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Elusive Free Bisimino-N-heterocyclic Carbene and Its Rearrangement by C−C Coupling. Characterization of Relevant Iridium(I) and Chromium(II) Complexes

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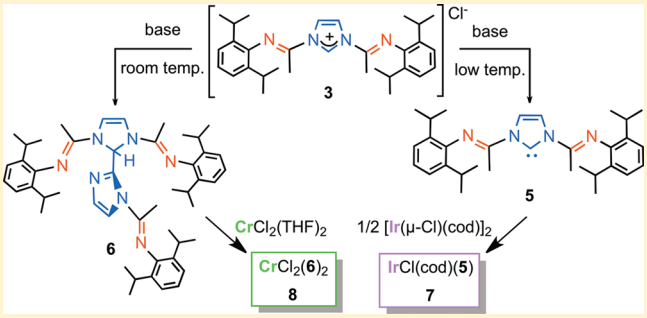
Supporting Information

ABSTRACT: The potentially pincer-type N-heterocyclic (NHC) precursor salt 1,3-bis((*E*)-1-((2,6-diisopropylphenyl)-imino)ethyl)-1*H*-imidazol-3-ium chloride, **3**(Cl$^-$), was prepared by reaction of *N*-(2,6-diisopropylphenyl)acetimidoyl chloride (**1**) with *N*-(1-(1*H*-imidazol-1-yl)ethylidene)-2,6-diisopropylaniline (**2**). Attempts to crystallize **3**(Cl$^-$) at different temperatures afforded single crystals of **3**(Cl$^-$)·MeCN from MeCN and the mixed salt **4** from toluene, in which **2**H$^+$(Cl$^-$) and **3**(Cl$^-$) have cocrystallized. Deprotonation of **3**(Cl$^-$) yielded 1,3-bis[1-(2,6-diisopropylphenylimino)-ethyl]imidazol-2-ylidene (**5**), the first bis(imino)-N-heterocyclic free carbene, and a novel product, **6**, resulting formally from the insertion of the carbene carbon atom of **5** into the C−H bond of the N=CHN moiety of **2** and formation of a new C−C bond. The structures and NMR spectra of **4** and **6** indicate that loss of one N-substituent from the bis(imino) NHC core by exocyclic imidazole N−C bond cleavage is relatively easy. Reaction of **5** with [Ir(μ-Cl)(cod)]$_2$ in pentane afforded in good yield the mononuclear, 16e Ir(I) NHC complex, [IrCl(cod)(**5**)] (**7**). The reaction of **6** with [CrCl$_2$(THF)$_2$] led to the isolation of the paramagnetic complex *trans*-[CrCl$_2$(**6**)$_2$] (**8**), in which the coordination geometry at the chromium is slightly distorted square planar. This complex is the first structurally characterized Cr(II) imidazole complex. The compounds **3**(Cl$^-$), **4**, **6**, **7**, and **8** were identified by X-ray diffraction methods.



INTRODUCTION

Pincer-based iridium complexes exhibit unique reactivity as catalysts in important organometallic transformations, including the dehydrogenation of alkanes to olefins,[1,2] of primary amines to nitriles,[1−3] and of borane-amine complexes,[1,2,4] the isomerization of olefins,[5] and the intermolecular C−H activation of substituted aromatic compounds.[6,7] The further development of new pincer-based iridium complexes with improved activity and selectivity is an attractive goal, which is also justified by the beneficial effects brought about by the thermal stability and structural rigidity of pincer ligands, their potential non-innocence,[8] and the metal−ligand cooperativity[9] in catalytic transformations. The design of new ligands and their controlled modifications have been used to fine-tune the behavior of metal complexes toward their successful use in catalysis.

In recent years, tailor-made N-substituted imidazol-2-ylidenes have been incorporated in various tridentate or pincer-type ligands, which include NCN,[10] CCC,[11,12] PCP,[13,14] CNN,[15] and CNC donor sets (C denotes a NHC-based donor).[16,17] In addition to the N-heterocyclic carbene (NHC) donor functionality, the N-substituents that are part of the pincer-type system play a key role for the modification of the stability, electronic properties, coordination behavior, and catalytic properties of the resulting complexes. The choice of imino functional groups as N-substituents could potentially lead to NHC diimine-type complexes, reminiscent of the α-diimine and pyridine diimine complexes well known for their remarkable catalytic properties.[18−20] The attractive features of the imino-NHCs as hybrid donor ligands are based on the association of a σ-donor/π-acceptor imine with a strong σ-donor/poor π-acceptor NHC functionality. Coleman, Green, et al. have isolated Ag(I), Pd(II), and Rh(I) complexes with imino-NHC ligands,[21−23] and Tilset et al. reported recently a chelated imine-functionalized NHC Rh(I) complex displaying a remarkable high reactivity and *cis*-selectivity in the cyclopropanation of alkenes.[24] Early transition metal complexes were isolated by Lavoie et al.[25,26]

Difficulties associated with extending the ligand design to pincer tridentate *N*,*N*′-bis(imino)azolium proligands or to the corresponding NHC ligands were reported by Bildstein et al. in 2004.[27] Recently, Lavoie's group reported 1,3-bis(*N*-arylimino)imidazolium salts and obtained NHC metal complexes with only one or no imino group coordinated to the metal. The clean preparation and isolation of a bis(imino)-N-heterocyclic free carbene ($N_{(imine)}CN_{(imine)}$) has not yet been

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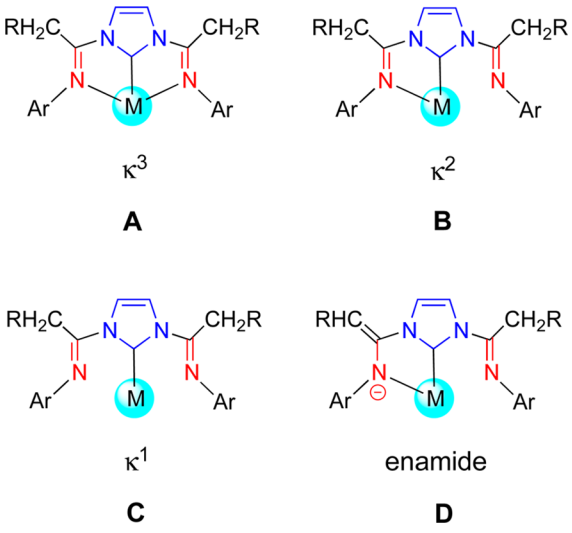
achieved.[28,29] The versatility of such bis(imino)-NHCs as new potential pincer ligands could reside in the diversity of coordination modes they could adopt: monodentate, bidentate, or tridentate through the carbene carbon and one or both iminic fragments (Scheme 1). In addition, plausible tautomeric forms of the ligand may be envisaged when an enolizable imine is present.

Scheme 1. Plausible Bonding Modes of Bis(imino)-NHC Ligands

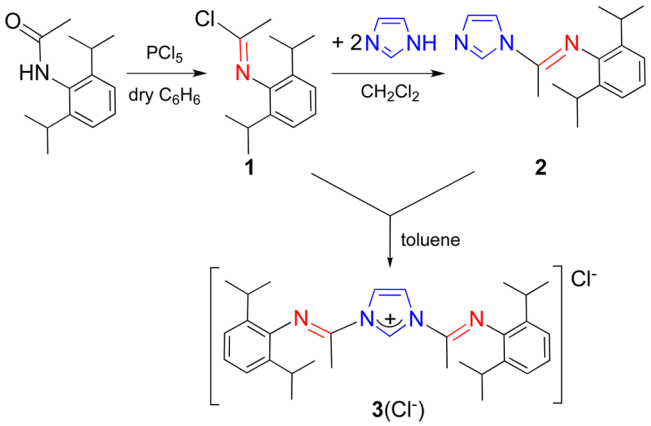


Although a number of stable carbene complexes of iridium are known, those with such bis(imino)-NHC ligands have not been investigated, to the best of our knowledge. The emerging interest in iridium NHC complexes associated with their catalytic properties[2,5,11,14] led us to attempt their synthesis with the bis(imino)-NHC ligands. Here we report a detailed study on the synthesis, isolation, and characterization of the elusive *free* carbene 1,3-bis[1-(2,6-diisopropylphenylimino)ethyl]-imidazol-2-ylidene (**5**), in the course of which an unexpected product resulting from C−C coupling of two imidazole-containing fragments was identified. The latter was used as a ligand toward Cr(II), and we also report one iridium complex obtained from **5**.

RESULTS AND DISCUSSION

1. Synthesis of the Bis-imino-imidazolium Salt 3(Cl⁻) and Its Stability toward Imidazole N−C$_{imino}$ Cleavage. The salt 1,3-bis((*E*)-1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-imidazol-3-ium chloride, **3**(Cl⁻), was prepared by established methods[30] as outlined in Scheme 2. Neat *N*-(2,6-diisopropylphenyl)acetimidoyl chloride, **1**, a colorless and air-sensitive oil, was reacted under nitrogen with a CH_2Cl_2 solution of imidazole to give the corresponding white, air-stable *N*-(1-(1*H*-imidazol-1-yl)ethylidene)-2,6-diisopropylaniline, **2**, in 80% yield. Reaction of the latter with a second equivalent of **1** in toluene afforded the desired 1,3-bis((*E*)-1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-imidazol-3-ium chloride, **3**(Cl⁻), in 83% yield as an insoluble, air-sensitive, white solid. The NMR data of **3**(Cl⁻) in $CDCl_3$ indicate a symmetrical structure in solution. The ^{1}H NMR spectrum contains the deshielded signal of the NC*H*N-imidazolium proton at δ 12.43 ppm and the resonance of the imidazole backbone protons (NC*H*C*H*N) at δ 8.29 ppm, while the ^{13}C NMR resonances of

Scheme 2. Synthesis of the Imidazolium Salt 3(Cl⁻)



the corresponding imidazolium backbone carbons appear at δ 138.9 and 118.1 ppm, respectively.[29]

Attempts were made to obtain single crystals of **3**(Cl⁻) by varying crystallization solvents and temperatures. Whereas single crystals of **3**(Cl⁻)·MeCN suitable for X-ray diffraction were grown from a saturated acetonitrile solution at −30 °C, dissolution of **3**(Cl⁻) in hot, dry toluene, followed by slow diffusion of pentane into a saturated solution at room temperature, afforded single crystals of the mixed salt **4**. The identity of **3**(Cl⁻) and **4** was unambiguously established by X-ray diffraction and spectroscopic methods. An ORTEP drawing of the imidazolium salt **3**(Cl⁻)·MeCN is shown in Figure 1, with selected bond distances and angles.

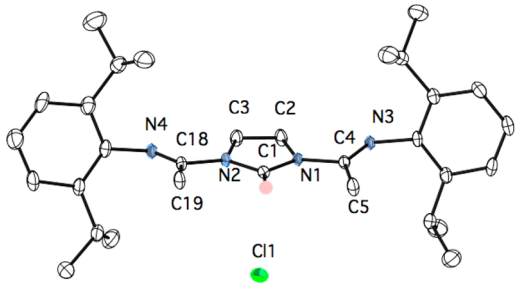


Figure 1. ORTEP of the crystal structure of **3**(Cl⁻) in **3**(Cl⁻)·MeCN. Hydrogen atoms, except the imidazolium proton, and one acetonitrile molecule of crystallization are omitted for clarity. Thermal ellipsoids are set at 30% probability. Selected bond distances (Å) and angles (deg): C1−N1 1.328(5), N1−C2 1.387(5), C2−C3 1.339(6), C3−N2 1.394(5), C1−N2 1.334(5), N1−C4 1.444(5), C4−C5 1.489(6), C4−N3 1.244(5), N2−C18 1.448(5), C18−N4 1.260(5), C18−C19 1.493(6); N1−C1−N2 108.1(4), N3−C4−N1 114.3(4), N1−C4−C5 114.0(3), N4−C18−N2 113.0(4), N2−C18−C19 114.9(4).

The salt **3**(Cl⁻) crystallizes with one molecule of acetonitrile in the monoclinic space group C_2, and both imine groups are in the *E* conformation. The C4−N3 and C18−N4 bond distances of 1.244(5) and 1.260(5) Å, respectively, are in the usual range for double bonds, and both imines are slightly tilted off the mean plane of the imidazolium ring, as indicated by the N3−C4−N1−C1 and N4−C18−N2−C1 torsion angles of 170.8(4)° and 177.7(4)°, respectively. The angles between the planes of the imidazole and the 2,6-diisopropylphenyl rings are 66.5° and 106.7°. Further discussion on the noncovalent interactions in the crystal structure will be presented below.

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The single crystals of the mixed salt **4** belong to the $P\bar{1}$ space group and the asymmetric unit contains two cations, **3** and $\mathbf{2H}^+$, two chlorides, and one toluene molecule, thus corresponding to the cocrystallization of $\mathbf{2H}^+(Cl^-)$ and $\mathbf{3}(Cl^-)$. The conditions for the cleavage of the imidazole N–C_{imino} bond in $\mathbf{3}(Cl^-)$ that led to $\mathbf{2H}^+$ will be discussed below. Similarly to **3**, all the imine groups in the constituents of **4** adopt the *E* configuration, and their C–N bond lengths are very similar to those in **3** (C4–N3 = 1.259(3) Å, C18–N4 = 1.260(3) Å, and C35–N7 = 1.252(3) Å), consistent with a significant double-bond character.[24,29,31] Further evidence for the constitution of **4** was obtained from ^{1}H NMR spectroscopy in CD_2Cl_2. For $\mathbf{2H}^+$, the NC*H*N proton (δ 10.31) and the backbone protons (NC*H*C*H*N) (δ 7.97 and 7.37) are upfield shifted ($\Delta\delta$ = 2.20 ppm and $\Delta\delta$ = 0.34 and nearly 0.29 ppm, respectively) with respect to **2**, owing to the protonation of the heterocycle. The corresponding ^{13}C NMR resonances are found at 136.3, 121.7, and 117.5 ppm, respectively. For the imidazolium cation **3**, the NC*H*N proton is upfield-shifted to δ 12.27, but the backbone protons (NC*H*C*H*N) at δ 8.26 are not affected compared to those in $\mathbf{3}(Cl^-)$. In addition, the ^{1}H NMR spectrum of **4** exhibits two overlapping septets in the range δ 2.69–2.53 (cf. the septet at δ 2.57 in $\mathbf{3}(Cl^-)$), assigned to the C*H*$(CH_3)_2$ protons and four doublets at δ 1.07, 1.02 ppm for $\mathbf{2H}^+$ and 1.11, 1.05 for **3**, respectively, for the CH(C*H*$_3)_2$ protons.

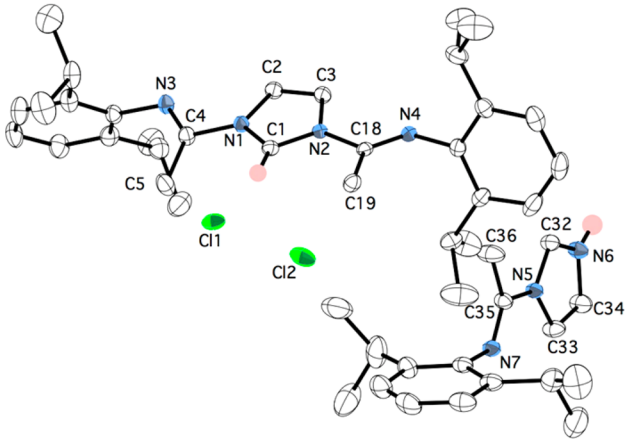

Figure 2. ORTEP of the structure of **4**, corresponding to the cocrystallization of $\mathbf{2H}^+(Cl^-)$ and $\mathbf{3}(Cl^-)$. H atoms, except the imidazolium protons, and one toluene molecule of crystallization are omitted for clarity. Thermal ellipsoids are set at 30% probability. Selected bond distances (Å) and angles (deg): C1–N1 1.334(3), C1–N2 1.327(3), C2–N1 1.398(3), C2–C3 1.335(4), C3–N2 1.389(3), C4–N1 1.443(3), C4–N3 1.259(3), C18–N2 1.440(3), C18–N4 1.260(3), C32–N5 1.349(3), C32–N6 1.305(3), C33–N5 1.382(3), C34–N6 1.376(4), C33–C34 1.333(4), C35–N7 1.252(3), C35–N5 1.437(3); N2–C1–N1 108.0(2), N3–C4–N1 114.5(2), N1–C4–C5 114.5(2), N4–C18–N2 113.7(2), N2–C18–C19 15.54(2), N6–C32–N5 108.3(2), N7–C35–N5 115.3(2), N5–C35–C36 115.3(2).

The successful isolation of $\mathbf{3}(Cl^-)$ from toluene (Scheme 2) is based on its poor solubility in this solvent and its rapid precipitation after formation. It was unexpected, however, that recrystallization of $\mathbf{3}(Cl^-)$ from anhydrous hot toluene would in part result in N–C bond cleavage and formation of $\mathbf{2H}^+(Cl^-)$, as found in **4**. Careful ^{1}H NMR experiments in a NMR Young's tube were conducted with a d_6-benzene suspension of $\mathbf{3}(Cl^-)$. After heating to 60 °C for ca. 1 h, a solution was obtained that contained a major component that gave rise to signals at δ 7.93, 7.52, 7.20, 2.69, 1.41, and 1.10–1.03 ppm, consistent with the formation of the neutral imidazole **2**. However, carrying out the recrystallization of $\mathbf{3}(Cl^-)$ from hot toluene in a glovebox resulted in the isolation of crystalline $\mathbf{3}(Cl^-)$·toluene, as established by ^{1}H NMR spectroscopy and X-ray diffraction analysis (SI). When the ^{1}H NMR spectrum of $\mathbf{3}(Cl^-)$ in d_8-THF was monitored at room temperature as a function of time, progressive formation of **2** was observed, which did not reach completion (see SI). We suggest therefore that nucleophilic attack of the chloride anion in $\mathbf{3}(Cl^-)$ on the C_{imino} carbon, with liberation of **2** and *N*-(2,6-diisopropylphenyl)acetimidoyl chloride (**1**), can occur in THF at room temperature, where $\mathbf{3}(Cl^-)$ is well soluble, but it requires thermal activation in toluene, also to solubilize $\mathbf{3}(Cl^-)$ (this N–C bond-breaking reaction corresponds to the reverse of the synthesis of $\mathbf{3}(Cl^-)$, the latter being driven by the poor solubility of the product in the reaction medium) (Scheme 3). The possibility of a nucleophilic attack of the chloride anion in $\mathbf{3}(Cl^-)$ on the C_{imino} carbon is further supported by the stability, under similar conditions, of $\mathbf{3}(BF_4^-)$, obviously due to the non-nucleophilic nature of the anion. Indeed, when $\mathbf{3}(BF_4^-)$ was dissolved in hot C_6D_6, no formation of **2** was observed by ^{1}H NMR spectroscopy (see SI). If traces of adventitious water are present when handling $\mathbf{3}(Cl^-)$, hydrolysis of the liberated **1** will readily produce HCl, which will form $\mathbf{2H}^+(Cl^-)$ upon reaction with **2**, as found in **4**. Previous reports have pointed to the fragmentation of *N*,*N*′-bis(imino)azolium species as being either responsible for their inaccessibility[27] or the result of their hydrolysis.[29]

2. C–H···Cl Hydrogen Bonding in the Solid-State Structures of $\mathbf{3}(Cl^-)$·MeCN and 4. Further to hydrogen-bonding interactions of the type X–H···Y (X, Y = O, N, S), which have been much investigated, in particular because of their importance in supramolecular chemistry, C–H···Cl interactions attract increasing attention.[32] The C–H···Cl hydrogen bond was first reported by Taylor and Kennard in 1982[33] and is defined by the distance between the proton and Cl being shorter than the sum of the van der Waals radii of H and Cl (3.0 Å) and by a donor–proton–Cl angle of at least 90°. H-bonding interactions involving imidazolium salts have also been shown of relevance to their reactivity and subsequent metalation.[34]

The chemical shift of 12.43 ppm (in CD_2Cl_2) for the imidazolium proton of $\mathbf{3}(Cl^-)$ contrasts with that of $\mathbf{3}(BF_4^-)$ at 10.10 ppm but is very similar to that found for 1,3-bis[1-(2,6-dimethylphenylimino)ethyl]imidazolium chloride (at 12.54 ppm in $CDCl_3$ and 12.85 ppm in THF-d_8),[29] here too being consistent with the occurrence of C–H···Cl^- hydrogen-bonding interactions.[34] A careful inspection of the structures of $\mathbf{3}(Cl^-)$·MeCN and **4** showed that they indeed provide a good opportunity to examine C–H···Cl^- interactions involving imidazole compounds. A C–H···Cl^- hydrogen bond is apparent in the single-crystal X-ray structure analysis of $\mathbf{3}(Cl^-)$·MeCN. Every Cl^- interacts with two neighboring imidazolium cations through three C–H···Cl^- hydrogen-bonding interactions (Cl···H1#1= 2.636 Å, Cl···H19B = 2.863 Å, and Cl···H19C#1 = 2.839 Å, respectively). The strongest C–H···Cl^- interaction (associated with the shortest H···Cl^- distance) involves the chloride interacting with proton H1 attached to crystallographic C1 (Figure 3a). This results in the formation of a one-dimensional left-handed helical supramolecular chain involving C–H···Cl^- hydrogen bonding

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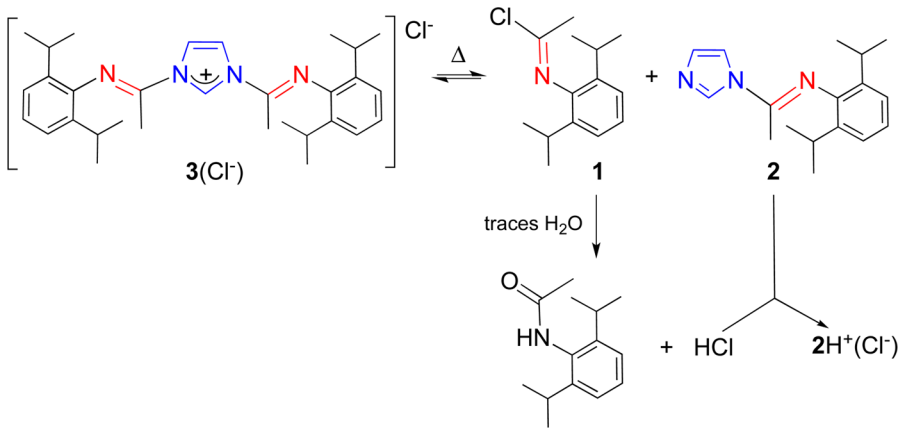
Scheme 3. Reversible Formation and Cleavage of the Imidazole−C_{imino} Bond



(Figure 3b). The helix has a calculated pitch of 10.131 Å, and it contains three Cl^- ions per turn. Every Cl^- also interacts with an acetonitrile molecule through C−H···Cl^- hydrogen bonds (Cl···H33B = 2.777 Å). In addition, C2−H···N3 hydrogen-bonding interactions (3.255 Å) occur between supramolecular chiral helical chains, which form a 2D layer (Figure 3c).

The intermolecular N−H···Cl^- and C−H···Cl^- H-bonds in the crystals of **4** are depicted in Figure 4. The chloride anion Cl2 forms an intermolecular N−H···Cl^- bond (the distance between Cl2 and H6 is 2.049 Å, with a bond angle of 172.27°). The chloride Cl1 bridges between two neighboring imidazolium cations **3** and one cation $\mathbf{2}H^+$ through four C−H···Cl^- hydrogen-bonding interactions. The distances between Cl1 and the proton of the adjacent C−H group are in the range 2.398−2.767 Å, with bond angles ranging from 138.72° to 172.51°, thus indicating that this chloride takes part in the formation of intermolecular N−H···Cl^- or C−H···Cl^- H-bonds

3. Deprotonation of the Imidazolium Salt 3(Cl^-): Isolation of the Free Carbene 5 and of the C−C Coupling Product 6. Although past attempts to isolate free carbenes from 1,3-bis(imino)imidazolium salts were unsuccessful,[28,29] we felt that the nature of the solvent may be critical for the isolation of the desired product. Therefore, we reacted a suspension of 3(Cl^-) in pentane with a suspension of potassium bis(trimethylsilyl)amide in the same solvent while maintaining careful temperature control (from −78 °C to room temperature over 12 h, not exceeding 1 h at room temperature; see Experimental Section and Scheme 4). The pure carbene **5** was isolated as a colorless, air- and moisture-sensitive microcrystalline solid in 85% yield. Its identity was established by ^{1}H and ^{13}C NMR techniques.

The ^{1}H NMR spectral features of **5** provide evidence for a symmetrically substituted heterocycle, and the disappearance of the resonance at δ 12.43 in the spectrum of 3(Cl^-) supports formation of a free carbene. In the ^{13}C NMR spectrum, the C_{NHC} was observed at δ 222.9 ppm. This free carbene is stable at room temperature in the solid state in a glovebox for at least 3 months. Its solutions in C_6D_6 may be stored at low temperature (frozen state, −40 °C) for weeks without noticeable decomposition but can be kept at room temperature for only ca. 1 h, as indicated by ^{1}H NMR monitoring, which revealed *inter alia* formation of **2** (see below Scheme 5).

When the synthesis of **5** was repeated in more concentrated solutions, new product **6** was formed slowly and was isolated by fractional crystallization from the light yellow pentane solution (see Experimental Section). The complicated ^{1}H NMR spectrum of **6** did not allow its straightforward identification. However, single crystals suitable for X-ray diffraction analysis were obtained (see below). After removal of the crystalline material initially formed from the pentane solution (i.e., **6**), the mother liquor was shown by ^{1}H NMR to contain a mixture of **5** and **6**. After the solution was taken to dryness, the resulting solid was washed with pentane several times to eliminate **5**, which afforded an additional amount of pure **6**. Compound **6** was obtained as the major product when the deprotonation of 3(Cl^-) was performed at room temperature; the minor product, compound **A**, is discussed below.

The solid-state structure of **6** is displayed in Figure 5. It features a 1,3-bis(imino)-2,3-dihydroimidazole moiety linked via the crystallographic C1 carbon to the C32 carbon of an *N*-imino-substituted imidazole ring. The structure of **6** may be understood as arising from the unexpected C−C bond formation formally resulting from insertion of the carbene carbon of **5** into the C−H bond of the N=CH-N moiety of **2**, the latter having been produced by cleavage of the exocyclic imidazole N−C_{imino} bond of the bis(imino) NHC backbone (see above, Scheme 3).

The ^{13}C NMR spectrum (C_6D_6, 298 K) of **6** shows a resonance at δ 72.0, characteristic for the C2 carbon in the 1,3-bis(imino)-2,3-dihydro-imidazole moiety, with the corresponding proton resonance at δ 7.79, while the C2 carbon in the (monoimino)imidazole moiety resonates at δ 149.0, a value similar to that found in the C−C coupling product obtained from *N,N′*-diethyl-3,4-dihydroimidazolium (δ = 66 and 173 ppm).[35] One set of ^{1}H NMR signals corresponds to the backbone protons of the 1,3-bis(imino)-2,3-dihydroimidazole moiety (at δ 5.78 ppm), and another set corresponds to the backbone protons of the (monoimino)imidazole group (at δ 8.17 ppm with ^3J(HH) = 1.5 Hz and another masked in the range 7.12−6.97 ppm); the latter are low-field shifted when compared to imidazole **2**.

The crystal structure of **6** is unprecedented. There are obvious questions to address regarding the sequence of C−H deprotonation, N−C_{imino} bond cleavage, and C−C bond formation as well as the driving forces for these events. Since we observed by ^{1}H NMR that mild thermolysis of **5** led to formation of **2**, we first envisaged the possibility that cleavage of the N−C_{imino} bond of **5** could occur and be followed by formal insertion of the carbene carbon of **5** into the C−H bond of the resulting imidazole **2** to give **6** (Scheme 5). The base present during the synthesis of **5** could also act as a catalyst.[35] However, the independent reaction of **5** with **2** in C_6D_6 (NMR

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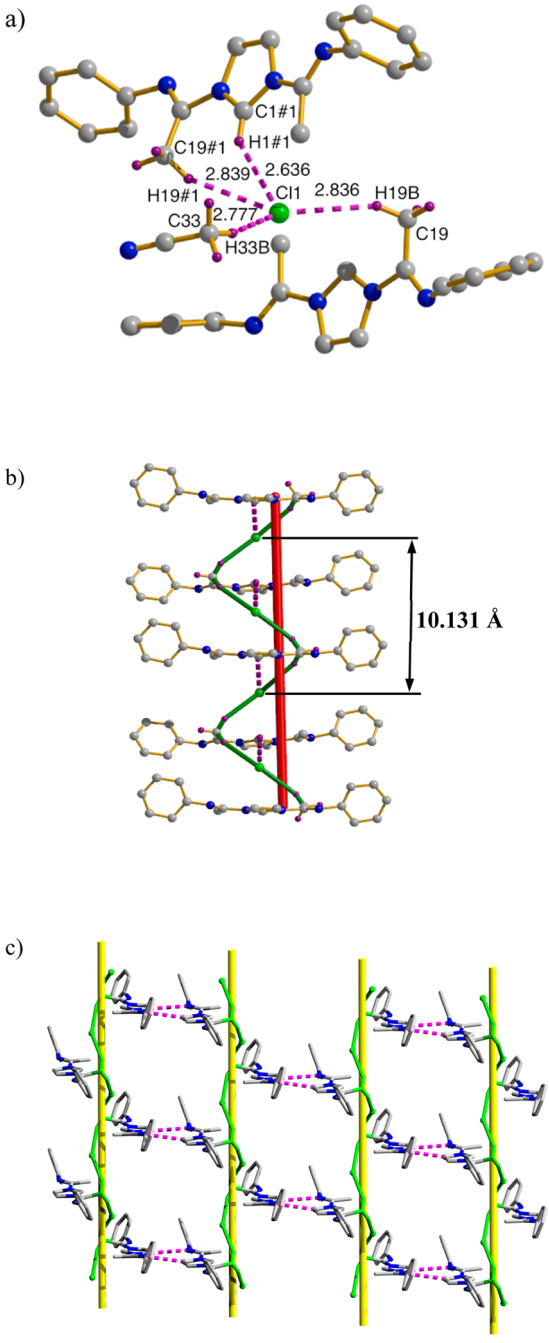

Figure 3. (a) C−H···Cl hydrogen bonds in **3**(Cl^-)·MeCN (H atoms, except those involved in hydrogen-bonding interactions, and *i*-Pr groups are omitted for clarity) (for **3**, #1: 1.5−*x*, 0.5+*y*, 1−*z*); (b) one-dimensional left-handed helical supramolecular chain formed by C−H···Cl^- hydrogen-bonding interactions (H atoms, except those involved in hydrogen bonding interactions, *i*-Pr groups, and the acetonitrile molecule are omitted for clarity); (c) 2D supramolecular layer constituted by the chiral helices of **3**(Cl^-)·MeCN.

experiment), in the presence or not of $KN(SiMe_3)_2$, did not lead to the formation of **6**, even after a few hours at room temperature (Scheme 5). In order to gain further insight into these observations, we monitored by ^{1}H NMR spectroscopy in C_6D_6, d_8-toluene, or d_8-THF various reactions between different precursors containing potential building blocks of **6**, i.e., **2**, **3**(Cl^-), and **5**, in the presence of $KN(SiMe_3)_2$. Transformations of **3**(Cl^-) or **5** to **2** were observed (Scheme

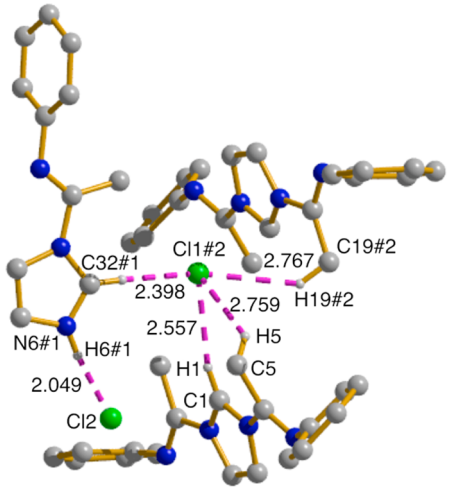

Figure 4. View of C−H···Cl hydrogen-bonding interactions involving a chloride ion in **4**. H atoms, except those involved in hydrogen-bonding interactions, and *i*-Pr groups are omitted for clarity. For **4**, #1: −1+*x*, *y*, *z*; #2: −*x*, 1−*y*, 1−*z*.

5), but in none of these experiments was the formation of **6** evident, except when the reaction of **3**(Cl^-) with $KN(SiMe_3)_2$ was performed in d_8-toluene at room temperature. This rules out that for the formation of **6** the initial formation of the C1−C32 bond between these components is necessary, as discussed in related systems.[36] To examine the possible role of the chloride anion of **3**(Cl^-) in the process leading to **6** and **A**, we reacted **3**(BF_4^-) with $KN(SiMe_3)_2$ in d_6-benzene at room temperature. Slow formation of **6** and **A** was monitored by ^{1}H NMR spectroscopy. These data suggest that the counterion associated with **3** does not play an essential role in the transformations considered.

Only small amounts of compound **A** were obtained, and crystallization by slow evaporation of its pentane solution afforded single crystals that readily lost pentane. Although the quality of the X-ray data was not satisfactory, they were sufficient to establish unambiguously the atom connectivity within the molecule (Scheme 5). The formation of **A** results from a complex sequence of reactions involving formally C−C bond formation between the carbene carbon atom of **5** and the carbon atom of the methyl group of an imine fragment, leading to a six-membered heterocycle fused with the five-membered ring of the NHC moiety. Activation of C−H bonds from methyl substituents has led to the C=CH_2 and CH_2−CH moieties. At this stage, the reaction mechanisms for the formation of **6** and **A** remain unclear and would require further thorough investigations.

4. Synthesis of Iridium Complexes. Initial attempts to prepare NHC iridium(I) complexes by reaction of $[Ir(\mu\text{-}Cl)(cod)]_2$ or $[Ir(\mu\text{-}Cl)(coe)_2]_2$ with the free carbene **5**, generated *in situ* by deprotonation of the imidazolium salt with a slight excess of base, were unsuccessful, probably owing to competitive decomposition of the free carbene. We then decided to use isolated **5** and react it with 0.5 equiv of $[Ir(\mu\text{-}Cl)(coe)_2]_2$ in pentane. This gave intractable reaction products. Fortunately, the reaction of isolated **5** with $[Ir(\mu\text{-}Cl)(cod)]_2$ afforded [IrCl(cod)(**5**)] (**7**), which was isolated as a yellow solid in good yield (Scheme 6).

The ^{1}H NMR data of **7** in solution were consistent with the presence of a mirror plane passing through the Ir, Cl, and C_{NHC} atoms. The coordination of the C_{NHC} donor to the metal center

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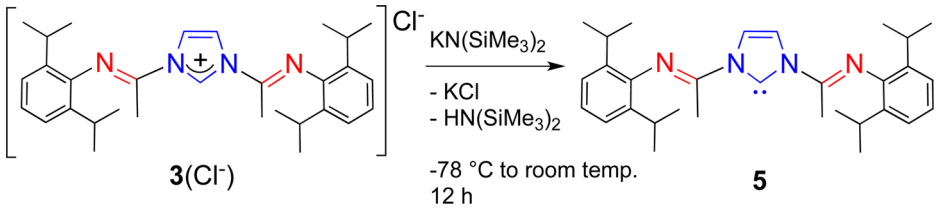
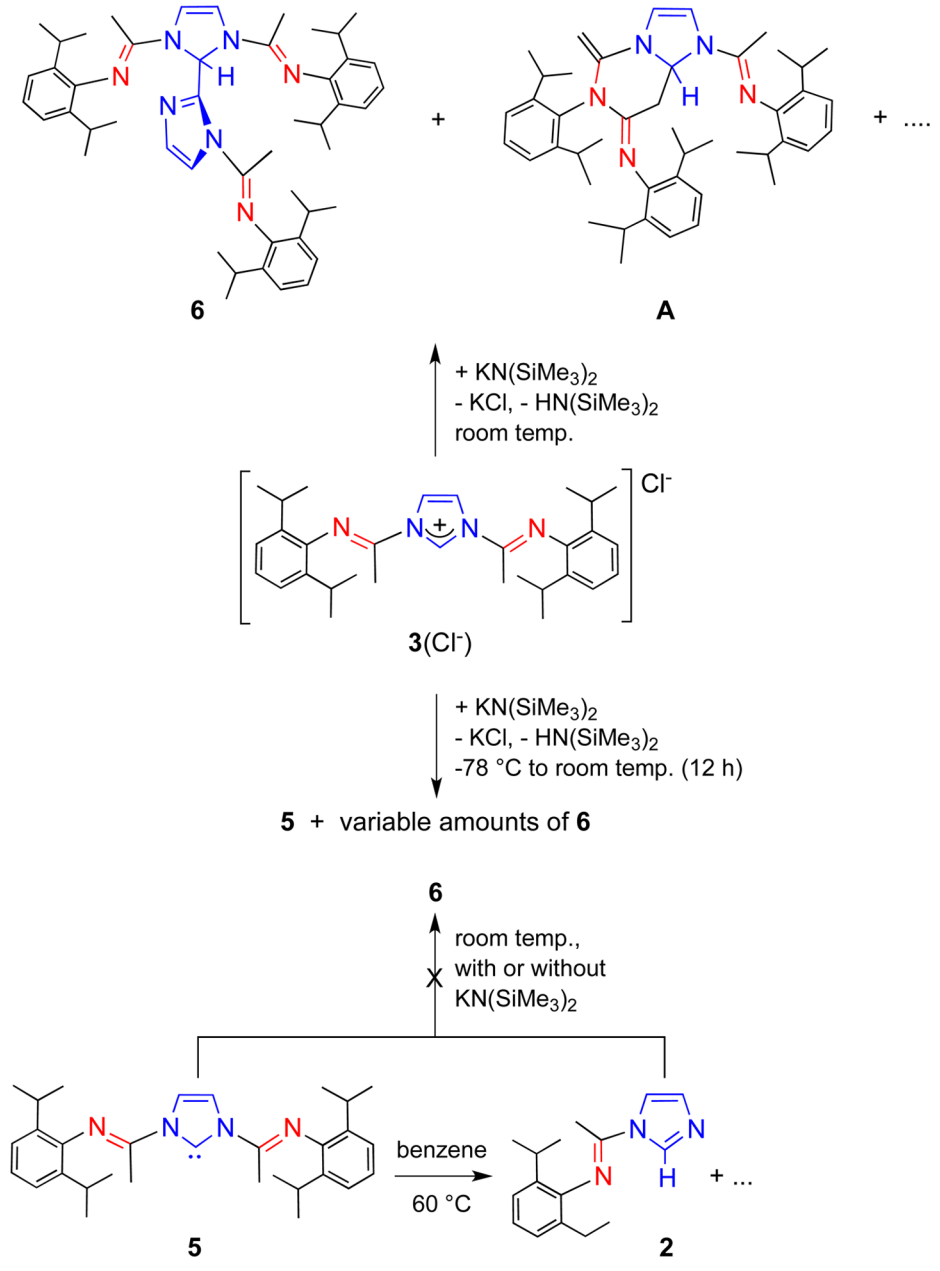
Scheme 4. Synthesis of the Free NHC Ligand 5 in Pentane



Scheme 5. Experiments Related to the Formation of Compound 6 (see text)



was evidenced by a low-field resonance at δ 184.8 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The NHC backbone protons (NC*H*C*H*N) were observed at δ 8.00 ppm, and the ^{13}C NMR signal of the corresponding C atoms appears at δ 120.6 ppm. The vinylic protons of the cod ligand appear at δ 4.63 and 2.86, and the corresponding olefinic carbons at δ 85.0 and 52.6 ppm. As observed in other Ir(I)−cod−NHC complexes,[37] the upfield resonance corresponds to the =CH protons *trans* to the NHC carbon. Single crystals of **7** suitable for X-ray diffraction were grown by slow diffusion of a pentane solution of **5** into a saturated THF solution of $[Ir(\mu\text{-}Cl)(cod)]_2$ at ambient temperature under nitrogen. The molecular structure of **7** and significant bond distances and angles are shown in Figure 6.

The coordination sphere around the iridium center is defined by the two olefinic bonds of the cyclooctadiene ligand, the C1

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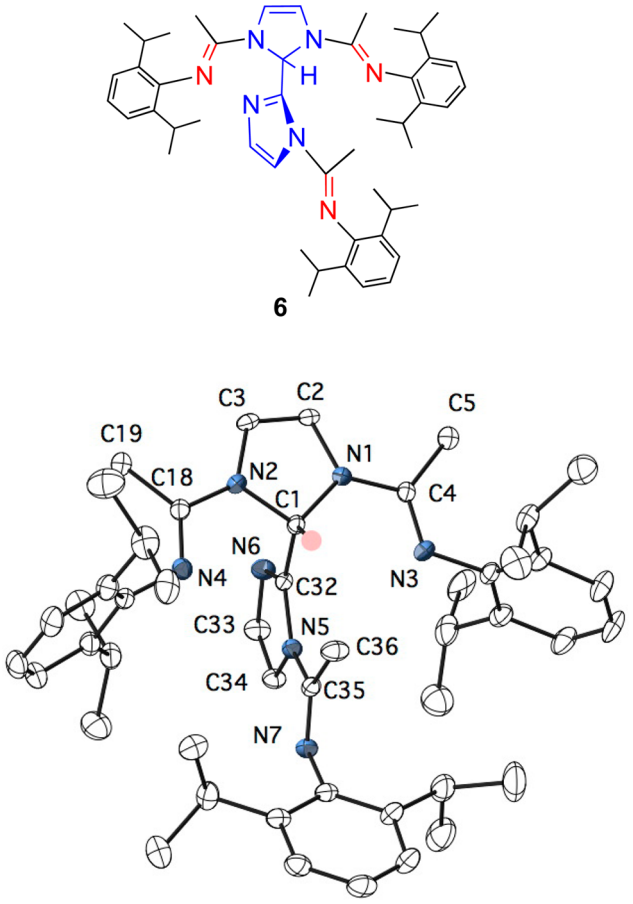
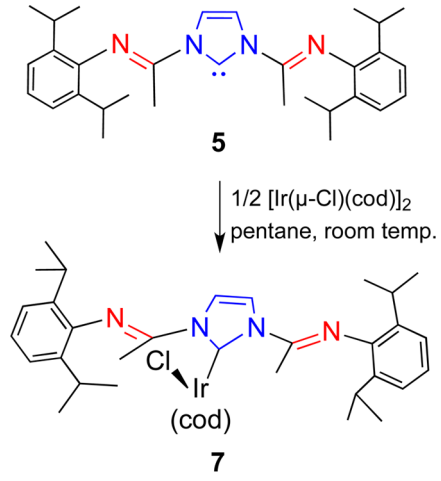


Figure 5. ORTEP of the molecular structure of **6**. H atoms are omitted for clarity, except the imidazolium proton. Three of the isopropyl groups (C15, C17, C27, C28, C44, C45) were found disordered in two positions having the tertiary atom in common and with equal occupancy factors. Thermal ellipsoids are set at 30% probability. Selected bond distances (Å) and angles (deg): C1−C32 1.511(3), C1−N1 1.474(3), C1−N2 1.473(3), C2−C3 1.318(3), C2−N1 1.404(3), C3−N2 1.403(3), C4−N3 1.292(3), C4−N1 1.366(3), C18−N4 1.282(3), C18−N2 1.370(3), C32−N6 1.314(3), C32−N5 1.391(3), C34−N5 1.393(3), C33−N6 1.373(3), C33−C34 1.345(4), C35−N7 1.260(3), C35−N5 1.434(3); N2−C1−N1 100.60(18), N2−C1−C32 111.14(18), N1−C1−C32 111.53(19), N3−C4−N1 116.7(2), N1−C4−C5 115.9(2), N4−C18−N2 117.6(2), N2−C18−C19 115.3(2), N6−C32−N5 111.1(2), N6−C32−C1 119.5(2), N5−C32−C1 129.4(2), N7−C35−N5 114.9(2), N5−C35−C36 118.1(2).

atom of the NHC ligand, and a terminal chloride atom, leading to a slightly distorted square-planar geometry, as evidenced by the *trans* bond angles Cl1−Ir1−C32/C33 160.15(1)°/160.21(1)° and C1−Ir1−C36/C37 161.3(2)°/160.8(2)°, consistent with the metal 16-valence-electron configuration. The molecule is bisected by a plane of symmetry passing through C1, Ir1, and Cl1 that renders the two imine ends of ligand **5** equivalent, in agreement with the NMR data in solution. The heterocycle of ligand **5** forms angles of 45.2° and 48.9° with the bulky 2,6-*i*-$Pr_2C_6H_3$ (diisopropylphenyl, dipp) rings.

In **7**, the NHC ligand binds to the metal in a monodentate κ^1-fashion through the carbene carbon, and the two imine groups assume an *E* configuration, directing the lone pairs away from the metal. Consistent with the NMR data in solution, the coordination of the cod ligand exhibits one double bond disposed *trans* to the carbene and the other *trans* to the chloride, which has implications in the Ir−C and C−C bond

Scheme 6. Synthesis of the Ir(I) NHC Complex 7



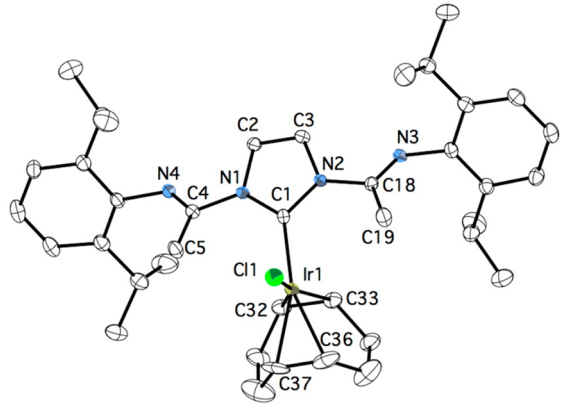


Figure 6. ORTEP of the molecular structure of **7**. H atoms are omitted for clarity. Thermal ellipsoids are set at 30% probability. Selected bond distances (Å) and angles (deg): Ir1−C1 2.019(4), Ir1−C32 2.113(5), Ir1−C33 2.114(4), Ir1−C36 2.166(5), Ir1−C37 2.169(5), Ir1−Cl1 2.3630(1), C32−C33 1.415(6), C36−C37 1.394(7), C1−N1 1.374(5), N1−C2 1.405(5), N1−C4 1.443(5), C4−N4 1.266(5), C2−C3 1.332(6), C3−N2 1.401(5), N2−C18 1.436(5), C18−N3 1.261(6), C1−N2 1.386(5); C1−Ir1−C32 90.22(2), C1−Ir1−C33 90.92(2), C1−Ir1−C36 161.3(2), C1−Ir1−C37 160.8(2), C1−Ir1−Cl1 92.64(1), C36−Ir1−Cl1 89.57(2), C37−Ir1−Cl1 90.43(2), C32−Ir1−Cl1 160.15(1), C33−Ir1−Cl1 160.21(1), C32−Ir1−C33 39.12(2), C36−Ir1−C37 37.5(2), N1−C1−N2 102.9(3), C1−N1−C4 128.4(3), N1−C4−N4 113.4(4), N1−C4−C5 117.3(4), N4−C4−C5 129.2(4), C1−N2−C18 128.6(3), N2−C18−N3 113.5(4), N2−C18−C19 117.7(4), N3−C18−C19 128.8(4).

distances owing to the different *trans* influences of NHC and Cl. Thus, the Ir1−C36/C37 distances are longer than Ir1−C32/C33 as a consequence of the larger *trans* influence of the NHC ligand, and consistently, the C36−C37 double bond is slightly shorter than C32−C33 owing to reduced back-bonding from the metal. The Ir−carbene bond length of 2.019(4) Å is similar to those found in other Ir(I) carbene complexes.[11,12,16] The imino groups are less twisted away from the mean plane of the azole ring (the torsion angles are N3−C18−N2−C1 (153.3°) and N4−C4−N1−C1 (151.6°), respectively) than in **3**(Cl^-) (170.8(4)° and 177.7(4)°). As expected, the C1−N1 and C1−N2 bonds in **7** (1.374(5) and 1.386(5) Å) are longer than in **3**(Cl^-) (1.328(5) and 1.334(5) Å) owing to the decreased π-delocalization over the azole ring. As a result, the

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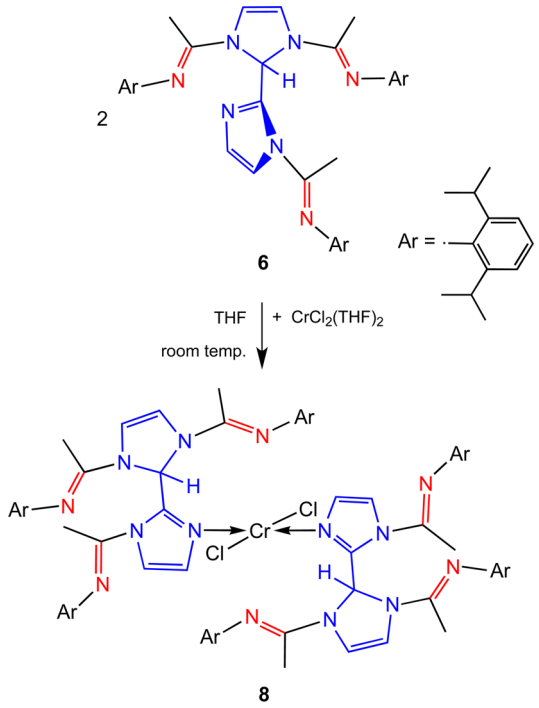
N1−C1−N2 bond angle of 102.9(3)° is also significantly less obtuse than in **3**(Cl⁻) (108.1(4)°).

The FTIR spectrum of **7** shows an absorption band at 1672 cm^{-1} for the C−N stretching vibration, a value consistent with an uncoordinated function. This value is slightly lower than or similar to those in **3**(Cl⁻) (1695 cm^{-1}) and **5** (1673 cm^{-1}).

5. Synthesis of the Chromium Complex *trans*-[$CrCl_2$(6)$_2$] (8) from the C−C Coupling Product 6. The unusual donor arrangement and steric features of **6** prompted us to initiate studies on its coordination chemistry. In view of our interest in the use of chromium complexes for the oligomerization of alkenes, we reacted **6** with [$CrCl_2(THF)_2$]. This led to the isolation of complex **8** after crystallization from THF/pentane (Scheme 7). Paramagnetic **8** was characterized by ^{1}H NMR spectroscopy and elemental analysis, and its structure was fully established by X-ray diffraction.

Scheme 7



The ^{1}H NMR data showed signals assignable to the protons of the isopropyl groups from the aromatic wingtips of the 1,3-bis(imino)-2,3-dihydroimidazole moiety that are furthest from the chromium center; these were only broadened but not shifted (see SI). In contrast, the signals associated with the protons of the directly coordinated (monoimino)imidazole moiety and of the imidazole and the methyl of the 1,3-bis(imino)-2,3-dihydroimidazole moiety were too broad to be observed at room temperature.

Single crystals of **8** suitable for X-ray diffraction were grown slowly from the THF solution. The molecular structure of **8** and significant bond distances and angles are shown in Figure 7.

The molecule is centrosymmetric, with the coordination geometry at the chromium being slightly distorted square planar with *trans* imidazole donors originating from **6**. The N−Cr− Cl angle is close to 90° (90.72°). Although square planar chromium(II) complexes are not rare,[38] the observed Cr−Cl bond lengths (2.3154(8) Å) are best compared with those

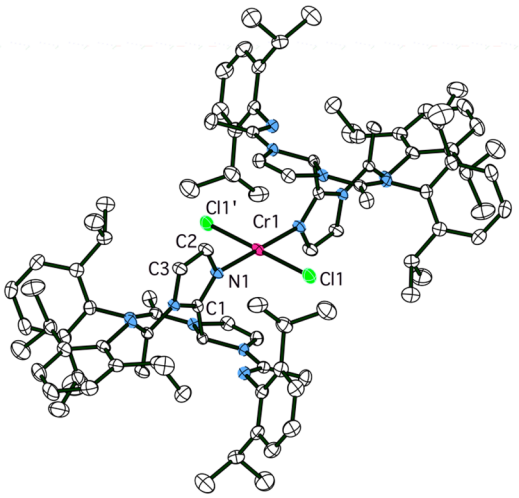


Figure 7. ORTEP of the centrosymmetric chromium complex **8** in **8**·4THF. H atoms and THF molecules of crystallization in the asymmetric unit are omitted for clarity. Thermal ellipsoids are set at 30% probability. Selected bond distances (Å) and angles (deg): Cr1−Cl1 2.3154(8), Cr1−N1 2.124(3), C1−N1 1.317(5), C2−N1 1.377(4), C2−C3 1.345(4), N1−Cr1−Cl1 90.72(7), N1−Cr1−Cl1′ 89.28(7).

found in other adducts of $CrCl_2$ with two bulky *trans* N-heterocyclic carbenes[39] (e.g., in *trans*-[$CrCl_2$(IPr)$_2$] [Cr(1)−Cl(1)/Cl(2) = 2.3140(5)/2.3108(5) Å (IPr = 1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-2-ylidene, :C[N{C_6H_3(*i*-Pr)$_2$-2,6}CH]$_2$) and are shorter than in analogues with less congested NHCs [e.g., in *trans*-[$CrCl_2$(IPrMe)$_2$], [Cr(1)−Cl(1)/Cl(2) 2.3477(8)/2.3461(9) Å (IPrMe = :C[N(*i*-Pr)C-(Me)]$_2$)]. Surprisingly, there are less than 10 Cr imidazole complexes in the CSD and none of them with Cr(II).[40] Compared to the free ligand **6**, the bond lengths in complex **8** were only slightly affected by the coordination to chromium [cf. C32−N6 1.314(3), C33−N6 1.373(3), C33−C34 1.345(4) Å and C1−N1 1.317(5), C2−N1 1.377(4), C2−C3 1.345(4) Å, respectively]. Therefore, the emerging coordination behavior of **6** is relevant to that of a bulky imidazole without interference from the dangling imine functions. Ongoing studies are under way in our group to further study the coordination properties of **6** as well as the catalytic reactivity of **8**.

CONCLUSIONS

The synthesis and study of the new *N*,*N*′-bis(imino)azolium salt **3**(Cl⁻), its corresponding bis(imino)-N-heterocyclic free carbene **5**, and iridium complex **7** demonstrate an unusual and complex chemistry of all the species (i.e., the ligand precursors, the free NHC, and the metal complexes) relevant to this potentially tridentate ligand framework. Deprotonation of the imidazolium salt **3**(Cl⁻) yielded the first bis(imino)-N-heterocyclic free carbene **5** and, importantly, the unexpected C−C coupling product **6**, which turns out to be an interesting new ligand, as shown with the Cr(II) complex **8**. The underlying features of the observed chemistry point to facile N(imidazole)−C(imine) bond cleavage under different conditions, e.g., thermolysis, nucleophilic attack by Cl⁻, and in one case (i.e., formation of **6**) accompanied by C−C bond formation, leading to a new imidazole ligand framework. Coordination of **5** to Ir(I) occurs via the C_{NHC} only (monodentate bonding mode κ^1), although κ^2 complexes with other metals have recently been reported.[25,26,28,29,31] The

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novel bulky imidazole **6** offers interesting ways to tune the metal environment. Further work on this and related chemistry is currently under way.

EXPERIMENTAL SECTION

General Procedures. All operations were carried out using standard Schlenk techniques under an inert atmosphere. Solvents were dried, degassed, and freshly distilled prior to use. THF and Et_2O were dried over sodium/benzophenone, and CH_2Cl_2, toluene, pentane, and acetonitrile were dried and freshly distilled. CD_3CN was degassed and stored over 4 Å molecular sieves. d_6-Benzene and d_8-toluene were vacuum distilled from KH. $CDCl_3$ and CD_2Cl_2 were dried over 4 Å molecular sieves, degassed by freeze−pump−thaw cycles, and stored under argon. NMR spectra were recorded at room temperature on a Bruker AVANCE 300 spectrometer or Bruker AVANCE 400 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.47 MHz or ^{1}H, 400 MHz; ^{13}C, 100.62 MHz) and referenced using the residual proton solvent (^{1}H) or solvent (^{13}C) resonance. Assignments are based on ^{1}H, ^{1}H-COSY, ^{1}H-NOESY, ^{1}H/^{13}C-HSQC, and ^{1}H/^{13}C-HMBC experiments. 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. Electrospray mass spectra (ESI-MS) were recorded on a micro-TOF (Bruker Daltonics, Bremen, Germany) instrument using nitrogen as drying agent and nebulizing gas. *N*-(2,6-Diisopropylphenyl)acetamide was prepared according to the methods described in the literature,[41] and *N*-(2,6-diisopropylphenyl)-acetimidoyl chloride (**1**) was obtained by a modification of a previously reported procedure.

*Preparation of N-(2,6-Diisopropylphenyl)acetimidoyl Chloride (**1**).* *N*-(2,6-Diisopropylphenyl)acetamide (15.5 g, 70.7 mmol) was dissolved in dry benzene (150 mL), PCl_5 (14.80 g, 71.1 mmol) was added gradually, and the mixture was stirred under N_2. Then the temperature of the oil-bath was raised to 60 °C, and the mixture was refluxed for 40 min, until evolution of HCl gas ceased. After the benzene was distilled off (oil-bath temperature 75 °C, bp 40 °C at 4.7 mbar), the oil-bath temperature was raised to 110 °C and a colorless oil of **1** distilled at 80−82 °C at 0.3 mbar (14.2 g, 59.7 mmol, 84% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.28−7.22 (m, 3H, *p*-C*H*$_{(dipp)}$ + *m*-C*H*$_{(dipp)}$), 2.91 (sept., ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_{2(dipp)}$), 2.70 (s, 3H, C*H*$_{3(imine)}$), 1.30 (br s, 12H, CH(C*H*$_3$)$_{2(dipp)}$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 143.7 (*C*═N), 143.4 (*ipso*-*C*$_{(dipp)}$), 137.5 (*o*-*C*$_{(dipp)}$), 125.4 (*p*-*C*H$_{(dipp)}$), 123.7 (*m*-*C*H$_{(dipp)}$), 29.6 (*C*H$_{3(amide)}$), 29.0 (*C*H(CH$_3$)$_{2(dipp)}$), 23.5 (CH(*C*H$_3$)$_{2(dipp)}$). IR (pure, orbit diamond): $\nu_{C=N}$ 1705 cm^{-1}. ESI-MS (CH_2Cl_2, 50 V, *m*/*z*): 461.31 [2 M − HCl + Na, 27%]$^+$, 242.15 [M − HCl + Na + H_2O, 100%]$^+$, 202.16 [M − Cl, 19%]$^+$. Anal. Calcd for $C_{14}H_{20}NCl$ (%): C, 70.72; H, 8.48; N, 5.89. Found (%): C, 70.52; H, 8.53; N, 5.66.

*Preparation of N-(1-(1H-Imidazol-1-yl)ethylidene)-2,6-diisopropylaniline (**2**) (ref 29).* Neat *N*-(2,6-diisopropylphenyl)acetimidoyl chloride (7.00 g, 29.4 mmol) was gradually added to a dichloromethane (80 mL) solution of imidazole (4.10 g, 59.6 mmol) at room temperature under N_2. A white precipitate formed immediately, and the reaction mixture was stirred overnight. Water was added to the mixture, and the product was extracted with dichloromethane. The combined dichloromethane layers were washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum to obtain **2** as a white solid (6.40 g, 23.76 mmol, 80.8%). ^{1}H NMR (CD_2Cl_2): δ 8.11 (br s, 1H, NC*H*N), 7.63 (t, ^3J = 1.5 Hz, 1H, NC*H*CHN$_{(near\ imine)}$), 7.08−6.98 (m, 4H, NCHC*H*N and C*H*$_{(dipp)}$), 2.68 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.08 (s, 3H, C*H*$_{3(imine)}$), 1.07 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.03 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 149.6 (*C*═N), 143.0 (*ipso*-*C*$_{(dipp)}$), 137.5 (*o*-*C*$_{(dipp)}$), 135.9 (NCHN), 130.5 (NCHCHN), 124.6 (*p*-*C*H$_{(dipp)}$), 123.6 (*m*-*C*H$_{(dipp)}$), 116.7 (NCH*C*HN$_{(near\ imine)}$), 28.7 (*C*H(CH$_3$)$_{2(dipp)}$), 23.4 (CH(*C*H$_3$)$_{2(dipp)}$), 23.0 (CH(*C*H$_3$)$_{2(dipp)}$), 16.6 (*C*H$_{3(imine)}$). IR (pure, orbit diamond): $\nu_{C=N}$ 1677 cm^{-1}. ESI-MS (CH_2Cl_2, 50 V, *m*/*z*): 561.37 [2 M + Na, 26%]$^+$, 292.18 [M + Na, 92%]$^+$, 202.16 [M − $C_3N_2H_{3(imidazole)}$, 100%]$^+$. Anal. Calcd for $C_{17}H_{23}N_3$: (%): C, 75.34; H, 8.64; N, 15.23. Found (%): C, 75.51; H, 8.95; N, 15.54.

*Preparation of 1,3-Bis[1-(2,6-diisopropylphenylimino)ethyl]-imidazolium Chloride (**3**·Cl$^-$).* *N*-(2,6-Diisopropylphenylimino)-acetimidoyl chloride (5.60 g, 23.5 mmol) was added to a toluene (50 mL) solution of *N*-(1-(1*H*-imidazol-1-yl)ethylidene)-2,6-diisopropylaniline (**2**) (6.30 g, 23.4 mmol) at room temperature. The reaction mixture was stirred for 48 h, and a light yellow precipitate formed. The solid was filtered, washed with benzene and pentane, respectively, under nitrogen, and dried under vacuum (9.84 g, 19.40 mmol, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.43 (br t, 1H, NC*H*N), 8.29 (d, ^4J = 1.4 Hz, 2H, NC*H*C*H*N), 7.20−7.06 (m, 6H, C*H*$_{(dipp)}$), 2.83 (s, 6H, C*H*$_{3(imine)}$), 2.57 (sept, ^3J = 6.9 Hz, 4H, C*H*(CH$_3$)$_{2(dipp)}$), 1.11 (d, ^3J = 6.9 Hz, 12H, CH(C*H*$_3$)$_{2(dipp)}$), 1.06 (d, ^3J = 6.9 Hz, 12H, CH(C*H*$_3$)$_{2(dipp)}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ149.8 (*C*═N), 140.6 (*ipso*-*C*$_{(dipp)}$), 138.9 (NCHN), 136.5 (*o*-*C*$_{(dipp)}$), 128.4 (C_6H_6), 125.8 (*p*-CH$_{(dipp)}$), 123.6 (*m*-CH$_{(dipp)}$), 118.1 (NCHCHN), 29.0 (CH-(CH$_3$)$_{2(dipp)}$), 23.3 (CH(CH$_3$)$_{2(dipp)}$), 23.0 (CH(CH$_3$)$_{2(dipp)}$), 17.9 (*C*H$_{3(imine)}$). IR (pure, orbit diamond): $\nu_{C=N}$ 1695 cm^{-1}. ESI-MS (CH_2Cl_2, 50 V, *m*/*z*): 489.36 [M + H_2O − Cl, 100%]$^+$, 471.35 [M − Cl, 57%]$^+$. Anal. Calcd for $C_{31}H_{43}N_4Cl$ (%): C, 73.27; H, 8.73; N, 11.03. Found (%): C, 72.30; H, 8.53; N, 9.73.

*Preparation of 1,3-Bis[1-(2,6-diisopropylphenylimino)ethyl]-imidazolium Tetrafluoroborate, **3**(BF$_4^-$).* A silver tetrafluoroborate (0.192 g, 0.98 mmol) solution in THF (10 mL) was added to a solution of 1,3-bis[1-(2,6-diisopropylphenylimino)ethyl]imidazolium chloride, **3**(Cl$^-$) (0.500 g, 0.98 mmol), in THF (50 mL) at room temperature. A white precipitate was formed within minutes, and the reaction mixture was allowed to stir at room temperature for 1 h protected from light. The precipitate was removed from the solution by filtration over Celite, and the solvent was removed under vacuum. An amorphous, white solid was obtained in almost quantitative yield (0.52 g, 9.89 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.10 (t, ^4J = 1.5 Hz, 1H, NC*H*N), 8.39 (d, ^4J = 1.5 Hz, 2H, NC*H*C*H*N), 7.28−7.16 (m, 6H, C*H*$_{(dipp)}$), 2.65 (sept, ^3J = 6.9 Hz, 4H, C*H*(CH$_3$)$_{2(dipp)}$), 2.55 (s, 6H, C*H*$_{3(imine)}$), 1.16 (d, ^3J = 6.9 Hz, 12H, CH(C*H*$_3$)$_{2(dipp)}$), 1.13 (d, ^3J = 6.9 Hz, 12H, CH(C*H*$_3$)$_{2(dipp)}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.1 (*C*═N), 140.6 (*ipso*-*C*$_{(dipp)}$), 136.7 (*o*-*C*$_{(dipp)}$), 135.7 (NCHN), 126.0 (*p*-*C*H$_{(dipp)}$), 123.8 (*m*-*C*H$_{(dipp)}$), 118.7 (NCHCHN), 28.7 (*C*H(CH$_3$)$_{2(dipp)}$), 23.5 (CH(*C*H$_3$)$_{2(dipp)}$), 23.0 (CH(*C*H$_3$)$_{2(dipp)}$), 15.9 (*C*H$_{3(imine)}$). IR (pure, orbit diamond): $\nu_{C=N}$ 1695 cm^{-1}. **3**(BF$_4^-$) can be recrystallized from toluene to give colorless needles of formula (**3**·BF$_4^-$)·toluene. IR (pure, orbit diamond): $\nu_{C=N}$ 1700 cm^{-1}. Anal. Calcd for $C_{38}H_{51}BF_4N_4$ (%): C, 70.15; H, 7.90; N, 8.61. Found (%): C, 69.84; H, 7.88; N, 9.02.

*Thermal Treatment of 1,3-Bis((E)-1-((2,6-diisopropylphenyl)-imino)ethyl)-1H-imidazol-3-ium Tetrafluoroborate, **3**(BF$_4^-$), in d_6-Benzene.* C_6D_6 (0.8 mL) was added to solid **3**(BF$_4^-$) (0.012 g, 0.02 mmol) in a NMR tube, and the suspension was heated at 80 °C until complete dissolution of the salt. The ^{1}H NMR spectrum was then recorded after cooling to room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 10.10 (br t, ^4J = 1.4 Hz, 1H, NC*H*N), 7.49 (d, ^4J = 1.4 Hz, 2H, NC*H*C*H*N), 7.13−7.05 (m, 6H, C*H*$_{(dipp)}$), 2.89 (sept, ^3J = 6.9 Hz, 4H, C*H*(CH$_3$)$_{2(dipp)}$), 2.59 (s, 6H, C*H*$_{3(imine)}$), 1.19 (d, ^3J = 6.9 Hz, 12H, CH(C*H*$_3$)$_{2(dipp)}$), 1.17 (d, ^3J = 6.9 Hz, 12H, CH(C*H*$_3$)$_{2(dipp)}$). The salt crystallizes as colorless needles from the solution at room temperature after about 1 h.

*Thermal Treatment of 1,3-Bis((E)-1-((2,6-diisopropylphenyl)-imino)ethyl)-1H-imidazol-3-ium Chloride, **3**(Cl$^-$), in C_6D_6.* C_6D_6 (0.8 mL) was added to solid **3**(Cl$^-$) (0.015 g, 0.03 mmol) in a NMR tube, and the suspension mixture was heated at 80 °C until complete dissolution (5−10 min). ^{1}H NMR (400 MHz, C_6D_6) shows a mixture of three products (see also SI): 10% of **3**(Cl$^-$): δ 12.88 (br s, 1H, NC*H*N), 7.40 (s, 2H, NC*H*C*H*N), 7.17−7.09 (m, aromatic H and C_6D_6), 3.19 (s, 6H, C*H*$_{3(imine)}$), 2.91 (overlapping sept, ^3J = 6.9 Hz, 4H, C*H*(CH$_3$)$_{2(dipp)}$), 1.20 (d, ^3J = 6.9 Hz, 12H, CH(C*H*$_3$)$_{2(dipp)}$), 1.17 (d, ^3J = 6.9 Hz, 12H, CH(C*H*$_3$)$_{2(dipp)}$); 45% of **2**: 8.13 (v br s, 1H, NC*H*N), 7.51 (br t, ^3J = 1.3 Hz, 1H, NC*H*CHN$_{(near\ imine)}$), 7.17−7.09 (m, aromatic H and C_6D_6), 2.69 (sept, ^3J = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 2.15 (s, 3H, C*H*$_{3(imine)}$), 1.09 (d, ^3J = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.05 (d,

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^3J = 6.9 Hz, 6H, CH(CH_3)$_2$); 45% of **1**: 7.17−7.09 (m, aromatic H and C_6D_6), 2.95 (sept, ^3J = 6.9 Hz, 2H, $CH(CH_3)_2$), 1.45 (s, 3H, $CH_{3(imine)}$), 1.26, (v br, CH(CH_3)$_2$), 1.19 (vbr, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6) (corresponding to **2**): δ 149.7 (*C*═N), 143.4 (*ipso*-$C_{(dipp)}$), 137.6 (*o*-$C_{(dipp)}$), 136.2 (NCHN), 131.2 (NCHCHN), 125.1 (*p*-$CH_{(dipp)}$), 124.0 (*m*-$CH_{(dipp)}$), 116.5 (NCHCHN$_{(near\ imine)}$), 29.1 ($CH(CH_3)_{2(dipp)}$), 23.7 ($CH(CH_3)_{2(dipp)}$), 23.2 ($CH(CH_3)_{2(dipp)}$), 15.9 ($CH_{3(imine)}$); attributed to **1**: δ 144.1 (*C*═N), 143.0 (*ipso*-$C_{(dipp)}$), 137.4 (*o*-$C_{(dipp)}$), 126.1 (*p*-$CH_{(dipp)}$), 125.8 (*m*-$CH_{(dipp)}$), 29.3 ($CH(CH_3)_{2(dipp)}$), 29.1 ($CH_{3(amide)}$), 23.9−23.5 large (CH-$(CH_3)_{2(dipp)}$). The signals due to **3**(Cl^-) are too small to be determined.

Spectrum of **2**: ^{1}H NMR (500 MHz, C_6D_6): 7.93 (s, 1H, NC*H*N), 7.53 (br t, ^3J = 1.4 Hz, 1H, NC*H*CHN$_{(near\ imine)}$), 7.20 (s, 1H, NC*H*CHN), 7.12−7.07 (m, aromatic H), 2.69 (sept, ^3J = 6.9 Hz, 2H, $CH(CH_3)_2$), 1.39 (s, 3H, $CH_{3(imine)}$), 1.09 (d, ^3J = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.04 (d, ^3J = 6.9 Hz, 6H, CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 149.6 (C═N), 143.5 (*ipso*-$C_{(dipp)}$), 137.6 (*o*-$C_{(dipp)}$), 136.1 (NCHN), 131.6 (NCHCHN), 125.1 (*p*-$CH_{(dipp)}$), 123.9 (*m*-$CH_{(dipp)}$), 116.5 (NCHCHN$_{(near\ imine)}$), 29.0 ($CH(CH_3)_{2(dipp)}$), 23.7 (CH-$(CH_3)_{2(dipp)}$), 23.2 ($CH(CH_3)_{2(dipp)}$), 15.8 ($CH_{3(imine)}$).

*Preparation of [**2**·HCl + **3**(Cl^-) + PhMe] (**4**).* Crystals of **4** suitable for X-ray diffraction studies were grown at room temperature by slow diffusion of pentane into a saturated toluene solution of **3**(Cl^-). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 12.27 (t, ^4J = 1.5 Hz, 1H, NC*H*N, for **3**(Cl^-)), 10.31 (dd, ^4J = 1.2, 1.5 Hz, 1H, NC*H*N, for **2**·HCl), 8.26 (d, ^3J = 1.5 Hz, 2H, NC*H*C*H*N, for **3**(Cl^-)), 7.97 (t, ^3J = ^4J = 1.7 Hz, 1H, NC*H*CHN$_{(near\ imine)}$, for **2**·HCl), 7.37 (dd, *J* = 1.5, 1.7 Hz, 1H, NCHC*H*N, for **2**·HCl), 7.15−7.04 (m, 9H for $CH_{(dipp)}$ + 4H for $CH_{(residual\ toluene)}$), 2.81 (s, 6H, $CH_{3(imine)}$, for **3**(Cl^-), 2.69−2.53 (two overlapping sept, ^3J = 6.9 Hz, 6H, $CH(CH_3)_{2(dipp)}$), 2.35 (s, 3H, $CH_{3(imine)}$, for **2**·HCl), 2.25 (s, 2.4H for $CH_{3(residual\ toluene)}$), 1.11 (d, ^3J = 6.9 Hz, 12H, CH(CH_3)$_{2(dipp)}$, for **3**(Cl^-)), 1.07 (d, ^3J = 6.9 Hz, 6H, CH(CH_3)$_{2(dipp)}$, for **2**·HCl), 1.05 (d, ^3J = 6.9 Hz, 12H, CH-$(CH_3)_{2(dipp)}$, for **3**(Cl^-)), 1.02 (d, ^3J = 6.9 Hz, 6H, CH(CH_3)$_{2(dipp)}$, for **2**·HCl). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 150.4 (C═N, for **3**(Cl^-)), 149.2 (C═N, for **2**·HCl), 141.6 (*ipso*-$C_{(dipp)}$, for **2**·HCl), 141.4 (*ipso*-$C_{(dipp)}$, for **3**(Cl^-)), 139.9 (NCHN, for **3**(Cl^-)), 138.3 (*ipso*-$C_{(residual\ toluene)}$), 137.0 (*o*-$C_{(dipp)}$ for both **3**(Cl^-) and **2**·HCl), 136.3 (NCHN, for **2**·HCl), 129.3 (*o*-$CH_{(residual\ toluene)}$), 128.5 (*m*-$CH_{(residual\ toluene)}$), 125.8 (*p*-$CH_{(dipp)}$, for **3**(Cl^-)), 125.6 (*p*-$CH_{(dipp)}$, for **2**·HCl), 125.1 (*p*-$CH_{(toluene)}$), 123.8 (*m*-$CH_{(dipp)}$, for both **3**·Cl^- and **2**·HCl), 121.7 (NCHCHN$_{(near\ imine)}$, for **2**·HCl), 118.3 (NCHCHN, for **3**(Cl^-)), 117.5 (NCHCHN, for **2**·HCl), 28.9 ($CH(CH_3)_{2(dipp)}$, for **3**·Cl^-), 28.8 ($CH(CH_3)_{2(dipp)}$, for **2**·HCl), 23.4 ($CH(CH_3)_{2(dipp)}$, for **3**(Cl^-)), 23.4 ($CH(CH_3)_{2(dipp)}$, for **2**·HCl), 23.0 ($CH(CH_3)_{2(dipp)}$, for **3**(Cl^-)), 22.9 ($CH(CH_3)_{2(dipp)}$, for **2**·HCl), 21.5 ($CH_{3(residual\ toluene)}$), 18.2 ($CH_{3(imine)}$, for **3**($Cl^-$), 17.1 ($CH_{3(imine)}$, for **2**·HCl). IR (pure, orbit diamond): $\nu_{C=N}$ 1688 cm^{-1}. ESI-MS (CH_2Cl_2, 50 V, *m*/*z*): 471.35 [M^2 − Cl, 18%]$^+$, 292.19 [M^1 + Na, 7%]$^+$, 202.16 {[M^1 − $C_3N_2H_{3(imidazole)}$]$^+$ + [M^2 − $C_{14}N_1H_{20(imine)}$ − $C_3N_2H_{3(imidazole)}$ − Cl]$^+$, 100%}. Anal. Calcd for $C_{54}H_{75}N_7Cl_2$ (%): C, 72.62; H, 8.46; N, 10.98. Found (%): C, 72.52; H, 8.43; N, 10.61.

*Preparation of 1,3-Bis[1-(2,6-diisopropylphenylimino)ethyl]-imidazol-2-ylidene (**5**).* A suspension of KN[$Si(CH_3)_3$]$_2$ (0.392 g, 1.97 mmol) in pentane (10 mL) was added slowly to a pentane (50 mL) suspension of **3**(Cl^-) (0.970 g, 1.91 mmol) at −78 °C. The suspension was stirred at −78 °C for 3 h and then was allowed to warm slowly with stirring overnight in the cooling bath in order to avoid decomposition of **5**. The reaction mixture was filtered, and **5** was obtained as a light yellow solid after removal of the solvent *in vacuo* (0.79 g, 1.68 mmol, 85%). ^{1}H NMR (300 MHz, C_6D_6): δ 8.06 (s, 2H, NC*H*C*H*N), 7.19−7.01 (m, 6H, $CH_{(dipp)}$), 2.94 (sept., ^3J = 6.9 Hz, 4H, $CH(CH_3)_{2(dipp)}$), 2.47 (s, 6H, $CH_{3(imine)}$), 1.17 (d, ^3J = 6.9 Hz, 12H, $CH(CH_3)_{2(dipp)}$), 1.13 (d, ^3J = 6.9 Hz, 12H, $CH(CH_3)_{2(dipp)}$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 225.9 (NCN), 156.1 (*C*═N), 144.4 (*ipso*-$C_{(dipp)}$), 137.6 (*o*-$C_{(dipp)}$), 124.9 (*p*-$CH_{(dipp)}$), 124.0 (*m*-$CH_{(dipp)}$), 117.8 (NCHCHN), 29.2 ($CH(CH_3)_{2(dipp)}$), 23.8 ($CH(CH_3)_{2(dipp)}$), 23.3 ($CH(CH_3)_{2(dipp)}$), 17.6 ($CH_{3(imine)}$). IR (pure, orbit diamond): $\nu_{C=N}$ 1673 cm^{-1}. ESI-MS (PhMe, 50 V, *m*/*z*): 489.36 [M + H_2O + H, 100%]$^+$, 471.35 [M + H, 13%]$^+$. Anal. Calcd for $C_{31}H_{42}N_4$ (%): C, 79.01; H, 8.99; N, 11.90. Found (%): C, 77.74; H, 9.18; N, 11.33.

*Compound **6**.* Compound **6** can be obtained in different ways: (a) as a byproduct in the preparation of compound **5** at lower temperatures especially in larger scales when the concentration of the reactant is higher (Scheme 5); (b) by the reaction of **3**(Cl^-) with KN($SiMe_3$)$_2$ at room temperature.

*a. Formation of **6** as a Byproduct in the Preparation of **5**.* The reaction described above for the synthesis of **5** was repeated with the reagents used in higher concentration as follows: A suspension of KN($SiMe_3$)$_2$ (1.920 g, 9.65 mmol) in pentane (20 mL) was added slowly to a pentane (50 mL) suspension of **3**(Cl^-) (4.84 g, 9.53 mmol) at −78 °C. The suspension was stirred at −78 °C for 3 h and then was allowed to warm slowly with stirring overnight in the cooling bath. The reaction mixture was filtered and taken to dryness under reduced pressure.

*b. Preparation of **6** at Room Temperature.* A suspension of KN($SiMe_3$)$_2$ (0.786 g, 3.94 mmol) in pentane (20 mL) was added slowly to a pentane (30 mL) suspension of **3**(Cl^-) (2.000 g, 3.94 mmol) at room temperature. The suspension was allowed to stir at room temperature for 48 h. The suspension was then filtered and the solvent evaporated under vacuum; 0.650 g of a first crop could be obtained that contained ca. 30% of **6** (determined by ^{1}H NMR) and 20% of compound **A** of similar solubility. The solid obtained from the filtration was triturated for several hours with pentane (3 × 75 mL) to extract **6**, which could be obtained in higher purity, around 95%. The combined yield of **6** is 55−62%. Isolated crystalline **6** can be obtained in 44% yield (0.70 g, 0.86 mmol). Crystals of **6** suitable for X-ray diffraction were grown from a saturated pentane solution at room temperature.

^{1}H NMR (300 MHz, C_6D_6): δ 8.21 (d, ^3J = 1.5 Hz, 1H, NC*H*CHN), 7.83 (s, 1H, NC*H*CN), 7.10−6.98 (m, 9H for $CH_{(dipp)}$ + 1H for NCHC*H*N + 2H for $C_6H_{6(residual\ benzene)}$), 5.81 (s, 2H, NC*H*C*H*N), 3.01 (s, 3H, $CH_{3(imine)}$), 2.84 (sept., ^3J = 6.8 Hz, 2H, $CH(CH_3)_{(dipp)}$), 2.56 (sept., ^3J = 6.8 Hz, 2H, $CH(CH_3)_{(dipp)}$), 2.12 (sept., ^3J = 6.8 Hz, 2H, $CH(CH_3)_{(dipp)}$), 1.34 (s, 6H, $CH_{3(imine)}$), 1.12 (d, ^3J = 6.8 Hz, 6H, CH(CH_3)$_{2(dipp)}$), 1.06 (d, ^3J = 6.8 Hz, 6H, CH(CH_3)$_{2(dipp)}$), 0.99 (d, ^3J = 6.8 Hz, 18H, CH(CH_3)$_{2(dipp)}$), 0.59 (d, ^3J = 6.8 Hz, 6H, CH(CH_3)$_{2(dipp)}$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 153.3(C═N), 149.3(C═N), 149.0(NCHCN), 145.5, 143.7, 140.1, 139.0, 138.1, 128.6, 127.7 (NCHCHN), 124.6, 123.8, 123.7, 123.5, 118.8 (NCHCHN), 112.1 (NCHCHN), 72.0 (NCHCN), 28.6, 28.3, 27.8, 24.8, 24.3, 24.2, 24.0, 23.2, 19.6, 15.4. IR (pure, orbit diamond): $\nu_{C=N,\ C=C}$ 1665, 1629, 1609, 1586 cm^{-1}. ESI-MS (PhMe, 50 V, *m*/*z*): 740.54 [M + H]$^+$. Anal. Calcd for $C_{48}H_{65}N_7$ (%): C, 77.79; H, 8.98; N, 13.23. Found (%): C, 77.24; H, 8.94; N, 12.63.

Compound **A** could not be isolated pure, but some crystals were identified in a mixture with **6**. X-ray diffraction analysis established the atom connectivity within the molecule, but the quality of the data did not allow metrical data of high accuracy for further discussion (see text). ^{1}H NMR (300 MHz, C_6D_6): δ 7.42−6.80 (m, 9H for $CH_{(dipp)}$), 6.37 (dd, ^3J = 10.2 Hz, ^3J = 2.6 Hz, 1H, NC*H*CH$_2$), 5.77 (d, ^3J = 2.9 Hz, 1H, NC*H*CHN), 5.46 (d, ^3J = 2.9 Hz, 1H, NCHC*H*N), 3.91 (dd, ^2J = 14.9 Hz, ^3J = 2.6 Hz, 1H, CC*H*HCH), 3.48 (d, ^2J = 2.4 Hz, 1H, NCC*H*H), 3.38 and 3.36 (two closely spaced sept, ^3J = 6.8 Hz, 2H, $CH(CH_3)_{2(dipp)}$), 3.18 (d, ^2J = 2.4 Hz, 1H, NCCH*H*), 3.10−2.96 (two overlapping sept, ^3J = 6.8 Hz, 2H, $CH(CH_3)_{2(dipp)}$), 2.80 (sept, ^3J = 6.8 Hz, 1H, $CH(CH_3)_{2(dipp)}$), 2.69 (dd, ^2J = 14.9 Hz, ^3J = 10.2 Hz,1H, NCC*H*H), 2.45 (sept, ^3J = 6.8 Hz, 1H, $CH(CH_3)_{2(dipp)}$), 1.43 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_{2(dipp)}$), 1.40 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_{2(dipp)}$), 1.39 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_{2(dipp)}$), 1.34 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_{2(dipp)}$), 1.21 (s, 3H, $CH_{3(imine)}$), 1.18 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_{2(dipp)}$), 1.17 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_{2(dipp)}$), 1.13−1.11 (two overlapping d, ^3J = 6.8 Hz, 6H, CH(CH_3)$_{2(dipp)}$), 1.08 (d, ^3J = 6.8 Hz, 6H, CH(CH_3)$_{2(dipp)}$), 0.87 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_{2(dipp)}$), 0.76 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_{2(dipp)}$). $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6): δ 151.4, 150.1, 148.5, 146.1, 145.7, 144.5 (two peaks), 139.5, 139.4, 138.6, 138.5, 136.5 (quaternary carbon), 129.4, 125.0, 124.8, 124.1, 124.0, 123.9, 123.7, 123.4, 123.3, 115.4, 111.3 (NCHCHN), 71.1 (NCCH_2),

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72.1 ($NCHCH_2$), 33.5 ($NCHCH_2$), 29.9, 29.8, 28.9, 28.7, 28.0, 26.2, 25.8, 25.7, 24.5, 24.2, 23.9 (two peaks), 23.4, 23.4, 23.2, 23.1, 15.1 (CH_3(imine)) (tertiary and primary carbon unless stated otherwise). ESI-MS (50 V, m/z): 672.50 (100%), 673.51 (49.4%), 674.51 (10.1%), pattern $[M + H]^+$ [theoretical pattern for $[M]^+$: 671.49 (100.0%), 672.50 (49.4%), 673.50 (11.9%)].

Preparation of [IrCl(cod)(5)] (7). The carbene ligand **5** (0.094 g, 0.200 mmol) was dissolved in a minimal amount of pentane (5 mL), and the mixture was added to a suspension of dark orange crystals of $[Ir(\mu\text{-}Cl)(cod)]_2$ (0.067 g, 0.100 mmol) in pentane (10 mL). A light yellow precipitate formed immediately, and the mixture was stirred at room temperature for 3 h. The solid was filtered, washed with pentane, and dried under vacuum to yield spectroscopically pure **7** as a yellow powder (0.058 g, 0.072 mmol, 72%). Crystals suitable for X-ray diffraction were grown at room temperature under nitrogen by slow diffusion of a pentane solution of the free carbene **5** into a saturated THF solution of $[Ir(\mu\text{-}Cl)(cod)]_2$. ^1H NMR (500 MHz, C_6D_6): δ 7.65 (s, 2H, NC*H*C*H*N), 7.20−7.00 (m, 6H, C$H_{(dipp)}$), 5.03 (m, 2H, C$H_{(cod)}$), 3.32 (s, 6H, C$H_{3(imine)}$), 3.06 (sept., ^3J = 6.9 Hz, 2H, C$H(CH_3)_{2(dipp)}$), 2.83 (m, 2H, C$H_{(cod)}$), 2.76 (sept, ^3J = 6.9 Hz, 2H, C$H(CH_3)_{2(dipp)}$), 2.15−2.01 (m, 4H, $CH_{2(cod)}$), 1.61−1.55 (m, 2H, $CH_{2(cod)}$), 1.48−1.43 (m, 2H, $CH_{2(cod)}$), 1.30 (d, ^3J = 6.9 Hz, 6H, CH(CH_3)$_{2(dipp)}$), 1.21 (d, ^3J = 6.9 Hz, 6H, CH(CH_3)$_{2(dipp)}$), 1.16 (d, ^3J = 6.9 Hz, 6H, CH(CH_3)$_{2(dipp)}$) 1.12 (d, ^3J = 6.9 Hz, 6H, CH(CH_3)$_{2(dipp)}$). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 185.2 (CIr), 155.5 (C═N), 143.0 (*ipso*-$C_{(dipp)}$), 136.6 (*o*-$C_{(dipp)}$), 136.2 (*o*-$C_{(dipp)}$), 124.8 (*p*-$CH_{(dipp)}$), 123.5 (*m*-$CH_{(dipp)}$), 123.3 (*m*-$CH_{(dipp)}$), 119.9 (NCHCHN), 84.6 (C$H_{(cod)}$), 51.7 (C$H_{(cod)}$), 33.4 ($CH_{2(cod)}$), 29.3 ($CH_{2(cod)}$), 28.5 (CH$(CH_3)_{2(dipp)}$), 28.4 (C$H(CH_3)_{2(dipp)}$), 23.3 ($CH_{3(imine)}$ + CH$(CH_3)_{2(dipp)}$), 23.1 (CH$(CH_3)_{2(dipp)}$), 22.9 (CH-$(CH_3)_{2(dipp)}$), 22.3 (CH$(CH_3)_{2(dipp)}$). IR (pure, orbit diamond): $\nu_{C=N}$ 1672 cm^{-1}. ESI-MS (CH_2Cl_2, 50 V, m/z): 805.40 $[M - H, 100\%]^+$, 771.40 $[M - Cl, 57\%]^+$. Anal. Calcd for $C_{39}H_{55}N_4ClIr$ (%): C, 58.00; H, 6.86; N, 6.94. Found (%): C, 57.08; H, 6.96; N, 5.97.

Preparation of [$CrCl_2$(6)$_2$] (8). A solution of compound **6** (0.100 g, 0.135 mmol) in 3 mL of THF was added under magnetic stirring to a solution of $[CrCl_2(THF)_2]$ (0.018 g, 0.067 mmol, 0.5 equiv) in THF (4 mL). Stirring was maintained for 2 h at room temperature. Light green crystals suitable for X-ray diffraction were formed slowly at room temperature after concentrating the solution under reduced pressure to ca. 4 mL. Following collection of the crystalline material, pentane was added to the green THF solution, and additional crystalline product separated and was collected (overall yield 75%, 0.080 g, 0.050 mmol). The crystals readily lose THF molecules of crystallization; therefore prior to elemental analysis they were maintained under vacuum for several hours. Anal. Calcd for $C_{96}H_{130}Cl_2CrN_4$ (%): C, 71.93; H, 8.17; N, 12.23. Found (%): C, 71.60; H, 8.15; N, 12.24. ^1H NMR (400 MHz, THF-d_8): see text above for discussion and ESI. IR (CsI, Nujol mull): $\nu_{C=N}$ 1664 cm^{-1}, ν_{Cr-Cl} 375 cm^{-1}.

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. The intensity data for **3**(Cl^-)·CH_3CN, **4**, **6**, and **8** were collected on a Kappa CCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) at 173(2) K.[42] Data for **3**(Cl^-)·toluene were collected on an APEX-II CCD (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structures are summarized in Table S1 (see SI). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[43] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined riding on the corresponding parent atoms. For all compounds, a MULTISCAN absorption correction was applied.[44] The structure of **3**(Cl^-) was treated as a racemic twin solved within the C_2 space group with a BASF of 0.62709. The SQUEEZE instruction in PLATON was applied for **6** and **8**.[44] The residual electron density was assigned to one molecule of pentane and two molecules of THF for **6** and **8**, respectively. In **6**, three of the isopropyl groups were found disordered in two positions having the tertiary atom in common and with equal occupancy factors. These methyl C atoms were refined anisotropically with constrained geometry and thermal parameters. A pentane molecule was found badly disordered on multiple positions. Attempts to locate its atomic coordinates failed and, instead, a SQUEEZE procedure was applied on the complete anisotropic model. The result gave missing electron density accounting for 69e per asymmetric unit, well consistent with the 72 demanded for a pentane molecule. The quality of the data for **A** is not sufficient for deposition with the CCDC, but the following unit cell data were obtained: space group orthorhombic, *Pbca*, a = 16.5497(10) Å, b = 16.6413(10) Å, c = 35.077(2) Å, $\alpha = \beta = \gamma$ = 90.00°, V = 9660.5(10) $Å^3$, Z = 8. CCDC 945109−945113 and 945115 contain the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

Crystal data and structure refinement for **3**(Cl^-)·MeCN, **4**, **6**, **7**, and **8** (Table S1). Crystallographic information files (CIF) of the compounds **3**(Cl^-)·MeCN, **3**(Cl^-)·toluene, **4**, **6**, **7**, and **8** have 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 945109−945113 and 945115. This material is also available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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