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Synthesis and Coordination Chemistry of 4-Azabenzimidazole Derivatives

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ABSTRACT: *A facile method for the preparation of N1- (***1a–6a***) and N3-alkylated (***1b–6b***) 4-azabenzimidazole derivatives is presented. Both isomers were obtained by alkylation of 4-azabenzimidazole. The isomers were separated, and the preferred formation of the N1-alkylated derivatives (***1a–6a***) was observed. The C2-proton in the alkylated benzimidazoles can be exchanged for an iodine atom by treatment with methyl lithium and iodine, leading to N-alkylated 2-iodo-4-azabenzimidazoles* **7a,b** *and* **8a**. *2,2′-Bis(4-azabenzimidazole) derivatives* **9a,b** *and* **10a** *were isolated as by-products of the proton–halogen exchange. Treatment of the N1- or N3-methyl-4-azabenzimidazoles* **1a,b** *with methyl lithium and N-chlorosuccinimide as a chlorine source proceeded to give 2-chloro-4-azabenzimidazoles* ***11a,b*** *without formation of the coupling products, but the yield of 2-chloro-1-methyl-4-azabenzimidazole* **11a** *is low (9%) whereas 2-chloro-3-methyl-4-azabenzimidazole* **11b** *has been obtained in reasonable yield (49%). The reaction of 3-butyl-2-iodo-4-azabenzimidazole* **7b** *with* $[IrCl_2Cp^*]_2$ *gave the iridium complex* **12**, *where 3-butyl-2-iodo-4-azabenzimidazole is coordinating to the metal center via the N1 atom. The reaction of the N1-alkylated 4-azabenzimidazole with chloroacetone gave the corresponding 1-alkyl-3-(2-oxopropyl)-4-azabenzimidazolium chlorides* **13–17** *in good yields. The chloride counterion was exchanged for a tetrafluoroborate anion for two derivatives leading to compounds* **18** *and* **19**. *Carbene complexes were obtained by treatment of 1-butyl-3-(2-oxopropyl)-4-azabenzimidazolium chloride* **15** *with silver oxide, followed by transmetalation with* $[AuCl(tht)]$ *or* $[IrCl_2Cp^*]_2$ *leading to the gold(I) (***20***) and iridium(III) complexes (***21***) with 1-butyl-3-(2-oxopropyl)-4-azabenzimidazolin-2-ylidene ligand. Removal of the 2-oxopropyl protecting group by treatment with silica gel proceeded in the case of the iridium complex to give complex* **22**, *possessing an NH,NR-stabilized carbene ligand, while it failed for the gold(I) complex.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:476–490, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20711

INTRODUCTION

N-Heterocyclic carbenes (NHCs) are established ligands in organometallic chemistry [1], allowing the synthesis of transition metal complexes with desirable catalytic properties [2]. Additional applications such as the use of polydentate carbene ligands as building blocks for metalosupramolecular architectures have emerged recently [3].

The ubiquitous unsaturated imidazolin-2-ylidenes normally exist as monomers [1], whereas their benzannulated congeners, the benzimidazolin-2-ylidenes **A** (Fig. 1), tend to dimerize to the

Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

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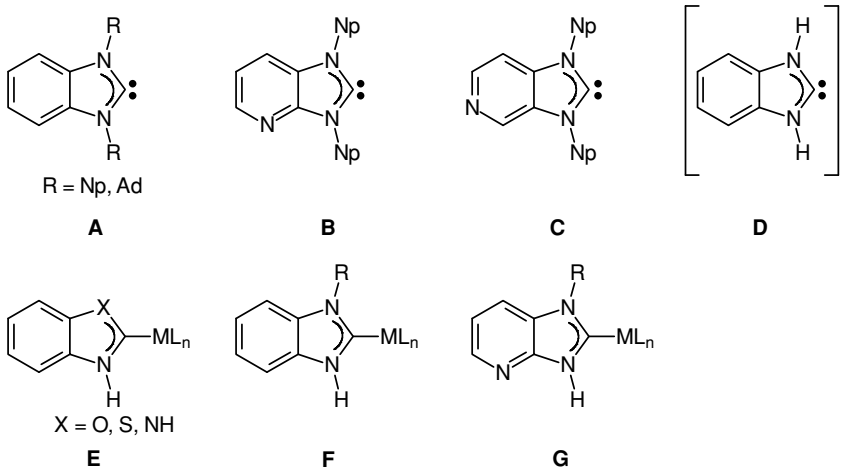


FIGURE 1 Selected types of annulated N-heterocyclic carbenes and their complexes.

dibenzotetraazafulvalenes if their *N*,*N*′-substituents are of reduced steric demand [4]. Kinetically stabilized monomeric benzimidazolin-2-ylidenes **A** can be obtained with bulky *N*,*N*′-substituents like neopentyl or adamantyl [5]. In contrast to the limited access to the free benzimidazolin-2-ylidenes, several complexes possessing benzimidazolin-2-ylidene ligands have been prepared [6].

Heinicke et al. demonstrated that free carbene ligands with a modified annulated ring are also stable if the nitrogen atoms bear bulky *N*,*N*′-substitutents, and the pyrido[*b*]- (**B**) [7,8] and pyrido[*c*]-annulated (**C**) carbenes [8] have been described recently (Fig. 1).

The carbenic carbon atom in the carbenes of the type **A**–**C** is normally stabilized by two alkylated, trigonal-planar nitrogen atoms as it is depicted in Fig. 1. Removal of one or both of the *N*,*N*′-substituents destabilizes the carbenes and consequently, free and stable NH,NH-functionalized diaminocarbenes of type **D** are unknown. Nevertheless, it is possible to stabilize such NH,NH-functionalized carbene ligands at a variety of metal centers. Carbene complexes of type **E** bearing one or more NH,NH- [9,10] or NH,O-stabilized [11] carbene ligands have been obtained by the metal template-controlled cyclization of suitably *β*-functionalized phenyl isocyanide ligands [12], whereas complexes with NH,S-stabilized carbene ligands were obtained from deprotonated benzothiazoles [13].

Complexes of type **E**, bearing a carbene ligand which is not stable in the free state, exhibit a number of interesting features. They can be alkylated at the NH-functions, leading to complexes with NR,NH- or NR,NR- [10], NR,O [11,12a], or NR,S-stabilized [13a] carbene ligands. This type of alkylation has enabled access to macrocyclic P_2C^{NHC} [14] and $P_2C_2^{NHC}$ ligands [15], featuring carbene and phosphine donors.

While complexes of type **F**, possessing an NH,NR-stabilized carbene ligand have been obtained by monoalkylation of the complexes of type **E**, it is more convenient to prepare this type of complex by lithiation of a *N*-alkylbenzimidazole and subsequent reaction with a suitable metal precursor followed by protonation of the ring nitrogen atom [16]. In selected cases, the access to complexes of type **F** with NR,NH-substituted NHC ligands is possible by base-induced tautomerization of N-coordinated *N*-heterocycles [17] or by oxidative addition of the C2–H bond of 1-alkylbenzimidazole at a suitable metal center, followed by reductive elimination under protonation of the unsubstituted ring nitrogen atom [18]. In addition, 2-chloro azole derivatives have been oxidatively added to low valent metal centers which yielded, after addition of a proton acid, metal complexes with an NH,X-stabilized carbene ligand (X = O, S, NR) [19]. No reductive elimination occurred in this case, and the metal remained in the higher oxidation state.

Complexes bearing an NH,NR-stabilized carbene ligand are not only easily N-alkylated to give the "classical" NHC ligands, but the N—H function of the carbene ligand in complexes of type **F** can act as a molecular recognition unit via the formation of hydrogen bonds to selected substrates [11a,16,20]. The close proximity of the NH group to the metal center is particularly useful for the recognition of substrates in competitive catalytic reactions [16].

In an effort to introduce a second recognition site in NHC ligands next to the N—H function, we

studied monoalkylated 4-azabenzimidazoles, which possess a nitrogen atom in close proximity to the carbene N—H function. After C2 deprotonation, coordination to a metal center, and protonation of the azole ring nitrogen atom, such ligands would lead to complexes of type **G** featuring two recognition units (NH and N), which are hydrogen bond donors and acceptors, respectively, and thus might be capable of selectively recognizing substrates with carboxyl groups via two $N—H\cdots O_{carboxyl}$ and $N\cdots H—O_{carboxyl}$ hydrogen bonds. Here we describe the preparation of N1- or N3-alkylated 4-azabenzimidazoles and their halogenation in C2-position to give the 2-iodo and 2-chloro derivatives. The synthesis of unsymmetrical N1,N3-substituted 4-azabenzimidazolium salts bearing a removable protecting group at one nitrogen atom and of carbene complexes derived from the 4-azabenzimidazole and 4-azabenzimidazolium salts is also described.

RESULTS AND DISCUSSION

Preliminary accounts on the synthesis of N-alkylated 4-azabenzimidazole derivatives have been published [21,22], but the yields of the desired 1-alkyl-4-azabenzimidazoles of type **1** (Scheme 1) were low [21] or a multiple-step synthesis has to be employed [22]. We found that treatment of 4-azabenzimidazole with potassium hydroxide as base and a suitable alkyl halide led to the desired N-alkylated 4-azabenzimidazoles **1a,b–6a,b** (Scheme 1). Since the alkylation could occur at the N1 or the N3 position, mixtures of two isomers **a** and **b** were obtained for each alkylation reaction. The isomers were separated by column chromatography, and the products were characterized by 2D NMR spectroscopy.

The yields obtained for the individual isomers and their ratio are summarized in Table 1. These data show that the N1-alkylation giving isomers **1a–6a** is preferred under the reaction conditions selected. This observation is in accord with a previous report by Müller et al., who found the preferred formation of the N1-alkylated derivatives at an elevated reaction temperature [21a].

All compounds have been characterized by NMR spectroscopy, mass spectrometry, and elemental analyses. A distinction between the two isomers, however, is only possible with the help of NMR spectroscopy. The $^{13}C\{^1H\}$ NMR resonances of the two quaternary carbon atoms linking the two cycles (C**3a**, C**7a**) are detected mostly downfield. Their chemical shifts depend directly on the N-substitution pattern, and thus these resonances

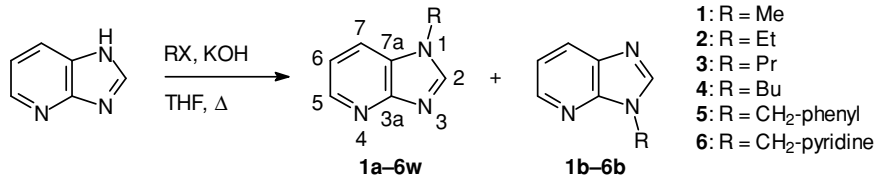
TABLE 1 Yields and Ratio of the Isomers **a** and **b** for Compounds **1–6**

Compound	*Yield Isomer **a** (%)*	*Yield Isomer **b** (%)*	*Ratio **a:b***
1	48	30	61:39
2	82	10	90:10
3	80	17	83:17
4	62	22	74:26
5	59	12	83:17
6	59	26	70:30

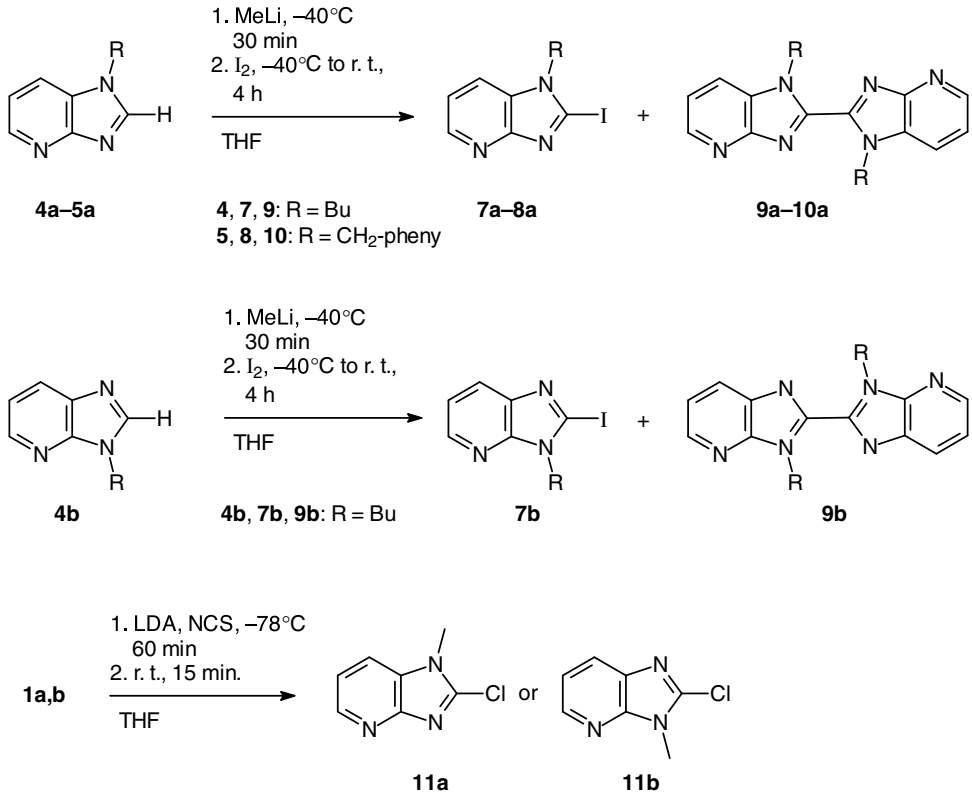
are an excellent probe for the detection of the isomers **a** and **b**. In the case of N1-substitution (isomer **a**), the resonances for atom C**3a** are detected at $\delta \approx 156$ ppm and at $\delta \approx 127$ ppm for C**7a**. If the 4-azabenzimidazole is alkylated at N3 (isomer **b**), the resonances for C**3a** are shifted highfield to $\delta \approx 147$ ppm ($\Delta\delta = 10$ ppm) whereas resonances of atoms C**7a** are detected downfield (compared to isomer **a**) at $\delta \approx 135$ ppm ($\Delta\delta = 8$–10 ppm). It can be concluded that N-alkylation leads to a highfield shift of the resonance belonging to the *ipso*-carbon atom in α-position of the alkylated nitrogen atom.

Apart from the template-controlled cyclization of 2-functionalized isocyanide, most complexes bearing NH,NR-functionalized NHC ligands have been prepared by an oxidative addition reaction of C–H or C–X bonds of azoles to transition metals, followed by protonation of one ring nitrogen atom [18,19]. At least for *N*,*N*′-alkylated azolium salts, this oxidative addition normally proceeds faster when 2-halogenated derivatives are used [23]. To facilitate the oxidative addition of *N*-alkyl-4-azabenzimidazole derivatives of types **1–6** to transition metals, we converted selected derivatives into their 2-halogen derivatives.

Initial attempts to synthesize 2-iodo-4-azabenzimidazoles by deprotonation of the N-alkylated 4-azabenzimidazole derivatives with both *n*-butyl lithium at –78°C or methyl lithium at –20°C failed and led to the 2-alkylated 4-azabenzimidazole derivatives [24]. However, treatment of the 4-azabenzimidazole derivatives with methyl lithium at a lower temperature of –40°C and subsequent addition of iodine to the cold reaction mixture gave the desired 2-iodo compounds (Scheme 2). The N-alkylated 2-iodo-4-azabenzimidazoles **7a,8a** (N1-alkylated) and **7b** (N3-alkylated) were isolated from the reaction mixture by column chromatography together with the 2,2′-bis(4-azabenzimidazole) derivatives **9a,b** and **10a** as by-products [13c,25]. Unfortunately, the yields for the 1-alkyl-2-iodo-4-azabenzimidazoles **7a** and **8a** are quite low (**7a**: 8%,



SCHEME 1 Synthesis of the N-alkylated 4-azabenzimidazole derivatives **1a–6a** and **1b–6b**.



SCHEME 2 Synthesis of the N-alkylated 2-iodo- (top and middle) and 2-chloro-4-azabenzimidazole derivatives (bottom).

8a: 13%), whereas the yield for the 3-butyl-2-iodo-4-azabenzimidazole **7b** (see Scheme 2) is significantly higher (36%).

The 2-iodo-4-benzimidazole derivatives of types **7** and **8** were characterized by NMR spectroscopy, EI mass spectrometry, and elemental analyses. The successful substitution of the C2 proton for iodine is indicated by the absence of the C2—H resonances (**4a** $\delta = 8.07$ ppm; **4b** $\delta = 8.06$ ppm; **5a** $\delta = 8.18$ ppm) in the ^{1}H NMR spectra of **7a,b** and **8a**. A significant upfield shift of $\Delta\delta \approx 37$ ppm has been observed for the C2—I carbon atom in the ^{13}C NMR spectra of the compounds **7a,b** and **8a** (**7a** $\delta = 107.5$ ppm; **7b** $\delta = 106.0$ ppm; **8a** $\delta = 108.5$ ppm) in comparison to the 4-azabenzimidazoles **4a,b** and **5a** (**4a** $\delta = 145.0$ ppm; **4b** $\delta = 144.2$ ppm; **5a** $\delta = 145.3$ ppm).

Alternatively, the 4-azabenzimidazole derivatives could also be transformed to 2-chloro analogues. The chlorination was performed in analogy to the reported synthesis of 2-chlorobenzimidazoles [26]. *N*-chlorosuccinimide (NCS) was used as chlorine source, which is more convenient than the use of chlorine gas. The *N*-methyl-4-azabenzimidazole derivatives **1a** or **1b** were C2-deprotonated with lithium diisopropylamide (LDA) at –78°C, and NCS was added to give the N-alkylated 2-chloro-4-azabenzimidazoles **11a** and **11b**, which were isolated as yellow brown solids (Scheme 2, bottom). As was observed for the iodo derivatives, the yield of N1-alkylated **11a** (9%) is significantly lower than the yield of N3-alkylated **11b** (49%).

In the ^{1}H NMR spectra of both **11a** and **11b**, the previously observed resonance for the C2 proton of the starting material (**1a** $\delta = 8.08$ ppm; **1b** $\delta = 8.05$ ppm) is absent. The resonances of the C2–Cl carbon atom are detected for **11a** and **11b**

at $\delta = 146.5$ ppm and $\delta = 142.8$ ppm, respectively, and thus are not significantly shifted when compared with the chemical shifts observed for the parent 4-azabenzimidazoles **1a,b** (**1a** $\delta = 145.7$ ppm; **1b** $\delta =$ 144.5 ppm). This behavior contrasts the situation in the 2-iodo-4-azabenzimidazole derivatives **7a,b** and **8a** (C2—I: $\delta = 106$–108 ppm), where a significant upfield shift was observed upon halogenation of C2. Apart from the C2—Cl ^{13}CNMR resonance, the other resonances for **11a** and **11b** resemble those of the parent 4-azabenzimidazoles.

All attempts to utilize the 2-halogenated 4-azabenzimidazoles for the preparation of carbene complexes by reacting them with Rh^{I}, Ir^{I}, or Ir^{III} complexes in the presence of phosphines as co-ligands have failed so far. The formation of a complex was only observed in the reaction of 3-butyl-2-iodo-4-azabenzimidazole **7b** with $[IrCl_2Cp^*]_2$. Unfortunately, no oxidative addition under formation of the carbene complex occurred, but instead complex **12** was obtained with 3-butyl-2-iodo-4-azabenzimidazole coordinating to iridium via the N1-nitrogen atom, while the C2–I bond of the ligand remained intact (Scheme 3).

The ^{13}C NMR spectrum of **12** exhibits no resonances in the range where the chemical shift of a carbene carbon atom bound to iridium(III) would be expected ($\delta \approx 160$–180 ppm). The aromatic carbon atoms, which are in close proximity to the Ir-coordinated nitrogen atom, resonate at $\delta = 127.9$ (C**7**), 139.9 (C**7a**), and 147.7 ppm (C**3a**) in the ^{13}C NMR spectrum. The MALDI-TOF mass spectrum of compound **12** confirms the formation of the complex, and the measured isotopic pattern matches perfectly to the calculated one for the complex fragment $[IrClCp^*(L)]^+$ (L = 3-butyl-2-iodo-4-azabenzimidazole) after loss of one chloro ligand $[M—Cl]^+$.

Crystals of **12** suitable for an X-ray diffraction study have been obtained by slow diffusion of diethyl ether into a dichloromethane solution of the complex. The molecular structure of **12** is depicted in Fig. 2.

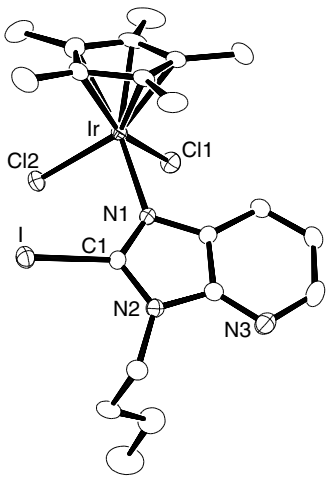
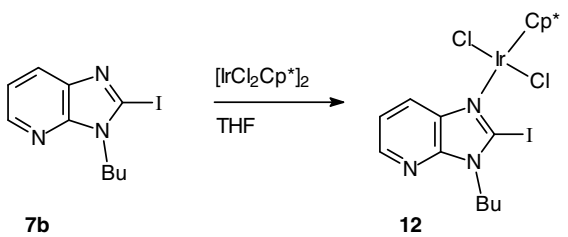


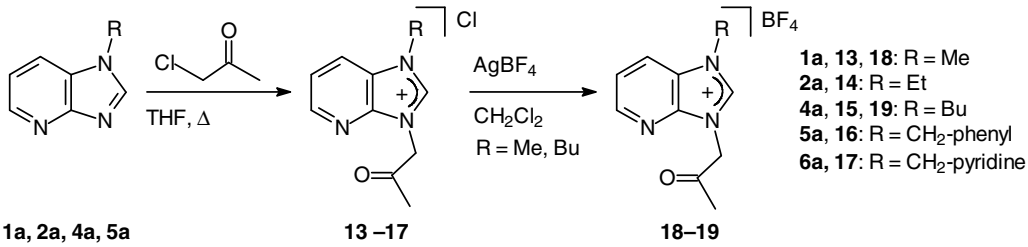
FIGURE 2 Molecular structure of the iridium complex **12**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ir–Cl1 2.4301(12), Ir–Cl2 2.4182(11), Ir–N1 2.132(4), I–C1 2.081(4), N1–C1 1.328(6), N2–C1 1.368(6); N1–C1–N2 112.6(4).



SCHEME 3 N1-coordination of 3-butyl-2-iodo-4-azabenzimidazole **7b** to iridium(III).

Up to now, only one molecular structure has been reported with a 4-azabenzimidazole ligand coordinating via the N1 atom to a metal center (mercury(II)) [21a]. The Ir–N1 bond length in **12** measures 2.132(4) Å and thus falls in the range reported for Ir–N bond distances in complexes featuring N-coordinated azoles [27]. The I–C1 bond distance measures 2.081(4) Å, but a comparison with similar compounds is not possible due to the lack of molecular structure determinations of 2-iodinated azoles.

Since the synthesis of complexes with NH,NR-functionalized carbene ligands by oxidative addition of 2-halogenated 4-azabenzimidazoles has failed so far, we decided to use a 4-azabenzimidazolium salt with one removable N-substituent. With this type of starting material, initially a classical NHC complex featuring an NR,NR-substituted NHC ligand is synthesized and subsequently, one N-substituent is removed to give the complex with an NH,NR-substituted NHC ligand. This protocol has been introduced by Wang et al. [28], who used the N1-(2-oxopropyl)-N3-butyl-substituted imidazolium salt for the preparation of an iridium(III) NR,NR-NHC complex. After "classical" carbene complex formation, the protecting group (2-oxypropyl) was removed giving the iridium complex bearing an NH,NR-functionalized NHC ligand. Recently, Crabtree et al. used a similar protocol and a benzoyl protecting group for the synthesis of NH,NR-NHC complexes [29].



SCHEME 4 Synthesis of the N3-(2-oxopropyl)-functionalized 4-azabenzimidazolium salts.

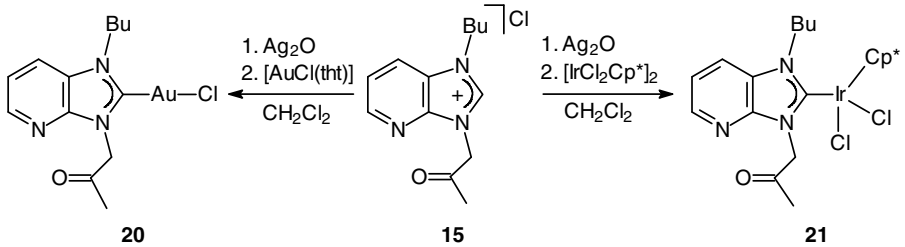
We selected the 2-oxopropyl-protecting group for the 4-azabenzimidazole derivatives. The N1-alkyl-4-azabenzimidazole derivatives **1a**, **2a**, and **4a**–**6a** were treated with chloroacetone (Scheme 4) to give the unsymmetrical N,N′-substituted 4-azabenzimidazolium chlorides **13**–**17**. These compounds were obtained as very hygroscopic brown solids in good yields (90–95%), except for the *N*-benzyl-substituted derivative **16**, which was only isolated in 56% yield.

The preparation of compounds **13**–**17** was verified by NMR spectroscopy. Formation of the benzimidazolium salts causes a downfield shift ($\Delta\delta$ = 0.50–1.25 ppm) for the aromatic protons in the ^{1}H NMR spectra, relative to the parent 4-azabenzimidazole derivatives. This downfield shift was also observed for the N—CH—N resonance ($\Delta\delta$ = 0.6–1.2 ppm) of compounds **13**–**17**, and the observed resonances fall in the typical range for the acidic N—CH—N protons of azolium salts [6,30]. The characteristic ^{13}C{^{1}H} NMR resonances for the carbonyl group of the 2-oxopropyl-protecting group were detected at $\delta \approx 199$ ppm, confirming the formation of the desired N1-alkyl-N3-(2-oxopropyl)-4-azabenzimidazolium chlorides **13**–**17**.

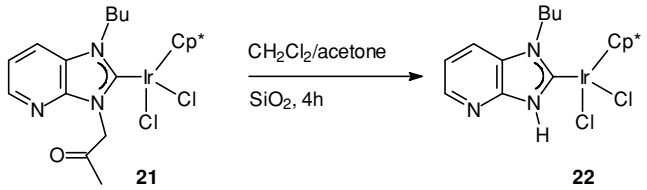
Since the 4-azabenzimidazolium chlorides are quite hygroscopic, the salts **13** and **15** were converted into the tetrafluoroborate salts, which is a common procedure for avoiding hygroscopic azolium salts and making them easily storable. Compounds **13** and **15** were dissolved in dichloromethane, and silver tetrafluoroborate was added to the solution. After separation of the silver chloride formed during this reaction, the N1-alkyl-N3-(2-oxopropyl)-4-azabenzimidazolium tetrafluoroborates **18** and **19** were isolated in quantitative yields as beige solids. A comparison of the NMR spectra of the salts **18** and **19** with those of the azolium chlorides **13** und **15** showed essentially no change in the NMR resonances upon anion exchange.

The N1-butyl-N3-(2-oxopropyl)-4-azabenzimidazolium chloride **15** was selected as a precursor for the synthesis of carbene complexes. In analogy to the reported procedure [28] and following the Ag_2O method developed by Lin et al. [31], gold(I) and iridium(III) complexes were prepared. Compound **15** reacted with silver oxide to give the silver carbene complex [31]. This complex was only of limited stability, and decomposed quickly after isolation, which is in marked contrast to the large number of stable and well characterized silver carbene complexes [32]. The silver(I) complex bearing the symmetrical *N*,*N*′-dineopentyl-4-azabenzimidazolin-2-ylidene ligand, for example, has been described as stable [8]. As a consequence of the instability of the silver(I) complex, this complex was not isolated but subsequently reacted with the transition metal precursors [AuCl(tht)] and [$IrCl_2Cp^*]_2$, respectively (Scheme 5).

The gold carbene complex **20** was obtained in a reasonable yield of 66%. Its formation was



SCHEME 5 Synthesis of gold(I) and iridium(III) with the asymmetrically substituted 4-azabenzimidazolin-2-ylidene ligand.



SCHEME 6 Synthesis of complex **22** by removal of the N-(2-oxopropyl)-substituent from **21**.

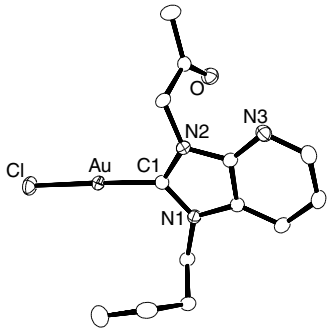


FIGURE 3 Molecular structure of complex **20**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au–Cl 2.2814(6), Au–C1 1.977(2), C1–N1 1.355(3), C1–N2 1.360(3), Cl–Au–C1 176.61(7), N1–C1–N2 106.5(2).

confirmed by NMR spectroscopy. The resonance for the carbene carbon atom in **20** was observed at δ = 181.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum, which is a value typical for complexes of the type [AuX(NHC)] (X = Cl, Br) bearing a benzimidazolin-2-ylidene ligand (δ = 175.8–181.2 ppm) [33]. The N-protecting group is still present and can be detected by the resonance for the carbonyl carbon atom at δ = 198.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

Crystals of **20**, which were suitable for X-ray diffraction study, have been obtained by slow diffusion of pentane into a saturated solution of **20** in chloroform. The molecular structure of **20** is depicted in Fig. 3. The Au—$C_{carbene}$ bond length (1.977(2) Å) in **20** is nearly identical to the Au–C separations in related gold(I) carbene complexes bearing the benzimidazolin-2-ylidene ligand [33, 34]. The Au–Cl bond length (2.2814(6) Å) also falls in the range previously reported for complexes of the type [AuCl(NHC)]. As expected, complex **20** exhibits an almost linear coordination geometry at the metal center (angle Cl–Au–C2 176.61(7)°). The N1–C1–N2 bond angle (106.5(2)°) in **20** falls in the range observed for related carbene ligands coordinating to transition metals [8]. Since the intermolecular distance between two gold atoms has been determined to be 3.438 Å, there can be only a weak Au···Au interaction [35] between the gold atoms in the crystal structure of **20**.

In analogy to the literature reports [28], we tried next to remove the N-(2-oxopropyl) group from the coordinated carbene ligand in **20** by treatment with silica gel but unfortunately, all attempts have failed so far. We, therefore, prepared the iridium(III) complex **21** by treatment of the silver complex obtained in situ from Ag_2O and **15** with $[IrCl_2Cp^*]_2$ (Scheme 5). The MALDI mass spectrum of the crude reaction product exhibits a peak at m/z = 594, which fits perfectly with the isotopic pattern for the ion [**21** – Cl]$^+$. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum of **21** exhibited a resonance at δ = 163.2 ppm, which can be assigned to the carbene carbon atom and thus verifies the formation of the iridium carbene complex **21**. The protecting group is still bound to the carbene ligand, since the ^{13}C NMR spectrum of **21** exhibits the characteristic resonance of the carbonyl group of the (2-oxopropyl)-substituent at δ = 203.9 ppm.

While the removal of the protecting group failed in the case of the gold complex **20**, it succeeded for the iridium(III) complex **21**. Treatment of **21** with silica gel led to complex **22**, the first metal complex with NH,NR-stabilized 4-azabenzimidazolin-2-ylidene ligand (Scheme 6). The successful removal of the protecting group with formation of **22** has been verified by NMR spectroscopy. The resonances assigned to the protecting group in complex **21** are absent in the NMR spectra of complex **22**. Instead, a broad singlet is observed in the ^1H NMR spectrum at δ = 11.39 ppm belonging to the proton bound to N3. The chemical shift for the resonance of the N—H proton falls in the typical range for NH,NR-stabilized carbene ligands (δ = 10–13 ppm) [18,19,28]. Formation of the complex with the NH,NR-stabilized carbene ligand is also verified by the MALDI mass spectrum of **22**, which exhibits peaks at m/z= 573 and 538 belonging to [**22**]$^+$ and [**22**-Cl]$^+$, respectively.

CONCLUSION

We have described the synthesis of several N1- and N3-alkylated 4-azabenzimidazole derivatives **1a,b**–**6a,b**. Selected N-alkylated 4-azabenzimidazole derivatives have been converted into the 2-iodo (**7a,b**

and **8a**) and 2-chloro derivatives (**11a,b**). During the iodination reaction, 2,2-bis(4-azabenzimidazole)s were obtained as by-products and both 2-iodination and 2-chlorination led to low product yields in case of the N1-alkylated 4-azabenzimidazoles, whereas C2-substitution proceeded with better yields for the N3-alkyl-4-azabenzimidazole derivatives. The oxidative addition of the 2-iodo-4-azabenzimidazoles to rhodium(I) or iridium(I) failed. The reaction of 3-butyl-2-iodo-4-azabenzimidazole **7b** with $[IrCl_2Cp^*]_2$ gave the iridium(III) complex **12** with an N-coordinated 4-azabenzimidazole ligand, leaving the C–I bond unaffected. Conversion of several 1-alkyl-4-azabenzimidazoles to the 1-alkyl-3-(2-oxopropyl)-4-azabenzimidazolium salts **13–17** by treatment with chloroacetone proceeded with good yields. Carbene complexes were synthesized with the N1-butyl-substituted 4-azabenzimidazolium salt **15**. The silver carbene complex is not stable, but acts as a carbene transfer agent in the preparation of the gold(I) (**20**) and iridium(III) complexes (**21**) bearing an NHC ligand derived from 4-azabenzimidazole. Removal of the 2-oxopropyl-protecting group failed for the gold complex **20**, but was possible with the iridium complex **21** leading to complex **22**, the first complex bearing an NH,NR-functionalized 4-azabenzimidazolin-2-ylidene ligand.

EXPERIMENTAL

Material and Instruments

Solvents were dried with standard methods and were freshly distilled prior to use. The metal precursors [AuCl(tht)] [36] and $[IrCl_2Cp^*]_2$ [37] were prepared following the published procedures. 4-Azabenzimidazole and silver oxide were purchased from Acros (Geel, Belgium) and Sigma-Aldrich (Munich, Germany). NMR spectra were recorded on Bruker Avance (II) 200 and Bruker Avance (I) 400 spectrometers with tetramethylsilane as the internal standard. MALDI mass spectra were measured on a MicroTof (Bruker Daltonics, Bremen), and EI mass spectra were measured on a Varian MAT 212 instrument. Elemental analyses (C, H, N) were obtained using a Vario EL III elemental analyzer at the Westfälische Wilhelms-Universität Münster except for the azolium salts **13–19**, which were either too hygroscopic or contained too much fluorine thereby preventing correct elemental analyses. For assignment of NMR resonances, see Scheme 1.

General Procedure for the Synthesis of the N-Alkyl-4-azabenzimidazoles **1a,b–6a,b**. 4-Azabenzimidazole (1.0 g, 8.4 mmol), an appropriate alkyl halide (9.2 mmol), and an excess of potassium hydroxide (1.9 g, 33.6 mmol) were dissolved in THF (50 mL), and the reaction mixture was heated under reflux for 48 h. Subsequently, the solvent was removed in vacuo and the residue was dissolved in water (25 mL). This aqueous solution was extracted four times with dichloromethane (15 mL each), and the combined organic layers were dried with $MgSO_4$, filtered, and the filtrate was dried in vacuo. The two isomers were separated by column chromatography (SiO_2, CH_2Cl_2:MeOH 10–30:1). The N1- and N3-alkyl-4-azabenzimidazole derivatives were obtained as brown oils or beige solids.

1-Methyl-4-azabenzimidazole (**1a**).Yield: 0.536 g (48%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 3.87 (s, 3H, NCH_3), 7.23 (dd, $^3J_{HH} = 8.1$, $^3J_{HH} = 4.8$ Hz, 1H, H6), 7.72 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, H7), 8.08 (s, 1H, H2), 8.55 (dd, $^3J_{HH} = 4.8$ Hz, $^4J_{HH} = 1.5$ Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 31.4 (NCH_3), 117.7 (C**6**), 118.1 (C**7**), 126.8 (C**7a**), 144.8 (C**5**), 145.7 (C**2**), 156.0 (C**3a**). MS (EI): *m/z* (%) = 133 ([**1a**]$^+$, 100]. Calcd for $C_7H_7N_3 \cdot 0.35H_2O$: C, 60.29; H, 5.56; N, 30.12%. Found: C, 59.94; H, 5.37; N, 30.09%.

3-Methyl-4-azabenzimidazole (**1b**).Yield: 0.337 g (30%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 3.91 (s, 3H, NCH_3), 7.23 (dd, $^3J_{HH} = 8.0$, $^3J_{HH} = 4.8$ Hz, 1H, H6), 8.05 (s, 1H, H2), 8.06 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, H7), 8.41 (dd, $^3J_{HH} = 4.8$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 29.7 (NCH_3), 118.2 (C**6**), 127.9 (C**7**), 135.2 (C**7a**), 144.4 (C**5**), 144.5 (C**2**), 147.7 (C**3a**). MS (EI): *m/z* (%) = 133 ([**1b**]$^+$, 43). Calcd for $C_7H_7N_3 \cdot 0.35H_2O$: C, 60.29; H, 5.56; N, 30.13%. Found: C, 59.96; H, 5.27; N, 29.98%.

1-Ethyl-4-azabenzimidazole (**2a**). Yield: 1.008 g (82%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 1.40 (t, $^3J_{HH} = 7.3$ Hz, 3H, NCH_2CH_3), 4.12 (q, $^3J_{HH} = 7.3$ Hz, 2H, NCH_2CH_3), 7.08 (dd, $^3J_{HH} = 8.1$ Hz, $^3J_{HH} = 4.7$ Hz, 1H, H6), 7.62 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, H7), 8.00 (s, 1H, H2), 8.41 (dd, $^3J_{HH} = 4.7$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.9 (NCH_2CH_3), 40.1 (NCH_2CH_3), 117.6 (C**6**/C**7**), 125.6 (C**7a**) 144.2 (C**2**), 144.4 (C**5**), 156.1 (C**3a**). MS (EI): *m/z* (%) = 147 ([**2a**]$^+$, 100), 132 ([**2a** – Me]$^+$, 18). Calcd for $C_8H_9N_3 \cdot 0.35H_2O$: C, 62.60; H, 6.37; N, 27.38%. Found: C, 62.33; H, 6.54; N, 27.35%.

3-Ethyl-4-azabenzimidazole (**2b**). Yield: 0.117 g (10%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 1.55 (t, $^3J_{HH} = 7.3$ Hz, 3H, NCH_2CH_3), 4.35 (q, $^3J_{HH} = 7.3$ Hz, 2H, NCH_2CH_3), 7.22 (dd, $^3J_{HH} = 8.2$ Hz, $^3J_{HH} = 4.8$ Hz, 1H, H6), 8.05 (dd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 1.3$ Hz, 1H, H7), 8.06 (s, 1H, H2), 8.39 (dd, $^3J_{HH} = 4.8$ Hz,

$^4J_{HH}$ = 1.3 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 15.5 (NCH_2CH_3), 38.7 (NCH_2CH_3), 118.1 (C**6**), 127.9 (C**7**), 135.5 (C**7a**), 143.4 (C**2**), 144.1 (C**5**), 146.9 (C**3a**). MS (EI): *m/z* (%) = 147 ([**2b**]$^+$, 100). Calcd for $C_8H_9N_3 \cdot 0.35H_2O$: C, 62.60; H, 6.37; N, 27.38%. Found: C, 62.19; H, 6.35; N, 27.40%.

1-Propyl-4-azabenzimidazole (**3a**). Yield: 1.079 g (80%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 0.90 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $NCH_2CH_2CH_3$), 1.87 (sext, $^3J_{HH}$ = 7.2 Hz, 2H, $NCH_2CH_2CH_3$), 4.11 (t, $^3J_{HH}$ = 7.2 Hz, 2H, $NCH_2CH_2CH_3$), 7.17 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 4.7 Hz, 1H, H6), 7.69 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H7), 8.05 (s, 1H, H2), 8.51 (dd, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 11.2 ($NCH_2CH_2CH_3$), 23.1 ($NCH_2CH_2CH_3$), 47.1 ($NCH_2CH_2CH_3$), 117.7 (C**6**), 117.8 (C**7**), 126.0 (C**7a**), 144.7 (C**5**), 145.0 (C**2**), 156.3 (C**3a**). MS (EI): *m/z* (%) = 161 ([**3a**]$^+$, 100), 132 ([(**3a** – Et]$^+$, 62); Calcd for $C_9H_{11}N_3 \cdot 0.7H_2O$: C, 62.19; H, 7.19; N, 24.18%. Found: C, 62.32; H, 7.07; N, 24.18%.

3-Propyl-4-azabenzimidazole (**3b**). Yield: 0.226 g (17%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 0.96 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $NCH_2CH_2CH_3$), 1.95 (sext, $^3J_{HH}$ = 7.2 Hz, 2H, $NCH_2CH_2CH_3$), 4.25 (t, $^3J_{HH}$ = 7.2 Hz, 2H, $NCH_2CH_2CH_3$), 7.21 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H6), 8.03 (s, 1H, H2), 8.04 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H7), 8.38 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H5). ^{13}C NMR(100.6 MHz, $CDCl_3$): δ 11.2 ($NCH_2CH_2CH_3$), 23.3 ($NCH_2CH_2CH_3$), 45.4 ($NCH_2CH_2CH_3$), 118.1 (C**6**), 127.8 (C**7**), 135.5 (C**7a**), 144.1 (C**2**), 147.1 (C**5**), 148.3 (C**3a**). MS (EI): *m/z* (%) = 161 ([**3b**]$^+$, 100), 132 ([**3b** – Et]$^+$, 57]. Calcd for $C_9H_{11}N_3 \cdot 0.6H_2O$: C, 62.84; H, 7.14; N, 24.43%. Found: C, 62.61; H, 7.03; N, 24.14%.

1-Butyl-4-azabenzimidazole (**4a**). Yield: 0.916 g (62%).^{1}H NMR (200.1 MHz, $CDCl_3$): δ 0.92 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.33 (sext, $^3J_{HH}$ = 7.2 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.84 (quint, $^3J_{HH}$ = 7.2 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 4.16 (t, $^3J_{HH}$ = 7.2 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 7.19 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H6), 7.70 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H7), 8.07 (s, 1H, H2), 8.53 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H5). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 13.4 ($NCH_2CH_2CH_2CH_3$), 19.9 ($NCH_2CH_2CH_2CH_3$), 31.8 ($NCH_2CH_2CH_2CH_3$), 45.3 ($NCH_2CH_2CH_2CH_3$), 117.8 (C**6**), 117.9 (C**7**), 126.1 (C**7a**), 144.8 (C**5**), 145.0 (C**2**), 156.4 (C**3a**). MS (EI): *m/z* (%) = 175 ([**4a**]$^+$, 100), 132 ([**4a** – Pr]$^+$, 27]. Calcd for $C_{10}H_{13}N_3 \cdot 0.35H_2O$: C, 66.16; H, 7.61; N, 23.15%. Found: C, 66.35; H, 7.74; N, 22.78%.

3-Butyl-4-azabenzimidazole (**4b**). Yield: 0.325 g (22%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 0.94 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.37 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.91 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 4.29 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 7.22 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H6), 8.05 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H7), 8.06 (s, 1H, H2), 8.39 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 13.5 ($NCH_2CH_2CH_2CH_3$), 19.9 ($NCH_2CH_2CH_2CH_3$), 32.0 ($NCH_2CH_2CH_2CH_3$), 43.5 ($NCH_2CH_2CH_2CH_3$), 118.2 (C**6**), 127.8 (C**7**), 135.3 (C**7a**), 143.9 (C**3a**), 144.2 (C**2**), 147.0 (C**5**). MS (EI): *m/z* (%) = 175 ([**4b**]$^+$, 100), 132 ([**4b** – Pr]$^+$, 31). Calcd for $C_{10}H_{13}N_3 \cdot 0.1H_2O$: C, 67.85; H, 7.52; N, 23.74%. Found: C, 67.88; H, 7.53; N, 23.56%.

1-Benzyl-4-azabenzimidazole (**5a**). Yield: 1.040 g (59%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 5.30 (s, 2H, NCH_2-Ph), 7.14 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 4.7 Hz, 1H, H6), 7.19–7.16 (m, 2H, Ph-H), 7.36–7.30 (m, 3H, Ph-H), 7.56 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H7), 8.18 (s, 1H, H2), 8.54 (dd, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 49.5 (NCH_2-Ph), 118.2 (C**6**), 118.4 (C**7**), 126.2 (C**7a**), 127.1 (Ph-C), 128.6 (Ph-C), 129.1 (Ph-C), 134.6 (Ph-C), 145.0 (C**5**), 145.3 (C**2**), 156.3 (C**3a**). MS (EI): *m/z* (%) = 209 ([**5a**]$^+$, 100), 91 ($CH_2C_6H_5$, 28). Calcd for $C_{13}H_{11}N_3 \cdot 0.2H_2O$: C, 73.36; H, 5.40; N, 19.74%. Found: C, 73.54; H, 4.94; N, 19.45%.

3-Benzyl-4-azabenzimidazole (**5b**). Yield: 0.214 g (12%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 5.48 (s, 2H, NCH_2-Ph), 7.26 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H6), 7.35–7.20 (m, 5H, Ph-H), 8.04 (s, 1H, H2), 8.09 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H7), 8.43 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 47.1 (NCH_2-Ph), 118.4 (C**6**), 127.8 (C**7**), 128.0 (Ph-C), 128.3 (Ph-C), 129.0 (Ph-C), 135.2 (C7a), 135.8 (Ph-C), 143.9 (C**2**), 144.6 (C**5**), 147.0 (C**3a**). MS (EI): *m/z* (%) = 209 ([**5b**]$^+$, 100). Calcd for $C_{13}H_{11}N_3 \cdot 0.2H_2O$: C, 73.36; H, 5.40; N, 19.74%. Found: C, 73.75; H, 5.01; N, 19.47%.

1-Picolyl-4-azabenzimidazole (**6a**). Yield: 1.045 g (59%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 5.46 (s, 2H, NCH_2-pyridine), 7.00 (d, $^3J_{HH}$ = 7.7 Hz, 1H, pyridine-H), 7.15 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H6), 7.21 (ddd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 0.5 Hz, 1H, pyridine-H), 7.61 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, pyridine-H), 7.66 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H7), 8.25 (s, 1H, H2), 8.51 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H5), 8.56 (d, $^3J_{HH}$ = 4.8 Hz, 1H, pyridine-H). ^{13}C

NMR (100.6 MHz, $CDCl_3$): δ 51.0 (NCH_2-pyridine), 118.3 (C**6**), 118.5 (pyridine-C), 121.3 (pyridine-C), 123.3 (C**7**), 129.6 (C**7a**), 137.3 (pyridine-C), 145.0 (C**5**), 145.5 (C**2**), 145.8 (pyridine-C), 149.9 (pyridine-C), 154.6 (C**3a**). MS (EI): *m/z* (%) = 210 ([**6a**]$^+$, 100). Calcd for $C_{12}H_{10}N_4$: C, 68.56; H, 4.79; N, 26.65%. Found: C, 68.15; H, 4.69; N, 26.47%.

3-Picolyl-4-azabenzimidazole (**6b**). Yield: 0.450 g (26%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 5.55 (s, 2H, NCH_2-pyridine), 7.17–7.10 (m, 2H, pyridine-H), 7.19 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, H6), 7.55 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, pyridine-H), 8.03 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H7), 8.20 (s, 1H, H2), 8.35 (dd, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H5), 8.51 (d, $^3J_{HH}$ = 4.7 Hz, 1H, pyridine-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 48.4 (NCH_2-pyridine), 118.2 (C**6**), 121.9 (pyridine-C), 122.9 (pyridine-C), 127.9 (C**7**), 135.1 (C**7a**), 137.0 (pyridine-C), 144.3 (C**5**), 144.4 (C**2**), 146.9 (pyridine-C), 149.6 (pyridine-C), 155.4 (C**3a**). MS (EI): *m/z* (%) = 210 ([**6b**]$^+$, 100). Calcd for $C_{12}H_{10}N_4$: C, 68.56; H, 4.79; N, 26.65%. Found: C, 68.23; H, 4.67; N, 26.39%.

General Procedure for the Synthesis of N-Alkyl-2-iodo-4-azabenzimidazole Derivatives. An *N*-alkyl-4-azabenzimidazole **4a,b** or **5a** (2.0 mmol) was dissolved in THF (20 mL). The solution was cooled to −40°C, and methyl lithium (1.6 M in hexane, 1.63 mL, 2.6 mmol) was added dropwise. The reaction mixture was stirred for 40 min at –40°C. After this time, elemental iodine (0.61 g, 2.4 mmol) was added to the solution and the reaction mixture was allowed to slowly warm up to ambient temperature. It was stirred for additional 4 h. The remaining iodine was removed from the reaction mixture by washing the THF solution with a saturated aqueous solution of sodium thiosulfate (5 mL). Then the THF solution was washed with brine (10 mL) and the 2-iodo-4-azabenzimidazole derivative was extracted with dichloromethane. The dichloromethane solution was dried with $MgSO_4$, the solvent was removed in vacuo, and the crude reaction product was purified by column chromatography (SiO_2, hexane:EtOAc 1:1 or CH_3CN:CH_2Cl_2 1:3). The 2-iodo-4-azabenzimidazoles were obtained as bright yellow compounds.

1-Butyl-2-iodo-4-azabenzimidazole (**7a**). Yield: 0.048 g (8%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 0.98 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.40 (sext, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.80 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 4.17 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 7.16 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, H6), 7.67 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H7), 8.49 (dd, $^3J_{HH}$ = 4.5 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 13.7 ($NCH_2CH_2CH_2CH_3$), 20.0 ($NCH_2CH_2CH_2CH_3$), 31.8 ($NCH_2CH_2CH_2CH_3$), 47.6 ($NCH_2CH_2CH_2CH_3$), 107.5 (C**2**), 117.2 (C**6**), 118.0 (C**7**), 128.2 (C**7a**), 144.9 (C**5**), 157.4 (C**3a**). MS (EI): *m/z* (%) = 301 ([**7a**]$^+$, 9), 174 ([**7a** – I]$^+$, 100). Calcd for $C_{10}H_{12}N_3I$: C, 39.88; H, 4.02; N, 13.96%. Found: C, 40.11; H, 3.85; N, 13.57%.

3-Butyl-2-iodo-4-azabenzimidazole (**7b**). Yield: 0.217 g (36%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 0.98 (t, $^3J_{HH}$ = 7.5 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.42 (sext, $^3J_{HH}$ = 7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.85 (quint, $^3J_{HH}$ = 7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 4.29 (t, $^3J_{HH}$ = 7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 7.17 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H6), 7.97 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H7), 8.32 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 13.7 ($NCH_2CH_2CH_2CH_3$), 20.0 ($NCH_2CH_2CH_2CH_3$), 31.8 ($NCH_2CH_2CH_2CH_3$), 45.9 ($NCH_2CH_2CH_2CH_3$), 106.0 (C**2**), 118.5 (C**6**), 126.5 (C**7**), 137.2 (C**7a**), 144.1 (C**5**), 147.9 (C**3a**). MS (EI): *m/z* (%) = 174 ([**7b** – I]$^+$, 100). Calcd for $C_{10}H_{12}N_3I$: C, 39.88; H, 4.02; N, 13.96%. Found: C, 40.24; H, 4.12; N, 13.76%.

1-Benzyl-2-iodo-4-azabenzimidazole (**8a**). Yield: 0.086 g (13%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 5.40 (s, 2H, NCH_2-Ph), 7.10 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H6), 7.16–7.12 (m, 2H, Ph-H), 7.36–7.30 (m, 3H, Ph-H), 7.54 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H7), 8.49 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 51.3 (NCH_2-Ph), 108.5 (C**2**), 118.1 (C**6**), 118.4 (C**7**), 126.8 (Ph-C), 127.6 (C**7a**), 128.5 (Ph-C), 129.2 (Ph-C), 134.5 (Ph-C), 145.1 (C**5**), 157.4 (C**3a**). MS (EI): *m/z* (%) = 335 ([**8a**]$^+$, 100), 208 ([**8a** – I]$^+$, 62), 91 ($CH_2C_6H_5$, 28). Calcd for $C_{13}H_{10}N_3I$: C, 46.58; H, 3.01; N, 12.54%. Found: C, 46.31; H, 2.72; N, 12.24%.

2,2′-Bis(1-butyl-4-azabenzimidazole) (**9a**). Yield: 0.077 g (11%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 0.89 (t, $^3J_{HH}$ = 7.4 Hz, 6H, $NCH_2CH_2CH_2CH_3$), 1.43–1.30 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.77 (quint, $^3J_{HH}$ = 7.4 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 4.15 (t, $^3J_{HH}$ = 7.4 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 7.32 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.7 Hz, 2H, H6), 7.84 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, H7), 8.62 (dd, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, H5). MS (EI): *m/z* (%) = 348 ([(**9a**]$^+$, 100), 291 ([**9a**-Bu]$^+$, 65).

2,2′-Bis(3-butyl-4-azabenzimidazole) (**9b**). Yield: 0.035 g (5%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 0.91 (t, $^3J_{HH}$ = 7.4 Hz, 6H, $NCH_2CH_2CH_2CH_3$), 1.36 (sext, $^3J_{HH}$ = 7.4 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 1.87 (quint,

$^3J_{HH}$ = 7.4 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 5.04 (t, $^3J_{HH}$ = 7.4 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 7.31 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 4.8 Hz, 2H, H6), 8.13 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, H7), 8.52 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, H5). MS (EI): *m/z* (%) = 348 ([**9b**]$^+$, 100), 291 ([**9b** – Bu]$^+$, 71).

2,2′-Bis(1-benzyl-4-azabenzimidazole) (**10a**). Yield: 0.019 g (2%). MS (EI): *m/z* (%) = 416 ([**10a**]$^+$, 15), 325 ([**10a**-Bn]$^+$, 100).

Synthesis of the N-Methyl-2-chloro-4-azabenzimidazoles **11a,b**. An *N*-methyl-4-azabenzimidazole derivative (0.185 g, 1.39 mmol) was dissolved in THF (3 mL). LDA (2.0 M in THF/heptane/ethylbenzene, 1.25 mL, 2.5 mmol) was added dropwise to this solution at –78°C, and the reaction mixture was then stirred for 1 h. Then *N*-chlorosuccinimide (0.37 g, 2.8 mmol) was added to the cold reaction mixture. The mixture was allowed to warm up to ambient temperature and was stirred for an additional 10 min. A saturated aqueous solution of ammonium chloride was added to the reaction mixture, and the resulting solution was extracted four times with dichloromethane (15 mL each). The combined organic layers were washed with brine and dried with sodium sulfate. The solvent was removed in vacuo, and the crude reaction product was purified by column chromatography (SiO_2, CH_2Cl_2:MeOH 20:1). The *N*-methyl-2-chloro-4-azabenzimidazole derivatives were obtained as orange brown solids.

2-Chloro-1-methyl-4-azabenzimidazole (**11a**). Yield: 0.021 g (9%). ^{1}H NMR (400.0 MHz, CD_3OD): δ 3.93 (s, 3H, NCH_3), 7.44 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, H6), 8.08 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H7), 8.47 (dd, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, CD_3OD): δ 31.4 (NCH_3), 120.1 (C**6**), 121.1 (C**7**), 130.5 (C**7a**), 145.0 (C**5**), 146.5 (C**2**), 153.8 (C**3a**). MS (EI): *m/z* (%) = 167 ([**11a**]$^+$, 100).

2-Chloro-3-methyl-4-azabenzimidazole (**11b**). Yield: 0.115 g (49%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 3.86 (s, 3H, NCH_3), 7.22 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H6), 7.95 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H7), 8.37 (dd, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, CD_3OD): δ 29.2 (NCH_3), 118.9 (C**6**), 126.8 (C**7**), 134.3 (C**7a**), 142.8 (C**2**), 144.1 (C**5**), 147.8 (C**3a**). MS (EI): *m/z* (%) = 167 ([**11b**]$^+$, 100).

κN1-(3-Butyl-2-iodo-4-azabenzimidazole) (pentamethylcyclopentadienyl)iridium Dichloride (**12**). The 3-butyl-2-iodo-4-azabenzimidazole **7b** (23 mg, 0.08 mmol) was dissolved in THF (4 mL). The metal precursor $[IrCl_2Cp^*]_2$ (30 mg, 0.4 mmol) was added to this solution, and the reaction mixture was heated under reflux for 12 h. The solvent was then removed in vacuo, and the remaining solid was recrystallized from THF leaving complex **12** as a yellow solid. Yield: 0.024 g (43%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 0.97 (t, $^3J_{HH}$ = 7.5 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.42 (sept, $^3J_{HH}$ = 7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.59 (s, 15H, Cp*-CH_3), 1.83 (quint, $^3J_{HH}$ = 7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 4.34 (t, $^3J_{HH}$ = 7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 7.17 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H6), 8.27 (s, br, 1H, H7), 8.31 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 9.5 (Cp*-CH_3), 13.7 ($NCH_2CH_2CH_2CH_3$), 20.0 ($NCH_2CH_2CH_2CH_3$), 31.7 ($NCH_2CH_2CH_2CH_3$), 46.5 ($NCH_2CH_2CH_2CH_3$), 86.1 (Cp*-C), 118.5 (C**6**), 127.9 (C**7**), 136.9 (C**7a**), 144.6 (C**5**), 147.7 (C**3a**). The resonance of the C2 carbon atom could not be detected. MS (MALDI-TOF, DCTB): *m/z* (%) = 664 ([**12** – Cl]$^+$, 17].

General Procedure for the Synthesis of the 1-Alkyl-3-(2-oxopropyl)-4-azabenzimidazolium Chlorides **13–17**. One of the 1-alkyl-4-azabenzimidazole derivatives **1a, 2a, 4a–6a** (2.0 mmol) was dissolved in THF (10 mL). An excess of chloracetone (0.63 mL, 8.0 mmol) was added dropwise to the solution, and the reaction mixture was heated under reflux for 48 h. The solvent was removed in vacuo, and the residue was dissolved in dichloromethane (3 mL). This solution was added dropwise to diethyl ether, and the precipitate obtained was separated from the solvent by filtration and dried in vacuo. The benzimidazolium salts were isolated as bright brown, very hygroscopic solids.

1-Methyl-3-(2-oxopropyl)-4-azabenzimidazolium Chloride (**13**). Yield: 0.428 g (95%). ^{1}H NMR (400.0 MHz, CD_3OD): δ 2.49 (s, 3H, $C(O)CH_3$), 3.39 (s, 2H, NCH_2), 4.17 (s, 3H, NCH_3), 7.88 (dd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 5.6 Hz, 1H, H6), 8.68 (s, 1H, H2), 8.83 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, H7), 8.92 (dd, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, CD_3OD): δ 27.4 ($C(O)CH_3$), 33.1 (NCH_3), 49.9 (NCH_2), 119.3 (C**6**), 129.4 (C**7**), 132.0 (C**7a**), 140.4 (C**2**), 149.2 (C**3a**), 151.4 (C**5**), 198.1 (C=O). MS (MALDI-TOF, DHB): *m/z* (%) = 190 ([**13** – Cl]$^+$, 100).

1-Ethyl-3-(2-oxopropyl)-4-azabenzimidazolium Chloride (**14**). Yield: 0.440 g (92%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 1.61 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2CH_3), 2.46 (s, 3H, $C(O)CH_3$), 4.67 (q, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2CH_3), 6.41 (s, 2H, NCH_2), 7.77 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, H6), 8.78 (s, 1H, H2),

9.04 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 0.5 Hz, 1H, H7), 9.53 (d, $^3J_{HH}$ = 6.1 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 15.4 (NCH_2CH_3), 27.8 ($C(O)CH_3$), 42.4 (NCH_2CH_3), 62.1 (NCH_2), 119.0 (C**6**), 129.6 (C**7**), 130.5 (C**7a**), 140.9 (C**2**), 148.9 (C**3a**), 149.7 (C**5**), 198.0 (C=O). MS (MALDI-TOF, DHB): *m/z* (%) = 204 ([**14** – Cl]$^+$, 100).

1-Butyl-3-(2-oxopropyl)-4-azabenzimidazolium Chloride (**15**). Yield: 0.480 g (90%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 0.87 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.32 (sext, $^3J_{HH}$ = 7.2 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.86 (quint, $^3J_{HH}$ = 7.2 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 2.42 (s, 3H, $C(O)CH_3$), 4.56 (t, $^3J_{HH}$ = 7.2 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 6.29 (s, 2H, NCH_2), 7.75 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 6.4 Hz, 1H, H6), 8.75 (s, 1H, H2), 8.97 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H7), 9.45 (d, $^3J_{HH}$ = 6.4 Hz, 1H, H5). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 13.3 ($NCH_2CH_2CH_2CH_3$), 19.2 ($NCH_2CH_2CH_2CH_3$), 27.3 ($C(O)CH_3$), 31.2 ($NCH_2CH_2CH_2CH_3$), 45.8 ($NCH_2CH_2CH_2CH_3$), 61.9 (NCH_2), 118.5 (C**6**), 129.8 (C**7**), 130.6 (C**7a**), 139.8 (C**2**), 148.5 (C**3a**), 151.3 (C**5**), 199.1 (C=O). MS (MALDI-TOF, DHB): *m/z* (%) = 232 ([**15** – Cl]$^+$, 100).

1-Benzyl-3-(2-oxopropyl)-4-azabenzimidazolium Chloride (**16**). Yield: 0.337 g (56%). ^{1}H NMR (200.1 MHz, DMSO-d_6): δ 2.40 (s, 3H, $C(O)CH_3$), 5.83 (s, 2H, NCH_2-Ph), 6.06 (s, 2H, NCH_2), 7.45–7.31 (m, 3H, Ph-H), 7.55–7.45 (m, 2H, Ph-H), 7.96 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, H6), 8.94 (d, $^3J_{HH}$ = 6.0 Hz, 1H, H7), 9.05 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H5), 9.39 (s, 1H, H2). ^{13}C NMR (100.6 MHz, CD_3OD): δ 27.3 ($C(O)CH_3$), 51.4 (NCH_2-Ph, NCH_2-C(O)), 120.1 (C**6**), 129.2 (Ph-C), 130.1 (C**7a**), 130.4 (Ph-C), 130.5 (Ph-C), 130.9 (C**7**), 135.6 (Ph-C), 141.2 (C**2**), 150.2 (C**3a**), 152.6 (C**5**), 199.5 (C=O). MS (MALDI-TOF, DHB): *m/z* (%) = 266 ([**16** – Cl]$^+$, 100).

1-Picolyl-3-(2-oxopropyl)-4-azabenzimidazolium Chloride (**17**). Yield: 0.496 g (82%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 2.45 (s, 3H, $C(O)CH_3$), 6.00 (s, 2H, NCH_2-pyridine), 6.37 (s, 2H, NCH_2-C(O)), 7.24–7.16 (m, 1H, pyridine-H), 7.74–7.57 (m, 2H, pyridine-H), 8.43 (d, $^3J_{HH}$ = 4.7 Hz, 1H, pyridine-H), 8.54 (dd, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 5.6 Hz, 1H, H6), 9.04 (s, 1H, H2), 9.14 (d, $^3J_{HH}$ = 9.5 Hz, 1H, H7), 9.42 (d, $^3J_{HH}$ = 5.6 Hz, 1H, H5). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 27.7 ($C(O)CH_3$), 51.8 (NCH_2-pyridine), 62.1 (NCH_2-C(O)), 118.8 (C**6**), 123.6 (pyridine-C), 123.8 (pyridine-C), 130.6 (C**7**), 131.1 (C**7a**), 137.6 (pyridine-C), 144.9 (C**2**), 145.6 (pyridine-C), 149.8 (pyridine-C), 151.0 (C**3a**), 152.9 (C**5**), 198.0 (C=O). MS (MALDI-TOF, DHB): *m/z* (%) = 267 ([**17** – Cl]$^+$, 100).

General Procedure for the Synthesis of the 1-Alkyl-3-(2-oxopropyl)-4-azabenzimidazolium Tetrafluoroborates **18–19**. One of the 1-alkyl-3-(2-oxopropyl)-4-azabenzimidazolium chlorides **13** or **15** (0.5 mmol) was dissolved in dichloromethane (15 mL). Silver tetrafluoroborate (0.117 g, 0.6 mmol) was added to this solution, and the reaction mixture was stirred for 12 h at ambient temperature. The reaction mixture was filtrated through Celite, and the filtrate was dried in vacuo. The reaction products were obtained as brown solids.

1-Methyl-3-(2-oxopropyl)-4-azabenzimidazolium Tetrafluoroborate (**18**). Yield: 0.137 g (98%). ^{1}H NMR (400.0 MHz, CD_3OD): δ 2.47 (s, 3H, $C(O)CH_3$), 3.39 (s, 3H, NCH_3), 5.99 (s, 2H, NCH_2), 7.93 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 8.2, 6.2 Hz, 1H, H6), 8.67 (d, $^3J_{HH}$ = 6.2 Hz, 1H, H7), 8.82 (s, 1H, H2), 8.91 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, CD_3OD): δ 27.2 ($C(O)CH_3$), 33.1 (NCH_3), 63.1 (NCH_2), 119.9 (C**6**), 124.3 (C**7**), 130.5 (C**7a**), 140.9 (C**2**), 150.1 (C**3a**), 153.2 (C**5**), 199.4 (C=O). ^{19}F NMR (376 MHz, CD_3OD): δ –154.5 (BF_4^-). MS (MALDI-TOF, DHB): *m/z* (%) = 190 ([**18** – BF_4]$^+$, 100).

1-Butyl-3-(2-oxopropyl)-4-azabenzimidazolium Tetrafluoroborate (**19**). Yield: 0.158 g (99%). ^{1}H NMR (400.0 MHz, CD_3OD): δ 1.03 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.46 (sept, $^3J_{HH}$ = 7.3 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 2.00 (quint, $^3J_{HH}$ = 7.3 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 2.47 (s, 3H, $C(O)CH_3$), 4.56 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 5.99 (s, 2H, NCH_2), 7.93 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.3 Hz, 1H, H6), 8.67 (d, $^3J_{HH}$ = 6.3 Hz, 1H, H7), 8.90 (s, 1H, H2), 8.96 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, CD_3OD): δ 13.8 ($NCH_2CH_2CH_2CH_3$), 20.8 ($NCH_2CH_2CH_2CH_3$), 27.2 ($C(O)CH_3$), 32.8 ($NCH_2CH_2CH_2CH_3$), 47.6 ($NCH_2CH_2CH_2CH_3$), 63.1 (NCH_2), 119.9 (C**6**), 124.5 (C**7**), 130.7 (C**7a**), 141.0 (C**2**), 150.2 (C**3a**), 152.5 (C**5**), 199.5 (C=O). ^{19}F NMR (376 MHz, CD_3OD): δ –154.4 (BF_4^-). MS (MALDI-TOF, DHB): *m/z* (%) = 232 ([**19** – BF_4]$^+$, 100).

{*[1-Butyl-3-(2-oxopropyl)-4-azabenzimidazolin-2-ylidene]gold(I) Chloride*} (**20**). 4-Azabenzimidazolium chloride **15** (42 mg, 0.156 mmol) was dissolved in dichloromethane (4 mL), and silver oxide (18 mg, 0.078 mmol) was added to this solution. The reaction mixture was stirred for 1 h at ambient temperature under exclusion of light. The mixture was then filtered through Celite, and the filtrate was treated with [AuCl(tht)] (50 mg, 0.156 mmol). The reaction mixture was stirred for 30 min under

exclusion of light and then filtered through Celite. Removal of the solvent in vacuo gave complex **20** as pale yellow solid. Yield: 0.048 g (66%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.43 (sept, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.94 (quint, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 2.37 (s, 3H, $C(O)CH_3$), 4.50 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 5.42 (s, 2H, NCH_2), 7.39 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.8 Hz, 1H, H6), 7.83 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H7), 8.45 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 13.7 ($NCH_2CH_2CH_2CH_3$), 20.0 ($NCH_2CH_2CH_2CH_3$), 27.4 ($C(O)CH_3$), 32.0 ($NCH_2CH_2CH_2CH_3$), 49.7 ($NCH_2CH_2CH_2CH_3$), 55.6 (NCH_2), 119.6 (C**6**), 119.9 (C**7**), 129.0 (C**7a**), 145.9 (C**5**), 149.6 (C**3a**), 181.5 (C**2**), 198.7 (C = O). MS (EI): *m/z* (%) = 428 ([**20** – Cl]$^+$, 95), 385 ([**20** – Cl – Pr]$^+$, 100), 328 ([**20** – Cl – Pr – C_2H_5O]$^+$, 16).

{*(Pentamethylcyclopentadienyl)-[1-butyl-3-(2-oxopropyl)-4-azabenzimidazolin-2-ylidene]-iridium(III) Dichloride*} (**21**). 4-Azabenzimidazolium chloride **15** (0.034 g, 0.126 mmol) was dissolved in dichloromethane (4 mL), and silver oxide (18 mg, 0.078 mmol) was added to this solution. The reaction mixture was stirred for 1 h at ambient temperature under exclusion of light and then filtered through Celite. $[IrCl_2Cp^*]_2$ (50 mg, 0.063 mmol) was added to the filtrate, and the reaction mixture was stirred for 30 min under exclusion of light. The reaction solution was filtered again through Celite, and the solvent was removed in vacuo to give complex **21**. Yield: 0.033 g (41%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 1.05 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.43–1.34 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.70 (s, 15H, Cp*-H), 1.93–1.84 (m, 2H, $NCH_2CH_2CH_2CH_3$), 2.17 (s, 3H, $C(O)CH_3$), 4.16 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 5.29 (s, 2H, NCH_2), 7.20 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.9 Hz, 1H, H6), 7.74 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H7), 8.32 (dd, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 9.1 (Cp*-CH_3), 13.7 ($NCH_2CH_2CH_2CH_3$), 20.1 ($NCH_2CH_2CH_2CH_3$), 27.3 ($C(O)CH_3$), 29.8 ($NCH_2CH_2CH_2CH_3$), 44.0 ($NCH_2CH_2CH_2CH_3$), 51.6 (NCH_2), 90.7 (Cp*-C), 113.1 (C**6**), 121.4 (C**7**), 137.0 (C**7a**), 148.0 (C**5**), 154.6 (C**3a**), 163.2 (C**2**), 203.9 (C=O). MS (MALDI-TOF, DCTB): *m/z* (%) = 594 ([**21** – Cl]$^+$, 19).

{*(Pentamethylcyclopentadienyl)-(1-butyl-4-azabenzimidazolin-2-ylidene)iridium(III) Dichloride*} (**22**). Compound **21** was subjected to slow column chromatography (SiO_2, CH_2Cl_2: acetone 5:1) over a period of 4 h to remove the protecting group. The column chromatography was repeated, upon which complex **22** was isolated as a yellow solid. Yield: 0.017 g (24%). ^{1}H NMR (400.0 MHz, $CDCl_3$): δ 1.02 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.57–1.46 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.72 (s, 15H, Cp*-CH_3), 2.02 (m, br, 2H, $NCH_2CH_2CH_2CH_3$), 4.49 (m, br, 2H, $NCH_2CH_2CH_2CH_3$), 7.23 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ =

TABLE 2 Summary of Crystallographic Data for **12** and **20**.

Formula	**12** $C_{20}H_{27}Cl_2IrN_3$	**20** $C_{13}H_{17}AuClN_3O$
M_r	699.45	463.71
Crystal size (mm)	0.16 × 0.02 × 0.02	0.11 × 0.07 × 0.06
a (Å)	7.3874(5)	11.2920(5)
b (Å)	20.2033(15)	7.9644(3)
c (Å)	15.1883(11)	15.9897(7)
α(°)	90	90
β(°)	93.7420(10)	96.3520(10)
γ(°)	90	90
V(Å^3)	2262.0(3)	1429.19(10)
Z	4	4
Space group	$P2_1/n$	$P2_1/c$
ρ_{calcd} (g cm^{-3})	2.054	2.155
μ (mm^{-1})	7.514 (Mo Kα)	10.476 (Mo Kα)
2θ range (°)	3.4–60.0	3.6–61.0
Data collected	22,543	16,726
Unique data	6,614	4,344
Observed data [$I \geq 2\sigma(I)$]	5,272	3,989
R (all data)	0.0497	0.0231
w*R* (all data)	0.0781	0.0501
No. of variables	250	174
Peak/hole (e·Å^{-3})	2.279, −1.363	1.428, −0.896

5.8 Hz, 1H, H6), 7.71 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H7), 8.70 (s, br, 1H, H5), 11.39 (s, br, 1H, N—H). MS (MALDI-TOF, DCTB): *m/z* (%) = 573 ([**22**]$^+$, 29), 538 ([**22** – Cl]$^+$, 100).

X-Ray Diffraction Studies

Diffraction data for **12** and **20** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K (**12**) or 153(2) K (**20**). Data were collected over the full sphere and were corrected for absorption. For further crystal data details, see Table 2. Structures of solutions were found with the SHELXS-97 [38] package using the heavy-atom method and were refined with SHELXL-97 [38] against all F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models at calculated positions, and their thermal parameters were fixed to 1.3 U_{eqiv} of the parent atom. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-797002 (**12**) and CCDC-797003 (**20**). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44–1223-336033, www.ccdc.cam.ac.uk./data/request/cif].

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