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Transition Metal Complexes of an (*S,S*)-1,2-Diphenylethylamine Functionalized N-Heterocyclic Carbene: a New Member of the Asymmetric NHC Ligand Family

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ABSTRACT: By a simple S_N2 reaction between N-methylimidazole and a chiral sulfamidate, the first proligand of a new class of enantiopure NHC-CHPh-CHPh-NH₂ ligands can be prepared in high yield. This proligand, with molecular formula [(*S,S*)-H₂NCHPhCHPh-NC₃H₃N-CH₃](PF₆), when reacted with a slight excess of lithium or potassium bis(trimethylsilyl)amide, produces the corresponding NHC-CHPh-CHPh-NH₂ ligand, “kaibene”. In the presence of the silver(I) starting materials AgPF₆ or AgI, two Ag(kaibene)₂X complexes (X = PF₆ or I) and one helical kaibene silver polymer [Ag(kaibene)]_n(PF₆)_n can be prepared. Using the suitable silver complex, we successfully transferred kaibene to ruthenium(II), iridium(I) and nickel(II). The ruthenium complex [Ru(*p*-cymene)(kaibene)(Cl)]PF₆ with a base in THF is a moderately active catalyst at 50 °C and 25 bar H₂ for the hydrogenation of acetophenone but with no enantioselectivity.

INTRODUCTION

Enantiopure alcohols and amines are essential building blocks for the synthesis of drugs, fragrances and agrochemicals. One of the many ways to efficiently generate such molecules is *via* the asymmetric hydrogenation of the corresponding ketones or imines using a transition metal catalyst.¹⁻⁸ However most hydrogenation catalysts, including recently reported iron-based catalysts, contain asymmetric chelating phosphine ligands which can potentially introduce harmful contaminants into products destined for medical applications.^{5,9-12} A possible solution to this problem is to replace the phosphines with N-heterocyclic carbenes (NHC) since these organic ligands might be less toxic while maintaining a σ -donor strength that is similar or greater than that of a phosphine.^{13,14} Our group previously reported achiral NHC-Q-NH₂ ligands with linking groups Q for use with precious metals like Ru (**1**, **2** and **4**) and Ir (**3**) (Scheme 1).¹⁵⁻¹⁸ The complexes of these ligands showed moderate to exceptional catalytic reactivity under mild conditions (25 – 50 °C, 9 – 26 atm) towards the complete hydrogenation of ketones, imines (only **2**), and esters (only **2**). Our theoretical calculations support the proposed mechanism involving an “N-H” effect in the hydrogenation of these substrates with polar bonds where a metal-hydride (M-H) and an amine-hydrogen (N-H) group deliver a pair of hydrogens from the catalyst to the polar unsaturated bond of a ketone, imine or ester in a cooperative fashion.^{8,19,20} Complexes **1**, **2** and **4** and a primary amino carbene ruthenium complex reported by Cross et al.²¹ are moderately active catalysts for the transfer hydrogenation of acetophenone using isopropanol, but the conversions for this equilibrium process are not complete.

Scheme 1. The Hydrogenation of Acetophenone Catalyzed by Complexes with Achiral NHC-Q-NH₂ Ligands.

Our objective is the synthesis of enantiomerically pure asymmetric ligands that chelate transition metals via NHC and amine donors in order to take advantage of this rate-enhancing “N-H” effect. Many asymmetric N-heterocyclic carbenes (NHC) ligand designs are known^{13,14,22-33} but there are only a few examples with the NHC-Q-NH₂ structure. A palladium complex containing such an NHC-Q-NH₂ ligand with a 1,2-trans-cyclohexyl linker Q between an NHC and primary amino group (Fig. 1, **5**) was described by Bonnet *et al* in 2004 but it was formed on the metal by a hydrolysis side reaction.³⁴ A related ligand with a 1,10-binaphthyl-2,2'-diamine linker was also formed on palladium by hydrolysis (Fig. 1, **6**).³⁵ Ligands with the amino group directly attached to an aromatic backbone such as that of **6** are not expected to form amido complexes that are reactive enough to efficiently split dihydrogen in a bifunctional catalytic reaction.¹² We are targeting ligands with the amino group attached to an aliphatic carbon to enhance the basicity of the amido group in the catalytic cycle.

Figure 1. Known asymmetric NHC-Q-NH₂ ligands in **5** and **6** (R¹ = ⁿPr, CHPh₂) and the targeted ligands for complexes **7**.

Here we describe the synthesis directly from methylimidazole of the first of a new class of such ligands **7** (R² = Me, “(S,S)-kaibene”) where Q is an (S,S)-1,2-diphenylethandiyld linker along with its silver, nickel, iridium and ruthenium complexes including a chiral, helical coordination silver polymer. Enantiopure 1,2-diphenylethylenediamine (dpn) has proven to be an effective group in catalyst structures for inducing asymmetry in the products of a wide variety of catalytic transformations³⁶ including asymmetric hydrogenation (AH).^{1,10} Kaibene’s similar structure to dpn when coordinated in a bidentate fashion suggests that it might have these valuable characteristics.

RESULTS AND DISCUSSION

Synthesis of a Chiral NH₂-tethered NHC Ligand “kaibene.” In order to synthesize the required imidazolium salt (*S,S*)-**9**, a sulfamidate precursor **8**^{37,38} in the configuration (*R, S*) was first refluxed in a solution of 50% v/v N-methylimidazole (about 10 equivalents) in toluene for 90 min (Scheme 2). During the course of heating, the initially insoluble sulfamidate suspension precipitated as a white powder. The white powder as the Boc protected intermediate can be isolated in almost quantitative yield by cooling the reaction mixture to room temperature and adding an excess of diethyl ether. To deprotect the Boc group, we simply used excess 37% HCl(aq) instead of the standard trifluoroacetic acid or HCl in dioxane treatment. After neutralization and salt metathesis, the product (*S,S*)-**9** can be collected in 90% yield. Its enantiopurity was confirmed by NMR after making the Mosher amide.³⁹ In principle the enantiomer (*R,R*)-**9** can also be prepared since the corresponding sulfamidate can be prepared from a commercially available amino alcohol. In addition other sulfamidates derived from amino alcohols could be prepared in principle. For example the synthesis of related imidazolium salts with a -CHPh-CHMe-NMeSO₃⁻ tether has been reported.⁴⁰

Scheme 2. Synthesis of the Imidazolium Salt Precursor to “(*S,S*)-kaibene”

The presence of the Boc protecting group is crucial in order to obtain an enantiopure product. In a different experiment where the Boc protection group on the sulfamidate was first removed by potassium imidazolide, subsequent reaction with N-methylimidazole consistently gave a mixture of *S,S* and *R,S* diastereomers in a 3:1 ratio independent of varying the reaction temperature and solvent polarity. This observation can be explained through a competing S_N1 reaction with the ongoing S_N2 reaction. We suspect that, without the Boc group, the nitrogen atom is better able to stabilize the carbocation intermediate formed during the S_N1 mechanism, thus yielding the undesired diastereomer. The use of the correct reaction time is also important to prevent side reactions. Prolonged heating led to an undesired side product which is formed by a slow but irreversible E2 elimination from (*S,S*)-**9** where the imidazolium functions as good leaving group.

Synthesis of Silver Complexes for use in Transmetallation Reactions. Typically NHC complexes are prepared by the transmetallation of the ligand from silver (e.g. complex **4** of Scheme 1) or nickel (complexes **1-3**) and usually silver oxide is utilized to make silver derivatives. We found that the imidazolium salt (*S,S*)-**9** is not sufficiently acidic to be deprotonated by silver (I) oxide in an aprotic, low dielectric constant solvent such as CH₂Cl₂ or THF. In order to synthesize

the corresponding silver complex, it is necessary to use a silver reagent in combination with the strong base hexamethyldisilylamide as the alkaline metal salt (MHMDS, M=Li, K); this likely produces the free (*S,S*)-kaibene (Scheme 3) which is rapidly trapped by a silver cation. We tried to directly deprotonate the imidazolium salt with various strong bases to generate the NHC *in situ* but the system decomposed. By using this method, three different silver complexes were made (Scheme 3).

Scheme 3. Synthesis of a Coordination Polymer (10) and Two Monometallic Silver Complexes (11, 12) Starting from (*S,S*)-9

In order to prepare **10** we reacted one equivalent of base and silver ion per imidazolium salt precursor in a THF solution over a period of four days until a white precipitate slowly formed. This substance was collected *via* filtration and all unreacted starting materials and lithium salt by-products were washed away by use of THF. A recrystallization using a slow diffusion of diethyl ether into a saturated acetonitrile solution gave colourless crystals which revealed the formation of a 1-D silver NHC-NH₂ polymer **10** as illustrated in Scheme 3. The crystal structure (Figure 2) reveals that the polymer is in a $\Lambda(M)$ -helical configuration with each silver ion coordinated by an

NHC carbon and an amino nitrogen of the (*S,S*)-kaibene with a nearly linear C-Ag-N angle of 177.0(2)°.

Figure 2. A $\Lambda(M)$ -helical coordination polymer **10** of silver with (*S,S*)-kaibene. Selected bond lengths (Å) and angles (°): Ag1-C1 2.053(5), Ag1-N3a 2.135(4), C1-Ag1-N1a 177.0(2). PF_6^- and a diethyl ether molecule are removed for clarity.

Complex **10** has an unusually short Ag-C bond distance of 2.053(5) Å in comparison to known Ag-NHC complexes with two coordinate silver in the literature. This is in the 6th percentile of Ag-NHC distances which range from 2.02 to 2.16 Å in 390 structures with two coordinate silver as determined by searching the 2015 Cambridge Structural Database. This is ascribed to the fact that amine donors have among the weakest trans influence of neutral donors.⁴¹ The only other complex with a crystallographically characterized $[\text{N}(\text{amine})\text{-Ag-C}(\text{NHC})]^+$ structure is the dimeric complex $[\text{Ag}_2(\text{NEt}_2\text{CH}_2\text{CH}_2\text{NC}_3\text{H}_2\text{NMe})_2](\text{NTf}_2)_2$.⁴² It has a comparable Ag-C distance but a longer Ag-N distance (2.178(3) vs 2.135(4) in **10**) because of the larger size of the substituents on nitrogen and their poorer ability to stabilize the positive charge. While some coordination polymers of silver and NHC ligands are known, none have adopted an asymmetric structure like that of **10**.⁴³⁻⁴⁵ Further investigation showed that the oligomerization process is extremely slow at room temperature as the white product did not appear in the solution until approximately the third day of the reaction. Attempts to isolate the product before this precipitate is observed yielded unidentified decomposition products. Although the formation of such a polymer is interesting and unprecedented, this polymer is only soluble in DMSO and acetonitrile which limits its use in the synthesis of other metal complexes.

In order to increase the solubility of a silver NHC complex, the ratio of silver to ligand was reduced to half to disfavour the formation of the polymer. The reaction of (*S,S*)-**9** with AgPF_6 and base resulted in the formation of the silver bis(kaibene) complex **11** as the PF_6^- salt while that with AgI and base produced the neutral silver bis(kaibene) iodide complex **12**. Complex **12** can also be prepared from **11** by reaction with potassium iodide (Scheme 3). It is noteworthy that the presence of excess KI is necessary to obtain **12** in high purity; if not, the product appears more metallic, probably due the formation of silver (0). In contrast to compound **10** which is light stable, compounds **11** and **12** are light sensitive; colourless solutions of **11** or **12** turned brown after 18 h when illuminated with overhead fluorescent lights. Both complexes were characterized by NMR

and by EA and single crystals of **12** suitable for X-ray diffraction were grown from a saturated CH₂Cl₂/hexane solution (Figure 3).

Figure 3. Molecular structure of **12**. (Left: atom numbering; right: orientation showing the T-shape with *trans* carbenes). Selected bond lengths (Å) and angles (°): Ag1A-C1A 2.103(1), Ag1A-C19A 2.095(2), Ag1A-I1A 3.251(8), C19A-Ag1A-C1A 165.9(6), C19A-Ag1A-I1A 93.3(4), C1A-Ag1A-I1A 100.6(4). CH₂Cl₂ molecules are removed for clarity.

Complex **12** contains a “T-shaped” three coordinate silver center with the two NHC ligands in an approximate *trans* orientation (Figure 3). There are two molecules A and B in each asymmetric unit with C-Ag-C angles 165.9(6)° for A and 160.3(5)° for B. The Ag-I bond forms two angles with the two Ag-C bonds, one in range of 94° and the other 103° for each molecule. The Ag-NHC distance appears to be longer in **12** (2.095(2) to 2.103(1) Å) than **10** (2.053(5)) because of the higher *trans* influence of carbene versus amine. Although a Ag-I bond is drawn by the crystallographic software in Fig. 3, the Ag-I distance (3.251(8) Å) is actually longer than the sum of the covalent radii of silver and iodine (2.84 Å, 1.45 Å for silver and 1.39 Å for iodine).⁴⁶ Therefore the iodide serves mainly as a counterion and its position can be attributed to a balance of electrostatic attractions and steric interaction. It should also be noted that the voids in this lattice host a large number of CH₂Cl₂ molecules. This compound has a characteristic NHC carbon shift at 181.5 ppm in the ¹³C NMR spectrum, which falls within the expected range of transition metal NHC compounds.⁴⁷

Synthesis of Ru, Ni and Ir Complexes of Kaibene. The ruthenium *p*-cymene complex with kaibene is prepared by reacting the dichloro(*p*-cymene)ruthenium dimer with compound **12** in THF at reflux (Scheme 4). Notably, it is important to add an excess of a non-halide salt such as KPF₆ or NaBPh₄ during the reaction to remove one chloride ligand from the dimer. This generates a vacant site on the ruthenium for kaibene, breaks apart the dimer, and makes the ruthenium center more Lewis acidic to facilitate ligand transmetalation. In contrast, trial reactions done without one of these salts, or with only a stoichiometric amount of them, tended to produce multiple products. Unfortunately, both **13** and **14** are obtained as equal quantities of two diastereomers having opposite chirality at ruthenium, independent of the choice of the counter anion. This might explain our failure to obtain single crystals for X-ray crystallography. As an alternative approach, we use 2D NMR and mass spectrometry techniques to elucidate the structures in solution.

Scheme 4. Synthesis of the Half-sandwich Ruthenium Complexes **13 and **14** using the Transmetallation Reagent **12****

The ^{13}C NMR spectrum of compound **13** in CD_2Cl_2 reveals two NHC signals at 174.2 and 171.3 ppm, one for each of the diastereomers. This is a significant chemical shift difference from that of the starting silver reagent at 181.5 ppm thus providing evidence for coordination. Also, this NMR shift is near to 174.0 ppm observed for its achiral analogue compound **4**.¹⁶ To further validate that kaibene is chelated to ruthenium via both the NHC and NH_2 parts, a 2D ^1H - ^{15}N gHSQC experiment was conducted (Figure 4). As expected for the presence of two diastereomers, two sets of NH_2 peaks are observed in the ^{15}N dimension of the spectrum at -2.61 and 3.76 ppm. More importantly, each of these nitrogen signals correlates to two diastereotopic hydrogen atoms through one-bond interactions. An NMR spectrum of **13** in $\text{DMSO}-d_6$ was also collected. In this spectrum, NH signals are found at 4.00, 4.13, 4.51, 5.60 ppm compared to 3.21, 3.93, 5.18, 5.60 ppm for **13** in CD_2Cl_2 . The NH peak at 4.51 ppm shows a clear doublet of doublet pattern as expected. This confirms the coordination of the NH_2 functional group in **13** since, upon binding to $\text{Ru}(\text{II})$, the two hydrogen atoms on the nitrogen are no longer able to achieve chemical equivalence via inversion at nitrogen.

Figure 4. ^1H - ^{15}N gHSQC spectrum of **13** in CD_2Cl_2 (f1 ^{15}N , f2 ^1H).

In addition to ruthenium, we also transferred kaibene from silver to nickel(II) and iridium(I) using silver complexes **11** and **12** respectively (Scheme 5). After reacting **11** with approximately two equivalents of nickel(II) chloride in the presence of KI over a five day period, we obtained a bis(kaibene) nickel (II) dimer with bridging iodides (**15**, Scheme 5) in approx. 64% yield, using kaibene as the limiting reagent. Experiments were also conducted in the absence of KI. However, the product mixture was never as pure as that obtained in the experiment performed with KI addition. In contrast to compounds **13** and **14**, we observed only one doublet ^1H NMR signal for the NH_2 group at 1.66 ppm ($J_{\text{HH}} = 5.1$ Hz) which integrates as two protons. The use of 2D ^1H - ^1H correlation determined that the CH hydrogen on the CHPh group adjacent to the NH_2 group is responsible for this coupling. It is likely that the amine groups are not coordinated and are freely inverting. We also observe similar NH_2 resonances for complexes **11** (1.56 ppm, $J = 4.3$ Hz) and **12** (1.77 ppm, $J = 5.5$ Hz) which are known to have no amine coordination because of the linear coordination mode favored by silver(I); this is seen in the solid state structure of compound **12**. The ^{13}C signal for **15** at 186.01 ppm provides evidence for NHC coordination while mass spectrometry reveals the presence of $[\text{Ni}(\text{kaibene})_2]^{2+}$ fragments. ^{19}F NMR and elemental analysis suggest the presence of PF_6^- as the counter anion for this system. All of these analytical data suggest that the nickel compound **15** contains a nickel (II) center and has a stoichiometric ratio kaibene:nickel = 2:1. On the basis that nickel (II) complexes tend to have a square planar arrangement due to their d^{10} configuration we propose that the structure of **15** is an iodide-bridged nickel dimer as illustrated in Scheme 5. A similar nickel (II) NHC dimeric structure was reported but it contains only one bulky IPr NHC ligand.^{48,49} Interestingly, the use of compound **11** as the transmetallation reagent to generate compound **15** was crucial. The use of the analogous compound **12** always led to a mixture of products. We speculate that the silver(I) cation in **11** without halide coordination can act as a halide abstracting agent to first convert NiCl_2 into the better Lewis acid $[\text{NiCl}]^+$ to favor the coordination of the kaibene.

Scheme 5. Synthesis and Proposed Structures of Nickel and Iridium Compounds **15** and **16**

Similarly, the analogous iridium complex **16** can be synthesized by refluxing chloro(1,5-cyclooctadiene)iridium(I) dimer with complex **12** in THF. Complex **11** can also be used but the yield is lower. In early attempts we reacted complex **11** with the iridium precursor at room temperature with an excess of KI but only obtained compound **12**. To rationalize this, we believe that the temperature of THF at reflux is required to make the cyclooctadiene ligand labile for substitution. Initially we attempted to isolate an $\text{Ir}(\text{cod})(\text{kaibene})\text{Cl}$ compound similar to our previous active catalyst **3**. However, we believe that the strong *trans* influence of the kaibene carbon labilizes the alkene ligand so that no $[\text{Ir}(\text{cod})(\text{kaibene})]^+$ complex is observed in the product.

We propose a structure $[\text{Ir}(\text{kaibene})_2\text{I}]_2$ for compound **16** with uncoordinated amino groups that is similar to that of compound **15** since we also observe a clean doublet representing the NH_2 at 1.78 ppm (d, $J_{\text{HH}} = 5.7$ Hz, 2H) in the ^1H NMR spectrum. The NHC ^{13}C shift in the NMR spectrum is 186.53 ppm. We observed an $[\text{Ir}(\text{kaibene})_2]^+$ fragment in mass spectrometry which indicates a ratio of kaibene:iridium = 2:1 and this is consistent with the elemental analysis. It is noteworthy that we also observe an $[\text{Ir}(\text{kaibene})_2(\text{cod})]^+$ fragment in the mass spectrum as the major species but no obvious cod signal in the proton NMR spectrum. Trace amounts of this complex must ionize much more efficiently under the ESI conditions than dimeric complex **16**. No similar iridium(I) structures have been reported but a reaction intermediate was proposed to have an $[\text{Ir}(\text{NHC})_2\text{Cl}]_2$ structure with bridging chlorides.⁵⁰ Compound **16** was tested for the hydrogenation of acetophenone and but no catalytic reactivity was observed under the conditions that we used (50°C , 25 bar H_2).

Catalytic hydrogenation of acetophenone using compound **13.** First we examined the transfer hydrogenation capability of ruthenium complex **13** since the analogous compound **4** showed moderate reactivity in transfer hydrogenation. At 75°C with 0.5% catalyst **13** loading along with 4% KOtBu , there was 40% conversion to 1-phenylethanol after 3.5 hours, using isopropanol

as the sacrificial hydrogen source as well as the solvent. We attribute the poor activity to the low solubility of the precatalyst in the solution. The enantioselectivity of this reaction is low (5%). This is possibly due to the diastereomeric composition of the precatalyst. However this is also consistent a mechanism, as proposed for the analogous achiral complex **4**, where the activated catalyst transfers a hydride to acetophenone in the inner coordination sphere with the amine group of the NHC ligand decoordinated and thus inducing little enantioselectively.¹⁶

We then tested precatalyst **13** for direct hydrogenation (Figure 5) and find that it is more effective here than in transfer hydrogenation. The e.e. is 0% indicating that the presence of diastereomers of the catalyst is detrimental to catalytic asymmetric applications or that this catalytic reaction also proceeds via an inner sphere hydride transfer mechanism with the tethered NH₂ decoordinated. The activity of the catalyst system (TOF 200 h⁻¹) is less than that of the achiral analogue **4** (Scheme 1, TOF 600 h⁻¹) possibly for steric reasons.

Figure 5. Catalytic hydrogenation of acetophenone using compound **13**

We lowered the catalyst loading and measured a reaction profile of conversion versus time and observed no activation period. This provides evidence against the formation of catalytically active nanoparticles which typically display an induction period. The reaction profile shows a continuously declining rate of reaction with conversion. The use of a higher substrate concentration gave a similar profile with no significant enhancement in TOF.

CONCLUSIONS

In summary, a new approach to synthesize primary amine tethered NHC prolignands is reported and this method can be used to generate enantiopure asymmetric ligands. Here we reported the first ligand of this class (*S,S*)-H₂N-CHPh-CHPh-NHC “kaibene” that can be prepared in 90% yield and analytical purity as the imidazolium salt. In the presence of HMDS base, three silver complexes can be produced depending on the source of silver and the stoichiometric ratio between the ligand and metal. With one equivalent of silver per ligand, the first Λ -helical coordination polymer of silver **10** was synthesized and structurally characterized by X-ray crystallography. The use of a half equiv. of silver per ligand generates compounds **11** and **12** with the molecular formula Ag(kaibene)₂X (X = I or PF₆) and these bis(kaibene) silver compounds are good transmetalation reagents that can be used for the synthesis of Ru(II), Ni(II) and Ir(I) kaibene complexes (**13-16**). The ruthenium complexes **13** and **14** [Ru(*p*-cymene)(kaibene)(Cl)](X) (X = PF₆, BPh₄) exist as two diastereomers and their amine coordination was confirmed by 2D ¹H-¹⁵N gHSQC. In contrast, Ni and Ir complexes display interesting dimeric structures with the formulae [NiI(kaibene)₂](PF₆)₂ and [IrI(kaibene)₂]₂ where the primary amine groups are not coordinating. Complex **13** showed poor transfer hydrogenation capacity and moderate direct hydrogenation activity (TOF 200 h⁻¹)

using acetophenone as the test substrate but the presence of the two diastereomers or decoordination of the amino group would explain why little or no enantioselectivity is observed.

EXPERIMENTAL SECTION

General Considerations. The synthesis of the ligand was conducted in the air. All of the syntheses of transition metal complexes were performed under an argon or nitrogen atmosphere using standard Schlenk-line and glove box techniques unless stated otherwise. The sulfamidate precursor was prepared according to the reported literature method.³⁷ All solvents were degassed and dried using standard procedures prior to all manipulations and reactions unless stated otherwise. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Sigma Aldrich, degassed, and dried over activated 3 Å molecular sieves prior to use. All other reagents were purchased from commercial sources and utilized without further purification. NMR spectra were recorded at ambient temperature and pressure using a Varian Gemini 400 MHz spectrometer (400 MHz for ¹H, 100 MHz for ¹³C, 376 MHz for ¹⁹F), Agilent DD2-500 MHz spectrometer (500 MHz for ¹H, 125 MHz for ¹³C) or an Agilent DD2-600 MHz spectrometer (600 MHz for ¹H, 151 MHz for ¹³C, 564 MHz for ¹⁹F) unless stated otherwise. The ¹H-¹⁵N gHSQC was measured using an Agilent DD2-700 MHz spectrometer. The ¹H and ¹³C NMR were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane (TMS). Only selected NMR data is listed below. A complete assignment of resonances and coupling constants for the compounds with numbered atoms is found in the Supporting Information.

3-((1S,2S)-2-amino-1,2-diphenylethyl)-1-methyl-1H-imidazol-3-ium hexafluorophosphate, (S,S)-9. A round bottom flask was charged with a magnetic stirring bar, the sulfamidate (4*S*,5*R*)-1,2,3-oxathiazolidine-3-carboxylic acid, 4,5-diphenyl-, 1,1-dimethylethyl ester, 2,2-dioxide (1.0 g, 2.66 mmol), N-methylimidazole (2.2 mL, 27.6 mmol) and 2 mL of toluene and then the solution was refluxed for 1.5 h. The reaction mixture turned from cloudy to clear and then to cloudy during the reflux. After cooling to room temperature, 20 mL of diethyl ether was added and the mixture was stirred for another 20 min. A white precipitate of the Boc-protected (S,S)-9 formed and was collected *via* filtration. 5 mL of conc. HCl (37% wt in H₂O) was used to dissolve this white powder and the mixture was stirred for another hour. The acidic solution was then neutralized with sodium carbonate and then to it was added 0.5 g of potassium hexafluorophosphate. The mixture stirred for 18 h to allow salt metathesis. The white precipitate that formed was filtered and the filtrate was extracted with 50 mL CH₂Cl₂ (CH₂Cl₂) three times and the extracts were combined with the precipitate. Evaporation of all volatiles under vacuum gave a white solid which was then dissolved in a minimum amount of CH₂Cl₂. Insoluble compounds were filtered off and then product was reprecipitated by the addition of an excess hexanes; this mixture was stirred for 2 h and then filtered and dried *in vacuo*. Yield: 1.02 g (90%). ¹H NMR (DMSO-*d*₆, 298K, δ): 9.42 (s, NCHN, 1H), 7.97 (dd, ³J_{HH}=2.4 Hz, ⁴J_{HH}=1.7 Hz, CH of imid., 1H), 7.71 (dd, ³J_{HH}=2.4 Hz, ⁴J_{HH}=1.6 Hz, CH of imid., 1H), 7.48-7.08 (m, Ph on the backbone, 10H), 5.72 (d, ³J_{HH}=10, CHPh-imid., 1H), 4.83 (d, ³J_{HH}=10.1 Hz, CHPh-NH₂, 1H), 3.88 (s, CH₃, 3H). ¹³C{¹H} NMR (DMSO-*d*₆, 298K, δ): 142.98 (NCHN), 137.05 (Ph), 136.71 (Ph), 129.5-127.5 (aromatic CH), 124.02 (CH of imid.), 122.10 (CH of imid.), 70.12 (CHPh-imid), 58.20 (CHPhNH₂), 36.40 (CH₃). ¹⁹F NMR (DMSO-*d*₆, 298K, δ): -70.16 (d, PF₆). ³¹P NMR (DMSO-*d*₆, 298K, δ): -114.17 (septet, PF₆). MS (ESI, methanol; *m/z*): 278.1653 [M – PF₆]⁺. Anal. Calcd for C₁₈H₂₀F₆N₃P: C, 51.07; H, 4.76; N, 9.93. Found: C, 50.68; H, 5.19; N, 9.89.

Note: All of the following syntheses of the Ag complexes were conducted at 28 °C without any heating.

[Ag(kaibene)(PF₆)]_n, 10. A 20 mL vial was charged with (S,S)-9 (40 mg, 0.094 mmol), AgPF₆ (26 mg, 0.10 mmol) and a stirring bar. The mixture was dissolved in 2 mL of THF. LiHMDS (16 mg, 0.10 mmol), dissolved in a minimum THF, was added with vigorous stirring. The vial was

then wrapped in aluminium foil to avoid photolytic side reactions and stirred for 4 days. Over time a white/gray precipitate formed. The precipitate was then collected by filtration and washed with cold THF. X-ray quality crystals were grown by slow diffusion of diethyl ether into a saturated solution of **10** in acetonitrile. Yield: 23.5 mg (94%). ^1H NMR (DMSO- d_6 , 298K, δ): 7.93 (s, CH of imid., 1H), 7.71 (s, CH of imid., 1H), 7.68-7.15 (m, Ph on the backbone, 10H), 5.97 (d, CHPh-imid., 1H), 5.56 (broad m, CHPhNH₂, 1H), 4.33 (broad m, NH₂, 2H), 3.83 (s, CH₃, 3H). ^1H - ^{13}C HSQC NMR (DMSO- d_6 , 298K, δ): 131.58-124.73 (aromatic CH), 126.64 (CH of imid.), 118.76 (CH of imid.), 73.32 (CHPh-imid.), 56.64 (CHPhNH₂), 39.52 (CH₃). MS failed due to low volatility and decomposition in protic solvents. Anal. Calcd for C₁₈H₁₉AgF₆N₃P: C, 40.78; H, 3.61; N, 7.93. Found: C, 41.74; H, 3.81; N, 9.99. Unsatisfactory analyses were measured even in the presence of V₂O₅ because of a combustion problem due to the presence of the hexafluorophosphate anion as previously reported in the literature.⁵¹

[Ag(kaibene)₂](PF₆), 11. A 20 mL vial was charged with (*S,S*)-**9** (300 mg, 0.709 mmol), AgPF₆ (99 mg, 0.39 mmol) and a stirring bar. With vigorous stirring, the mixture was dissolved in 5 mL of THF and then a solution of KHMDS (177 mg, 0.887 mmol) in 3 mL THF was added. The vial was then protected with aluminium foil to avoid photolytic side reactions and the solution was stirred for 18 h. Over time an insoluble precipitate formed. The reaction mixture was then filtered to remove insoluble materials and the residue was washed with more THF. The volatiles were then removed *in vacuo* and the residue was dissolved in CH₂Cl₂ again. The CH₂Cl₂ solution was filtered through a pad of celite to remove any insoluble compounds and then treated with an excess of hexanes to cause the formation of an oily substance at -30°C. Removal of the supernatant and drying the residue in the dark gave a fluffy yellow-white solid. Yield: 240 mg (84%). ^1H NMR (DMSO- d_6 , 298K, δ): 7.97 (s, CH of imid., 2H), 7.54 (s, CH of imid., 2H), 7.5-7.0 (m, Ph on the backbone, 20H), 5.68 (d, $^3J_{\text{HH}}=9.4$ Hz, CHPh-imid., 2H), 5.03 (dt, $^3J_{\text{HH}}=9.4$, 4.8 Hz, CHPh-NH₂, 2H), 3.82 (s, CH₃, 6H), 1.98 (d, $^3J_{\text{HH}}=4.8$ Hz, NH₂, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 298K, δ): C_{NHC} was not detected due to the low solubility of **11**, 142.72 (Ph), 138.73 (Ph), 129.0-126.5 (aromatic CH), 123.38 (CH of imid.), 120.37 (CH of imid.), 72.03 (CHPh-imid.), 57.70 (CHPh-NH₂), 38.29 (CH₃). MS unavailable due to water sensitivity. Anal. Calcd for C₃₆H₃₈AgF₆N₆P•0.5CH₂Cl₂: C, 51.57; H, 4.62; N, 9.89. Found: C, 50.92; H, 5.27; N, 9.33.

Ag(kaibene)₂I, 12: Route (a) from 11. A magnetic stirring bar, **11** (200 mg, 0.248 mmol), potassium iodide (KI) (100 mg, 0.602 mmol) and 7 mL of THF were added to a round bottom flask and the mixture was stirred 18 h while protecting the reaction from light. The reaction mixture was then filtered to remove unreacted KI and the residue was washed with more THF. The volatiles were then removed *in vacuo* and residue was dissolved in CH₂Cl₂. The CH₂Cl₂ solution was filtered through a pad of celite to remove any insoluble matter and then the addition of excess hexanes caused the formation of a white powder. Yield: 132 mg (68%). **Route (b) from (*S,S*)-9.** A 40 mL vial was charged with (*S,S*)-**9** (500 mg, 1.18 mmol), KI (500 mg, 3.01 mmol) and a stirring bar and then 10 mL THF was added to form a suspension. With vigorous stirring, AgI (144 mg, 0.613 mmol) was added followed by a KHMDS solution (KHMDS (1.43 mmol, 285 mg) dissolved in 4 mL THF). More THF was added to make up a total volume at about 40 mL. The vial was then protected with aluminium foil to avoid photolytic side reactions and the mixture was stirred for 18 h. The reaction mixture was then filtered to remove insoluble compounds and the residue was washed with CH₂Cl₂ (5 mL x 3). The washings were combined and then evaporated and the residue was dissolved in CH₂Cl₂. The CH₂Cl₂ solution was filtered through a pad of celite to remove any insoluble compounds and then treated with an excess of hexanes to cause the formation of product as a white precipitate. Yield: 423 mg (91%). ^1H NMR (DMSO- d_6 , 298K, δ): 7.96 (d, $^3J_{\text{HH}}=1.8$ Hz,

CH of imid., 2H), 7.52 (d, $^3J_{\text{HH}}=1.6$ Hz, CH of imid., 2H), 7.45-7.05 (m, Ph on the backbone, 20H), 5.76 (d, $^3J_{\text{HH}}=9.6$ Hz, CHPh-imid., 2H), 5.02 (dt, $^3J_{\text{HH}}=9.6, 5.8$ Hz, CHPh-NH₂, 2H), 3.81 (s, CH₃, 6H), 1.97 (d, $^3J_{\text{HH}}=5.8$ Hz, NH₂, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO-*d*₆, 298K, δ): 181.49 (C_{NHC}), 142.87 (Ph), 138.88 (Ph), 129.0-126.5 (aromatic CH), 123.27 (CH of imid.), 120.1 (CH of imid.), 72.10 (CHPh-imid.), 57.76 (CHPh-NH₂), 38.26 (CH₃). MS unavailable due to water sensitivity. Anal. Calcd for C₃₆H₃₈N₆AgI·0.5CH₂Cl₂: C, 52.69; H, 4.73; N, 10.10. Found: C, 53.07; H, 4.63; N, 10.07. Single crystals for the X-ray diffraction study were obtained by slow evaporation of a saturated hexane/CH₂Cl₂ solution.

[Ru(*p*-cymene)(kaibene)(Cl)]PF₆, 13. In a 25 mL Schlenk flask charged with a stirring bar, **12** (40 mg, 0.051 mmol), [Ru(*p*-cymene)Cl₂]₂ (30 mg, 0.049 mmol) and KPF₆ (40 mg, 0.26 mmol) were suspended in 4 mL THF. The reaction mixture was then refluxed for 3 h and stirred at room temperature for 18 h. Then, all of the THF was evaporated and the residue was redissolved in CH₂Cl₂ and filtered through a pad of celite. The addition of excess diethyl ether to the CH₂Cl₂ filtrate caused the formation of a yellow powder. The solution was then cooled to -30°C for further crystallization. The precipitate was then collected *via* filtration, washed with diethyl ether and dried in vacuum. Yield: 48 mg (71%). ^1H NMR (CD₂Cl₂, 298K, δ): see Supporting Information. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): 174.20 (C_{NHC}, isomer B), 171.31 (C_{NHC}, isomer A) and see Supporting Information. MS (ESI, methanol; *m/z*): 548.1412 [M – PF₆]⁺. Anal. Calcd for C₂₈H₃₃F₆N₃PRuCl: C, 48.52; H, 4.80; N, 6.06. Found: C, 45.35; H, 4.23; N, 5.62. Unsatisfactory analyses were measured even in the presence of V₂O₅ because of a combustion problem.⁵¹

[Ru(*p*-cymene)(kaibene)(Cl)] BPh₄, 14. This was synthesized using the same procedure to make compound **13**, starting with **12** (40 mg, 0.051 mmol), [Ru(*p*-cymene)Cl₂]₂ (30 mg, 0.049 mmol) and NaBPh₄ (70 mg, 4.18 mmol). Yield: 76 mg (89%). The ^1H NMR spectrum is nearly identical to that of **12** except for the extra aromatic peaks due to the BPh₄ anion.

[NiI(kaibene)₂](PF₆)₂, 15. A 20 mL vial was charged with NiCl₂ (12 mg, 0.093 mmol), **11** (35 mg, 0.043 mmol), KI (63 mg, 0.38 mmol) and a stirring bar and the mixture was suspended in 3 mL of THF with vigorous stirring for 18 h, protected from light. The reaction mixture was then filtered to remove insoluble materials and the residue was washed with more THF. All of the volatiles were then evaporated and the residue was dissolved in CH₂Cl₂ again. The CH₂Cl₂ solution was filtered through a pad of celite to remove any insoluble compounds and then stirred for five days. The CH₂Cl₂ solution was filtered through a pad of celite again and all of the CH₂Cl₂ was removed under vacuum. The residue was then recrystallized from THF/diethyl ether as a light yellow powder. Yield: 25 mg (64%). ^1H NMR (CD₂Cl₂, 298K, δ): 7.37-7.15 (m, Ph, 40H), 7.49 (d, $^3J_{\text{HH}}=1.8$ Hz, CH of imid., 4H), 7.04 (d, $^3J_{\text{HH}}=1.8$ Hz, CH of imid., 4H), 5.99 (d, $^3J_{\text{HH}}=8.5$ Hz, CHPh-imid., 4H), 4.93 (dt, $^3J_{\text{HH}}=8.5, 5.1$ Hz, CHPhNH₂, 4H), 3.77 (s, CH₃, 12H), 1.68 (d, $^3J_{\text{HH}}=5.1$ Hz, NH₂, 8H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): 186.01 (C_{NHC}), 142.21 (Ph), 138.67 (Ph, isomer A), 130.0-127.0 (Ph), 122.70 (CH of imid.), 120.54 (CH of imid.), 71.95 (CHPh-imid.), 59.50 (CHPh-NH₂), 39.34 (CH₃). ^{19}F NMR (CD₂Cl₂, 298K, δ): -72.95 (d, PF₆). MS (ESI, methanol; *m/z*): 306.1255 [Ni(kaibene)₂]²⁺. Anal. Calcd for C₇₂H₇₆F₁₂N₁₂P₂Ni₂I₂: C, 48.84; H, 4.33; N, 9.49. Found: C, 47.40; H, 4.60; N, 9.13. Unsatisfactory carbon analyses but acceptable hydrogen and nitrogen content were measured, even in the presence of V₂O₅, because of a combustion problem due to the presence of the hexafluorophosphate anion.⁵¹

[IrI(kaibene)₂], 16. A 20 mL vial was charged with chloro(1,5-cyclooctadiene)iridium(I) dimer (50 mg, 0.074 mmol), **12** (120 mg, 0.152 mmol), KI (240 mg, 1.45 mmol) and a stirring bar and the mixture was suspended in 12 mL of THF with vigorous stirring for 18 h at 66 °C, protected

from light. The reaction mixture was then filtered to remove insoluble materials and the residue was washed with more THF. All of the volatiles were then evaporated and the residue was dissolved in CH₂Cl₂ again. The CH₂Cl₂ solution was filtered through a pad of celite again and all of the CH₂Cl₂ was removed under vacuum. The residue was then recrystallized from CH₂Cl₂/diethyl ether as a light yellow powder. Yield: 104 mg (80%). ¹H NMR (CD₂Cl₂, 298K, δ): 7.51 (d, ³J_{HH}=1.8 Hz, CH of imid., 4H), 7.45-7.10 (m, Ph on the backbone, 40H), 7.06 (d, ³J_{HH}=1.8 Hz, CH of imid., 4H), 6.18 (d, ³J_{HH}=9.0 Hz, CHPh-imid., 4H), 4.87 (dt, ³J_{HH}=9.0, 5.6 Hz, CHPh-NH₂, 4H), 3.75 (s, CH₃, 12H), 1.78 (d, ³J_{HH}=5.6 Hz, NH₂, 8H). ¹³C{¹H} NMR (CD₂Cl₂): 186.53 (C_{NHC}), 142.60 (Ph), 139.14 (Ph), 130.0-127.5 (Ph), 122.66 (CH of imid.), 120.21 (CH of imid.), 71.52 (CHPh-imid.), 59.87 (CHPh-NH₂), 39.36 (CH₃). MS (ESI, methanol; *m/z*): 747.2795 [Ir(kaibene)₂]²⁺. Anal. Calcd for C₇₂H₇₆N₆Ir₂I₂: C, 49.48; H, 4.38; N, 9.62. Found: C, 48.66; H, 4.82; N, 8.58.

ASSOCIATED CONTENT

NMR data for the complexes. CIF files of crystal structure data. 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.

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TOC Graphic

Transition Metal Complexes of an (*S,S*)-1,2-Diphenylethylamine Functionalized N-Heterocyclic Carbene: a New Member of the Asymmetric NHC Ligand Family

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Supporting Information

Figure S1: ^1H NMR spectrum (400 MHz, DMSO- d_6 , 298K) of (<i>S,S</i>)- 9	S2
Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, DMSO- d_6 , 298K) of (<i>S,S</i>)- 9	S3
Figure S3: gCOSY (^1H - ^1H) NMR spectrum (400 MHz, DMSO- d_6 , 298K) of (<i>S,S</i>)- 9	S4
Figure S4: gHSQC (^1H - ^{13}C) NMR spectrum (400 MHz, DMSO- d_6 , 298K) of (<i>S,S</i>)- 9	S5
Figure S5: ^{19}F NMR spectrum (376 MHz, DMSO- d_6 , 298K) of (<i>S,S</i>)- 9	S6
Figure S6: ^{31}P NMR spectrum (162 MHz, DMSO- d_6 , 298K) of (<i>S,S</i>)- 9	S7
Figure S7: ^1H NMR spectrum (400 MHz, DMSO- d_6 , 298K) of 10	S8
Figure S8: gCOSY (^1H - ^1H) NMR spectrum (400 MHz, DMSO- d_6 , 298K) of 10	S9
Figure S9: gHSQC (^1H - ^{13}C) NMR spectrum (700 MHz, DMSO- d_6 , 298K) of 10	S10
Figure S10: ^1H NMR spectrum (500 MHz, DMSO- d_6 , 298K) of 11	S11
Figure S11: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, DMSO- d_6 , 298K) of 11	S12
Figure S12: gHSQC (^1H - ^{13}C) NMR spectrum (500 MHz, DMSO- d_6 , 298K) of 11	S13
Figure S13: ^1H NMR spectrum (700 MHz, DMSO- d_6 , 298K) of 12	S14
Figure S14: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, DMSO- d_6 , 298K) of 12	S15
Figure S15: gHSQC (^1H - ^{13}C) NMR spectrum (500 MHz, DMSO- d_6 , 298K) of 12	S16
Figure S16: ^1H NMR spectrum (500 MHz, CD_2Cl_2 , 298K) of 13	S17
Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CD_2Cl_2 , 298K) of 13	S19
Figure S18: gCOSY (^1H - ^1H) NMR spectrum (500 MHz, CD_2Cl_2 , 298K) of 13	S20
Figure S19: gHSQC (^1H - ^{13}C) NMR spectrum (500 MHz, CD_2Cl_2 , 298K) of 13	S21
Figure S20: ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298K) of 15	S22
Figure S21: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CD_2Cl_2 , 298K) of 15	S23
Figure S22: ^{19}F NMR spectrum (376 MHz, CD_2Cl_2 , 298K) of 15	S24
Figure S23: gCOSY (^1H - ^1H) NMR spectrum (400 MHz, CD_2Cl_2 , 298K) of 15	S25
Figure S24: gHSQC (^1H - ^{13}C) NMR spectrum (400 MHz, CD_2Cl_2 , 298K) of 15	S26
Figure S25: ^1H NMR spectrum (500 MHz, CD_2Cl_2 , 298K) of 16	S27
Figure S26: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CD_2Cl_2 , 298K) of 16	S28
Figure S27: gCOSY (^1H - ^1H) NMR spectrum (400 MHz, CD_2Cl_2 , 298K) of 16	S29
Figure S28: gHSQC (^1H - ^{13}C) NMR spectrum (400 MHz, CD_2Cl_2 , 298K) of 16	S30

3-((1*S*,2*S*)-2-amino-1,2-diphenylethyl)-1-methyl-1*H*-imidazol-3-ium hexafluorophosphate (*S,S*)-9. %). ^1H NMR ($\text{DMSO-}d_6$, 298K, δ): 9.42 (s, 1H; H2), 7.97 (dd, 1H; H4, $^3J_{\text{HH}}=2.4$ Hz, $^4J_{\text{HH}}=1.7$ Hz), 7.71 (dd, 1H; H3, $^3J_{\text{HH}}=2.4$ Hz, $^4J_{\text{HH}}=1.6$ Hz), 7.48-7.08 (m, 10H; H9-H18), 5.72 (d, 1H; H5, $^3J_{\text{HH}}=10.1$ Hz), 4.83 (d, 1H; H6, $^3J_{\text{HH}}=10.1$ Hz), 3.88 (s, 3H; H1).

Figure S1: ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 298K) of (*S,S*)-9

3-((1*S*,2*S*)-2-amino-1,2-diphenylethyl)-1-methyl-1*H*-imidazol-3-ium hexafluorophosphate, (*S,S*)-9 $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 298K, δ): 142.98 (C2), 137.05 (C7), 136.71 (C8), 129.5-127.5 (C9-C18), 124.02 (C3), 122.10 (C4), 70.12 (C5), 58.20 (C6), 36.40 (C1).

Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, DMSO- d_6 , 298K) of (*S,S*)-9

Figure S3: gCOSY (^1H - ^1H) NMR spectrum (400 MHz, DMSO- d_6 , 298K) of (*S,S*)-**9**

Figure S4: gHSQC (^1H - ^{13}C) NMR spectrum (400 MHz, DMSO- d_6 , 298K) of (*S,S*)-9

Figure S5: ^{19}F NMR spectrum (376 MHz, $\text{DMSO-}d_6$, 298K) of **(S,S)-9**

Figure S6: ^{31}P NMR spectrum (162 MHz, DMSO- d_6 , 298K) of (S,S)-9

[Ag(kaibene)(PF₆)]_n, 10. ¹H NMR (DMSO-*d*₆, 298K, δ): 7.93 (s, 1H; H4), 7.71 (s, 1H; H3), 7.68-7.15 (m, 10H; H9-H18), 5.97 (broad s, 1H; H5), 5.56 (broad s, 1H; H6), 4.33 (broad s, 2H; H19), 3.83 (s, 3H; H1).

Figure S7: ¹H NMR spectrum (400 MHz, DMSO-*d*₆, 298K) of **10**

Figure S8: gCOSY (¹H-¹H) NMR spectrum (400 MHz, DMSO-*d*₆, 298K) of **10**

[Ag(kaibene)(PF₆)]_n, **10**. ¹H - ¹³C HSQC NMR (DMSO-*d*₆, 298K, δ): 131.58-124.73 (C9-C18), 126.64 (C3), 118.76 (C4), 73.32 (C5), 56.64 (C6), 39.52 (C1).

Figure S9: gHSQC (¹H-¹³C) NMR spectrum (700 MHz, DMSO-*d*₆, 298K) of **10**

[Ag(kaibene)₂](PF₆), 11. ¹H NMR (DMSO-*d*₆, 298K, δ): 7.97 (s, 2H; H4), 7.54 (s, 2H; H3), 7.50-7.00 (m, 20H; H9-H18), 5.68 (d, 2H; H5, ³*J*_{HH}=9.4 Hz), 5.03 (dt, 2H; H6, ³*J*_{HH}=9.4, 4.8 Hz), 3.83 (s, 6H; H1), 1.98 (d, 4H; H19, ³*J*_{HH}=4.8 Hz).

Figure S10: ¹H NMR spectrum (500 MHz, DMSO-*d*₆, 298K) of **11**

[Ag(kaibene)₂](PF₆), 11. ¹³C{¹H} NMR (DMSO-*d*₆, 298K, δ): C_{NHC} was not detected due to the low solubility of **11**, 142.72 (C7), 138.73 (C8), 129.0-126.5 (C9-C18), 123.38 (C3), 120.37 (C4), 72.03 (C5), 57.70 (C6), 38.29 (C1).

Figure S11: ¹³C{¹H} NMR spectrum (126 MHz, DMSO-*d*₆, 298K) of **11**

Figure S12: gHSQC (^1H - ^{13}C) NMR spectrum (500 MHz, $\text{DMSO-}d_6$, 298K) of **11**

Ag(kaibene)₂I, 12. ¹H NMR (DMSO-*d*₆, 298K, δ): 7.96 (d, 2H; H4, ³*J*_{HH}=1.8 Hz), 7.52 (d, 2H; H3, ³*J*_{HH}=1.6 Hz), 7.45-7.05 (m, 20H; H9-H18), 5.76 (d, 2H; H5, ³*J*_{HH}=9.6 Hz), 5.02 (dt, 2H; H6, ³*J*_{HH}=9.6, 5.8 Hz), 3.81 (s, 6H; H1), 1.97 (d, 4H; H19, ³*J*_{HH}=5.8 Hz).

Figure S13: ¹H NMR spectrum (700 MHz, DMSO-*d*₆, 298K) of **12**

Ag(kaibene)₂I, 12. $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 298K, δ): 181.49 (C2), 142.87 (C7), 138.88 (C8), 129.0-126.5 (C9-C18), 123.27 (C3), 120.13 (C4), 71.73 (C5), 57.76 (C6), 38.26 (C1).

Figure S14: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, DMSO- d_6 , 298K) of **12**

Figure S15: gHSQC (^1H - ^{13}C) NMR spectrum (500 MHz, $\text{DMSO}-d_6$, 298K) of **12**

[Ru(p-cymene)(kaibene)(Cl)] PF₆, **13**. ¹H NMR (CD₂Cl₂, 298K, δ):

Figure S16: ¹H NMR spectrum (500 MHz, CD₂Cl₂, 298K) of **13**

[Ru(p-cymene)(kaibene)(Cl)] PF₆, 13. ¹H NMR (CD₂Cl₂, 298K, δ):

Isomer A			
Shift (ppm)	Integration	Assignment	Multiplet
7.45-7.10	6	H9, H10, H12, H13, H14, H15, H17, H18	m
7.19	1	H4	d, ³ J _{HH} =2.1 Hz
7.01 and 7.00	2	H11, H16	dd, ³ J _{HH} =1.0, 1.8 Hz/2.2, 1.5 Hz
6.64	1	H3	d, ³ J _{HH} =2.1 Hz
5.84	1	H22	d, ³ J _{HH} =6.0 Hz
5.30	1	H23	s
5.20-5.10	4	H5, H19, H25, H26	m
4.39	1	H6	t, ³ J _{HH} =10.8 Hz
4.00	3	H1	s
3.93	1	H19	m
3.81	1	H27	m
2.22	3	H20	s
1.34	3	H28	d, ³ J _{HH} =7.0 Hz
1.22	3	H29	d, ³ J _{HH} =6.8 Hz

Isomer B			
Shift (ppm)	Integration	Assignment	Multiplet
7.45-7.10	6	H9, H10, H12, H13, H14, H15, H17, H18	m
7.04	1	H4	d, ³ J _{HH} =2.1 Hz
6.91 and 6.90	2	H11, H16	dd, ³ J _{HH} =1.1, 1.8 Hz/2.2, 1.5 Hz
6.36	1	H3	d, ³ J _{HH} =2.1 Hz
5.68-3.63	4	H22, H23, H25, H26	m
5.76	1	H6	t, ³ J _{HH} =7.0 Hz
5.60	1	H19	m
5.48	1	H5	d, ³ J _{HH} =5.9 Hz
3.98	3	H1	s
3.21	1	H19	t, ³ J _{HH} =11.3 Hz
2.78	1	H27	m
2.14	3	H20	s
1.29	3	H20	d, ³ J _{HH} =7.0 Hz
1.12	3	H29	d, ³ J _{HH} =6.9 Hz

[Ru(*p*-cymene)(kaibene)(Cl)]PF₆, **13**. ¹³C{¹H} NMR (CD₂Cl₂):

Figure S17: ¹³C{¹H} NMR spectrum (126 MHz, CD₂Cl₂, 298K) of **13**

[Ru(*p*-cymene)(kaibene)(Cl)]PF₆, **13**. ¹³C{¹H} NMR (CD₂Cl₂):

Isomer A		Isomer B	
Shift (ppm)	Assignment	Shift (ppm)	Assignment
171.31	C2	174.20	C2
138.36	C7	138.90	C7
136.94	C8	133.90	C8
131.0-127.5	C9-C18	131.0-127.5	C9-C18
125.49	C3	123.17	C3
124.16	C4	122.11	C4
111.67	C21	112.30	C21
102.59	C24	102.81	C24
90.0-82.0	C22, C23, C25, C26	90.0-82.0	C22, C23, C25, C26
69.12	C5	68.54	C5
65.59	C6	62.16	C6
39.91	C1	39.27	C1
31.92	C27	31.87	C27
24.63	C28	24.14	C28
20.95	C29	21.01	C29
19.49	C20	18.86	C20

Figure S18: gCOSY (¹H-¹H) NMR spectrum (500 MHz, CD₂Cl₂, 298K) of **13**

Figure S19: gHSQC (^1H - ^{13}C) NMR spectrum (500 MHz, CD_2Cl_2 , 298K) of **13**

[Ni(kaibene)₂](PF₆)₂, **15.** ¹H NMR (CD₂Cl₂, 298K, δ): 7.49 (d, 4H; H4, ³J_{HH}=1.8 Hz), 7.37-7.15 (m, 40H; H9-H18), 7.04 (d, 4H; H3, ³J_{HH}=1.8 Hz), 5.99 (d, 4H; H5, ³J_{HH}=8.5 Hz), 4.93 (dt, 1H; H6, ³J_{HH}=8.5, 5.1 Hz), 3.77 (s, 12H; H1), 1.68 (d, 8H; H19, ³J_{HH}=5.1 Hz).

Figure S20: ¹H NMR spectrum (400 MHz, CD₂Cl₂, 298K) of **15**

[NiI(kaibene)₂](PF₆)₂, **15.** ¹³C{¹H} NMR (CD₂Cl₂): 186.01 (C2), 142.21 (C7), 138.67 (C8), 130.0-127.0 (C9-C18), 122.70 (C3), 120.54 (C4), 71.95 (C5), 59.50 (C6), 54.00 (C1), 39.34 (C1).

Figure S21: ¹³C{¹H} NMR spectrum (100 MHz, CD₂Cl₂, 298K) of **15**

Figure S22: ^{19}F NMR spectrum (376 MHz, CD_2Cl_2 , 298K) of **15**

Figure S23: gCOSY (^1H - ^1H) NMR spectrum (400 MHz, CD_2Cl_2 , 298K) of **15**

Figure S24: gHSQC (^1H - ^{13}C) NMR spectrum (400 MHz, CD_2Cl_2 , 298K) of **15**

[IrI(kaibene)₂]₂, 16. ¹H NMR (CD₂Cl₂, 298K, δ): 7.51 (d, 4H; H4, ³J_{HH}=1.8 Hz), 7.45-7.10 (m, 40H; H9-18), 7.06 (d, 4H; H3, ³J_{HH}=1.8 Hz), 6.18 (d, 4H; H5, ³J_{HH}=9.0 Hz), 4.87 (dt, 4H; H6, ³J_{HH}=9.0, 5.6 Hz), 3.75 (s, 12H; H1), 1.78 (d, 8H; H19, ³J_{HH}=5.6 Hz).

Figure S25: ¹H NMR spectrum (500 MHz, CD₂Cl₂, 298K) of **16**

[IrI(kaibene)₂]₂, 16. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): 186.53 (C2), 142.60 (C7), 139.14 (C8), 130.0-127.5 (C9-C18), 122.66 (C3), 120.21 (C4), 71.52 (C5), 59.87 (C6), 39.36 (C1).

Figure S26: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CD_2Cl_2 , 298K) of **16**

Figure S27: gCOSY (^1H - ^1H) NMR spectrum (400 MHz, CD_2Cl_2 , 298K) of **16**

Figure S28: gHSQC (^1H - ^{13}C) NMR spectrum (400 MHz, CD_2Cl_2 , 298K) of **16**