

Short Note

## 1,3-Bis(pyren-1-yl)imidazolium Chloride (IPyr·HCl)

Peter Schroll and Burkhard König \*

Institute of Organic Chemistry, University of Regensburg, Universitätsstraße 31, 93040 Regensburg, Germany

\* Author to whom correspondence should be addressed; E-Mail: Burkhard.Koenig@chemie.uni-regensburg.de.

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**Abstract:** A novel UV-A-light absorbing N-heterocyclic carbene precursor imidazolium salt **2** was synthesized by reaction of 1,4-bis(pyren-1-yl)-1,4-diazadiene **1** with paraformaldehyde in the presence of chlorotrimethylsilane. The title compound was characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, 2D-NMR, mass spectrometry, IR and UV/VIS spectroscopy.

**Keywords:** N-heterocyclic carbene; catalysis; light absorption; photochemistry

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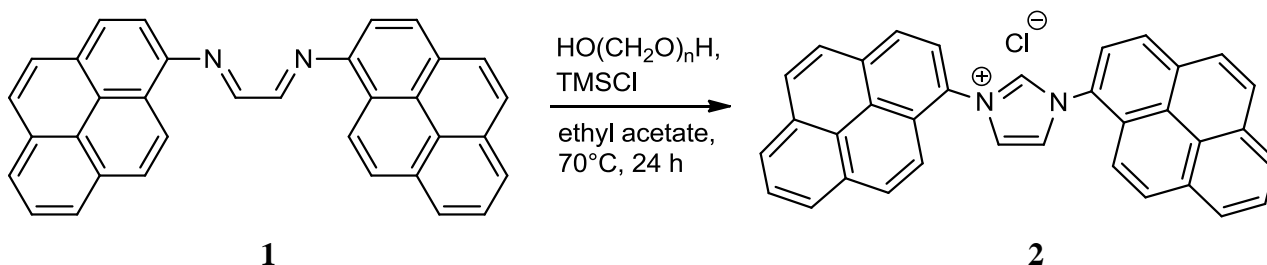
### 1. Introduction

N-Heterocyclic carbenes (NHCs) have attracted great interest since the isolation of the first stable free NHC [1] and the discovery of the catalytic activity of their metal complexes [2]. Since they act as excellent two electron  $\sigma$ -donor ligands in metal-based catalytic reactions [3], many applications in C-H-activation processes for bond-formation reactions have been found. Amongst others, the 2<sup>nd</sup> generation Grubbs catalyst has become illustrious in metathesis reactions [4]. Moreover, nucleophilic carbenes are used as organocatalysts to accomplish Umpolung reactions, for example [5]. A widespread synthetic route to N-heterocyclic carbenes is the formation of the five-membered heterocycle by condensation of glyoxal with an amine followed by ring-closure with paraformaldehyde in the presence of chlorotrimethylsilane [6] or HCl [7]. The free carbene is generated from the imidazolium salt precursor by deprotonation [1].

## 2. Results and Discussion

We herein report a new imidazolium salt precursor 1,3-bis(pyren-1-yl)imidazolium chloride (IPyr·HCl) **2** for N-heterocyclic carbenes containing a pyrene chromophore bound to the nitrogen atoms of the imidazolium heterocycle. Carbene ligands absorbing light might be useful tools for photochemistry as it is already shown for UV-A-absorbing phosphine ligands, which have been proved to accelerate Suzuki- and Stille-coupling reactions upon irradiation of their palladium complexes [8]. The conjugated  $\pi$ -system of the reported ligand might allow the use of light as energy source for catalytic reactions. Therefore, the following precursor might serve as a model system for the investigation of light-absorbing carbene ligands for future application in photocatalysis. As far as the synthetic route is concerned, the reactant 1,4-bis(pyren-1-yl)-1,4-diazadiene **1** was obtained as a red solid from the condensation of 1-aminopyrene (2.0 eq.) and glyoxal (1.0 eq.) in isopropanol with catalytic amount of acetic acid at ambient temperature. The imidazolium salt was synthesized as shown in scheme 1.

**Scheme 1.** Synthesis of the title compound 1,3-bis(pyren-1-yl)imidazolium chloride (IPyr·HCl) **2**.



## 3. Experimental

1,4-bis(pyren-1-yl)-1,4-diazadiene **1** (0.23 g, 0.5 mmol) in dry ethyl acetate (90 mL) was warmed to 70 °C in a pre-dried Schlenk flask. Paraformaldehyde (15 mg, 0.5 mmol) was added followed by dropwise addition of chlorotrimethylsilane (63  $\mu\text{L}$ , 0.5 mmol) in ethyl acetate (1.3 mL). The mixture was stirred for another 24 h at 70 °C. After cooling the reaction mixture to ambient temperature, the solid was filtered off and purified by flash column chromatography using dichloromethane / methanol (6:1) as the eluent. Final purification was achieved by preparative high pressure liquid chromatography (HPLC) to give **2** as a white solid in 42% yield.

1,4-bis(pyren-1-yl)-1,4-diazadiene **1**:

IR:  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 3034 (w); 2360 (w); 1598 (m); 1511 (m); 1275 (m); 830 (s).

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.80–8.10 (m, 18H,  $\text{H}_{\text{aryl}}$ ), 8.96 (s, 2H).

Anal. calcd. for  $\text{C}_{34}\text{H}_{20}\text{N}_2$ : C, 89.45; H, 4.42; N, 6.14. Found: C, 88.89; H, 5.15; N, 5.96.

MS (EI):  $m/z$  (%) = 456.2 (100) [ $\text{M}^+$ ].

UV/VIS ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  [nm] ( $\lg \epsilon$ ) = 267 (4.517); 344 (4.284); 449 (4.142).

1,3-bis(pyren-1-yl)imidazolium chloride (IPyr-HCl) **2**:

IR:  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 2992 (w); 2365 (m); 1275 (m); 750 (s).

$^1\text{H-NMR}$  (600 MHz, DMSO- $d_6$ ):  $\delta$  [ppm] = 8.26 (t,  $J$  = 7.6 Hz, 2H), 8.34 (d,  $J$  = 9.2 Hz, 2H), 8.41 (d,  $J$  = 8.9 Hz, 2H), 8.45 (d,  $J$  = 8.9 Hz, 2H), 8.53 (m, 6H), 8.64 (s, 4H), 8.78 (d,  $J$  = 1.3 Hz, 2H,  $\text{H}_{\text{imidazole}}$ ), 10.50 (t,  $J$  = 1.3 Hz, 1H,  $\text{H}_{\text{imidazole}}$ ).

$^{13}\text{C-NMR}$  (150 MHz, DMSO- $d_6$ ):  $\delta$  [ppm] = 120.8 (+), 123.2 (q), 124.1 (q), 125.0 (+), 125.2 (q), 125.8 (+), 125.9 (q), 126.7 (+), 127.0 (+), 127.1 (+), 127.5 (+), 128.1 (q), 129.5 (+), 130.2 (+), 130.3 (+), 130.7 (q), 132.5 (q), 139.9 (+).

HRMS calcd. for  $\text{C}_{35}\text{H}_{21}\text{N}_2^+$  [ $\text{M}^+$ ]: 469.1699. Found: 469.1703.

UV/VIS (DMSO):  $\lambda_{\text{max}}$  [nm] ( $\lg \epsilon$ ) = 279 (4.794); 332 (4.570); 348 (4.722).

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