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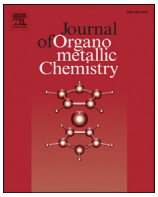

A benzothiadiazole-supported *N*-heterocyclic carbene and its rhodium and iridium complexes

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ABSTRACT

A new *N*-heterocyclic carbene containing a fused benzothiadiazole (BTD) moiety, 5,7-bis(1,1-dimethylethyl)-5*H*-imidazo[4,5-*f*]-2,1,3-benzothiadiazol-6-ylidene (**1**), was generated by deprotonation of the corresponding tetrafluoroborate salt. The salt precursor was accessed in six steps from the commercially available 1,2-phenylenediamine. This carbene was found to be stable under inert conditions and it was fully characterized by NMR spectroscopy. The sulfur adduct of this carbene was also synthesized and fully characterized. The X-ray structure analysis of the thione revealed that the carbene carbon and the sulfur atom deviate from the plane containing the BTD moiety and the two nitrogen atoms of the imidazole ring by 0.231 and 0.890 Å, respectively. Complexes of type [MCl(COD)(**1**)] (where M = Rh and Ir) were prepared and characterized using spectroscopic and crystallographic methods. The donor strength of this new carbene was determined by IR spectroscopy (ν_{av}) and cyclic voltammetry ($E_{1/2}$). Preliminary catalytic studies show that the new carbene is a suitable ligand for rhodium and iridium catalysts in the hydrosilylation of acetophenones.

1. Introduction

The use of *N*-heterocyclic carbenes (NHC) as ancillary ligands in organometallic chemistry and homogeneous catalysis is still an area of intense activity 25 years after the isolation and crystallographic characterization of the first stable NHC in early 1991 [1]. NHCs comprise a remarkably varied class of carbon-based ligands with unique electronic and steric properties [2–8]. Many NHC metal complexes are now well recognized as efficient catalysts in a plethora of reactions such as cross-coupling, olefin metathesis, and hydrogenation [4,6,9]. To extend the possibilities of ligand tuning and the scope of NHC-based catalysts, structural variations influencing the electronic and steric properties are desirable. One such approach is annulation at the C4–C5 position of the of the typical 5-membered ring parent system (Fig. 1, **I**) with aromatic carbo- or heterocycles. It was observed that this type of annulation has a significant impact on the stability and the electronic nature of NHCs [10–23]. The electron density at the carbene center varies with the π donor or acceptor properties of the annulated rings [10–23]. Despite their proven utility in catalysis, coordination and polymer chemistry and materials science, only a few monoNHCs that incorporate a fused polycyclic heteroaromatic moiety have been studied so far (Fig. 1, **II-VIII**) [10–18].

This contribution reports our investigation toward the synthesis and reactivity of a new polycyclic heteroaromatic carbene: 5,7-bis(1,1-dimethylethyl)-5*H*-imidazo[4,5-*f*]-2,1,3-benzothiadiazol-6-ylidene (**1**). 2,1,3-Benzothiodiazole (BTD) and its derivatives are a class of aromatic compounds with interesting electronic properties [24]. In recent years, these compounds have attracted significant attention in the area of heterocyclic, coordination, and materials chemistry. For example, they have been used as components of organic-light-emitted diodes and as structural units of low-band gap polymers for photovoltaic applications [24–33]. They have also found applicability as ligands in transition metal complexes [34–40]. Annulation of a BTD moiety to an imidazol-2-ylidene provides a promising framework in which the carbene center is a component of an electron-rich, extended aromatic system. It is expected that the extended π-system should have a significant

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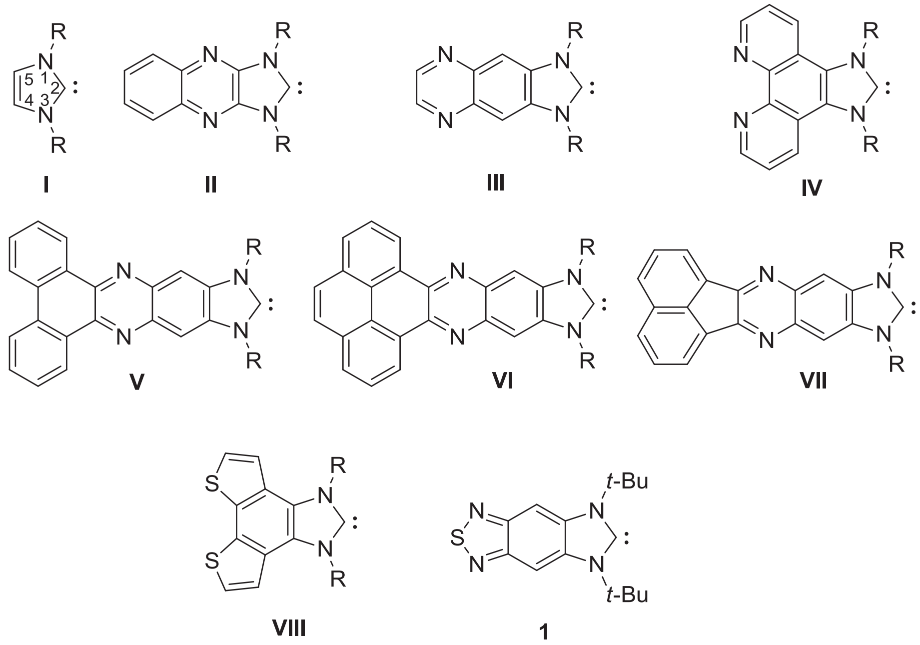


Fig. 1. Examples of monoNHCs featuring fused polycyclic heteroaromatic moieties.

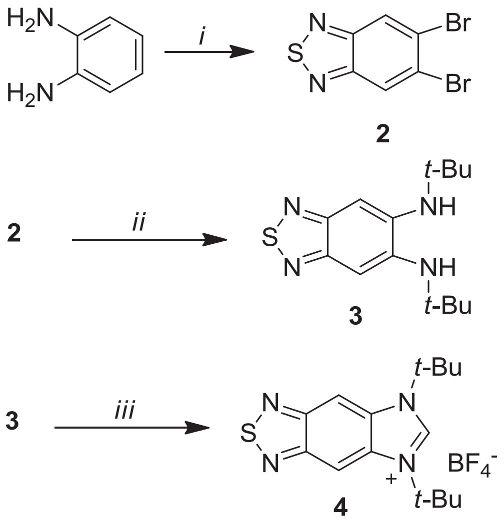
effect on the donor properties of the carbene center. In addition, carbene **1** displays several potential coordination sites which could lead to the synthesis of novel heterobimetallic complexes or metal-organic frameworks. The focus of this work is the synthesis and full characterization of this novel carbene. In addition, the synthesis and characterization of its corresponding monometallic complexes [MCl(COD)(**1**)] (with M = Rh and Ir) are also described. Preliminary studies of the catalytic performance of these metal complexes in the hydrosilylation of acetophenone and its derivatives are reported as well.

2. Results and discussion

2.1. Chemical synthesis studies

2.1.1. Synthesis of the carbene precursor

Imidazolium salts are the most common precursors used to generate NHCs [1]. Scheme 1 summarizes the six steps necessary to access imidazolium salt **4** from the commercially available 1,2-phenylenediamine. Using published protocols 1,2-phenylenediamine was converted into 5,6-dibromo-2,1,3-benzothiadiazole (**2**) [41]. A Buchwald-Hartwig amination was employed to convert **2** to diamine **3**, which was used without further purification to generate the imidazolium salt precursor **4** by a ring closing reaction with triethylorthoformate and tetrafluoroboric acid. The tetrafluoroborate salt **4** was targeted to avoid potential halide exchange and any subsequent separation problems in reactions involving metal chlorides. The ^{1}H and ^{13}C NMR spectra of **4** are consistent with the proposed structure. In the ^{1}H NMR spectrum, the characteristic imidazolium proton appears at δ 9.02 ppm in DMSO-d_6, while the ^{13}C NMR signal of NCN carbon appears at δ 146.64 ppm (DMSO-d_6). Interestingly, this value is the median of the chemical shifts of the NCN carbons of 1,3-bis(1,1-dimethylethyl) benzimidazolium chloride (δ 139.1 ppm in DMSO-d_6) and the saturated 1,3-bis(1,1-dimethylethyl) imidazolinium chloride (δ 153.5 ppm in DMSO-d_6) [8]. The unsaturated analogue, 1,3-*bis*(1,1-dimethylethyl) imidazolium chloride, displays the NCN carbon at δ 132.7 ppm in DMSO-d_6.



(i) 1) TsCl, Py; 2) Br_2, acetic acid, NaOAc; 3) H_2SO_4 4) $SOCl_2$, Et_3N; *(ii)* *t*-$BuNH_2$, NaO*t*Bu, Pd catalyst; (iii) $HC(OEt)_3$, HBF_4.

Scheme 1. Synthesis of imidazolium salt **4**.

2.1.2. Generation of carbene 1 and its corresponding thione 8

Having isolated **4**, subsequent efforts focused on exploring the synthesis and characterization of the target carbene **1**. The treatment of **4** with potassium *t*-butoxide (KO*t*Bu) or potassium bis(-trimethylsilyl)amide (KHMDS) in anhydrous toluene at room temperature afforded the free carbene **1** (Scheme 2), as evidenced by the disappearance of the acidic proton signal at δ 9.02 ppm in the compound's ^{1}H NMR spectrum. In addition, the ^{13}C NMR spectrum of **1** revealed a signal for the carbenic carbon at δ 243.44 ppm (d_6-benzene), a 96.8 ppm downfield shift relative to **4**. Surprisingly, this chemical shift is much higher than those displayed by 1,3-bis(1,1-dimethylethyl)imidazol-2-ylidene (**5**) (δ ^{13}C2 = 212.58 ppm,