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1,1′-(Pyridine-2,6-diyl)bis(3-benzyl-2,3-dihydro-1*H*-imidazol-2-ylidene), a new multidentate *N*-heterocyclic biscarbene and its silver(I) complex derivative

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Dedicated to Professor José Elguero on the occasion of his 65th birthday

Abstract

1,1′-(Pyridine-2,6-diyl)bis(3-benzyl-2,3-dihydro-1*H*-imidazole-2-ylidene) (**5**) is a new polydentate *N*-heterocyclic biscarbene, stable at −20°C in THF solution and obtained by deprotonation of the corresponding bisimidazolium salt **4**. Reaction of **5** with silver(I) triflate yields the silver(I) complex **7**.

Keywords: Imidazol-2-ylidene; Pyridine; Silver

1. Introduction

The chemistry of stable *N*-heterocyclic carbenes have experienced a remarkable growth after their initial synthesis as transition metal complexes by Wanzlick [1] and Öfele [2] and as free-carbenes by Arduengo [3]. These facts were the beginning of the chemistry of imidazol-2-ylidene, a useful ligand due to its ability to form transition metal complexes [4] and its use in catalysis applications [4,5].

Several multidentate *N*-heterocyclic carbene systems have been used in coordination chemistry: *N*,*C*-bidentate systems containing oxazoline and imidazol-2-ylidene [6], pyridine and imidazol-2-ylidene [7], *C*,*C*-bidentate systems containing two imidazol-2-ylidene [4,8], benzimidazol-2-ylidene [9] or 1,2,4-triazol-5-ylidene [10] and polidentate ligands [4]. Here we report the synthesis of a new multidentate *N*-heterocyclic biscarbene system and its silver(I) complex.

2. Results and discussion

Imidazolium salts are appropriate starting materials for the synthesis of imidazol-2-ylidenes by deprotonation with bases [4]. In this way 1,1′-(pyridine-2,6-diyl)bis(3-alkyl-1*H*-imidazolium) salt has been chosen as a precursor of multidentate carbene systems. Recently a similar approach has been reported for the synthesis of a dicarbene mercury complex [11].

Firstly, we prepared 2,6-bis(1*H*-imidazol-1-yl)pyridine (**3**) by reaction of 2,6-dichloropyridine with two equivalents of imidazolate anion, generated in situ using potassium hydroxide and tetrabutylammonium bromide (TBAB) at 80°C. Bisimidazolium salt **4** was synthesised refluxing **3** with benzyl bromide (Scheme 1). Compounds **3** and **4** were fully characterised by ^{1}H- and ^{13}C-NMR spectroscopy (see Section 4).

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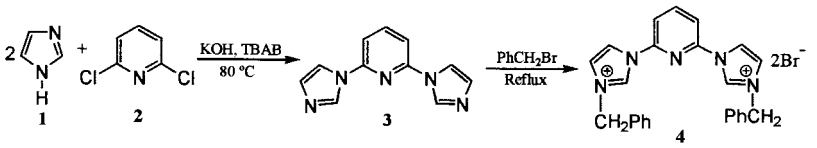


Scheme 1. Synthesis of 1,1′-(pyridine-2,6-diyl)bis(3-benzyl-1*H*-imidazolium) bromide.

Deprotonation of the 2,6-bis(1*H*-imidazolium-1-yl)pyridine salt (**4**) has been tried with *n*-butyl lithium, sodium hydride and potassium *tert*-butoxide. *n*-Butyl lithium afforded decomposition products in any conditions. Reaction of the bisimidazolium salt **4** with sodium hydride, working in a −20°C RT temperature range, yields the dithione **6** when sulphur [12] is present in the reaction system. However if the reaction mixture is filtered before the sulphur quenching, unaltered bisimidazolium salt **4** is recovered. We have no explanation for this fact. When **4** was treated with potassium *tert*-butoxide at room temperature, the suspension quickly turned into a clear solution, where the 1,1′-(pyridine-2,6-diyl)bis(3-benzyl-1*H*-2,3-dihydroimidazole-2-ylidene) (pbbdiy) (**5**) is present as we can verify by (i) NMR spectroscopies and (ii) quenching with sulphur (Scheme 2). The NMR spectra of **5** showed a low intensity signal at 217.4 ppm in the ^{13}C-NMR spectrum and the absence of signals in the imidazole H2 region in the ^{1}H-NMR, in agreement with a carbene structure. All typical signals from benzyl, pyridine and imidazol-2-ylidene moieties are also present in both spectra (See Section 4).

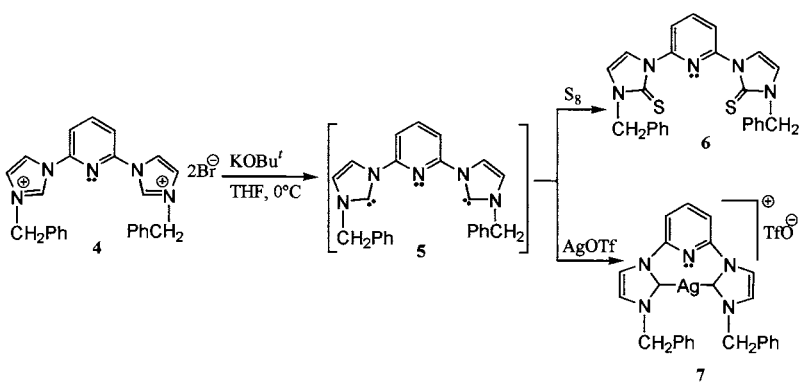
THF solutions of carbene are stable during 1–2 h at 0°C and no less than 24 h at −20°C. The addition of diethylether to a solution of **5** in THF provokes the precipitation of the biscarbene. Redisolution in THF followed by sulphur quenching afforded the dihione **6**. However all attempts to isolate **5** were unsuccessful. In any way, only tars were obtained.

Taking into account the ability of this kind of carbene to coordinate metals, we envisaged the reaction of **5** with silver(I) triflate. For this purpose biscarbene **5** was generated with potassium *tert*-butoxide in THF at 0°C and then an equivalent amount of silver(I) triflate was added. We have chosen silver because the silver(I) complexes may be used as carbene transfer agents [13]. 1,1′-(Pyridine-2,6-diyl)bis(3-benzyl-2,3-dihydro-1*H*-imidazol-2-ylidene)-silver(I) triflate {[Ag(pbbdiy)]OSO_2CF_3} (**7**) was obtained after filtration of the reaction crude and precipitation from THF–pentane. The ^{1}H- and ^{13}C-NMR spectra are consistent with the silver carbene complex. Thus the C2 of the imidazol-2-ylidene ring appears as two low intensity duplets (186.8 ppm, $^{1}J_{107_{AgC}} = 186.6$ Hz, $^{1}J_{109_{AgC}} = 216.1$ Hz) which the coupling constant ratio is in agreement with the ratio of the giromagnetic constant of both silver isotopes. These resonances are in agreement with reported silver(I)-imidazol-2-ylidenes [14] and especially with the first biscarbene silver complex reported by Bertrand [14c]. In addition proton and carbon resonances of benzyl, pyridine and imidazol-2-ylidene are present. FAB-MS showed mass peak according to the cation of the proposed structure ($m/z = 498$).

Searches for evidence of coordination of the metal by the nitrogen atom of the pyridine ring, and the synthesis of complexes with other metals are in progress.

3. Conclusions

The new multidentate *N*-heterociclic biscarbene 1,1′-(pyridine-2,6-diyl)bis(3-benzyl-2,3-dihydro-1*H*-imidazol-2-ylidene) is obtained in THF solution. Sil-



Scheme 2. Preparation of 1,1′-(pyridine-2,6-diyl)bis(3-benzyl-2,3-dihydro-1*H*-imidazol-2-ylidene) and synthesis of [Ag(pbbdiy)]OSO_2CF_3.

ver(I) complex may be synthesised by the reaction of silver(I) triflate with the in situ generated carbene.

4. Experimental

Solvents were purified by distillation from appropriate drying reagents before use. Melting points were determined in capillary tubes on a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyzer. NMR spectra were recorded on a Varian Unity 300. Chemical shifts are expressed in parts per million (δ) relative to TMS as internal standard. The resonances of compounds **3**, **4**, **6** and **7** were assigned by their coupling constants, and different NOE- and Hetcor experiments. FAB-MS was recorded on a VG Autospect instrument using *m*-nitrobenzylalcohol as matrix.

4.1. Preparation of 2,6-bis(imidazol-1-yl)pyridine (3)

In a 50 ml round bottom flask, provided with a condenser of reflux, imidazole (45 mmol), KOH (90 mmol) and TBAB (1,35 mmol) were stirred at room temperature (r.t.) for 15 min, then 2,6-dichloropyridine (21 mmol) was added and the mixture was stirred for 2 h at 80°C. The residue was extracted with EtOH and after removing the solvent the crude product was purified by flash chromatography on silica gel (AcOEt:MeOH, 10:1) to afford the compound **3** as a white powder. M.p. 142–143°C ($CHCl_3$–Et_2O); 85% yield. ^{1}H-NMR (δ, $CDCl_3$): 7.21 (*bs*, 2H, H4-Im), 7.27 (*d*, $J = 8.1$ Hz, 2H, H3-Py), 7.65 (pseudot, $J = 1.3$ Hz, 2H, H5-Im), 7.96 (*t*, $J = 8.1$ Hz, 1H, H4-Py), 8.36 (*bs*, 2H, H2-Im). ^{13}C{H}-NMR (δ, $CDCl_3$): 109.6 (C3-Py), 116.1 (C5-Im), 131.1 (C4-Im), 134.9 (C2-Im), 142.0 (C4-Py), 148.3 (C2-Py). Anal. Calc. for $C_{11}H_9N_5$: C, 62.56; H, 4.30; N, 33.16. Found: C, 62.45; H, 4.62; N, 32.81%.

4.2. Preparation of 1,1′-(pyridine-2,6-diyl)bis(3-benzyl-1H-imidazolium) dibromide (4)

In a 250ml round bottom flask, provided with a condenser of reflux, a mixture of **3** (10 mmol) and benzyl bromide (200 mmol) was heated at 100°C for 24 h. The reaction mixture was washed with CH_2Cl_2 to give **4** which was purified by crystallisation. M.p. 288–289°C (EtOH–AcOEt); 78% yield. ^{1}H-NMR (δ, DMSO-d_6): 5.68 (*s*, 4H, CH_2), 7.40–7.66 (*m*, 10H, Ph), 8.20 (pseudot, $J = 1.8$ Hz, 2H, H4-Im), 8.29 (*d*, $J = 8.1$ Hz, 2H, H3-Py), 8.61 (*t*, $J = 8.1$ Hz, 1H, H4-Py), 8.91 (pseudot, $J = 1.8$ Hz, 2H, H5-Im), 11.20 (*bs*, 2H, H2-Im). ^{13}C{H}-NMR (δ, DMSO-d_6): 53.1 (CH_2), 114.9 (C3-Py), 120.6 (C5-Im), 124.4 (C4-Im), 129.3 (C2-Ph), 129.6 (C4-Ph), 129.7 (C3Ph), 135.0 (C1-Ph), 136.6 (C2-Im), 145.4 (C2-Py), 145.9 (C4-Py). Anal. Calc. for $C_{25}H_{23}N_5Br_2$: C, 54.27; H, 4.19; N, 12.66. Found: C, 54.15; H, 4.24; N, 12.59%.

4.3. Preparation of 1,1′-(pyridine-2,6-diyl)bis-(3-benzyl-2,3-dihydro-1H-imidazol-2-ylidene) (5)

A THF-d_8 (0.5 ml) solution of potassium *tert*-butoxide (0.056 mmol) was transferred at −78°C to a NMR tube containing 4 (0.027 mmol) After 5 min the following spectra were recorded: ^{1}H-NMR (δ, THF-d_8, 0°C): 5.33 (*s*, 4H, CH_2), 7.11 (*d*, $J = 1.8$ Hz, 2H, H4-Im), 7.25–7.36 (*m*, 10H, Ph), 7.91 (*t*, $J = 8.1$ Hz, 1H, H4-Py), 8.20 (*d*, $J = 1.8$ Hz, 2H, H5-Im), 8.29 (*d*, $J = 8.1$ Hz, 2H, H3-Py). ^{13}C{H}-NMR (δ, THF-d_8, 0°C): 55.8 (CH_2), 111.1(C3-Py), 117.6 (C5-Im), 120.6 (C4-Im), 128.3 (C4-Ph), 128.5 (C2-Ph), 129.3 (C3-Ph), 139.4 (C1-Ph), 141.0 (C4-Py), 153.2 (C2-Py), 217.4 (C2-Im).

4.4. Preparation of 1,1′-(pyridine-2,6-diyl)bis-(3-benzylimidazole-2-thione) (6)

To a solution of **4** (0.7 mmol) in THF (75 ml) and potassium *tert*-butoxide (1.4 mmol) was added at r.t. The mixture was stirred for 5 min and then sulphur (1.5 mmol) was added. After 2 h the solution was filtered and the solvent removed to give a crude product which was purified by flash chromatography (70:1 CH_2Cl_2–MeOH). M.p. 159–160°C ($CHCl_3$–Hexane); 77% yield. ^{1}H-NMR (δ, $CDCl_3$): 5.35 (*s*, 4H, CH_2), 6.68 (*d*, $J = 2.7$ Hz, 2H, H4-Im), 7.36–7.39 (*m*, 10H, Ph), 7.48 (*d*, $J = 2.7$ Hz, 2H, H5-Im), 8.06 (*t*, $J = 8.1$ Hz, 1H, H4-Py), 8.95 (*d*, $J = 8.1$ Hz, 2H, H3-Py). ^{13}C{H}-NMR (δ, $CDCl_3$): 51.0 (CH_2), 116.3(C5-Im), 117.0 (C3-Py), 117.2 (C4-Im), 128.3 (C4-Ph), 128.4 (C2-Ph), 128.9 (C3-Ph), 135.3 (C1-Ph), 139.8 (C4-Py), 148.4 (C2-Py), 162.8 (C2-Im). Anal. Calc. for $C_{25}H_{21}N_5S_2$: C, 65.91; H, 4.65; N, 15.37; S, 14.08. Found: C, 65.83; H, 4.61; N, 15.31; S, 14.11%.

4.5. Preparation of [Ag(pbbdiy)]OSO_2CF_3 (7)

To a 250 ml Schlenk tube light protected, containing **4** (0.36 mmol) a solution of potassium *tert*-butoxide (0.75 mmol) in THF (75 ml) was added at 0°C. Then silver trifluoromethanesulfonate (0.54 mmol) was added and the mixture was stirred for 5 min. The solution was filtered and the solvent removed to give a brown powder, which was washed with 1:10 tetrahydrofuran–pentane. The product was obtained as brown powder. M.p. 191–192°C (decomposition) (THF–Pentane); 60% yield. ^{1}H-NMR (δ, DMSO-d_6): 4.89 (*bs* 4H, CH_2), 6.85 (*d*, $J = 7.3$ Hz, 4H, H2-Ph), 7.07 (*t*, $J = 7.3$ Hz, 4H, H3-Ph), 7.17 (*t*, $J = 7.3$ Hz, 2H, H4-Ph), 7.73 (*s*, 2H, H4-Im), 7.99 (*d*, $J = 8.0$ Hz, 2H, H3-Py), 8.34 (*s*, 2H, H5-Im), 8.42 (*t*, $J = 8.0$ Hz, 1H, H4-Py). ^{13}C{H}-NMR

(δ, DMSO-d_6): 55.1 (CH_2), 114.1 (C3-Py), 120.5 (C5-Im), 120.7 (*c*, $^1J_{FC} = 322.1$ Hz, CF_3), 123.7 (C4-Im), 127.5 (C2-Ph), 128.0 (C4-Ph), 128.5 (C3-Ph), 135.6 (C1-Ph), 143.6 (C2-Py), 148.5 (C4-Py), 186.8 (*dd* $^1J_{107_{AgC}} = 186.6$ Hz, $^1J109_{AgC} = 216.1$ Hz, C2-Im). ^{19}F-NMR (δ, DMSO-d_6): -78.93 (CF_3). MS (FAB^+): $m/z = 498$ (M^+ of cation).

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