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Short Note

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

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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 ^{1}H-NMR, ^{13}C-NMR, 2D-NMR, mass spectrometry, IR and UV/VIS spectroscopy.

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

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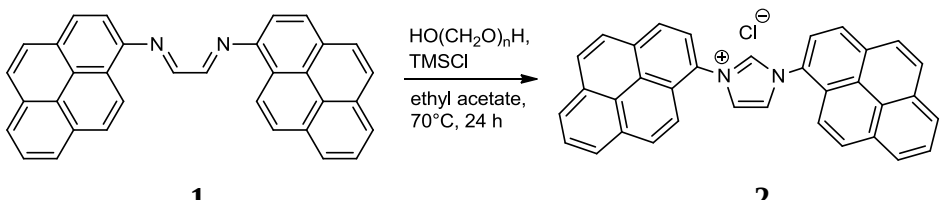
1. Introduction

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 σ-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 2nd 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 π-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 ℃ in a pre-dried Schlenk flask. Paraformaldehyde (15 mg, 0.5 mmol) was added followed by dropwise addition of chlorotrimethylsilane (63 µL, 0.5 mmol) in ethyl acetate (1.3 mL). The mixture was stirred for another 24 h at 70 ℃. 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: $\tilde{\nu}$ [cm^{-1}] = 3034 (w); 2360 (w); 1598 (m); 1511 (m); 1275 (m); 830 (s).

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.80–8.10 (m, 18H, H_{aryl}), 8.96 (s, 2H).

Anal. calcd. for $C_{34}H_{20}N_2$: 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) [M^+].

UV/VIS (CH_2Cl_2): λ_{max} [nm] (lg ε) = 267 (4.517); 344 (4.284); 449 (4.142).

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

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

^{1}H-NMR (600 MHz, DMSO-d$_6$): δ [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, $H_{imidazole}$), 10.50 (t, *J* = 1.3 Hz, 1H, $H_{imidazole}$).

^{13}C-NMR (150 MHz, DMSO-d$_6$): δ [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 $C_{35}H_{21}N_2^+$ [M^+]: 469.1699. Found: 469.1703.

UV/VIS (DMSO): λ_{max} [nm] (lg ε) = 279 (4.794); 332 (4.570); 348 (4.722).

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