



# Synthesis and reactivity of (benz)imidazol-2-ylidenes with exocyclic *N*-acyl or *N*-sulfonyl groups



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## ABSTRACT

Imidazolium and benzimidazolium salts featuring exocyclic *N*-acyl or *N*-sulfonyl groups were prepared and converted in situ to the corresponding *N*-heterocyclic carbenes by deprotonation. The NHCs were further converted to group six adducts (sulfur and selenium) and metal complexes with Rh(I), Ir(I), Cu(I), Ni(II) and Fe(II). The *N*-acyl derivatives were found to be much more sensitive towards hydrolytic degradation than the *N*-sulfonyl compounds. IR spectroscopic analysis of NHC-carbonyl complexes revealed the *N*-acyl NHCs to be slightly better donors (TEP 2054–2055 cm<sup>-1</sup>) compared to the *N*-sulfonyl based ligands (TEP: 2056–2061 cm<sup>-1</sup>). Both classes are comparable to cyclic mono- and diamido carbenes regarding their donor properties.

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## 1. Introduction

*N*-Heterocyclic carbenes (NHCs) continue to be a class of fascinating compounds. Since Arduengos [1] pivotal report of the first archetypical example in 1991, a plethora of derivatives have been reported [2]. Apart from being increasingly applied in organo [3]- as well as transition metal catalysis [4], considerable research effort is directed towards a better understanding of the electronic properties of these compounds. In recent years, investigations into electron poor NHCs revealed that these systems may feature a decent  $\pi$ -acceptor character when coordinated to transition metal atoms. Furthermore, it became evident, that a small singlet-triplet (S-T) gap leads to some electrophilic character of those carbenes in addition to their well established nature as good nucleophiles/Lewis bases. Incorporation of the carbene-stabilizing nitrogen atoms into amide functions turned out to be one suitable approach to design electron poor NHCs and a couple of cyclic mono [5] and diamido [6] NHCs have been reported.

In extension of our previous work, we intended to investigate amido NHCs that feature an acyl group attached to at least one imidazole nitrogen atom and to compare these exocyclic amido carbenes with the related cyclic amido NHCs mentioned above. There are only a few previous literature reports concerning NHCs with exocyclic acyl groups. Crabtree

and coworkers used the *N*-benzoyl function as a protecting group that enabled protic NHC species to be obtained after deprotection [7]. This already points to a potential pitfall of these exocyclic amido species, i.e. their potential susceptibility towards nucleophilic cleavage. Indeed, this property has already been exploited for the preparation of 2-substituted imidazoles [8]. On the other hand, Batey et al. presented an air- and moisture-stable Pd complex of a carbamoyl-substituted NHC [9]. The enhanced stability of this system can be attributed to the presence of the additional N atom of the pyrrolidine moiety leading to a barely electrophilic urea function. Interestingly, Au(I) complexes with an *N*-benzoyl NHC ligand have been reported as early as 1993 [10]. However, no systematic study of the electronic properties of *N*-acyl NHCs has been reported to date. In contrast to carboxamides, sulfonamides are known to be much more robust entities which also exert a strong electron withdrawing effect. Therefore, we wish to report our first results concerning the syntheses and properties of NHCs featuring exocyclic acyl and sulfonyl groups, respectively, derived from ferrocene carboxylic and sulfonic acid chloride. The ferrocenyl residue was chosen as it provides considerable steric demand. Ferrocenylated NHCs were first investigated by Bildstein [11] and coworkers and have since then attracted attention [12] as chiral ligands for catalysis [13] and as redox-switchable systems [14]. Furthermore, an NHC comprising a ferrocenophane backbone was found to display a unique reactivity [15].

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## 2. Results and discussion

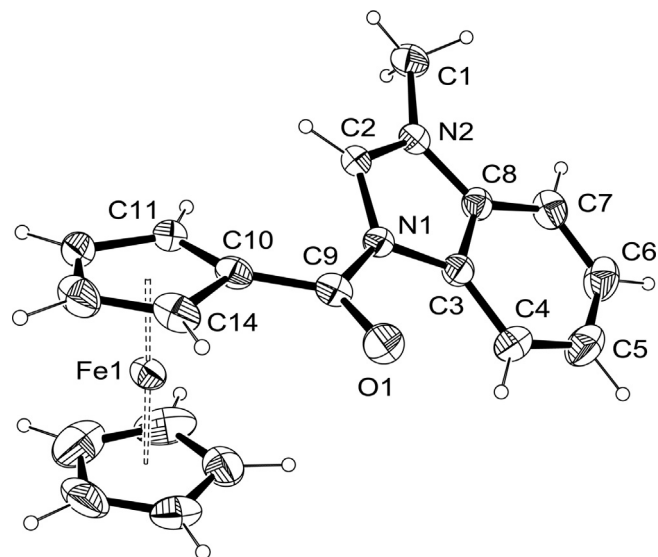
### 2.1. Synthesis of carboxamide and sulfonamide based NHC precursors

The carboxamide based NHC precursors **3a** and **3b** were synthesized starting from easily available ferrocenylcarboxylic acid chloride **1** [16]. The imidazolium salt **3a** simply precipitated as a red solid in 92% yield upon treatment of the acid chloride with *N*-methylimidazole in diethyl ether. The benzimidazolium salt **3b** was synthesized in two steps: first, the acid chloride reacted with benzimidazole in the presence of triethylamine to afford the literature-known neutral amide **2** [17], which was subsequently converted to the benzimidazolium derivative **3b** by alkylation with methyl trifluoromethanesulfonate (Scheme 1).

The related sulfonamides **6a** and **6b** were straightforwardly prepared starting from ferrocenesulfonylchloride **4** by treatment with imidazole and benzimidazole, respectively, and subsequent methylation of the neutral sulfonamides **5** with methyl triflate (Scheme 1). The synthesis of **5b** has been reported earlier by Yang [18]. The reaction of sulfonylchloride **4** and methylimidazole to provide the cationic species **6a** in one step was not successful in this case. However, treatment of MeSO<sub>2</sub>Cl and *p*-TosCl with methylimidazole in ether cleanly afforded the related imidazolium salts **6c** and **6d** [19] which precipitated from solution.

All precursors **3a,b** and **6a–d** were completely characterized by <sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H}-NMR spectroscopy, mass spectrometry and elemental analysis. The MALDI-TOF mass spectra are dominated by a base peak (100%) centered at *m/z* 295 (345) for the cationic moiety in **3a** (**3b**) and at *m/z* 331 (381, 161) for the corresponding cations in **6a** (**6b**, **6c**).

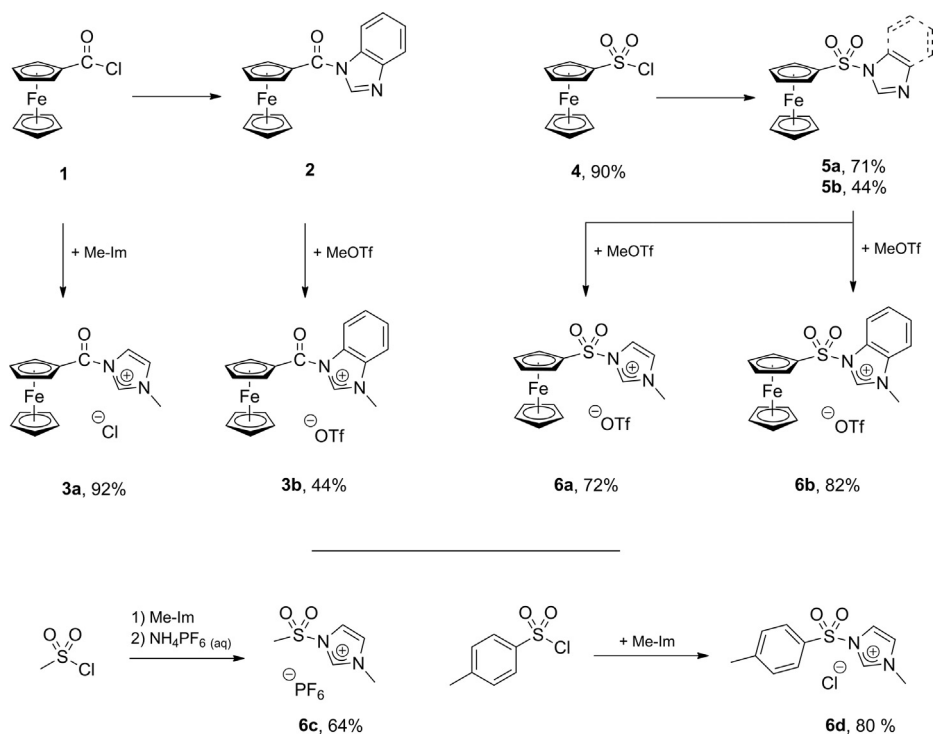
The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra show no significant differences to those of other imidazolium or benzimidazolium salts. The resonances for the amidinium proton (NCHN) were detected between 8.93 ppm and 9.74 ppm. The corresponding amidinium carbon atom gave a resonance between 137.6 ppm and 143.1 ppm. Furthermore, the free



**Fig. 1.** Molecular structure of the cation **3b** in the solid state. Thermal ellipsoids are drawn at the 30% probability level. The OTf<sup>-</sup> anion has been omitted for clarity. Selected interatomic distances [Å] and bond angles [deg]: O1–C9 1.216(6), N1–C2 1.349(6), N1–C3 1.403(6), N1–C9 1.447(6), N2–C2 1.322(6), N2–C8 1.385(6), N2–C1 1.463(6), C9–C10 1.439(7), C10–C9–N1 117.0(4), N2–C2–N1 109.9(4).

rotation in solution of the ferrocenyl precursors **3a,b** and **6a,b** led to effective C<sub>5</sub>-symmetry as only two resonances in the <sup>1</sup>H NMR spectra and three resonances in the <sup>13</sup>C NMR spectra were recorded for the substituted cyclopentadienyl rings.

Suitable crystals for X-ray diffraction studies could be obtained for the salts **3b** and **6b** by diffusion of hexane into dichloromethane solutions. The molecular structures are depicted in Figs. 1 and 2 together with selected geometrical parameters. The benzimidazole fragment and the ferrocene unit are linked via a trigonal planar carboxy group in the amide **3b** and a



**Scheme 1.** Synthesis of the precursors **3a,b** and **6a–d** (a = imidazole, b = benzimidazole).

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