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ARTICLE

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The first isolation and structural characterization of a series of chiral trinitrogen 1,3-bis(4,5-dihydrooxazol-2-ylimino)isoindoline-based pincer ligands are reported. Cadmium complexes, isolated as $Cd(L)_2$ where L is the deprotonated form of LH = 1,3-bis(4,5-dihydro-4-(*R*)-phenyloxazol-2-ylimino)-isoindoline ((*R*,*R*)-**5H**) or 1,3-bis(4,5-dihydro-4-(*S*)-*iso*-propyloxazol-2-ylimino)isoindoline ((*S*,*S*)-**6H**) were prepared in-situ via traditional or microwave-based techniques with the latter being more efficient but less able to be scaled up at this time. Ligands (*R*,*R*)-**5**H and (*S*,*S*)-**6**H were isolated via deligation from their respective cadmium complexes using a thiol-based ligand exchange protocol. The characterization of ligands and their respective cadmium complexes, in both the solid (X-ray crystallography) and solution (NMR spectroscopy) states are reported. Pd((*S*,*S*)-**6**)(OAc) is reported as a proof-of-concept of the ability to prepare 1:1 ligand:metal complexes that are believed to be necessary as potential enantioselective catalysts.

Introduction

Control of the steric and electronic environments about a metal centre are keys to develop efficient and selective catalyst systems for use in enantioselective homogeneous catalysis. Since the first boom of reports in the late 1960s, the design of new ligand architectures has been highly successful in modulating the reactivity and selectivity of transition metal catalysts in homogeneous catalysis as most notably recognized by the pioneering 2001 Nobel Prize award work of Knowles,[1a] Noyori,[1b] and Sharpless.[1c] To this day, new ligand architectures are necessary to increase the overall efficiency and selectivity of developed catalysis reactions as well as for the development of new catalytic reactions. Of the ligand systems developed, the *mer*-coordinating pincer-type ligand systems have become increasingly impactful in recent years.[2] Some of the earliest systems, like the 1,3-bis(2-arylimino)isoindoline pincer ligands[3] (e.g. aryl = pyridine), have been studied for over 60 years. Studies on these systems has found a resurgence due in part to their rich palladium chemistry[4] and their success in homogeneous catalysis including oxidations,[5] hydrogenations,[6] and radical polymerizations.[7] Architectural derviatization on these systems by Bröring's[8] and Gade's[9] groups have generated chiral bis(pyridylimino)isoindoline ligands for use in enantioselective homogeneous catalysis. Other mer-tridentate pincer ligands used in enantioselective catalysis include Gade's bis(oxazolinylmethyl)pyrrole- and bis(oxazolinylmethylidene)-isoindole-based ligands,[10] Nakada's bis(oxazolinyl)carbazole ligands,[11] the independently developed bis(oxazolinyl)phenyl ('phebox') ligands,[12] and Nishiyama's highly successful chiral C_2 symmetric 2,6-bis(2-oxazolinyl)-pyridine ('pybox') ligand;[13] a standard in the chiral "tool kit" of stereodirecting ligands.

Based on Bröring's and Gade's success in enantioselective catalysis with chiral bis(pyridylimino)isoindoline ligands and the structural similarity of 1,3-bis(2-pyridylimino)isoindoline to the pybox ligand we pursued the synthesis of a new class of chiral *mer*-coordinating ligands, 1,3-bis(4,5-dihydrooxazol-2-ylimino)isoindolines for potential use in enantioselective catalysis. Replacement of the 2-aminopyridine units of 1,3-bis(2-pyridylimino)isoindoline for enantiopure 2-amino-4-substituted-oxazoline was chosen as the oxazolines (i) are readily commercially available, or are easily prepared, in enantiopure form and (ii) are successful in enantioselective homogeneous catalysis as demonstrated by examples that include the bis(oxazoline),[14] bis(oxazolinylmethyl)pyrrole,[15] bis(oxazolinylmethylidene)isoindole,[16] and pybox[13] ligand systems. Our earlier investigations showed that reaction of 2 equivalents of enantiopure 4-substituted-2-aminooxazoline with 1 equivalent of phthalonitrile, through the use of conventional heating methods, with $ZnCl_2$ as catalyst produces the desired 1,3-bis(4,5-dihydrooxazol-2-ylimino)isoindoline (LH) ligand architecture *in-situ* as neutral $Zn(L)_2$ complexes, having 2 equivalents of the ligand coordinated in mer-fashion in their deprotonated anionic form in low-to-modest yields.[17]

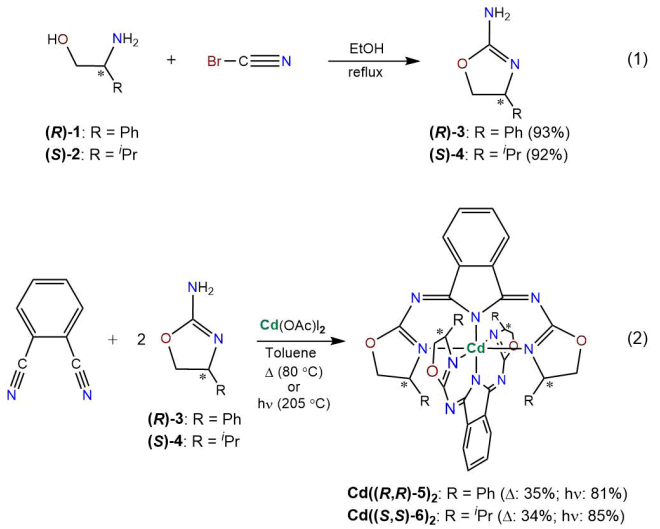
Herein we report our continued studies on the development of this new class of chiral ligand through (i) the improved synthesis of $Cd(L)_2$ complexes, structurally analogous to the $Zn(L)_2$ systems reported earlier, and (ii) the deligation, isolation, and characterization of the ligands in their free neutral protio forms. Finally, a proof-of-concept 1:1, ligand:metal complex is reported as a model of a potential enantioselective catalyst precursor.

Results and discussion

In-situ synthesis of cadmium metal complexes: Cd((*R*,*R*)-5)$_2$ and Cd((*S*,*S*)-6)$_2$.

The precursor chiral oxazoline ligand stereodirecting units (*R*)-**3** and (*S*)-**4** are prepared in high yields on reacting 1 equiv of amino alcohol, (*R*)-**1** and (*S*)-**2**, respectively, with 1.2 equiv of cyanogen bromide in refluxing ethanol (Scheme 1: reaction 1).[17] The direct preparation of the desired chiral ligands (*R*,*R*)-**5**H and (*S*,*S*)-**6**H from reaction of phthalonitrile and 2 equiv of (*R*)-**3** or (*S*)-**4**, respectively was not successful using reported methods that afford the similar achiral bis(2-pyridylimino)isoindoline systems.[18] However, using $ZnCl_2$ as catalyst, we successfully made the complexes $Zn(L)_2$, where L = (*R*,*R*)-**5**$^-$ and (*S*,*S*)-**6**$^-$), which contain the desired ligand, formed *in-situ*, bound in their deprotonated form.[17] Attempts to prepare the ligands directly, in their free, unbound, neutral form, using several other metal salts as potential catalysts, under similar reaction conditions were unsuccessful. Several reactions afforded low yields of complexes analogous to the ZnL_2 compounds however when $Cd(OAc)_2$ was used as catalyst it fared the best of all investigated including the reported zinc systems. Using a similar protocol as for the $Zn(L)_2$ complexes (Scheme 1: reaction 2; four equivalents of (*R*)-**5** or (*S*)-**6** reacted with two equivalents of phthalonitrile with one equivalent of $Cd(OAc)_2$ in dry toluene at 80 ºC) resulted in the isolation, after chromatographic workup and recrystallization, of Cd((*R*,*R*)-**5**)$_2$ (35%) and Cd((*S*,*S*)-**6**)$_2$ (34%), respectively in modest yields.

As was observed with the analogous zinc complexes,[17] trying to boost the yields of Cd((*R*,*R*)-**5**)$_2$ and Cd((*S*,*S*)-**6**)$_2$ by increasing the temperature of reaction using traditional heating was ineffective; resulting in lower yields and an increase in byproduct formation. The methodology of conventional heating at 80 °C was used to prepare and characterize the cadmium complexes however exploration of alternative methods to increase the efficiency of the reactions continued. Initial attempts to use microwave methodologies, at the time the zinc complexes were reported, were hampered by the microwave reactor system that we had available as it could not reach sufficiently elevated temperature to form the metal complexes. However, since that time, we obtained a new microwave reactor and it was found that heating the reaction at 200-205 ºC for a short period of time (10 min) successfully prepared the Furthermore, less decomposition and byproduct formation was observed resulting in a significantly improved efficiency for the isolation and purification of the complexes. Only recrystallization of the product mixture was necessary to obtain the desired complexes as opposed to the need for column chromatography followed by recrystallization using the traditional heating method. Unlike the traditional heating method, the microwave method does not allow for single, large scale product preparation but with the use of an auto-sampler, gram quantities of the complexes can be prepared in a day. The characterization of Cd((*R*,*R*)-**5**)$_2$ and Cd((*S*,*S*)-**6**)$_2$ are detailed in the subsequent sections. desired complexes in good yield (81% and 85% for Cd((*R*,*R*)-**5**)$_2$ and Cd((*S*,*S*)-**6**)$_2$, respectively).



Scheme 1. Synthesis of the Cd((*R*,*R*)-**5**)$_2$ and Cd((*S*,*S*)-**6**)$_2$ by conventional and microwave heating methods, with the latter being most successful.

Characterization of cadmium metal complexes: Cd((*R*,*R*)-5)$_2$ and Cd((*S*,*S*)-6)$_2$.

Each complex was structurally characterized both in the solution (NMR) and solid (X-ray) states. In $CDCl_3$ solution (Figure 1) each complex was determined to have C_2 symmetry based on the number of signals observed in the ^{1}H NMR. Analogous to Zn((*R*,*R*)-**5**)$_2$, the aromatic signals of Cd((*R*,*R*)-**5**)$_2$ are shifted upfield relative to free (*R*)-**3**, a further indication of bound ligand. Similarly, analogous to Zn((*S*,*S*)-**6**)$_2$, the isopropyl signals of Cd((*S*,*S*)-**6**)$_2$ are shifted upfield relative to free (*S*)-**2**. Signal assignments for each Cd(II) complex are analogous to those of the zinc series: Zn((*R*,*R*)-**5**)$_2$ and Zn((*S*,*S*)-**6**)$_2$) previously reported.[17]

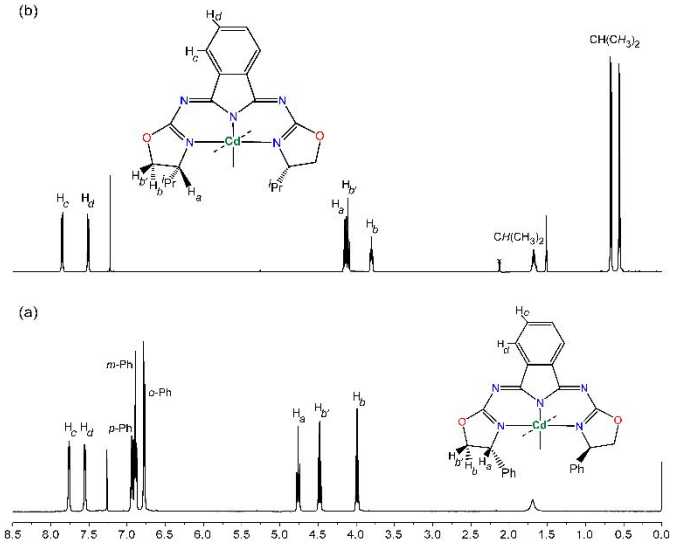


Figure 1. ^{1}H NMR spectra of cadmium complexes Cd((*R*,*R*)-**5**)$_2$ (a) and Cd((*S*,*S*)-**6**)$_2$ (b) in $CDCl_3$ with assignments made based on their analogous zinc complexes.[17]

Crystals suitable for X-ray diffraction were obtained via slow evaporation of concentrated CH_2Cl_2:acetone solutions of the cadmium complexes in an analogous fashion as to those reported for Zn((*R*,*R*)-**5**)$_2$ and Zn((*S*,*S*)-**6**)$_2$.[17] The structures of each were determined and are depicted in Figure 2 and selected structural data are contained in Table 1. The enantiopurity of each complex was confirmed via anomalous dispersion analysis. As was the case for the zinc complexes, the use of the SQUEEZE[19] program was required to account for the void volumes associated with each structure. They were modelled as containing 3 molecules of CH_2Cl_2 in both the Cd((*R*,*R*)-**5**)$_2$ and Cd((*S*,*S*)-**6**)$_2$ crystals along with an addition 6 acetone molecules in the latter. Complexes Cd((*R*,*R*)-**5**)$_2$ and Cd((*S*,*S*)-**6**)$_2$ were determined to be isomorphous with their reported Zn analogues. One phenyl group substituent of each ligand in the structure of Cd((*R*,*R*)-**5**)$_2$ is disordered and is modelled as being in two positions in 54.7% and 45.3% occupancy (Figure 2). The geometry of each complex is slightly disordered octahedral about the Cd metal centres; with the sum of the angles around each set of 4-planar bound N-atoms of one ligand and the central N-bound atom of the second ligand being ~360° (Plane in Cd((*R*,*R*)-**5**)$_2$ = 360.1°, Cd((*S*,*S*)-**6**)$_2$ = 360.0°. The bite-angle of each ligand accounts for the largest deviation from ideal (180°) octahedral, being 159.0° and 158.9°, respectively for each complex with the bond angle between each bound isoindoline-*N* atom and the Cd centre being closer to ideal at 175.4° and 173.9°, respectively. Of note is the slight distortion of the ideal 90° angle between each bound ligand, as defined by a calculated plane containing each N-atom bound and the Cd centre, being 82.0° and 82.2° for the smallest angle, respectively for Cd((*R*,*R*)-**5**)$_2$ and Cd((*S*,*S*)-**6**)$_2$.

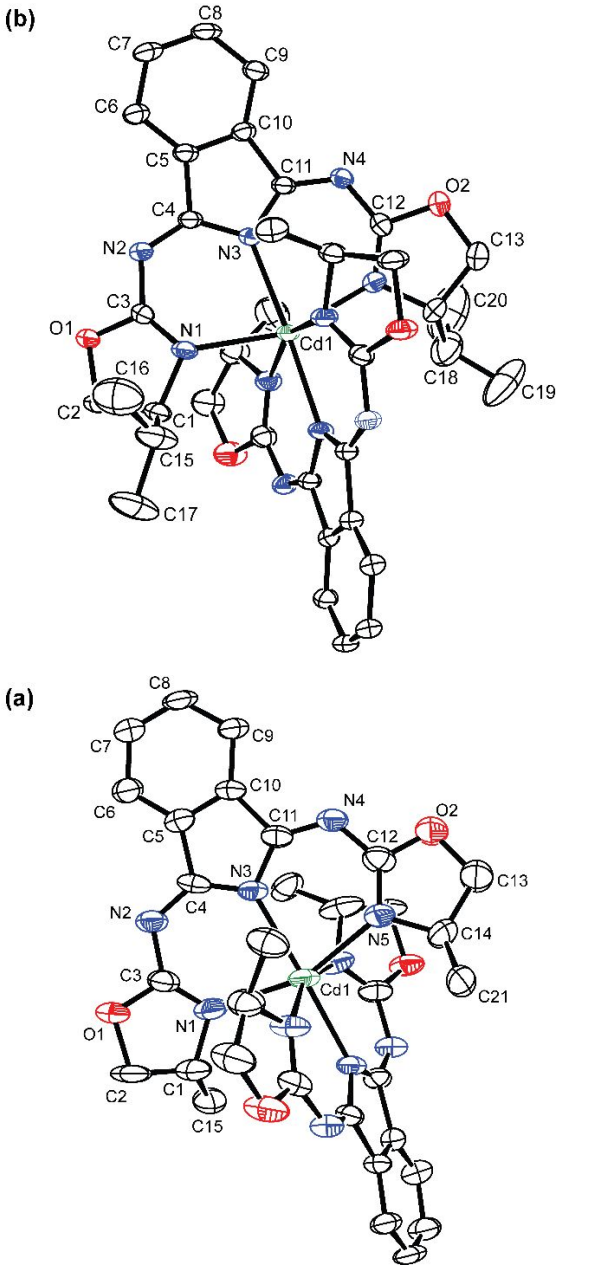
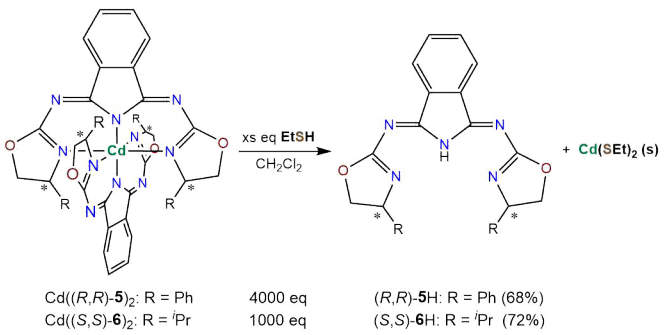


Figure 2. Ortep diagram of structure Cd((*R*,*R*)-**5**)$_2$ (a) and Cd((*S*,*S*)-**6**)$_2$ (b) determined by single crystal x-ray diffraction at 150 K and 120 K, respectively. All atoms are shown at 30% probability with the exception of H-atoms which are removed for clarity. Details of each analysis are found in Table 1 and in the supplementary material.

Ligand isolation.

A major goal of the work was to prepare the chiral substituted 1,3-bis(4,5-dihydrooxazoline)isoindoline-based ligands in their free, neutral form. As direct synthesis was not achieved in our hands, attempts were directed to unbind the ligand from the metal centre. The goal was to find a reagent that would separate out the resulting cadmium centre byproduct, ideally by precipitation, while leaving the free ligand in its neutral form in solution to be collected on concentration. Sulphur compounds were investigated for the deligation reaction as

cadmium is highly thiophilic and the Cd(S-thiolate)$_2$ byproducts were expected to have very low solubilities based on that of CdS (K_{sp} = 8.0 x 10^{-27})[20] and similar compounds. Initial studies on the reactions of complex Cd((*R*,*R*)-**5**)$_2$ or Cd((*S*,*S*)-**6**)$_2$ with excess sodium sulfide in MeOH at room temperature resulted in CdS precipitation as anticipated but free ligand recovery was poor; low yield and numerous decomposition products were observed via ^{1}H NMR analysis. Adjustments to the solvent used and trials with added proton sources (e.g. NH_4Cl) to aid in protonation of the bound anionic ligand to its neutral form did not produce significantly better results. However, on combining the sulfide-protic solvent methodology into one species, namely thiols, results quickly improved. Benzyl mercaptan (HSBz) was the first thiol tested and yielded direct conversion of Cd((*S*,*S*)-**6**)$_2$ to free ligand (*S*,*S*)-**6**H, with precipitation of Cd(SBz)$_2$ byproduct from solution, based on ^{1}H NMR analysis. However, no reactivity was observed between benzyl mercaptan and Cd((*R*,*R*)-**5**)$_2$, leaving unreacted starting materials even on addition of > 500 equiv of thiol and heating to 45 °C. It is hypothesized, based on the analysis of the x-ray structures of the Zn and Cd complexes, that the phenyl substituents of Cd((*R*,*R*)-**5**)$_2$, being very bulky, likely block benzyl mercaptan from interacting with the cadmium metal centre thus preventing the deligation reaction. As such, attention turned to smaller thiols and success was obtained with ethanethiol as the deligating agent. Reactions of the cadmium complexes with excess ethanethiol resulted in clean conversion to free ligand and precipitation of Cd(SEt)$_2$ (Scheme 2). Removal of ethanethiol under reduced pressure yielded the desired free ligand in good yield making the reaction highly efficient.



Scheme 2. Thiol-based ligand exchange methodology used to isolate ligands (*R*,*R*)-**5**H and (*S*,*S*)-**6**H.

In order to push the reactions to completion (100% conversion based on ^{1}H NMR analysis of crude reaction mixture), shifting the equilibrium from bound, anionic ligand to free, neutral ligand and insoluble cadmium thiolate byproduct, a large excess of ethanethiol was required. Efficient deligation reactions required 1000 equiv and 4000 equiv of ethanethiol for Cd((*R*,*R*)-**5**)$_2$ and Cd((*S*,*S*)-**6**)$_2$, respectively. The amount of thiol required may relate to the relative binding strengths of the ligands, with the phenyl substituted ligand (*R*,*R*)-**5**H being greater relative to the *iso*-propyl substituted ligand (*S*,*S*)-**6**H. However, kinetic factors, including sterics where the phenyl groups in Cd((*R*,*R*)-**5**)$_2$ likely hinder access to the Cd more than the *iso*-propyl groups of Cd((*S*,*S*)-**6**)$_2$, cannot be ruled out as the reason for the required relative amounts of thiol. Regardless, in all cases, empirical evidence suggests the ligand binding is strong based on comparison to the very strong binding of thiolates to cadmium.[18] This is supported by the observation that failure to filter the solid Cd(SEt)$_2$ byproduct from solution before removing the excess ethanethiol under vacuum results in the re-binding of ligand to the cadmium centre with displacement of the ethanthiol on adding solvent to the mixture. Overall, the new series of ligands show great potential to bind to metals in a *mer*-coordinated tridentate fashion as is desired for their use as chiral auxiliaries in enantioselective catalysis reactions like similar systems successfully reported elsewhere.[8-13]

Characterization of free ligands: (*R*,*R*)-5H and (*S*,*S*)-6H.

Each ligand, in its neutral protio form (*R*,*R*)-**5**H or (*S*,*S*)-**6**H, was characterized both in the solution (NMR) and the solid (X-ray) states. As with their corresponding cadmium and zinc complexes, each of the free ligands was determined to have C_2 symmetry based on the number of signals observed in the ^{1}H NMR (Figure 3). However, in contrast to the metal complexes, which displayed characteristic upfield shifting of the ^{1}H signals of the phenyl and *iso*-propyl pendant arms, the signals for the pendant groups in (*R*,*R*)-**5**H and (*S*,*S*)-**6**H were in the predicted region for freely rotating substituents as expected. ^{1}H NMR signal assignments are made based on comparison to their corresponding cadmium metal complex.

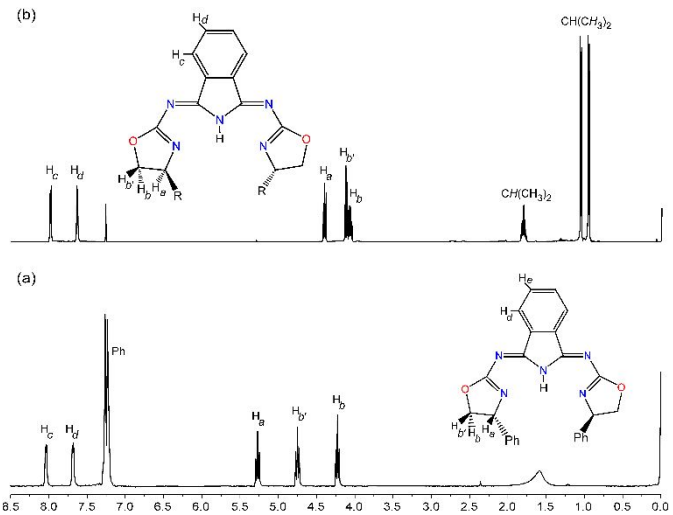


Figure 3. ^{1}H NMR spectra of (*R*,*R*)-**5**H (a) and (*S*,*S*)-**6**H (b) in $CDCl_3$ with assignments made based on their cadmium complexes.

For (*R*,*R*)-**5**H and (*S*,*S*)-**6**H, crystals suitable for X-ray diffraction were obtained via slow evaporation of concentrated CH_2Cl_2:acetone solutions (Figure 4 and Table 1). The data confirmed the enantiopurity of the ligands as well as the structure of each. The X-ray data of (*R*,*R*)-**5**H and (*S*,*S*)-**6**H are consistent with the bonds lengths and angles expected and showed no unusual features.

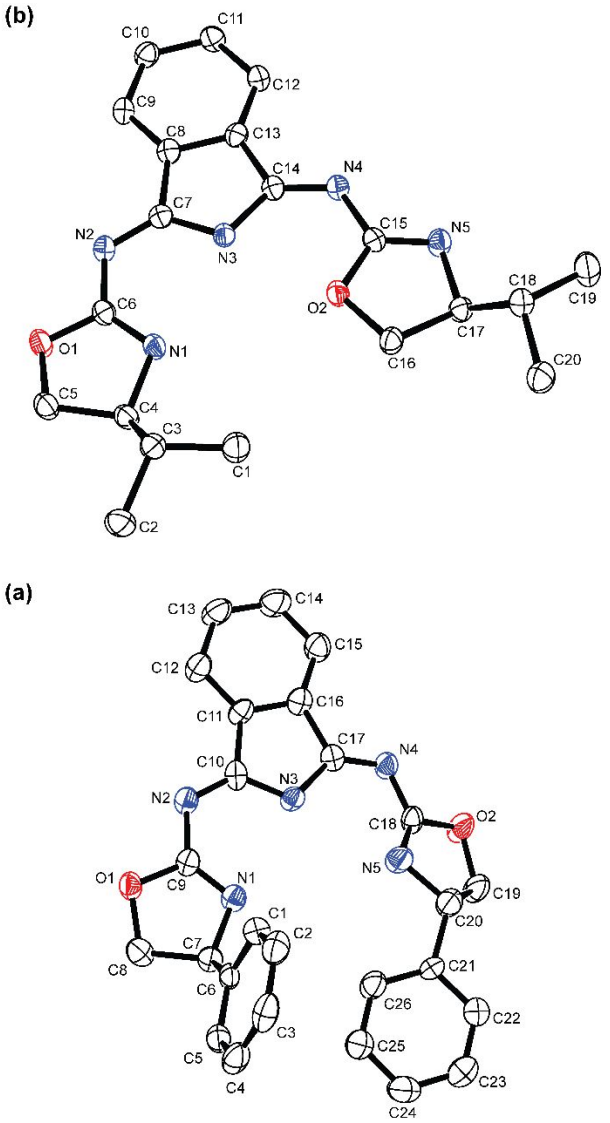
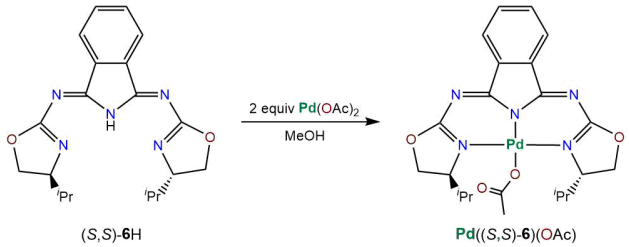


Figure 4. Ortep diagram of the structures of (*R*,*R*)-**5**H (a) and (*S*,*S*)-**6**H (b) determined by single crystal x-ray diffraction at 100 K and 120 K, respectively. All atoms are shown at 50% probability with the exception of H-atoms which are removed for clarity.

Proof-of-Concept Potential Catalyst Complex Structure.

With isolation of the ligands, in their neutral protio form, accomplished, the goal of preparing a monomeric ligand:metal 1:1 complex as a model enantioselective catalyst precursor was pursued. The target complex was a palladium(II)-based system owing to the numerous catalytic applications reported with palladium(II) ligand systems.[21] The complex was prepared (Scheme 3) following the reported work of Bröring and Kleeberg,[8] where 2 equiv of $Pd(OAc)_2$ was reacted with 1 equiv of (*S*,*S*)-**6**H to form Pd((*S*,*S*)-**6**)(OAc). The use of excess metal precursor to ligand is to avoid the binding of 2 equiv of ligand to the metal (Pd((*S*,*S*)-**6**)$_2$), which has a strong potential based on the observed cadmium and zinc complexes formed during the *in-situ* ligand preparation.



Scheme 3. Synthesis of model catalyst complex: Pd((*S*,*S*-**6**)(OAc) based on methodology reported Bröring and Kleeberg.[8]

The complex was isolated via column chromatography and both ^{1}H NMR and X-ray analyses were used to characterize the complex. The ^{1}H NMR showed the characteristic C_2-symmetric binding of deprotonated (*S*,*S*)-**6**H Figure 5 (a) with proton signals appearing in the expected areas. Signal assignments were made based on assignments of Zn((S,S)-**6**)$_2$. The C_2-symmetric binding was further confirmed by single crystal x-ray analysis (Figure 5 (b) and Table 1). The compound is a slightly distorted square planar in geometry as expected for 4-coordinate Pd(II) complexes; confirmed based on the sum of the angles between adjacent bound atoms (N1, N3, N5, and O3) and the Pd being 360.1° and with the adjacent N1-Pd-N3 and N3-Pd-N5 angles being 88.9° and 88.4°, respectively. The angle between the central bound N-isoindoline atom (N3) and trans coordinated acetate is 172.2° (N3-Pd-O3) confirming the slightly distorted square planar nature of the complex. Isolation of this species is proof-of-concept that potential catalyst 1:1 ligand:metal complexes of our ligand system can be prepared. Future work will be focused on the synthesis and study of such complexes in enantioselective catalysts.

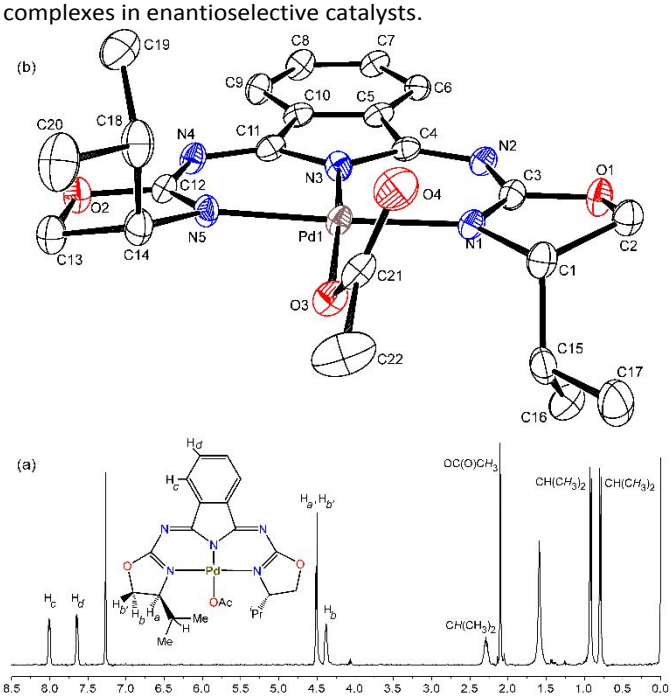


Figure 5. ^{1}H NMR spectrum in $CDCl_3$ (a) and ortep diagram (b) of Pd((*S*,*S*-**6**)(OAc). The structure was determined by single crystal x-ray diffraction at 100 K. All atoms are shown at 50% probability with the exception of H-atoms which are removed for clarity.

Experimental section

Methods and Materials

Chemicals and analysis. All reagents were purchased from commercial sources and used as received. Solvents (Et_2O and CH_2Cl_2) were dried by passing through an Innovative Technologies solvent purification system and collected just prior to use. Toluene (EMD: DriSolv) was deoxygenated by bubbling with a stream of N_2 for 30 min prior to use. NMR spectra were collected on a 400 MHz or 500 MHz Varian NMR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are referenced to TMS. Microwave reactions were performed on a CEM Discover system. Column chromatography were performed on a Biotage Sephora Flash system. High resolution mass spectrometry analyses (TOF-MS ES) were performed at the Mass Spectrometry Facility at the University of California, Irvine (Irvine, CA, 92697).

Ligand synthesis and characterization

Conventional heating synthesis of bis(1,3-bis(4,5-dihydro-4-(*R*)-phenyloxazol-2-ylimino)isoindoline) cadmium(II) (Cd((*R*,*R*)-5)$_2$). To a 200 mL side arm flask with stir bar was added (*R*)-**3** (1.0001 g, 6.1667 mmol), phthalonitrile (0.3252 g, 2.540 mmol), and $Cd(OAc)_2$ (0.2803 g, 1.216 mmol) and sealed with a septum. Under inert N_2 atmosphere, toluene (90 mL) was added via cannula. The mixture was stirred at 80 °C for ~4 days in an oil bath. The solution was cooled to room temperature the solvent was removed under reduced pressure on a rotary evaporator. The residue that remained was re-dissolved in CH_2Cl_2 (10 mL), loaded onto a silica KP-SIL pre-packaged cartridge (10 g), and dried 24 h prior to separation on the Biotage flash column chromatography system (hexane: ethyl acetate- 9:1 over 1 column volume (CV), ramped over 24 CV to 100% EtOAc, and maintained at 100% EtOAc over remaining period). Product eluted as the second peak. Fractions were collected, combined, and solvent removed under reduced pressure producing Cd((*R,R*)-**5**)$_2$ (0.4265 g, 0.4483 mmol, 37%). Product can be purified further by recrystallization from CH_2Cl_2:acetone. HRMS m/z experimental (calculated): $[M+Na]^+$ 1005.2163 (1005.2180). ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.4, 3.0 Hz, 4H), 7.56 (dd, *J* = 5.4, 3.0 Hz, 4H), 6.96 (m, 4H), 6.88 (m, 8H), 6.78 (dt, *J* = 6.9, 1.4 Hz, 8H), 4.76 ('t', *J* = 9.4 Hz, 4H), 4.49 (dd, *J* = 8.9 Hz, *J* = 9.4 Hz, 4H), 3.99 (t, *J* = 8.9 Hz, 4H).

Conventional heating synthesis of bis(1,3-bis(4,5-dihydro-4-(*S*)-isopropyloxazol-2-ylimino)isoindoline) cadmium(II) (Cd((*S,S*)-6)$_2$). The synthesis was performed in a similar fashion as Cd((*R*,*R*)-5)$_2$. To a 500mL side arm flask with stir bar was added (*S*)-**4** (2.5033 g, 19.530 mmol), phthalonitrile, (1.2498 g, 9.7610 mmol) and $Cd(OAc)_2$ (1.1237 g, 4.8751 mmol) and sealed with a septum. Under inert N_2 atmosphere, toluene (175 mL) was added via cannula. The mixture was stirred at 80 °C for ~4 days in an oil bath. The solution was cooled to room temperature and the removed under reduced pressure on a rotary evaporator. The remaining solid residue was dissolved in CH_2Cl_2 (10 mL), loaded onto a silica KP-SIL pre-packaged cartridge (10 g), and dried 18 h prior to separation on the Biotage flash column chromatography system (hexane: ethyl acetate- 9:1 over 1 column volume (CV), ramped over 24 CV to 100% EtOAc, and maintained at 100% EtOAc over remaining period). Product eluted as the second peak. Fractions were collected, combined, and solvent removed under reduced pressure producing Cd((*S,S*)-**6**)$_2$ (1.5012 g, 1.7760 mmol, 36%). Product can be purified further by recrystallization from CH_2Cl_2:acetone. HRMS m/z experimental (calculated): $[M+Na]^+$ 869.2808 (869.2803). ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 5.5, 3.0 Hz, 4H), 7.57 (dd, *J* = 5.5, 3.0 Hz, 4H), 4.25 – 4.14 (m, 8H), 3.86 (m, 4H), 1.74 (m, 4H), 0.74 (d, *J* = 6.8 Hz, 12H), 0.62 (d, *J* = 6.8 Hz, 12H).

General microwave heating synthesis of Cd((*R*,*R*)-5))$_2$ and Cd((*S*,*S*)-6))$_2$. To a 20mL CEM microwave reaction vial was added $Cd(OAc)_2 \bullet 2H_2O$ (1 equiv), phthalonitrile (2 equiv), and (*R*)-**3** or (*S*)-**4** (4 equiv), along with a magnetic stirbar. To this was added toluene (7 mL) and the vial was sealed with the CEM microwave vial plastic cap. The mixture was stirred for 1 min and then placed in the microwave reactor. The sample was heated to 205 °C and held there for 10 min before being cooled back to room temperature with a flow of $N_{2\,(g)}$. A minimum of 3 synthesis trials were run per compound and their product mixtures were combined into a RB flask. The solvent was removed under reduced pressure on a rotary evaporator and the solid residue was purified by recrystallization (CH_2Cl_2:acetone) to yield pure product Cd((*R*,*R*)-**5**))$_2$ or Cd((*S*,*S*)-**6**))$_2$.

Microwave synthesis of Cd((*R*,*R*)-5))$_2$. $Cd(OAc)_2 \bullet 2H_2O$ (0.0822 g, 0.308 mmol), phthalonitrile (0.0793 g, 0.619 mmol), and (*R*)-**3** (0.2001 g, 1.234 mmol) reacted in toluene (7 mL). Product Cd((*R*,*R*)-**5**)$_2$ collected (0.2434 g, 0.2558 mmol) in an average of 82 % yield as a minimum of three trials. Product confirmed based on comparison of ^1H NMR analysis of pure Cd((*R*,*R*)-**5**)$_2$ product from traditional heating method.

Microwave synthesis of Cd((*S*,*S*)-6))$_2$. $Cd(OAc)_2 \bullet 2H_2O$ (0.0784 g, 0.294 mmol), phthalonitrile (0.0751 g, 0.587 mmol), and (*S*)-**4** (0.1506 g, 1.175 mmol) reacted in toluene (7 mL). Product Cd((*S*,*S*)-**6**)$_2$ collected (0.2144 g, 0.2536 mmol) in an average of 85 % yield as a minimum of three trials. Product confirmed based on comparison of ^1H NMR analysis of pure Cd((*S*,*S*)-**6**)$_2$ product from traditional heating method.

Deligation study of (*S*,*S*)-6 from Cd((*S*,*S*)-6)$_2$ via benzyl mercaptan ligand exchange. Cd((*S,S*)-**6**)$_2$ (0.0343 g, 40.6 µmol) was dissolved in $CDCl_3$ (0.5 mL) in an NMR sample tube. Benzyl mercaptan (54 µL, 460 µmol) was added via syringe to the NMR tube and the tube was heated at 45 ºC for 40 min. 1H NMR analysis was performed and indicated ~30% clean conversion to free (*S*,*S*)-**6**H occurring. Additional aliquots of benzyl mercaptan were added (total final combined volume: 1.20 mL, 10.2 mmol, 252 equiv) with heating for 30-40 min and ^1H NMR analysis

performed between each addition. The final ^{1}H NMR analysis indicated almost complete, clean, dissociation (>90% by NMR) of the ligand from the cadmium center based on ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CCDl_3$) δ 7.98 (dd, *J* = 5.6, 3.0 Hz, 4H), 7.64 (dd, *J* = 5.6, 3.0 Hz, 4H), 4.41 (dd, *J* = 9.4, 8.1 Hz, 4H), 4.13 ('t', *J* = 8.1 Hz, 4H), 4.08 (m, 4H), 1.80 (hept, *J* = 6.7 Hz, 4H), 1.06 (d, *J* = 6.7 Hz, 12H), 0.96 (d, *J* = 6.7 Hz, 12H). The spectrum is consistent with that of isolated and purified (*S,S*)-**6**H from the deligation method described hereafter.

General procedure for deligation of (*R*,*R*)-**5**H and (*S*,*S*)-**6**H from Cd((*R*,*R*)-**5**)$_2$ and Cd((*S*,*S*)-**6**)$_2$, respectively, via ethanthiol ligand exchange. To a 250 mL RB flask containing a stir bar was added Cd(L)$_2$ (L = (*R*,*R*)-**5**$^-$ or (*S*,*S*)-**6**$^-$; 1 equiv) and CH_2Cl_2 (10-20 mL). The solution was stirred for 5 min then excess ethanethiol (4000 or 1000 equiv for Cd((*R*,*R*)-**5**)$_2$ and Cd((*S*,*S*)-**6**)$_2$, respectively) was added via glass syringe. The flask was sealed with a septum and left to stir for 24 h. The solution became noticeably cloudy as a precipitate formed. Vacuum filtration was performed to remove the solid Cd(SEt)$_2$ byproduct. The filtrate solvent was either allowed to stir to react further for 24 h, refiltered and the filtrate solvent was removed under reduced pressure or it was not stirred further with only solvent removal under reduced pressure being completed. To the remaining residue, pentane (10 mL) was added and swirled after which another vacuum filtration was performed to collect the solid product LH, where LH is (*R*,*R*)-**5**H or (*S*,*S*)-**6**H as a first crop. The remaining filtrate solvent was removed under reduced pressure and the solid was recrystallized as a second crop. The crops were combined and stored for use.

Deligation of (*R*,*R*)-5H. Cd((*R*,*R*)-**5**)$_2$ (0.2001 g, 0.02039 mmol) was dissolved in CH_2Cl_2 (20 mL). Ethanethiol (59.0 mL, 818 mmol) was added and the reaction was stirred for 24 h. The solution was filtered and the filtrate was left to stir and react for a further 24 h. Combined crops 1 and 2 of product (*R*,*R*)-**5**H (0.1213 g) were collected in 68% yield. HRMS m/z experimental (calculated): $[M+Na]^+$ 458.1577 (458.1593). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 5.6, 3.1 Hz, 4H), 7.68 (dd, *J* = 5.6, 3.1 Hz, 4H), 7.30 – 7.18 (m, 20H), 5.27 (t, *J* = 9.4 Hz, 4H), 4.75 (dd, *J* = 10.1, 8.5 Hz, 4H), 4.22 (t, *J* = 8.5 Hz, 1H).

Deligation of (*S*,*S*)-6H. Cd((*S*,*S*)-**6**)$_2$ (0.4877 g, 0.5770 mmol) was dissolved in CH_2Cl_2 (10 mL). Ethanethiol (42.0 mL, 582 mmol) was added and the reaction was stirred for 48 h. The solution was filtered and the filtrate was left to stir and react for a further 24 h. Combined crops 1 and 2 of product (*S*,*S*)-**6**H (0.3041 g) were collected in 72% yield. HRMS m/z experimental (calculated): $[M+Na]^+$ 390.1894 (390.1906). ^{1}H NMR (500 MHz, $CCDl_3$) δ 7.98 (dd, *J* = 5.6, 3.0 Hz, 4H), 7.64 (dd, *J* = 5.6, 3.0 Hz, 4H), 4.41 (dd, *J* = 9.4, 8.1 Hz, 4H), 4.13 ('t', *J* = 8.1 Hz, 4H), 4.08 (m, 4H), 1.80 (hept, *J* = 6.7 Hz, 4H), 1.06 (d, *J* = 6.7 Hz, 12H), 0.96 (d, *J* = 6.7 Hz, 12H).

Synthesis of Pd((*S*,*S*)-6)(OAc). To a 25 mL side-arm tube was added (*S*,*S*)-**6**H (0.0409 g, 0.0111 mmol) and Pd(OAc)$_2$ (0.0493 g, 0.0220 mmol). The flask was placed under vacuum and refilled with N_2 (x 3) to remove O_2 and water. Deoxygenated methanol (5 mL) was transferred to the side-arm tube via cannula yielding a brown solution that was left to stir under nitrogen for 24 h. During that time a black solid, likely plated out Pd, formed on the sides of the flask. The solution was filtered through a pad of Celite into a 25 mL side-arm tube to remove the black solid byproduct. The reaction tube was rinsed with methanol (3 x 2 mL) and filtered into the same tube used to collect the reaction filtrate. The solvent was removed under reduced pressure and the remaining light brown powdery solid residue was washed with diethyl ether (5 mL) and filtered to collect the red powdery solid Pd((*S*,*S*)-**6**)(OAc). The filtrate was transferred to a 50 mL side-arm flask and a second crop of product was precipitated by the addition of pentane (6 mL) to the filtrate, which was isolated via vacuum filtration. The total yield of red-brown solid Pd((*S*,*S*)-**6**)(OAc) collected was 45 % (0.0269 g, 0.00506 mmol). The compound was identified by X-ray crystallography and characterized by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.64 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.51 (m, 4H), 4.38 (m, 2H), 2.29 (m, 2H), 2.10 (s, 3H), 0.92 (d, *J* = 7.0 Hz, 6H), 0.79 (d, *J* = 7.0 Hz, 6H).

X-ray structural characterizations

X-ray structure analyses of Cd((*R*,*R*)-5)$_2$, Cd((*S*,*S*)-6)$_2$, (*R*,*R*)-5H, (*S*,*S*)-6H, and Pd((*S*,*S*)-6)(OAc). Crystals of Cd((*R*,*R*)-**5**)$_2$, Cd((*S*,*S*)-**6**)$_2$, (*R*,*R*)-**5**H, (*S*,*S*)-**6**H, and Pd((*S*,*S*)-**6**)(OAc) suitable for single crystal X-ray analysis were prepared via slow evaporation of a concentrated CH_2Cl_2:acetone (~10:1) solution of each compound. All crystals were mounted on a Cryoloop with Paratone-N oil. The data were collected on a Bruker Apex II CCD system using either a molybdenum or copper source in a nitrogen gas stream at low temperature (100 K to 120 K). Data were collected in a series of phi and omega scans. The data were integrated using the Bruker SHELXTL[22] software program and scaled using the SADABS[23] software program. The structure was solved by direct methods (SHELXS) and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 (SHELXL-97).[24] In the cases of Cd((*R*,*R*)-5)$_2$ and Cd((*S*,*S*)-**6**)$_2$, SQUEEZE[25] was used and found voids that have been modelled as containing 3 disordered methylene chloride in the Cd((*R*,*R*)-5)$_2$ crystal and 3 methylene chloride and 6 acetone molecules in the Cd((*S*,*S*)-**6**)$_2$ crystal. The absolute stereochemistry of compounds Cd((*R*,*R*)-5)$_2$, Cd((*S*,*S*)-**6**)$_2$, and Pd((*S*,*S*)-**6**)(OAc) were confirmed to be of the correct stereochemistry, in comparison to their enantiopure starting material ((*R*)-**1** and (*S*)-**2**, respectively), from analysis of their Flack[26] parameter. The absolute stereochemistry of (*R*,*R*)-**5**H and (*S*,*S*)-**6**H are assigned based on the configuration assignments of their starting material and corresponding cadmium complexes. The crystal data is summarized in Table 1.

Conclusions

This work reports the first synthesis and isolation of a series of chiral 1,3-bis(4,5-dihydro-4-substituted-2-ylimino)isoindoline ligands via an intermediate cadmium metal complexes. The resulting ligands are enantiopure and have the expected similar structural features of the pybox and other chiral 1,3-bis(pyridine-2 ylimino)isoindoline systems. The Pd((*S*,*S*)-**6**)(OAc) complex is proof-of-concept of the ability to synthesize 1:1 ligand:metal complexes that are expected to be necessary for use as potential catalyst systems.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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Electronic Supplementary Information (ESI) available: X-ray diffraction analysis files for compounds Cd((*R*,*R*)-**5**)$_2$, Cd((*S*,*S*)-**6**)$_2$, (*R*,*R*)-**5**H, (*S*,*S*)-**6**H, and Pd((*S*,*S*)-**6**)(OAc) are available at CCDC: 1952889, 1952586, 1953322, 2016087, and 2016649, respectively.

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Table 1. Selected Crystal Data for Cd((*R*,*R*)-**5**)$_2$, Cd((*S*,*S*)-**6**)$_2$, (*R*,*R*)-**5**H, (*S*,*S*)-**6**H, and Pd((*S*,*S*-**6**)(OAc).

Compound Data	Cd((*R*,*R*)-**5**)$_2$	Cd((*S*,*S*)-**6**)$_2$	(*R*,*R*)-**5**H	*S*,*S*-**6**H	Pd((*S*,*S*)-**6**)(OAc)
Empirical formula	$C_{52}H_{40}CdN_{10}O_4$	$C_{40}H_{48}CdN_{10}O_4$	$C_{26}H_{21}N_5O_2$	$C_{20}H_{25}N_5O_2$	$C_{22}H_{27}N_5O_4Pd$
Formula weight	981.34	845.28	435.48	367.45	531.88
Temperature (K)	150	120	120	100	100
Radiation (λ; Å)	Mo; 0.71073	Mo; 0.71073	Cu; 1.54178	Cu; 1.54178	Mo; 0.71073
Crystal system	Trigonal	Trigonal	Orthorhombic	Triclinic	Monoclinic
Space group	$P3_121$	$P3_221$	$P2_12_12_1$	P_1	P_12_11
Cell dimensions (Å, °)					
a =	19.2930(15)	19.1032(14)	6.1731(2)	9.2785(4)	6.6646(5)
b =	19.293	19.1032	9.1085(3)	10.8229(4)	12.23835(10)
c =	11.7970(9)	11.8529(9)	37.2539(12)	11.2472(4)	13.5762(10)
α =	90	90	90	100.313(2)	90
β =	90	90	90	109.063(2)	95.441(2)
γ =	120	120	90	110.537(2)	90
Volume (Å^3)	3802.8(7) Å^3	3746.0(6)	2094.70(12)	943.06(7)	1106.40(15)
Z	3	3	4	2	2
d (calculated; Mg/m^3)	1.286	1.124	1.381	1.294	1.597
Absorption coeff. (mm^{-1})	0.484	0.480	0.730	0.697	0.878
F(000)	1506	1314	912	392	544
Total reflections	32483	25490	6476	10393	12875
Independent reflections	4673 (R_{int}=0.0509)	5594 (R_{int}=0.0285)	3056 (R_{int}=0.0298)	4863 (R_{int}=0.0225)	5069 (R_{int}=0.0333)
Goodness-of-fit on F^2	0.989	1.060	1.098	1.054	1.018
Final *R* indices [I >2σ(I)]	R_1=0.0309; wR_2=0.0684	R_1=0.0249; wR_2=0.0629	R_1=0.0533; wR_2=0.1262	R_1=0.0299; wR_2=0.0730	R_1=0.0289; wR_2=0.0584
R indices (all data)	R_1=0.0390; wR_2=0.0709	R_1=0.0271; wR_2=0.0642	R_1=0.0591; wR_2=0.1293	R_1=0.0323; wR_2=0.0750	R_1=0.380; wR_2=0.0608
Abs. struct. param.	-0.009(11)	-0.002(7)	0.7(2)	0.21(15)	0.020(16)
Largest diff. peak & hole (e Å^3)	0.286, -0.238	0.639, -0.336	0.389, -0.180	0.151, -0.169	0.412; -0.441