In depth study on chloride abstractions from (NHC)Ir(COD)Cl complexes

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Supporting Information Placeholder

ABSTRACT: While attempting to prepare a series of cationic NHC-Ir complexes of general formula [(NHC)Ir(COD)]⁺ via the silver salt metathesis reaction of its precursor (NHC)Ir(COD)Cl in dichloromethane, we unexpectedly synthesized [(μ-Cl)-{(2,7-SiCyNap)Ir(COD)}₂·{Ag(OTf)}], a chloride-bridged Ir-Ag adduct. This result led us to investigate the chloride abstraction from the (NHC)Ir(COD)Cl system in detail. We show how the outcome of this ubiquitous reaction is dependent on a fine balance between nucleophilicity of the weakly coordinating anion (WCA) and the polarity / coordinating ability of the reaction medium. A frequently encountered alternative to using silver salts is also presented and compared. The experimental difference in the reactivities of cationic catalysts in a representative intramolecular hydroamination reaction shows how cationic Ir-Ag adduct can fail to deliver the reaction product through what appears to be a stabilization of the catalytically inactive iridium-silver intermediate by the educt.

1. INTRODUCTION

Ionic transition metal complexes play a vital role in organometallic chemistry and catalysis,¹ and both academically and industrially important processes such as olefin polymerizations,² Diels-Alder,³ carbonylation,⁴ and hydrogenation reactions,⁵ often rely on such catalytic species. The high reactivity of cationic metal complexes is generally attributed to the increased electrophilicity of the metal center, and oftentimes encompasses the creation of additional coordinative unsaturation.

Especially valuable cationic catalysts are the ones of group 9. The history of efficient cationic group 9 complexes dates back to the years after the initial discovery of Wilkinson's catalyst where research led to more active, cationic [L₂Rh(diene)]⁺ Schrock-Osborn type precatalysts.⁶ The idea was immediately transferred to the asymmetric hydrogenation studies that were underway at the time and it was these cationic rhodium species that led to a real breakthrough in this nascent field, as evidenced inter alia by work of Knowles and Noyori on rhodium catalyzed asymmetric hydrogenations using chiral chelating phosphine ligands DIPAMP and BINAP.⁷ Efficient iridium complexes for hydrogenations remained elusive until the discovery of the cationic [Ir(COD)(py)(PR₃)]⁺[BF₄]⁻ (COD = 1,5-cyclooctadiene, py = pyridine) by Crabtree and coworkers.⁸ Since then, and particularly in the last twenty years, very efficient cationic iridium systems have appeared in the literature for various (asymmetric) reactions.^{5c,7,9}

Cationic metal complexes are usually accessed via abstraction of an anionic ligand (most typically a hydride, alkyl or

halide), which is replaced by a weakly coordinating anion.¹⁰ Among these methods, halide abstractions are probably the most widely applied and are commonly carried out by reacting a neutral L_nMX formulated complex with a univalent metal incorporating a weakly coordinating anion (WCA) as shown in Chart 1.

Chart 1. Typical outcomes in halide abstraction reactions.

M = metal center
M' = univalent metal, e.g. Ag, Na, Tl
L = spectator ligand
L' = solvent or neutral ligand
X = halide
Y = weakly coordinating anion

Equation 2 depicts the ideal case scenario, where the halide abstraction not only leads to increased electrophilicity of the resulting complex, but also generates a coordinative unsaturation and increased reactivity on the metal. Unfortunately, the increased reactivity of the metal in the ideal case of equation 2 more often than not leads to unwanted decomposition of the complex. For example, one or more ligands (L) can be activated by the metal center which can result in cyclometallation, subsequent dehydrogenation or other decomposition pathways.¹¹ Alternatively, anions with low stability may be activated and go through decomposition.^{10c} In order to avoid such

outcomes, halide abstractions are frequently carried out in donor solvents or in the presence of other neutral, two electron donor ligands (Chart 1, eq 3). This strategy however results in compounds of lesser activity.

Of the univalent metals employed for halide abstraction, silver salts are the most widely used for mid- to late-transition metals. Unfortunately, even this method of choice has its shortcomings. For example, it can be plagued by decomposition of the resulting product as discussed above, or also by incomplete halide abstraction leading to dimerized complexes with the general formula $[M-Cl-M]^+$ or by the formation of heterobimetallic complexes. The mechanism of the silver salt metathesis was studied to some extent. For instance, from solution phase spectroscopic experiments, the intermediacy of $[CpFe(CO)_2(\mu-I)Ag]^+$ was proposed for the reaction between $CpFe(CO)_2I$ and $AgBF_4$ or $Ag(CB_{11}H_{12})$ in chlorinated solvents.^{12,13} A series of heterobimetallic Mo-Ag complexes were synthesized by Weller using $CpMo(CO)_3I$ and silver-carboranes as precursors.¹⁴ For noble metals, the compound that has been studied in some detail is Vaska's complex *trans*- $[(PPh_3)_2Ir(CO)Cl]$, where early studies by Vaska and Peone had shown that salt metathesis proceeds readily in benzene with $AgClO_4$ to provide a perchlorate complex (Chart 1, eq 1), that undergoes complete ionization in the presence of coordinating solvents such as acetone or methanol (product of eq 3).¹⁵ When halide abstractions with more weakly coordinating anions were attempted later on by Reed and most recently by Bohle, arrested Ir-Ag intermediates were isolated in both toluene or acetonitrile.^{13,16,17} Further studies on silver-promoted ligand metathesis in square-planar complexes were reported on Pt(II) by Albano, Ruffo et al.,¹⁸ and halide abstraction attempts on more electrophilic, octahedral Rh(III) and Ir(III) complexes were also described.^{19,20}

The studies cited above established the importance of the nucleophilicity and binding ability of the counteranion, but overall, a general mechanism for the halide abstraction can not be deduced and very little is known about other factors influencing the ability of this metathesis to take place. Coordinative unsaturation (generation of a virtually vacant site) is though highly desirable, especially in catalysis, and salt metathesis is one of the most straightforward methods to achieve that goal.¹⁰ As such and to avoid the difficulties associated with the isolation of highly active, often unstable cationic catalysts, in situ methods to abstract halides from catalyst precursors are oftentimes preferred. Recent research has though drawn attention toward the “silver effect” in gold catalysis, where these in situ methods have been extensively utilized in the last decade.^{21,22}

Our recent research has focused on the synthesis and catalytic application of highly unsaturated $[(NHC)Ir(COD)]^+$ (NHC = N-heterocyclic carbene) complexes (Figure 1).²³ These formally 14 electron, 3-coordinate compounds are stabilized by an interaction between one of the aromatic wingtips and the metal center that leads to a sideways tilt of the NHC-Ir bond.²⁴ When employed in the intramolecular hydroamination of unactivated aminoalkenes, (pre)catalyst $2[PF_6]$, which was generated from catalytically inactive $(NHC)Ir(COD)Cl$ (**1**) via silver salt metathesis with $AgPF_6$, showed remarkably high catalytic activity.²⁵

In order to gain a better understanding on how the nature of the anion in $[(2,7-SiCyNap)Ir(COD)]PF_6$ (**2** $[PF_6]$) influences the catalytic activity of these species, we decided to synthesize

a series of $[(NHC)Ir(COD)]^+$ compounds with counterions of different nucleophilicity. The current contribution reports how a serendipitous discovery during these studies led to the synthesis a heterobimetallic $(\mu-Cl)-Ir-Ag$ adducts. These unexpected results led us to investigate the silver metathesis reaction on the starting complex **1** in detail. The studies revealed not only the influence of the chosen counteranion on the reaction outcome, but also highlighted the profound influence the reaction medium as well as the univalent metal choice can have on the results of this seemingly straightforward reaction. Finally, we present comparative catalytic studies employing these complexes which underline the importance of applying well defined (pre)catalysts.

Figure 1. Previous work with a formally 14 VE Ir(I) complex: a) Structure of $[(2,7-SiCyNap)Ir(COD)][PF_6]$ (**2** $[PF_6]$). b) Molecular structure of the cation of **2** $[PF_6]$. c) Hydroamination/cyclization reaction with **2** $[PF_6]$.

2. RESULTS AND DISCUSSION

2.1 Silver salt metathesis reactions in dichloromethane

In our earlier work on accessing the catalytically competent compound **2** $[PF_6]$ and its enantiopure derivatives,²³ we performed the halide abstraction in DCM (dichloromethane), giving very clean reactions and high yields of the product(s). We therefore fixed these reaction conditions and started to investigate silver salts containing anions of increasing nucleophilicity (and basicity) when compared to the PF_6 anion.

*Synthesis and characterization of $[(2,7-SiCyNap)Ir(COD)][BF_4]$ (**2** $[BF_4]$):* The BF_4 anion, while slightly more nucleophilic than the PF_6 anion, is normally considered a non-binding counterion for late-transition metals.^{10a} Indeed, treatment of $(2,7-SiCyNap)Ir(COD)Cl$ (**1**) with $AgBF_4$ in DCM led to clean formation of the (expected) cationic complex $[(2,7-SiCyNap)Ir(COD)][BF_4]$ (**2** $[BF_4]$) in high yield (Scheme 1). Rather unexpectedly though, **2** $[BF_4]$ proved to be much less stable than **2** $[PF_6]$ in both solution and the solid state. The compound, when analyzed, showed very similar features and data to **2** $[PF_6]$. The molecular structure of **2** $[BF_4]$ is shown on Figure 2.²⁶ X-ray crystallographic analysis of **2** $[BF_4]$ revealed that the cation adopts a very similar structure to **2** $[PF_6]$ such that one of the aromatic wingtips approaches the metal center and displays a metal-arene interaction [$Ir-C58 = 2.551(5)$ and $Ir-C58A = 2.428(5)$ Å], that leads to a pseudo-square-planar coordination geometry (Table 1).

Scheme 1. Synthesis of monometallic iridium-only and bimetallic iridium-silver complexes.

*Synthesis and characterization of $[(2,7\text{-SiCyNap})\text{Ir}(\text{COD})][\text{NTf}_2]$ (**2** [NTf_2]):* Next, we chose AgNTf_2 for this investigation, as it still offers relatively low basicity/nucleophilicity,²⁷ all the while already showing more diverse coordination chemistry with metals.²⁸ Indeed, the NTf_2 anion is by now a well-established, labile pseudohalide ligand in catalysis of group 11 metals.²⁹ However, the catalytic potential of NTf_2 anion containing group 9 metals is rather underdeveloped.^{16c,30} Furthermore, a recent investigation into using AgNTf_2 in the silver metathesis reaction with Vaska's complex caught our attention.^{16c} Contrary to what was reported for Vaska's complex (i.e. isolation of a Ir-Ag adduct),¹⁶ the chloride atom in **1** was susceptible to abstraction by AgNTf_2 in DCM and upon workup, $[(2,7\text{-SiCyNap})\text{Ir}(\text{COD})][\text{NTf}_2]$ (**2** [NTf_2]) was isolated as a red solid in high yield with analytical data consistent with its formulation (Scheme 1). Crystals suitable for an X-ray structure analysis were grown by layering pentane onto a concentrated solution of **2** [NTf_2] in DCM.²⁶ The cation is the same as that in **2** [PF_6] and **2** [BF_4] (Figure 3, Table 1), and there are no significant deviations in bond lengths and angles. However, while the NTf_2 anion has no close contact to the metal center, there are some weak interactions present between the oxygen atoms of the NTf_2 anion and hydrogen atoms of the NHC ligand of the complex (shortest intermolecular distances $\text{O11}\cdots\text{H23} = 2.470$ and $\text{O12}\cdots\text{H3A} = 2.475$ Å; corresponding distances $\text{O11}\cdots\text{C23} = 3.418(4)$ and $\text{O12}\cdots\text{C3} = 3.269(3)$ Å). Overall, bond lengths and angles represent the expected values for a free anion.³¹

*Synthesis and characterization of $[(\mu\text{-Cl})\text{-}\{(2,7\text{-SiCyNap})\text{Ir}(\text{COD})\}\text{-}\{\text{Ag}(\text{OTf})\}}]$ (**3**):* The unexpectedly easy ionization of **1** in the presence of AgNTf_2 naturally led us to explore the possibility of synthesizing the same cationic iridium complex with the triflate counterion, an ion which still displays relatively low nucleophilicity, but that clearly shows an increased covalent character in its metal complexes when compared to its triflimide cousin.^{27,32} It should also be noted that complexes with the OTf anion are known to show diverse and sometimes unexpected catalytic activity.³³ Treatment of $(2,7\text{-SiCyNap})\text{Ir}(\text{COD})\text{Cl}$ (**1**) with an equimolar amount of AgOTf in DCM led to a quick color change from yellow to deep orange, which is typical in case of the formation of cationic complexes **2** described above (Scheme 1). Surprisingly though, we did not observe precipitation of AgCl to any extent during the reaction. While a detailed discussion of the NMR spectroscopic features is given further down, the location of the carbene signal at 205 ppm in the ^{13}C NMR spectrum clearly excluded generation of the tilted cationic structure of **2**, where the diagnostic carbenic signal appears significantly further upfield (188–187 ppm). Slow diffusion of pentane into a concentrated solution of the complex revealed its unusual structure as being the iridium-silver adduct $[(\mu\text{-Cl})\text{-}\{(2,7\text{-SiCyNap})\text{Ir}(\text{COD})\}\text{-}\{\text{Ag}(\text{OTf})\}}]$ (**3**), a formulation that is fully consistent with its spectroscopic (^1H , ^{13}C NMR) features and its composition as determined by elemental analysis.²⁶ Figure 4 depicts this complex (**3a**) and a discussion and comparison of the different solvates of **3** is given in section 2.3.

Synthesis and characterization of (2,7-SiCyNap)Ir(COD)(TFA) (4): To complete our investigation on halide abstractions using anions with different nucleophilicity, we finally used the TFA ($\text{TFA} = \text{CF}_3\text{CO}_2^-$) anion in the same reaction (as its AgTFA salt). TFA is usually considered a coordinating anion that in some cases however can form separated ion pairs.³⁴ The reaction of $(2,7\text{-SiCyNap})\text{Ir}(\text{COD})\text{Cl}$ (**1**) with AgTFA in DCM gave $(2,7\text{-SiCyNap})\text{Ir}(\text{COD})(\text{TFA})$ (**4**) as a yellow product in high yield (Scheme 1). Covalent coordination of the anionic ligand was deduced from ^1H NMR spectroscopy,³⁵ and was unambiguously confirmed by X-ray crystallographic analysis.²⁶ The ^1H NMR spectrum at room temperature indicated fluxional behavior of the compound. Upon cooling to -40°C , the broad signals sharpened and two species with an approximately 1:0.2 ratio were observed.³⁶ Elemental analysis of the bulk material is in good agreement with the sum formula of $(2,7\text{-SiCyNap})\text{Ir}(\text{COD})(\text{TFA})$. In the solid state, complex **4** (Figure 5) shows a slightly distorted square planar coordination around the iridium center with an η^1 -coordination of the TFA anion. The C-O bond length of the bound oxygen is somewhat elongated [$\text{O101-C101} = 1.272(5)$ vs $\text{O102-C101} = 1.196(6)$ and $\text{Ir1-O101} = 2.097(2)$ Å].

Figure 2. Crystal structure of the cation of **2**[BF_4]. Hydrogen atoms are omitted for clarity and the cyclohexyl groups are represented differently for the same reason. Ellipsoids are drawn at the 50 % probability level.

Figure 3. Crystal structure of the cation of **2**[NTf_2]. Hydrogen atoms are omitted for clarity and the cyclohexyl groups are represented differently for the same reason. Ellipsoids are drawn at the 50 % probability level.

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Figure 4. Crystal structure of the neutral complex **3a**. Hydrogen atoms are omitted for clarity and the cyclohexyl groups are represented differently for the same reason. Ellipsoids are drawn at the 50 % probability level.

2.2 Silver salt metathesis reactions in coordinating solvents

From these first experiments which were exclusively run in very weakly coordinating DCM as the solvent, it is already apparent that the equations in Chart 1 represent a simplified picture of the overall reaction. In our case, while the NTf_2^- anion followed equation 2 and the more nucleophilic TFA anion led to generation of the neutral complex according to equation 1, the reaction between **1** and AgOTf did not go to completion and gave the arrested intermediate **3** instead. When discussing Chart 1, we mentioned that frequently, these halide abstraction reactions are run in coordinating solvents (equation 3), the general consensus being that this approach helps deliver the ionized species.

Figure 5 Crystal structure of neutral complex **4**. Hydrogen atoms and the minor components of the disordered atoms are omitted for clarity and the cyclohexyl groups are represented differently for the same reason. Ellipsoids are drawn at 20 % probability level.

Synthesis of [(2,7-SiCyNap)Ir(COD)(CH_3CN)]/[OTf]([5]/ PF_6)] and of [(2,7-SiCyNap)Ir(COD)(CH_3CN)]/[PF₆]/[5]/[OTf]].^[37] One of the most popular coordinating solvents in silver-promoted anion exchange reactions where solvent-stabilized cationic LTMs are generated is acetonitrile. Not

surprisingly given the ample literature precedents, **5**[PF₆] can be prepared in high yield from (2,7-SiCyNap)Ir(COD)Cl if the halide abstraction using AgPF₆ is carried out in acetonitrile instead of DCM (Scheme 1). Alternatively, treatment of 'naked' cation **2**[PF₆] in DCM with excess CH₃CN cleanly gave the same solvento complex **5**[PF₆] (Scheme 1). A more interesting question that arises from these results is whether acetonitrile is capable of abstracting AgCl from our arrested iridium-silver intermediate **3**, where non-coordinating DCM was not able to bring about ionization of the complex. Indeed, upon addition of excess CH₃CN to [(μ-Cl)-{(2,7-SiCyNap)Ir(COD)}·{Ag(OTf)}] (**3**) in DCM, almost instant precipitation of AgCl occurred. The ¹H NMR spectrum clearly indicated the formation of an CH₃CN complex, similar to [(2,7-SiCyNap)Ir(COD)(CH₃CN)][PF₆] (**5**[PF₆]). Compared to complexes **2**, the NHC ligand in **5**[PF₆] and **5**[OTf] loses its apparent C₂ symmetry in the solution phase.²³ The carbene carbon atom was found at 200.5 ppm in the ¹³C NMR spectra, confirming the existence of the cationic metal center and the disappearance of the tilted NHC-Ir bond, where the carbenic signal is significantly shifted to lower ppm values.³⁸ In the solid state, **5**[PF₆] crystallizes with 2.75 equivalents of DCM (Figure 6).²⁶ The triflate analogue, **5**[OTf] (Figure S3), crystallizes with one molecule of DCM.²⁶ In the cations of both **5**[PF₆] and **5**[OTf], the expected square planar coordination around the metal can be observed. The Ir1-C1 distances {Ir1-C1 = 2.059(3) and 2.054(3) Å for **5**[PF₆] and **5**[OTf], respectively} are not significantly different from the distances seen in **2**[PF₆] and the common precursor (2,7-SiCyNap)Ir(COD)Cl (**1**) [2.038(2) and 2.052(5) Å, respectively]. The acetonitrile ligand is *cis* to the NHC, and bond distances are Ir1-N101 = 2.041(3) and 2.034(2), and N101-C101 = 1.131(4) Å and 1.122(4) Å for **5**[PF₆] and **5**[OTf], respectively. Surprisingly, these are the first X-ray structures of an [(NHC)Ir(CH₃CN)(COD)]⁺ complex with an Arduengo-type NHC.

Figure 6. Crystal structure of the cation of **5**[PF₆]. Hydrogen atoms are omitted for clarity and the cyclohexyl groups are represented differently for the same reason. Ellipsoids are drawn at the 50 % probability level.

Synthesis of [(2,7-SiCyNap)Ir(COD)][(CH₃)₂CO][PF₆] (6**[PF₆]):** We next moved to the weaker binding acetone molecule as a potential neutral 2-electron donor ligand (Scheme 1, top left). Unfortunately, switching to acetone as a reaction medium / donor solvent already led to incomplete halide abstraction between complex **1** and AgPF₆ and isolation of an intractable mixture of products.³⁹ The acetone-stabilized analogue of **5**[PF₆] was nevertheless obtained by dissolving

2[PF₆] in (CH₃)₂CO. Subsequent workup and crystallization gave **6**[PF₆] as yellow crystals in good yield (64% yield).²⁶ Low temperature ¹H NMR data at 233 K in DCM-d₂ and in acetone-d₆ at 273 K confirmed the formation of **6**[PF₆]. The carbene carbon atom was found at 202.1 ppm in the ¹³C NMR spectra (DCM-d₂) with the carbonyl carbon of the acetone molecule located at 223.4 ppm. The crystal structure of the cation of **6**[PF₆] is shown in Figure 7. The coordination geometry around the iridium is square planar. The Ir1-C1 distance is 2.061(5) Å. The acetone ligand is *cis* to the NHC; the Ir1-O10 = 2.110(3) Å and O10-C10 = 1.237(6) Å. The plane of the acetone molecule is oriented approximately parallel to one of the naphthyl wingtips. The dihedral angle is 14.6°, the closest approach C10...C58A 3.273(6) Å. Most notably, it is rather surprising that complex **6**[PF₆] seems to represent the first X-ray structure of any iridium(I)-acetone complex in the literature.⁴⁰

2.3 Silver salt metathesis reactions in aromatic solvents

Aromatic solvents such as toluene, benzene or fluorobenzene are a group of solvents that have been used quite extensively in silver salt metathesis reactions. One of the main reasons for this choice might lie in the simple fact that they are able to solubilize the starting silver salts. Another noteworthy aspect is that at least in cases where η⁶-coordination of the aromatic ring to the metal is not possible as is the case with our system, these solvents can be considered as non- or very weakly coordinating. We therefore set out to see if toluene or benzene could be used instead of DCM with a particular focus on the question of whether reaction between **1** and AgOTf would favor complete ionization when carried out in toluene or benzene.

Figure 7. Crystal structure of the cation of **6**[PF₆]. Hydrogen atoms are omitted for clarity and the cyclohexyl groups are represented differently for the same reason. Ellipsoids are drawn at the 50 % probability level.

*Reaction of (2,7-SiCyNap)Ir(COD)Cl (**1**) with AgOTf in benzene or toluene:*

In the hope of being able to access a cationic complex **2** with the OTf counterion, we repeated the procedure of treating (2,7-SiCyNap)Ir(COD)Cl (**1**) with AgOTf in benzene-d₆ or toluene-d₈ instead of DCM. Unfortunately, after appropriate workup, the identical product produced using DCM as solvent, namely [(μ-Cl)-{(2,7-SiCyNap)Ir(COD)}·{Ag(OTf)}] (**3**),

was isolated in high yields (87%, 87%) with matching spectroscopic and elemental analyses data (Scheme 1). These experiments confirm that the formation of **3** is independent of the reaction media used, meaning that DCM, toluene as well as benzene do not promote abstraction of AgCl in this case. To make sure that slight variations in the structure of **3** are not going unnoticed, we prepared crystals suitable for X-ray diffraction from slow diffusion of pentane into a concentrated toluene solution containing **3** (from the reaction run in toluene) or from directly growing crystals from a mixture of starting materials in benzene (see the Supporting Information for details).²⁶

The structure of **3** was therefore solved as DCM (**3a**), pentane (**3b**, grown from toluene/pentane) and C₆D₆ solvates, the last being determined as both low temperature (**3c**) and high temperature (**3c'**) polymorphs. In the solid state, **3** contains a (μ-Cl)AgIr motif. Bond distances and angles in this motif are in the range of Ir-Cl = 2.3739(5)-2.3859(9) Å, Ir-Ag = 2.7963(3)-2.8159(2) Å, Ag-Cl = 2.5836(7)-2.6113(6) Å and Ir-Cl-Ag = 68.59(1)-68.87(2)°. The Ag cation is also coordinated to the OTf anion [Ag-O = 2.195(5)-2.301(2) Å]. There is a close contact between the Ag-center and the C8a atom of the naphthyl ring [Ag-C8a = 2.645(4)-2.748(2) Å]. Selected bond lengths and angles for **3a** are shown in Table 2.

The solvates and polymorphs of **3** differ in the incorporated solvent molecules and in the OTf anion's orientation with the structure of **3a** showing a weak interaction between the Ag and a second oxygen atom of the OTf [Ag-O2 = 2.8787(2) Å]. As noted above, a single crystal of the C₆D₆ solvate went through an interesting phase transition by warming up the crystal from 100 K to 200 K. The cell dimensions of both are similar ~16.7 × ~21 × ~18 Å, α, γ ~90°, β ~115°, but **3c'** is monoclinic (Z'=1) and **3c** is triclinic (Z'=2). Figures of the crystal structures of the solvates and polymorphs **3b**, **3c**, **3c'** are included in the Supplementary Information (Figures S1-S2).

Reaction of (2,7-SiCyNap)Ir(COD)Cl (**1**) with AgTFA in benzene or toluene:

Obviously, generation of **3** in toluene and benzene raised the question of whether reaction outcomes between **1** and our other silver salts would follow the same logic and furnish complexes analogous to the ones we had seen in DCM (Scheme 1). Indeed, this was the case with AgTFA, where reaction with **1** in benzene (or toluene) gave the same complex **4** in high yield (in this case, we did not deem it necessary to reconfirm its solid state).

Synthesis and characterization of [(μ-Cl)-{(2,7-SiCyNap)Ir(COD)}-{Ag(η²-tol)}][PF₆] (**7[PF₆]**) and [(μ-Cl)-{(2,7-SiCyNap)Ir(COD)}-{Ag(η²-tol)}][PF₆] (**7[NTf₂]**):

A distinctively different reaction pathway to the one seen in DCM was observed when we tried to extract the chloride using the least nucleophilic WCAs, the PF₆ and the NTf₂ anions. When (2,7-SiCyNap)Ir(COD)Cl (**1**) was treated with AgPF₆ or AgNTf₂ in toluene, orange solutions formed and AgCl precipitation was not observed (Scheme 1). The upfield shift of one of the H8 atoms (see discussion under 2.4) and the otherwise general downfield shift in their ¹H NMR spectra indicated the formation of iridium-silver adducts. The composition of the compounds was further confirmed by elemental analyses. Both complexes readily crystallized from toluene upon standing or by diffusion of pentane into a toluene solution containing the compounds and ensuing X-ray diffraction

analyses identified them as the unusual solvent-stabilized Ir-Ag complexes [(μ-Cl)-{(2,7-SiCyNap)Ir(COD)}-{Ag(η²-tol)}][PF₆] (**7[PF₆]**) and [(μ-Cl)-{(2,7-SiCyNap)Ir(COD)}-{Ag(η²-tol)}][PF₆] (**7[NTf₂]**) respectively.²⁶

A sample of complex **7[PF₆]** crystallized with two independent molecules in the asymmetric unit as a 2×C₇H₈ solvate.^[41] Similarly to **3**, compound **7[PF₆]** contains a (μ-Cl)AgIr motif, although **7[PF₆]** is an ionic complex, where the Ag cation is coordinated to a toluene molecule instead of the anion. The structure of one of the cations (**7[PF₆]**a****) is shown in Figure 8, while the structure of the other cation (**7[PF₆]**a'****) is shown in the Supplementary Information (Figure S4). The difference between the structures of the two cations is largely confined to the orientation of the toluene molecule which is η²-bound to the Ag-center. In cation **7[PF₆]**a****, the two toluene atoms (meta and para) closest to the Ag1 atom are C103 [2.446(15) Å] and C104 [2.525(18) Å]. In cation **7[PF₆]**a'****, the closest atoms (ortho and meta) to Ag2 are C202 [2.486(14) Å] and C203 [2.404(12) Å]. There is also a relatively close contact between the Ag-center and the C8 carbon atom of one of the naphthyl rings [Ag1-C128 = 2.691(9) Å] for cation **7[PF₆]**a****. Larger distances, and possibly an η²-interaction, are present in cation **7[PF₆]**a'**** [Ag2-C228 = 2.864(9) Å and Ag2-C220 = 2.800(9) Å]. Selected bond lengths and angles are shown in Table 2.

Figure 8. Crystal structure of the cation of **7[PF₆]**a****. Hydrogen atoms are omitted for clarity and the cyclohexyl groups are represented differently for the same reason. Ellipsoids are drawn at 20 % probability level.

The structure of **7[NTf₂]** is similar to that of **7[PF₆]**a****. The Ir and the Ag atoms are bridged by the Cl atom to create a three membered metallacycle motif [Ir-Ag = 2.8305(4), Ir-Cl = 2.373(1), and Ag-Cl = 2.601(1) Å] (Figure 9). The Ag-center is η²-bound to a toluene molecule. There is a close contact between the Ag atom and the C8 carbon atom of the naphthyl ring [Ag1-C28 = 2.698(5) Å]. The anion is disordered over two sites and has no contact with either metal atoms.

In terms of reactivity, complexes **7[PF₆]** and **7[NTf₂]** show similar behavior to complex **3** when dissolved in acetonitrile, where precipitation of AgCl is instantaneous and gives the corresponding solvent-stabilized complexes **5[PF₆]** and **5[NTf₂]**.³⁶ Obviously and in contrast to complex **3**, simple dissolution of complexes **7** in DCM is also bringing about complete ionization and formation of compounds **2** as also discussed in the catalytic section below.

Table 1. Relevant bond lengths and angles in neutral and cationic iridium-only compounds.

	1 (X = Cl)	2[PF ₆]	2[BF ₄]	2[NTf ₂]	4 (X = O)	5[PF ₆] (X = N)	5[OTf] (X = N)	6[PF ₆] (X = O)
Ir-C1 (Å)	2.052(5)	2.038(2)	2.043(5)	2.043(2)	2.045(3)	2.059(3)	2.054(3)	2.061(5)
Ir-C11 (Å)	2.194(5)	2.181(2)	2.163(5)	2.195(2)	2.188(4)	2.202(3)	2.195(3)	2.199(5)
Ir-C12 (Å)	2.173(6)	2.224(2)	2.213(5)	2.227(2)	2.180(3)	2.192(3)	2.189(3)	2.194(5)
Ir-C15 (Å)	2.121(5)	2.091(2)	2.095(5)	2.102(2)	2.113(3)	2.146(4)	2.139(3)	2.112(5)
Ir-C16 (Å)	2.113(6)	2.114(2)	2.105(5)	2.118(2)	2.110(3)	2.143(3)	2.134(3)	2.112(5)
Ir-X (Å) ^a	2.350(1)	-	-	-	2.097(2)	2.041(3)	2.034(3)	2.110(3)
Ir-C8 (Å) ^b		2.544(2)	2.551(5)	2.527(2)				
Ir-C8a (Å) ^b		2.413(2)	2.428(5)	2.449(2)				
Ir-C1-N2 (°)	126.0(4)	145.0(1)	144.0(4)	142.0(2)	125.9(2)	124.7(2)	124.23(19)	127.3(3)
Ir-C1-N5 (°)	127.2(4)	106.7(1)	106.5(3)	108.7(1)	126.9(2)	127.9(2)	129.23(19)	125.6(3)

^a X = Cl or heteroatom coordinated to Ir. ^b C8 and C8a are not according to crystallographic numbering. On the corresponding figures, these are typically numbered C58 and C58A.

Figure 9. Crystal structure of the cation of 7[NTf₂]. Hydrogen atoms and the atoms of the minor component of the disorder are omitted for clarity and the cyclohexyl groups are represented differently for the same reason. Ellipsoids are drawn at the 20 % probability level.

Synthesis and characterization of (2,7-SiCyNap)Ir(COD)Cl·TIBF₄ (8):

Having completed the studies on the halide abstraction and its outcome from **1** using different solvent classes and anions of varying nucleophilicity, we also wanted to assess the viability of alternative cations (to Ag) in this metathesis reaction. To do so and in line with literature data, we chose a representative thallium salt (TIBF₄), with a cation that is considered to be an excellent halide abstracting agent and is indeed preferred in cases where the potentially oxidizing silver ion is not desired.^{10,20,42}

When a suspension of TIBF₄ in DCM was treated with (2,7-SiCyNap)Ir(COD)Cl (**1**), the color changed from yellow to orange in less than an hour (Scheme 2). Upon filtration and

evaporation of the solvent, an orange crystalline solid was isolated in high yield (98%). ¹H NMR clearly indicated formation of a new species. All analytical data were in agreement with the formation of an adduct compound with formula (2,7-SiCyNap)Ir(COD)Cl·TIBF₄ (**8**). This result is in stark contrast to the one recorded for **1** and AgBF₄ in DCM, where halide abstraction is instantaneous and leads to the cationic compound 2[BF₄].

Scheme 2. Reaction between 1 and AgBF₄ (left) or TIBF₄ (right) in DCM.

2.4 Discussion of the solid state structure of complexes 1-7

The solid-state structures of solvent stabilized, cationic complexes 5[PF₆], 5[OTf] and 6[PF₆], as well as of the neutral complex **4** are very similar to the parent chloro-iridium compound **1** (Types 1 and 3 respectively in Figure 10). All of these complexes show an only very slightly distorted square-planar coordination around the iridium atom. The nature of the small monodentate ligand (chloride, CH₃CN, acetone or trifluoroacetate) does not substantially alter the electronic situation in the complexes, with the Ir-(olefin) distances trans to the sigma-donating oxygen-donor ligands (acetone in 6[PF₆], trifluoroacetate in **4**) only slightly shorter than observed in the chloro (**1**) and the acetonitrile compounds 5[PF₆] and 5[OTf].

Moving to the Type 4 cationic complexes 2[PF₆], 2[BF₄], and 2[NTf₂] (Figure 10, bottom center), the main feature consists of the tilt of the NHC structure that allows one of the aromatic wingtips to approach the metal center and to engage in an arene-metal interaction that involves the C8 and C8a carbon atoms of the corresponding naphthyl unit. This affords disparate Ir-C1-N2 and Ir-C1-N5 angles and leads to a pseudo-square-planar coordination around the metal center. The major

interaction between the iridium center and the naphthyl unit in these structures reveals bond distances of 2.413(2)–2.449(2) Å between Ir–C8a, while a second, weaker interaction is present with the adjacent C8 (>2.53 Å). The Ir–C1(NHC) bond distance does not change significantly upon halide abstraction, but in order to accommodate the interaction with the naphthyl side chain, the N-heterocycle of the ligand is rotated by about 90° compared to the COD ligand. There is a slight shortening of the Ir-(olefin) distance of COD trans to the aromatic interaction with the wingtip group, indicating higher electron back-donation from the iridium center into the π^* orbital of the olefinic binding site.

Figure 10. Schematic representation of types of neutral complexes (top row) and cationic complexes (bottom row) synthesized in this study.

Table 2. Bond lengths and angles in Ir–Ag complexes.

	3a (L = η^1 -OTf)	7[PF₆]a (L = η^2 -tol)	7[PF₆]a' (L = η^2 -tol)	7[NTf₂] (L = η^2 -tol)
Ir–C (Å) ^[a]	2.035(2)	2.035(8)	2.038(9)	2.041(5)
Ir–Cl (Å)	2.3739(5)	2.379(2)	2.371(3)	2.373(1)
Ir–Ag (Å)	2.8159(2)	2.892(1)	2.806(1)	2.8305(4)
Ag–Cl (Å)	2.6113(6)	2.562(3)	2.583(3)	2.601(1)
Ag–C8 (Å) ^[b]	3.323(2)	2.69(1)	2.864(9)	2.698(5)
Ag–C8a (Å) ^[b]	2.748(2)	2.90(1)	2.800(9)	2.929(5)
Ag–L (Å)	2.301(2)	2.45(2)	2.49(2)	2.453(6)
Ag–L (Å)	-	2.52(2)	2.40(1)	2.527(7)
Ir–C–N2 (°) ^[c]	130.9(2)	131.4(7)	132.3(7)	130.4(3)
Ir–C–N5 (°) ^[c]	121.9(1)	121.0(6)	119.5(7)	122.0(3)
Ir–Cl–Ag (°)	68.59(1)	71.53(7)	68.86(7)	69.20(3)
Ag–Ir–Cl (°)	59.70(1)	57.17(6)	59.15(6)	59.19(3)

[a] C = carbene atom. [b] C8 and C8a are not according to crystallographic numbering. [c] The crystallographic numbering for N2 and N5 is as follows: in **7[PF₆]a** N2 = N12, N5 = N15; in **7[PF₆]a'** N2 = N22, N5 = N25

The iridium–silver bimetallic complexes **3** (Type 2), **7[PF₆]**, and **7[NTf₂]** (Type 5) represent some unique features where we also observed that various crystallization techniques led to the crystallization of different polymorphs or solvates (for **3** and **7[PF₆]**). For a general discussion of these structures, we selected complex **7[NTf₂]** and the crystal structure of **3a**. The-

se structures can be considered as being constituted of three structural motifs: a) a [(2,7-SiCyNap)Ir(COD)(μ -Cl)] moiety; b) a chloride bridged Ir–Ag core; c) and a four-coordinate silver cation.

The overall coordination geometry around the two metals does not fall into one of the classical categories found for 5-coordinate complexes. Around the iridium metal center, it is best viewed as a distorted square pyramidal arrangement, where the (NHC)Ir(COD)Cl forms the plane of the square and the silver is at the vertex of the pyramid.

a) Description of the [(2,7-SiCyNap)Ir(COD)(μ -Cl)] moiety: The parent (2,7-SiCyNap)Ir(COD)Cl motif is only marginally affected by the coordination of the fifth silver(I) ligand. E.g., the Ir–Cl bond length is slightly longer than in **1** {by ca. 0.03 Å, e.g. 2.373(1) Å for **7[NTf₂]**, 2.3739(5) Å for **3a**, 2.350(1) Å for **1**}. The orientation of the NHC ligand is perturbed by the underlying silver cation (under the B ring of one of the naphthyl groups). This results in tilting of the NHC ring and gives disparate Ir–C1–N2 and Ir–C1–N5 angles in the range of 130–133° and 121–123° respectively, the larger angle being on the side where the silver cation is present {e.g. 130.4(3)° and 122.0(3)° for **7[NTf₂]**, 130.9(2)° and 121.9(1)° for **3a**}.

b) The chloride bridged Ir–Ag core: The Ir–Ag distances are ranging from 2.75–2.89 Å for our complexes {e.g. complex **7[NTf₂]**: 2.8305(4) Å; and complex **3a**: 2.8159(2) Å}, while the Ag–Cl distances are at 2.56–2.64 Å {typical examples: 2.601(1) Å for **7[NTf₂]**, 2.6113(6) Å for **3a**}. These distances result in acute Ir–Cl–Ag angles for the chloro-bridged motif {e.g. 69.20(3)° for **7[NTf₂]**, 68.59(2)° for **3a**}.

To compare these values to the most relevant other examples in the literature, we compiled data of attempted halide abstraction from Vaska's complex showing the Ir–Ag motif,¹⁶ and crystallographic information gathered from d⁸-metal [Pt(II)]–Ag complexes.⁴³ As can be seen on Figure 11, our Ag–Cl distances may best be compared to some of the platinum structures reported by Usón et al. In fact, the Vaska-type compounds do not show bonding between Ag and Cl (Ag–Cl distances described in the literature are in the range of 2.28 – 3.00 Å).^{44,45,46,47c} The Ir–Ag distances that we observe are in turn significantly longer than the ones seen in the Vaska-type compounds and again correspond more to the values reported for some of the Pt(II) complexes. Overall, the Ir–Ag distances are perfectly in line with reported values that vary between 2.61–3.03 Å.^{16,17,47}

c) The four-coordinate silver cation: The silver cation is in principle tetra-coordinated with bond distances well within the corresponding van der Waals radii.⁴⁸ One of these bonds, namely the one between the silver atom and the C8 or C8a atoms of the naphthyl wingtip, shows long distances (in the order of 2.7 Å) and consequently a weak η^1 -interaction. Furthermore, the Ag center is either coordinated to a solvent molecule (**7[PF₆]** and **7[NTf₂]**) or to the anion (**3**). In **3a**, a short Ag–O distance was observed [Ag–O = 2.301(2) Å] and the triflate anion was coordinated in a monodentate fashion.⁴⁹

The toluene coordinated complexes **7[PF₆]** and **7[NTf₂]** display an η^2 -arene–silver coordination. Silver–arene interactions were studied in detail in the past, most notably by Kochi et al.⁵⁰ These authors found that there was no apparent preference for η^1 - or η^2 -coordination and saw that the distance of the silver atom from the mean plane of the aromatic ring(s) varied only very slightly in all crystallographically characterized

complexes ($d = 2.41 \pm 0.05 \text{ \AA}$). This is in line with what we observe for the silver-toluene interactions in **7**[PF₆] and **7**[NTf₂], while the numbers that we see for our Ag-NHC(wingtip) interactions clearly underline the fact that these are well outside normal covalent bonding distances.⁴⁸

X	Ag-Ir (Å)	Ag-Cl (Å)	Cl-Ir-Ag (°)	Ref.
Br ₅ CB ₉ H ₅	2.631(5)	3.73(2)	94.4(4)	[16b]
B ₁₁ H ₁₂	2.683(1)	3.975(2)	104.33(4)	[16a]
NTf ₂	2.6074(3)	3.920(1)	104.82(3)	[16c]

Aryl	Ag-Pt (Å)	Ag-Cl (Å)	Cl-Pt-Ag (°)	Ref.
C ₆ F ₅	2.797(2)	2.474(5)	56.8(2)	[43b]
C ₆ Cl ₅	2.781(1)	2.667(3)	62.15(6)	[43c]

Ag-Pt (Å)	Ag-Cl (Å)	Cl-Pt-Ag (°)	Ref.
2.945(2)	2.514(3)	55.37(8)	[43d]

Figure 11. Bonding situation in related Ag(I)-Ir(I) and Ag(I)-Pt(II) complexes.

Stereochemistry in Ir-Ag complexes:

What we have not mentioned so far is another feature of these complexes that sets them apart from the reported complexes shown in Figure 11. Contrary to these, our compounds incorporate a *cis*-chelating ligand (COD), that in conjunction with the other monodentate ligands render these complexes chiral at the metal center. Together with the fact that they have, at the same time, a chiral but racemic NHC ligand means that we can in principle expect diastereomeric mixtures in these compounds. It is noteworthy to indicate that the crystals that were measured (for **3**, **7**[PF₆], **7**[NTf₂]) show racemic mixtures of only one of the possible enantiomeric pairs, namely the *C,R_a,R_a* and *A,S_a,S_a* pair.

2.5 Structural discussion of complexes 1-8 in solution

NMR spectroscopic analysis of complexes:

Solution phase analyses of the Type 4 cationic complexes **2**[PF₆], **2**[BF₄] and **2**[NTf₂] corresponds well with the solid-state architectures that we observe. The cation of these compounds is essentially the same for all three complexes. The NHC ligand appears to be *C*₂-symmetric on the ¹H NMR time-scale,^{23b} while the COD ligand remains static. However, in the ¹³C NMR spectra, the interaction with the naphthyl ligand is evidenced by an upfield shift and broadening for the C8 and C8a carbon atoms [δ (C8) = 107 and δ (C8a) = 123 ppm]. In line with earlier observations (and calculations) for complex **2**[PF₆],²³ the tilt of the N-heterocycle of the NHC leads to a carbene atom that shows a high upfield shift and is located at ca. 16-22 ppm lower than cases where the NHC is not significantly tilted (Types 1,2,3,5). Finally, the corresponding signals for the anions can be found in the ¹³C (for compound **2**[NTf₂]) and ¹⁹F NMR spectra.

Figure 12. Stacked view of the ¹H NMR spectra of **1** (red) and **3** (blue) in DCM-d₂, showing the shifting of the signal for the H8 atoms.

Unambiguous NMR spectroscopic analysis of the hetero-bimetallic complexes (Types 2 and 5; complexes **3**, **7**) proved to be rather difficult with some of these complexes showing what appear to be signals of the minor diastereomer pair in solution. When the ¹H NMR spectra of parent **1** and Ir-Ag adduct **3** in DCM-d₂ are compared (Figure 12), the most evident change is the upfield shift of a naphthyl H8 proton from 8.18 to 7.86 ppm (δ values given for **1** and **3** respectively). This translates well into the ¹³C NMR spectra of these compounds, where the C8 vs C8' signals in **1** [δ (C8) = 125.1 and 120.71 ppm] are showing at rather different ppm values, while the C8/C8' signals in **3** [δ (C8) = 120.42 and 119.37 ppm] are within 1 ppm of each other. Because both **1** and **3** do not show significant tilting of the NHC, the carbenic carbon signal is appearing at the expected downfield range.

Rotation around the NHC-Ir bond:

The complexes synthesized in this study showed diverse rotational behavior around the Ir-NHC bond as evidenced by ¹H NMR spectroscopy. Fast rotation, even at low temperatures, was observed in Type 4 (Figure 10) complexes. Type 3 compounds and the TFA compound **4** featured broad signals at 298 K, however resolution of the peaks occurred upon cooling in the temperature range of 273 - 233 K. On the other extreme,

complexes **1** and **3** proved to be rotationally rigid as evidenced when looking at the ^1H - ^1H NOESY NMR spectrum **1** in Figure 13. In this case, cross-peaks arising from NOE interactions between the H8' atom (7.63 ppm) and specific hydrogens of the CH=CH moiety of the COD ligand were distinct and could be located, underlining the static nature of the NHC-Ir in solution.

Figure 13. Excerpt from the ^1H - ^1H NOESY spectra of **1**. Cross-peaks between H8' atom and olefinic protons are highlighted in red. Dashed lines show the ^1H NMR resonance of the CH=CH units of the COD ligand.

Spectroscopic discussion of (2,7-SiCyNap)Ir(COD)Cl-TlBF₄ (**8**):

While the solid-state structure of the thallium adduct **8** was not determined, the ^1H NMR spectrum of **8** in DCM- d_2 is similar but noticeably different to that of the starting chloro complex **1**. There is an upfield shift of the H8 protons [$\delta(\text{H8}) = 8.18$ ppm for **1**, $\delta(\text{H8}) = 8.06$ ppm in **8**], a value that incidentally lies between that of **1** and the silver-iridium adduct **3**. [$\delta(\text{H8}) = 7.86$ ppm for **3**]. The olefinic signals located trans to the Cl ligand move

progressively downfield when going from **1** to **8** to **3**. This deshielding is consistent with an increasingly stronger interaction of the univalent metal center with the chloride ligand and the loss of electron density at the olefinic end resulting from it. In the ^{13}C NMR spectrum, the carbene atom was located at 206.25 ppm, meaning well below the value of **1** and in line with values recorded for the Ir-Ag compounds. Whether **8** shows similar structural features to our Ir-Ag complexes is not clear, but the lack of two distinct C8 atoms around 121-119 ppm, together with the ^1H NMR data on the only small upfield shift of the H8 atom would indicate a binding situation where interactions of the thallium metal with the ligand framework are negligible or absent.

2.6 Catalytic performance of Ir-only and Ir-Ag adduct complexes

The series of Ir(I) complexes featuring different WCAs as well as the unusual Ir-Ag complexes that we were able to characterize above naturally led us to wonder how these compounds would behave when used as well-defined species in catalysis.

Table 3. Catalytic performance of (NHC)Ir and (NHC)Ir-Ag complexes in the hydroamination/cyclization of amino alkene **9**.

Precatalyst	Method	Conversion (%) ^{a,b}
[(2,7-SiCyNap)Ir(COD)]PF ₆ (2 [PF ₆])	A	>99
[(2,7-SiCyNap)Ir(COD)][BF ₄] (2 [BF ₄])	A	65
[(2,7-SiCyNap)Ir(COD)][NTf ₂] (2 [NTf ₂])	A	>99
(2,7-SiCyNap)Ir(COD)(TFA) (4)	A	trace
[(μ-Cl)-{(2,7-SiCyNap)Ir(COD)}]·[Ag(η ² -tol)] [PF ₆] (7 [PF ₆])	B	>99
[(μ-Cl)-{(2,7-SiCyNap)Ir(COD)}]·[Ag(η ² -tol)] [PF ₆] (7 [PF ₆])	C	trace

General conditions: 0.3 mmol **9**, 0.5 mL DCM- d_2 . Method A: 2 mol% catalyst added from a stock solution. Method B: 4 mol% catalyst in DCM- d_2 was stirred for an hour, then added to **9**. Method C: 4 mol% catalyst was added as a solid to **9** in DCM- d_2 . ^a Determined by ^1H NMR analysis after 1.5 hours. ^b 3:2 diastereomeric ratio.

As a model reaction for our investigations, we chose the cyclization of N-benzyl-2-phenylpent-4-en-1-amine (**9**) in DCM- d_2 (0.5 M), following the conversion by ^1H NMR spectroscopy. The results of these intramolecular hydroaminations are shown in Table 3. The first entry using catalyst **2**[PF₆] was not surprising given our previously published results.²³ Complex **2**[BF₄], which is more prone to decomposition, showed attenuated reactivity. Complex **2**[NTf₂], the other cationic Type 4 compound (Figure 10) that incorporates a weakly coordinating anion, was as effective as **2**[PF₆] in the reaction, giving quantitative conversion to product **10**. When the neutral TFA complex **4** (Type 1 in Figure 10) was used instead, reactivity shut down entirely, highlighting the fact that the cationic species with the empty coordination site is not generated (TFA remains tightly bound). The most revealing and intriguing results came when we switched to the arrested Ir-Ag intermediate **7**[PF₆], itself the immediate precursor to reference catalyst **2**[PF₆]. Here, we purposely chose two different loading procedures for the catalytic runs. In one, we premixed **7**[PF₆] for one hour in DCM- d_2 before transferring the content into an NMR tube containing substrate **9**. This clearly led to complete product formation (**10**) over the next 90 minutes, with precipitation of AgCl already at the first stage. This result is indeed expected as formation of **2**[PF₆] from **7**[PF₆] is straightforward in DCM. The second catalytic run was initiated by adding catalyst **7**[PF₆] as a solid into a stirred DCM- d_2 solution containing substrate **9**. Analysis of this latter reaction mixture

after 90 minutes not only showed no visible precipitation of AgCl, but also led to no product formation even if left over 24 hrs. The most straightforward interpretation of this result would be to propose that the aminoalkene substrate **9** is able to stabilize the Ir-Ag species to such an extent that formation of cationic (and catalytically active) **2**[PF₆] in DCM is no longer possible.

3. CONCLUSIONS

When planning the synthesis of cationic complexes that are not solvent stabilized, the choice of the WCA is usually thoroughly considered and relevant documentation in the literature on the importance of the nucleophilicity (or lack thereof) of the WCA abounds.^{10,27} In turn, relevant references that discuss the influence of the reaction medium and go beyond the simple distinction of coordinating vs non-coordinating solvent are rare. Furthermore, only passing references are made with regards to the subject of choosing the univalent metal (M') in eq. 2 of Chart 1) in these salt metathesis reactions.

With the study presented in this paper, we have seen how all three of these factors (nucleophilicity of the WCA, solvent used, univalent metal used) can have a large impact on the outcome of these salt metathesis reactions using a single precursor molecule.

For instance, the study here shows how the outcome of the silver metathesis reaction can lead to either an intermediate or to the product of the metathesis reaction event when employing silver salts that incorporate very weakly nucleophilic anions (PF₆, NTf₂). In these cases, a seemingly innocent switch of solvent from DCM to benzene/toluene (both considered non- or very weakly coordinating solvents) leads to generation of highly unusual, cationic Type 5 complexes. These complexes show no apparent contact between the cationic part of the structure and the anion.⁵¹

When moving to the more nucleophilic OTf anion, generation of the Type 4 compound was not attainable any longer. Independent of the reaction medium used (DCM, toluene, benzene), a bimetallic Ir-Ag complex (Type 2) was isolated. Only a further increase in nucleophilicity of the anion (TFA) brings about a situation favorable enough to drive the reaction to completion with covalent bonding of the TFA moiety to iridium in a simple Type 1 complex.

As an alternative to using more nucleophilic anions such as TFA, dissolving Type 2 and Type 5 complexes in a coordinating solvent such as acetonitrile drives the metathesis reaction to completion and generates the expected solvent stabilized iridium salts **5**.

Mechanistically, the results that we have gathered here are of particular note as they do not, at first glance, seem to follow silver-halide bonding proposed in the classical reaction pathway that involves a halide-bridged acid-base intermediate (Scheme 3, structure **A**). Reed et al. and more recently Bohle have observed silver-metal adducts for Vaska's complex during these arrested metathesis reactions (Scheme 3, structure **B**), but no clear mechanistic scenario that would propose involvement of such a species in the overall mechanism was put forth.¹⁶

The intermediates that we have isolated here during salt metathesis of (NHC)Ir(COD)Cl are the first examples of hybrid structures, i.e. of structures with a chlorine-bridged metallacyclic motif, evolving from such reaction with silver salts. This would lend credence to the notion that these species are actual later-stage intermediates during the silver promoted halide abstraction. Supporting this idea is not only the observation that a non-coordinating solvent such as DCM can already drive the reaction to completion (in **7**[PF₆] and **7**[NTf₂]), but also the fact that the overall electronic situation of the starting complex (slightly more electron-rich as compared to Vaska's complex) would favor such a scenario with a later-stage intermediate. As depicted in Scheme 3, both the early silver-halide (**A**) as well as the silver-metal intermediates (**B**) would therefore collapse to either form the cationic, solvent stabilized structure **C** (with very weakly coordinating anions) or the neutral type structure **D**. Whether structure **D** is an earlier intermediate than structure **C** or whether generation of these (**C** or **D**) simply depends on the bonding situation of the silver salt is not clear at this point.

Scheme 3. A plausible, general mechanistic scenario for the silver salt metathesis reaction.

A further insightful result of our study comes from directly comparing the reactivity of AgBF₄ and TlBF₄ in DCM. While halide abstraction using the silver salt proceeds smoothly to give the cationic species, univalent thallium is not able to provide more than an adduct where spectroscopic data, while not conclusive, would suggest an early arrested intermediate of either type **A** or type **B**.

Finally, and going beyond the discussion on mechanistic aspects of these halide abstraction reactions, our catalytic results highlight once more that well-defined and silver-free (pre)catalysts should be used whenever catalytic performances of cationic complexes are being assessed. As pointed out in the introduction, some studies do exist that try to clarify and interpret different experimental approaches to the generation of catalytically active cationic Au(I) catalysts using the silver salt metathesis approach. The last entry in Table 3 adds another layer of complexity to the discourse by showing that the presence of substrate may by itself inhibit proper generation of the active catalytic species by favoring and stabilizing inactive M-Ag intermediates.

4. EXPERIMENTAL SECTION

General considerations. All reactions were carried out using standard Schlenk or glovebox (Innovative Technology) techniques under nitrogen (Schlenk lines) or argon (gloveboxes).

(2,7-SiCyNap)Ir(COD)Cl (**1**), [(2,7-SiCyNap)Ir(COD)][PF₆]₂ [PF₆], and N-benzyl-2-phenylpent-4-en-1-amine (**9**) was prepared according to literature procedures.²³ [(2,7-SiCyNap)Ir(COD)(CH₃CN)][PF₆] (**5**[PF₆]) has been described previously,²³ a modified procedure and further characterization is included in the Supporting Information. TIBF₄ was used as received from Prof. Paul Low. **CAUTION:** TIBF₄ is highly toxic! All other reagents were used as received unless otherwise noted. Solvents were purchased in the best quality available, degassed by purging thoroughly with nitrogen and dried over molecular sieves. Benzene and CH₃CN were distilled from CaH₂ under a nitrogen atmosphere and it was stored over molecular sieves inside the glovebox. DCM, THF, pentane, and toluene were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Acetone was distilled from DrieriteTM and stored inside the glovebox (no molecular sieves were added).

Solvents for NMR spectroscopy were degassed with nitrogen and dried over molecular sieves. Acetone-d₆ was degassed with nitrogen (molecular sieves were not added). NMR spectra were recorded using Bruker Avance IIIHD 600 and Bruker Avance IIIHD 500 instruments. Chemical shifts are given in ppm. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (b). Overlapping signals are noted as multiplets. Elemental analyses were performed at London Metropolitan University (UK) by Stephen Boyer.

The synthesis of all iridium complexes was carried out several times. Representative procedures and analytical data given below do not necessarily derive from a same single experiment. ¹H NMR and/or elemental analysis was used to assess compound purity. To detect possible hydride formation during the characterization of the iridium complexes, a spectral window of 15 – (-50) ppm was used for ¹H NMR measurements. The assignment of ¹H and ¹³C NMR signals of iridium complexes was accomplished by using the appropriate 1D and 2D correlation experiments.

Synthesis of [(2,7-SiCyNap)Ir(COD)][BF₄] (2**[BF₄]).** Inside a screw-capped vial, AgBF₄ (8 mg, 0.0426 mmol, 1.05 equiv.) was stirred in DCM (1 mL). To this was added (2,7-SiCyNap)Ir(COD)Cl [**1**], 40 mg, 0.0405 mmol, 1.00 equiv] in DCM (3+1 mL). The originally orange solution turned into a red slurry. After 1.5 hrs, the mixture was filtered through cotton/Celite® in a Pasteur pipette to eliminate AgCl and the red solution was concentrated to dryness. The solid was dissolved in DCM (ca. 0.5-1.0 mL) and pentane (ca. 7-8 mL) was added to form an orange precipitate. The mixture was centrifuged for 10 min and the supernatant was decanted. The orange solid was dried under vacuum to give the product in 98% yield (41 mg, 0.0395 mmol). Recrystallization from DCM by layering with pentane gave orange crystals of **2**[BF₄] (29 mg, 69% overall yield, 0.0279 mmol). ¹H NMR (CDCl₃, 600 MHz): δ 7.95-7.89 (m, 4H, CH of naphthyl), 7.66 (d, *J* = 8.7 Hz, 2H, CH of naphthyl), 7.57 (s, 2H, C8-H of naphthyl), 7.53 (d, *J* = 8.2 Hz, 2H, CH of naphthyl), 4.61-4.46 (m, 4H, CH₂-CH₂ of NHC), 3.41-3.32 (m, 2H, CH of cyclohexyl), 3.14-3.08 (m, 1H, CH=CH of COD), 2.86-2.78 (m, 2H, CH of cyclohexyl), 2.64-2.59 (m, 1H, CH=CH of COD), 2.20-1.09 (m, 48H), 0.92-0.83 (m, 1H), 0.68-0.58 (m, 1H). ¹³C NMR (CDCl₃, 150 MHz): δ 187.36 (NCN), 153.71 (C of naphthyl), 144.22 (C of naphthyl), 133.47 (C of naphthyl), 131.11 (C of naphthyl), 129.52 (C of naphthyl), 126.98 (C of naphthyl), 126.52 (C of naphthyl), 125.88 (C of naphthyl), 123.66 (C of naphthyl), 107.00 (C8 of naphthyl), 92.18 (CH=CH of COD), 85.22 (CH=CH of COD), 58.91, 58.90, 55.46, 53.57, 46.06, 39.92, 36.34, 34.94, 34.54, 34.32, 34.22, 31.40, 29.90, 28.29, 26.72, 26.47, 26.45, 26.32, 26.23, 26.03. ¹⁹F NMR (CDCl₃, 565 MHz): δ -153.6. Due to the complex's instability, satisfactory elemental analysis was not obtained. Measured values for four individual samples are given in the Supporting Information.

Synthesis of [(2,7-SiCyNap)Ir(COD)][NTf₂], (2**[NTf₂]).** Inside the glovebox, AgNTf₂ (32 mg, 0.0836 mmol, 1.1 equiv) was stirred in

DCM (4 mL). To this was dropwise added (2,7-SiCyNap)Ir(COD)Cl [**1**], 75 mg, 0.0760 mmol, 1.0 equiv] in DCM (5 + 1 mL). The cloudy orange solution was stirred for ca. 2 hrs, during which time the solution became red and a white precipitate (AgCl) formed. The mixture was filtered through cotton/Celite® in a Pasteur pipette, then the solvent was removed under vacuum. The residual red powder was dissolved in DCM (ca. 1-2 mL) and then precipitated by slow addition of pentane (ca. 18 mL). The mixture was centrifuged and the solvent was decanted. The dissolution-precipitation-decantation sequence was repeated one more time. The residue was then dried under vacuum to give product **2**[NTf₂] as a red powder (86 mg, 0.0698 mmol, 92% yield). Suitable crystals for X-ray diffraction studies were grown by slow diffusion of pentane into a concentrated solution of [(2,7-SiCyNap)Ir(COD)][NTf₂] (**2**[NTf₂]) in DCM. ¹H NMR (CD₂Cl₂, 600 MHz): δ 8.02-7.98 (m, 4H, C4-H and C5-H of naphthyl), 7.73 (d, *J* = 8.7 Hz, 2H, C3-H of naphthyl), 7.61 (bd, *J* = 8.3 Hz, 2H, C6-H of naphthyl), 7.50 (s, 2H, C8-H of naphthyl), 4.42 (s, 4H, CH₂-CH₂ of NHC), 3.33-3.25 (m, 2H, CH of cyclohexyl), 3.20-3.14 (m, 1H, CH=CH of COD), 2.85-2.78 (m, 2H, CH of cyclohexyl), 2.71-2.67 (m, 1H, CH=CH of COD), 2.26-2.15 (m, 4H), 2.08-1.15 (m, 44H), 0.95-0.87 (m, 1H), 0.71-0.63 (m, 1H). ¹³C NMR (CD₂Cl₂, 150 MHz): δ 188.13 (NCN), 153.92 (C of naphthyl), 144.36 (C of naphthyl), 133.83 (C of naphthyl), 131.61 (C of naphthyl), 130.27 (C of naphthyl), 127.18 (C of naphthyl), 126.55 (C of naphthyl), 126.17 (C of naphthyl), 123.60 (C of naphthyl), 120.28 (q, *J* = 321.6 Hz, CF₃), 106.76 (bs, C8 of naphthyl), 94.09 (CH=CH of COD), 86.87 (CH=CH of COD), 59.91 (CH=CH of COD), 56.92 (CH=CH of COD), 55.41 (CH₂-CH₂ of NHC), 46.52 (CH of cyclohexyl), 40.78 (CH of cyclohexyl), 36.81, 35.33, 34.84, 34.55, 34.21, 31.35, 30.28, 28.75, 27.16, 26.70, 26.61, 26.29, 26.19. ¹⁹F NMR (CD₂Cl₂, 565 MHz): δ -79.15. Elemental analysis (%) calculated for C₅₇H₇₀F₆IrN₃O₄S₂: C, 55.59; H, 5.73; N, 3.41. Found: C, 55.67, 55.63; H, 5.81, 5.84; N, 3.52, 3.48.

Synthesis of [(μ-Cl)-(2,7-SiCyNap)Ir(COD)]·{Ag(OTf)} (3**) in DCM.** Inside a screw-capped vial, to a mixture of AgOTf (8.2 mg, 0.0319 mmol, 1.05 equiv) in DCM (0.3 mL) was added dropwise (2,7-SiCyNap)Ir(COD)Cl [**1**], 30 mg, 0.0304 mmol, 1.0 equiv] in DCM (1.2 + 0.5 mL). The deep orange solution was stirred in the dark for 0.5 hrs. The mixture was filtered through cotton/Celite® in a Pasteur pipette, then the solvent was removed under vacuum. The product was collected as a red powder (37 mg, 0.0297 mmol, 97% yield). Suitable crystals (**3a**) for diffraction studies were grown by slow diffusion of pentane into a concentrated solution of [(μ-Cl)-(2,7-SiCyNap)Ir(COD)]·{Ag(OTf)} (**3**) in DCM. The ¹H NMR spectrum of the title compound contains two isomers (in an approximate ratio of 5:1). Overlapping of signals prevents detailed analysis, the signals listed below are for the major isomer (the characteristic ¹H NMR shift for the minor isomer can be found at δ 7.75 (d, *J* = 8.5 Hz) ppm). ¹H NMR (CD₂Cl₂, 600 MHz): δ 8.12 (d, *J* = 8.6 Hz, 1H, CH of naphthyl), 8.05 (d, *J* = 8.6 Hz, 2H, CH of naphthyl), 7.97 (d, *J* = 8.5 Hz, 1H, CH of naphthyl), 7.91 (s, 1H, C8-H of naphthyl), 7.70-7.61 (m, 4H, CH of naphthyl), 7.58-7.54 (m, 1H, CH of naphthyl), 4.51-4.22 (m, 5H), 3.91-3.85 (m, 1H), 3.78-3.70 (m, 1H), 3.58-3.50 (m, 1H), 3.20-3.14 (m, 1H), 3.10-3.03 (m, 1H), 2.99-2.91 (m, 1H), 2.88-2.81 (m, 1H), 2.42-2.34 (m, 1H), 2.25-0.91 (m, 46H), 0.68-0.56 (m, 1H). ¹³C NMR (CD₂Cl₂, 150 MHz): δ 205.00 (NCN), 148.18 (C-Ar), 147.22 (C-Ar), 145.30 (C-Ar), 143.83 (C-Ar), 132.60 (C of naphthyl), 132.48 (C of naphthyl), 131.96 (C of naphthyl), 131.65 (C of naphthyl), 131.28 (C of naphthyl), 130.99 (C of naphthyl), 130.09 (C of naphthyl), 129.90 (C of naphthyl), 129.28 (C of naphthyl), 128.14 (C of naphthyl), 127.04 (C of naphthyl), 125.55 (C of naphthyl), 125.11 (C of naphthyl), 124.75 (C of naphthyl), 120.42 (C8 of naphthyl), 119.37 (C8 of naphthyl), 95.03 (CH=CH of COD), 89.62 (CH=CH of COD), 61.83, 58.63, 54.53 (CH₂-CH₂ of NHC), 54.31 (CH₂-CH₂ of NHC), 46.38, 46.30, 41.58, 40.77, 38.45, 37.88, 37.24, 35.37, 35.31, 34.39, 34.33, 32.46, 32.06, 21.16, 29.73, 28.13, 28.00, 27.53, 27.31, 27.22, 27.16, 27.10, 27.05, 26.85, 26.67, 26.53, 26.39, 26.36, 25.67. (Signal for CF₃ is not detected). ¹⁹F NMR (CD₂Cl₂, 565 MHz): δ -78.0. Elemental analysis (%) calculated for C₅₆H₇₀AgClF₃IrN₂O₃S: C, 54.08; H, 5.67; N, 2.25. Found: C, 54.12, 54.19; H, 5.72, 5.77; N, 2.32, 2.36.

Synthesis of 3 in toluene. Inside a screw-capped vial, to a mixture of AgOTf (8.2 mg, 0.0319 mmol, 1.05 equiv) in toluene- d_8 (0.3 mL) was added dropwise (2,7-SiCyNap)Ir(COD)Cl [(1), 30 mg, 0.0304 mmol, 1.0 equiv] in toluene- d_8 (0.7 + 0.5 mL). The deep orange solution was stirred in the dark for 1 hrs. The mixture was filtered through a piece of cotton wool in a Pasteur pipette, and then the solvent was removed under vacuum. Product **3** was collected as an orange solid (33 mg, 0.0265 mmol, 87% yield). Suitable crystals (**3b**) for diffraction studies were grown by slow diffusion of pentane into a solution of $[(\mu\text{-Cl})\text{-}\{(2,7\text{-SiCyNap})\text{Ir(COD)}\})\cdot\{\text{Ag(OTf)}\}]$ (**3**) in toluene- d_8 . ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 600 MHz): δ 7.98 (d, J = 8.5 Hz, 1H, CH of naphthyl), 7.95 (d, J = 8.4 Hz, 1H, CH of naphthyl), 7.85 (s, 1H, C8-H of naphthyl), 7.74 (d, J = 8.5 Hz, 1H, CH of naphthyl), 7.68 (d, J = 8.4 Hz, 1H, CH of naphthyl), 7.52 (s, 1H, C8-H of naphthyl), 7.43-7.37 (m, 3H, CH of naphthyl), 7.26 (d, J = 8.3 Hz, 1H, CH of naphthyl), 4.36 (t, J = 7.2 Hz, 1H, CH=CH of COD), 3.91-3.82 (m, 2H), 3.78-3.61 (m, 4H), 3.57-3.49 (m, 2H), 3.10-3.03 (m, 1H), 2.99-2.87 (m, 2H), 2.80-2.71 (m, 1H), 2.47-2.38 (m, 1H), 2.29-0.64 (m, 45H), 0.60-0.52 (m, 1H). ^{19}F NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 565 MHz): δ -76.9. Elemental analysis (%) calculated for $\text{C}_{56}\text{H}_{70}\text{AgClF}_3\text{IrN}_2\text{O}_3\text{S}$: C, 54.08; H, 5.67; N, 2.25. Found: C, 54.20, 54.25; H, 5.71, 5.77; N, 2.30, 2.36.

Synthesis of 3 in benzene: Inside a screw-capped vial, to a mixture of AgOTf (8.2 mg, 0.0319 mmol, 1.05 equiv) in benzene- d_6 (0.3 mL) was added dropwise (2,7-SiCyNap)Ir(COD)Cl [(1), 30 mg, 0.0304 mmol, 1.0 equiv] in benzene- d_6 (0.7 + 0.5 mL). The orange solution was stirred in the dark for 1 hrs and then the ^1H NMR spectrum was recorded. The mixture was filtered through a piece of cotton wool in a Pasteur pipette, then the solvent was removed. Product **3** was collected as an orange solid (33 mg, 0.0265 mmol, 87% yield). ^1H NMR (C_6D_6 , 600 MHz): δ 8.08 (d, J = 8.6 Hz, 1H, CH of naphthyl), 8.02 (d, J = 8.5 Hz, 1H, CH of naphthyl), 7.88 (s, 1H, C8-H of naphthyl), 7.75 (d, J = 8.5 Hz, 1H, CH of naphthyl), 7.69 (d, J = 8.5 Hz, 1H, CH of naphthyl), 7.52 (s, 1H, C8-H of naphthyl), 7.48-7.42 (m, 3H, CH of naphthyl), 7.28 (d, J = 8.6 Hz, 1H, CH of naphthyl), 4.48-4.42 (m, 1H, CH=CH of COD), 3.97-3.90 (m, 1H), 3.73-3.52 (m, 4H), 3.52-3.44 (m, 1H), 3.10-3.03 (m, 1H), 3.00-2.88 (m, 2H), 2.80-2.73 (m, 1H), 2.50-2.42 (m, 1H), 2.32-1.16 (m, 44H), 0.98-0.90 (m, 1H), 0.75-0.65 (m, 2H), 0.58-0.50 (m, 1H). ^{19}F NMR (C_6D_6 , 565 MHz): δ -76.8. Elemental analysis (%) calculated for $\text{C}_{56}\text{H}_{70}\text{AgClF}_3\text{IrN}_2\text{O}_3\text{S}$: C, 54.08; H, 5.67; N, 2.25. Found: C, 53.87, 53.88; H, 5.48, 5.46; N, 2.27, 2.31.

Crystallization of 3 from benzene. Inside an HPLC vial, to a mixture of AgOTf (4.1 mg, 0.0160 mmol, 1.05 equiv) in benzene- d_6 (0.1 mL) was added (2,7-SiCyNap)Ir(COD)Cl [(1), 15 mg, 0.0152 mmol, 1.0 equiv] in benzene- d_6 (0.3 + 0.35 mL). After covering the vial with its cap, it was shaken vigorously and left to sit in the dark. Orange crystals [polymorph **3c** (100 K) and **3c'** (200K)] formed within a couple of hours.

Synthesis of (2,7-SiCyNap)Ir(COD)(TFA) (4) in DCM. AgTFA (9.4 mg, 0.0426 mmol, 1.05 equiv.) was stirred in DCM (1 mL). To this was added dropwise a solution of (2,7-SiCyNap)Ir(COD)Cl [(1), 40 mg, 0.0405 mmol, 1.00 equiv.] in DCM (2+1 mL). The resulting orange mixture was stirred in the dark for 2 hours. During this time, a grey precipitation formed. The mixture was filtered through cotton/Celite® in a Pasteur pipette. The solvent was removed under vacuum to give an orange/yellow solid. This was washed twice with pentane (1 mL, then 2 mL). The solid was dried to give product **4** as a yellow solid in 91% yield (39 mg, 0.0366 mmol). Suitable crystals of **4** for X-ray diffraction studies were grown by slow diffusion of pentane into a concentrated solution of (2,7-SiCyNap)Ir(COD)(TFA) (**4**) in DCM. ^1H NMR (CD_2Cl_2 , 600 MHz, 273 K): δ 7.95-7.91 (m, 1H, CH of naphthyl), 7.91-7.85 (m, 2H, CH of naphthyl), 7.82-7.76 (m, 1H, CH of naphthyl), 7.68-7.63 (m, 1H, CH of naphthyl), 7.63-7.53 (m, 3H, CH of naphthyl), 7.47-7.42 (m, 1H, CH of naphthyl), 7.42-7.37 (m, 1H, CH of naphthyl), 4.30-4.20 (m, 1H, CH₂-CH₂ of NHC), 4.18-4.03 (m, 3H, CH₂-CH₂ of NHC overlapping with CH=CH of COD), 4.03-3.95 (m, 1H, CH=CH of COD), 3.52-3.41 (m, 1H, integrates to 0.9, CH of cyclohexyl), 3.27-3.12 (m, 2H, integrates to 1.6), 2.83-2.70 (m, 2H), 2.70-2.58 (m, 1H), 2.54-2.44 (m, 1H), 2.40-2.37 (m, 1H), 2.17-0.80 (m, 47H). ^{13}C NMR (CD_2Cl_2 , 150 MHz, 273 K): δ

203.93 (NCN), 159.09 (detected as d, should be a q, CO, J = 35 Hz), 147.39 (C-Ar), 146.52 (C-Ar), 144.47 (C-Ar), 143.18 (C-Ar), 133.50 (C-Ar), 132.69 (C-Ar), 132.24 (C-Ar), 131.31 (2 overlapping C-Ar), 131.19 (C-Ar), 128.93 (CH-Ar), 128.45 (CH-Ar), 128.37 (CH-Ar), 127.96 (CH-Ar), 125.98 (CH-Ar), 124.98 (CH-Ar), 124.34 (CH-Ar), 123.71 (CH-Ar), 120.51 (C8 of naphthyl), 118.73 (C8 of naphthyl), 115.70 (detected as d, should be a q, CF₃, J = 293 Hz), 85.91 (CH=CH of COD), 82.54 (CH=CH of COD), 54.75 (CH₂-CH₂ of NHC), 53.71 (CH₂-CH₂ of NHC), 51.37 (CH=CH of COD), 47.96 (CH=CH of COD), 45.23 (CH of cyclohexyl), 45.12 (CH of cyclohexyl), 40.06 (CH of cyclohexyl), 39.48 (CH of cyclohexyl), 37.26, 36.53, 35.73, 35.34, 33.97, 33.19, 32.79, 32.56, 32.34, 31.78, 28.20, 27.66, 27.28, 26.98, 26.91, 26.84, 26.78, 26.21, 26.17, 26.03, 25.36. ^{19}F NMR (CD_2Cl_2 , 565 MHz, 273 K): δ -74.1. Elemental analysis (%) calculated for $\text{C}_{57}\text{H}_{70}\text{F}_3\text{IrN}_2\text{O}_2$: C, 64.32; H, 6.63; N, 2.63. Found: C, 64.09, 64.15; H, 6.63, 6.73; N, 2.71, 2.72.

Synthesis of 4 in benzene. AgTFA (7.4 mg, 0.0334 mmol, 1.1 equiv.) was stirred in C_6D_6 (0.5 mL). To this was dropwise added a solution of (2,7-SiCyNap)Ir(COD)Cl [(1), 30 mg, 0.0304 mmol, 1.0 equiv.] in C_6D_6 (1.5 + 0.5 mL). The resulting orange mixture was stirred overnight. During this time a grey precipitation formed. The mixture was filtered through cotton/Celite® in a Pasteur pipette. The solvent was removed under vacuum to give product **4** as a pale orange solid (31 mg, 0.029 mmol, 96%). ^1H NMR (C_6D_6 , 600 MHz): δ 7.86 (d, J = 8.5 Hz, 1H, CH of naphthyl), 7.80-7.76 (m, 2H, CH of naphthyl), 7.72 (d, J = 8.5 Hz, 1H, CH of naphthyl), 7.67 (d, J = 8.3 Hz, 1H, CH of naphthyl), 7.65 (s, 1H), 7.55-7.50 (m, 2H, CH of naphthyl), 7.43 (d, J = 8.2 Hz, 1H, CH of naphthyl), 7.23 (d, J = 8.2 Hz, 1H, CH of naphthyl), 4.52-4.46 (m, 1H), 4.45-4.40 (m, 1H), 3.72-3.50 (m, 5H), 3.41-3.36 (m, 1H), 3.33-3.25 (m, 1H), 3.07-2.99 (m, 1H), 2.93-2.85 (m, 1H), 2.78-2.70 (m, 1H), 2.70-2.63 (m, 1H), 2.61-2.55 (m, 1H), 2.41-0.77 (m, 46H).

Synthesis [(2,7-SiCyNap)Ir(COD)(CH₃CN)][NTf₂] (5**[(NTf₂)]).** The title compound was prepared in situ in an NMR tube experiment. Inside an NMR tube, freshly prepared $[(\mu\text{-Cl})\text{-}\{(2,7\text{-SiCyNap})\text{Ir(COD)}\})\cdot\{\text{Ag}(\eta^2\text{-tol-}d_8)\}][\text{NTf}_2]$ (ca. 5-10 mg) was dissolved in CD_3CN (ca. 0.6 mL). The NMR tube was sealed and shaken. A fluffy white precipitate (AgCl) and an orange solution formed. The ^1H NMR spectrum was identical to **5**[PF₆]. ^{23}Na NMR (CD_2Cl_2 , 565 MHz): δ -80.36 (s).

Synthesis of [(2,7-SiCyNap)Ir(COD)(CH₃CN)][OTf] (5**[OTf]).** A recrystallized sample of $[(\mu\text{-Cl})\text{-}\{(2,7\text{-SiCyNap})\text{Ir(COD)}\})\cdot\{\text{Ag(OTf)}\}]$ (**3**), approx. 10 mg] was dissolved in $\text{DCM-}d_2$ (0.5 mL). The ^1H NMR spectrum was recorded, then (inside the glovebox) a drop of CH_3CN was added. Immediately, a white fluffy precipitate formed. ^1H NMR analysis indicated the formation of the title compound; the spectrum is comparable to that of [(2,7-SiCyNap)Ir(COD)(CH₃CN)][PF₆] (**5**[OTf]). The supernatant was decanted, transferred into a clean NMR tube and layered with pentane. Suitable crystals for X-ray diffraction studies formed overnight. Further characterization or a preparative synthesis was not carried out. ^1H NMR (CD_2Cl_2 , 600 MHz, 273 K): δ 8.00 (d, J = 8.6 Hz, 1H, CH of naphthyl), 7.97 (d, J = 8.5 Hz, 2H, CH of naphthyl), 7.89 (d, J = 8.4 Hz, 1H, CH of naphthyl), 7.71 (s, 1H, C8-H of naphthyl), 7.63 (d, J = 8.6 Hz, 1H, CH of naphthyl), 7.61-7.57 (m, 2H, CH of naphthyl), 7.53 (d, J = 8.5 Hz, 1H, CH of naphthyl), 7.47 (d, J = 8.3 Hz, 1H, CH of naphthyl), 4.48-4.39 (m, 1H, CH₂-CH₂ of NHC), 4.34-4.14 (m, 3H, CH₂-CH₂ of NHC), 3.84-3.77 (m, 1H), 3.71-3.65 (m, 1H), 3.64-3.59 (m, 1H), 3.19-3.13 (m, 1H), 3.11-2.98 (m, 2H), 2.90-2.81 (m, 1H), 2.80-2.71 (m, 1H), 2.53-2.44 (m, 1H), 2.31-2.23 (m, 1H), 2.14-0.87 (m, 49). ^{19}F NMR (CD_2Cl_2 , 565 MHz, 273 K): δ -79.1.

Synthesis of [(2,7-SiCyNap)Ir(COD)(CH₃)₂CO][PF₆] (6**[PF₆]).** *In situ:* Inside an NMR tube, [(2,7-SiCyNap)Ir(COD)][PF₆] (**2**[PF₆]), 15 mg, 0.017 mmol) was dissolved in acetone- d_6 (0.5 mL). ^1H NMR spectroscopy indicated clean formation of the title compound. The NMR tube was then transferred into the glovebox and the solution was layered with hexanes. Yellow needles, suitable for single crystal X-ray diffraction studies grew overnight. ^1H NMR ($\text{CD}_3\text{C(O)CD}_3$, 600 MHz): δ 8.19-8.14 (m, 2H, CH of naphthyl), 8.13 (d, J = 8.4 Hz, 1H, CH of naphthyl), 8.04 (d, J = 8.3 Hz, 1H, CH of naphthyl), 7.86 (d, J = 8.4 Hz, 1H, CH of naphthyl), 7.84-7.78 (m,

2H, CH of naphthyl), 7.71 (d, $J = 8.3$ Hz, 1H, CH of naphthyl), 7.64 (s, 1H, C8-H of naphthyl), 7.58 (d, $J = 8.3$ Hz, 1H, CH of naphthyl), 4.68-4.59 (m, 1H, $\text{CH}_2\text{-CH}_2$ of NHC), 4.49-4.29 (m, 3H, $\text{CH}_2\text{-CH}_2$ of NHC), 4.21-4.15 (m, 1H), 4.10-4.04 (m, 1H), 3.45-3.35 (m, 1H), 3.16-3.07 (m, 1H), 3.02-2.94 (m, 1H), 2.94-2.88 (m, 2H), 2.88-2.81 (m, 1H), 2.59-2.51 (m, 1H), 2.29-1.19 (m, 44H), 1.12-1.02 (m, 1H), 0.71-0.62 (m, 1H), 0.34-0.24 (m, 1H). **Preparative experiment:** The deep red complex $[(2,7\text{-SICyNap})\text{Ir}(\text{COD})][\text{PF}_6]$ ($2[\text{PF}_6]$, 56 mg, 0.051 mmol) was dissolved in acetone or acetone- d_6 (1.5 mL). A clean, orange solution formed immediately. After 10 min stirring at room temperature, the solution was layered with hexanes. Yellow crystals formed overnight. The solvent was decanted, the crystals were washed with hexanes and dried under vacuum (38 mg, 0.0327 mmol, 64% yield). When the title compound $6[\text{PF}_6]$ was dissolved in DCM-d_2 , a red solution formed. ^1H NMR spectrum resembled that of $[(2,7\text{-SICyNap})\text{Ir}(\text{COD})][\text{PF}_6]$, however significant broadening of the H8 signal and of signals in the downfield region (5-1 ppm) of the spectrum occurred. Cooling the sample to 233 K led to sharpening of the signals and the spectrum was very similar to the one recorded in acetone- d_6 at 273 K. A stacked view of ^1H NMR spectra in the temperature range 298 – 233 K can be found in the Supporting Information. ^1H NMR (CD_2Cl_2 , 600 MHz, 233 K): δ 8.05-7.95 (m, 3H, CH of naphthyl), 7.90 (d, $J = 8.4$ Hz, 1H, CH of naphthyl), 7.68 (d, $J = 8.6$ Hz, 1H, CH of naphthyl), 7.61 (d, $J = 8.6$ Hz, 1H, CH of naphthyl), 7.59-7.30 (m, 2H, CH of naphthyl), 7.46 (d, $J = 8.3$ Hz, 1H, CH of naphthyl), 7.37 (s, 1H, C8-H of naphthyl), 4.49-4.41 (m, 1H, $\text{CH}_2\text{-CH}_2$ of NHC), 4.27-4.06 (m, 4H), 3.96-3.89 (m, 1H), 3.24-3.14 (m, 1H), 2.96-2.87 (m, 1H), 2.82-2.68 (m, 3H), 2.64-2.57 (m, 1H), 2.43-2.36 (m, 1H), 2.18-1.02 (m, 51H), 0.67-0.57 (m, 1H), 0.28-0.19 (m, 1H). ^{13}C NMR (CD_2Cl_2 , 150 MHz, 233 K): δ 223.44 (CO), 202.14 (carbene), 148.0 (C-Ar), 147.70 (C-Ar), 144.68 (C-Ar), 144.20 (C-Ar), 132.29 (C-Ar), 132.24 (C-Ar), 131.27 (C-Ar), 131.21 (C-Ar), 130.65 (2 overlapping C-Ar), 129.98 (CH-Ar), 129.26 (2 overlapping CH-Ar), 128.49 (CH-Ar), 127.06 (CH-Ar), 125.16 (CH-Ar), 124.99 (CH-Ar), 124.54 (CH-Ar), 119.87 (CH-Ar), 117.89 (CH-Ar), 88.55 (CH=CH of COD), 80.36 (CH=CH of COD), 58.13 (CH=CH of COD), 54.37 ($\text{CH}_2\text{-CH}_2$ of NHC), 53.94 ($\text{CH}_2\text{-CH}_2$ of NHC), 51.79 (CH=CH of COD), 45.61 (CH of cyclohexyl), 44.43 (CH of cyclohexyl), 40.66 (CH of cyclohexyl), 40.30 (CH of cyclohexyl), 36.89, 36.58, 35.49 (CH_3CO), 35.37, 33.35, 33.04, 32.14, 31.71, 29.48, 28.80, 27.60, 27.26, 27.03, 26.80, 26.53, 26.49, 26.46, 26.35, 25.92, 25.83, 25.70, 25.25. Elemental analysis (%) calculated for $\text{C}_{58}\text{H}_{76}\text{F}_6\text{IrN}_2\text{O}_2\text{P}$: C, 60.34; H, 6.64; N, 2.43. Found: C, 59.83, 59.93; H, 7.00, 7.07; N, 2.67, 2.60.

Synthesis of $[(\mu\text{-Cl})\text{-}\{(2,7\text{-SICyNap})\text{Ir}(\text{COD})\}\cdot\{\text{Ag}(\eta^2\text{-tol-d}_8)\}][\text{PF}_6]$ ($7[\text{PF}_6]$). The synthesis of this complex was repeated several times. Due to instability and low solubility of $7[\text{PF}_6]$, slightly different procedures are given below for analysis. ^1H NMR spectroscopy indicated the existence of one major and one minor species in equilibrium. The ratio between these isomers (see discussion on the stereochemistry of these complexes in the main text) can be influenced by temperature and concentration. Attempts to unambiguously identify these isomers failed. **Synthesis 1.** To a solution of $(2,7\text{-SICyNap})\text{Ir}(\text{COD})\text{Cl}$ (**1**, 18 mg, 0.0180 mmol) in toluene- d_8 (0.3 mL) prepared inside an NMR tube was added AgPF_6 (5 mg, 0.0198 mmol, 1.1 equiv) in toluene- d_8 (0.5 + 0.3 mL). The solution eventually became cloudy and an orange substance oiled out. ^1H NMR analysis of this mother liquor was recorded. The mother liquor was then decanted and the oily substance at the bottom of the NMR tube redissolved in fresh toluene- d_8 (0.5 mL). ^1H NMR analysis showed this to be the same compound as seen in the mother liquor. ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 600 MHz): δ 8.58 (bs, 1H, CH of naphthyl), 8.25 (d, $J = 7.7$ Hz, 1H, CH of naphthyl), 7.96 (s, 1H, C8-H of naphthyl), 7.89 (d, $J = 6.7$ Hz, 1H, CH of naphthyl), 7.82 (d, $J = 8.5$ Hz, 1H, CH of naphthyl overlapping with the minor isomer), 7.73 (d, $J = 8.4$ Hz, 1H, CH of naphthyl), 7.72 (s, 1H, C8-H of naphthyl), 7.54 (d, $J = 8.3$ Hz, 1H, CH of naphthyl), 7.46 (d, $J = 8.6$ Hz, minor isomer), 7.41 (d, $J = 8.6$ Hz, 1H, CH of naphthyl), 7.35 (d, $J = 8.6$ Hz, 1H, CH of naphthyl), 7.29 (d, $J = 8.3$ Hz, minor isomer), 4.52-4.25 (m, 3H), 4.20-4.09 (m, 1H), 3.99-3.87 (m, 2H), 3.49-3.41 (m, 1H), 3.17-3.10 (m, 1H), 3.05-2.88 (m, 3H), 2.73-2.63 (m, 1H), 2.29-0.81 (m, 45H), 0.73-0.61

(m, 2H), 0.39-0.31 (m, 1H). **Synthesis 2.** Inside a screw-capped vial to a solution of AgPF_6 (4.0 mg, 0.0158 mmol, 1.04 equiv.) in toluene (0.5 mL) was added a solution of $(2,7\text{-SICyNap})\text{Ir}(\text{COD})\text{Cl}$ (**1**, 15 mg, 0.0152 mmol) in toluene (1.5 + 0.5 mL). The resulting orange solution was stirred for 2 hrs, then filtered through Celite®/cotton in a Pasteur pipette. The solvent was removed under vacuum to give the product in quantitative yield. Elemental analysis (%) calculated for $\text{C}_{62}\text{H}_{78}\text{AgClF}_6\text{IrN}_2\text{P}$: C, 55.91; H, 5.90; N, 2.10. Found: C, 56.02, 56.04; H, 5.93, 6.03; N, 2.14, 2.17. **Synthesis 3.** Inside a screw-capped vial to a solution of AgPF_6 (5.5 mg, 0.0218 mmol, 1.2 equiv.) in toluene (1.0 mL) was added a solution of $(2,7\text{-SICyNap})\text{Ir}(\text{COD})\text{Cl}$ (**1**, 18 mg, 0.0182 mmol, 1.0 equiv) in toluene (0.8 + 0.2 mL). The resulting orange solution was stirred for 0.5 hrs, then the stir bar was removed and the vial was placed in the freezer (-30 °C). Suitable crystals for X-ray crystallography were grown over a couple of weeks.

Synthesis of $[(\mu\text{-Cl})\text{-}\{(2,7\text{-SICyNap})\text{Ir}(\text{COD})\}\cdot\{\text{Ag}(\eta^2\text{-tol-d}_8)\}][\text{NTf}_2]$ ($7[\text{NTf}_2]$). Inside a screw-capped vial, to a suspension of AgNTf_2 (19.5 mg, 0.0502 mmol, 1.1 equiv) in toluene- d_8 (0.9 mL) was added dropwise $(2,7\text{-SICyNap})\text{Ir}(\text{COD})\text{Cl}$ (**1**, 45 mg, 0.0456 mmol, 1.0 equiv) in toluene- d_8 (2 + 0.7 mL). After stirring the solution for 5 minutes, a sample (ca. 0.5 mL) was transferred into an NMR tube. The sample was analysed by ^1H and ^{19}F NMR spectroscopy. Within 0.5 hours, the formation of crystals was observed in the NMR tube. At this stage, the rest of the mixture from the screw-capped vial was filtered through a small piece of cotton wool in a Pasteur pipette into a crystallization tube, where it was layered with pentane. Orange crystals of $7[\text{NTf}_2]$ grew overnight and were collected (40 mg, 0.027 mmol) in 60% overall, 69% corrected yield (accounting for the sample used for NMR spectroscopy). ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 600 MHz): δ 8.13 (d, $J = 8.5$ Hz, 1 H, CH of naphthyl), 8.00 (d, $J = 8.3$ Hz, 1 H, CH of naphthyl), 7.92 (s, 1H, C8-H of naphthyl), 7.75 (d, $J = 8.5$ Hz, 1 H, CH of naphthyl), 7.67 (d, $J = 8.4$ Hz, 1 H, CH of naphthyl), 7.54-7.47 (m, 3H, CH of naphthyl), 7.41 (d, $J = 8.6$ Hz, 1 H, CH of naphthyl), 7.27 (d, $J = 8.3$ Hz, 1 H, CH of naphthyl), 4.44 (t, $J = 7.1$ Hz, 1 H), 3.90 (t, $J = 6.5$ Hz, 1 H), 3.79-3.73 (m, 2H), 3.72-3.60 (m, 2H), 3.58-3.48 (m, 2H), 3.14-3.08 (m, 1H), 2.99 (t, $J = 12.0$ Hz, 1 H), 2.89 (t, $J = 11.5$ Hz, 1 H), 2.75 (t, $J = 11.8$ Hz, 1 H), 2.38-2.32 (m, 1H), 2.30-2.25 (m, 1H), 2.18-1.17 (m, 40H), 0.98-0.88 (m, 1H), 0.80-0.66 (m, 2H), 0.50-0.41 (m, 1H). ^{19}F NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 471 MHz): δ -74.6. Elemental analysis (%) calculated for $\text{C}_{64}\text{H}_{78}\text{AgClF}_6\text{IrN}_2\text{O}_4\text{S}_2$: C, 52.40; H, 5.36; N, 2.86. Found: C, 52.31, 52.28; H, 5.41, 5.49; N, 3.04, 2.95. The orange crystals were only sparingly soluble in toluene- d_8 . The addition of DCM-d_2 as a co-solvent led to generation of a new minor species (ca. 0.15 equiv) which probably corresponds to the other diastereomer that can be present in $7[\text{NTf}_2]$ (see discussion in the main text). We note that the ^1H NMR shifts in the aromatic region seem to highly depend on the concentration and ratios of these two solvents. The spectra are calibrated for DCM-d_2 (5.32 and 53.84 ppm for ^1H and ^{13}C , respectively). ^1H NMR ($\text{CD}_2\text{Cl}_2/\text{C}_6\text{D}_5\text{CD}_3$, 500 MHz): δ 8.69 (d, $J = 8.5$ Hz, 1H, CH of naphthyl), 8.59 (d, $J = 8.4$ Hz, 1H, CH of naphthyl), 8.45 (s, 1H, C8-H of naphthyl), 8.42 (d, $J = 8.6$ Hz, 1H, CH of naphthyl), 8.35 (d, $J = 8.4$ Hz, 1H, CH of naphthyl), 8.19 (d, $J = 8.7$ Hz, 1H, CH of naphthyl), 8.14 (d, $J = 8.4$ Hz, 1 H, CH of naphthyl), 8.08-8.04 (m, 2H, CH of naphthyl), 7.99-7.94 (m, 1H, CH of naphthyl), 5.00-4.88 (m, 1H, CH=CH of COD), 4.65-4.44 (m, 3H, NHC backbone), 4.42 (t, $J = 6.5$ Hz, 1H), 4.39-4.30 (m, 1H, NHC backbone), 4.05-3.96 (m, 1H), 3.74-3.64 (m, 2H), 3.57-3.49 (m, 1H), 3.49-3.42 (m, 1H), 3.38-3.29 (m, 1H), 2.80-1.63 (m, 44H), 1.45-1.28 (m, 3H), 1.00-0.90 (m, 1H). The residual toluene- d_8 signals were found at 7.73, 7.64, 2.78 (p, $J = 4.4$ Hz) ppm. ^{13}C NMR ($\text{CD}_2\text{Cl}_2/\text{C}_6\text{D}_5\text{CD}_3$, 150 MHz): Due to the complexity of the spectrum, individual shifts are not reported; copies of the spectra can be found at the end of the supporting information. Representatively, the carbene atom can be found at 204.8 ppm. ^{19}F NMR ($\text{CD}_2\text{Cl}_2/\text{C}_6\text{D}_5\text{CD}_3$, 471 MHz): δ -74.9.

Synthesis of $(2,7\text{-SICyNap})\text{Ir}(\text{COD})\text{Cl}\cdot\text{TIBF}_4$ (8**).** Inside a screw-capped vial, TIBF_4 (12.4 mg, 0.0426 mmol, 1.05 equiv.) was stirred in DCM (1 mL). To this was added $(2,7\text{-SICyNap})\text{Ir}(\text{COD})\text{Cl}$ (**1**, 40 mg, 0.0405 mmol, 1.00 equiv) in DCM (2 + 1 mL). The resulting orange solution was stirred at room temperature for 2.5 hrs. The mixture was

filtered through cotton/Celite® in a Pasteur pipette and the solvent was removed under vacuum. The orange solid was washed with pentane (2 × 2 mL), and dried under vacuum. Product **8** was collected as a crystalline orange solid (49 mg, 0.0394 mmol, 98% yield). ¹H NMR (CD₂Cl₂, 600 MHz): δ 8.06 (s, 1H, C8-H of naphthyl), 7.97 (m, 2H, CH of naphthyl), 7.90 (d, *J* = 8.4 Hz, 1H, CH of naphthyl), 7.87 (d, *J* = 8.4 Hz, 1H, CH of naphthyl), 7.65–7.56 (m, 3H, CH of naphthyl), 7.54–7.47 (m, 2H, CH of naphthyl), 4.42–4.16 (m, 5H), 3.66–3.56 (m, 1H), 3.45–3.34 (m, 2H), 3.09–3.00 (m, 1H), 3.00–2.86 (m, 2H), 2.84–2.74 (m, 1H), 2.30–2.22 (m, 1H), 2.18–0.95 (m, 45H), 0.72–0.62 (m, 1H), 0.51–0.41 (m, 1H). ¹³C NMR (CD₂Cl₂, 150 MHz): δ 206.25 (NCN), 147.36 (C-Ar), 147.26 (C-Ar), 145.96 (C-Ar), 143.76 (C-Ar), 133.53 (C-Ar), 133.02 (C-Ar), 132.26 (C-Ar), 132.23 (C-Ar), 131.70 (C-Ar), 131.04 (C-Ar), 130.05 (CH-Ar), 129.62 (CH-Ar), 129.16 (CH-Ar), 128.31 (CH-Ar), 126.73 (CH-Ar), 125.53 (CH-Ar), 125.14 (CH-Ar), 124.55 (CH-Ar), 124.15 (CH-Ar), 120.29 (CH-Ar), 88.92 (CH=CH of COD), 82.31 (CH=CH of COD), 56.62, 56.20, 54.36 (CH₂-CH₂ of NHC), 54.14 (CH₂-CH₂ of NHC), 46.38, 46.16, 41.31, 39.92, 37.82, 37.66, 35.08, 35.04, 34.88, 34.78, 34.12, 32.55, 32.30, 30.78, 29.70, 28.03, 27.98, 27.35, 27.33, 27.21, 27.14, 27.11, 26.77, 26.70, 26.59, 26.5, 26.50, 26.38. ¹⁹F NMR (CD₂Cl₂, 471 MHz): δ -150.13, -150.19. Elemental analysis (%) calculated for C₅₅H₇₀BF₄IrN₂TI: C, 53.16; H, 5.68; N, 2.25. Found: C, 53.29, 53.35; H, 5.82, 5.84; N, 2.32, 2.36.

Catalytic experiments. *Method A.* Representative procedure for the hydroamination/cyclization with compounds **2**[PF₆], **2**[NTf₂], **2**[BF₄] and **4**: Inside the glovebox, N-benzyl-2-phenylpent-4-en-1-amine (**9**) (75 mg, 0.3 mmol) was put into an NMR tube. To this was added a stock solution containing the catalyst in DCM-d₂ [6.6 mg, 0.006 mmol {(2,7-SiCyNap)Ir(COD)}[PF₆] (**2**[PF₆]) in 0.5 mL DCM-d₂, corresponding to 2 mol% catalyst loading}. The NMR tube was sealed, taken outside the glovebox and immediately placed into an NMR spectrometer. The conversion was monitored by ¹H NMR spectroscopy. *Method B.* Catalytic run with **7**[PF₆] with pre-mixing: Freshly prepared **7**[PF₆] (24 mg, 0.018 mmol, orange solid) was stirred in DCM-d₂ (750 μL). A red suspension formed which was stirred in the dark for one hour. Out of this red suspension 500 μL (equivalent to 16 mg, 0.012 mmol of **7**[PF₆], corresponding to 4 mol% catalyst loading) was added to N-benzyl-2-phenylpent-4-en-1-amine (**9**) (75 mg, 0.30 mmol) in a screw-capped vial. The mixture was stirred for an hour in the dark, then transferred into an NMR tube. The ¹H NMR spectrum showed full conversion of **9** to 1-benzyl-2-methyl-4-phenylpyrrolidine (**10**). *Method C.* Catalytic run with **7**[PF₆] without pre-mixing: To a solution of N-benzyl-2-phenylpent-4-en-1-amine (**9**) (75 mg, 0.30 mmol) in DCM-d₂ (0.5 mL) was added freshly prepared **7**[PF₆] (16 mg, 0.012 mmol, 4 mol% catalyst loading) as an orange solid. The yellow/orange mixture (no apparent precipitation was observed) was stirred in the dark for 75 min. Subsequently, the mixture was transferred into an NMR tube. The ¹H NMR spectrum did not indicate any appreciable conversion of the starting material to 1-benzyl-2-methyl-4-phenylpyrrolidine (**10**). The NMR tube was left at room temperature in the dark and re-measured after ca. 24 hrs. No appreciable conversion was observed.

X-ray Crystallography. Crystallographic data for the structures were collected at 100(2) K (200(2)K for **5**[OTf], **3c**, **4**) on an Oxford Diffraction Gemini or Xcalibur diffractometer using Mo Kα or Cu Kα radiation. Following absorption corrections and solution by direct methods, the structures were refined against *F*² with full-matrix least-squares using the program SHELXL-2014.⁵² Unless stated, anisotropic displacement parameters were employed for the non-hydrogen atoms. All hydrogen atoms were added at calculated positions and refined by use of riding models with isotropic displacement parameters based on those of the parent atoms. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre with supplementary publication numbers given below. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Rd, Cambridge CB21EZ, UK (fax +441223336033; email deposit@ccdc.cam.ac.uk).

Key details of the crystal and structure refinement data are summarized in the Supporting Information. CCDC files 1501767–1501779 contain crystallographic data for the crystal structures reported herein.

5. ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional experimental and crystallographic data (PDF)

Copies of NMR spectra (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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