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A zwitterionic cyclopentadienyl annulated imidazolium salt

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Abstract—The first directly annulated cyclopentadienyl–imidazolium salt has been synthesized and fully characterized. In the solid-state, this zwitterion arranges itself in a hydrogen-bridged head to tail trimer which optimizes ionic interactions. Substantial π–π interactions are absent. The UV spectrum of the imidazolium innersalt reflects the intimate electronic interaction arising from direct fusion of cationic and anionic fragments of the molecule.
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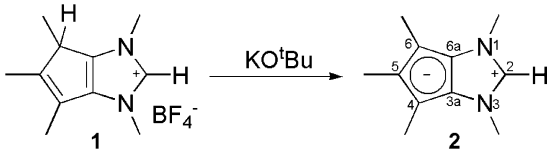
Imidazolium salts have become increasingly important since the resurgence of interest in imidazole-based carbenes following the report of the isolation of a stable crystalline imidazol-2-ylidene in 1991.[1] Although new routes to imidazole-based carbenes have been developed in recent years,[2] the deprotonation of imidazolium ions remains an important synthetic strategy.[1,3] A variety of interesting functional groups have now been incorporated as substituents on imidazolium ions and thereby ultimately on imidazole-based carbenes.[4] The ferrocene moiety has been incorporated as a pendent group on imidazoles,[5] but no directly annulated cyclopentadienyl–imidazol-2-ylidene or imidazolium innersalt is known. The more intimate electronic interaction arising from direct cyclopentadienyl–imidazole ring fusion suggests that compounds containing this type of functionality will make interesting subjects for chemical study and may offer useful properties for 'tuning' the electronic properties of imidazole-based carbenes. A significant synthetic challenge arises from the planar fusion of two 5-membered rings. In this 5–5 fusion, the external angles at the angular positions are expected to be about 143°. Additionally, cyclopentadienyl rings functionalized with nitrogens are rare.[6] We recently reported, a successful methodology for the assembly of this basic bicyclic ring system[7] and we now report, a complementary strategy that allows easy access to a useful zwitterionic cyclopentadienyl–imidazole.



Scheme 1. Synthesis of the zwitterion **2**.

Imidazolium salt **1** reacts with potassium *tert*-butoxide in tetrahydrofuran to form cyclopentadienyl annulated imidazolium zwitterion **2** (Scheme 1).[†] The synthesis of **1** is achieved starting from 2 chloro-methyl imidazole by a reaction sequence that involves as a key step a Nazarov-type cyclization (Scheme 2)[8] similar to that which we recently reported for an imidazole-2-thione.[7]

Zwitterion **2** is isolated as a yellow solid that can be recrystallized from toluene. It has a melting point of 176–178 °C. The imidazole H^2 resonates at δ 5.44 in C_6D_6 solution at room temperature and in DMSO-d_6 at δ 7.70. In benzene solution the NMR chemical shift of the imidazole ^{13}C-2 appears at δ 121.49. Both of these resonances are upfield of those for other imidazolium salts[9] and are probably the result of an electron-releasing effect of cyclopentadienide ring.

Keywords: Imidazolium cyclopentadienide; Zwitterion; Annulated.
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† Experimental procedures and characterizations for new compounds are described in Supplementary data.

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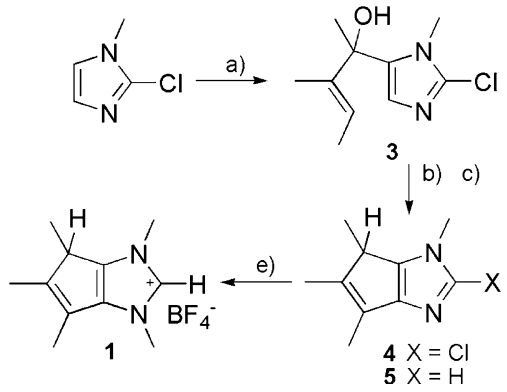

Scheme 2. Synthesis of the precursor **1**. Reagents: (a) BuLi, 3-methyl-3-penten-2-one, THF; (b) TsOH, CH_2Cl_2; (c) $LiAlH_4$, THF; (d) $(CH_3)_3O^+BF_4^-$, CH_2Cl_2.

Crystals of **2** suitable for X-ray crystallographic structure determination were grown by cooling a saturated toluene solution. The solid-state structure of **2** is depicted by the KANVAS[10] drawing in Figure 1 and the representative bond lengths and angles from one of the trimer subunits are given in Table 1. The ring-internal bond distances and angles presented for the zwitterion in Table 1 do not differ by more than 0.7 pm and 0.5°, respectively, from the other two crystallographically unique molecules.

The X-ray structure of **2** reveals that the asymmetric unit contains three molecules.[11] The three unique molecules form a trimeric unit in the packing of the unit cell. This trimer appears to be assembled by ionic interactions between the acidic hydrogen in the C^2 position of the imidazolium cation and the cyclopentadienyl ring. The hydrogen center is coordinated in a η^5-fashion to the cyclopentadienyl ring of another zwitterion. This cyclopentadienide–imidazole orientation is similar to previously reported carbene–lithium complexes.[12] This arrangement is in accord with Streitwieser's modeling studies[13] that indicate that the central C–H bond of an imidazolium cation in an imidazolium–cyclopentadienide ion-pair is directed toward the cyclopentadienyl ring rather than interacting through π–π stacking. For the zwitterion the average H^2–$Cp^{(centroid)}$ distance is 224 pm between trimer partners (assuming a normalized C–H distance of 107 pm). The average C–H distance to

Table 1. Selected bond lengths (pm) and angles (deg) in **2**

Property	2	Property	2
$r(C^2–H)$	95.0 (20)	θ ($N^1–C^2–N^3$)	110.37 (19)
$r(C^2–N^{1(3)})$	133.6 (3)	θ ($C^2–N^{1(3)}–C^{6a(3a)}$)	108.53 (19)
	134.0 (3)		108.11 (18)
$r(N^{1(3)}–C^{6a(3a)})$	139.6 (3)	θ ($N^{1(3)}–C^{6a(3a)}–C^{3a(6a)}$)	106.52 (19)
	140.3 (3)		106.45 (18)
$r(C^{6a}–C^{3a})$	140.3 (3)	θ ($C^{6(4)}–C^{6a(3a)}–C^{3a(6a)}$)	109.67 (18)
			109.95 (19)
$r(C^{3a(6a)}–C^{4(6)})$	140.7 (3)	θ ($C^{6a(3a)}–C^{6(4)}–C^5$)	104.04 (18)
	140.9 (3)		103.84 (19)
$r(C^{4(6)}–C^5)$	141.9 (3)	$\theta(C^4–C^5–C^6)$	112.50 (18)
	141.6 (3)		
$r(H^{C(2)}–C^{Cp})$	264.9		

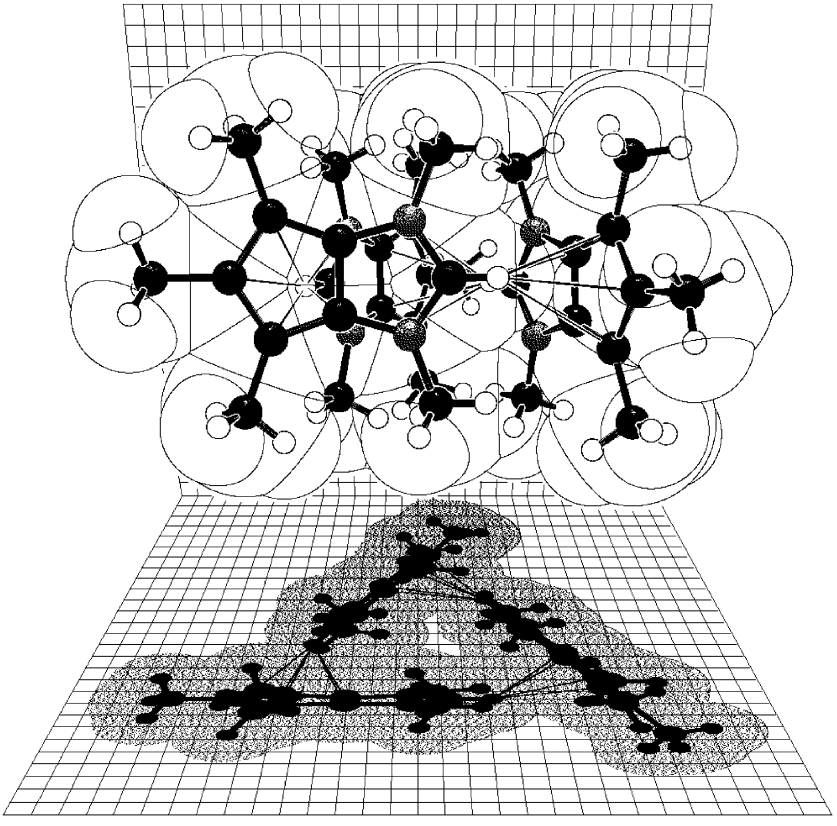

Figure 1. KANVAS[10] drawing of the zwitterion **2**.

the Cp ring atoms is 264.9 pm (varying between 254.5 and 278.1 pm for the hydrogens in their refined positions). Cowley and co-workers have reported ion-paired imidazolium cyclopentadienide, indenide, and fluorenide structures which parallel some of the features exhibited in the packing motif observed for **2**.[14] Absent in **2**, however, are any substantial π–π interactions. The peripheral methylation in **2** causes a half-molecule offset (along the ring fusion direction) between adjacent trimers that precludes extensive π–π interactions. The average angle between planes in the **2**-trimer is 60°. The trimeric nature of the crystal packing in **2** thus reinforces the energy minimum predicted by Streitweiser et al. for the imidazolium–cyclopentadienide ion-pairs (62.2°).

In acetonitrile, the zwitterion exhibits a $\lambda_{max} = 314$ nm (ε 12,530 M^{-1} cm^{-1}). This absorption is red-shifted from isoelectronic naphthalene (275 nm; ε 6000 M^{-1} cm^{-1}) as one might expect for this zwitterionic homolog. Preliminary molecular orbital calculations (DFT, DZVP2) are consistent with the smaller frontier orbital gap in **2** relative to naphthalene and also predict a greater extinction coefficient for **2**.

In conclusion, a synthetic route to the first cyclopentadienyl-fused imidazolium salt has been developed. In the solid-state, the zwitterion **2** arranges itself in a hydrogen-bridged head-to-tail trimer which optimizes ionic interactions. Unlike some previously observed imidazolium–cyclopentadienide salts, **2** does not show dominant π–π stacking interactions in the solid-state. The UV spectrum of **2** reflects the intimate electronic interaction between the cationic and anionic moieties in the molecule and thus supports the expectation that **2** will function as a mediator for electron transfer and 'communication' between metals coordinated to the cyclopentadienyl π-system and the latent carbene σ-lone pair.

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Supplementary data

Description of the preparation, NMR spectra and elemental analyses of **1**–**5**, and a complete description of the X-ray crystallographic determination on **2** including tables of fractional coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles are included as supplementary data. The supplementary data are available online with the paper at ScienceDirect. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.08.018.

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10. This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universitat Freiburg, Germany), which was modified by A. J. Arduengo, III to produce the back and shadowed planes. The planes bear a 50 pm grid and the lighting source is at infinity so that shadow size is meaningful.
11. Crystallographic data for **2** are included in Supplementary data and have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 275108. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].
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