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Synthesis of a lithium–cyclopentadienide complex by addition of LiNTf$_2$ to a zwitterionic fulvalene†‡

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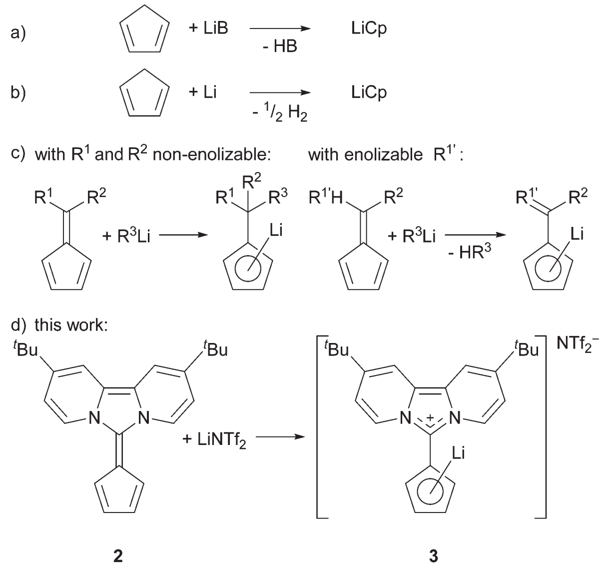
The synthesis of a η^5-coordinated LiCp complex by simple addition of a Li-salt in benzene is presented. A strongly zwitterionic fulvalene serves as the Cp-precursor. Evidence for the coordination of Li$^+$ was obtained by the characterisitic ^{7}Li NMR chemical shifts, variable temperature experiments in solution and by X-ray structure analysis in the solid state.

Lithium cyclopentadienide derivatives are important Cp-transfer reagents in the synthesis of metallocenes and half-sandwich complexes of transition metals.[1] Usually, their preparation follows one of the three major routes (Scheme 1)[2]: (a) deprotonation of cylcopentadiene with a strong base, (b) reduction of cyclopentadiene with lithium metal (dehydrogenation), or (c) nucleophilic carbolithiation at the exocyclic double bond of a fulvene or its enolisation (deprotonation), wherein the five-membered ring plays the role of the carbonyl group.[3] Usually, all these reactions are carried out in coordinating solvents, for example THF, diethylether or liquid NH$_3$.[2b]



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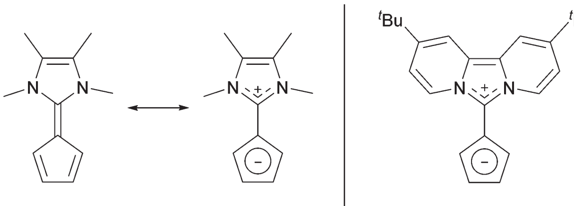
3

Scheme 1 Methods for the synthesis of LiCp compounds.

In 1972 Müller–Westerhoff showed that dipolar 6,6-bis(dimethylamino)fulvene can serve as a Cp-precursor upon reaction with FeCl$_2$,[4a] a reaction that takes advantage of the high stability of ferrocenes and the dipolar character of the aminofulvene.

Over the past few years, we reported zwitterionic fulvalenes **1** and **2** (Fig. 1, Scheme 1d) and their straightforward conversion to imidazolium-substituted metallocenes[4b] and half-sandwich complexes.[5] Together with their structural features, we concluded that they can be regarded as organic cyclopentadienide equivalents and are best depicted in their zwitterionic resonance forms **1′** and **2′**.[6] Thus, they are similar to phosphonium cyclopentadienylides,[7] for which the addition to transition metal complexes has been shown in the past,[8] and only one case of a neutral Li-adduct was reported for the solid state.[9] As fulvalenes provide a high versatility in metallocene chemistry, we set out to test their potentials and limitations in coordination chemistry. For this purpose, we wanted to probe whether Li$^+$ ions are able to form stable cyclopentadienide complexes by simple addition of lithium salts to fulvalene **2**



1

1'

2'

Fig. 1 Zwitterionic diazafulvalenes **1′** and **2′** are organic Cp analogues.

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† Dedicated to Professor Rolf Gleiter on the occasion of his 80th birthday.

‡ Electronic supplementary information (ESI) available: Synthetic procedure and analytical data of **3**. CCDC 1485216. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt03355e

(Scheme 1d) that bears the strongest ylidic character of all 6,6-diaminofulvenes or -fulvalenes.

At first, we reacted **2** and LiOTf in acetonitrile-d_3 as well as **2** and $LiNTf_2$ in THF-d_8, but a prolonged reaction time neither at room temperature nor at 60 °C caused any significant shift of the peaks in the ^1H NMR and ^7Li NMR spectra. To avoid any competing coordination of the solvent to the Li^+ cation, we chose benzene-d_6 as a solvent. Heating **2** and LiOTf at 60 °C in benzene-d_6 did not show any reaction, possibly due to the extremely low solubility of lithium triflate. However, keeping a mixture of **2** and $LiNTf_2$ for 16 h at room temperature leads to differences in the chemical shift of all but the *tert*-butyl signals of 0.05 to 0.25 ppm in the ^1H NMR spectrum. Heating the mixture up to 60 °C for 16 h increased these differences to 0.10–0.41 ppm (Fig. 2).

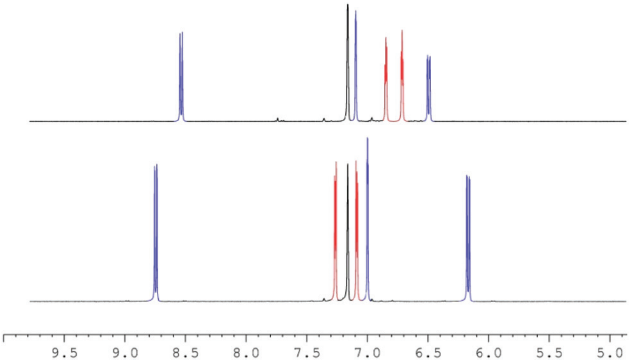


Fig. 2 Detail of the ^1H NMR spectrum (400.1 MHz) of **2** in C_6D_6 before (bottom) and after addition of $LiNTf_2$ and at 16 h at 60 °C (top) showing the imidazolium (blue), the Cp signals (red) as well as the solvent peak (C_6HD_5) (black).

The Cp–H signals are shifted upfield by 0.4 ppm, while the signals of the dipyridoimidazolinylidene moiety are shifted partly both upfield and downfield. These shifts indicate the formation of the coordination complex **3** rather than a mere change in the polarity of the solution upon addition of $LiNTf_2$. The ^7Li NMR spectrum of **3** shows a singlet at −5.6 ppm in toluene-d_8 as well as in benzene-d_6. In both cases, no signal was detected at the beginning of the reaction due to the poor solubility of $LiNTf_2$ in both solvents. This chemical shift is characteristic of a contact ion pair (−5 to −8.5 ppm)[10] in which the Li resides above the centre of an aromatic ring, and has also been observed for Cp-substituted Li-phosphoniumylides recently.[11] In contrast, solvent separated ion pairs show the Li signal typically between 1 and −1 ppm.[10] To gain more insight into the bonding situation in solution, we carried out variable temperature NMR experiments. Cooling down the sample in 10 °C steps reveals a significant broadening of the ^1H NMR signals at −50 °C down to −80 °C (Fig. 3, left). Below −70 °C an additional broad signal set appears. Due to the different shapes of the *t*-Bu signals, a hindered rotation about the exocyclic C–C bond that leads to two non-equivalent sides of the dipyrido moiety cannot explain this result. For comparison, we also cooled a sample of fulvalene **2** in toluene-d_8 to −80 °C and did not observe any significant broadening of the signals. A ^7Li NMR experiment shows not only the broadening of the Li

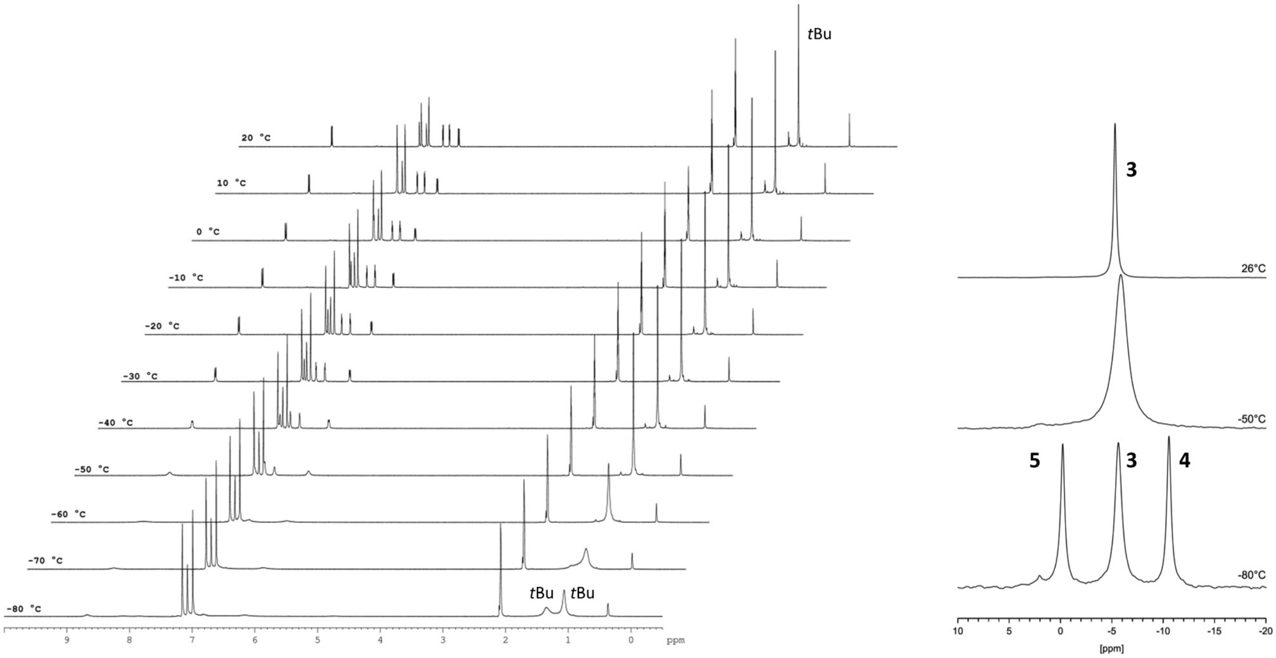
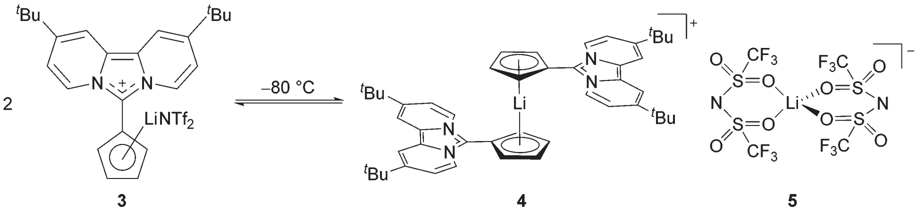


Fig. 3 VT NMR experiments of **3** in toluene-d_8. In the ^1H NMR spectrum (400.1 MHz) (left) an additional (broader) signal set indicating the presence of a second species at −80 °C is observed. In the ^7Li NMR spectrum (194.4 MHz) two new peaks in a 1 : 1 ratio at −0.5 ppm and −11 ppm are observed in addition to the signal at −5.8 ppm at −80 °C. The respective lithium atoms exchange at this temperature as revealed by an EXSY experiment (see the ESI‡).



Scheme 2 Fast equilibrium between the LiCp complex **3** and a solvent separated salt that consists of monocationic lithiocene **4** and lithiate **5** at –80 °C.

signal at –50 °C but also the formation of two additional peaks in a 1 : 1 ratio at –0.5 and –11 ppm at –80 °C (Fig. 3, right). This behavior was reported in the literature before and is diagnostic for the formation of a lithiocene species (–10 to –12 ppm) and a solvent separated Li-cation.[12] By applying these results to our case, we conclude that a mono-cationic lithiocene **4** and the negative counterion **5**[13] that consists of a lithium cation coordinated by two NTf_2^- ligands are formed (Scheme 2). Moreover, an EXSY experiment at –80 °C reveals lithium exchange of all three species (see the ESI‡).

By slow diffusion of dichloromethane into a solution of **3** in C_6D_6 at room temperature, we obtained single crystals suitable for X-ray diffraction analysis.

The molecular structure (Fig. 4) clearly shows a η^5-coordination between the Li^+ cation and the cyclopentadienide ring. The Li–$Cp_{Centroid}$ distance of 2.057 Å is in complete agreement with those of other LiCp complexes (1.910 Å to 2.086 Å).[14] The Li–carbon distances range from 2.354(4) Å to 2.422(4) Å, which is a typical range for η^5-coordinated $LiCpL_n$ compounds.[14]

The remaining coordination sphere of the Li-cation is occupied by three oxygen atoms of the two bridging bis(trifluoromethanesulfonyl)imide anions with Li–O distances between 2.033(4) Å and 2.057(4) Å. Complex **3** crystallises as a dimeric variation of the "donor ligand stabilised neutral monomer" motif of alkali metal cyclopentadienides.[2] Following the nomenclature established for $LiNTf_2$ crystalline solvates, complex **3** shows an aggregate coordination (AGG) in the transoid form (C_2) regarding the position of the CF_3 groups relative to the S–N–S plane.[15] As three oxygen atoms are coordinated to two Li^+ cations, the so called AGG-Ib-C_2 coordination mode is realised in the solid state of complex **3**.[15]

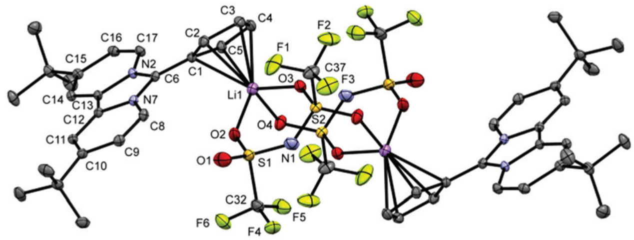


Fig. 4 X-ray crystal structure of complex **3** with anisotropic atomic displacement parameters at the 50% probability level. Hydrogen atoms and three benzene molecules (1.5 per asymmetric unit) are omitted for clarity.

Although the coordination of the lithium cation to the Cp ring could be demonstrated clearly for **3** both in solution and in solid states, this bond formed is rather weak. This can be deduced from the fact that during monitoring the course of the reaction of **2** and $LiNTf_2$ only one species is observed in the ^1H NMR spectra, which implies a fast equilibrium between the free fulvalene and the coordinated species. This leads to the continuous shifting of the signals until the final values for compound **3** (fulvalene : Li = 1 : 1) are reached. Using two equivalents of $Li(NTf)_2$ does not lead to further shifting of the signals. Another argument is the fast Li^+ exchange at –80 °C revealed by the EXSY spectrum. Furthermore, already one equivalent of added THF leads to a recognisable shift of the signals into the direction of the free fulvalene **2** in the ^1H NMR spectrum. With 8 equivalents of THF, the signals of pure **2** are almost obtained back. This is also corroborated by the ESI^+ mass spectrum of complex **3** in which only the signal of the decoordinated, protonated fulvalene **2** $[M + H]^+$ is detected.

In conclusion, we have presented a simple method for the preparation of a η^5-cyclopentadienide lithium complex by addition of $LiNTf_2$ to a highly zwitterionic fulvalene. While a dimeric structure forms in the solid state, the complex undergoes fast exchange in solution at room temperature. Evidence for an equilibrium between **3** and a monocationic lithiocene species **4** together with the $[Li(NTf_2)_2]^-$ counter ion (**5**) at –80 °C was obtained by the characteristic ^7Li NMR chemical shifts. An EXSY experiment at –80 °C revealed Li exchange between all of these three species.

We will now put our efforts in applying this method to other group 1 and group 2 metal salts, and also on probing the utility of **3** as a Cp-transfer reagent in non-polar solvents.

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