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Iridium and Rhodium Complexes Containing Enantiopure Primary Amine-Tethered *N*-Heterocyclic Carbenes: Synthesis, Characterization, Reactivity, and Catalytic Asymmetric Hydrogenation of Ketones

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Supporting Information

ABSTRACT: The imidazolium salt [(*S*,*S*)-*t*BuNC$_3$H$_3$NCHPhCHPhNH$_2$]PF$_6$, (*S*,*S*)-**11**·HPF$_6$ is a precursor to the enantiopure "Kaibene" ligand, *t*Bu-Kaibene, (*S*,*S*)-**11** featuring a *tert*-butyl group on the *N*-heterocyclic carbene (NHC) ring-nitrogen atoms. It has been prepared in high yield and purity by refluxing a chiral cyclic sulfamidate with 1-*tert*-butylimidazole. Similarly (*S*,*S*)-**12**·HPF$_6$ with a mesityl group at the imidazolium ring-nitrogen atom has been prepared in the same fashion and serves as a source of Mes-Kaibene, (*S*,*S*)-**12**. These bidentate Kaibene ligands feature an NHC and a primary amine separated by a chiral linker. Salts (*S*,*S*)-**11**·HPF$_6$ or (*S*,*S*)-**12**·HPF$_6$ react with base and AgI or CuI to give a total of four M(Kaibene)$_2$I compounds (M = Ag or Cu). At 22 °C, the amine-functionalized imidazolium cations undergo oxidative addition to iridium(I) in [IrCl(cod)]$_2$ (cod = 1,5-cyclooctadiene) to generate iridium(III) hydride R-Kaibene compounds [IrHCl(cod)((*S*,*S*)-**11**)](PF$_6$) (**17**) and [IrHCl(cod)-((*S*,*S*)-**12**)](PF$_6$) (**18**), respectively, each as a mixture of six configurational isomers. In contrast, the salt (*S*,*S*)-**11**·HPF$_6$ reacts with [Ir(O*t*Bu)(cod)]$_2$ to produce a bimetallic iridium compound with (*S*,*S*)-**11** as the bridging ligand. This compound contains interesting NH···Cl and NH···Ir noncovalent intramolecular interactions. Salt (*S*,*S*)-**12**·HPF$_6$ reacts with silver oxide to yield [Ag$_2$((*S*,*S*)-**12**)$_2$](PF$_6$)$_2$ (**20**). Reagent **20** serves as an efficient transmetalation reagent to deliver to each rhodium in [RhCl(cod)]$_2$ 1 equiv of (*S*,*S*)-**12** as a bidentate ligand to give [Rh(cod)((*S*,*S*)-**12**)](PF$_6$). In the reaction between [IrCl(cod)]$_2$ and **20**, (*S*,*S*)-**12** ends up coordinated in an iridium(III) hydride complex (**22**) as a tridentate ligand via the NHC, NH$_2$, and a cyclometalated phenyl group. The two iridium hydride compounds, **18** and **22**, are catalysts for the hydrogenation of a range of ketones (turnover number up to 499, turnover frequency up to 249 h^{-1}, with er (enantiomeric ratio) up to 35:65 *R*:*S*).

INTRODUCTION

The synthesis of chiral molecules receives broad industrial interest due to its applications in the pharmaceutical, agricultural, and fragrance sectors.[1−4] As a result, many enantio- and diastereoselective catalytic processes have been developed on the basis of transition metals with chiral ligands that convert the corresponding prochiral substrate to the desired homochiral product.[5−16] Most of the chiral ligands used in asymmetric catalysis, however, are based on phosphines, some of which are air-sensitive and are produced using environmentally harmful reagents.[13,17−21] In recent years, the substitution of phosphine by *N*-heterocyclic carbene (NHC) in asymmetric transition metal catalysis has received much interest.[22,23] The NHC ligands have tunable electronic and steric properties and their precursor imidazolium salts are usually air-stable.[22−27]

In the past few years, some of us have focused on the discovery of primary amine-functionalized NHC ligands due to their ability to access a six-membered ring transition state with a low energy barrier for ketone and imine reduction (Figure 1).[28] The N−H group in the transition state structure serves to activate the polar bond of the substrate in the outer coordination sphere to hydride attack and to position the groups on the substrate for enantioselective reaction.

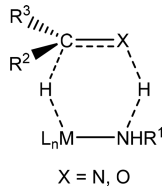

Figure 1. Outer-sphere low energy barrier six-membered ring transition state during ketone and imine hydrogenation utilizing the "N−H" effect.

The investigation of homogeneous catalysts containing an NHC bearing a pendant N−H functionality dates back to 2009.[29] Initially, an achiral ligand (**1**) was synthesized through

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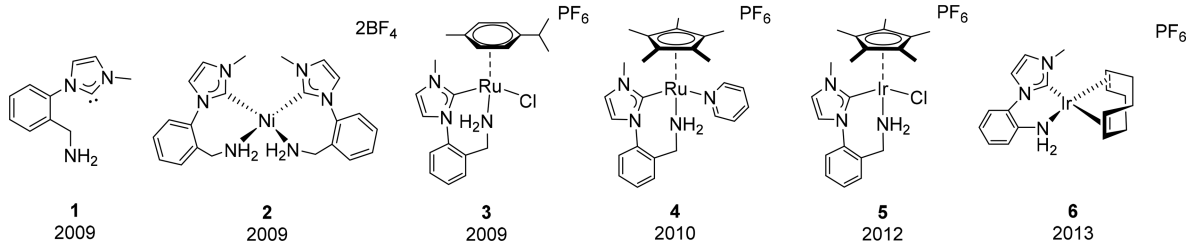


Figure 2. Achiral N−H-functionalized compound **1** and its group 8 and 9 compounds.

the *in situ* reduction of a nitrile-functionalized NHC coordinated to nickel, to generate excellent transmetalation reagent **2** (Figure 2).[29] The NHC^amine ligand in complex **2** can then be transferred to ruthenium or iridium in order to synthesize compounds **3**−**6**, all of which catalyze ketone reduction using either 2-propanol or hydrogen gas as the reductant.[29−34] Of the two iridium complexes, compound **6** exhibits a higher reactivity than that of **5**. Computational studies supported the proposal that within the catalytic cycle the Cp* (1,2,3,4,5-pentamethylcyclopentadienyl) ligand in compound **5** was converted into 1,2,3,4,5-pentamethylcyclopentadiene that acted as a spectator diene ligand. One consistent observation in these catalytic systems was that complexes bearing the NHC^NH_2 chelate ligand outperformed the corresponding complexes bearing PPh_2^NH_2 chelates where the NHC donor was replaced by a diphenylalkylphosphine donor.[32,33]

After the success in improving catalytic performance by using NHCs instead of PPh_2 in these systems, we were interested in learning whether these systems could be rendered enantioselective to create highly active, enantioselective catalysts based on NHCs. In 2016, some of us reported the synthesis of the first isolable imidazolium salt of this type that contains a primary amine functional group, (*S*,*S*)-7·HPF_6 (Figure 3).[35] By using either silver or copper transmetalation techniques, we produced two ruthenium-based ketone hydrogenation catalysts, **8** and **9**.[35,36] Complex **9** exhibited an exceptionally high turnover number (TON up to 10 000) and turnover frequency (TOF up to 48 s^{-1}) for ketone reduction at very low catalyst concentration (0.057 mM, catalyst/base/ketone = 1:8:5000 in 2-propanol) and under relatively mild conditions (25 bar H_2, 50 °C). However, in spite of its high reactivity in ketone reduction, complexes of ligand (*S*,*S*)-7 only provide low enantioselectivity (up to 60% ee at the beginning of catalysis with **9**).

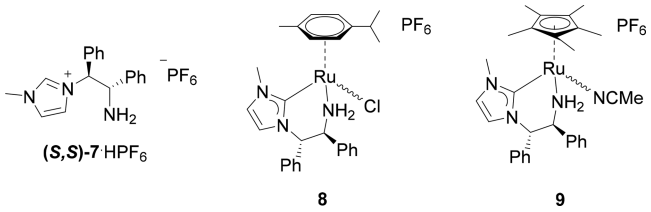


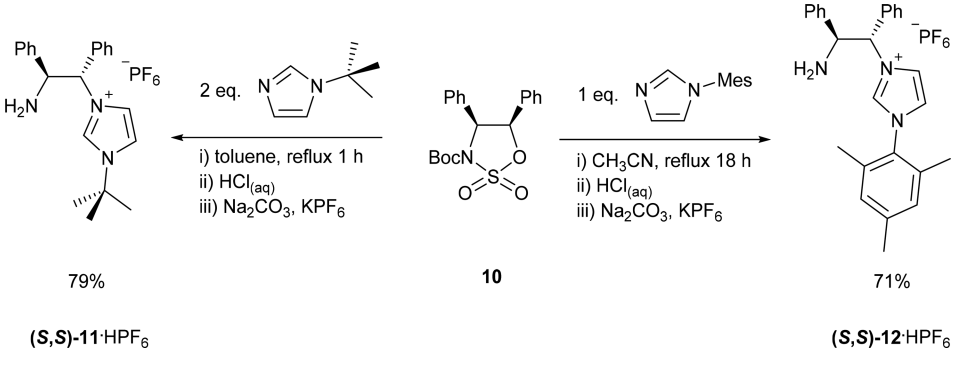
Figure 3. Enantiopure N−H functionalized compound (*S*,*S*)-7·HPF_6 and ruthenium complexes of Me-Kaibene, (*S*,*S*)-7.

In this study, two analogues of "Me-Kaibene" ((*S*,*S*)-7) have been synthesized in an attempt to improve the effectiveness for asymmetric ketone hydrogenation. One analogue (*S*,*S*)-**11** has a *tert*-butyl group in place of a methyl at the N3 ring atom of the NHC while the other, (*S*,*S*)-**12**, features a mesityl group on the NHC. These new R-Kaibene ligands have been used to prepare several copper, silver, rhodium, and iridium compounds. Two of the prepared iridium compounds have been tested as catalysts for the asymmetric hydrogenation of a range of ketones.

RESULTS AND DISCUSSION

Synthesis of Bulky Imidazolium Salts Based on Kaibene. Two new ligands were synthesized with different inductive effects compared to (*S*,*S*)-7: the basic derivative *t*Bu-Kaibene, (*S*,*S*)-**11**, with a *tert*-butyl group, and the less basic Mes-Kaibene, (*S*,*S*)-**12**, with a Mes group bound to ring-nitrogen atom N3 (Scheme 1). Imidazolium salt (*S*,*S*)-**11**·HPF_6 was prepared in analogy to (*S*,*S*)-7·HPF_6.[35] A sample of 1-*tert*-butylimidazole and chiral, Boc-protected (*R*,*S*)-sulfamidate **10**[37] was refluxed in toluene for 1 h to allow a concerted nucleophilic substitution (S_N2) reaction, which results in the full inversion of one stereocenter. Then, 2 equiv of 1-*tert*-butylimidazole per 1 equiv of **10** was used as the optimal nucleophile/electrophile ratio. Subsequent Boc deprotection was performed using concentrated hydrochloric acid. Finally, neutralization with sodium carbonate and salt metathesis with potassium

Scheme 1. Synthesis of (*S*,*S*)-11·HPF_6 and (*S*,*S*)-12·HPF_6



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hexafluorophosphate provided (*S,S*)-**11**·HPF_6 in high purity as a white powder in 79% yield. The mesityl derivative, (*S,S*)-**12**·HPF_6, however, was synthesized using a lower reaction temperature and acetonitrile as the solvent. The starting nucleophile and electrophile in a 1:1 stoichiometric ratio were refluxed overnight to facilitate the substitution reaction. By using similar workup procedures to those of (*S,S*)-**11**·HPF_6, the reaction afforded imidazolium salt (*S,S*)-**12**·HPF_6 in 71% yield as a white powder. This synthesis method for the generation of Kaibene derivatives with different diamine backbones and imidazole substituents is highly versatile.

Both (*S,S*)-**11**·HPF_6 and (*S,S*)-**12**·HPF_6 were fully characterized by NMR spectroscopy, high-resolution mass spectroscopy, and elemental analysis. The HR-ESI mass spectrum of (*S,S*)-**11**·HPF_6 showed the signal with the highest intensity at m/z = 320.2128 (calcd for $[M - PF_6]^+$: 320.2127) with the correct isotope distribution. The ^1H NMR (CD_2Cl_2) spectrum of (*S,S*)-**11**·HPF_6 revealed a signal for the imidazolium hydrogen at δ = 8.82 ppm as a pseudotriplet ($^4J_{HH}$ = 1.7 Hz) due to the coupling to the other two hydrogens in the imidazolium ring. Similarly, the mass spectrum of (*S,S*)-**12**·HPF_6 revealed the most intense peak at m/z = 382.2283 (calcd for $[M - PF_6]^+$: 382.2278, HR-ESI) and the imidazolium hydrogen was detected at δ = 9.76 ppm (pseudotriplet, $^4J_{HH}$ = 1.4 Hz) in the ^1H NMR (DMSO-d_6) spectrum. The elemental analysis together with the signals in the $^{31}P\{^1H\}$ and the ^{19}F NMR spectra confirmed that the anions initially present were completely replaced by the PF_6 anion for both (*S,S*)-**11**·HPF_6 and (*S,S*)-**12**·HPF_6.

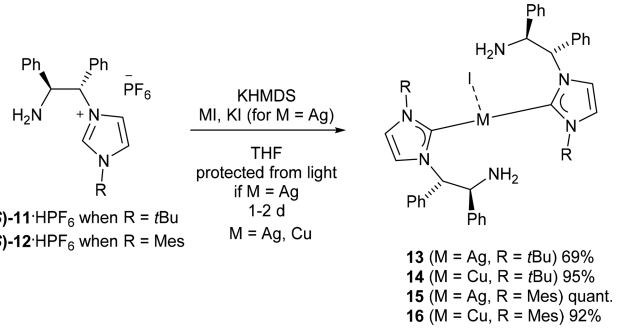
Synthesis of Bis(Kaibene) Group 11 Complexes Containing (*S,S*)-11 or (*S,S*)-12. Free carbene (*S,S*)-**11** with the donating *tert*-butyl group on the NHC is strongly basic like (*S,S*)-**7**, and silver oxide was found to be insufficiently basic to deprotonate the imidazolium salt. Therefore, silver iodide and potassium bis(trimethylsilyl)amide were used to generate silver complex **13** in good yield (69%) from (*S,S*)-**11**·HPF_6. Potential silver intermediates were stabilized by addition of 2.5 equiv of KI (Scheme 2). Complex **13** was characterized by NMR spectroscopy. It is exceptionally light-sensitive so that additional analytical data could not be obtained. Reactions of (*S,S*)-**11**·HPF_6 with silver bromide, silver hexafluorophosphate, or silver tetrafluoroborate were also attempted, but the products were substantially more unstable compared to the complex obtained from silver iodide. The ^1H NMR spectrum of **13** no longer showed any signal for the imidazolium hydrogen atom in (*S,S*)-**11**·HPF_6, which indicated the formation and coordination of an NHC to the silver ion. The signal for the primary amine group was detected as a doublet ($^3J_{HH}$ = 4.5 Hz) at δ = 1.58 ppm due to the coupling to a methine hydrogen atom in the backbone. The observed doublet with a relative intensity of two indicates a dangling amine group that is not coordinated to the silver atom and can rotate freely. The $^{13}C\{^1H\}$ NMR spectrum of complex **13** revealed a resonance at δ = 181.8 ppm for the carbene carbon atom in the typical region for silver NHC complexes. Remarkably, the resonance of the carbene carbon atom shows no sign of coupling to the NMR active silver isotopes. This indicates a fluxional exchange process of the silver carbene and partially explains the instability of complex **13**.[38]

Since silver complex **13** is extremely light-sensitive, the analogous copper complex **14** was also synthesized. This complex was obtained in high yield (95%) by reaction of imidazolium salt (*S,S*)-**11**·HPF_6 with 0.5 equiv of CuI and a slight excess of KHMDS in THF at ambient temperature. The formation of the NHC copper iodide complex was signaled by the disappearance of the resonance for the imidazolium C2 hydrogen atom and the appearance of a doublet at δ = 1.55 ppm assigned to the primary amine in ^1H NMR spectrum. The carbene carbon resonance was found at δ = 177.9 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The carbene resonance of **14** falls in the expected range of copper carbene complexes.[38−40] With improved stability in light, compound **14** can be characterized by MALDI-TOF spectrometry where a signal for the cationic fragment $[\mathbf{14} - I]^+$ was observed at m/z = 701. The elemental analysis is also consistent with the proposed composition.

Through similar procedures and characterization techniques, bisNHC silver and copper iodide complexes of (*S,S*)-**12** were also prepared in good yields (quantitative for **15**, Ag; and 92% for **16**, Cu). Complexes **15** and **16** feature carbene signal at δ = 184.3 and 181.8 ppm, respectively, in their $^{13}C\{^1H\}$ NMR spectra. Compared to complex **13**, complex **15** is less sensitive but still decomposes after prolonged exposure to light. Complexes **13**−**16** are assumed to have similar structures to those of previously reported MI(Me-Kaibene)$_2$ compounds (M = Cu and Ag) where the two NHC donors in the complex are coordinated *trans* to each other while the iodide ion is within ion-pairing distance which produces an overall T-shaped structure.[35,36] Complexes **13**−**16** are highly water sensitive. Although carbene compounds were observed by NMR spectroscopy, only imidazolium salts were observed by ESI mass spectrometry. So far complexes **13**−**16** have not been successfully used as transmetalation reagents.

Oxidative Addition of the Imidazolium Groups of *t*Bu- and Mes-Kaibene to Iridium(I). A different approach based on the C2−H activation of the imidazolium moiety was used to generate an organometallic compound containing *t*Bu-Kaibene, (*S,S*)-**11**. Iridium(I) is renowned for its ability to oxidatively add polarized C−H bonds and some literature precedents exist where an imidazolium salt and an iridium(I) precursor reacted at ambient temperature to afford iridium(III) carbene hydride species.[41−44] The C2−H oxidative addition of azolium salts is aided by the presence of a donor function tethered to one of the azolium ring-nitrogen atoms.[45] For the synthesis of carbene-hydride complexes by oxidative addition, a Schlenk flask was charged with (*S,S*)-**11**·HPF_6 and 0.5 equiv of $[IrCl(cod)]_2$ in chloroform-*d*. After approximately 30 min, the resulting mixture contained six hydride species of the type 17 (Scheme 3) that were observable by ^1H NMR spectroscopy with approximately 29% conversion from the imidazolium salt (major ones at δ = −13.29 ppm with 62% of the total hydride

Scheme 2. Group 11 Compounds Synthesized Using (*S,S*)-11·HPF_6 and (*S,S*)-12·HPF_6



(*S,S*)-**11**·HPF_6 when R = *t*Bu
(*S,S*)-**12**·HPF_6 when R = Mes

13 (M = Ag, R = *t*Bu) 69%
14 (M = Cu, R = *t*Bu) 95%
15 (M = Ag, R = Mes) quant.
16 (M = Cu, R = Mes) 92%

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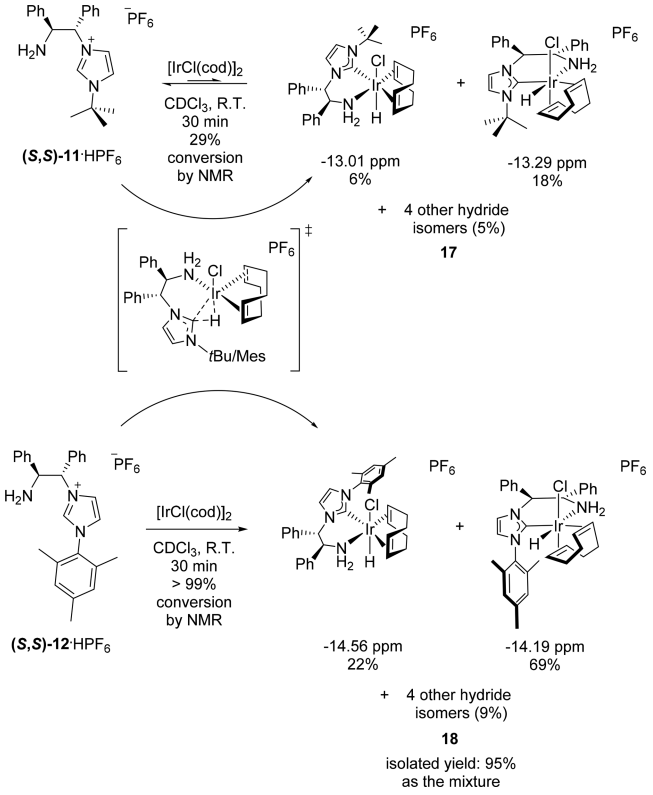
Scheme 3. C−H Activation of (*S*,*S*)-11·HPF$_6$ and (*S*,*S*)-12·HPF$_6$ by Iridium in CDCl$_3$



integration and δ = −13.01 ppm with 22%). The other four isomers are shown in Figure S1. The ratio between the iridium carbene hydrides and the imidazolium salt remained constant regardless of the reaction temperature. This constitutes evidence for an equilibrium between the imidazolium salt and an iridium carbene hydride species (Scheme 3) as previously suggested by others.[41,43,46,47] The mechanism of the formation of the hydride complex is also illustrated in Scheme 3 where an amine adduct is assumed to form first between iridium and the amine-tethered imidazolium salt. Subsequently, an intramolecular C−H bond oxidative addition to the iridium atoms affords complexes of the type **17**. The corresponding mechanism of this type of C−H bond oxidative addition to Pd(0) had been investigated by computational chemistry,[46,47] showing that the oxidative addition is in equilibrium with the reductive elimination step. Therefore, a clean hydride sample from complete conversion was not obtained in the reaction of (*S*,*S*)-**11**·HPF$_6$. The cationic hydride is estimated to have a pK_a of ∼2 in CDCl$_3$;[48] thus, a weak base like triethylamine is sufficient to deprotonate the M−H bond. Similar reactions have been performed by Peris et al.[41] After adding triethylamine to a mixture of the imidazolium salt and the iridium precursor in THF, we observed after 3 h a small peak in the mass spectrum at m/z = 620.2614 au with an isotopic pattern that corresponds to the formula of [Ir(*t*Bu-Kaibene)(cod)]$^+$ (calculated $C_{29}H_{37}IrN_3$ 620.2612). However, complete conversion to this compound could not be achieved.

The same experiment was subsequently performed in dichloromethane-d_2 but an even smaller extent of C−H oxidative addition was observed by ^{1}H NMR spectroscopy (approximately 8% with two major iridium(III) hydrides at δ = −14.46 and −15.01 ppm). The remaining iridium was converted to the amine adduct shown in Figure 4. Its identity was determined by ^{1}H and ^{1}H−^{1}H gCOSY NMR experiments.

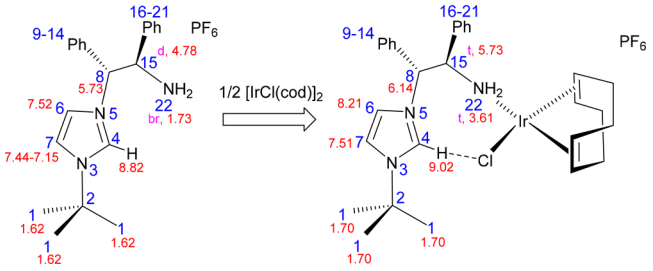


Figure 4. Proposed structure of an (*S*,*S*)-**11**·HPF$_6$−IrCl(cod) adduct.

The two hydrogen atoms of the amino group are diastereotopic because the coordination to the iridium prevents amine inversion. As illustrated in Figure 4, the splitting pattern of the methine hydrogen H15 switches from a doublet to a triplet on going from the free amine to the complex, which is an indication of additional coupling ($^3J_{HH}$ = 11.5 Hz) to a hydrogen atom at the noninverting nitrogen. The ^{1}H NMR signal corresponding to the amine protons should change from a broad signal at 1.73 ppm to a pair of triplets upon coordination. Only one of these N−H protons can be observed at 3.61 ppm ($^3J_{HH}$ = 11.5 Hz), while the other N−H proton is buried within the CH$_2$ signals of the cod. Also, there is a global downfield shift of hydrogen resonances of (*S*,*S*)-**11** compared to (*S*,*S*)-**11**·HPF$_6$ and a desymmetrization of the cod signals of the IrCl(cod) moiety was observed. The former observation can be explained by the formation of a hydrogen bond between H4 and the chloride ligand. The latter is further evidence for the coordination of the amine of (*S*,*S*)-**11**·HPF$_6$, resulting from the splitting of the chloride bridges of the dimeric iridium precursor. The reaction mixture was then added to a solution of KHMDS in THF to deprotonate the imidazolium group and generate *t*Bu-Kaibene. No imidazolium group signals remained after the addition of the base, and mass spectrometry revealed a peak at m/z = 620.2612 for [Ir(*t*Bu-Kaibene)(cod)]$^+$ with the correct isotope pattern. However, multiple peaks were observed in the ^{1}H NMR spectrum. A pure sample of [Ir(*t*Bu-Kaibene)(cod)](PF$_6$) was not obtained.

Compared to (*S*,*S*)-**11**·HPF$_6$, the imidazolium (*S*,*S*)-**12**·HPF$_6$ is expected to be more acidic and more prone to oxidative addition since the mesityl group of (*S*,*S*)-**12**·HPF$_6$ is less donating than the *t*-butyl group of (*S*,*S*)-**11**·HPF$_6$. Therefore, a reaction between (*S*,*S*)-**12**·HPF$_6$ and [IrCl(cod)]$_2$ could potentially yield an oxidative addition product in higher yield. The first attempt of a reaction between (*S*,*S*)-**12**·HPF$_6$ and [IrCl(cod)]$_2$ in CD$_2$Cl$_2$ proved unsuccessful as less than 10% of the (*S*,*S*)-**12**·HPF$_6$ was converted to a mixture of hydride isomers **18**. When CDCl$_3$ was used, a similar set of isomers **18** was observed but with a significantly higher conversion (>99% consumption of (*S*,*S*)-**12**·HPF$_6$, Scheme 3). Six hydride species produced singlets between δ = −12.90 and −15.70 ppm with two dominant peaks at δ = −14.56 and −14.19 ppm (Scheme 3). Despite the presence of isomers, the purity of **18** was confirmed by both HR-ESI (calcd for [Ir(H)(Cl)(Mes-Kaibene)(cod)]$^+$ m/z = 718.2528, found 718.2526) and elemental analysis. Thus, both **17** and **18** consist of a mixture of six isomers of hydride complexes. The structures of the two most abundant isomers are assigned to those illustrated in Scheme 3, with reference to DFT

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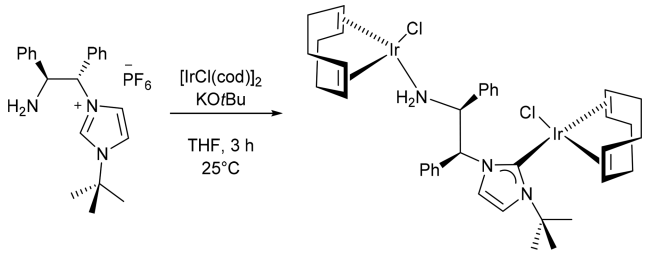
calculations performed previously on a similar achiral system.[33] The most stable structures feature the high *trans*-influence hydride in *trans* positions to donors of low *trans*-influence (Cl, NH_2).

Although the C−H oxidative addition of imidazolium salts to transition metals has been known for decades, most of these reactions were based on zero-valent group 10 metals with strongly donating, tethered donor ligands such as phosphines or NHCs.[46,47,49−53] While some literature examples of Ir(I) and Rh(I) are known for this type of reaction, in most cases, heating or the use of a donor-functionalized NHC imidazolium salt is required.[41−43,54] The formation of mixtures **17** and **18** is the first example of the use of a primary-amine tether in facilitating the oxidative addition at ambient temperature.

Synthesis of Silver, Rhodium, and Iridium Compounds of Kaibene with Amine Coordination. Song et al.[43,55] generated $[Ir(OtBu)(cod)]_2$ *in situ* from $[IrCl(cod)]_2$ and KO*t*Bu and used this alkoxide-bridged intermediate to generate carbene compounds from imidazolium salts. With the goal of isolating a mononuclear iridium complex bearing a chelating Kaibene ligand, **(*S*,*S*)-11**·HPF_6 was stirred with *in situ* generated $[Ir(OtBu)(cod)]_2$ in THF at ambient temperature with a 1:1 ligand/metal ratio. Instead of a mononuclear chelate complex, complex **19** with two [IrCl(cod)] fragments bridged by the amine-tethered NHC ligand was isolated (Scheme 4).

Scheme 4. Formation of Bridging *t*Bu-Kaibene Di(iridium) Compound



(*S*,*S*)-11·HPF_6 **19** 38%

Adjustment of the stoichiometry to 1:2 imidazolium salt/iridium resulted in the isolation of complex **19** in low yield (38%). Although multiple species were observed in the ^1H NMR spectrum of a sample from the reaction mixture, only this bimetallic compound could be isolated cleanly.

Complex **19** was characterized by MALDI-TOF mass spectrometry, NMR spectroscopy, elemental analysis, and X-ray crystallography (Figure 5). The MALDI-TOF mass spectrum showed a signal for cationic complex $[\mathbf{19}]^+$ at m/z = 991 with the correct isotope distribution. The molecular structure of **19** shows the iridium atoms coordinated in a distorted square-planar coordination environment with one cod ligand, one chloride ligand, and one NHC or amine donor, respectively. The bond distance between iridium and the NHC carbon measures 2.045(3) Å, which agrees well with the median value (2.044 Å) of iridium−carbon NHC bond distances found in the 2017 Cambridge Crystallographic Database (CCD). Interestingly, several noncovalent interactions are observed in the molecular structure. The distance between an amine hydrogen H2N and chloride Cl2 measures 2.57(4) Å and the N1−H2N···Cl2 angle of 153(3)° fit the criteria for hydrogen bonding.[56,57] Remarkably, there is also a noncovalent

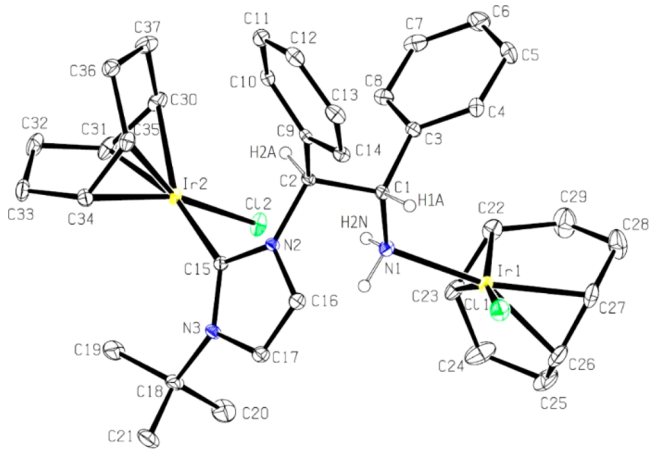


Figure 5. Molecular structure of **19**: displacement ellipsoids are shown with 50% probability. Nonrelevant hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−N1 2.136(3), Ir2−C15 2.045(3), Ir2···H2A 2.653, Cl2···H2N 2.57(4), C15−Ir2−Cl2 88.03(9), H1−Ir1−Cl1 87.62(8), C2−H2A···Ir2 123.1, N1−H2N···Cl2 153(3).

interaction between Ir2 and the methine hydrogen H2A. The distance between Ir2 and H2A measures 2.653 Å. This interaction represents a rare example of a preagostic interaction as described by Crabtree and Bergman.[58,59] We believe these two noncovalent interactions are maintained in solution and are responsible for the abnormal downfield shifts of the H2N and H2A hydrogen atoms observed in the ^1H NMR spectrum of the complex in CD_2Cl_2 solution as described below. The ligand conformation in **19** is very similar to that of **(*S*,*S*)-7** in a silver polymer $[Ag(Me\text{-}Kaibene)]_n(PF_6)_n$[35] where **(*S*,*S*)-7** is bridging between silver ions to generate a Λ-helical polymeric structure. In both structures, the two methine hydrogen atoms are *anti* to each other with the phenyl groups mutually gauche. This arrangement minimizes steric repulsions and explains the high stability of **(*S*,*S*)-7** silver polymer, as well as the formation of **19** as the major product. The ^1H NMR spectrum of complex **19** revealed two signals for the hydrogen atoms of the coordinating primary amine at δ = 4.76 and 2.57 ppm, respectively. The coupling pattern showed geminal coupling between the two hydrogens ($^2J_{HH}$ = 11.5 Hz) as well as a coupling between the methine hydrogen H1A ($^3J_{HH}$ = 11.8 Hz) and the NH proton at δ = 4.76 ppm. The signal for the methine hydrogen H1A was detected at δ = 5.24 ppm with an appropriate pattern for coupling to the amine and the methine hydrogen H2A ($^3J_{HH}$ = 11.8 Hz). Interestingly, the resonance for H2A was detected at δ = 8.17 ppm with a downfield shift of $\Delta\delta$ = 2.44 ppm compared to the resonance of imidazolium salt (δ = 5.73 ppm). This downfield shift and the downfield-shifted signal for one of the amine hydrogens indicate strong noncovalent interactions such as hydrogen bonding in complex **19**. The characteristic downfield shift in the ^1H NMR spectrum of the C−H group in a preagostic bond with d^8 square planar metal complexes has been reported by Zhang et al.[60] The $^{13}C\{^1H\}$ NMR spectrum of complex **19** has a signal for the carbene carbon atom C15 at δ = 181.3 ppm.

In the chemistry of *t*Bu-Kaibene described above, two challenges were encountered. These are the sensitivity of its coordination compounds and its weakly chelating primary amine group when in competition with chloride. Therefore, the preparation of organometallic compounds based on the less

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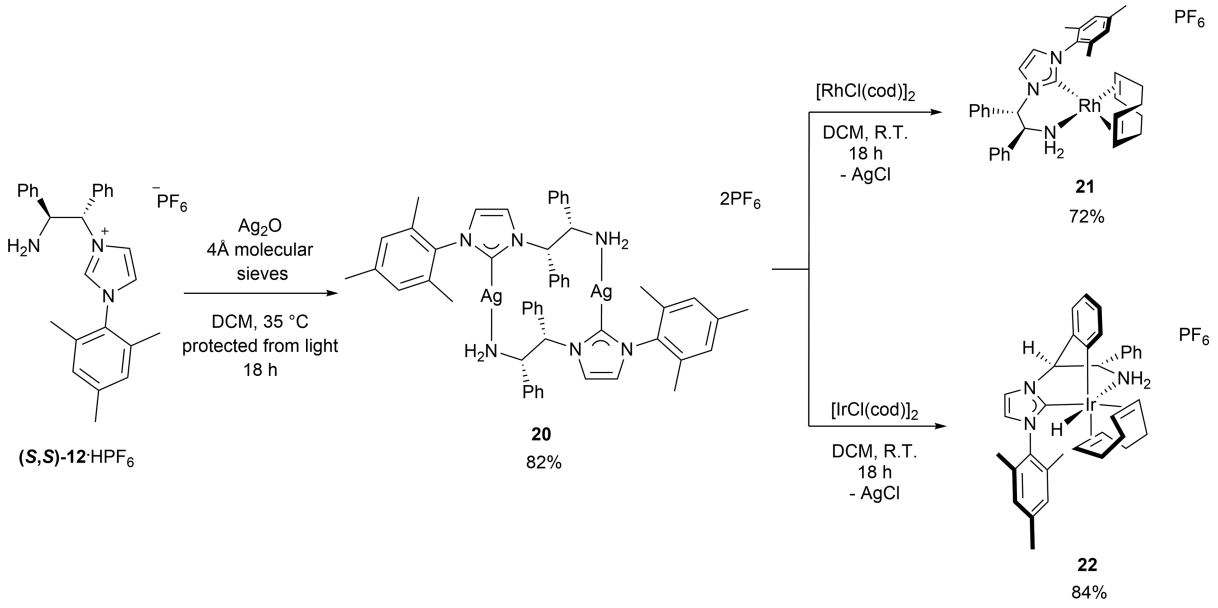
Organometallics XXXX, XXX, XXX−XXX

Scheme 5. Organometallic Compounds of Mes-Kaibene (*S*,*S*)-12



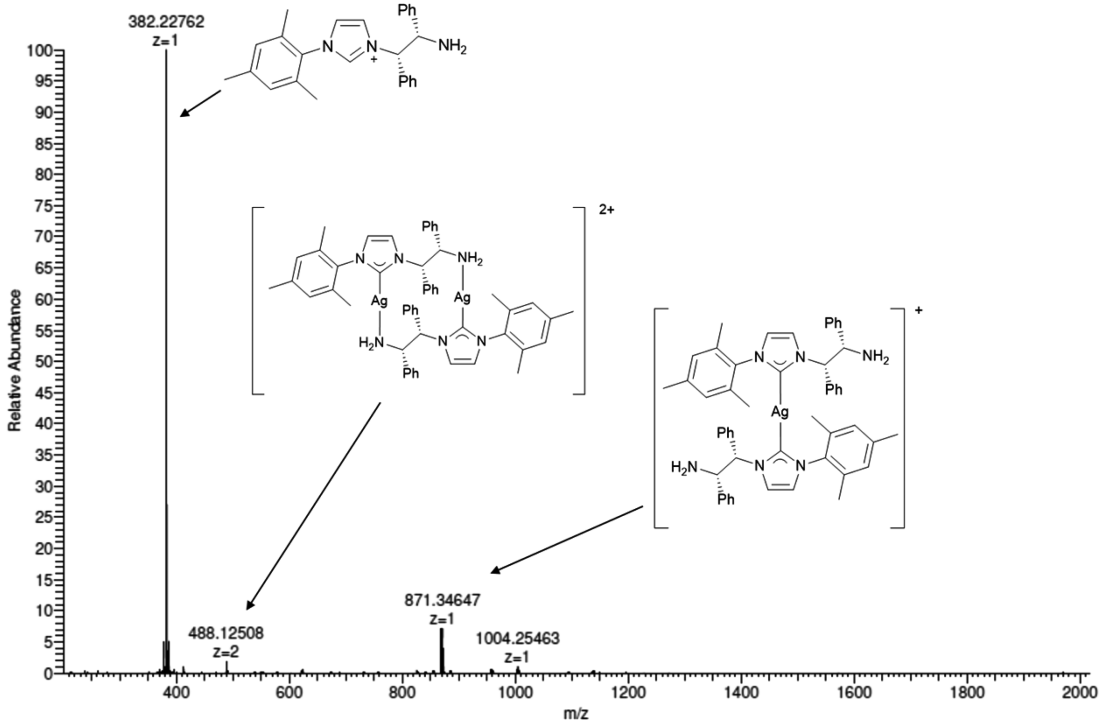


Figure 6. ESI-MS spectrum of **20**.

basic Mes-Kaibene (*S*,*S*)-**12** seemed more promising. Indeed, gently heating (*S*,*S*)-**12**·HPF_6 with silver oxide in the presence of activated 4 Å molecular sieves afforded silver compound **20** cleanly in good yield (Scheme 5).

Note that in order to ensure complete conversion of (*S*,*S*)-**12**·HPF_6 to **20**, it is necessary to use molecular sieves that have been activated under high vacuum and by heating. Once the silver complex is formed, it can be stored in air and is stable in wet DMSO-d_6. One of the possible structures of compound **20** is the head-to-tail dimer illustrated in Scheme 5. However, a higher molecular weight structure, such as a trimer or other oligomers may also be possible. In the ^{1}H NMR spectrum of **20**, a broad peak representing the NH_2 groups was observed at δ = 4.67 ppm, a chemical shift close to that of the NH_2 group of the crystallographically characterized [Ag(Me-Kaibene)]$_n$(PF_6)$_n$ polymer.[35] However, complex **20** has a higher solubility in nonpolar organic solvents like dichloromethane compared to the Me-Kaibene polymer, which is only soluble in highly polar organic solvents such as DMSO or acetonitrile. Thus, if **20** is a polymer, then it likely has a lower degree of polymerization than the Me-Kaibene polymer. The broad NH_2 peak and methine peaks of the backbone of (*S*,*S*)-**12** in the ^{1}H NMR spectrum of **20** also provide evidence for a polymeric structure where these hydrogens experience different chemical

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environments depending on the ligands' positions in the macromolecule. Fortunately, several fragments were observed in the mass spectra that provide insight into the structure. In the ESI-MS spectrum (Figure 6), peaks due to fragments possibly representing the dimeric structure were observed, along with that of a [bis(Mes-Kaibene)Ag]$^+$ fragment. The imidazolium salt was also observed in the spectrum due to the acidic conditions of the solution used in the ESI analysis. Similar fragments were also observed by MALDI-MS where the imidazolium salt signal was significantly smaller, and the [bis(Mes-Kaibene)Ag]$^+$ fragment is the dominant species observed. The $^{13}C\{^1H\}$ NMR spectrum of **20** displayed the carbene carbon resonance at δ = 181.5 ppm, which falls within the expected range of Ag-NHC complexes.[38]

In the reaction with $[RhCl(cod)]_2$ or $[IrCl(cod)]_2$, compound **20** proved to be a better transmetalation reagent for (*S*,*S*)-**12** than **15** or **16**. This could be due to the release $AgPF_6$ as a secondary reactant which in turn caused the precipitation of silver chloride which was observed after 18 h of reaction and allowed not only the NHC but also the amine of Mes-Kaibene to coordinate. Removal of silver chloride and subsequent purification by washing with diethyl ether yielded rhodium and iridium complexes **21** and **22**, respectively, in high purity and good yields (Scheme 5). Although the starting materials have similar dimeric structures $[MCl(cod)]_2$ (M = Rh, Ir), the products generated from their reactions with **20** are significantly different regarding the oxidation state and geometry of rhodium versus iridium. The expected [Rh(cod)(Mes-Kaibene)](PF_6) (**21**) compound was obtained as a result of halide abstraction and ligand coordination. In contrast, an Ir(III) hydride compound [Ir(H)(cod)(*o*-metalated Mes-Kaibene)](PF_6) (**22**) was obtained with one phenyl group orthometalated. An [Ir(cod)(Mes-Kaibene)](PF_6) complex with a structure similar to that of **21** might be an intermediate in the formation of **22**. In compound **22**, Mes-Kaibene is coordinated to iridium as a tridentate ligand, forming three stable and rigid six-membered metalacycles.

Both compounds **21** and **22** were fully characterized by NMR spectroscopy, HR-ESI, elemental analysis, and X-ray crystallography. The HR-ESI spectrum of **21** features a peak at m/z = 592.2195 which corresponds to the mass of the fragment of [Rh(Mes-Kaibene)(cod)]$^+$ (calcd 592.2194). The ^1H NMR spectrum of **21** reveals two N−H hydrogen atoms of the coordinated amine at δ = 4.90 and 4.33 ppm. The $^{13}C\{^1H\}$ NMR spectrum of **21** shows the carbene carbon resonance at δ = 173.4 ppm with a single bond coupling to rhodium ($^1J_{Rh-C}$ = 53.2 Hz). The molecular structure of **21** (Figure 7) exhibits a distorted square planar geometry, consistent with the d^8 Rh(I) configuration. The Rh−C(NHC) distance of 2.056(4) Å falls within the expected range of Rh−NHC bonds and is slightly longer than the mean Rh−C(NHC) distance (2.033 Å) determined by searching the 2017 CCD. The Rh-NH_2 distance of 2.165(4) falls within the longest 10% of Rh−amine bonds according to the 2017 CCD. The bond distances between the metal center and the olefin carbons are longer where the olefin is *trans* to the NHC, consistent with the stronger *trans* influence and the σ-donor ability of the NHC. The two phenyl groups on the backbone are oriented *anti* to each other and axial in the five-member Rh−C−N−C−C−N ring.

The HR-ESI mass spectrum of **22** reveals the presence of the major component with a peak at m/z = 680.2750 with an isotopic pattern matching for [Ir(H)(cod)(*o*-metalated Mes-Kaibene)]$^+$ (calcd 680.2744). In the ^1H NMR spectrum of **22**,

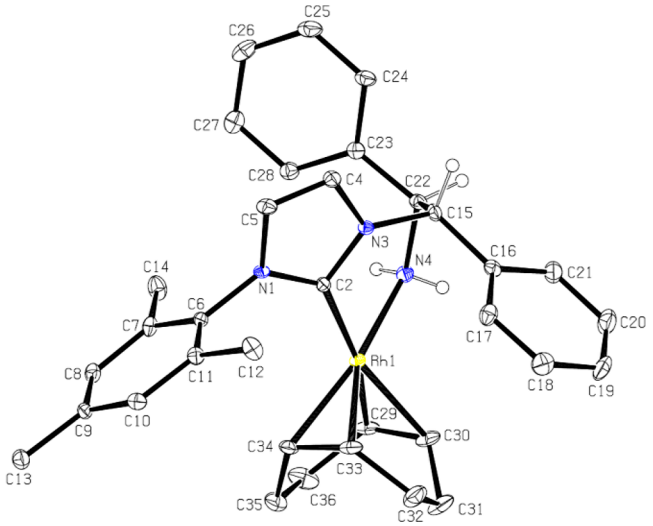

Figure 7. Molecular structure of **21**. The PF_6^- anion and irrelevant hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1−C2 2.056(4), Rh1−N4 2.165(4), Rh−C29 2.190(4), Rh1−C30 2.210(5), Rh1−C33 2.134(4), Rh1−C34 2.146(4), C2−Rh1−N4 88.0(2)

a hydride signal is observed at δ = −15.49 ppm and the two N−H hydrogens for the coordinated amine are found at δ = 6.02 and 5.15 ppm. The carbene carbon of **22** causes a resonance at δ = 153.61 ppm in the $^{13}C\{^1H\}$ NMR spectrum. An X-ray crystallographic study shows that **22** has a distorted octahedral structure (Figure 8), consistent with iridium(III) with a d^6

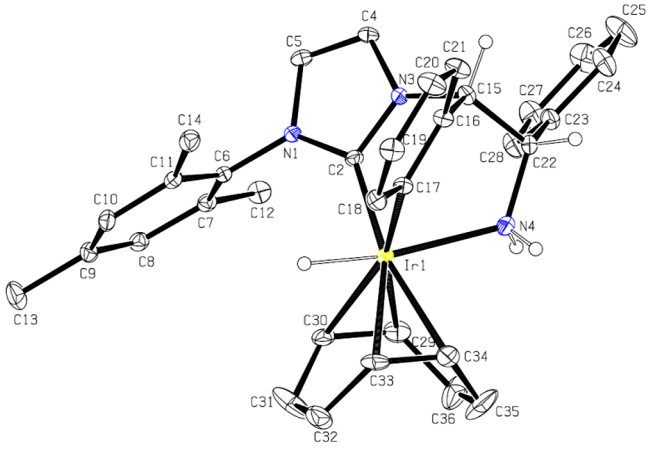

Figure 8. Molecular structure of **22**. Nonrelevant hydrogen atoms, one PF_6^- anion, half of a dichloromethane, and half of a pentane molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−hydride 1.51(4), Ir1−C2 2.027(4), Ir1−N4 2.256(4), Ir1−C17 2.070(5), Ir1−C29 2.296(6), Ir1−C30 2.308(5), Ir1−C33 2.266(5), Ir1−C34 2.253(5), hydride−Ir1−C2 87(2), hydride−Ir1−N4 170(2), hydride−Ir1−C17 88(2), C2−Ir1−N4 87.4(2), C2−Ir1−C17 82.9(2), N4−Ir1−C17 83.4(2).

electron configuration. The Ir−hydride distance measures 1.51(4) Å and falls within the expected range of iridium hydride distances determined by X-ray crystallography according to the 2017 CCD. Similarly, the 2.027(4) Å Ir−C(NHC) distance and 2.070(5) Å Ir−C(Ph) distance fall within the expected range according to previously reported data. Interestingly, the 2.256(4) Å Ir−NH_2 distance is much longer than most of the Ir−NH_2R bond reported in literature

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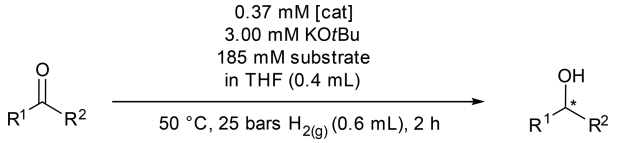
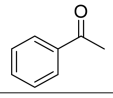
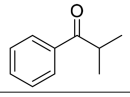
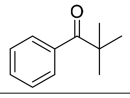
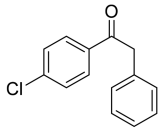
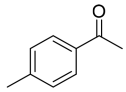
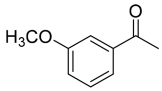
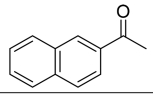
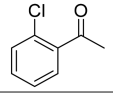
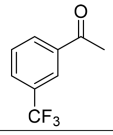
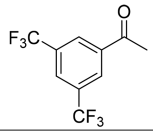
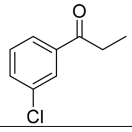
Table 1. Hydrogenation of Ketone Substrates by Compound 18 and 22: Select Substrates



No.	Substrate	Catalyst	% conv.	er (*R* : *S*)	TOF (h^{-1})	TON
1		**18**	92	52 : 48	231	462
		22	30	53 : 47	76	151
2		**18**	92	51 : 49	229	459
		22	56	49 : 51	140	280
3		**18**	96	52 : 48	241	481
		22	66	46 : 54	164	328
4		**18**	76	53 : 47	190	380
		22	86	63 : 37	214	428
5		**18**	85	52 : 48	211	423
		22	66	46 : 54	164	329
6		**18**	96	52 : 48	239	478
		22	88	49 : 51	220	440
7		**18**	76	53 : 47	189	379
		22	88	53 : 47	221	441
8		**18**	100	49 : 51	249	499
		22	99	35 : 65	248	496
9		**18**	92	54 : 46	230	460
		22	93	58 : 42	232	464
10		**18**	90	47 : 53	225	450
		22	86	39 : 61	215	429
11		**18**	83	53 : 47	208	416
		22	1	48 : 52	1.5	3

and falls within the longest 0.5% percentile due to the strong *trans* influence of the hydride ligand. The other three examples with comparable Ir−NH_2R distance all have the primary amine *trans* to either hydride or aryl ligands.[61−63] In **22**, the phenyl, the NHC, and the amine donor groups from Mes-Kaibene are coordinated to the metal center in a *mer* configuration, forming three six-membered metalacycles. The other ligands in **22** take up positions with strong *trans* influence donors *trans* to weak donors. Thus, the stronger σ-donors from Mes-Kaibene phenyl and NHC, are arranged *trans* to the weaker olefin groups of the cod ligand. The weak σ-donor amine is found in *trans* position to the strong σ-donor hydride.

Catalytic Direct Ketone Hydrogenation by 18 and 22. Iridium complexes **18** and **22** were then tested in the direct hydrogenation of 25 different ketones with varied steric and electronic properties. The catalysts:base:substrate ratio was controlled at 1:8:500 at 0.37 mM of the catalyst. The catalytic mixture was heated at 50 °C under 25 bar of H_2 for 2 h, and the product mixture was analyzed by gas chromatography. Selected catalytic results are listed in Table 1 and the comprehensive list of catalytic outcomes of all substrates are included in the Supporting Information.

In general, compound **18** and **22** are effective in reducing aryl-alkyl ketones (entries 1−3, Table 1) but with low enantioselectivity. These two complexes are also efficient in

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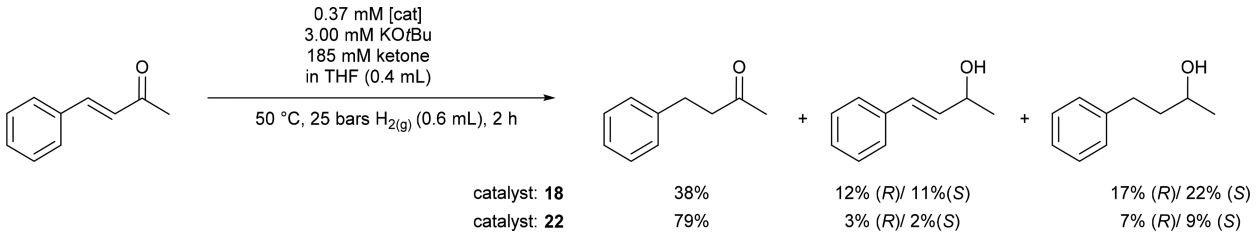
Organometallics XXXX, XXX, XXX−XXX

Scheme 6. Hydrogenation of Benzylideneacetone by 18 and 22



reducing benzyl 4-chlorophenyl ketone (entry 4, Table 1) with some degree of enantioselectivity. In comparison, compound **22** provides a higher stereoselectivity to the reduction most likely due to its more rigid structure compared to compound **18**. Compounds **18** and **22** can also reduce a range of derivatized acetophenone compounds including chloro-, methoxy-, *o*-phenylene-, methyl-, and trifluoromethyl- substituents (entries 5−11, Tables 1 and S1). Overall compounds **18** and **22** are effective ketone hydrogenation catalysts with TON up to 499 and TOF up to 249 h^{-1}.

We also tested compound **18** and **22** for the hydrogenation of benzylideneacetone to observe their selectivity between olefin and ketone (Scheme 6). As expected, the iridium hydrides are effective alkene hydrogenation catalysts. The alkene functional group in benzylideneacetone was almost completely hydrogenated along with the ketone to a small extent to give both the allyl alcohol and the saturated alcohol.

CONCLUSIONS

Two bulky new members of the class of Kaibene ligands, *t*Bu-Kaibene (*S*,*S*)-**11** and Mes-Kaibene (*S*,*S*)-**12**, composed of an NHC and a primary amine which are connected by a chiral backbone have been prepared in high yield and purity. In the presence of base and group 11 metal halides, four compounds containing a ligand/metal ratio of 2 have been prepared. The oxidative addition of the imidazolium salts to iridium(I) to generate iridium(III) hydride Kaibene compounds was also observed with 29% conversion for (*S*,*S*)-**11** and 99% conversion for (*S*,*S*)-**12**. Using an internal alkoxide base as in $[Ir(OtBu)(cod)]_2$ allows the preparation of a bimetallic iridium compound with (*S*,*S*)-**11** as the bridging ligand. This ligand exhibits interesting noncovalent interactions within the bimetallic molecule, which can be observed through spectroscopy and by X-ray diffraction studies. Using silver oxide as the base, efficient silver-based transmetalation reagent **20** has been generated for the transfer of ligand (*S*,*S*)-**12**. This transmetalation reagent can deliver 1 equiv of (*S*,*S*)-**12** to rhodium and iridium as a bidentate NHC^amine chelate ligand. The iridium compound prepared using $[IrCl(cod)]_2$ and **20** also facilitates an oxidative addition of an *ortho* C−H bond of the phenyl substituent on the ligand backbone to produce an iridium(III) hydride complex. The two iridium hydride compounds, **18** and **22** were tested for ketone hydrogenation and were shown to be effective ketone hydrogenation catalysts (TON 499, TOF 249 s^{-1}) but ineffective for their asymmetric hydrogenation. The bifunctional activity of these ligand places them among the family of Smart NHC ligands, which were recently reviewed by Peris.[64]

EXPERIMENTAL SECTION

General Considerations. All of the syntheses of transition metal complexes were performed under an argon or nitrogen atmosphere using standard Schlenk-line or glovebox techniques unless stated otherwise. Synthesis of sulfamidate **10** was reported previously.[37] All other reagents used were purchased from commercial sources and used without further purifications. 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 molecular sieves prior to use. NMR spectra were recorded at ambient temperature and pressure using a Bruker AVANCE I 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F), Bruker AVANCE III 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F), Varian Gemini 400 MHz spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F), Agilent DD2−500 MHz spectrometer (500 MHz for ^{1}H, 126 MHz for ^{13}C), an Agilent DD2−600 MHz spectrometer (600 MHz for ^{1}H, 151 MHz for ^{13}C, 564 MHz for ^{19}F), or an Agilent DD2−700 MHz. All assignments of signals were completed by 2D experiments. The ^{1}H and ^{13}C NMR spectra were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane (TMS). GC-FID equipped with a chiral column was used to analyze the conversion and enantioselectivity. The details of GC temperature and chromatographs were identical to those found in Demmans et al.[65] Abbreviations: Phi = ipso carbon of ring; Pho = ortho carbon; etc.

3-((1*S*,2*S*)-1,2-Diphenyl-2-aminoethyl)-1-*tert*-butylimidazolium hexafluorophosphate, *t*Bu-KaibeneHPF$_6$, (*S*,*S*)-11·HPF$_6$. A round-bottomed flask was charged with 1-*tert*-butylimidazole (621 mg, 5.0 mmol, 2 equiv), the sulfamidate (4*S*,5*R*)-1,2,3-oxathiazolidine-3-carboxylic acid,4,5-diphenyl-1,1-dimethylethylester-2,2-dioxide (**10**, 938 mg, 2.5 mmol, 1 equiv), and toluene (4 mL). The mixture was heated to reflux for 1 h after which time a precipitate formed. After cooling to room temperature, diethyl ether (40 mL) was added, and the resulting precipitate was collected by filtration. The solid was treated with HCl (37% in H_2O, 5 mL) and stirred for 1 h. Na_2CO_3 was added to neutralize the mixture and make the solution basic. KPF_6 (460 mg, 2.5 mmol, 1 equiv) was added, and the suspension was stirred for 18 h. The solid was collected by filtration and purified by recrystallization in CH_2Cl_2/diethyl ether to yield (*S*,*S*)-**11**·HPF$_6$ as an off-white solid. Yield: 918 mg (1.97 mmol, 79%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 8.82 (t, $^3J_{HH}$ = 1.7 Hz, 1H, NCHN), 7.52 (t, $^3J_{HH}$ = 1.9 Hz, 1H, NCHCHN), 7.44−7.15 (m, 11H, Ph−CH and NCHCHN), 5.73 (d, $^3J_{HH}$ = 8.4 Hz, 1H, ImidC*H*PhCHPhNH$_2$), 4.78 (d, $^3J_{HH}$ = 8.4 Hz, 1H, ImidCHPhC*H*PhNH$_2$), 1.73 (br, 2H, NH$_2$), 1.63 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) δ 141.1 (NCN), 134.5 (NCHCHN), 134.1 (NCHCHN), 129.3 (Ph$_o$ or Ph$_m$), 129.2 (Ph$_i$), 128.9 (Ph$_o$ or Ph$_m$), 127.9(Ph$_i$), 127.8 (Ph$_o$ or Ph$_m$), 126.5 (Ph$_o$ or Ph$_m$), 121.9 (Ph$_p$), 119.1 (Ph$_p$), 70.0 (ImidCHPhCHPhNH$_2$), 60.4 (C(CH$_3$)$_3$), 58.3 (ImidCHPhCHPhNH$_2$), 29.4 (C(CH$_3$)$_3$). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ −71.4 (d, $^1J_{FP}$ = 713.3 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2, 298 K): δ −144.2 (heptet, $^1J_{PF}$ = 713.3 Hz). HRMS (ESI, *m*/*z*): calc. for $C_{21}H_{36}N_3^+$ [M]$^+$ 320.2127, found 320.2128. Anal. Calcd for $C_{21}H_{36}N_3PF_6$: C, 54.19; H, 5.63; N, 9.03%. Found: C, 54.07; H, 5.88; N, 8.94%.

3-((1*S*,2*S*)-1,2-Diphenyl-2-aminoethyl)-1-mesityl-imidazolium Hexafluorophosphate, Mes-KaibeneHPF$_6$, (*S*,*S*)-12 HPF$_6$. The sulfamidate **10** (624 mg, 1.66 mmol, 1 equiv) and 1-(Mes)-imidazole (309 mg, 1.66 mmol, 1 equiv) were suspended in about 5 mL of MeCN. The mixture was refluxed overnight. After cooling to

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room temperature, 5 mL concentrated HCl was added, and the reaction mixture was stirred for few hours. Then, sufficient sodium carbonate solution was added to neutralize the solution, and KPF_6 (320 mg, 1.74 mmol, 1.05 equiv) was added. The solution was stirred overnight, and the product was extracted with dichloromethane (product forms a yellow solution in DCM). The extracts were quickly dried over magnesium sulfate, and all DCM were removed under vacuum. The yellow oil obtained was reprecipitated from DCM/hexane. Yield: 619 mg (1.17 mmol, 71%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 9.76 (t, $^4J_{HH}$ = 1.4 Hz, 1H, NCHN), 8.23 (t, $^3J_{HH}$ = 1.7 Hz, 1H, NCHCHN), 7.96 (t, $^3J_{HH}$ = 1.5 H, 1H, NCHCHN), 7.46 (m, 2H, *o*-Ph−CH adjacent to Imid.), 7.34 (d, 2H, *o*-Ph−CH adjacent to NH_2), 7.31 (t, 2H, *m*-Ph−CH adjacent to Imid.), 7.27 (t, 1H, *p*-Ph−CH adjacent to Imid.), 7.24 (t, 2H, *m*-Ph−CH adjacent to NH_2), 7.17 (s, 2H, Mes−CH), 7.15 (t, 1H, *p*-Ph−CH adjacent to NH_2), 5.89 (d, $^3J_{HH}$ = 9.7 Hz, 1H, ImidC*H*PhCHPhNH$_2$), 4.90 (d, $^3J_{HH}$ = 9.7 Hz, 1H, ImidCHPhC*H*PhNH$_2$), 2.35 (s, 3H, *p*-Me in Mes), 2.34 (br, 2H, NH_2), 2.02 (s, 3H, *o*-Me in Mes), 2.00 (s, 3H, *o*-Me in Mes). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 298 K) δ 142.5 (Ph_i in Ph adjacent to NH_2), 140.3 (Mes_p), 137.3 (NCHN), 136.1 (Ph_i in Ph adjacent to Imid.), 134.1 (Mes_o), 131.1 (Mes_i), 129.2 (*m*-Mes−CH), 128.7 (*m*-Ph−CH adjacent to Imid.), 128.6 (*p*-Ph−CH adjacent to Imid.), 128.2 (*m*-Ph−CH adjacent to NH_2), 127.7 (*o*-Ph−CH adjacent to Imid.), 127.1 (*p*-Ph−CH adjacent to NH_2), 126.9 (*o*-Ph−CH adjacent to NH_2), 123.7 (NCHCHN), 122.8 (NCHCHN), 69.6 (ImidCHPhCHPhNH$_2$), 57.6 (ImidCHPhCHPhNH$_2$), 20.5 (*p*-CH_3 in Mes), 16.8 (*o*-CH_3 in Mes), 16.7 (*o*-CH_3 in Mes). ^{1}H−^{15}N HMBC NMR (400 MHz, DMSO-d_6, 298 K) δ 192.7 (NCHCHN, chiral backbone substituted), 181.7 (NCHCHN, Mes substituted), 35.3 (NH_2). ^{19}F NMR (376 MHz, DMSO-d_6, 298 K) δ −70.1 (d, P*F*$_6$, $^1J_{FP}$ = 711 Hz). ^{31}P NMR (162 MHz, DMSO-d_6, 298 K) δ −144.1 (heptet, *P*F$_6$, $^1J_{FP}$ = 711 Hz). HRMS (ESI, *m*/*z*): calcd for $C_{26}H_{28}N_3^+$ $[M]^+$ 382.2278, found 382.2283. Anal. Calcd for $C_{26}H_{28}N_3PF_6$: C, 59.20; H, 5.35; N, 7.97%. Found: C, 60.01; H, 5.41; N, 7.86%.

Bis[3-((1*S*,2*S*)-1,2-diphenyl-2-aminoethyl)-1-*tert*-butylimidazol-2-ylidene]iodosilver, AgI(*t*Bu-Kaibene)$_2$, 13. In a nitrogen glovebox and protected from light, **11·HPF$_6$** (100 mg, 0.215 mmol, 1 equiv), AgI (26 mg, 0.107 mmol, 0.5 equiv), KI (89 mg, 0.538 mmol, 2.5 equiv), and KHMDS (47 mg, 0.237 mmol, 1.1 equiv) were dissolved in THF (10 mL). The initially clear solution was stirred at room temperature for 18 h. The resulting suspension was filtered through a pad of Celite, and the volatiles were removed *in vacuo*. The residue was redissolved in CH_2Cl_2 (2 mL) and filtered through a pad of Celite. Addition of pentane (20 mL) gave **13** as an off-white, very light sensitive solid. Yield: 65 mg, (0.074 mmol, 69%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.66 (d, $^3J_{HH}$ = 2.0 Hz, 2H, NCHCHN), 7.33 (d, $^3J_{HH}$ = 2.0 Hz, 2H, NCHCHN), 7.30−7.06 (m, 20H, Ph−CH), 5.93 (d, $^3J_{HH}$ = 7.7 Hz, 2H, ImidC*H*PhCHPhNH$_2$), 4.99 (dt, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 4.5 Hz, 2H, ImidCHPhC*H*PhNH$_2$), 1.64 (s, 18H, *t*Bu), 1.58 (d, $^3J_{HH}$ = 4.5 Hz, 4H, NH_2). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ 181.8 (NCN), 141.7 (Ph_i), 138.0 (Ph_i), 129.2 (Ph_o or Ph_m), 128.9 (Ph_o or Ph_m), 128.6 (Ph_p), 127.9 (Ph_p), 127.9 (Ph_o or Ph_m), 127.7 (Ph_o or Ph_m), 120.0 (NCHCHN), 119.3 (NCHCHN), 73.7 (ImidCHPhCHPhNH$_2$), 58.9 (ImidCHPhCHPhNH$_2$), 58.1 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$).

Bis[3-((1*S*,2*S*)-1,2-diphenyl-2-aminoethyl)-1-*tert*-butylimidazol-2-ylidene]iodocopper, CuI(*t*Bu-Kaibene)$_2$, 14. In a nitrogen Schlenk flask, **11·HPF$_6$** (100 mg, 0.214 mmol, 1 equiv), CuI (21 mg, 0.107 mmol, 0.5 equiv), and KHMDS (50 mg, 0.251 mmol, 1.17 equiv) were dissolved in THF (10 mL). The initially clear, orange solution was stirred at room temperature overnight. The resulting suspension was filtered over a pad of Celite, and the volatiles were removed *in vacuo*. The residue was redissolved in CH_2Cl_2 (2 mL) and filtered. Removal of all volatiles *in vacuo* and washing with Et_2O (3 × 5 mL) gave **14** as a white solid. Yield: 83 mg, (0.102 mmol, 95%). ^{1}H NMR (399 MHz, CD_2Cl_2): δ 7.66−6.91 (m, 24H, Ph−CH and NCHCHN), 5.77 (d, $^3J_{HH}$ = 6.6 Hz, 2H, ImidC*H*PhCHPhNH$_2$), 4.93 (m, 2H, ImidCHPhC*H*PhNH$_2$), 1.62 (s, 18H, *t*Bu), 1.55 (m, 4H, NH_2). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 177.9 (NCN), 141.2 (Ph_i), 138.1 (Ph_i), 129.5 (Ph_o or Ph_m), 128.9 (Ph_o or Ph_m), 128.8 (Ph_p), 128.4 (Ph_p), 127.8 (Ph_o or Ph_m), 127.6 (Ph_o or Ph_m), 120.4 (NCHCHN), 119.3 (NCHCHN), 72.4 (ImidCHPhCHPhNH$_2$), 59.1 (ImidCHPhCHPhNH$_2$), 58.2 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$). MS (MALDI-TOF, DCTB, *m*/*z*): 701 $[M - I]^+$. Anal. Calcd for $C_{42}H_{50}CuIN_6 \cdot 0.5\ CH_2Cl_2$: C, 58.55; H, 5.90; N, 9.64%. Found: C, 58.39; H, 6.26; N, 9.29%.

Bis[3-((1*S*,2*S*)-1,2-diphenyl-2-aminoethyl)-1-mesityl-butylimidazol-2-ylidene]iodosilver, AgI(Mes-Kaibene)$_2$, 15. Compound **15** is synthesized as an off-white powder using a similar procedure as that for making **13** with 300 mg of **12·HPF$_6$**. Yield: 283 mg (quantitative). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) δ 7.63−6.73 (m, 28H, Ph−CH, NCHCHN, Mes−CH), 5.68 (br, 2H, ImidC*H*PhCHPhNH$_2$), 5.04 (m, 2H, ImidCHPhC*H*PhNH$_2$), 2.31 (s, 6H, *p*-CH_3 in Mes), 1.90 (d, $^3J_{HH}$ = 3.2 Hz, 4H, NH_2), 1.71 (s, 6H, *o*-CH_3 in Mes), 1.32 (s, 6H, *o*-CH_3 in Mes). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ 184.3 (NCN), 141.3 (Ph_i, Mes_i, Mes_o, or Mes_p), 139.9 (Ph_i, Mes_i, Mes_o, or Mes_p), 137.9 (Ph_i, Mes_i, Mes_o, or Mes_p), 136.1 (Ph_i, Mes_i, Mes_o, or Mes_p), 135.5 (Ph_i, Mes_i, Mes_o, or Mes_p), 135.3 (Ph_i, Mes_i, Mes_o, or Mes_p), 129.7 (Ph−CH or Mes−CH), 129.6 (Ph−CH or Mes−CH), 129.6 (Ph−CH or Mes−CH), 129.0 (Ph−CH or Mes−CH), 128.8 (Ph−CH or Mes−CH), 128.1 (Ph−CH or Mes−CH), 127.2 (Ph−CH or Mes−CH), 127.1 (Ph−CH or Mes−CH), 122.9 (NCHCHN), 122.8 (NCHCHN), 71.5 (ImidCHPhCHPhNH$_2$), 58.3 (ImidCHPhCHPhNH$_2$), 21.4 (*p*-CH_3 in Mes), 18.1 (*o*-CH_3 in Mes), 17.9 (*o*-CH_3 in Mes). Anal. Calcd for $C_{52}H_{54}AgIN_6$: C, 62.59; H, 5.46; N, 8.42%. Found: C, 57.33; H, 5.81; N, 6.71%. Satisfactory elementary analysis cannot be obtained due to the relatively high instability of **15** in light and in air.

Bis[3-((1*S*,2*S*)-1,2-diphenyl-2-aminoethyl)-1-mesityl-butylimidazol-2-ylidene]iodocopper, CuI(Mes-Kaibene)$_2$, 16. Compound **16** is synthesized as an off-white powder with a procedure similar to that for making **14** with 300 mg of **12·HPF$_6$**. Yield: 250 mg (92%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) δ 7.95 (d, $^3J_{HH}$ = 1.8 Hz, 2H, NCHCHN), 7.42 (d, $^3J_{HH}$ = 1.8 Hz, 2H, NCHCHN), 7.35−7.23 (m, 6H, Ph−CH), 7.23−7.03 (m, 14H, Ph−CH), 6.97 (s, 2H, Mes−CH), 6.93 (s, 2H, Mes−CH) 5.42 (br, 2H, ImidC*H*PhCHPhNH$_2$), 5.01 (m, 2H, ImidCHPhC*H*PhNH$_2$), 2.23 (s, 6H, *p*-CH_3 in Mes), 1.87 (d, $^3J_{HH}$ = 3.2 Hz, 4H, NH_2), 1.75 (s, 6H, *o*-CH_3 in Mes), 1.64 (s, 6H, *o*-CH_3 in Mes). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6, 298 K): δ 181.8 (NCN), 140.6 (Ph_i, Mes_i, Mes_o, or Mes_p), 138.3 (Ph_i, Mes_i, Mes_o, or Mes_p), 137.9 (Ph_i, Mes_i, Mes_o, or Mes_p), 135.9 (Ph_i, Mes_i, Mes_o, or Mes_p), 134.9 (Ph_i, Mes_i, Mes_o, or Mes_p), 134.1 (Ph_i, Mes_i, Mes_o, or Mes_p), 128.9 (Ph_o, Ph_m, Ph_p, NCHCHN or Mes−CH), 128.4 (Ph_o, Ph_m, Ph_p, NCHCHN or Mes−CH), 127.7 (Ph_o, Ph_m, Ph_p, NCHCHN or Mes−CH), 126.8 (Ph_o, Ph_m, Ph_p, NCHCHN or Mes−CH), 126.6 (Ph_o, Ph_m, Ph_p, NCHCHN or Mes−CH), 121.8 (Ph_o, Ph_m, Ph_p, NCHCHN or Mes−CH), 68.7 (ImidCHPhCHPhNH$_2$), 57.0 (ImidCHPhCHPhNH$_2$), 20.7 (*p*-CH_3 in Mes), 17.1 (*o*-CH_3 in Mes), 16.8 (*o*-CH_3 in Mes). Anal. Calcd for $C_{52}H_{54}CuIN_6 \cdot 2H_2O$: C, 63.12; H, 5.91; N, 8.49%. Found: C, 62.84; H, 6.00; N, 8.36%.

Chloridohydrido(η^2,η^2-cycloocta-1,5-diene)[3-((1*S*,2*S*)-1,2-diphenyl-2-aminoethyl)-1-mesityl-imidazol-2-ylidene]iridium-(III), [Ir(cod)(Cl)(H)(Mes-Kaibene)](PF$_6$), 18. $[IrCl(cod)]_2$ (128 mg, 0.191 mmol, 0.5 equiv) and **12·HPF$_6$** (200 mg, 0.379 mmol, 1 equiv) were dissolved in 5 mL of anhydrous chloroform and stirred at room temperature for 18 h. The solution was then filtered through a pad of Celite to remove any insolubles. The residue yellow solid was then washed with diethyl ether for 3 h, collected by filtration, and dried in vacuum for 18 h. Yield: 310 mg (0.359 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ Major (69%): 7.51−6.76 (m, 14H, Ph−CH, Mes−CH, and NCHCHN), 7.09 (s, 1H, NCHCHN), 6.25 (s, 1H, NCHCHN), 6.13 (d, 1H, ImidC*H*PhCHPhNH$_2$), 5.39 (m, 1H, NH_2), 5.11 (m, $^3J_{HH}$ = 9.7 Hz, 1H, ImidCHPhC*H*PhNH$_2$), 5.17 (m, 1H, cod−CH), 4.44 (m, 1H, cod−CH), 4.41 (m, 1H, cod−CH), 4.28 (m, 1H, cod−CH), 3.66 (d, $^3J_{HH}$ = 10.9 Hz, 1H, NH_2), 2.92 (m, 1H, cod−CH_2), 2.91 (m, 1H, cod−CH_2), 2.81 (m, 1H, cod−CH_2), 2.67 (m, 1H, cod−CH_2), 2.44 (m, 1H, cod−CH_2), 2.30 (m, 1H, cod−CH_2), 2.19 (m, 1H, cod−CH_2), 2.18 (m, 1H, cod−CH_2), 2.29 (s, *p*-CH_3 in Mes), 2.02 (s, *o*-CH_3 in Mes), 1.96 (s, *o*-CH_3 in Mes); hydride region:

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Major (*cis*-H/Cl, 69%): −14.25 (s, 1H, IrH); Minor (*trans*-H/Cl, 22%): −14.63 (s, 1H, IrH); other isomers: −12.94, −13.25, −14.73, −15.65 (s, 1H, IrH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K) δ Major (69%): 154.7 (NCN), 141.0 (Ph_i), 129.8 (Ph_i), 129.3 (NCHCHN), 123.3 (NCHCHN), 130.5−123.5 (Ph_o, Ph_m, Ph_p, Mes_i, Mes_o, Mes_m, and Mes_p), 96.9 (cod−CH), 94.7 (cod−CH), 76.3 (cod−CH), 74.6 (cod−CH), 67.8 (ImidCHPhCHPhNH$_2$), 61.3 (ImidCHPhCHPhNH$_2$), 34.1 (cod−CH_2), 31.7 (cod−CH_2), 30.9 (cod−CH_2), 27.3 (cod−CH_2), 21.1 (*p*-CH_3 in Mes), 17.5 (*o*-CH_3 in Mes), 17.5 (*o*-CH_3 in Mes). $^1H-^{15}N$ HSQC/HMBC NMR (700 (HSQC) and 400 (HMBC) MHz, $CDCl_3$, 298 K) δ Major (69%): 204.2 (NCHCHN, Mes-substituted), 182.4 (NCHCHN, chiral backbone substituted), 0.75 (NH_2). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ −71.6 (d, PF_6). ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ −144.1 (heptet, PF_6). HRMS (ESI, *m*/*z*): Calcd for $[C_{34}H_{40}N_3ClIr]^+$ 718.2528, found 718.2526; calcd for $[C_{34}H_{39}N_3Ir]^+$ 682.2769, found 682.2766; calcd for $[C_{34}H_{39}N_3Cl_2Ir]^+$ 752.2132, found 752.2136. Anal. Calcd for $C_{34}H_{40}ClN_3PF_6Ir$: C, 47.30; H, 4.67; N, 4.87%. Found: C, 47.21; H, 4.70; N, 4.93%.

Chlorido(η^2,η^2-cycloocta-1,5-diene)iridium(I)-μ-[3-((1*S*,2*S*)-1,2-diphenyl-2-amino-κN-ethyl)-1-*tert*-butylimidazol-2-ylidene-κC]chlorido(η^2,η^2-cycloocta-1,5-diene)iridium(I), (cod)IrCl(κ-*t*Bu-Kaibene)IrCl(cod), 19. In a nitrogen glovebox a 3 mL scintillation vial was charged with **11·HPF$_6$** (50 mg, 0.107 mmol, 1 equiv), $[IrCl(cod)]_2$ (72 mg, 0.107 mmol, 1 equiv), and KO*t*Bu (14 mg, 0.128 mmol, 1.2 equiv). The mixture was dissolved in THF (1 mL) and stirred at room temperature for 3 h. The volatiles were removed in vacuo; the residue was redissolved in CH_2Cl_2 (1 mL) and filtered over a pad of Celite. The Celite was washed with 1 mL of CH_2Cl_2. *n*-Pentane (10 mL) was added to the filtrate, and the resulting suspension was filtered. The second filtrate was reduced to 2 mL, and *n*-pentane was added (10 mL). Compound **19** precipitated as a bright yellow powder and was collected via filtration and dried in vacuo. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of pentane into a saturated solution of **19** in THF under a nitrogen atmosphere. Yield: 40 mg (0.04 mmol, 38%). ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.17 (d, $^3J_{HH}$ = 11.3 Hz, 1H, ImidC*H*PhCHPhNH$_2$), 7.76−7.71 (m, 2H, Ph−CH), 7.66 (d, $^3J_{HH}$ = 2.2 Hz, 1H, NCHCHN), 7.46−7.41 (m, 2H, Ph−CH), 7.41−7.35 (m, 2H, Ph−CH and NCHCHN), 7.29−7.20 (m, 5H, Ph−CH), 5.24 (m, $^3J_{HH}$ = 11.8 Hz, $^3J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 2.6 Hz, 1H, ImidCHPhC*H*PhNH$_2$), 4.93 (td, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, cod−CH), 4.76 (dd, $^3J_{HH}$ = 11.8 Hz, ^2J = 11.5 Hz, 1H, NH_2), 4.41 (m, 1H, cod−CH), 3.93 (td, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, cod−CH), 3.79 (td, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 3.9 Hz, 1H, cod−CH), 3.44 (td, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, cod−CH), 3.12 (m, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 2.0 Hz, 1H, cod−CH), 2.74 (td, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 4.0 Hz, 1H, cod−CH), 2.57 (d, ^2J = 11.5 Hz, 1H, NH_2), 2.52−2.41 (m, 1H, cod−CH_2), 2.37−2.22 (m, 2H, cod−CH and cod−CH_2), 2.18−1.84 (m, 4H, cod−CH_2), 1.92 (s, 9H, *t*Bu), 1.74−1.66 (m, 2H, cod−CH_2), 1.53−1.42 (m, 1H, cod−CH_2), 1.34−1.11 (m, 6H, cod−CH_2), 0.98−0.90 (m, 1H, cod−CH_2). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ 181.3 (NCN), 139.4 (Ph_i), 138.0 (Ph_i), 130.1 (Ph_o or Ph_m), 129.3 (Ph_o or Ph_m), 129.1 (Ph_p), 129.1 (Ph_o or Ph_m), 128.8 (Ph_p), 128.3 (Ph_o or Ph_m), 123.1 (NCHCHN), 118.8 (NCHCHN), 84.5 (cod−CH), 79.3 (cod−CH), 71.4 (ImidCHPhCHPhNH$_2$), 67.1 (cod−CH), 64.6 (cod−CH), 63.3 (ImidCHPhCHPhNH$_2$), 60.2 (C(CH_3)$_3$), 58.1 (cod−CH), 57.4 (cod−CH), 54.4 (cod−CH), 54.0 (cod−CH), 34.9 (cod−CH_2), 33.0 (C(CH_3)$_3$), 32.2 (cod−CH_2), 31.9 (cod−CH_2), 31.5 (cod−CH_2), 31.5 (cod−CH_2), 31.2 (cod−CH_2), 30.7 (cod−CH_2), 28.0 (cod−CH_2). MS (MALDI-TOF, DCTB, *m*/*z*): 991 $[M]^+$. Anal. Calcd for $C_{37}H_{49}Cl_2Ir_2N_3$: C, 44.84; H, 4.98; N, 4.24%. Found: C, 44.63; H, 5.39; N, 3.73%.

[3-((1*S*,2*S*)-1,2-Diphenyl-2-aminoethyl)-1-mesityl-butylimidazol-2-ylidene]silver Hexafluorophosphate Dimer, [Ag(Mes-Kaibene)]$_2$(PF$_6$)$_2$, 20. 12·HPF$_6$ (400 mg, 0.76 mmol, 1 equiv), Ag_2O (300 mg, 1.29 mmol, 1.71 equiv), and 1 g of activated 4 Å molecular sieves were suspended in 10 mL of anhydrous dichloromethane, and the reaction mixture was stirred at 35 °C for 18 h, protected from light. Then, all the insolubles were removed by filtration, and the residue was washed by more anhydrous dichloromethane (5 mL × 2). The organic washings and filtrate were then combined, and volatiles were removed under reduced pressure. The residue obtained was then suspended in a pentane/diethyl ether mixture (10 mL, 1:1 ratio) and stirred vigorously for 3.5 h. The white power formed was collected by filtration and dried under vacuum for 18 h. Yield: 395 mg (0.31 mmol, 82%). ^1H NMR (400 MHz, DMSO-d_6, 298 K) δ 8.06 (s, 1H, NCHCHN), 7.80−6.80 (m, 13H, Ph−CH, Mes−CH group, and NCHCHN), 5.94 (br, 1H, ImidC*H*PhCHPhNH$_2$), 5.61 (br, 1H, ImidCHPhC*H*PhNH$_2$), 4.67 (br, 2H, NH_2), 2.30 (s, 3H, *p*-CH_3 in Mes), 1.96 (s, 3H, *o*-CH_3 in Mes), 1.71 (s, 3H, *o*-CH_3 in Mes). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6, 298 K) δ 181.5 (NCN), 138.7 (Ph_i), 134.1 (Ph_i), 126.7 (NCHCHN), 119.8 (NCHCHN), 129−127 (Ph_o, Ph_m, Ph_p, Mes_o, Mes_m, and Mes_p), 73.0 (br, 1H, ImidCHPhCHPhNH$_2$), 55.6 (br, 1H, ImidCHPhCHPhNH$_2$), 20.5 (*p*-CH_3 in Mes), 18.0 (*o*-CH_3 in Mes), 17.0 (*o*-CH_3 in Mes). (These peaks were determined through a combination of $^{13}C\{^1H\}$ NMR, gHSQC ($^1H-^{13}C$) NMR, and gHMBC ($^1H-^{13}C$) NMR). ^{19}F NMR (376 MHz, DMSO-d_6, 298 K) δ −70.1 (d, PF_6). ^{31}P NMR (162 MHz, DMSO-d_6, 298 K) δ −144.2 (heptet, PF_6). HRMS (ESI, *m*/*z*): calcd for $[C_{26}H_{27}N_3Ag]_2^{2+}$ 488.1250, found 488.1251. Calcd for $[C_{52}H_{54}N_6Ag]^+$ 869.3455, found 869.3464. MS (MALDI-TOF, DCTB, *m*/*z*): Calcd for $[C_{26}H_{27}N_3Ag]_2^{2+}$ 488.1250, found 488.125. Calcd for $[C_{52}H_{54}N_6Ag]^+$ 869.3455, found 869.364. Anal. Calcd for $C_{26}H_{27}AgF_6N_3P$: C, 49.23; H, 4.29; N, 6.62%. Found: C, 52.86; H, 4.44; N, 6.77%. Unsatisfactory carbon analyses but acceptable hydrogen and nitrogen content were measured, even in the presence of V_2O_5, because of a combustion problem due to the presence of the hexafluorophosphate anion.[66]

(η^2,η^2-Cycloocta-1,5-diene)[3-((1*S*,2*S*)-1,2-diphenyl-2-aminoethyl)-1-mesityl-butylimidazol-2-ylidene]rhodium Hexafluorophosphate, [Rh(cod)(Mes-Kaibene)](PF$_6$), 21. $[RhCl(cod)]_2$ (20 mg, 0.041 mmol, 1.03 equiv) and **20** (50 mg, 0.039 mmol, 1 equiv) were dissolved in 2 mL of anhydrous dichloromethane and stirred at room temperature for 18 h, protected from light. White precipitate slowly formed over time was filtered off, and the residue was washed with more anhydrous dichloromethane. Dichloromethane was then evaporated under reduced pressure, and the residue was redissolved in dichloromethane. More precipitate that might form was removed by filtration. This process was repeated until no suspension was observed when the solid was dissolved in DCM. Then, the yellow solid was washed with diethyl ether for 3 h, collected by filtration, and dried under vacuum for 18 h. Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of pentane into a saturated solution of **21** in dichloromethane. Yield: 42 mg (0.057 mmol, 72%). ^1H NMR (400 MHz, DMSO-d_6, 298 K) δ 7.54 (t, 2H, *m*-Ph−CH adjacent to Imid.), 7.47 (m, 2H, *o*-Ph−CH adjacent to Imid.), 7.44 (t, 1H, *p*-Ph−CH adjacent to Imid.), 7.32 (t, 2H, *m*-Ph−CH adjacent to NH_2), 7.30 (t, 1H, *p*-Ph−CH adjacent to NH_2), 7.29 (d, 1H, NCHCHN), 7.26 (d, 2H, *o*-Ph−CH adjacent to NH_2), 7.17 (d, 1H, NCHCHN), 7.17 (s, 1H, Mes−CH), 7.01 (s, 1H, Mes−CH), 5.83 (d, $^3J_{HH}$ = 1.0 Hz, 1H, ImC*H*PhCHPhNH$_2$), 5.10 (d, $^3J_{HH}$ = 7.5 Hz, 1H, ImCHPhC*H*PhNH$_2$), 4.90 (dd, $^3J_{HH}$ = 12.9, 8.1 Hz, 1H, NH_2), 4.55 (m, 1H, cod−CH), 4.33 (d, $^3J_{HH}$ = 12.9 Hz, 1H, NH_2), 4.07 (m, 1H, cod−CH), 3.37 (m, 1H, cod−CH), 2.62 (m, 1H, cod−CH), 2.50 (s, 3H, *p*-CH_3 in Mes), 2.31 (s, 3H, *o*-CH_3 in Mes), 2.26 (m, 1H, cod−CH_2), 1.94 (m, 1H, cod−CH_2), 1.92 (s, 3H, *o*-CH_3 in Mes), 1.65 (m, 1H, cod−CH_2), 1.45 (m, 3H, cod−CH_2), 1.29 (m, 2H, cod−CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6, 298 K) δ 173.4 (d, $^1J_{Rh-C}$ = 53.2 Hz, NCN), 139.0 (Ph_i in Ph adjacent to Imid.), 138.7 (Mes_p), 138.7 (Ph_i in Ph adjacent to NH_2), 135.5 (Mes_i), 134.8 (Mes_o), 134.4 (Mes_o), 128.9 (Mes_m), 128.8 (Mes_m), 128.3 (Ph_m in Ph adjacent to Imid.), 128.0 (Ph_m in Ph adjacent to NH_2), 127.6 (Ph_p), 127.1 (Ph_o in Ph adjacent to Imid.), 126.7 (Ph_o in Ph adjacent to NH_2), 124.4 (NCHCHN), 123.2 (NCHCHN), 92.9 (d, $^1J_{Rh-C}$ = 7.6 Hz, cod−CH), 92.3 (d, $^1J_{Rh-C}$ = 7.8 Hz, cod−CH), 73.1 (d, $^1J_{Rh-C}$ = 12.3 Hz, cod−CH), 71.4 (d, $^1J_{Rh-C}$ = 12.9 Hz, cod−CH), 68.6 (ImidCHPhCHPhNH$_2$), 51.9 (ImidCHPhCHPhNH$_2$), 32.4 (cod−CH_2), 30.0 (cod−CH_2), 29.6 (cod−CH_2), 25.8 (cod−CH_2), 20.5 (*p*-CH_3 in Mes), 18.9 (*o*-CH_3 in Mes), 17.3 (*o*-CH_3 in Mes). $^1H-^{15}N$

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HMBC NMR (400 MHz, DMSO-d_6, 298 K) δ 194.5 (NCHCHN, Mes substituted), 190.9 (NCHCHN, chiral backbone substituted), 4.8 (NH_2). ^{19}F NMR (376 MHz, DMSO-d_6, 298 K) δ −70.2 (d, PF_6, $^1J_{FP}$ = 711 Hz). ^{31}P NMR (162 MHz, DMSO-d_6, 298 K) δ −144.2 (heptet, PF_6, $^1J_{FP}$ = 711 Hz). HRMS (ESI, m/z): Calcd for $[C_{34}H_{39}N_3Rh]^+$ 592.2194, found 592.2195. Anal. Calcd for $C_{34}H_{39}N_3PF_6Rh$: C, 55.37; H, 5.33; N, 5.70%. Found: C, 55.13; H, 5.38; N, 5.55%.

Hydrido(η^2,η^2-cycloocta-1,5-diene)[*o*-metalated-3-((1*S*,2*S*)-1,2-diphenyl-2-aminoethyl)-1-mesityl-butylimidazol-2-ylidene]iridium Hexafluorophosphate, [Ir(cod)(H)(*o*-metalated Mes-Kaibene)](PF$_6$), 22. $[IrCl(cod)]_2$ (106 mg, 0.158 mmol, 1 equiv) and **20** (200 mg, 0.158 mmol, 1 equiv) were dissolved in 5 mL of anhydrous dichloromethane and stirred at room temperature for 18 h, protected from light. White precipitate slowly formed overtime was filtered off, and the residue was washed with more anhydrous dichloromethane. Dichloromethane was then evaporated under reduced pressure, and the residue was redissolved in dichloromethane. More precipitate that might form was removed by filtration. This process was repeated until no suspension was observed when the solid was dissolved in DCM. Then, the yellow solid was washed with diethyl ether for 3 h and collected by filtration, dried in vacuum for 18 h. Single crystals suitable for an X-ray diffraction study were obtained by slow diffusion of pentane into a saturated solution of **22** in dichloromethane. Yield: 219 mg (0.265 mmol, 84%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 7.47 (d, 1H, *o*-Ph−CH in Ph adjacent to Imid.), 7.33 (t, 1H, *p*-Ph−CH in Ph adjacent to NH_2), 7.32 (m, 3H, *m*-Ph−CH in Ph adjacent to NH_2, CH adjacent to phenyl ligand), 7.14 (m, 4H, Mes−CH, NCHCHN), 7.10 (d, 2H, *o*-Ph−CH in Ph adjacent to NH_2), 6.98 (t, 1H, *m*-Ph−CH in Ph adjacent to Imid.), 6.88 (t, 1H, *p*-Ph−CH in Ph adjacent to Imid.), 6.02 (dd, $^2J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 9.0 Hz, 1H, NH_2), 5.70 (d, $^3J_{HH}$ = 2.5 Hz, 1H, ImC*H*PhCHPhNH$_2$), 5.32 (m, 1H, cod−CH), 5.15 (d, $^2J_{HH}$ = 12.5 Hz, 1H, NH_2), 4.41 (d, $^3J_{HH}$ = 9.0 Hz, 1H, ImCHPhC*H*PhNH$_2$), 4.37 (m, 1H, cod−CH), 4.34 (m, 1H, cod−CH), 4.06 (m, 1H, cod−CH), 2.90 (m, 1H, cod−CH_2), 2.65 (m, 1H, cod−CH_2), 2.40 (m, 1H, cod−CH_2), 2.36 (s, 3H, *p*-CH_3 in Mes), 2.35 (m, 2H, cod−CH_2), 2.06 (s, 3H, *o*−CH_3 in Mes), 1.77 (s, 3H, *o*−CH_3 in Mes), 1.72 (m, 2H, cod−CH_2), 1.63 (m, 1H, cod−CH_2) −15.49 (s, 1H, IrH). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 298 K) δ 153.6 (NCN), 139.2 (Mes_p), 138.3 (Ph_i in Ph adjacent to NH_2), 138.1 (Ph_i in Ph adjacent to Imid.), 137.2 (Ph_o in phenyl ligand), 135.5 (Mes_i), 135.5 (Ph_o and Ph_m in phenyl ligand), 135.2 (Mes_o), 134.6 (Mes_o), 129.3 (Mes_m), 128.7 (Mes_m), 128.1 (Ph_m in Ph adjacent to NH_2), 127.7 (Ph_p in Ph adjacent to NH_2), 126.7 (Ph_p in Ph adjacent to Imid., and Ph_o in Ph adjacent to NH_2), 125.9 (Ph_o in Ph adjacent to Imid.), 123.2 (Ph_m in Ph adjacent to Imid.), 122.9 (NCHCHN), 122.6 (NCHCHN), 90.8 (cod−CH), 89.2 (cod−CH), 87.7 (cod−CH), 85.3 (cod−CH), 73.8 (ImidCHPhCHPhNH$_2$), 50.8 (ImidCHPhCHPhNH$_2$), 37.0 (cod−CH_2), 30.3 (cod−CH_2), 27.0 (cod−CH_2), 25.6 (cod−CH_2), 20.5 (*p*-CH_3 in Mes), 17.6 (*o*-CH_3 in Mes), 17.0 (*o*-CH_3 in Mes). ^{1}H−^{15}N HSQC/HMBC NMR (400 MHz, DMSO-d_6, 298 K) δ 189.8 (NCHCHN, Mes-substituted), 185.1 (NCHCHN, chiral backbone substituted), −24.7 (NH_2). ^{19}F NMR (376 MHz, DMSO-d_6, 298 K) δ −70.2 (d, PF_6, $^1J_{FP}$ = 711 Hz). ^{31}P NMR (162 MHz, DMSO-d_6, 298 K) δ −144.2 (heptet, PF_6, $^1J_{FP}$ = 711 Hz). HRMS (ESI, m/z): calcd for $[C_{34}H_{39}N_3Ir]^+$ 680.2744, found 680.2750. Anal. Calcd for $C_{34}H_{39}N_3PF_6Ir$: C, 49.39; H, 4.75; N, 5.08%. Found: C, 49.14; H, 4.67; N, 5.12%.

General Procedure for Ketone Hydrogenation Testing. The experiments were conducted at the Centre for Catalysis Research and Innovation at the University of Ottawa. Into a 1 mL glass liner was added 0.1 mL of THF solution of 1.48 mM catalyst, 0.1 mL of THF solution of 12 mM KO*t*Bu, 0.2 mL of THF solution of 370 mM substrate, and two glass beads. This glass liner was placed within a 96-well stainless plate with other testing solutions. Then, the plate was sealed with one layer of paraffin and one layer of PTFE with one small hole above each well for the introduction of hydrogen. The plate was then placed in a large hydrogenation block and sealed to withstand elevated pressures. The block was then pressurized with H_2(g), heated, and shaken. The conversion of the reaction mixture at the end of the catalytic run was analyzed by chiral GC.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00915.

The proposed structures of all of the isomers of **17** and **18**, ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra and table of hydrogenation results (PDF)

Accession Codes

CCDC 1813983−1813985 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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