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Synthesis, Characterisation, and Coordination Behaviour of Novel Pyridyl-formamidine Based Mn(I), Cu(II), Zn(II), and Pd(II) Complexes

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We report a new synthetic approach for the synthesis of less-explored unsymmetrical pyridyl-formamidine ligands and their coordination behaviour to form Mn(I), Cu(II), Zn(II), and Pd(II) complexes. The one-step process for synthesising the unsymmetrical pyridyl-formamidine compounds offers the advantage of being functional-group tolerant and less cumbersome. Generally, the pyridyl-formamidine ligands coordinate to the metal centres in a bidentate fashion to form a six-membered chelate as established by spectroscopic and crystallographic analysis. It was observed that the formamidine functionality is prone to hydrolysis in the presence of methoxy substituent on the phenyl ring and/or acetate-containing metal precursors.

Introduction

Metal-ligand bonding interactions that arise when a ligand coordinates to a metal can modulate the metal's electronic properties and influence its steric environment. This allows for control over the structure and reactivity of metal complexes. Consequently, organometallic chemistry, as well as homogeneous metal-mediated catalysis, has been greatly enriched by the design and study of new ligand motifs.[1] An understanding of how ligands influence the properties of metal species has led to the discovery of new and improved metal-catalysed reactions used in the synthesis of pharmaceuticals and materials, as well as the isolation and interrogation of vital reactive intermediates. Additionally, it has enabled chemists to uncover fundamentally new modes of bonding between metal centres and organic or main-group compounds.[1]

Coordination compounds containing nitrogen donor ligands have been of great interest to researchers due to their usefulness in many applications, including catalysis. Usually, nitrogen donor ligands are based on amide, amine, imine, and imide functionalities, which have seen massive development over the years, to improve upon properties such as reactivity and stability.[2] The formamidine nitrogen donor ligand combines amine and amide functionalities where the arrangement of the motif displays a central carbon atom that bonds to a nitrogen atom *via* a single bond and at the same time is doubly bonded with another nitrogen atom, forming an –N=C(H)–N-(H)– backbone. This structural motif has attracted a great deal of interest since the first reported synthesis in 1858[3] due to its rich conformational, configurational, and tautomeric diversity.[4–6] Noteworthy are the symmetrical N,N′-diarylformamidines, which have been extensively explored due to their convenient synthesis from aniline derivatives and trialkyl orthoformates.[7–9] The aryl groups can also be modified to have electron-donating and electron-withdrawing substituents. Usually, when formamidines are used as neutral ligands, they bind in a monodentate fashion through the imine nitrogen.[10,11] However, when deprotonated, the resulting formamidinates have a conjugated N–C–N backbone that presents even more interesting coordination behaviours such as bidentate, η^3-allyl, and bridging modes.[12–15] Their corresponding metal complexes have found applications in catalysis such as polymerisation,[16] cross-coupling,[17] hydrogen evolution reactions,[18] hydroformylation,[19] among others.[20] Similar to symmetrical N,N′-diarylformamidines, the symmetrical bis-2-pyridyl-formamidine, and its anion have also been studied and found to exhibit a variety of coordination modes.[21] Even though formamidines and formamidinates are versatile ligands and exhibit a variety of coordination modes in metal complexes, the unsymmetrical formamidines have been less explored, likely due to the more demanding synthesis routes.[22–25]

Our group is interested in developing novel pyridyl-formamidine ligands, their corresponding metal complexes, and their potential applications, especially in catalysis. Herein, as a first example, we report the improved synthesis of a series of unsymmetrical pyridyl-formamidines bearing both electron-donating and electron-withdrawing substituents. The synthesis, characterisation, and coordination behaviour of copper (Cu), zinc (Zn), manganese (Mn), and palladium (Pd), complexes incorporating these pyridyl-formamidine ligands have also been

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explored. The synthetic strategies employed, the challenges encountered in the processes, and the conditions applied to achieve the desired coordination environments or otherwise are described.

Results and Discussion

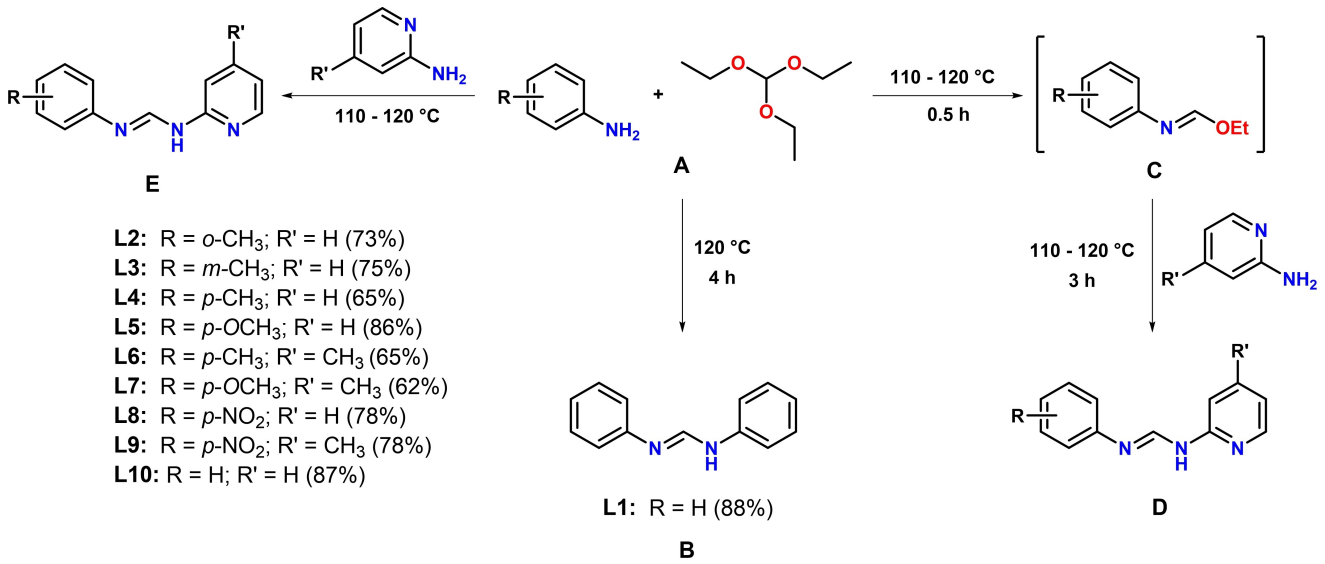
Ligand Development Strategies

Our starting point in ligand development was the preparation of N,N′-diphenylformimidamide (**L1**) using a slight modification of a previously reported method for the synthesis of symmetrical formamidines,[26] as illustrated in Scheme 1, **A** to **B**. Compound **L1** has been reported previously[27,28] and is also commercially available, however for this study, we employed the outlined procedure in Scheme 1 and obtained **L1** in high yield (*ca.* 88%). It is more cost-efficient to synthesise **L1** using our approach than to purchase from commercial vendors. (See pricing info in the supplementary information). The (E)-isomers are shown for all the ligands illustrated in Scheme 1. Two approaches have been used in synthesising the unsymmetrical pyridyl-formamidines, **L2**–**L10**, as illustrated in Scheme 1. Procedure one, (**A** to **D**) is a modification of a previously reported method for the synthesis of unsymmetrical formamidines,[29] while procedure two (**A** to **E**) is a novel method we have developed for synthesising unsymmetrical pyridyl-formamidines. Procedure one is a two-step approach where the first primary amine is reacted with triethyl orthoformate (TEOF) at 110–115 °C for 30 minutes or until an imidate intermediate (**C**) is formed. Evidence for the formation of this intermediate is seen in the production of ethanol during the reaction, which is then distilled off.[30] The second amine is added without isolation of the intermediate, and the reaction continued for 3 hours. Procedure two is a one-step approach in which all the reactants are initially charged into the reaction vessel. Continuous ethanol removal from the reaction mixture ensures rapid conversion to the formamidine product, while preventing the reverse reaction from occurring and leading to increased yields of the desired, unsymmetrical, product.[31] Typically, procedure one gives higher overall yields (*ca.* 10–15% more) than procedure two albeit with lower selectivity, requiring tedious purification methods and product loss. Procedure two is a more convenient route to the synthesis of unsymmetrical pyridyl-formamidines since it is a less cumbersome approach to desired product formation and isolation, while being more atom-economical. To the best of our knowledge this is the first reported synthesis of unsymmetrical pyridyl-formamidine ligands using a one-step approach.

Cotton and coworkers[32] reported a two-step approach to synthesising unsymmetrical pyridyl-formamidines, including **L4**, **L5**, and **L10** with yields greater than 80%. The first step involved the synthesis of pyridyl-formimidate by reacting aminopyridine derivatives with TEOF, using catalytic amounts of acid and temperatures as high as 180 °C. In the second step, the pyridyl-formimidate is reacted with the required aniline derivatives in an acid-free environment to produce the unsymmetrical formamidines. For example, using our approach, as shown in Scheme 1, a comparable yield (*ca.* 86%) was obtained for **L5** using milder reaction conditions and without the need to use an acid.[32–34] With the exceptions of compounds **L1**, **L4**, **L5** and **L10**, all the other compounds are novel to the best of our knowledge. These compounds were characterised using a combination of FTIR and NMR spectroscopy, CHNS elemental analysis, APCI-MS, and GC-MS spectrometry.

Characterisation of Ligands

The FTIR spectra of compounds **L1**–**L10** exhibited weak absorption bands around 3010 to 3310 cm^{-1}, which is attributed to N–H stretching frequencies.[26] The formamidinyl C–H



Scheme 1. Outline for solvent-free synthesis of compounds **L1**–**L10**.

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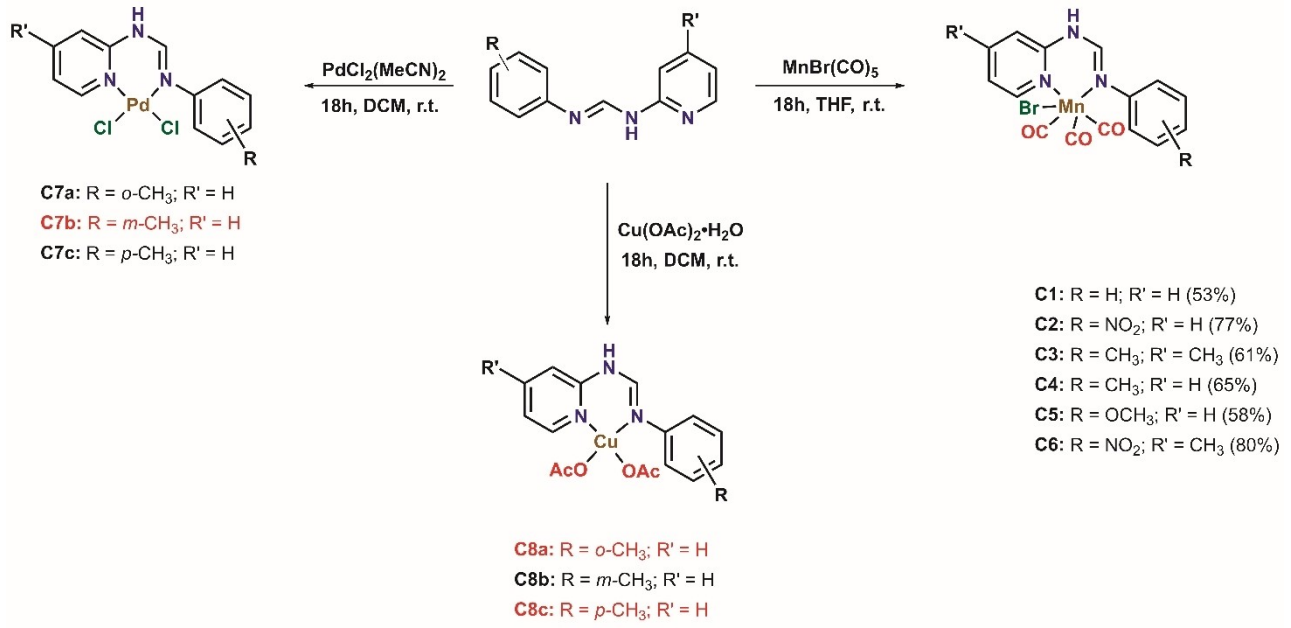
stretch is seen around 2830–2970 cm^{-1} and the azomethine (C=N) symmetric vibration frequencies are around 1610–1660 cm^{-1}. Additionally, strong absorption bands between 1550–1590 cm^{-1} were assigned to pyridinyl C=N stretching frequencies (Figure S1). The ^{1}H NMR data provided complementary evidence for the successful synthesis of the ligands (Figure S2). Generally, the N–*H* signal is a characteristic broad singlet observed downfield between 8.85 and 10.80 ppm, with the compounds bearing nitro substituents further downfield whilst the methyl and methoxy derivatives appear slightly upfield (Figure S3). The difference is attributed to the high solvent polarity and electronic effects of the substituents on the proton.[32] In addition, the imine proton signals, N=C(*H*)–N, were observed between 8.07 and 8.25 ppm in all the ligands, while all other protons were duly accounted for. ^{13}C NMR spectra of the ligands show the imine ^{13}C shifts around 156–149 ppm, aromatic ^{13}C signals between 150–110 ppm while the methoxy and methyl signals were observed around 55 and 20 ppm respectively.

To further corroborate the successful synthesis of **L1**–**L10**, elemental analysis, APCI–MS and/or GC–MS were performed. The bulk purity of the new ligands was confirmed by CHNS elemental analysis. The results of the elemental analysis mostly tally well with the calculated values and fall within acceptable limits, as advocated by the scientific community recently (Table S3.1).[35,36] The GC–MS and APCI–MS analyses showed peaks corresponding to the ligand of interest, as illustrated in Figures S4 and S5. The findings from the various analytical and spectroscopic methods signal the successful synthesis of all compounds.

Establishing the Coordination Behaviour of Pyridyl-Formamidine Ligands, L1–L10

The complexes were synthesised by reacting the required amount of metal precursor and ligand in a 1:1 metal:ligand ratio at room temperature overnight. The chelates are readily formed under the conditions outlined in Scheme 2 and do not require heating or additives. In preparing the manganese(I) complexes (**C1**–**C6**), it is desirable to filter the crude through Celite® at the end of the reaction to remove manganese black, after which recrystallisation in THF/hexane mixture affords the pure product. Attempts to synthesise other manganese complexes with the remaining ligands proved futile. The ligands chelated in a bidentate fashion through the imine nitrogen of the formamidine moiety and the pyridyl nitrogen, forming a six-membered ring. The complexes are very unstable in air, making them extremely difficult to handle and requiring inert conditions for their synthesis, purification, and storage. To further expand the scope of the metals, we attempted to synthesise copper and palladium complexes with the ligands bearing methyl and methoxy groups, to obtain insights into the substituent effects on the coordination behaviour. However, most of these have been unsuccessful (highlighted in red in Scheme 2), even after several efforts using different reaction conditions. The successfully synthesised Pd(II) and Cu(II) compounds, **C7a** and **C8b** (hereafter **C7** and **C8** respectively) were obtained by reacting the required ligand and metal precursor in DCM at room temperature overnight using standard Schlenk techniques. The pure products were then obtained by reducing the solvent *in vacuo* and washing the precipitate with dry hexane or diethyl ether. The complexes were characterised using a combination of FTIR, NMR, ESI–MS, elemental analysis, and ScXRD techniques.



Scheme 2. Synthetic routes to manganese (**C1**–**C6**), palladium (**C7**), and copper (**C8**) pyridyl-formamidine complexes.

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In the IR spectra of **C1**–**C8**, the N–H and imine stretching frequencies are generally red-shifted relative to the respective ligands. Furthermore, the IR spectra of the manganese(I) complexes reveal three characteristic peaks between 2020–1880 cm^{-1} which are attributed to the carbonyl groups coordinated to the manganese centre.[27,28] Thus both symmetric and asymmetric stretching vibrations occur simultaneously (Figure S6). The CO stretching vibrations also confirm a mutual facial orientation as observed in the crystal structures .[29]

From the ^{1}H NMR spectra, the coordination of Mn(I) to the ligand through the imine and pyridyl N-atoms is evident. The N–H proton signals of the complexes shift further downfield compared to the free ligands, while the imine proton signals shift slightly upfield. For example, in complex **C3**, the N–*H* and C*H*=N proton signals are observed at 11.18 and 8.63 ppm respectively, whereas in the corresponding ligand (**L8**), the chemical shifts are 10.79 and 8.94 ppm, respectively. Generally, peak broadening has been observed in the ^{1}H NMR spectra for manganese complexes, **C1**–**C6** (Figure S7). Attempts to resolve this by switching the NMR solvents from $CDCl_3$ to CD_2Cl_2 and DMSO-d_6 (Figure S8) did not improve the spectra, nor did delaying the acquisition time and running the samples at low or high temperatures. In the ^{13}C NMR spectra, the signals corresponding to the imine carbon (*C*=N_{im}) are observed around 159.13–155.46 ppm while the *C*=N_{py} signals resonate around 151.66–154.97 ppm. The aromatic carbons resonate within the range from 126 to 114 ppm (Figure S9). The N–*H* and C*H*=N proton signals of the palladium(II) complex **C8** both shifted further downfield compared to the free ligand, **L2**.

The ESI-MS data recorded in the positive ion mode for manganese complexes, **C1**–**C6**, indicates the loss of the bromide ligand as shown by the masses of the base peaks (Figure S10).[28] Additionally, the calculated ESI-MS values for **C7** and **C8** agree with the experimentally observed ones. The results of the elemental analysis tally well with the calculated values and fall within acceptable limits, confirming the bulk purity and further corroborating the successful synthesis of **C1**–**C8**.

The molecular structures of Mn(I) complexes **C1** and **C2** are shown in Figure 1 and Figure S11 respectively. In these complexes, the manganese centre assumes an octahedral geometry, with the three CO ligands in mutual *facial* configuration.[27] The formamidine ligand chelates the metal centre in a bidentate fashion through the N-donor atoms resulting in a six-membered ring neutral complex, with the bromide completing the coordination sphere. Complexes **C1** and **C2** crystallise in the triclinic crystal system. The Mn–Br bond lengths in both complexes are comparable, measuring 2.5443(3) Å in **C1** and 2.5460(5) Å in **C2**. Similarly, the Mn–N_{py} bond lengths are similar, with **C2** showing a slightly longer length of 2.0885 Å compared to **C1** (2.0833 Å). Additionally, the N–M–N angles in **C1** and **C2** are 86.58°and 87.19° respectively, suggesting a greater extent of chelate distortion in **C1** relative to **C2**.

Single crystals of the Pd(II) and Cu(II) complexes, **C7** and **C8**, suitable for X-ray diffraction analysis were obtained from DCM layered with *n*-hexane. Their molecular structures are shown in Figure 1. The complexes exhibit good stability in the solid state and show no sign of degradation under ambient conditions. Their crystal structures show a distorted square planar geometry around the metal centre. Both complexes crystallise in the monoclinic crystal system with the $P2_1/_c$ space group for **C7** and the $P2_1/_n$ space group for **C8** respectively. The crystallographic data and structure refinement parameters are detailed in Table S2 and selected bond lengths and angles are provided in Table S3. The N–M–N angle observed for **C7** is 87.37°, which is slightly smaller than the ideal geometry but also consistent with reports of similar palladium complexes.[30] On the contrary, the N–M–N angle observed for **C8** is 93.37° which is *ca.* 3° larger than expected in the ideal geometry but consistent with those found in some copper complexes.[25] The torsion angle around **C7**'s phenyl plane is 51.1°, while that of **C8** is 42.0°. In addition, the metallocycle torsion angle in **C7** is 39.83°, pointing to the Pd being significantly out-of-plane whereas in **C8** it is 1.9°, suggesting that the Cu is nearly planar.

Attempted Synthesis of $Cu(OAc)_2$(L5) and $Zn(OAc)_2$(L7) Complexes

As mentioned, efforts were made to synthesise novel complexes with the prepared ligands, with varying success. In some cases, unexpected products were obtained. Two reactions worth noting are the unexpected behaviour of the methoxy-substituted ligands **L5** and **L7** in the presence of copper- and zinc acetate precursors to afford compounds **C9** and **C10**.

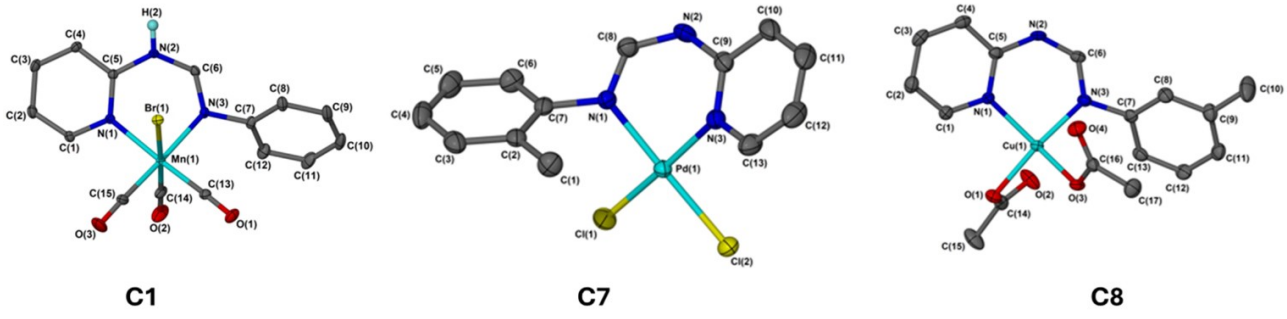

Figure 1. Representative molecular structures of pyridyl-formamidine-ligated metal complexes: Mn(I): **C1**, Pd(II): **C7** and Cu(II): **C8** with atomic labelling drawn at 50 % probability ellipsoids. Hydrogen atoms, besides H(2) in **C1**, are omitted for clarity.

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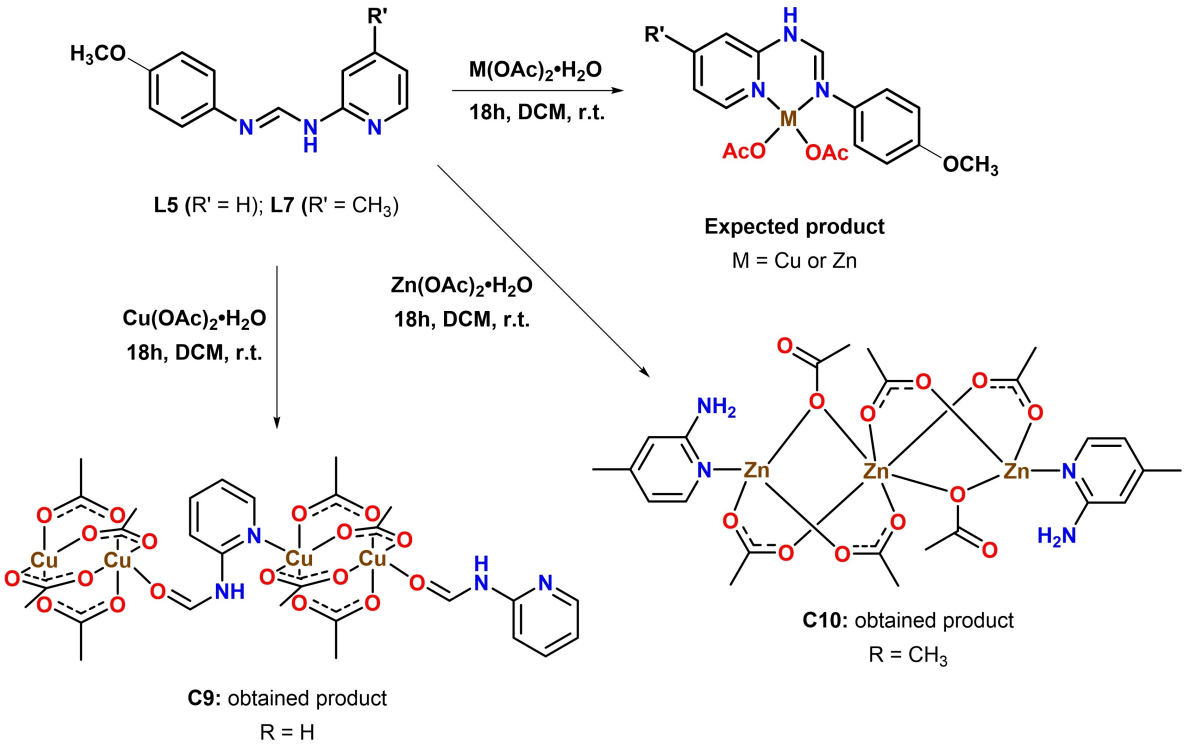
Compound **C9** was synthesised by reacting $Cu(OAc)_2{\cdot}H_2O$ with **L5** in dichloromethane at room temperature (Scheme 3). It was expected that the ligand would coordinate to the metal centre in a bidentate fashion to form a six-membered ring complex as observed with compounds **C1**–**C8**. However, the molecular structure revealed that the formamidine ligand, **L5** underwent base-mediated hydrolysis in the presence of the basic acetate group into pyridine-formamide and *p*-anisidine (Scheme S1). The pyridine-formamide then coordinates with the Cu precursor, yielding complex **C9**. The ORTEP image of **C9** is shown in Figure 2. The arrangement of compound **C9** displays a 1D polymeric chain structure with a $Cu_2(OAc)_4$ paddlewheel core where one Cu centre is coordinated to the N-atom of the pyridine-formamide ligand and the other Cu is coordinated to the O-atom of the formamide ligand, in a monodentate mode. Thus, an alternating arrangement of the dinuclear $Cu_2(OAc)_4$ paddlewheel core and the pyridine-formamide ligand results in a coordination polymer. Each metal centre displays a distorted square-pyramidal geometry such that four acetate groups coordinate at the base of the pyramid and the apex is occupied by the pyridine-formamide ligand. The compound also presents a shorter intermetallic Cu·Cu distance (2.584 Å) than other reports of $Cu_2(OAc)_4$ paddlewheel core type complexes.[31,32] The Cu–OAc distances are between 1.95 and 1.98 Å which is consistent with literature reports[18,31] while the Cu–O_{form} distance is 2.183 Å. Additionally, the Cu–N_{py} distance, Cu(2)–N(1) (2.2263(4)) is slightly longer than most Cu–N_{py} bonds. Again, AcO–Cu–OAc angles range between ~88° and 93° showing a distortion from the ideal square-pyramidal geometry values. Similarly to **L5**, **L7** is also hydrolysed in the presence of the acetate-containing Zn precursor to form 4-methoxyphenyl formamide and 2-amino-4-methylpyridine as illustrated in



Scheme 3. Synthetic routes to compounds **C9** and **C10**.

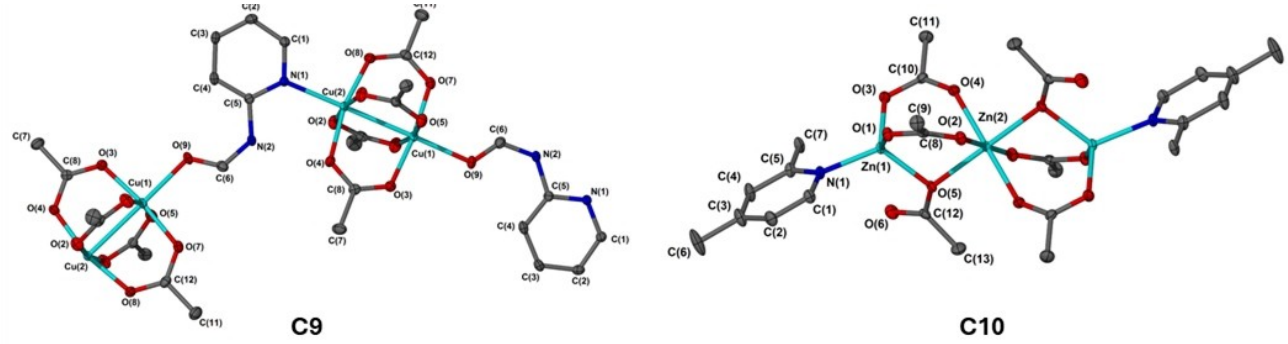


Figure 2. Molecular structures of **C9** and **C10** with atomic labelling drawn at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

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Scheme S1. The manner in which the hydrolysis occurs in both instances indicate the presence of two tautomeric forms of the ligands, as previously reported and described in Scheme S1.[4–6] It is possible that the presence of the methoxy substituent plays a role in the hydrolysis reaction since the hydrolysis did not occur with compound **C8** which is an analogous copper complex, without the methoxy substituent. It should be noted that in our hands, the targeted synthesis of **C9** and **C10** led to the isolation of intractable mixtures. This is attributable to a lack of control over the tautomerisation process and subsequent hydrolysis events. This lack of control is illustrated in divergent ligand hydrolysis products as illustrated in Scheme 3. As such, bulk purity could not be established for **C9** and **C10**. The ORTEP image of **C10** is shown in Figure 2. The 4-methoxyphenyl formamide coordinates to the Zn acetate precursor forming **C10**, a trinuclear Zn(II) complex with the Zn centres arranged linearly. The structure reveals two types of bridging modes where the acetate ions occupy the bridges in both monodentate and bidentate fashion, similar to a Zn(II) formamidine complex reported previously.[18] The two outer Zn(II) centres exhibit a distorted tetrahedral geometry while the central Zn atom adopts a distorted octahedral geometry. The crystallographic data and structure refinement parameters for **C9** and **C10** are detailed in Table S4, and selected bond lengths and angles are provided in Table S5.

Conclusions

We have developed a new synthetic method to prepare the less-explored unsymmetrical pyridyl-formamidine ligands. Among the synthesised ligands, **L1**, **L4**, **L5** and **L10**, have been previously reported while the remaining ligands are novel to the best of our knowledge. Furthermore, we have successfully synthesised and characterised a variety of novel pyridyl-formamidine-metal chelate complexes using a combination of NMR, FTIR, ESI–MS, elemental analysis, and ScXRD techniques. For the Mn(I) complexes, **C1**–**C6**, and Pd(II) and Cu(II) complexes, **C7**–**C8**, the ligands coordinate to the metal centre in a bidentate chelating mode resulting in a six-membered ring, with either distorted octahedral or square planar geometry at the metal. Interestingly, the analysis of the molecular structures of Cu(II) and Zn(II) complexes, **C9** and **C10**, revealed that the ligands underwent base-mediated hydrolysis. This result is significant and confirms that formamidines lead to the formation of unintended by-products when metal acetate salts are used, emphasising careful choice of metal salts during complexation reactions. Current efforts in our group are directed at establishing the coordination behaviour of our ligand scaffold with other metals and evaluating the Mn(I) complexes as catalyst precursors in direct- and transfer hydrogenation of unsaturated compounds for fuel and fine-chemical synthesis.

Experimental Section

Synthesis of N,N′-Diphenylformimidamide (L1)

A round-bottomed flask fitted with a distillation head was charged with aniline (60 mmol; 5.5 mL), TEOF (30 mmol; 5 mL) and one drop of 2 M HCl. The mixture was heated in an oil bath at about 120 °C for 4 h. Excess TEOF was removed under vacuum and the product was cooled to room temperature. The crude solidified upon cooling and was then triturated in hexane and recrystallised in ethanol to afford an off-white crystalline product. Yield: 5.18 g (88 %). FTIR (ATR, ν cm^{-1}) 3158 υ(N–H) stretching, 1657 υ(C=N) stretching. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.17 (d, J = 11.7 Hz, CH_{py},1H), 7.29 (dd, J = 9.7, 5.4 Hz, CH_{py}, 4H), 7.05 (dd, J = 15.0, 7.2 Hz, CH_{arom}, 6H). EA calculated (found): C 79.56(79.65), H 6.16(6.23), N 14.27(14.11). HRMS (APCI + mode, m/z): Calculated for $[M+H]^+$ 197.1000, found 197.1097.

General Procedure for Synthesis of Pyridyl-Formamidine Ligands L2–L7

A series of unsymmetrical formamidine ligands were prepared using a modification of the method described by Munzeiwa *et al.*[26] Therefore, the first primary amine (substituted aniline/aniline) and TEOF are charged into a round-bottomed flask with a simple distillation setup. The mixture is slowly heated using an oil bath. At about 115 °C, ethanol begins to distill or if distillation does not start, one drop of 2 M HCl is added to aid the distillation process. When about 95 % of the ethanol is distilled, the excess TEOF is removed *via* vacuum distillation. After the removal of the excess TEOF, the required aminopyridine is added and the reaction continued at 115 °C for 3 h. The work-up is described for the individual products below.

Synthesis of N-(Pyridin-2-yl)-N′-(o-Tolyl)Formimidamide (L2)

Compound **L2** was synthesised as described in the general procedure above, using *o*-toluidine (20 mmol; 2.143 g), TEOF (60 mmol, 10 mL), one drop of 2 M HCl and 2-aminopyridine (20 mmol, 1.82 g). At the end of the reaction, the flask was slowly cooled, ethyl acetate and hexane were added, and the mixture was kept in the fridge for 72 h. The product crystallised out and was filtered, washed with 3×10 mL hexane and dried to afford a white solid. Yield: 3.085 g (73 %). FTIR (ATR, ν cm^{-1}) 3168 υ(N–H) stretching, 1666 υ(C(H)=N) stretching. ^{1}H NMR (600 MHz, DMSO, ppm) δ 10.27 (s, N–*H*, 1H), 8.63 (s, *H*C=N$_{im}$, 1H), 8.20 (d, J = 3.5 Hz, CH_{py}, 1H), 7.73–7.63 (m, CH_{py}, 1H), 7.15 (dd, J = 17.1, 7.7 Hz, CH_{arom}, 3H), 6.96 (dt, J = 12.0, 6.4 Hz, CH_{arom}, 3H), 2.24 (s, –CH_3, 3H). ^{13}C NMR (151 MHz, DMSO) δ 149.83 (*C*=N$_{im}$), 148.81 (*C*=N$_{py}$), 148.01 (–N–*C*$_{arom}$), 147.75 (*C*H$_{py}$), 129.12 (H*C*–N$_{py}$), 128.98 (*C*H$_{arom}$), 122.65 (*C*H$_{arom}$), 119.76 (*C*H$_{arom}$), 118.94 (*C*H$_{arom}$), 20.56 (–*C*H$_3$). EA calculated (found): C 73.91(73.37), H 6.20(6.64), N 19.89(19.95). HRMS (APCI + mode, m/z): Calculated for $[M+H]^+$ 212.1101, found 212.1177.

Synthesis of N-(Pyridin-2-yl)-N′-(m-Tolyl)Formimidamide (L3)

Compound **L3** was synthesised as described in the general procedure in above using *m*-toluidine (20 mmol; 2.143 g), TEOF (60 mmol, 10 mL), one drop of 2 M HCl and 2-aminopyridine (20 mmol, 1.82 g). The product was triturated in cold *n*-pentane and washed with diethyl ether to afford a white solid. Yield: 3.169 g (75 %). FTIR (ATR, ν cm^{-1}) 3147 υ(N–H) stretching, 1658 υ(C(H)=N) stretching. ^{1}H NMR (600 MHz, DMSO, ppm) δ 10.29 (s, N–*H*, 1H), 8.84 (s, *H*C=N$_{im}$, 1H), 8.23 (s, CH_{py}, 1H), 7.69–7.64 (m, CH_{py}, 1H), 7.18 (t, J = 7.7 Hz, CH_{py}, 1H), 6.92 (dd, J = 71.2, 13.8 Hz, CH_{arom}, 5H), 2.29

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(s, –CH_3, 3H). ^{13}C NMR (151 MHz, DMSO) δ 150.85 (C=N_{im}), 149.52 (C=N_{py}), 148.63 (–N–C_{arom}), 147.90 (CH_{py}), 129.64 (CH_{py}), 128.98 (CH_{arom}), 123.12 (CH_{arom}), 119.97 (CH_{arom}), 118.99 (CH_{arom}), 20.59 (–CH_3). EA calculated (found): C 73.91(73.48), H 6.20(6.52), N 19.89(20.05). HRMS (APCI + mode, m/z): Calculated for $[M+H]^+$ 212.1101, found 212.1190.

Synthesis of N-(Pyridin-2-yl)-N′-(p-Tolyl)Formimidamide (L4)

Compound **L4** was synthesised as described in the general above using *p*-toluidine (20 mmol; 2.143 g), TEOF (60 mmol, 10 mL) and 2-aminopyridine (20 mmol, 1.82 g). At the end of the reaction, the flask was slowly cooled, and the product solidified upon cooling. The product was then triturated in n-hexane, recrystallised in toluene, filtered, and air dried to afford the product as an off-white solid. Yield: 3.05 g (72%). FTIR (ATR, *v* cm^{-1}) 3047 υ(N–H) stretching, 1661 υ(C(H)=N) stretching. ^{1}H-NMR (600 MHz, $CDCl_3$, ppm) δ 8.94 (s, N–*H*, 1H), 8.27 (d, *J* = 4.0 Hz, *H*C=N_{im}, 1H), 7.53 (t, *J* = 7.4 Hz, CH_{py}, 1H), 7.13 (d, *J* = 7.8 Hz, CH_{py}, 3H), 7.03 (s, CH_{arom}, 2H), 6.90 (dd, *J* = 14.5, 8.2 Hz, CH_{arom}, 2H), 2.33 (s, –CH_3, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.36 (C=N_{im}), 148.40 (CH_{py}), 138.15 (CH_{py}), 133.59 (CH_{py}), 130.02 (CH_{py}), 120.07 (CH_{arom}), 118.21 (CH_{arom}), 113.26 (CH_{arom}), 20.94 (–CH_3). EA calculated (found): C 73.91(73.69), H 6.20(6.23), N 19.89(19.92). HRMS (APCI + mode, m/z): Calculated for $[M+H]^+$ 212.1101, found 212.1190.

Synthesis of n-(Pyridin-2-Yl)-n′-(p-Anisidyl)Formimidamide (L5)

Compound **L5** was synthesised as described in the general procedure above using *p*-anisidine (20 mmol; 2.463 g), TEOF (60 mmol, 10 mL), and 2-aminopyridine (20 mmol, 1.82 g). At the end of the reaction, the flask is slowly cooled, and the solidified product is then triturated in n-hexane, recrystallised in toluene, filtered and dried in air to afford the pure product. Yield: 3.909 g (86%). FTIR (ATR, *v* cm^{-1}) 3164 υ(N–H) stretching, 1666 υ(C(H)=N) stretching. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.89 (s, N–*H*, 1H), 8.25 (s, *H*C=N_{im}, 1H), 7.51 (s, CH_{py}, 1H), 7.07 (d, *J* = 5.8 Hz, CH_{py}, 2H), 6.95–6.78 (m, CH_{arom}, 5H), 3.80 (s, O–CH_3, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.75 (C=N_{im}), 148.70 (CH_{py}), 148.06–147.93 (CH_{py}), 138.14 (CH_{py}), 121.61 (CH_{arom}), 120.50 (CH_{arom}), 117.98 (CH_{arom}), 114.76 (CH_{arom}), 112.57 (CH_{arom}), 55.68 (–OCH_3). EA calculated (found): C 68.70(68.71), H 4.16(4.92), N 23.13(22.95). HRMS (APCI + mode, m/z): Calculated for $[M+H]^+$ 228.1100, found 228.1132.

Synthesis of N-(4-Methylpyridin-2-yl)- N′-(p-Tolyl)Formimidamide (L6)

Compound **L6** was synthesised as described in the general procedure above using *p*-toluidine (20 mmol; 2.143 g), TEOF (60 mmol, 10 mL), one drop of 2 M HCl and 2-amino-4-methylpyridine (20 mmol, 2.163 g). At the end of the reaction, the flask is slowly cooled, and the solidified product is then triturated in n-hexane, recrystallised in toluene, filtered, and dried in air to afford the pure product. Yield: 2.925 g (65%). FTIR (ATR, *v* cm^{-1}) 3174 υ(N–H) stretching, 1666 υ(C(H)=N) stretching. ^{1}H NMR (600 MHz, DMSO, ppm) δ 10.25 (s, N–*H*, 1H), 8.82 (s, *H*C=N_{im}, 1H), 8.07 (s, CH_{py}, 1H), 7.10 (d, *J* = 7.8 Hz, CH_{py}, 2H), 6.97 (s, CH_{arom}, 2H), 6.80 (d, *J* = 15.7 Hz, CH_{arom}, 2H), 2.25 (s, –CH_3, 6H). ^{13}C NMR (151 MHz, DMSO) δ 148.72 (C=N_{im}), 147.78 (CH_{py}), 129.52 (CH_{py}), 118.84 (CH_{arom}), 20.48 (–CH_3). EA calculated (found): C 74.64(74.77), H 6.71(7.01), N 18.65(19.20). HRMS (APCI + mode, m/z): Calculated for $[M+H]^+$ 226.1300, found 226.1340.

Synthesis of N-(4-Methylpyridin-2-yl)- N′-(4-Methoxyphenyl)Formimidamide (L7)

Compound **L7** was synthesised as described in the general procedure above using *p*-anisidine (20 mmol; 2.463 g), TEOF (60 mmol, 10 mL) and 2-amino-4-methylpyridine (20 mmol, 2.163 g). At the end of the reaction, the flask is slowly cooled, and the solidified product is then triturated in n-hexane, recrystallised in toluene, filtered, and dried in air to afford the pure product. Yield: 2.992 g (62%). FTIR (ATR, *v* cm^{-1}) 3065 υ(N–H) stretching, 1673 υ(C(H) =N) stretching. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.89 (s, N–*H*, 1H), 8.09 (d, *J* = 4.9 Hz, *H*C=N_{im}, 1H), 7.07 (d, *J* = 7.7 Hz, CH_{py}, 2H), 6.88 (d, *J* = 8.6 Hz, CH_{arom}, 3H), 6.70 (d, *J* = 4.3 Hz, CH_{arom}, 1H), 6.57 (s, CH_{arom}, 1H), 3.80 (s, O–CH_3, 3H), 2.18 (s, –CH_3, 3H). ^{13}C NMR (151 MHz, DMSO) δ 155.75 (C=N_{im}), 148.71 (CH_{py}), 147.63 (CH_{py}), 147.39 (CH_{py}), 120.81 (CH_{arom}), 118.59 (CH_{arom}), 114.43 (CH_{arom}), 114.43 (CH_{arom}), 113.95 (CH_{arom}), 55.20 (–OCH_3), 20.59 (–CH_3). EA calculated (found): C 69.69(69.46), H 6.27(6.80), N 17.41(17.81). HRMS (APCI + mode, m/z): Calculated for $[M+H]^+$ 242.1200, found 242.1295.

Novel Method of Synthesis of Unsymmetrical Pyridyl-Formamidines (L8–L10)

All the reactants (the first primary amine, TEOF, and aminopyridine) are charged into a round-bottomed flask and the reaction is performed using a simple distillation set-up. The specific conditions and work-up are described for the individual compounds.

Synthesis of N-(Pyridin-2-yl)-N′-(p-Nitro)Formimidamide (L8)

Compound **L8** was synthesised as described in the novel method procedure above using 4-nitroaniline (20 mmol; 2.76 g), TEOF (60 mmol, 10 mL), 2-aminopyridine (20 mmol, 1.82 g) and toluene (10 mL). The reaction was performed overnight at 100 °C. At the end of the reaction, the crude was triturated in diethyl ether and washed with ethanol to afford a yellow solid. Yield: 3.34 g (75%). FTIR (ATR, *v* cm^{-1}) 3097 υ(N–H) stretching, 1665 υ(C(H)=N) stretching. ^{1}H-NMR (600 MHz, DMSO, ppm) δ 10.79 (s, N–*H*, 1H), 8.94 (s, *H*C=N_{im}, 1H), 8.22 (dd, *J* = 35.3, 26.4 Hz, CH_{py}, 4H), 7.73 (t, *J* = 7.7 Hz, CH_{arom}, 1H), 7.40–7.22 (m, CH_{arom}, 1H), 7.05 (s, CH_{arom}, 2H). ^{13}C NMR (151 MHz, DMSO) δ 149.36 (C=N_{im}), 148.17 (CH_{py}), 138.42 (CH_{py}), 125.19 (CH_{arom}), 118.82 (CH_{arom}). EA calculated (found): C 59.50(59.29), H 4.16(3.89), N 23.13(23.14). HRMS (APCI + mode, m/z): Calculated for $[M+H]^+$ 243.0800, found 243.0880.

Synthesis of N-(4-Nitrophenyl)-N′-(4-Methylpyridin-2-yl)Formimidamide (L9)

Compound **L9** was synthesised as described in the novel method procedure above using 4-nitroaniline (20 mmol; 2.76 g), TEOF (60 mmol, 10 mL), 2-amino-4-methylpyridine (20 mmol, 2.163 g) and THF (5 mL). The mixture was stirred at 90 °C for 4 h. At the end of the reaction, the crude was triturated in diethyl ether, followed by warm ethanol to afford a pure product. Yield: 4.01 g (78%). FTIR (ATR, *v* cm^{-1}) 3073 υ(N–H) stretching, 1672 υ(C(H)=N) stretching. ^{1}H-NMR (600 MHz, DMSO, ppm) δ 10.74 (s, N–*H*, 1H), 8.94 (s, *H*C=N_{im}, 1H), 8.25–8.06 (m, CH_{py}, 3H), 7.42–7.18 (m, CH_{arom}, 2H), 6.89 (s, CH_{arom}, 2H), 2.29 (s, –CH_3, 3H). ^{13}C NMR (151 MHz, DMSO) δ 149.42 (–C(NO_2)), 149.15(C=N_{im}) 147.82 (CH_{py}), 126.37 (CH_{arom}), 125.17 (CH_{arom}), 121.72 (CH_{arom}), 120.07 (CH_{arom}), 112.36 (CH_{arom}), 20.56 (–CH_3). EA calculated (found): C 60.93(60.88), H 4.72(4.93), N 21.86(22.03). HRMS (APCI + mode, m/z): Calculated for $[M+H]^+$ 257.1000, found 257.1037.

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Synthesis of (E)-N-Phenyl-N′-(Pyridin-2-yl)Formimidamide (L10)

Compound **L10** was synthesised as described in the novel method procedure above using aniline (20 mmol; 1.85 g), TEOF (60 mmol, 10 mL) and 2-aminopyridine (20 mmol, 1.82 g). The mixture was stirred at 110 °C for 4 h. At the end of the reaction, the flask was cooled, and the crude was triturated in a 2:1 mixture of hexane: diethyl ether and dried to afford a white solid. Yield: 3.40 g (87 %). FTIR (ATR, ν cm^{-1}) 3069 υ(N–H) stretching, 1672 υ(C(H)=N) stretching. ^{1}H NMR (600 MHz, DMSO) δ 10.29 (s, N–*H*, 1H), 8.79 (s, *H*C=N_{im}, 1H), 8.26 (d, J = 31.6 Hz, C*H*$_{py}$,1H), 7.70–7.65 (m, C*H*$_{py}$, 1H), 7.31 (t, J = 7.8 Hz, C*H*$_{py}$, 2H), 7.03 (dd, J = 31.0, 23.6 Hz, C*H*$_{arom}$, 5H). ^{13}C NMR (151 MHz, DMSO) δ 149.43 (*C*=N_{im}), 148.51 (*C*H$_{py}$), 148.22–147.52 (*C*H$_{py}$), 138.52–138.09 (*C*H$_{py}$), 130.51–129.92 (*C*H$_{arom}$), 117.91 (*C*H$_{arom}$). EA calculated (found): C 73.07(73.04), H 5.62(5.60), N 21.30(21.28). HRMS (APCI + mode, m/z): Calculated for $[M+H]^+$ 198.2400, found 198.1029.

Synthesis of Mn Complexes

[MnBr(CO)$_3$(L10)] (C1)

To a stirring THF solution of $Mn(CO)_5Br$ (0.365 mmol; 100 mg) was added a THF solution of the **L10** (0.365 mmol; 71.99 mg). The mixture was then allowed to stir overnight at room temperature under nitrogen. At the end of the reaction, the resulting solution was filtered through celite and recrystallised by layering of hexane in a closed system. The product was isolated as a dark-orange crystalline solid. Yield: 80.50 mg (53 %). FTIR (ATR, ν cm^{-1}) 2972 υ(N–H) stretching, 2016 υ(Mn–C=O) stretching, 1928 υ(Mn–C=O) stretching, 1893 υ(Mn–C=O) stretching, 1647 υ(C(H)=N) stretching. ^{1}H NMR (400 MHz, THF) δ 10.17 (s, N–*H*, 1H), 8.91 (s, *H*C=N_{im}, 1H), 7.76 (d, J = 21.9 Hz, C*H*$_{py}$, 2H), 7.46–6.89 (m, C*H*$_{arom}$, 7H). ^{13}C NMR (101 MHz, THF) δ 155.46 (s, *C*=N_{im}), 151.66 (d, J = 12.6 Hz, s, *C*=N_{py}), 140.19 (s, –N–C_{arom}), 129.38 (s, H*C*–N_{py}), 126.54 (s, *C*H$_{py}$), 124.16 (s, *C*H$_{arom}$), 119.30 (s, *C*H$_{arom}$), 115.19 (s, *C*H$_{arom}$). EA calculated for $C_{15}H_{10}BrMnN_4O_5$.2H2O (found): C 39.85 (39.85), H 3.34 (3.35), N 9.29 (9.72). HRMS (ESI + mode, m/z): Calculated for $[M–Br]^+$ 336.2100, found 336.0181.

[MnBr(CO)$_3$(L6)] (C2)

Compound **C2** was synthesised in a similar manner as described for **C1** using $Mn(CO)_5Br$ (0.365 mmol; 100 mg) and ligand **L6** (0.365 mmol; 88.42 mg). The product was isolated as a dark-orange crystalline solid. Yield: 129.59 mg (77 %). FTIR (ATR, ν cm^{-1}) 2998 υ(N–H) stretching, 2016 υ(Mn–C=O) stretching, 1926 υ(Mn–C=O) stretching, 1888 υ(Mn–C=O) stretching, 1654 υ(C(H) = N) stretching. ^{1}H NMR (400 MHz, THF) δ 10.31 (s, N–*H*, 1H), 8.92 (s, *H*C=N_{im}, 1H), 8.25 (s, C*H*$_{py}$, 2H), 7.72 (d, J = 77.1 Hz, C*H*$_{arom}$, 4H), 7.12 (s, C*H*$_{arom}$, 2H). ^{13}C NMR (151 MHz, THF) δ 160.21 (–*C*(NO_2)), 155.81 (*C*=N_{im}), 149.55 (*C*=N_{py}), 147.11 (–N–C_{arom}), 144.50 (*C*H$_{py}$), 144.50 (*C*H$_{py}$), 140.69 (*C*H$_{py}$), 125.88 (*C*H$_{py}$), 125.65 (*C*H$_{arom}$), 125.27 (*C*H$_{arom}$), 120.17 (*C*H$_{arom}$), 115.96 (*C*H$_{arom}$). EA calculated for $C_{15}H_{10}BrMnN_4O_5.H_2O$ (found): C 37.60 (37.33), H 2.52 (1.90), N 11.69 (11.56). HRMS (ESI + mode, m/z): Calculated for $[M–Br]^+$ 381.2100, found 381.0032.

[MnBr(CO)$_3$(L8)] (C3)

Compound **C3** was synthesised in a similar manner as described for **C1** using $Mn(CO)_5Br$ (0.365 mmol; 100 mg) and ligand **L8** (0.365 mmol; 82.23 mg). The product was isolated as a yellow solid. Yield: 98.89 mg (61 %). FTIR (ATR, ν cm^{-1}) 2998 υ(N–H) stretching, 2016 υ(Mn–C=O) stretching, 1926 υ(Mn–C=O) stretching, 1884 υ(Mn–C=O) stretching, 1654 υ(C(H)=N) stretching. ^{1}H NMR (600 MHz, DMSO) δ 11.18 (s, N–*H*, 1H), 8.63 (d, J = 5.4 Hz, *H*C=N_{im}, 1H), 7.84 (s, C*H*$_{py,}$ 1H), 7.29–6.98 (m, C*H*$_{arom}$, 6H), 2.32 (dd, J = 35.5, 25.7 Hz, –C*H*$_3$, 6H). ^{13}C NMR (151 MHz, DMSO) δ 159.13 (*C*=N_{im}), 153.31 (*C*=N_{py}), 152.16 (–N–C_{arom}), 151.81(HC–N_{py}), 149.52 (*C*H$_{py}$), 144.80 (–*C*(CH_3)), 124.78 (*C*H$_{arom}$), 124.40 (*C*H$_{arom}$), 120.82 (*C*H$_{arom}$), 114.84 (*C*H$_{arom}$), 24.74 (py–CH_3), 20.07 (–CH_3). EA calculated for $C_{17}H_{26}BrMnN_3O_3$ (found): C 45.97 (45.54), H 3.40 (3.43), N 9.46 (9.80). HRMS (ESI + mode, m/z): Calculated for $[M–Br]^+$ 364.2600, found 364.0507.

[MnBr(CO)$_3$(L4)] (C4)

Compound **C4** was synthesised in a similar manner as described for **C1** using $Mn(CO)_5Br$ (0.365 mmol; 100 mg) and ligand **L4** (0.365 mmol; 77.06 mg). The product was isolated as a yellow solid. Yield: 102 mg (65 %). FTIR (ATR, ν cm^{-1}) 3058 υ(N–H) stretching, 2018 υ(C=O) stretching, 1930 υ(C=O) stretching, 1884 υ(C=O) stretching, 1654 υ(C(H) =N) stretching. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 10.82 (s, N–*H*, 1H), 8.85 (s, HC = N_{im}, 1H), 7.66 (d, J = 52.6 Hz, C*H*$_{py}$, 2H), 7.18 (t, J = 47.4 Hz, C*H*$_{arom}$, 6H), 2.35 (s, –C*H*$_3$, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 154.75 (*C*–N_{py}), 139.68 (–N–C_{arom}), 136.16 (*C*H$_{py}$), 129.71 (*C*H$_{py}$), 123.68 (*C*H$_{arom}$), 118.91 (*C*H$_{arom}$), 20.86 (–CH_3). EA calculated for $C_{16}H_{13}BrMnN_3O_3.H_2O$ (found): C 42.88 (42.26), H 3.37 (2.64), N 9.38 (10.34). HRMS (ESI + mode, m/z): Calculated for $[M–Br]^+$ 350.2400, found 350.0341.

[MnBr(CO)$_3$(L5)] (C5)

Compound **C5** was synthesised in a similar manner as described for **C1** using $Mn(CO)_5Br$ (0.365 mmol; 100 mg) and ligand **L5** (0.365 mmol; 82.89 mg). The product was isolated as a yellow solid. Yield: 95 mg (58 %). FTIR (ATR, ν cm^{-1}) 2997 υ(N–H) stretching, 2016 υ(C=O) stretching, 1925 υ(C=O) stretching, 1886 υ(C=O) stretching, 1654 υ(C(H) =N) stretching. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.86 (s, *H*C=N_{im}, 1H), 7.66 (d, J = 53.2 Hz, C*H*$_{py}$, 2H), 7.31 (d, J = 7.3 Hz, C*H*$_{arom}$, 2H), 6.97 (dd, J = 26.5 Hz, C*H*$_{arom}$, 6H), 3.80 (s, –OC*H*$_3$, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 158. 50 (*C*=N_{im}), 154.97 (*C*=N_{py}), 151.56 (–N–C_{arom}), 151.02 (HC–N_{py}) 148.85 (*C*H$_{py}$), 139.74 (–*C*(CH_3)), 124.94 (*C*H$_{arom}$), 119.02 (*C*H$_{arom}$), 114.56 (*C*H$_{arom}$), 55.92 (–OCH_3). EA calculated for $C_{16}H_{13}BrMnN_3O_4$ (found): C 43.08 (43.08), H 2.94 (2.94), N 9.42 (9.42). HRMS (ESI + mode, m/z): Calculated for $[M–Br]^+$ 366.2400, found 366.0240.

[MnBr(CO)$_3$(L9)] (C6)

Compound **C6** was synthesised in a similar manner as described for **C1** using $Mn(CO)_5Br$ (0.365 mmol; 100 mg) and ligand **L9** (0.365 mmol; 93.48 mg). The product was isolated as a yellow solid. Yield: 139.50 mg (80 %). FTIR (ATR, ν cm^{-1}) 2998 υ(N–H) stretching, 2016 υ(C=O) stretching, 1926 υ(C=O) stretching, 1884 υ(C=O) stretching, 1654 υ(C(H)=N) stretching. ^{1}H NMR (600 MHz, DMSO) δ 11.47 (s, N*H*, 1H), 8.66 (s, *H*C=N_{im}, 1H), 8.34 (s, C*H*$_{py}$, 1H), 8.08 (d, J = 104.0 Hz, C*H*$_{py}$, 2H), 7.58 (s, H$_{arom}$, 2H), 7.08 (d, J = 25.2 Hz, H$_{arom}$, 2H), 2.31 (d, J = 57.1 Hz, –C*H*$_3$, 3H). ^{13}C NMR (151 MHz, DMSO) δ 159.13 (–*C*(NO_2)), 153.31 (C=N_{im}), 152.16 (*C*=$_{py}$), 151.81 (–N–C_{arom}), 149.52 (HC–N_{py}), 144.80 (*C*H$_{py}$), 124.78 (–*C*(CH_3)), 124.40 (*C*H$_{py}$), 120.82 (–*C*H$_{arom}$), 114.84 (–*C*H$_{arom}$), 20.07 (–*C*H_3). EA calculated for $C_{16}H_{12}BrMnN_4O_5$ (found): C 40.45 (41.30), H 2.55 (2.14), N 12.79 (12.79). HRMS (ESI + mode, m/z): Calculated for $[M–Br]^+$ 395.2300, found 395.0163.

General Procedure for the Synthesis of Pd, Cu and Zn Complexes (C7–C10)

To a stirring DCM solution of the metal precursor is added a DCM solution of the required ligand. The mixture is then allowed to stir overnight at room temperature under Argon. At the end of the reaction, the solvent is reduced under vacuum and the product precipitated with hexane or diethyl ether.

[$PdCl_2$(L2)] (C7)

Compound **C7** was synthesised as described in the general procedure using $Pd(NCCH_3)_2Cl_2$ (0.193 mmol; 50 mg) and ligand **L2** (0.193 mmol; 41 mg). The product was isolated as an orange solid. Yield: 54.00 mg (73%). FTIR (ATR, ν cm^{-1}) 3082 υ(N–H) stretching, 1645 υ(C(H)=N) stretching. ^{1}H NMR (600 MHz, DMSO) δ 11.79 (s, 1H), 9.00 (d, J = 6.0 Hz, 1H), 8.06 (t, J = 7.7 Hz, 1H), 7.69 (s, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.28 (t, J = 6.6 Hz, 1H), 7.20–7.10 (m, 4H), 2.49 (s, 3H). Yield: 0.054 g (72.6%). ^{13}C NMR (151 MHz, DMSO) δ 153.70 (C=N_{im}), 151.87 (C=N_{py}), 151.19 (–N–C_{arom}), 150.05 (HC–N_{py}), 139.82 (–C(CH_3)), 134.62 (CH_{py}), 128.89 (CH_{py}), 122.71 (CH_{arom}), 118.62 (CH_{arom}), 114.70 (CH_{arom}), 20.04 (–CH_3). EA calculated for $C_{13}H_{13}PdN_3Cl_2$ (found): C 40.18 (40.44), H 3.37 (3.40), N 10.81 (10.81). HRMS (ESI + mode, m/z): Calculated for [M-(Cl) + CH_3N]$^+$ 393.0100, found 393.0081.

$Cu(OAc)_2$(L3) (C8)

Compound **C8** was synthesised as described in the general procedure using $Cu(OAc)_2{\cdot}H_2O$ (1.25 mmol; 250 mg) and ligand **L3** (1.25 mmol; 264 mg). The mixture was then allowed to stir overnight at room temperature under nitrogen. At the end of the reaction, the solvent is reduced under vacuum and the product precipitated with hexane or diethyl ether. The product was isolated as a green solid. Yield: 385 mg (78.4%). FTIR (ATR, ν cm^{-1}) 3088 υ(N–H) stretching, 1655 υ(C(H)=N) stretching. EA calculated for $C_{17}H_{19}CuN_3O_4$ (found): C 51.97 (51.50), H 4.87 (4.87), N 10.70 (10.80). HRMS (ESI + mode, m/z): Calculated for [M + H]$^+$ 393.0700, found 393.3003.

$Cu(OAc)_2$(L5) C9

Compound **C10** was synthesised as described in the general procedure using $Cu(OAc)_2{\cdot}H_2O$ (0.625 mmol; 0.125 g) and ligand **L5** (1.25 mmol; 0.026 g). The product was isolated as a dark brown solid. Yield: 0.134 g.

$Zn(OAc)_2$(L7) (C10)

Compound **C10** was synthesised as described in the general procedure using $Zn(OAc)_2{\cdot}2H_2O$ (1.0 mmol; 0.219 g) and ligand **L7**(1.0 mmol; 0.241 g). The product was isolated as an off-white solid. ^{1}H NMR (600 MHz, DMSO) δ 7.70 (d, J = 5.6 Hz, N–H_2, 2H), 6.55 (s, $H_{arom,}$ 3H), 6.42–6.35 (m, H_{arom}, 3H), 2.16 (s, 6H), 1.81 (s, 18H). HRMS (ESI + mode, m/z): Calculated for [M–$C_7H_8N_2O_2Zn$]$^+$ 549.9300, found 549.9605.

X-Ray Crystal Structure Determination

Data for single-crystal X-ray diffraction were collected using a Bruker Apex DUO diffractometer equipped with a CCD area detector[37] utilizing graphite-monochromated Mo–Kα radiation (λ = 0.71073 Å). Data collection, reduction, and refinement were conducted with the SMART and SAINT software packages.[38] Absorption corrections[39] and other systematic errors were addressed using SADABS.[40] The structures were solved via direct methods and refined using full-matrix least-squares on F^2 with SHELXS-13 and SHELXL-16,[41,42] operated within the X-Seed graphical user interface.[43–44] Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions using riding models. High-resolution molecular diagrams were generated with POV-Ray.[45] Crystallographic data are deposited at the CCDC under the accession numbers: 2251445 (**C8**), 2251446 (**C7**), 2382057 (**C2**), 2382058 (**C1**), 2251447 (**C9**) and 2251448 (**C10**).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Pyridyl-formamidine ligands · Coordination behaviour · Complexes · Synthesis · Characterisation

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