information), respectively. The X-ray crystal structures of *trans*-1, *cis*-1, and *trans*-2 are shown in Figure 2.

NHCs are well-known as very strong σ -donating ligands^{7,9} and for their marked *trans* influence (structural) and *trans* effect (kinetic), with the *trans* effect exerted by NHCs being

particularly important in catalytic applications.⁵¹ Amidate donors are also known for their strong σ -donating properties and their capacity to form stable metal complexes with metal ions in high oxidation states.^{52–56} Analysis of the *cis* and *trans* forms of 1 show little evidence of a marked NHC *trans* influence. In the case of *cis*-1, the NHCs are *trans* to the amidate groups and the average Pd–N_{amidate} bond distance is 2.096(2) Å, while for *trans*-1, where the amidate donor groups adopt a mutually *trans* disposition, the average Pd–N_{amidate} bond distance is 2.063(2) Å. Given the strong σ -donating properties of the anionic amidate groups and the metallocyclic nature of these complexes, the NHC *trans* influence is not expected to be as pronounced as that seen in other systems.

Complex 3 crystallizes in the chiral space group $P4_32_12$ (tetragonal), and two views of the molecular structure are shown in Figure 3. The Ni(II) center adopts a distorted-squareplanar geometry (Figure 3a), with the distortion resulting from steric interactions between the R groups (methyl) of the NHC



Figure 2. ORTEP⁵⁰ representations of the X-ray crystal structures of (a) *trans*-1, (b) *cis*-1, and (c) *trans*-2. Cocrystallized DMF (*trans*-1), methanol (*cis*-1), and DCM and H₂O (*trans*-2) are omitted for clarity. Atomic displacement ellipsoids are shown at the 40% probability level.



Figure 3. ORTEP⁵⁰ representations of the X-ray crystal structures of (a) 3 (top view), (b) 3 (edge view) (cocrystallized methanol molecule omitted for clarity), and (c) 4 (hydrogen atoms omitted for clarity; one of the carbonyl oxygen atoms is disordered, and the site occupancy factors are 0.62 (O1) and 0.38 (O2)). Atomic displacement ellipsoids are shown at the 40% probability level.

units. The carbene carbon atoms (C1 and C1') are displaced by 0.511 and 0.512 Å above and below the plane defined by N3, N3', and Ni1 (Figure 3b). This distortion of the square-planar geometry results in axial chirality or helicity. Here a right- or left-handed helical twist is induced by one NHC group being displaced "up" and the other "down" relative to a chirality axis passing through the Ni(II) center (Scheme 5).

Complex 4 crystallizes in the cubic space group $Pa\overline{3}$, and the crystal is composed of a racemic mixture of each stereoisomeric form of the complex. The distortion of the square-planar geometry is less pronounced than that seen for 3, with the carbene carbon atoms displaced 0.479 and 0.460 Å above and below the plane defined by N3, N3', and Ni1. The decreased distortion for 4 may result from a π - π stacking interaction between the phenyl ring from one arm of the tetradentate ligand with the NHC unit of the other arm. The intramolecular distances between these groups are relatively short: C1···C9' is 3.127 Å, and C1'···C9 is 3.118 Å. For compounds 3 and 4, the

Scheme 5. Stereoisomeric Forms of the Complexes 3, 4, and $6_{n,n}$, Which Possess Axial Chirality^{*a*,57}



"Stereodescriptors: M, left-handed helical twist; P, right-handed helical twist.

¹H NMR studies show that the methylene protons are nonequivalent (AX pattern), indicating that the stereoisomeric forms of these complexes do not interconvert.

Representative crystal structures were obtained for the three possible constitutional isomeric forms of 5 and 6, these being $5_{n,a}$ and $5_{a,a}$ ($5_{n,n}$ was not formed) and $6_{n,n}$ and $6_{a,a}$ (Figure 4). Compound $6_{n,n}$ adopts a structure closely resembling that of 4 and also crystallizes in space group $Pa\overline{3}$. The Pd-C_{carbene} and the Pd-N_{amidate} bond distances (Table 1) are longer than those of 4; however, they are the shortest among the Pd(II) complexes prepared in this work. The distortion associated with the R group (Ph) steric interactions is less pronounced than that seen for 4, with the carbene carbon atoms C1 and C1' being displaced by 0.340 and 0.349 Å from the plane defined by N3, N3', and Pd1. For compound $\boldsymbol{5}_{n,a\prime}$ in addition to the amidate donors, the Pd center is bound to the "normal" C1 carbon of one NHC group and the "abnormal" C2' carbon of the other NHC. The square-planar geometry is distorted, with C1 and C2' being displaced by 0.324 and 0.385 Å above and below the plane defined by N3, N3', and Pd1, respectively. Coordination of the abnormal carbene appears to relieve the congestion associated with steric interactions between the NHC methyl groups. This result is consistent with those of several other studies, which have demonstrated that the abnormal coordination mode often arises to lessen steric congestion at the metal center. $^{21,58-61}$ Decreased steric congestion for $S_{n,a}$ is also clearly evidenced by the ¹H NMR data. Singlets are observed for each pair of methylene protons on carbons C4 and C4', indicating that the NHC groups are able to reorientate freely. As discussed in the Introduction, there is evidence to suggest that aNHCs are among the most basic of all known neutral donors. As such, a difference between the Pd-N_{amidate} bond distances trans to the abnormal carbene in comparison to those for the normal carbene might be expected. However, the bond distance data (Table 1) show that the $Pd-N_{amidate}$ bond distances are identical.

Complexes $5_{a,a}$ and $6_{a,a}$ adopt similar "saddle"-shaped structures, with both NHC groups coordinated as abnormal carbenes (Figure 4b,d). The bis-abnormal coordination mode results in a structure free from strain associated with steric interactions between the NHC R groups, and relatively undistorted square-planar geometries about the Pd(II) atoms are obtained. Significant curvature of the ligand is observed for these structures, with the methylene carbon atoms (C4 and C4') being displaced from the best plane defined by C2, C2', N3, and N3' by 1.094 and 1.272 Å, respectively, for $5_{a,a}$ and 0.930 and 1.168 Å, respectively, for $6_{a,a}$. Additionally, the NHC units are twisted out of the metal coordination plane by 17 and 36° for $5_{a,a}$ and 14 and 29° for $6_{a,a}$. Slightly shorter Pd–C_{carbene}



Figure 4. ORTEP⁵⁰ representations of the X-ray crystal structures (a) $\mathbf{5}_{n,a'}$ (b) $\mathbf{5}_{a,a'}$ (c) $\mathbf{6}_{n,n'}$ and (d) $\mathbf{6}_{a,a}$. For $\mathbf{6}_{n,n}$ and $\mathbf{6}_{a,a}$ a cocrystallized molecule of methanol is omitted for clarity in each case. Atomic displacement ellipsoids are shown at the 40% probability level.

bond distances are seen for compound $\mathbf{6}_{a,a}$ in comparison to those for $\mathbf{5}_{a,a}$ (Table 1), with the average values being 1.981(6) and 1.992(2) Å, respectively. In both cases the Pd-C_{carbene} bond distances in the "abnormal" form are slightly longer than those for the "normal" form ($\mathbf{6}_{n,n}$), where the average Pd-C_{carbene} bond distance is 1.961(4) Å. When the *bis*-abnormal complexes $\mathbf{5}_{a,a}$ and $\mathbf{6}_{a,a}$ are compared to the bis-normal complex $\mathbf{6}_{n,n}$, there does appear to be a slightly stronger *trans* influence exerted by the abnormal NHCs in comparison to the normal NHCs. For compounds $\mathbf{5}_{a,a}$ and $\mathbf{6}_{a,a}$ the average Pd-N_{amidate} bond distances (*trans* to the aNHCs) are 2.050(9) and 2.05(1) Å, respectively. For $\mathbf{6}_{n,n}$ the average Pd-N_{amidate} bond distance (*trans* to the normal NHCs) is shorter at 2.033(2) Å.

Previously, Pd(II) complexes of a chelating 2-picolylfunctionalized aNHC ligand⁶² and a methylene-bridged bisaNHC ligand¹⁶ have been structurally characterized. For both ligand types, a similar twisting of the aNHC units and displacement of the methylene group away from the metal coordination plane was observed. The Pd^{II}–aNHC bond length for the structurally characterized complexes were within the range 1.961(7)–2.007(4) Å, with variation observed primarily resulting from the *trans* influence from the opposing ligand: i.e., Cl⁻ versus I⁻. Consistent with the present study, little difference was seen between the Pd^{II}–aNHC bond lengths for the bis-aNHC–Pd^{II} complex and those of an analogous complex with "normally" coordinated NHCs.

Electrochemistry. The redox properties of the three isomeric forms of **6** were studied using cyclic voltammetry, with results summarized in Table 2. The anodic portions of the

Table 2. Electrochemical Anodic Peak Potentials (mV) for $6_{n,n'}$, $6_{n,a'}$ and $6_{a,a}$

complex	$E_{\rm pa}(1)$	$E_{\rm pa}(2)$
6 _{n,n}	313	457
6 _{n,a}	249	442
6 _{a,a}	203	360

cyclic voltammograms for $\mathbf{6}_{n,n}$, $\mathbf{6}_{n,a}$, and $\mathbf{6}_{a,a}$ (100 mV/s, 1 mM in anhydrous DMF with 0.1 M [Bu₄N][PF₆] supporting electrolyte) are shown in Figure 5. Similar voltammograms were obtained for each isomer, with two irreversible oxidative processes ($E_{pa}(1)$ and $E_{pa}(2)$) evident. Studies of the scan rate dependence of these oxidations (Figure S1, Supporting Information) show evidence for quasi-reversibility for $E_{pa}(1)$ at higher scan rates (20 V/s). The E_{pa} values (Table 2) show that the highest oxidation potentials are associated with the normal coordination mode of the carbene donors ($\mathbf{6}_{n,n}$), with an intermediate value obtained for the mixed coordination mode ($\mathbf{6}_{n,a}$) and the lowest value associated with both NHC groups being coordinated in an abnormal manner.

DFT studies (see below) for $6_{n,n}$, $6_{n,a}$, and $6_{a,a}$ yield orbital energies of the highest occupied molecular orbital (HOMO) that are consistent with the oxidation potentials, with $6_{n,n}$ predicted to have the lowest energy HOMO (-5.38 eV) followed by $6_{n,a}$ (-5.31 eV) and then $6_{a,a}$ (-5.26 eV); from B3LYP/def2-TZVPP//B3LYP/6-31G(d),LANL2DZ with DMF IEF-PCM solvent.



Figure 5. Anodic portion of the cyclic voltammogram for $\mathbf{6}_{n,n'}$, $\mathbf{6}_{n,n'}$ and $\mathbf{6}_{a,a'}$. Conditions: complex concentrations 1 mM, scan rate 100 mV s⁻¹, DMF, 0.1 M [Bu₄N][PF₆], glassy-carbon (3 mm diameter) working electrode.

Analysis of the MOs suggests that in all cases the HOMO is predominantly (>90%) ligand-based (Figure 6). For the isomeric forms of **6** the character of the HOMO is similar, being primarily π -orbitals associated with the amide units and the phenyl linker group of the ligand and, to a lesser extent, the metal center.



Figure 6. Molecular orbital isosurfaces of the highest occupied molecular orbitals (HOMO) for the isomeric forms of 6: (a) $6_{n,n}$; (b) $6_{n,a}$; (c) $6_{a,a}$.

It is possible that the strong trend observed in the values of the oxidation potentials may result from the *trans* influence exerted by the carbenes on the amide groups. Here the abnormally coordinated NHC groups exert the strongest *trans* influence, thereby decreasing the oxidation potential, while the anodic shift seen for $6_{n,a}$ and $6_{n,n}$ results from the less pronounced *trans* influence exerted by the normally coordinated NHC groups.

Density Functional Theory Studies. To gain further insights into the relative stabilities of complexes displaying either "normal" or "abnormal" NHC coordination modes, DFT was used to calculate the optimized geometries for **3–6**.

For the complexes of the methyl-substituted ligands (3 and 5) both gas-phase and solvated (IEF-PCM SCRF solvation model with DMF solvent) optimized geometries were calculated to investigate the effect of solvent on geometries. For complex 5, the relative single-point energies (inclusive of solvent) at the gas phase and solvated optimized geometries agreed to within 0.1 kJ/mol, while for the Ni complex 3 the relative energies agreed to within 0.5 kJ/mol. Such variation is insignificant in comparison to the relative isomeric energies (25-50 kJ/mol). Subsequently, only gas-phase-optimized geometries were calculated for the larger complexes of the phenyl-substituted ligands (4 and 6).

Optimized geometries were determined for all possible NHC coordination modes (nNHC/nNHC, nNHC/aNHC, and aNHC/aNHC) using the B3LYP hybrid exchange correlation functional with the 6-31G(d) basis set on nonmetal atoms and the LANL2DZ basis set and effective core potential on metal atoms. In the cases where X-ray crystal structures were available, the calculated geometries are in good agreement with the solid-state structures. The Cartesian coordinates of all optimized geometries are available as Supporting Information.

Although the aNHC coordination mode was not observed experimentally for the Ni(II) complexes of the tetradentate ligands (3 and 4), similar optimized geometries were calculated for both the Ni(II) and Pd(II) (5 and 6) complexes with the three possible NHC coordination modes. For the isomers with nNHC/nNHC coordination, distorted four-coordinate squareplanar geometries were obtained, with the distortion a result of steric interactions between the ligand R groups (Me and Ph). In contrast, the nNHC/aNHC and aNHC/aNHC coordination modes result in decreased steric congestion and lower levels of distortion of the square-planar structures.

Given the congestion associated with the NHC R-groups for the nNHC/nNHC isomers, complexes displaying aNHC coordination might be predicted to be more stable on the basis of steric grounds. This notion was not supported by the DFT results. B3LYP/6-31G(d),LANL2DZ calculated relative energies for the nNHC/nNHC, nNHC/aNHC, and aNHC/ aNHC isomeric forms of 3-6 are summarized in Table 3.

Table 3. B3LYP/6-31G(d),LANL2DZ Calculated Relative Electronic and Gibbs Free Energies (kJ/mol) for the nNHC/ nNHC, nNHC/aNHC, and aNHC/aNHC Isomeric Forms of Complexes $3-6^a$

		coordination mode					
complex	metal	nNHC/nNHC	nNHC/aNHC	aNHC/aNHC			
3	Ni(II)	0.0	25.0 (20.7)	50.3 (47.9)			
4	Ni(II)	0.0	28.6 (25.6)	55.5 (53.1)			
5	Pd(II)	0.0	22.3 (22.9)	39.6 (38.6)			
6	Pd(II)	0.0	25.3 (22.3)	41.2 (36.9)			
^{<i>a</i>} Single-po	int energi	es with DMF s	olvent at gas-pl	hase optimized			

geometries. Gibbs free energies are given in parentheses.

Solvent effects were found to be significant for relative energies, for which only energies inclusive of solvent effects are reported (gas-phase energies are available as Supporting Information, Table S2). The aNHC/aNHC isomer is calculated to be the least stable, with nNHC/nNHC being the most stable. It is notable that the relative electronic and Gibbs free energies are very similar. Basis set effects were considered with B3LYP/ def2-TZVP calculations, with relative energies for 3 and 5 (R =Me) deviating by less than 1 kJ/mol while for 4 and 6 (R = Ph) the difference is typically 3-5 kJ/mol. Test MP2/6-31G-(d),LANL2DZ calculations for 5 give relative electronic energies within 2.5 kJ/mol of the B3LYP/6-31G(d),LANL2DZ results. In comparison to the relative isomer energies, the variation with method and basis set is sufficiently small to give confidence that the calculated trends are reliable. In all cases complexes displaying aNHC coordination are predicted to be less stable than their nNHC counterparts.

The association of "abnormal" coordination with higher calculated energies is consistent with previous studies and is likely to result from the different arrangements of the heteroatoms in the imidazolylidene ring.^{15,63} A detailed analysis

of the bonding and electronic structure is the subject of further investigation.

Despite the DFT prediction of lower stability associated with aNHC coordination, ¹H NMR analysis of the crude products obtained for both 5 and 6 showed that higher yields were obtained for isomers displaying aNHC in comparison with those displaying nNHC coordination. These findings are consistent with the result of a previous study, which suggest that the isomers displaying aNHC coordination are kinetic rather than thermodynamic reaction products.²¹ In an effort to experimentally define which coordination mode (nNHC/ nNHC, nNHC/aNHC, or aNHC/aNHC) represents the actual thermodynamic product, solutions of $6_{n,n}$, $6_{n,a}$, and $6_{a,a}$ were prepared in d_6 -DMSO and these samples were incubated at 80 °C for 5 days. It was anticipated that rearrangement of the ligand binding mode might occur, yielding the thermodynamically more stable isomer. The samples were monitored by ¹H NMR spectroscopy, and no changes in the spectra for any of the isomeric forms were observed, showing that ligand rearrangement does not occur under these conditions. An identical NMR experiment was conducted with the addition of the weak base Cs₂CO₃, and again no changes in the ¹H NMR spectra were observed. The lack of ligand rearrangement is consistent with previous studies^{21,64} and is suggestive of metalation at the aNHC position taking place via a process that does not involve deprotonation and formation of the "free" aNHC followed by coordination to the metal. Crabtree and coworkers have postulated that aNHC binding occurs via a mechanism involving C–H bond activation.²³ It is possible that differences between the Ni(II) and Pd(II) observed in this work, i.e. Pd(II) induces aNHCs binding while Ni(II) does not, result from Pd(II) being more active in C-H bond activation processes than Ni(II). The preferential formation of the aNHC isomers seems likely to result from steric congestion between the NHC R groups during complex formation.⁶⁰ Transition state structures can be envisioned where steric congestion between the NHC R groups favors the formation of constitutional isomers displaying aNHC coordination (kinetic products), while steric crowding in the transition state disfavors nNHC coordination (thermodynamic product). Additionally, complexes 1 and 2 of the much less sterically demanding bidentate ligands show no evidence of aNHC binding.

CONCLUSION

A family of Ni(II) and Pd(II) complexes of bidentate and tetradentate NHC/amidate ligands have been prepared. Two geometric isomeric forms (cis and trans) of the Pd(II) complexes of the bidenate ligands (1 and 2) were obtained. The Pd(II) complexes of the tetradentate ligands (5 and 6) showed a remarkable interplay in the nature of the NHC coordination mode, where these groups were bound to the metal as either "normal" or "abnormal" NHCs. In contrast, only the "normal" NHC coordination mode was obtained for the Ni(II) tetradentate complexes (3 and 4). The constitutional isomeric forms of 5 and 6 provide an interesting series that allow the influence that "abnormal" versus "normal" NHCs have on structural and electronic properties of the resultant isomers to be examined. The square-planar coordination geometries of the Ni(II) and Pd(II) complexes with normally coordinated NHCs were strongly distorted as a result of steric congestion between the NHC R groups. ¹H NMR and structural studies show that the "abnormal" coordination mode results in decreased steric interactions between the

NHC R groups and that these compounds are fluxional on the NMR time scale. Abnormally coordinated NHCs are thought to be among the most basic of all known neutral donors. The structural studies conducted here show little evidence for a difference in the *trans* influence exerted by the normally or abnormally coordinated NHC groups. Cyclic voltammetric measurements showed that "abnormal" NHC coordination reduces the oxidation potential relative to the "normal" NHC binding mode for constitutional isomeric forms of **6**. DFT studies indicate that aNHC coordination results in higher energy structures relative to the nNHC counterparts and, taken together with the experimental results, suggest that the "abnormal" NHC binding occurs in kinetic rather than thermodynamic reaction products.

EXPERIMENTAL SECTION

General Procedures. All reagents were purchased from Sigma-Aldrich, were of analytical grade or higher, and were used without further purification unless otherwise stated. Anhydrous DMF was prepared by standing the analytical grade solvent over molecular sieves (3 Å, activated at 300 °C) for 2 days, followed by vacuum distillation. NMR spectra were recorded using a Bruker ARX-300 spectrometer (300.14 MHz for ¹H, 75.48 MHz for ¹³C) and were internally referenced to solvent resonances. All reactions were performed under nitrogen unless otherwise stated. 1-Phenylimidazole,⁶⁵ *N*-(2chloroacetyl)aniline,³⁷ and *N,N'*-bis(2-chloroacetyl)-1,2-phenylenediamine⁴⁸ were prepared according to the literature procedures.

Electrochemical experiments were performed using an AUTOLAB type II electrochemical station potentiostat (MEP Instruments, North Ryde, NSW, Australia) with General Purpose Electrochemical Systems (GPES) software (version 4.9). A conventional three-electrode configuration was used, consisting of a glassy-carbon 3 mm diameter working electrode shrouded in Teflon (CH Instruments, Austin, TX, USA), a 1 cm² platinum-gauze auxiliary electrode, and a silver-wire quasi reference electrode. Potentials were referenced to the ferrocene/ ferrocenium couple measured in situ (1 mM) in each case. Complexes 4, $6_{n,n'}$, $6_{n,a}$, and $6_{a,a}$ were prepared at a concentration of 1 mM in distilled dimethylformamide, with 0.1 M [Bu₄N][PF₆] as the supporting electrolyte.

Microanalyses were performed by the Microanalytical Laboratory at the ANU Research School of Chemistry, Canberra, Australia.

X-ray Crystallography. Single crystals suitable for X-ray crystallography were grown as follows: trans-1, slow evaporation of a DMF solution containing a mixture of *cis*- and *trans*-1; *cis*-1, 5_{aa} , $6_{n,n'}$ and $6_{a,a}$, slow evaporation of methanol solutions of the title compounds; trans-2 and $\mathbf{5}_{n,a}$, slow evaporation of dichloromethane solutions of the title compounds; 3, diffusion of vapors between hexane and a solution of 3 in methanol; 4, diffusion of vapors between ether and a solution of 4 in dichloromethane. Refinement data are given in Table S1 (Supporting Information). Diffraction data were measured using an Oxford Gemini diffractometer mounted with Mo K α radiation (λ = 0.71073 Å). Following multiscan absorption corrections and solution by direct methods or Patterson methods, the structures were refined using full-matrix least-squares refinement techniques on F^2 using SHELXL97.⁶⁶ The non-hydrogen atoms were refined with anisotropic displacement parameters, with hydrogen atoms placed geometrically and refined using a riding model. All calculations were carried out using the program Olex^{2,67} Images were generated by using ORTEP-3.⁵⁰ CCDC 889432–889440 contain 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.

Density Functional Theory. Density functional theory (DFT) calculations were carried out within the Gaussian 09 suite of programs.⁶⁸ Ground state geometries were optimized in the absence of solvent with the B3LYP^{69–71} hybrid exchange-correlation functional in conjunction with the 6-31G(d) basis set^{72–74} for non-metal atoms and the LANL2DZ basis set and core potential for nickel and

palladium.^{75,76} The def2-TZVP basis set and effective core potential⁷⁷ was utilized in single-point energy calculations. The polarizable continuum model (PCM)⁷⁸ self-consistent reaction field (SCRF) was used to model solvent effects, with a solvent of DMF to be consistent with the experimental system. Select species were optimized inclusive of solvent effects. Solvent effects are included in single-point energies at the gas-phase optimized geometries. An SCF convergence criteria of 10⁻⁸ au was employed throughout. **Synthesis.** *Imidazolium Salt* [*I*]*Cl.*³⁹ A solution of 2-chloro-*N*-

Synthesis. *Imidazolium Salt* [*I*]*Cl.*³⁹ A solution of 2-chloro-*N*-phenylacetamide (0.843 g, 4.97 mmol) and 1-methylimidazole (0.40 mL, 4.97 mmol) in acetonitrile (70 mL) was heated at reflux (100 °C) for 16 h. A white precipitate formed, which was collected and washed with diethyl ether (3 × 5 mL) to afford a white powder. Yield: 1.06 g (85%). ¹H NMR (*d*₆-DMSO): δ 3.91 (s, 3H, CH₃), 5.27 (s, 2H, CH₂), 7.07 (t, 1H, ³J_{HH} = 6.9 Hz, *H*_{aryl}), 7.32 (dd, 2H, ³J_{HH} = 6.9 Hz, *J* = 8.4 Hz, *H*_{aryl}), 7.63 (d, 2H, ³J_{HH} = 8.4 Hz, *H*_{aryl}), 7.73 (s, 1H, *H*_{imi}), 7.77 (s, 1H, *H*_{imi}), 9.19 (s, 1H, NCHN), 11.04 (s, 1H, NH). ¹³C NMR (*d*₆-DMSO): δ 35.9 (CH₃), 51.2 (CH₂), 119.2 (*C*_{aryl}), 123.0 (*C*_{imi}), 123.7 (*C*_{aryl}), 123.9 (*C*_{imi}), 128.9 (*C*_{aryl}), 137.8 (NCN), 138.5 (*C*_q), 163.7 (C=O). Anal. Found: C, 57.41; H, 5.55; N, 16.78. Calcd for C₁₂H₁₄ClN₃O: C, 57.26; H, 5.61; N, 16.69.

Imidazolium Salt [II]Cl. This compound was prepared from 1-phenylimidazole (0.50 g, 3.47 mmol) and 2-chloro-*N*-phenylacetamide (0.59 g, 3.47 mmol) using the method described for [I]Cl. The product was obtained as a white powder. Yield: 0.82 g (75%). ¹H NMR (*d*₆-DMSO): δ 5.37 (s, 2H, CH₂), 7.08 (t, 1H, ³J_{HH} = 7.5 Hz, H_{aryl}), 7.33 (dd, 2H, ³J_{HH} = 7.5 Hz, ³J_{IHH} = 8.1 Hz, H_{aryl}), 7.60–7.65 (m, 5H, H_{aryl}), 7.81 (d, 2H, ³J_{HH} = 8.1 Hz, H_{aryl}), 8.07 (s, 1H, H_{imin}), 8.38 (s, 1H, H_{imi}), 10.01 (s, 1H, NCHN), 11.15 (s, 1H, NH). ¹³C NMR (*d*₆-DMSO): δ 51.6 (CH₂), 119.1 (C_{aryl}), 120.7 (C_{imi}), 122.0 (C_{aryl}), 123.7 (C_{aryl}), 125.0 (C_{imi}), 128.8 (C_{aryl}), 129.9 (C_{aryl}), 130.5 (C_{aryl}), 134.6 (C_q), 136.6 (NCN), 138.6 (C_q), 163.5 (C=O). Anal. Found: C, 65.00; H, 5.21; N, 13.45. Calcd for C₁₇H₁₆ClN₃O: C, 65.07; H, 5.14; N, 13.39.

*Imidazolium Salt [III]Cl*₂. This compound was prepared from *N*,*N*′-bis(chloroacetyl)1,2-phenylenediamine (0.6 g, 2.3 mmol) and 1-methylimidazole (0.366 mL, 4.6 mmol) using the method described for **[I]**Cl. The crude product was recrystallized from boiling ethanol to give **[II]**Cl₂ as a pale purple powder. Yield: 0.639 g (65%). ¹H NMR (d_{6} -DMSO): δ 3.91 (s, 6H, CH₃), 5.49 (s, 4H, CH₂), 7.15–7.18 (m, 2H, H_{aryl}), 7.58–7.62 (m, 2H, H_{aryl}), 7.73 (s, 2H, H_{imil}), 7.90 (s, 2H, H_{imil}), 9.35 (s, 2H, NCHN), 10.75 (s, 2H, NH). ¹³C NMR (d_{6} -DMSO): δ 35.9 (CH₃), 51.5 (CH₂), 123.0 (C_{imi}), 123.8 (C_{imil}), 124.7 (C_{aryl}), 125.2 (C_{aryl}), 129.8 (C_q), 137.8 (NCN), 164.3 (C=O). Anal. Found: C, 49.09; H, 5.19; N, 19.00. Calcd for $C_{18}H_{22}Cl_2N_6O_2$ ·H₂O: C, 48.77; H, 5.46; N, 18.96.

Imidazolium Salt [*IV*]*Cl*₂. This compound was prepared from 1phenylimidazole (0.55 g, 3.81 mmol) and *N*,*N*'-bis(chloroacetyl)1,2phenylenediamine (0.50 g, 1.91 mmol) using the method described for [III]*Cl*₂ to give [*IV*]*Cl*₂ as a pale pink powder. Yield: 0.735 g (70%). ¹H NMR (*d*₆-DMSO): δ 5.57 (s, 4H, *CH*₂), 7.18–7.21 (m, 2H, *H*_{aryl}), 7.57–7.69 (m, 8H, *H*_{aryl}), 7.81–7.83 (m, 4H, *H*_{aryl}), 8.18 (s, 2H, *H*_{imi}), 8.37 (s, 2H, *H*_{imi}), 10.18 (s, 2H, NCHN), 10.81 (s, 2H, NH). ¹³C NMR (*d*₆-DMSO): δ 52.0 (*CH*₂), 120.6 (*C*_{imi}), 122.0 (*C*_{aryl}), 124.8 (*C*_{imi}, *C*_q), 125.5 (*C*_{aryl}), 129.9 (2 × *C*_{aryl}), 130.5 (*C*_{aryl}), 134.7 (*C*_q), 136.8 (NCN), 164.0 (*C*=O). Anal. Found: C, 57.24; H, 5.43; N, 14.04. Calcd for C₂₈H₂₆Cl₂N₆O₂·2H₂O: C, 57.44; H, 5.16; N, 14.35.

Pd(ll) Complex trans-1. To a solution of [I]Cl (0.15 g, 0.59 mmol) in anhydrous dimethylformamide (15 mL) were added K₂CO₃ (0.41 g, 2.96 mmol) and a solution of K₂PdCl₄ (0.097 g, 0.30 mmol) in anhydrous dimethylformamide (10 mL). The resultant mixture was heated at 110 °C for 16 h, and after it was cooled to room temperature, the mixture was filtered and the solvent removed under reduced pressure. ¹H NMR analysis of the crude product showed it to be a mixture of *cis* and *trans* isomers of the title compound. The *trans* isomer was isolated by adding methanol (10 mL), and after stirring for 15 min the insoluble solid was collected and washed with diethyl ether to give *trans*-1 as a cream-colored powder. Yield: 0.032 g (20%). ¹H NMR (MeOD + *d*₆-DMSO): δ 3.63 (*s*, 6H, CH₃), 4.23 (*d*, 2H, ²*J*_{HH} = 14.1 Hz, CH₂), 5.42 (*d*, 2H, ²*J*_{HH} = 14.1 Hz, CH₂), 6.70 (t, 2H, ³*J*_{HH} =

7.5 Hz, H_{aryl}), 6.73 (d, 2H, ${}^{3}J_{HH}$ = 1.5 Hz, H_{imi}), 6.94 (dd, 4H, ${}^{3}J_{HH}$ = 7.5 Hz, ${}^{3}J_{HH}$ = 8.1 Hz, H_{aryl}), 7.07 (d, 2H, ${}^{3}J_{HH}$ = 1.5 Hz, H_{imi}), 7.62 (d, 4H, ${}^{3}J_{HH}$ = 8.1 Hz, H_{aryl}) ppm. 13 C NMR (d_{6} -DMSO): δ 36.3 (CH₃), 58.5 (CH₂), 122.0 (C_{imi}), 122.3 (C_{imi}), 123.6 (C_{aryl}), 126.4 (C_{aryl}), 127.7 (C_{aryl}), 151.0 (C_{q}), 171.1 (Pd-C), 171.4 (C=O) ppm. Anal. Found: C, 53.69; H, 4.73; N, 15.55. Calcd for $C_{24}H_{24}N_{6}O_{2}$ Pd: C, 53.89; H, 4.52; N, 15.71.

Pd(II) Complex cis-1. The methanol solution (from the trituration step in the synthesis of *trans-*1 above) was evaporated to dryness, and the residue was further recrystallized from methanol to give *cis-*1 as a white powder. Yield: 0.018 g (12%). ¹H NMR (*d₆-*DMSO): δ 3.31 (s, 6H, CH₃), 4.31 (d, 2H, ²J_{HH} = 14.4 Hz, CH₂), 5.26 (d, 2H, ²J_{HH} = 14.4 Hz, CH₂), 6.69 (t, 2H, ³J_{HH} = 7.2 Hz, *H_{aryl}*), 6.82 (dd, 4H, ³J_{HH} = 7.2 Hz, ³J_{HH} = 7.8 Hz, *H_{aryl}*), 6.98 (d, 4H, ³J_{HH} = 7.8 Hz, *H_{aryl}*), 7.32 (d, 2H, ³J_{HH} = 1.8 Hz, *H_{imi}*), 7.61 (d, 2H, ³J_{HH} = 1.8 Hz, *H_{imi}*) ppm. ¹³C NMR (*d₆-*DMSO): δ 36.1 (CH₃), 57.8 (CH₂), 120.6 (*C_{aryl}*), 122.0 (*C_{imi}*), 122.7 (2 × *C_{aryl}*), 147.8 (*C_q*), 163.1 (Pd-C), 166.5 (*C*=O) ppm. Anal. Found: C, 51.55; H, 5.82; N, 13.10. Calcd for C₂₄H₂₄N₆O₂Pd·3CH₃OH: C, 51.39; H, 5.75; N, 13.32.

Pd(II) Complex trans-2. This compound was prepared from [**II**]·Cl (0.11 g, 0.36 mmol), K₂CO₃ (0.25 g, 1.78 mmol), and K₂PdCl₄ (0.058 g, 0.18 mmol) in anhydrous dimethylformamide (25 mL) using the method described for **1** to give *trans-2* as a cream-colored powder. Yield: 0.026 g (23%). ¹H NMR (*d*₆-DMSO): δ 4.36 (d, 2H, ²J_{HH} = 14.1 Hz, CH₂), 5.41 (d, 2H, ²J_{HH} = 14.1 Hz, CH₂), 6.65 (t, 2H, ³J_{HH} = 7.1 Hz, *H*_{aryl}), 6.82 (dd, 4H, ³J_{HH} = 7.1 Hz, ³J_{HH} = 7.5 Hz, *H*_{aryl}), 7.40 (s, 2H, *H*_{imi}), 7.51 (t, 4H, ³J_{HH} = 7.2 Hz, *H*_{aryl} and *H*_{imi}), 7.63 (dd, 4H, ³J_{HH} = 7.2 Hz, ³J_{HH} = 7.8 Hz, *H*_{aryl}), 7.82 (d, 4H, ³J_{HH} = 7.8 Hz, *H*_{aryl}), 122.4 (*C*_{imi}), 123.4 (*C*_{aryl}), 125.6 (*C*_{aryl}), 126.0 (*C*_{aryl}), 127.9 (*C*_{aryl}), 128.6 (*C*_{aryl}), 137.7 (*C*_q), 149.8 (*C*_q), 167.2 (Pd-C), 169.1 (*C*==O) ppm. Anal. Found: *C*, 60.11; H, 4.33; N, 12.39. Calcd for C₃₄H₂₈N₆O₂Pd·H₂O: <u>C</u>, 60.31; H, 4.47; N, 12.41.

Ni(II) Complex 3. To a solution of $[III]Cl_2$ (0.13 g, 0.301 mmol) in anhydrous dimethylformamide (15 mL) were added K2CO3 (0.21 g, 1.50 mmol) and a solution of NiCl₂ (0.039 g, 0.301 mmol) in anhydrous dimethylformamide (10 mL). The resultant mixture was heated at 110 °C for 16 h, and after it was cooled to room temperature, the mixture was filtered and the solvent was removed under reduced pressure. The residue was recrystallized from a mixture of dichloromethane and diethyl ether to give 3 as a light brown powder. Yield: 0.027 g (21%). ¹Η NMR (d₆-DMSO): δ 3.18 (s, 6H, CH_3), 4.66 (d, 2H, ${}^2J_{HH}$ = 17.1 Hz, CH_2), 5.13 (d, 2H, ${}^2J_{HH}$ = 17.1 Hz, CH_2), 6.63–6.66 (m, 2H, H_{aryl}), 7.32 (d, 2H, ${}^{3}J_{HH}$ = 1.8 Hz, H_{imi}), 7.42 (d, 2H, ${}^{3}J_{HH}$ = 1.8 Hz, H_{imi}), 8.30–8.33 (m, 2H, H_{aryl}) ppm. ${}^{13}C$ NMR $(d_6$ -DMSO): δ 36.1 (CH₃), 54.5 (CH₂), 119.9 (C_{aryl}), 121.3 (C_{imil}), 121.6 (C_{aryl}) , 123.7 (C_{imi}) , 143.4 (C_q) , 162.7 (Ni-C), 166.4 (C=O) ppm. Anal. Found: C, 49.57; H, 4.32; N, 18.75. Calcd for C18H18N6O2Ni 0.5CH2Cl2: C, 49.21; H, 4.24; N, 18.61. The reported elemental analysis results are provided to illustrate the best values obtained to date. Copies of the NMR spectra (1H and 13C) are provided in the Supporting Information (Figure S2) as additional evidence of purity.

Ni(II) Complex **4**. This compound was prepared from a solution of [**IV**]Cl₂ (0.12 g, 0.21 mmol), K₂CO₃ (0.15 g, 1.06 mmol), and NiCl₂ (0.028 g, 0.21 mmol) using the method described for **3**, except the reaction was conducted at 125 °C for 16 h. The crude product was recrystallized from a mixture of dichloromethane and diethyl ether to give **4** as a brown powder. Yield: 0.026 g (23%). ¹H NMR (*d*₆-DMSO): δ 4.55 (dd, 2H, ²J_{HH} = 17.1 Hz, CH₂), 4.65 (dd, 2H, ²J_{HH} = 17.1 Hz, CH₂), 6.69–6.73 (m, 2H, H_{aryl}), 7.07 (d, 2H, ³J_{HH} = 1.8 Hz, H_{imi}), 7.25 (d, 2H, ³J_{HH} = 7.5 Hz, ³J_{HH} = 7.8 Hz, H_{aryl}), 7.56 (dd, 4H, ³J_{HH} = 7.5 Hz, ³J_{HH} = 7.8 Hz, H_{aryl}), 8.40–8.43 (m, 2H, H_{aryl}) ppm. ¹³C NMR (*d*₆-DMSO): δ 54.2 (CH₂), 120.1 (C_{aryl}), 121.5 (C_{imi}), 121.6 (C_{aryl}), 122.4 (C_{imi}), 124.3 (C_{aryl}), 127.9 (C_{aryl}), 128.8 (C_{aryl}), 138.8 (C_q), 143.6 (C_q), 164.1 (Ni-C), 166.0 (C=O) ppm. Anal. Found: C, 62.03; H, 4.28; N, 15.40. Calcd for C₂₈H₂₂N₆O₂Ni·0.5H₂O: C, 62.02; H, 4.28; N, 15.50. The reported elemental analysis results are provided to illustrate the best values obtained to date. Copies of the NMR spectra (¹H and ¹³C)

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are provided in the Supporting Information (Figure S2) as additional evidence of purity.

Pd(II) Complex 5. $5_{a,a}$ To a solution of [III]Cl₂ (0.16 g, 0.37 mmol) in anhydrous dimethylformamide (20 mL) were added K₂CO₃ (0.26 g, 1.9 mmol) and a solution of K₂PdCl₄ (0.12 g, 0.37 mmol) in anhydrous dimethylformamide (20 mL). The resulting mixture was heated at 70 °C for 16 h, and after it was cooled to room temperature, the mixture was filtered and the solvent was removed under reduced pressure. ¹H NMR analysis of the crude product showed that two isomers were formed $(5_{n,a}/5_{a,a})$ in the ratio 0.39/0.61. The crude product was triturated with dichloromethane (30 mL), and a brown solid that did not dissolve was collected and recrystallized from methanol to give $5_{a,a}$ as a pale brown powder. Yield: 0.046 g (27%). ¹H NMR (*d*₆-DMSO): δ 3.76 (s, 6H, CH₃), 4.63 (s, 4H, CH₂), 6.58–6.60 (m, 2H, H_{arvl}), 7.10 (s, 2H, H_{imi}), 8.13-8.15 (m, 2H, H_{arvl}), 8.84 (s, 2H, NCHN) ppm. ¹³C NMR ($\overline{d_6}$ -DMSO): δ 34.4 (CH₃), 56.7 (CH₂), 119.8 (C_{aryl}), 122.2 (C_{aryl}), 124.5 (C_{imi}), 134.3 (NCN), 143.7 (C_{q}), 144.9 (Pd-C), 164.6 (C=O) ppm. Anal. Found: C, 40.88; H, 4.68; N, 15.58. Calcd for C₁₈H₁₈N₆O₂Pd·4H₂O: C, 40.88; H, 4.96; N, 15.89.

5_{*n,a*}. The dichloromethane solution (from the trituration step in the synthesis of **5**_{*a,a*}, above) was evaporated to dryness, and the residue was further recrystallized from dichloromethane to give **5**_{*n,a*} as a cream-colored powder. Yield: 0.007 g (4%). ¹H NMR (*d₆*-DMSO): δ 3.70 (*s*, 6H, CH₃), 4.67 (*s*, 2H, CH₂), 4.81 (*s*, 2H, CH₂), 6.63 (*s*, 1H, H_{imi}), 6.68–6.70 (m, 2H, H_{aryl}), 7.28 (d, 1H, ³J_{HH}= 0.9 Hz, H_{imi}), 7.41 (d, 1H, ³J_{HH}= 0.9 Hz, H_{imi}), 7.93–7.95 (m, 1H, H_{aryl}), 8.54–8.56 (m, 1H, H_{aryl}), 8.69 (*s*, 1H, NCHN) ppm. ¹³C NMR (*d₆*-DMSO + MeOD): δ 33.9 (2 × CH₃), 120.2 (*C*_{aryl}), 120.6 (*C*_{aryl}), 121.5 (*C*_{imi}), 122.2 (*C*_{imi}), 122.5 (*C*_{aryl}), 123.3 (*C*_{aryl}), 126.0 (*C*_{imi}), 133.8 (NCN), 140.4 (*C_q*), 143.3 (*C_q*), 144.5 (Pd-C), 165.3 (Pd-C), 165.6 (*C*=O), 165.8 (*C*=O) ppm. Anal. Found: C, 47.04; H, 3.81; N, 18.22. Calcd for C₁₈H₁₈N₆O₂Pd: C, 47.33; H, 3.97; N, 18.40.

Pd(II) Complex **6**. **6**_{*a,a*}. This compound was prepared from a solution of [**IV**]Cl₂ (0.39 g, 0.071 mmol), K₂CO₃ (0.49 g, 3.54 mmol), and K₂PdCl₄ (0.23 g, 0.071 mmol) using the method described for **5**. ¹H NMR analysis of the crude product showed that three isomers were formed (**6**_{*n,n*}/**6**_{*n,a*}/**6**_{*a,a*}) in the ratio 0.25/0.35/0.40. **6**_{*a,a*} was obtained as a dark brown powder. Yield: 0.085 g (21%). ¹H NMR (*d*₆-DMSO): *δ* 4.77 (s, 4H, CH₂), 6.62–6.64 (m, 2H, H_{aryl}), 7.52 (t, 2H, ³J_{HH}= 4.5 Hz, H_{aryl}), 7.62 (dd, 4H, ³J_{HH} = 4.5 Hz, ³J_{HH} = 4.8 Hz, H_{aryl}), 7.76 (d, 2H, ³J_{HH} = 0.9 Hz, H_{imil}), 7.78 (d, 4H, ³J_{HH} = 4.8 Hz, H_{aryl}), 8.10–8.12 (m, 2H, H_{aryl}), 9.54 (d, 2H, ³J_{HH}= 0.9 Hz, NCHN) ppm. ¹³C NMR (*d*₆-DMSO): *δ* 57.2 (CH₂), 120.1 (C_{aryl}), 121.8 (C_{imi}), 121.9 (C_{aryl}), 122.3 (C_{aryl}), 128.8 (C_{aryl}), 130.0 (C_{aryl}), 133.4 (NCN), 135.6 (C_q), 144.5 (C_q), 144.8 (Pd-C), 164.3 (C=O) ppm. Anal. Found: C, 55.80; H, 4.31; N, 13.74. Calcd for C₂₈H₂₂N₆O₂Pd·H₂O: C, 56.15; H, 4.04; N, 14.03.

 $\boldsymbol{6}_{n,a}$. The dichloromethane solution (from the trituration step in the synthesis of $6_{a,a}$, above) was evaporated to dryness, and ¹H NMR showed the residue obtained to be a mixture of two geometric isomeric forms of 6. Initial recrystallization of the residue from acetonitrile gave $6_{n,a}$ as a pale brown powder. Yield: 0.020 g (5%). ¹H NMR (d_6 -DMSO): δ 4.75 (s, 2H, CH₂), 4.83 (s, 2H, CH₂), 5.99 (d, 1H, ${}^{3}J_{HH} = 0.9$ Hz, H_{imi}), 6.70–6.72 (m, 2H, H_{aryl}), 7.24 (t, 1H, ${}^{3}J_{HH} =$ 4.5 Hz, H_{aryl}), 7.32 (d, 2H, ${}^{3}J_{HH}$ = 4.8 Hz, H_{aryl}), 7.39 (dd, 2H, ${}^{3}J_{HH}$ = 4.5 Hz, ${}^{3}J_{HH} = 4.8$ Hz, H_{aryl}), 7.45 (t, 1H, ${}^{3}J_{HH} = 4.5$ Hz, H_{aryl}), 7.53 $(dd, 2H, {}^{3}J_{HH} = 4.8 \text{ Hz}, {}^{3}J_{HH} = 4.5 \text{ Hz}, H_{aryl}), 7.75 (d, 1H, {}^{3}J_{HH} = 1.2$ Hz, $H_{\rm imi}$), 7.76 (d, 1H, ${}^{3}J_{\rm HH} = 1.2$ Hz, $H_{\rm imi}$), 7.80 (d, 2H, ${}^{3}J_{\rm HH} = 4.8$ Hz, H_{arvl}), 8.10–8.12 (m, 1H, H_{arvl}), 8.34–8.36 (m, 1H, H_{arvl}), 9.19 (d, 1H, ${}^{3}J_{HH} = 0.9$ Hz, NCHN) ppm. ${}^{13}C$ NMR (d_{6} -DMSO): δ 56.5 (CH_2) , 56.9 (CH_2) , 120.3 $(2 \times C_{arvl})$, 121.0 (C_{arvl}) , 122.0 (C_{imi}) , 122.7 $(2 \times C_{imi}, C_{aryl}), 123.0 (C_{aryl}), 126.2 (C_{aryl}), 128.1 (C_{aryl}), 128.5 (C_{aryl}), 128.7 (C_{aryl}), 130.0 (C_{aryl}), 131.6 (NCN), 135.0 (C_q), 140.0 (C_q),$ 141.9 (C_q) , 144.1 (C_q) , 144.7 (Pd-C), 149.5 (C_q) , 164.8 (Pd-C), 164.9 (C=O), 165.3 (C=O) ppm. Anal. Found: C, 57.00; H, 4.21; N, 14.21. Calcd for C₂₈H₂₂N₆O₂Pd·0.5H₂O: C, 57.01; H, 3.93; N, 14.25. The reported elemental analysis results are provided to illustrate the best values obtained to date. Copies of the NMR spectra (¹H and ¹³C) are provided in the Supporting Information (Figure S3) as additional evidence of purity.

6_{*n,n*}. The acetonitrile filtrate (from the recrystallization of **6**_{*a*,a} above) was evaporated to dryness, and the resultant residue was recrystallized from methanol to afford **6**_{*n*,n} as a dark brown powder. Yield: 0.015 g (4%)/ ¹H NMR (*d*₆-DMSO): δ 4.72 (dd, 2H, ²J_{HH} = 9.9 Hz, CH₂), 4.97 (dd, 2H, ²J_{HH} = 9.9 Hz, CH₂), 6.76–6.78 (m, 2H, H_{aryl}), 7.25–7.28 (m, 2H, H_{aryl}), 7.29 (d, 2H, ³J_{HH} = 1.2 Hz, H_{imi}), 7.36 (d, 2H, ³J_{HH} = 1.2 Hz, H_{imi}), 7.42–7.48 (m, 8H, H_{aryl}), 8.40–8.42 (m, 2H, H_{aryl}) ppm. ¹³C NMR (*d*₆-DMSO): δ 56.4 (CH₂), 120.5 (C_{aryl}), 121.2 (C_{imi}), 121.8 (C_{imi}), 123.0 (C_{aryl}), 125.0 (C_{aryl}), 128.0 (C_{aryl}), 128.1 (C_{aryl}), 137.9 (C_q), 143.8 (C_q), 163.5 (C=O), 165.1 (Pd–C) ppm. Anal. Found: C, 52.88; H, 4.59; N, 13.29. Calcd for C₂₈H₂₂N₆O₂Pd·3H₂O: C, 52.96; H, 4.44; N, 13.24.

ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving X-ray crystallographic data for *trans*-1, *cis*-1, *trans*-2, 3, 4, $5_{a,a}$, $5_{n,a}$, $6_{n,n}$ and $6_{a,a}$, scan rate dependence of cyclic voltammograms for $6_{n,n}$, $6_{n,a'}$ and $6_{a,a'}$ relative energies for calculated geometries, and the Cartesian coordinates of optimized Ni(II) and Pd(II) complexes. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr. Gregory Barbante and Dr. Conor Hogan for help with the electrochemical measurements. We thank the Australian Research Council for LIEF funding for the X-ray diffractometer used in this work.

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