ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Trifunctional pNHC, Imine, Pyridine Pincer-Type Iridium(III) Complexes: Synthetic, Structural, and Reactivity Studies

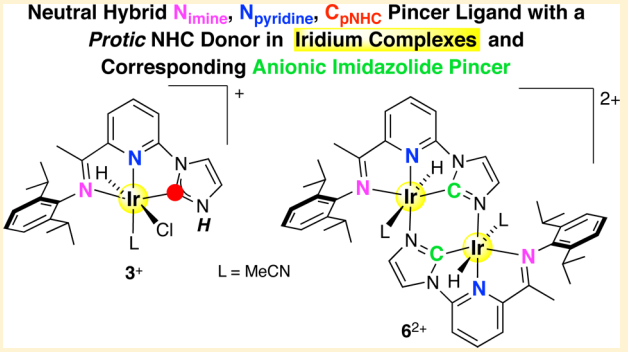
Fan He,[†] Andreas A. Danopoulos,*[,†,‡] and Pierre Braunstein*[,†]

[†]Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal, 67081 Strasbourg Cedex, France

[‡]Université de Strasbourg Institute for Advanced Study (USIAS), 4 rue Blaise Pascal, 67081 Strasbourg Cedex, France

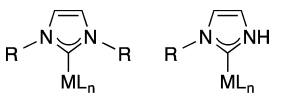
Supporting Information

ABSTRACT: Iridium(III) complexes with a trifunctional pincer ligand containing protic N-heterocyclic carbene (pNHC), pyridine, and imine donor groups were obtained in two sequential steps: (i) protonation of 2-(1-(2,6-diisopropylphenylimino)ethyl)-6-(1-imidazolyl)pyridine ($\mathbf{L}^{CH}$; the superscript specifies the position of the tautomerizable H atom in the imidazole ring) with $HBF_4{\cdot}Et_2O$ to give the imidazolium salt $[HL^{CH}]^+[BF_4]^-$ (protonation always occurs at the imidazole N atom) and (ii) metalation of the latter with $[Ir(cod)(\mu\text{-}Cl)]_2$ to give the hydrido pincer complex $[Ir(H)(Cl)(NCMe)\{\mathbf{L}^{NH}\text{-}\kappa^3N_{imine},N_{Py},C_{NHC}\}]^+[BF_4]^-$ ($\mathbf{3}^+[BF_4]^-$). Substitution of MeCN in $\mathbf{3}^+[BF_4]^-$ by treatment with triisopropylphosphine gave the analogue $[Ir(H)(Cl)P(i\text{-}Pr)_3\{\mathbf{L}^{NH}\text{-}\kappa^3N_{imine},N_{Py},C_{NHC}\}]^+[BF_4]^-$ ($\mathbf{4}^+[BF_4]^-$). Chloride abstraction from $\mathbf{3}^+[BF_4]^-$ by $AgBF_4$ gave $[Ir(H)(NCMe)_2\{\mathbf{L}^{NH}\text{-}\kappa^3N_{imine},N_{Py},C_{NHC}\}]^{2+}[BF_4^-]_2$ ($\mathbf{5}^{2+}[BF_4^-]_2$). The centrosymmetric dinuclear Ir(III) complex $[Ir(H)(NCMe)\{\mu\text{-}(\mathbf{L}^{CH}\text{-}H)\text{-}\kappa^3N_{imine},N_{Py},C2,\kappa N3\}]_2^{2+}[B(C_6F_5)_3F^-]_2$ ($\mathbf{6}^{2+}[B(C_6F_5)_3F^-]_2$) was obtained after deprotonation of $\mathbf{5}^{2+}[BF_4^-]_2$ with KO-*t*-Bu, followed by addition of $B(C_6F_5)_3$. It contains two Ir pincer moieties, each with a $N_{imine},N_{Py},C2$ donor set, which are connected by the Ir−N bonds involving the imidazolide rings, leading to a μ-C,N bridging mode for the latter. Remarkably, all of the donor atoms in the tetradentate bridging chelating ligands are chemically different. The molecular structures of $\mathbf{3}^+[BF_4]^-{\cdot}CH_2Cl_2$, $\mathbf{4}^+[BF_4]^-{\cdot}CH_2Cl_2$, $\mathbf{5}^{2+}[BF_4^-]_2{\cdot}2CH_2Cl_2$, and $\mathbf{6}^{2+}[B(C_6F_5)_3F^-]_2{\cdot}4CH_2Cl_2$ have been determined by X-ray diffraction.



INTRODUCTION

As tunable and strong σ-donor ligands, N-heterocyclic carbenes (NHCs) have triggered fast-growing interest in organometallic chemistry in the last two decades.[1] A considerable number of NHC metal complexes have been produced where, in most cases, both N sites carry a substituent R (R = alkyl, aryl in **I**) that allows fine tuning of the steric and electronic properties of the NHC ligand. In contrast, protic NHC (pNHC; R = alkyl, aryl, H in **II**) metal complexes are less common.



I II

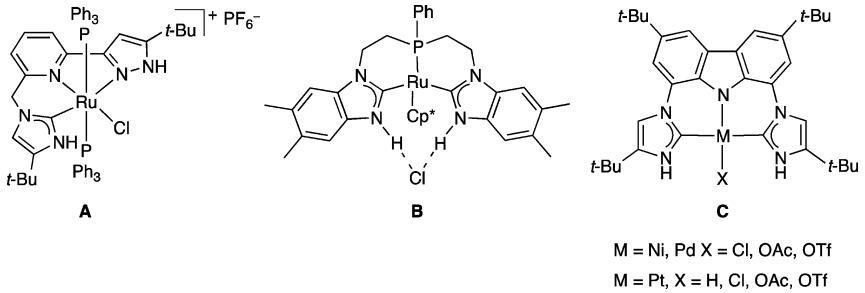
Owing to the presence of the acidic N*H*, pNHCs are not stable as free ligands, in contrast to their corresponding imidazole tautomers; pNHCs cannot generally be obtained by simple deprotonation of the corresponding imidazolium salts.[2] Thus, pNHC complexes have been comparatively less investigated and their synthesis can occasionally be challenging; their coordination chemistry has been recently reviewed.[3] Conversely, the NH moiety in a pNHC complex can act as a reactive site of potential relevance to bifunctional catalysis[4] and substrate recognition.[3a,c,5] Furthermore, metal complexes with pincer-type ligands are attracting continuing interest, largely driven by their unique photophysical and chemical properties, the latter in particular with respect to catalytic transformations.[6] Interestingly, among the limited number of pNHC metal complexes reported, the only ones of the pincer type are depicted in Scheme 1 and some of them possess interesting catalytic properties, rendering this family of complexes attractive synthetic targets for further developments.[7] In a pNHC-based pincer-type donor system, the carbene donor occupies a terminal (wingtip) rather than the central (bridgehead) position, in contrast to the many known NHC-based pincer ligands.[6,8]

The Ru(II) complex with pincer-type pNHC ligand and heterotopic wingtips reported by Kuwata and Ikariya (**A** in Scheme 1) has two different NH groups: one on the pNHC and the other on a pyrazole. Treatment of **A** with 1 equiv of base led to the deprotonation of the pyrazole, indicating that the N*H* of the pNHC is less acidic.[7a] The Ru(II) complex with

Received: November 6, 2015

DOI: 10.1021/acs.organomet.5b00926
Organometallics XXXX, XXX, XXX−XXX

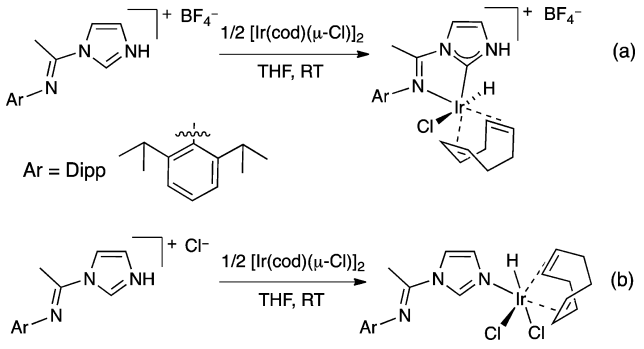
Scheme 1. Transition-Metal Complexes Containing Pincer-Type pNHC Ligands



the symmetrical pincer pNHC ligand reported by Flowers and Cossairt (**B** in Scheme 1) features in the solid state hydrogen-bonding interactions between the two N*H*s of the pNHC and the chloride counterion. Double deprotonation of **B** followed by a salt metathesis reaction with $FeCl_2$ and $CoCl_2$ afforded Ru(II)/Fe(II) and Ru(II)/Co(II) heterometallic complexes, respectively.[7b] The Ni(II) complex with the symmetrical pincer pNHC ligand reported by Grotjahn (**C** in Scheme 1) is the first such example for a 3d metal. The Pt(II) triflate analogue of **C** was successfully used as a catalyst in the anti-Markovnikov addition of O−H to alkynes and the hydration of alkynes.[7c]

Following studies on bisimino-NHC Ir(I) complexes,[9] we have recently reported a one-step procedure involving direct metalation of the imidazolium salt to prepare Ir(III) complexes with bidentate monoimine-functionalized pNHC ligands (Scheme 2a).[10] In this approach, a remarkable influence of

Scheme 2. Anion-Dependent One-Step Access (a) to a Bidentate Imine-Functionalized pNHC Ir(III) Complex or (b) to an Imidazole Complex via Selective N−H Bond Activation[10]



the nature of the associated anion on the nature of the product obtained was observed since, when X = BF_4, a formal oxidative addition of the C2−H bond to Ir(I) led to a pNHC complex, whereas when X = Cl, selective N−H bond activation afforded a N3-bound imidazole complex (Scheme 2b). These studies were extended to the stepwise synthesis of homo- and heterodinuclear Ir and Ir/Rh complexes.[11]

Considering the important features associated with nonsymmetrically substituted pincer ligands,[6k] we sought to extend our methodology to the synthesis of trifunctional pincer-type pNHC Ir(III) complexes with heterotopic wingtips.

RESULTS AND DISCUSSION

Synthesis of the pNHC Ligand Precursors. The synthetic sequence developed in order to access the ligand precursors $\mathbf{L}^{CH}$ (the superscript specifies the position of the tautomerizable H atom in the imidazole ring) and the corresponding imidazolium salt $[HL^{CH}]^+X^-$ (protonation always occurs at the imidazole N atom) are given in Scheme 3. After the preparation of the starting materials 2-acetyl-6-bromopyridine[12] and 2-(1-(2,6-diisopropylphenylimino)ethyl)-6-bromopyridine[13] from the commercially available 2,6-dibromopyridine, the introduction of the imidazole moiety was accomplished by modification of the method introduced by Herrmann and Kühn for the synthesis of 2-imidazolylpyridines.[14] Thus, reaction of 2-(1-(2,6-diisopropylphenylimino)-ethyl)-6-bromopyridine with 3 equiv of imidazole and 2 equiv of K_2CO_3 at 190 °C for 18 h gave in satisfactory overall yield 2-(1-(2,6-diisopropylphenylimino)ethyl)-6-(1-imidazolyl)-pyridine ($\mathbf{L}^{CH}$) (Scheme 3 and Experimental Section).

Then $\mathbf{L}^{CH}$ was protonated by $HBF_4{\cdot}Et_2O$ or HCl in ether to give the imidazolium salts $[HL^{CH}]^+X^-$ (X = Cl, BF_4) in high yield. In their ^{1}H NMR spectrum in DMSO-d_6, the C2−*H* proton of the imidazole exhibits characteristic apparent triplet resonances at δ 10.06 ppm (^4J = 1.7 Hz) (X = BF_4) or δ 10.04 ppm (^4J = 1.7 Hz) (X = Cl), respectively, which are shifted significantly downfield in comparison to the corresponding resonance in $\mathbf{L}^{CH}$ (δ 8.44 ppm in $CDCl_3$). The shifts of the $^{13}C\{^1H\}$ NMR resonances of $[HL^{CH}]^+X^-$ due to C_{imine} and *C*2 (at δ 165.9 and 134.7 ppm, respectively) are of diagnostic value for the subsequent formation of pincer-type metal complexes, in which C2 has been metalated and the imine coordinated (see below).

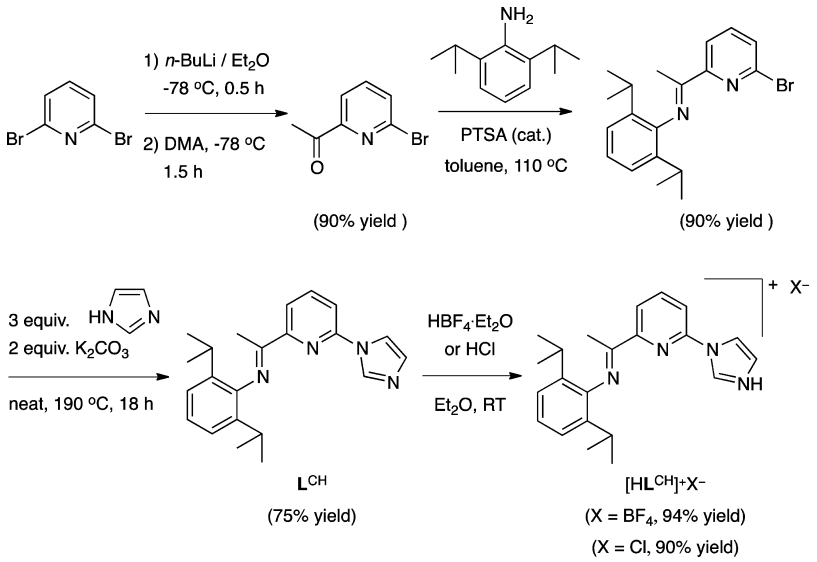
Reactivity of $\mathbf{L}^{CH}$ with Ir Precursors. The reaction of $\mathbf{L}^{CH}$ with 0.5 equiv of $[Ir(cod)(\mu\text{-}Cl)]_2$ led to the isolation of the N-bound Ir(I) imidazole complex $[IrCl(cod)\{\mathbf{L}^{CH}\text{-}\kappa N3\}]$ (**1**) (Scheme 4), which is analogous to other N-bound Ir(I) imidazole complexes isolated during our studies on bidentate imine functionalized pNHC Ir complexes.[10,11,15]

In contrast, the reaction of $\mathbf{L}^{CH}$ with $[Ir(cod)(\mu\text{-}Cl)]_2$ in a 1:1 molar ratio under similar conditions afforded a mixture of **1**, $[Ir_2(H(Cl)_2(cod)_2\{\mu\text{-}(\mathbf{L}^{CH}-H)\text{-}\kappa^2C3_{Py},N_{imine},\kappa N3\}]$ (**2**) and unreacted $[Ir(cod)(\mu\text{-}Cl)]_2$, but **2** could not be isolated in pure form from the reaction mixture. Neither heating nor addition of another 1/2 equiv of $[Ir(cod)(\mu\text{-}Cl)]_2$ led to full conversion of **1**. In the ^{1}H NMR spectrum of the mixture in CD_2Cl_2, the hydride signal at δ −14.81 ppm and the resonances (AB pattern) due to C4 and C5 pyridyl protons at δ 7.47 ppm (d, ^3J = 8.2 Hz) and 7.32 ppm (d, ^3J = 8.2 Hz) are consistent with oxidative addition of the $C3_{Py}$−H bond to the Ir(I) center. Such behavior has previously been observed in pyridyl-NHC Ir complexes.[16] Complex **2** is thus a mixed-valent Ir(I)−Ir(III) complex with a chelating-bridging N,C,N ligand.

Reactivity of $[HL^{CH}]^+X^-$ with Ir Precursors. Attempted reactions to metalate $[HL^{CH}]^+[BF_4]^-$ with either $[Ir(coe)_2(\mu\text{-}Cl)]_2$ or $[Ir(C_2H_4)_2(\mu\text{-}Cl)]_2$ were monitored by ^{1}H NMR

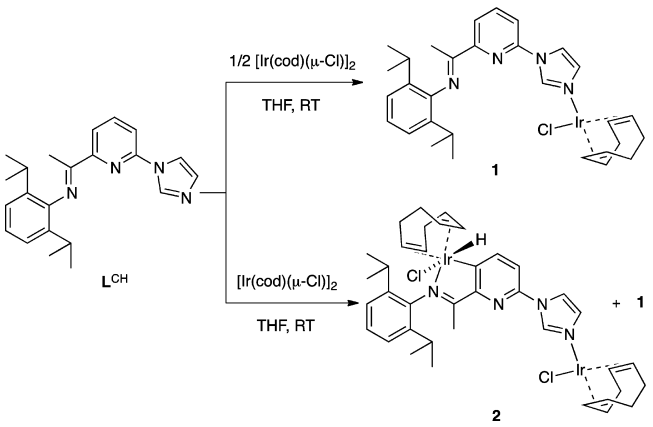
DOI: 10.1021/acs.organomet.5b00926
Organometallics XXXX, XXX, XXX−XXX

Scheme 3. Synthesis of L^{CH} and $[HL^{CH}]^+X^-$ [a]



[a]DMA = *N,N′*-dimethylacetamide; PTSA = *p*-toluenesulfonic acid.

Scheme 4. Synthesis of 1 and 2 [a]



[a]The metalated N atom is called N3 in the following.

spectroscopy in various deuterated solvents, such as CD_3CN, C_6D_6, toluene-d_8, and THF-d_8. All of these reactions resulted in intractable mixtures, regardless of the reaction time or temperature. The metalation by $[Ir(cod)(\mu\text{-}Cl)]_2$ was best performed in acetonitrile. After its solution was heated at 80 °C for 12 h, $[Ir(H)(Cl)(NCMe)\{\mathbf{L}^{NH}\text{-}\kappa^3N_{imine},N_{Py},C_{NHC}\}]^+[BF_4]^-$ ($\mathbf{3}^+[BF_4]^-$) was isolated from the reaction mixture in good yield (Scheme 5).

In the ^1H NMR spectrum of $\mathbf{3}^+[BF_4]^-$ in CD_2Cl_2, the N*H* proton gives rise to a broad singlet at δ 11.59 ppm. There were no signals for the cod ligand and the C2−*H* proton, but two characteristic new singlet resonances were found at δ 2.31 and −22.73 ppm that were assigned to the coordinated CH_3CN and Ir−*H*, respectively. The $^{13}C\{^1H\}$ NMR spectrum contains resonances for C_{imine} at δ 176.9 ppm and for C_{NHC} at δ 141.9 ppm. All of these data are consistent with $\mathbf{3}^+[BF_4]^-$ being an Ir(III) pincer complex with a pNHC donor group. This was confirmed by the structural determination of $\mathbf{3}^+[BF_4]^-\cdot CH_2Cl_2$ by X-ray diffraction (Figure 1).

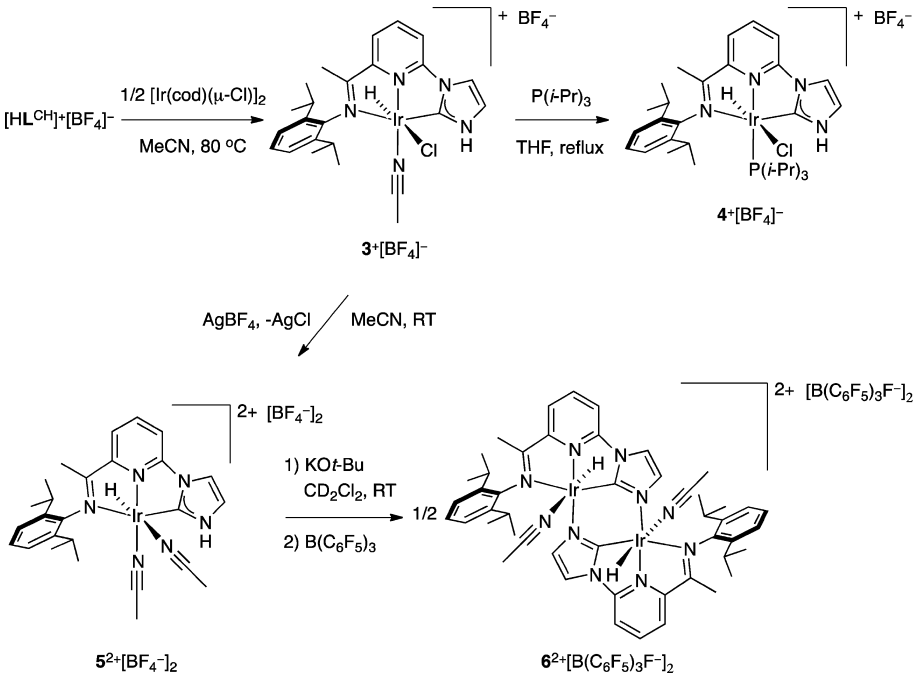
The structure of $\mathbf{3}^+[BF_4]^-\cdot CH_2Cl_2$ shows tridentate $\kappa^3N_{imine},N_{Py},C_{NHC}$ coordination of the ligand and a distorted-octahedral coordination geometry at the metal. The *cis* disposition of the Ir−C and Ir−H bonds is consistent with this 18-valence-electron Ir(III) complex resulting from C−H oxidative addition to Ir(I). The Ir1−C1 bond distance of 1.970(3) Å is similar to that in the bidentate imine-functionalized pNHC Ir(III) complex shown in Scheme 2 (1.983(2) Å).[10] The shortest N−H···F(BF_3) distance of 2.01(4) Å is consistent with a hydrogen-bonding interaction.

When the reaction between $[HL^{CH}]^+Cl^-$ and $[Ir(cod)(\mu\text{-}Cl)]_2$ in CD_3CN was performed at room temperature instead of 80 °C, a product of oxidative addition of the N−H bond to Ir was initially formed, as evidenced by a ^1H NMR resonance at δ −12.07 ppm, in a way analogous to that for the related N-bound imidazole Ir(III) complex (Scheme 2b).[10] This Ir hydride complex converted gradually upon heating to another Ir hydride species (Ir−*H* at δ −22.85 ppm), which is assignable to a pincer-type Ir(III) pNHC complex (cf. δ −22.73 ppm in $\mathbf{3}^+[BF_4]^-$). However, the reaction, albeit clean, was quite slow (50% conversion after heating for 2 weeks in CD_3CN at 80 °C).

Deprotonation of $\mathbf{3}^+[BF_4]^-$ by KO-*t*-Bu at room temperature in CD_2Cl_2 was monitored by ^1H NMR spectroscopy. After addition of a stoichiometric amount of KO-*t*-Bu, the disappearance of the resonance due to the N*H* proton and the appearance of a characteristic doublet due to C5−*H* (C5 is at the imidazole backbone carbon closer to the pyridine ring) at δ 7.75 ppm (d, ^3J = 2.3 Hz) (cf. 7.77 ppm (dd, J = 2.2, 0.9 Hz) in $\mathbf{3}^+[BF_4]^-$) indicate the formation of an Ir(III) complex containing a C-bound "anionic" imidazolide ligand in solution. Unfortunately, attempts to isolate this iridium species under different conditions (KO-*t*-Bu/CH_2Cl_2, room temperature or KHMDS/THF, −78 °C) led to intractable reaction mixtures. Therefore, in order to better stabilize the iridium center, the complex $[Ir(H)(Cl)P(i\text{-}Pr)_3\{\mathbf{L}^{NH}\text{-}\kappa^3N_{imine},N_{Py},C_{NHC}\}]^+[BF_4]^-$ ($\mathbf{4}^+[BF_4]^-$) was prepared by treatment of $\mathbf{3}^+[BF_4]^-$ with triisopropylphosphine in refluxing THF for 12 h (Scheme 5). The ^1H NMR spectrum of $\mathbf{4}^+[BF_4]^-$ showed the Ir−*H* resonance at δ −22.41 ppm (d, $^2J_{H-P}$ = 19.5 Hz). In the $^{31}P\{^1H\}$ NMR spectrum, the coordinated triisopropylphosphine gave rise to a singlet at δ 12.8 ppm. The C_{NHC} resonance

DOI: 10.1021/acs.organomet.5b00926
Organometallics XXXX, XXX, XXX−XXX

Scheme 5. Synthesis of Ir(III) Complexes



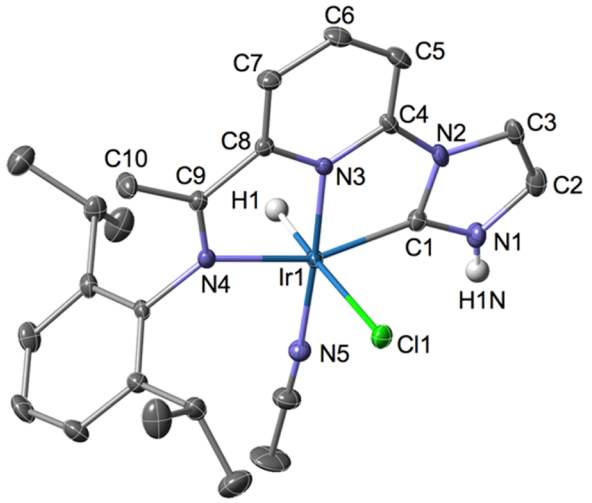


Figure 1. Molecular structure of the cation in $3^{+}[BF_4]^{-}\cdot CH_2Cl_2$. H atoms are omitted for clarity, except for H1 and H1N. Thermal ellipsoids are at the 30% probability level. Selected bond distances (Å) and angles (deg): C1−N1 1.332(4), C1−N2 1.380(4), Ir1−C1 1.970(3), Ir1−N3 1.956(2), Ir1−N4 2.124(2), Ir1−N5 2.006(3), Ir1−Cl1 2.4990(8); N1−C1−N2 104.3(3), C1−Ir1−N3 79.8(1), N3−Ir1−N4 77.9(1), N4−Ir1−N5 100.5(1), N5−Ir1−C1 101.7(1), Cl1−Ir1−C1 88.5(1), Cl1−Ir1−N3 89.50(8), Cl1−Ir1−N4 93.57(7), Cl1−Ir1−N5 93.56(9).

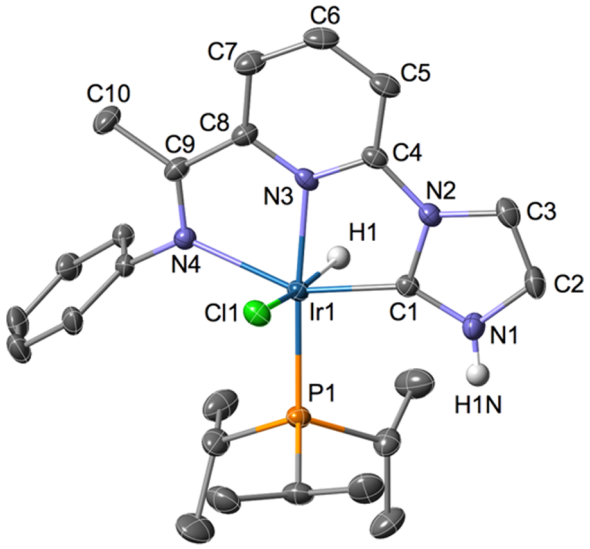


Figure 2. Molecular structure of the cation in $4^{+}[BF_4]^{-}\cdot CH_2Cl_2$. Two isopropyl groups of the Dipp and H atoms, except for H1 and H1N, are omitted for clarity. Thermal ellipsoids are at the 30% probability level. Selected bond distances (Å) and angles (deg): C1−N1 1.348(4), C1−N2 1.391(3), Ir1−C1 1.973(3), Ir1−N3 2.052(2), Ir1−N4 2.206(2), Ir1−P1 2.3259(9), Ir1−Cl1 2.487(1); N1−C1−N2 102.5(2), C1−Ir1−N3 78.9(1), N3−Ir1−N4 74.40(9), N4−Ir1−P1 109.51(6), P1−Ir1−C1 97.00(8), Cl1−Ir1−C1 92.24(8), Cl1−Ir1−N3 82.45(7), Cl1−Ir1−N4 88.92(6), Cl1−Ir1−P1 99.23(3).

in the $^{13}C\{^{1}H\}$ NMR spectrum at δ 146.4 ppm (d, $^{2}J_{C-P}$ = 9.9 Hz) is consistent with a *cis* arrangement of the triisopropylphosphine and the C_{NHC} of the pNHC. As expected, the structure of $4^{+}[BF_4]^{-}\cdot CH_2Cl_2$ (Figure 2) confirmed the substitution of the coordinated acetonitrile in $3^{+}[BF_4]^{-}\cdot CH_2Cl_2$ by triisopropylphosphine.

The coordination geometry of Ir in 4^{+} is distorted octahedral and comprises a $\kappa^3 N_{imine}, N_{Py}, C_{NHC}$ trifunctional pincer with heterotopic wingtips, one triisopropylphosphine, and mutually *trans* hydride and chloride ligands. The Ir−C_{NHC} bond distance of 1.973(3) Å is similar to that in $3^{+}[BF_4]^{-}\cdot CH_2Cl_2$. The presence of a N−H···F(BF_3) hydrogen-bonding interaction can also be deduced from the metrical data (N−H···F(BF_3) distance 2.03 Å).

Unfortunately, deprotonation of $4^{+}[BF_4]^{-}$ under the same conditions as described above for $3^{+}[BF_4]^{-}$ led also to intractable reaction mixtures.

Chloride abstraction from $3^{+}[BF_4]^{-}$ by $AgBF_4$ was performed in acetonitrile at room temperature to afford

DOI: 10.1021/acs.organomet.5b00926
Organometallics XXXX, XXX, XXX−XXX

$[Ir(H)(NCMe)_2\{L^{NH}\text{-}\kappa^3N_{imine},N_{Py},C_{NHC}\}]^{2+}[BF_4^-]_2$ ($\mathbf{5}^{2+}[BF_4^-]_2$) (Scheme 4). Evidence from NMR spectroscopy in CD_2Cl_2 indicates that this complex contains two acetonitrile ligands, and the Ir–*H* resonance is shifted slightly upfield in comparison to that in $\mathbf{3}^+[BF_4]^-$ (δ −23.11 ppm vs −22.73 ppm), while the resonance of C_{NHC} is shifted downfield (δ 146.1 ppm vs. 141.9 ppm). The 18-valence-electron Ir(III) center in $\mathbf{5}^{2+}[BF_4^-]_2$ adopts a distorted-octahedral coordination geometry with two mutually *cis* acetonitrile ligands (Figure 3). The Ir–C_{NHC} bond distance of 1.982(4) Å is similar to that in $\mathbf{4}^+[BF_4]^-$.

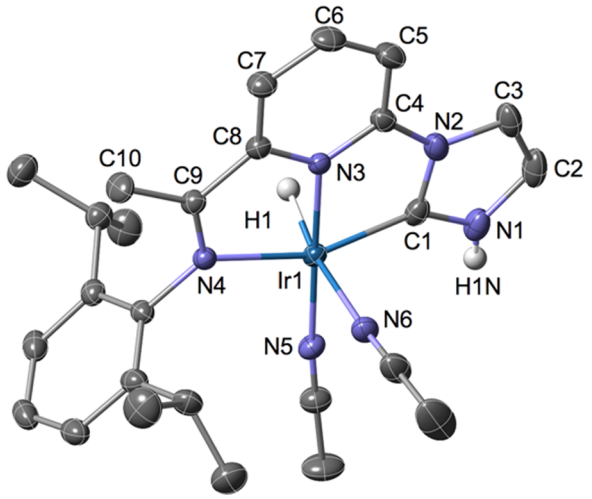


Figure 3. Molecular structure of the cation in $\mathbf{5}^{2+}[BF_4^-]_2{\cdot}2CH_2Cl_2$. H atoms are omitted for clarity, except for H1 and H1N. Thermal ellipsoids are at the 30% probability level. Selected bond distances (Å) and angles (deg): C1–N1 1.328(5), C1–N2 1.382(6), Ir1–C1 1.982(4), Ir1–N3 1.984(3), Ir1–N4 2.122(3), Ir1–N5 2.015(3), Ir1–N6 2.154(4); N1–C1–N2 105.5(4), C1–Ir1–N3 78.8(2), N3–Ir1–N4 78.3(1), N4–Ir1–N5 102.8(1), N5–Ir1–C1 100.1(2), N6–Ir1–C1 91.4 (2), N6–Ir1–N3 92.7(1), N6–Ir1–N4 92.7(1), N5–Ir1–N6 87.7(2).

Initially for the purpose of obtaining a pincer-type anionic NHC complex containing a N–$B(C_6F_5)_3$ moiety, with the boron Lewis acid acting as a readily removable protecting group, deprotonation of $\mathbf{5}^{2+}[BF_4^-]_2$ with KO-*t*-Bu followed by addition of $B(C_6F_5)_3$ was attempted in a ^{1}H NMR scale experiment in CD_2Cl_2 ($B(C_6F_5)_3$/Ir molar ratio 1/1). Unexpectedly, the dinuclear, centrosymmetric complex $[Ir(H)(NCMe)\{\mu\text{-}(L^{CH}\text{–}H)\text{-}\kappa^3N_{imine},N_{Py},C2,\kappa N3\}]_2^{2+}[B(C_6F_5)_3F^-]_2$ ($\mathbf{6}^{2+}[B(C_6F_5)_3F^-]_2$) was isolated from the reaction mixture, as could be established crystallographically. Two Ir(III) pincer-type moieties are connected by μ-C,N bridging imidazolide moieties (Figure 4). Each Ir has a distorted-octahedral coordination geometry defined by a $\kappa^3N_{imine},N_{Py},C2$ pincer ligand, *trans* hydride and acetonitrile ligands, and one nitrogen atom from the imidazolide arm of another ligand. The separation between the metal atoms of 3.992 Å is too long to invoke direct interaction between the metal centers. This value is much larger than separations observed in recently reported dinuclear Ir(I) complexes with related bridging arylimidazolide-N^3,C^2 ligands (3.1844(9) and 3.1407(2) Å).[15] The C1–N1 distance of 1.328(3) Å is shorter than that of C1–N2 (1.404(3) Å), which would be consistent with a more pronounced double-bond character for the C–N bond in the bridging part of the ligands. A likely source of F^- which leads to the anion

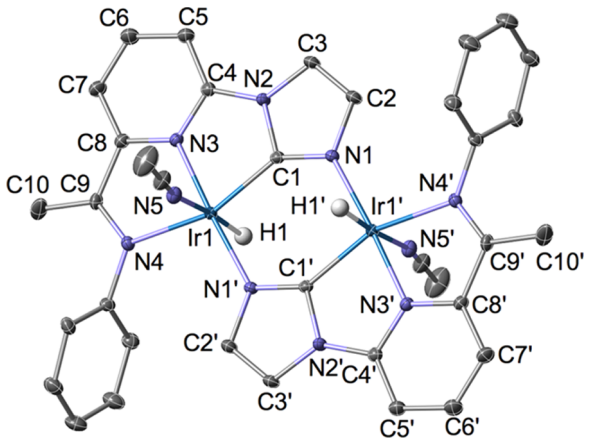


Figure 4. Molecular structure of the cation in $\mathbf{6}^{2+}[B(C_6F_5)_3F^-]_2{\cdot}4CH_2Cl_2$. Two isopropyl groups in Dipp and H atoms are omitted for clarity, except for H1. Thermal ellipsoids are at the 30% probability level. Selected bond distances (Å) and angles (deg): C1–N1 1.328(3), C1–N2 1.404(3), Ir1–C1 1.980(2), Ir1–N3 1.978(2), Ir1–N4 2.155(2), Ir1–N1′ 2.059(2), Ir1–N5 2.161(2); N1–C1–N2 107.3(2), C1–Ir1–N3 80.33(8), N3–Ir1–N4 76.88(7), N4–Ir1–N1′ 105.85(7), N1′–Ir1–C1 96.86(7), N5–Ir1–C1 90.38(8), N5–Ir1–N3 92.29(7), N5–Ir1–N4 94.80(7), N5–Ir1–N1′ 88.60(7).

$[B(C_6F_5)_3F]^-$ is the BF_4^- present in the reaction medium. The formation of this large anion allowed crystallization, which did not occur otherwise.

In the ^{1}H NMR spectrum of $\mathbf{6}^{2+}[B(C_6F_5)_3F^-]_2$ in CD_2Cl_2, the imidazolide backbone protons at the C4 and C5 positions (crystallographic C2 and C3) give rise to two doublets at δ 5.31 ppm (d) and 7.30 ppm (d, ^3J = 1.6 Hz). In the $^{13}C\{^1H\}$ NMR spectrum, the resonances at δ 129.2 and 116.3 ppm are assigned to C4 and C5, respectively. The $^{13}C\{^1H\}$ NMR resonance of the imidazolide C2 carbon (crystallographic C1) in $\mathbf{6}^{2+}[B(C_6F_5)_3F^-]_2$ (δ 154.1 ppm) is shifted downfield in comparison to that of C_{NHC} in $\mathbf{5}^{2+}[BF_4^-]_2$ (δ 146.1 ppm).

CONCLUSION

We have extended the one-step metalation of functionalized imidazolium salts to the synthesis of Ir(III) pNHC complexes containing a trifunctional pincer system with heterotopic wingtips, as in $\mathbf{3}^+[BF_4]^-$, and explored their reactivity. Their successful synthesis from the imidazolium salts $[HL^{CH}]^+X^-$ is in contrast with the results obtained from the neutral imidazole derivative L^{CH}. Deprotonation of the NH of the pNHC group in $\mathbf{5}^{2+}$ resulted in the formation of a dinuclear complex containing two tetradentate chelating-bridging ligands characterized by four chemically different donor atoms. These results are useful for the further development of synthetic methodologies to access pNHC, trifunctional pincer, and C-bound "anionic" imidazolide complexes.

EXPERIMENTAL SECTION

General Considerations. All manipulations involving organometallics were performed under argon in a Braun glovebox or using standard Schlenk techniques. Solvents were dried using standard methods and distilled over sodium/benzophenone under argon prior to use or passed through columns of activated alumina and subsequently purged with argon. $[Ir(cod)(\mu\text{-}Cl)]_2$ is commercially available from Johnson Matthey PLC. The starting materials 2-acetyl-6-bromopyridine[12] and 2-(1-(2,6-diisopropylphenylimino)ethyl)-6-bromopyridine[13] were prepared according to the literature. NMR spectra of organic compounds and metal complexes were recorded on

DOI: 10.1021/acs.organomet.5b00926
Organometallics XXXX, XXX, XXX–XXX

Bruker 300, 400, or 500 MHz instruments at ambient temperature and referenced using the residual proton (^{1}H) or the carbon (^{13}C) resonance of the solvent. Chemical shifts (δ) are given in ppm. Assignments are based on ^{1}H, ^{1}H-COSY, ^{1}H-NOESY, ^{1}H/^{13}C-HSQC, and ^{1}H/^{13}C-HMBC experiments. ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance 300 instrument at 121.49 MHz using H_3PO_4 (85% in D_2O) as an external standard. IR spectra were recorded in the region 4000−100 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the "Service de microanalyses", Université de Strasbourg.

Synthesis of 2-(1-(2,6-Diisopropylphenylimino)ethyl)-6-(1-imidazolyl)pyridine (L^{CH}). A 50 mL round Schlenk flask equipped with a stirring bar was loaded with 2-(1-(2,6-diisopropylphenylimino)-ethyl)-6-bromopyridine (1.00 g, 2.78 mmol), imidazole (0.57 g, 8.37 mmol), and K_2CO_3 (0.77 g, 5.56 mmol). The reaction mixture was degassed under 10^{-3} mbar and placed under an argon atmosphere; this cycle was repeated three times. Then the mixture was stirred at 190 °C for 18 h. After it was cooled to room temperature, the mixture was diluted in 10 mL of water and extracted with dichloromethane (3 × 10 mL), and then the extract was washed with a saturated aqueous Na_2CO_3 solution (3 × 20 mL). The combined organic phases were dried over $NaSO_4$ and filtered, and the solvent was removed under reduced pressure to leave a crude brown solid. It was dissolved in 50 mL of Et_2O, the solution was passed through a plug of Celite, and then the solvent was removed under reduced pressure and the resultant solid was washed with pentane (3 × 5 mL) to yield a yellowish powder (0.72 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (apparent t, ^4J = 1.4 Hz, 1H, NC*H*N$_{(near\ Py)}$), 8.31 (dd, J = 7.8, 0.5 Hz, 1H, C*H* Py), 7.95 (apparent t, ^3J = 7.8 Hz, 1H, C*H* Py), 7.72 (apparent t, $^{3,4}J$ = 1.4 Hz, 1H, NC*H*CHN$_{(near\ Py)}$), 7.46 (dd, J = 7.8, 0.5 Hz, 1H, C*H* Py), 7.24 (apparent t, $^{3,4}J$ = 1.4 Hz, 1H, NCHC*H*N$_{(near\ Py)}$), 7.20−7.08 (m, 3H, C*H* Ar), 2.72 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.23 (s, 3H, C*H*$_{3(imine)}$), 1.16 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.1 (*C*=N), 155.9 (*C* Ar), 148.2 (*C* Ar), 146.3 (*C* Ar), 139.6 (*C*H Ar), 135.8 (*C* Ar), 135.1 (NCHN$_{(near\ Py)}$), 131.0 (NCHCHN$_{(near\ Py)}$), 123.9 (*C*H Ar), 123.2 (*C*H Ar), 119.4 (*C*H Ar), 116.3 (NCHCHN$_{(near\ Py)}$), 113.1 (*C*H Ar), 28.5 (*C*H(CH$_3$)$_2$), 23.3 (CH(*C*H$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$), 17.3 (*C*H$_{3(imine)}$). IR: ν_{max} (pure, orbit diamond)/cm^{-1} 1643 ν(C=N). Anal. Calcd for $C_{22}H_{26}N_4$ (346.48): C, 76.27; H, 7.56; N, 16.17. Found: C, 75.97; H, 7.73; N, 16.12.

Synthesis of $[HL^{CH}]^+[BF_4]^-$. To a stirred solution of L^{CH} (0.34 g, 1.00 mmol) in Et_2O (30 mL) was added dropwise a solution of HBF_4·Et_2O (0.16 g, 1.00 mmol) in Et_2O (5 mL). The reaction mixture was stirred for 2 h at room temperature. Then the resultant precipitate was collected by filtration, washed with Et_2O, and dried in vacuo to obtain a yellow powder (0.41 g, 0.94 mmol, 94%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.06 (apparent t, ^4J = 1.7 Hz, 1H, NHC*H*N$_{(near\ Py)}$), 8.61 (apparent t, $^{3,4}J$ = 1.7 Hz, 1H, NHCHC*H*N$_{(near\ Py)}$), 8.44 (d, J = 7.9 Hz, 1H, C*H* Py), 8.35 (apparent t, ^3J = 7.9 Hz, 1H, C*H* Py), 8.21 (d, J = 7.9 Hz, 1H, C*H* Py), 7.99 (apparent t, $^{3,4}J$ = 1.7 Hz, 1H, NHC*H*CHN$_{(near\ Py)}$), 7.21−7.07 (m, 3H, C*H* Ar), 2.65 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.23 (s, 3H, C*H*$_{3(imine)}$), 1.11 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.09 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$). The N*H* resonance was not observed. ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 165.9 (*C*=N), 154.7 (*C* Ar), 146.0 (*C* Ar), 145.5 (*C* Ar), 141.4 (*C*H Ar), 135.1 (*C* Ar), 134.7 (NHCHN$_{(near\ Py)}$), 124.0 (*C*H Ar), 123.1 (*C*H Ar), 121.5 (NHCHCHN$_{(near\ Py)}$), 121.2 (*C*H Ar), 119.2 (*C*H Ar), 116.0 (NHCHCHN$_{(near\ Py)}$), 27.9 (*C*H(CH$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$), 22.7 (CH(*C*H$_3$)$_2$), 17.1 (*C*H$_{3(imine)}$). IR: ν_{max} (pure, orbit diamond)/cm^{-1} 3253 ν(N−H) and 1653 ν(C=N). Anal. Calcd for $C_{22}H_{27}BF_4N_4$ (434.29): C, 60.84; H, 6.27; N, 12.90. Found: C, 60.46; H, 6.19; N, 12.66.

Synthesis of $[HL^{CH}]^+Cl^-$. To a stirred solution of L^{CH} (0.10 g, 0.30 mmol) in Et_2O (10 mL) was added dropwise a solution of HCl (1.0 M in Et_2O, 0.3 mL, 0.30 mmol). The reaction mixture was stirred for 2 h at room temperature. Then the resultant precipitate was collected by filtration, washed with Et_2O, and dried in vacuo to give a yellow powder (0.10 g, 0.27 mmol, 90%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.04 (apparent t, ^4J = 1.7 Hz, 1H, NHC*H*N$_{(near\ Py)}$), 8.58 (apparent t, $^{3,4}J$ = 1.7 Hz, 1H, NHCHC*H*N$_{(near\ Py)}$), 8.41 (d, J = 7.9 Hz, 1H, C*H* Py), 8.33 (apparent t, ^3J = 7.9 Hz, 1H, C*H* Py), 8.24 (d, J = 7.9 Hz, 1H, C*H* Py), 7.92 (apparent t, $^{3,4}J$ = 1.7 Hz, 1H, NHC*H*CHN$_{(near\ Py)}$), 7.21−7.07 (m, 3H, C*H* Ar), 2.65 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.22 (s, 3H, C*H*$_{3(imine)}$), 1.11 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.08 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$). The N*H* resonance was not observed. ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 165.9 (*C*=N), 154.6 (*C* Ar), 146.2 (*C* Ar), 145.6 (*C* Ar), 141.2 (*C*H Ar), 135.0 (*C* Ar), 134.7 (NHCHN$_{(near\ Py)}$), 124.0 (*C*H Ar), 123.0 (*C*H Ar), 121.7 (NHCHCHN$_{(near\ Py)}$), 121.2 (*C*H Ar), 119.0 (*C*H Ar), 115.9 (NHCHCHN$_{(near\ Py)}$), 27.9 (*C*H(CH$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$), 22.7 (CH(*C*H$_3$)$_2$), 17.1 (*C*H$_{3(imine)}$). IR: ν_{max} (pure, orbit diamond)/cm^{-1} 3270 ν(N−H) and 1642 ν(C=N). Anal. Calcd for $C_{22}H_{27}ClN_4$ (382.94): C, 69.00; H, 7.11; N, 14.63. Found: C, 69.08; H, 6.86; N, 14.98.

Synthesis of [IrCl(cod)(L^{CH}-$\kappa N3$)] (1). To a stirred solution of L^{CH} (0.072 g, 0.21 mmol) in THF (3 mL) was added a solution of [Ir(cod)(μ-Cl)]$_2$ (0.070 g, 0.10 mmol) in THF (2 mL). The reaction mixture was stirred for 1 h at room temperature, and then the solvent was removed under reduced pressure. The residue was washed with Et_2O (3 × 1 mL) and dried under vacuum to give a yellow solid (0.122 g, 0.18 mmol, 88%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.11 (apparent t, ^4J = 1.4 Hz, 1H, NC*H*N$_{(near\ Py)}$), 8.40 (dd, J = 7.8, 0.5 Hz, 1H, C*H* Py), 8.03 (apparent t, ^3J = 7.8 Hz, 1H, C*H* Py), 7.84 (apparent t, $^{3,4}J$ = 1.4 Hz, 1H, NC*H*CHN$_{(near\ Py)}$), 7.56 (dd, J = 7.8, 0.5 Hz, 1H, C*H* Py), 7.27 (apparent t, $^{3,4}J$ = 1.4 Hz, 1H, NCHC*H*N$_{(near\ Py)}$), 7.20−7.07 (m, 3H, C*H* Ar), 4.27 (br s, 2H, C*H*$_{(cod)}$), 3.66 (br s, 2H, C*H*$_{(cod)}$), 2.72 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.28 (m, 4H, CH$_{2(cod)}$), 2.21 (s, 3H, C*H*$_{3(imine)}$), 1.66 (m, 2H, CH$_{2(cod)}$), 1.52 (m, 2H, CH$_{2(cod)}$), 1.15 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 166.1 (*C*=N), 156.4 (*C* Ar), 147.2 (*C* Ar), 146.5 (*C* Ar), 140.4 (*C*H Ar), 137.6 (NCHN$_{(near\ Py)}$), 136.0 (*C* Ar), 128.1 (NCHCHN$_{(near\ Py)}$), 124.2 (*C*H Ar), 123.4 (*C*H Ar), 121.0 (*C*H Ar), 117.4 (NCHCHN$_{(near\ Py)}$), 114.0 (*C*H Ar), 67.9 (*C*H$_{(cod)}$), 58.5 (*C*H$_{(cod)}$), 32.4 (CH$_{2(cod)}$), 31.5 (CH$_{2(cod)}$), 28.7 (*C*H(CH$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$), 17.3 (*C*H$_{3(imine)}$). IR: ν_{max} (pure, orbit diamond)/cm^{-1} 1645 ν(C=N). Anal. Calcd for $C_{30}H_{38}ClIrN_4$ (682.33): C, 52.81; H, 5.61; N, 8.21. Found: C, 52.58; H, 5.42; N, 8.37.

Reaction between L^{CH} and [Ir(cod)(μ-Cl)]$_2$ in a 1:1 Molar Ratio. To a stirred solution of L^{CH} (0.030 g, 0.087 mmol) in THF (3 mL) was added a solution of [Ir(cod)(μ-Cl)]$_2$ (0.060 g, 0.089 mmol) in THF (2 mL). After the reaction mixture was stirred for 1 h at room temperature, it contained **1** and **2** in an approximate 2:1 ratio and unreacted [Ir(cod)(μ-Cl)]$_2$. The solvent was then removed under reduced pressure, and the residue was washed with Et_2O (3 × 1 mL) and dried under vacuum to give a mixture of **1** and **2** in an approximate 1:1 ratio. NMR spectroscopic data of **2** are as follows. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.99 (apparent t, ^4J = 1.4 Hz, 1H, NC*H*N$_{(near\ Py)}$), 7.75 (apparent t, $^{3,4}J$ = 1.4 Hz, 1H, NC*H*CHN$_{(near\ Py)}$), 7.47 (d, ^3J = 8.2 Hz, 1H, C*H* Py), 7.32 (d, ^3J = 8.2 Hz, 1H, C*H* Py), 7.30−7.25 (m, 3H, C*H* Ar), 7.24 (apparent t, $^{3,4}J$ = 1.4 Hz, 1H, NCHC*H*N$_{(near\ Py)}$), 4.53 (m, 1H, C*H*$_{(cod)}$), 4.33 (m, 1H, C*H*$_{(cod)}$), 4.24 (m, 3H, C*H*$_{(cod)}$), 3.98 (m, 1H, C*H*$_{(cod)}$), 3.82 (sept, ^3J = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 3.65 (br s, 2H, C*H*$_{(cod)}$), 3.06 (sept, ^3J = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 2.97 (m, 2H, CH$_{2(cod)}$), 2.55 (m, 2H, CH$_{2(cod)}$), 2.42 (s, 3H, C*H*$_{3(imine)}$), 2.27 (m, 4H, CH$_{2(cod)}$), 2.13 (m, 2H, CH$_{2(cod)}$), 1.73 (m, 2H, CH$_{2(cod)}$), 1.66 (m, 2H, CH$_{2(cod)}$), 1.52 (m, 2H, CH$_{2(cod)}$), 1.40 (d, ^3J = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.33 (d, ^3J = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.10 (d, ^3J = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.05 (d, ^3J = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), −14.81 (s, 1H, Ir−*H*). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 187.5 (C=N), 164.4 (Ir−*C*), 151.6 (*C* Ar), 144.4 (*C* Ar), 142.3 (*C*H Ar), 142.2 (*C* Ar), 142.1 (*C* Ar), 140.6 (*C* Ar), 137.2 (NCHN$_{(near\ Py)}$), 128.5 (NCHCHN$_{(near\ Py)}$), 127.7 (*C*H Ar), 125.1 (*C*H Ar), 124.6 (*C*H Ar), 117.4 (NCHCHN$_{(near\ Py)}$), 115.5 (*C*H Ar), 96.6 (*C*H$_{(cod)}$), 95.0 (*C*H$_{(cod)}$), 75.7 (*C*H$_{(cod)}$), 75.3 (*C*H$_{(cod)}$), 67.7 (*C*H$_{(cod)}$), 58.4 (*C*H$_{(cod)}$), 37.9 (CH$_{2(cod)}$), 29.0 (CH$_{2(cod)}$), 28.8 (CH$_{2(cod)}$), 28.3 (CH$_{2(cod)}$), 28.1 (*C*H(CH$_3$)$_2$), 27.6 (CH(*C*H$_3$)$_2$), 25.6

DOI: 10.1021/acs.organomet.5b00926
Organometallics XXXX, XXX, XXX−XXX

Table 1. Crystal Data and Structure Refinement Details for $3^+[BF_4]^-\cdot CH_2Cl_2$, $4^+[BF_4]^-\cdot CH_2Cl_2$, $5^{2+}[BF_4^-]_2\cdot 2CH_2Cl_2$, and $6^{2+}[B(C_6F_5)_3F^-]_2\cdot 4CH_2Cl_2$

	$3^+[BF_4]^-\cdot CH_2Cl_2$	$4^+[BF_4]^-\cdot CH_2Cl_2$	$5^{2+}[BF_4^-]_2\cdot 2CH_2Cl_2$	$6^{2+}[B(C_6F_5)_3F^-]_2\cdot 4CH_2Cl_2$.
CCDC no.	1432524	1432526	1432523	1432525
empirical formula	$C_{25}H_{32}BCl_3F_4IrN_5$	$C_{32}H_{50}BCl_3F_4IrN_4P$	$C_{28}H_{37}B_2Cl_4F_8IrN_6$	$C_{88}H_{66}B_2Cl_8F_{32}Ir_2N_{10}$
fw	787.91	907.09	965.25	2561.12
T/K	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	18.4630(6)	9.234(5)	12.037(9)	12.3805(5)
b/Å	8.4248(3)	12.118(5)	12.849(10)	14.7768(6)
c/Å	24.8389(7)	18.115(5)	14.281(10)	14.8245(6)
α/deg	90	93.175(5)	77.179(18)	79.6020(10)
β/deg	127.008(2)	93.492(5)	71.935(17)	69.5660(10)
γ/deg	90	93.730(5)	66.434(18)	71.7040(10)
V/Å^3	3085.30(18)	2015.4(15)	1913(2)	2405.26(17)
Z	4	2	2	1
μ/mm^{-1}	4.635	3.596	3.838	3.099
no. of rflns collected	52902	52682	50012	63046
no. of unique rflns	10720	13891	13241	16590
R(int)	0.0322	0.0336	0.0307	0.0239
goodness of fit on F^2	1.187	1.024	1.061	1.131
final R indices ($I > 2\sigma(I)$)	R1 = 0.0364, wR2 = 0.0691	R1 = 0.0319, wR2 = 0.0743	R1 = 0.0401, wR2 = 0.1119	R1 = 0.0268, wR2 = 0.0548
R indices (all data)	R1 = 0.0474, wR2 = 0.0716	R1 = 0.0423, wR2 = 0.0774	R1 = 0.0485, wR2 = 0.1176	R1 = 0.0355, wR2 = 0.0599

($CH(CH_3)_2$), 25.3 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 23.4 ($CH(CH_3)_2$), 20.1 ($CH_{3(imine)}$).

Synthesis of [Ir(H)(Cl)(NCMe){L^{NH}-κ^3N_{imine},N_{Py},C_{NHC}}]$^+$[BF_4]$^-$ ($3^+[BF_4]^-$). To a stirred solution of $[H^{N3}L^{CH}]^+[BF_4]^-$ (0.065 g, 0.15 mmol) in acetonitrile (3 mL) was added a solution of $[Ir(cod)(\mu\text{-}Cl)]_2$ (0.050 g, 0.075 mmol) in acetonitrile (2 mL). The reaction mixture was stirred for 12 h at 80 °C, and then the volatiles were removed under reduced pressure. The residue was washed with Et_2O (3 × 2 mL) to yield a red solid, which was collected by filtration and dried in vacuo (0.086 g, 0.12 mmol, 82%). Single crystals of $3^+[BF_4]^-\cdot CH_2Cl_2$ suitable for X-ray diffraction were obtained by slow diffusion of a layer of Et_2O into a dichloromethane solution of $3^+[BF_4]^-$ and a small amount of acetonitrile at ambient temperature under argon. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 11.59 (br s, 1H, N*H*), 8.05 (apparent t, ^3J = 8.0 Hz, 1H, C*H* Py), 7.87 (dd, J = 8.0, 0.6 Hz, 1H, C*H* Py), 7.84 (dd, J = 8.0, 0.6 Hz, 1H, C*H* Py), 7.77 (dd, J = 2.2, 0.9 Hz, 1H, NHCHC*H*N$_{(near\ Py)}$), 7.40−7.26 (m, 3H, C*H* Ar), 7.23 (apparent t, ^3J = 2.2 Hz, 1H, NHC*H*CHN$_{(near\ Py)}$), 3.59 (sept, ^3J = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 2.73 (sept, ^3J = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 2.58 (s, 3H, C*H*$_{3(imine)}$), 2.31 (s, 3H, C*H*$_3$CN), 1.28 (d, ^3J = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.18 (d, ^3J = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.16 (d, ^3J = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.12 (d, ^3J = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), −22.73 (s, 1H, Ir−*H*). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 176.9 (*C*═N), 157.5 (*C* Ar), 154.9 (*C* Ar), 141.9 (NHC$_{(near\ Py)}$), 141.7 (*C*H Ar), 141.2 (*C* Ar), 139.4 (*C* Ar), 128.6 (*C*H Ar), 125.2 (*C*H Ar), 122.4 (*C*H Ar), 120.9 (NHCHC*H*N$_{(near\ Py)}$), 120.6 (*C*H$_3$CN), 117.5 (NHC*H*CHN$_{(near\ Py)}$), 112.0 (*C*H Ar), 28.6 (*C*H$(CH_3)_2$), 27.7 (CH(*C*H$_3$)$_2$), 25.6 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 24.3 (*C*H$(CH_3)_2$), 24.2 (CH(*C*H$_3$)$_2$), 18.8 (*C*H$_{3(imine)}$), 3.4 (*C*H$_3$CN). IR: ν_{max} (pure, orbit diamond)/cm^{-1} 3267 ν(N−H), 2196 ν(Ir−H) and 1585 ν(C═N). Anal. Calcd for $C_{24}H_{30}BClF_4IrN_5$ (703.01): C, 41.00; H, 4.30; N, 9.96. Found: C, 40.57; H, 4.31; N, 9.75.

Synthesis of [Ir(H)(Cl)P(*i*-Pr)$_3$){L^{NH}-κ^3N_{imine},N_{Py},C_{NHC}}]$^+$[BF_4]$^-$ ($4^+[BF_4]^-$). To a stirred solution of $3^+[BF_4]^-$ (0.070 g, 0.10 mmol) in THF (5 mL), was added dropwise a solution of triisopropylphosphine (0.1 M in toluene, 1.1 mL, 1.1 mmol). The reaction mixture was refluxed with stirring for 12 h. The volatiles were removed under reduced pressure, and the residue was washed with Et_2O (3 × 2 mL) to yield an orange solid, which was collected by filtration and dried in vacuo (0.062 g, 0.075 mmol, 75%). Single crystals of $4^+[BF_4]^-\cdot CH_2Cl_2$ suitable for X-ray diffraction were obtained by slow diffusion of a layer of Et_2O into a dichloromethane solution of $4^+[BF_4]^-$ at ambient temperature under argon. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 10.26 (br s, 1H, N*H*), 8.18 (apparent t, ^3J = 8.0 Hz, 1H, C*H* Py), 7.99 (dt, J = 8.0, 0.9 Hz, 1H, C*H* Py), 7.93 (dt, J = 8.0, 0.9 Hz, 1H, C*H* Py), 7.84 (dd, J = 2.3, 0.9 Hz, 1H, NHCHC*H*N$_{(near\ Py)}$), 7.40−7.22 (m, 4H, C*H* Ar and NHC*H*CHN$_{(near\ Py)}$), 3.50 (sept, ^3J = 6.7 Hz, 1H, C*H*$(CH_3)_2$), 2.64 (sept, ^3J = 6.7 Hz, 1H, C*H*$(CH_3)_2$), 2.45 (s, 3H, C*H*$_{3(imine)}$), 2.27 (m, 3H, PC*H*$(CH_3)_2$), 1.34−1.18 (m, 15H, PC*H*$(CH_3)_2$ CH$(CH_3)_2$), 1.16−1.00 (m, 15H, PC*H*$(CH_3)_2$ CH$(CH_3)_2$), −22.41 (d, $^2J_{H-P}$ = 19.5 Hz, 1H, Ir−*H*). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 180.4 (d, $^3J_{C-P}$ = 2.5 Hz, *C*═N), 155.1 (d, $^3J_{C-P}$ = 1.3 Hz, *C* Ar), 151.5 (d, $^3J_{C-P}$ = 1.9 Hz, *C* Ar), 146.4 (d, $^2J_{C-P}$ = 9.9 Hz, NHC*N*$_{(near\ Py)}$), 142.7 (*C*H Ar), 141.0 (*C* Ar), 139.8 (*C* Ar), 139.7 (*C* Ar), 129.0 (*C*H Ar), 125.6 (*C*H Ar), 124.7 (*C*H Ar), 123.1 (d, $^4J_{C-P}$ = 2.5 Hz, *C*H Ar), 122.0 (NHCHC*H*N$_{(near\ Py)}$), 117.0 (NHC*H*CHN$_{(near\ Py)}$), 112.5 (d, $^4J_{C-P}$ = 1.9 Hz, *C*H Ar), 28.9 (*C*H$(CH_3)_2$), 27.8 (CH(*C*H$_3$)$_2$), 26.1 (d, $^1J_{C-P}$ = 30.2 Hz, P*C*H$(CH_3)_2$), 24.9 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 22.3 (*C*H$_{3(imine)}$), 19.9 (PCH(*C*H$_3$)$_2$), 19.3 (PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 12.8. IR: ν_{max} (pure, orbit diamond)/cm^{-1} 3233 ν(N−H), 2204 ν(Ir−H) and 1593 ν(C═N). Anal. Calcd for $C_{31}H_{48}BClF_4IrN_4P$ (822.20): C, 45.29; H, 5.88; N, 6.81. Found: C, 44.92; H, 5.63; N, 6.45.

Synthesis of [Ir(H)(NCMe)$_2$){L^{NH}-κ^3N_{imine},N_{Py},C_{NHC}}]$^{2+}$[BF_4^-]$_2$ ($5^{2+}[BF_4^-]_2$). To a solution of $3^+[BF_4]^-$ (0.070 g, 0.10 mmol) in acetonitrile (5 mL), was added $AgBF_4$ (0.020 g, 0.10 mmol). The reaction mixture was stirred in the absence of light for 3 h at room temperature. After filtration through Celite, the filtrate was evaporated to dryness and then the residue was washed with Et_2O (3 × 2 mL) to yield an orange solid, which was collected by filtration and dried in vacuo (0.063 g, 0.079 mmol, 79%). Single crystals of $5^{2+}[BF_4^-]_2\cdot 2CH_2Cl_2$ suitable for X-ray diffraction were obtained by slow diffusion of a layer of Et_2O into a dichloromethane solution of $5^{2+}[BF_4^-]_2$ and a small amount of acetonitrile at ambient temperature under argon. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 11.98 (br s, 1H, N*H*), 8.27 (apparent t, ^3J = 8.0 Hz, 1H, C*H* Py), 8.07 (dd, J = 8.0, 0.5 Hz, 1H, C*H* Py), 8.03 (dd, J = 8.0, 0.5 Hz, 1H, C*H* Py), 7.92 (dd, J = 2.3, 1.3 Hz, 1H, NHCHC*H*N$_{(near\ Py)}$), 7.43 (apparent t, ^3J = 2.3 Hz, 1H, NHC*H*CHN$_{(near\ Py)}$), 7.42−7.30 (m, 3H, C*H* Ar), 2.98 (sept, ^3J = 6.7 Hz, 1H, C*H*$(CH_3)_2$), 2.73 (sept, ^3J = 6.7 Hz, 1H, C*H*$(CH_3)_2$), 2.64 (s, 3H, C*H*$_{3(imine)}$), 2.35 (s, 3H, C*H*$_3$CN), 2.23 (s, 3H, C*H*$_3$CN), 1.26 (d, ^3J = 6.7 Hz, 3H, CH(C*H*$_3$)$_2$), 1.25 (d, ^3J = 6.7 Hz, 3H,

DOI: 10.1021/acs.organomet.5b00926
Organometallics XXXX, XXX, XXX−XXX

$CH(CH_3)_2$), 1.15 (d, ^3J = 6.7 Hz, 3H, $CH(CH_3)_2$), 1.12 (d, ^3J = 6.7 Hz, 3H, $CH(CH_3)_2$), −23.11 (s, 1H, Ir−*H*). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 180.7 (*C*═N), 157.5 (*C* Ar), 154.9 (*C* Ar), 146.1 ($NHCN_{(near\ Py)}$), 143.7 (*CH* Ar), 140.7 (*C* Ar), 139.7 (*C* Ar), 139.6 (*C* Ar), 129.1 (*CH* Ar), 125.6 (*CH* Ar), 125.2 (*CH* Ar), 124.5 (*CH* Ar), 121.3 ($NHCHCHN_{(near\ Py)}$), 120.5 (CH_3CN), 120.4 (CH_3CN), 118.4 ($NHCHCHN_{(near\ Py)}$), 113.7 (*CH* Ar), 28.5 ($CH(CH_3)_2$), 27.8 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$), 23.9 ($CH(CH_3)_2$), 18.9 ($CH_{3(imine)}$), 3.7 (CH_3CN), 3.3 (CH_3CN). IR: ν_{max} (pure, orbit diamond)/cm^{-1} 3249 ν(N−H), 2196 ν(Ir−H) and 1585 ν(C═N). Anal. Calcd for $C_{26}H_{33}B_2F_8IrN_6$ (795.42): C, 39.26; H, 4.18; N, 10.57. Found: C, 38.85; H, 4.14; N, 10.82.

Synthesis of [Ir(H)(NCMe){μ-(L^{CH}−H)-κ^3*N*$_{imine}$,*N*$_{Py}$,*C*2,κ*N*3}]$_2^{2+}$[B(C$_6$F$_5$)$_3$F$^-$]$_2$ (6^{2+}[B(C$_6$F$_5$)$_3$F$^-$]$_2$). To a CD_2Cl_2 (0.5 mL) solution of $5^{2+}[BF_4^-]_2$ (0.014 g, 0.018 mmol) in a Young NMR tube was added KO-*t*-Bu (0.002 g, 0.018 mmol); the disappearance of the N*H* resonance was confirmed by ^1H NMR spectroscopic data. Then $B(C_6F_5)_3$ (0.010 g, 0.019 mmol) was added to this reaction mixture. The product crystallized in the NMR tube as single crystals at 0 °C (0.013 g, 0.006 mmol, 65%). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.90 (apparent t, ^3J = 8.2 Hz, 1H, C*H* Py), 7.78 (d, ^3J = 8.0 Hz, 1H, C*H* Py), 7.58−7.36 (m, 4H, C*H* Ar), 7.30 (d, ^3J = 2.2 Hz, 1H, $NCHCHN_{(near\ Py)}$), 5.31 (d, ^3J = 2.2 Hz, 1H, $NCHCHN_{(near\ Py)}$), 2.88 (sept, ^3J = 6.9 Hz, 1H, $CH(CH_3)_2$), 2.77 (sept, ^3J = 6.9 Hz, 1H, $CH(CH_3)_2$), 2.63 (s, 3H, $CH_{3(imine)}$), 1.93 (s, 3H, CH_3CN), 1.25 (d, ^3J = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.16 (d, ^3J = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.12 (d, ^3J = 6.9 Hz, 3H, $CH(CH_3)_2$), 0.94 (d, ^3J = 6.9 Hz, 3H, $CH(CH_3)_2$), −24.02 (s, 1H, Ir−*H*). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 178.3 (*C*═N), 156.7 (*C* Ar), 156.3 (*C* Ar), 154.1 ($NCN_{(near\ Py)}$), 149.2 (*C* C_6F_5), 147.3 (*C* C_6F_5), 143.0 (*C* Ar), 141.1 (*CH* Ar), 139.8 (*C* Ar), 139.1 (*C* Ar), 138.0 (*C* C_6F_5),136.0 (*C* C_6F_5), 129.2 ($NCHCHN_{(near\ Py)}$), 128.6 (*CH* Ar), 126.3 (*CH* Ar), 125.6 (*CH* Ar), 121.3 (*CH* Ar), 117.4 (CH_3CN), 116.3 ($NCHCHN_{(near\ Py)}$), 110.9 (*CH* Ar), 28.6 ($CH(CH_3)_2$), 27.6 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 23.3 ($CH(CH_3)_2$), 18.7 ($CH_{3(imine)}$), 3.0 (CH_3CN). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ −0.31 (br s) $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2): δ −136.6 (quintet, $^3J_{F-F}$ = 12.9 Hz, 6F, *o*-C_6F_5), −163.3 (t, $^3J_{F-F}$ = 20.1 Hz, 3F, *p*-C_6F_5), −167.8 (td, $^3J_{F-F}$ = 20.4 Hz, $^4J_{F-F}$ = 4.3 Hz, 6F, *m*-C_6F_5), −190.8 (br s, 1F, B*F*). IR: ν_{max} (pure, orbit diamond)/cm^{-1} 2200 ν(Ir−H) and 1591 ν(C═N). Anal. Calcd for $C_{84}H_{58}B_2F_{32}Ir_2N_{10}$ (2221.46): C, 45.42; H, 2.63; N, 6.31. Found: C, 44.99; H, 2.79; N, 6.12.

X-ray Data Collection, Structure Solution, and Refinement for All Compounds. Suitable crystals for the X-ray analysis of all compounds were obtained as described above. Data for $3^+[BF_4]^-\cdot CH_2Cl_2$, $4^+[BF_4]^-\cdot CH_2Cl_2$, $5^{2+}[BF_4^-]_2\cdot 2CH_2Cl_2$, and $6^{2+}[B(C_6F_5)_3F^-]_2\cdot 4CH_2Cl_2$ were collected on an APEX-II CCD instrument (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) at 173(2) K. Crystallographic and experimental details for these structures are summarized in Table 1. The structures were solved by direct methods (SHELXS-97[17]) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97) with anisotropic thermal parameters for all of the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures).

The following specific comments apply for the structures.

$3^+[BF_4]^-\cdot CH_2Cl_2$. The asymmetric unit contains one molecule of CH_2Cl_2. The hydrogen atom H1N was found (not placed in a calculated position). There is an intermolecular hydrogen bond interaction between the NH group and F2 in the $[BF_4]^-$ group. The hydride H1 was found and then fixed; otherwise, the bond distance Ir1−H1 changes during the refinement.

$4^+[BF_4]^-\cdot CH_2Cl_2$. The asymmetric unit contains one molecule of CH_2Cl_2. The hydrogen atom H1N was found (not placed in a calculated position). There is an intermolecular hydrogen bond interaction between the NH group and F2 in the $[BF_4]^-$ group. The hydride H1 was found (not placed in a calculated position) and then fixed. The SQUEEZE instruction in PLATON was applied to eliminate residual electronic density. The residual electron density was assigned to half a disordered molecule of diethyl ether.

$5^{2+}[BF_4^-]_2\cdot 2CH_2Cl_2$. One $[BF_4]^-$ is disordered. The asymmetric unit contains two molecules of CH_2Cl_2. The hydrogen atom H1N and the hydride H1 were found (not placed in a calculated position). There is an intermolecular hydrogen bond interaction between the NH group and F4 in $[BF_4]^-$.

$6^{2+}[B(C_6F_5)_3F^-]_2\cdot 4CH_2Cl_2$. The asymmetric unit contains half a molecule of the iridium dimer, one $[B(C_6F_5)_3F]^-$ anion, and two molecules of CH_2Cl_2. By symmetry, there are two $[B(C_6F_5)_3F]^-$ anions for one entire Ir dimer and four molecules of CH_2Cl_2. The hydride H1 was found and then fixed. Although the ellipsoid of C10 is distorted (alert B in the checkcif), it is a CH_3 group, as also confirmed by the NMR spectra.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00926. Crystallographic information files (CIF) have also been deposited with the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 1432523−1432526.

Crystallographic data for $3^+[BF_4]^-\cdot CH_2Cl_2$, $4^+[BF_4]^-\cdot CH_2Cl_2$, $5^{2+}[BF_4^-]_2\cdot 2CH_2Cl_2$, and $6^{2+}[B(C_6F_5)_3F^-]_2\cdot 4CH_2Cl_2$ (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for A.A.D.: danopoulos@unistra.fr.

*E-mail for P.B.: braunstein@unistra.fr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The USIAS, CNRS, UdS, Région Alsace, and the Eurométropole de Strasbourg are gratefully acknowledged for the award of fellowships and a Gutenberg Excellence Chair (2010−2011) to A.A.D. and support. We also thank the ucFRC (www.icfrc.fr) for support, the China Scholarship Council for a Ph.D. grant to F.H., and Dr. L. Karmazin (Service de Radiocrystallographie, Institut de Chimie, Strasbourg, France) for the determination of the crystal structures.

■ REFERENCES

(1) (a) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*; Cazin, C. S. J., Ed.; Springer: Berlin, 2011. (b) *N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2014. (c) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122−3172. (d) de Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862−892. (e) Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 8810−8849. (f) Crabtree, R. H. *Coord. Chem. Rev.* **2013**, *257*, 755−766.

(2) Karmakar, S.; Datta, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 9587−9591.

(3) (a) Hahn, F. E. *ChemCatChem* **2013**, *5*, 419−430. (b) Hahn, F. E. Complexes with Protic N-Heterocyclic Carbene (NR,NH-NHC) Ligands. In *Advances in Organometallic Chemistry and Catalysis*; Pombeiro, A. J. L., Ed.; Wiley: Hoboken, NJ, 2013; pp 113−132. (c) Jahnke, M. C.; Hahn, F. E. *Coord. Chem. Rev.* **2015**, *293−294*, 95−115.

(4) (a) Kuwata, S.; Ikariya, T. *Chem. - Eur. J.* **2011**, *17*, 3542−3556. (b) Kuwata, S.; Ikariya, T. *Chem. Commun.* **2014**, *50*, 14290−14300.

DOI: 10.1021/acs.organomet.5b00926
Organometallics XXXX, XXX, XXX−XXX

(c) Zhao, B.; Han, Z.; Ding, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 4744−4788.
(5) Meier, N.; Hahn, F. E.; Pape, T.; Siering, C.; Waldvogel, S. R. *Eur. J. Inorg. Chem.* **2007**, *2007*, 1210−1214.
(6) (a) *Organometallic Pincer Chemistry*; van Koten, G., Milstein, D., Eds.; Springer: Berlin, 2013. (b) *Pincer and Pincer-Type Complexes: Applications in Organic Synthesis and Catalysis*; Szabó, K. J., Wendt, O. F., Eds.; Wiley-VCH: Weinheim, Germany, 2014. (c) Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610−641. (d) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761−1779. (e) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588−602. (f) Selander, N.; Szabó, K. J. *Chem. Rev.* **2011**, *111*, 2048−2076. (g) Gunanathan, C.; Milstein, D. *Chem. Rev.* **2014**, *114*, 12024−12087. (h) Khusnutdinova, J. R.; Milstein, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 12236−12273. (i) Zell, T.; Milstein, D. *Acc. Chem. Res.* **2015**, *48*, 1979−1994. (j) Werkmeister, S.; Neumann, J.; Junge, K.; Beller, M. *Chem. - Eur. J.* **2015**, *21*, 12226−12250. (k) Asay, M.; Morales-Morales, D. *Dalton Trans.* **2015**, *44*, 17432−17447.
(7) (a) Toda, T.; Kuwata, S.; Ikariya, T. *Chem. - Eur. J.* **2014**, *20*, 9539−9542. (b) Flowers, S. E.; Cossairt, B. M. *Organometallics* **2014**, *33*, 4341−4344. (c) Marelius, D. C.; Darrow, E. H.; Moore, C. E.; Golen, J. A.; Rheingold, A. L.; Grotjahn, D. B. *Chem. - Eur. J.* **2015**, *21*, 10988−10992.
(8) (a) Raynal, M.; Cazin, C. S. J.; Vallée, C.; Olivier-Bourbigou, H.; Braunstein, P. *Chem. Commun.* **2008**, 3983−3985. (b) Raynal, M.; Pattacini, R.; Cazin, C. S. J.; Vallée, C.; Olivier-Bourbigou, H.; Braunstein, P. *Organometallics* **2009**, *28*, 4028−4047. (c) Zuo, W.; Braunstein, P. *Organometallics* **2012**, *31*, 2606−2615. (d) Liu, X.; Braunstein, P. *Inorg. Chem.* **2013**, *52*, 7367−7379. (e) Simler, T.; Danopoulos, A. A.; Braunstein, P. *Chem. Commun.* **2015**, *51*, 10699−10702.
(9) Liu, P.; Wesolek, M.; Danopoulos, A. A.; Braunstein, P. *Organometallics* **2013**, *32*, 6286−6297.
(10) He, F.; Braunstein, P.; Wesolek, M.; Danopoulos, A. A. *Chem. Commun.* **2015**, *51*, 2814−2817.
(11) He, F.; Wesolek, M.; Danopoulos, A. A.; Braunstein, P. *Chem. - Eur. J.* **2015**, DOI: 10.1002/chem.201504891.
(12) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Organomet. Chem.* **1973**, *56*, 53−66.
(13) Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci, F.; Laschi, F. *Organometallics* **2003**, *22*, 2545−2547.
(14) Raba, A.; Anneser, M. R.; Jantke, D.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E. *Tetrahedron Lett.* **2013**, *54*, 3384−3387.
(15) He, F.; Ruhlmann, L.; Gisselbrecht, J.-P.; Choua, S.; Orio, M.; Wesolek, M.; Danopoulos, A. A.; Braunstein, P. *Dalton Trans.* **2015**, *44*, 17030−17044.
(16) (a) Danopoulos, A. A.; Winston, S.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2002**, 3090−3091. (b) Danopoulos, A. A.; Pugh, D.; Wright, J. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9765−9767.
(17) Sheldrick, G. M. *SHELXL-97, Program for crystal structure refinement*; University of Göttingen, Göttingen, Germany, 1997.

DOI: 10.1021/acs.organomet.5b00926
Organometallics XXXX, XXX, XXX−XXX