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Synthesis of a new zwitterionic cyclopentadienyl-imidazolium compound and isolation of the 3,3′-(*trans*-3,5-cyclopentenyl)-di(1-*tert*-butylimidazolium)bromide intermediate

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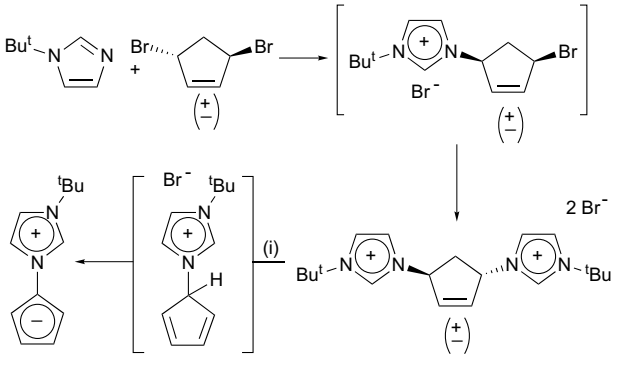
Abstract—The new zwitterionic compound 1-*tert*-butylimidazolium-cyclopentadienylide, shown to have a polar ground state and a non-polar fulvene-like excited state, has been synthesised and the intermediate 3,3′-(*trans*-3,5-cyclopentenyl)di(1-*tert*-butylimidazolium)bromide isolated and structurally characterised.

Zwitterionic cyclopentadienide compounds with positively charged groups, such as triphenylphosphonium[1] or pyridinium,[2] attached to the Cp ring are known. These compounds are prepared by an elimination reaction from an intermediate, assumed to be a 3,5-bis-substituted cyclopentenyl species[3] (although two geometric isomers are possible depending on the mechanism of substitution), followed by an in situ deprotonation. However, the cyclopentenyl intermediates used in the elimination step have not been isolated or characterised.

Our interests lie in the synthesis of novel substituted imidazolium compounds as potential ligand precursors for *N*-heterocyclic carbene metal complexes.[4] Herein we report the synthesis and isolation of the bis-substituted intermediate 3,3′-(*trans*-3,5-cyclopentenyl)di(1-*tert*-butylimidazolium)bromide **1** and the synthesis of the zwitterionic cyclopentadienyl-imidazolium compound 1-*tert*-butylimidazolium-cyclopentadienylide **2**.

The bis-substituted intermediate **1** was prepared by the addition of 2 equiv of 1-*tert*-butylimidazole to a chloroform solution of 3,5-*trans*-dibromocyclopentene and isolation of the resulting precipitate (Scheme 1). ^{1}H and $^{13}C\{^{1}H\}$ NMR data (COSY, HSQC, HMBC and NOESY experiments) showed the presence of only one species and were consistent with the formation of the 3,5-bis-substituted product **1**. Unfortunately, it was not possible to determine, by NMR spectroscopy, whether the imidazolium rings were attached to the cyclopentenyl ring in a *cis* or *trans* manner. However, the relative configuration of the imidazolium rings was readily determined by single crystal X-ray diffraction.



(**2**) (**1**)

Scheme 1. Reagents and conditions: (i) 2 equiv KO^{t}Bu in MeCN (60 °C).

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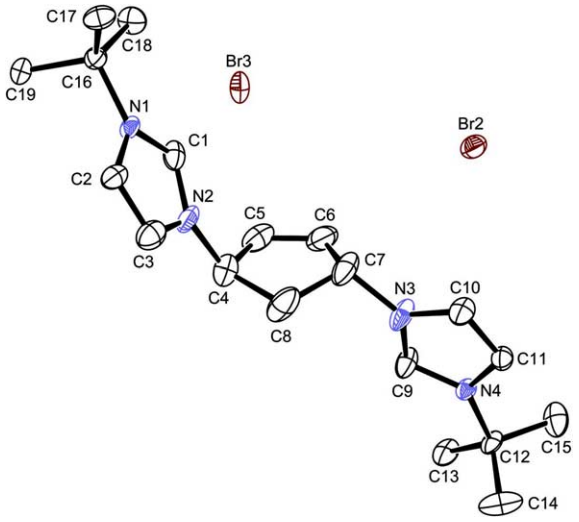

Figure 1. ORTEP diagram of the molecular structure of **1**. Thermal ellipsoids are set at 40%. Hydrogen atoms and the solvent of crystallisation are omitted for clarity. Selected distances (Å): C(1)–N(1) 1.336(5), C(2)–C(3) 1.348(6), N(2)–C(4) 1.492(6), N(3)–C(7) 1.478(5), N(3)–C(9) 1.330(5) and C(10)–C(11) 1.341(5).

Suitable crystals of **1** were grown from a concentrated methanol solution.[15] The molecular structure confirms the 3,5 regiochemistry of the compound and shows that the imidazolium rings are arranged *trans* to one another. Note compound **1** is racemic as it was prepared from a racemic mixture of 3,5-*trans*-dibromocyclopentene. The asymmetric unit contains two molecules of methanol and two molecules of **1**, as a pair of enantiomers. A view of one enantiomer is shown in Figure 1.

The bond lengths and angles of the imidazolium rings are similar to those described previously[4] and to other structurally characterised imidazolium salts.[5,6] The imidazolium rings are attached to sp^3 hybridised carbon atoms in the cyclopentene ring and point above and below the plane of this ring. The imidazolium rings are arranged in a staggered conformation about the C–N bond that joins them to the cyclopentene ring. Presumably each imidazolium ring is orientated to minimise the eclipsing interactions with the cyclopentene ring and any close axial hydrogens. The bond lengths in the cyclopentene ring are unexceptional with atoms in this ring forming a puckered arrangement to reduce torsional strain a feature common in non-aromatic five-membered rings.[7]

Reaction of **1** with potassium *tert*-butoxide, and subsequent workup, resulted in elimination of *tert*-butylimidazole and deprotonation to afford the zwitterionic compound 1-*tert*-butylimidazolium-cyclopentadienylide **2** as an air and water sensitive pale red solid (Scheme 1). The ^1H and $^{13}C\{^1H\}$ NMR data showed the presence of only one species and were consistent with the formation of the zwitterionic cyclopentadienyl-imidazolium compound of **2**. MS (ES+ in MeCN) confirmed the presence of the zwitterion **2** with the observation of the parent ion (*m/z* 189). Interestingly, no *N*-heterocyclic carbene products, resulting from competing deprotonation of the imidazolium ring, were observed.

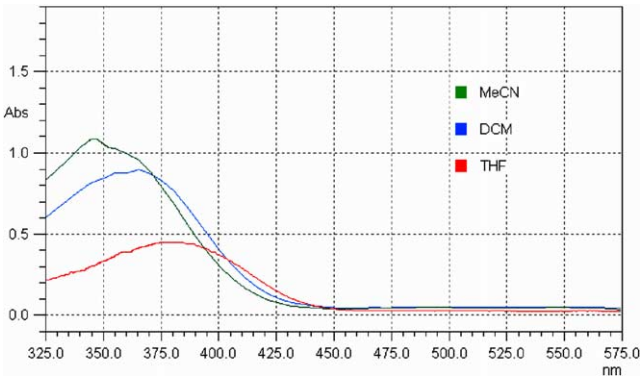

Figure 2. UV–vis spectra of **2** in various solvents showing the solvatochromic shift.

The electronic structure of the zwitterion **2**, containing two oppositely charged delocalised systems connected by a single bond, was probed by UV–vis spectroscopy (Fig. 2). The spectrum shows a single absorption peak near 350 nm (in MeCN), which was dependent on the solvent, with the absorption maximum shifting to longer wavelengths with decreasing solvent polarity. In the solvents used (MeCN, dichloromethane and THF with $E_T(30)$ values of 45.6, 40.7 and 37.4 kcal/mol, respectively) the magnitude of this hypsochromic shift was 35 nm. The magnitude of the extinction coefficient ($\log\varepsilon \sim 3.7$) suggests that the absorption is probably due to a $\pi \rightarrow \pi^*$ transition between the electron donating cyclopentadienide group and the accepting imidazolium ring. The solvatochromic shift and its direction[8] suggest a dipolar ground state structure, as it is stabilised by polar solvents, with the structure probably near to that drawn in Scheme 1. Whereas the excited state is more likely to be less polar and more fulvene like in character as it is not greatly affected by the nature of the solvent.

Theoretical calculations on **2** (Gaussian 98, B3LYP 6-31(G))[9–11] were consistent with the expected zwitterionic ground state structure with a torsional angle around the interannular bond of ca. 15° and with opposite charges localised in separate parts of the molecule. The HOMO was derived mainly from the degenerate cyclopentadienide HOMOs and the LUMO is mainly imidazolium

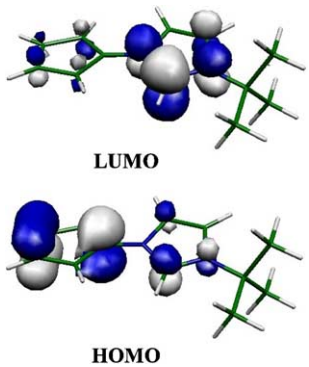

Figure 3. Frontier orbitals of the zwitterion **2** calculated using the B3LYP method and the 6-31G(d) basis set in the Gaussian 98 suite of programs.

based and derives from the LUMO of the cyclopentadienide anion and the LUMO of an imidazolium cation (Fig. 3). The HOMO–LUMO gap was calculated to be 3.2 eV and, although based on gas phase calculations, is comparable to the energy of the electronic transitions observed in the UV–vis spectrum.

To conclude, we have prepared, to the best of our knowledge, the first example of an imidazolium ring attached directly to a free cyclopentadienyl ring forming a novel zwitterionic species **2** and isolated and structurally characterised 3,3′-(*trans*-3,5-cyclopentenyl)di(1-*tert*-butylimidazolium)bromide **1**, an intermediate in the reaction pathway. Electronic spectroscopy reveals that **1** has a dipolar ground state with a less polar fulvene-like excited sate.

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15. Crystallographic data were collected in an Enras-Nonius KappaCCD diffractometer using graphite monochromatised Mo-Kα radiation ($\lambda = 0.71073$). Intensity data were processed using the DENZO-SMN package.[12] The structure was solved by direct methods using the SIR92 program.[13] Full matrix least-squares refinement was carried out using the CRYSTALS program suite.[14] A Chebychev polynomial weighting scheme was applied. Crystal data for **1**. CH_3OH: $C_{20}H_{34}Br_2N_4O$, $M = 506.31$, $T = 150$ K, triclinic, P-1, $a = 12.3273(2)$ Å, $b = 13.9296(2)$ Å, $c = 14.9319(2)$ Å, $\alpha = 71.9665(6)°$, $\beta = 73.6931(6)°$, $\gamma = 89.3546(7)°$, $V = 2331.93(6)$ Å^3, $Z = 4$, $D_c = 1.442$ g cm^{-3}, 19,836 reflections measured, 10,672 unique reflections [$R_{int} = 0.047$]. F refinement, $R1$ ($wR2$) = 0.0490 (0.0544), for the 7854 unique data with $I > 3\sigma(I)$ and 487 parameters.
Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 238863. Data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
Preparation of 3,3′-(*trans*-3,5-cyclopentenyl)di(1-*tert*-butylimidazolium)bromide **1**: 3,5-*trans*-Dibromocyclopentene (8.49 g, 37.6 mmol) was dissolved in 250 mL of $CHCl_3$ in a 500 mL reaction vessel covered with aluminium foil. 1-*tert*-Butylimidazole (9.44 g, 76.0 mmol) was added under nitrogen and the solution immediately changed colour from grey to a light brown. The reaction mixture was stirred for 24 h at room temperature upon which a cream coloured precipitated formed. The remaining solution was filtered off and the resulting solid washed with Et_2O (3×50 mL) and with CH_2Cl_2 (2×20 mL) to afford **1** as a white solid (9.81 g, 55%).
^{1}H NMR (500 MHz,$(CD_3)_2SO$, 30 °C): δ 1.61 [s, 18H, C(CH_3)$_3$], 2.77 [t, $^3J_{HH} = 6.03$ Hz, 2H, Cp–CH_2], 6.06 [t, $^3J_{HH} = 6.03$ Hz, 2H, Cp–CH], 6.47 [s, 2H, Cp–C=CH], 7.91 [m, $^3J_{HH} = 2.13$ Hz, $^4J_{HH} = 1.77$ Hz, 2H, Imd–CH], 8.15 [m, $^4J_{HH} = 1.77$ Hz, $^3J_{HH} = 2.13$ Hz, 2H, Imd–CH], 9.43 [m, $^4J_{HH} = 1.77$ Hz, $^4J_{HH} = 1.77$ Hz, 2H, Imd–CH]. ^{13}C{^{1}H} NMR (125.7 MHz, $(CD_3)_2SO$, 30 °C): 28.87 [s, C(CH_3)$_3$], 38.43 [s, Cp–CH_2], 59.63 [s, C(CH_3)$_3$], 64.13 [s, Cp-CH], 120.69 [s, Imd–CH], 120.73 [s, Imd–CH], 133.82 [s, Imd–CH] and 135.20 [s, Cp–C=C]. MS (ES+) (MeOH): $m/z = 393$ [M$^+$−Br] (22%). Elemental analysis (%): Found (Calc.) C, 46.78 (48.12); H, 6.55 (6.38); N, 11.59 (11.81).
Preparation of 1-*tert*-butylimidazolium-cyclopentadienylide **2**: KO^{t}Bu (1.30 g, 11.6 mmol) was added, under nitrogen, to a suspension of **1** (2.50 g, 5.3 mmol) in 50 mL of MeCN. The reaction mixture was warmed to 60 °C under nitrogen and stirred for 4 days. The colour of the suspension gradually changed from brown to a deep red. After allowing the reaction to cool to room temperature, the red solution was filtered leaving a white solid. Removal of the volatiles under vacuum left a purple residue. The solid was washed with toluene (2×10 mL) and then extracted into THF (10×10 mL) and cooled to

−78 °C. Prolonged exposure of the compound to THF at room temperature sometimes resulted in decomposition to give a dark solution containing a black solid. The THF was removed under vacuum to afford **2** as a light pink solid (0.41 g, 41%).

^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ 1.60 [s, 9H, $C(CH_3)_3$], 5.60 [br m, 2H, Cp–C*H*], 5.85 [br m, 2H, Cp–C*H*], 7.39 [s, 1H, Imd–C*H*], 7.49 [s, 1H, Imd–C*H*] and 8.48 [s, 1H, Imd–C*H*]. $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_3CN, 25 °C): δ 29.78 [s, $C(CH_3)_3$], 59.53 [s, $C(CH_3)_3$], 96.74 [s, Cp–*C*H], 105.63 [s, Cp–*C*H], 117.08 [s, Cp–*C*–N], 119.55 [s, Imd–*C*H], 120.89 [s, Imd–*C*H] and 128.04 [s, Imd–*C*H]. MS (ES+) (CH_3CN): m/z = 189 [MH^+] (100%). Elemental analysis (%): Found (Calc.) C, 73.10 (76.55); H, 8.11 (8.57); N, 14.18 (14.88)%.