Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthesis of a lithium-cyclopentadienide complex by addition of $LiNTf_2$ to a zwitterionic fulvalene

Dominic Schmid,[a] Alexander Seyboldt[a], Klaus Eichele[a] and Doris Kunz*[, a]

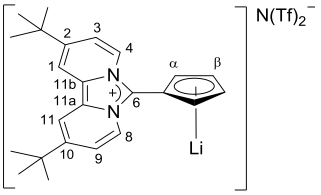
Institut für Anorganische Chemie, Eberhard Karls Universität Tübingen,
Auf der Morgenstelle 18, 72076 Tübingen, Germany
E-Mail: Doris.Kunz@uni-tuebingen.de

Contents

1. Experimental procedures and analytical data

General Procedures: Unless otherwise noted, all reactions were carried out under an argon atmosphere in dried and degassed solvents using Schlenk techniques. NMR solvents were purchased from Euroisotop, dried according to literature procedures[1] and stored under argon atmosphere. All lithium salts used were obtained from commercial suppliers, dried in vacuum and used without further purification. Diazafulvalene **2** was synthesized according to the literature procedure.[2] ^{1}H, ^{7}Li and ^{13}C NMR spectra were recorded using a Bruker DRX 250, AVII+400 or 500 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm and calibrated to TMS on the basis of the (residual) solvent signal as an internal standard (7.16 ppm, C_6D_6; 2.08 ppm, toluene-D_8). ^{7}Li NMR chemical shifts are reported in ppm and calibrated to LiCl as external standard. Assignment of peaks was made using 2D NMR correlation spectra.

Synthesis of lithium complex 3:



3

5.5 mg (16 µmol) **2** and 4.6 mg (16 µmol) Lithiumbis(trifluoromethanesulfonyl)imide are put in a *J.Young*®-NMR-tube, dissolved in 0.5 mL benzene-d_6 and heated to 60 °C for 16 h.

For the VT NMR experiments, the same procedure was used but with toluene-d_8 instead of benzene-d_6.

^{1}H NMR (benzene-d_6, 400.13 MHz): δ = 1.05 (s, 18 H, *t*-Bu), 6.49 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.9 Hz, 2 H, H-3/9), 6.72 (m, N = $|^3J_{HH} + {}^4J_{HH}|$ = 5.6 Hz, 2 H, Cp-β), 6.85 (m, N = $|^3J_{HH} + {}^4J_{HH}|$ = 5.6 Hz, 2 H, Cp-α), 7.09 (br s, 2 H, H-1/11), 8.53 (br d, $^3J_{HH}$ = 7.7 Hz, 2 H, H-4/8).

^{1}H NMR (toluene-d_8, 400.13 MHz): δ = 1.07 (s, 18 H, *t*-Bu), 6.45 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.9 Hz, 2 H, H-3/9), 6.67 (m, N = $|^3J_{HH} + {}^4J_{HH}|$ = 5.6 Hz, 2 H, Cp-β), 6.77 (m, N = $|^3J_{HH} + {}^4J_{HH}|$ = 5.6 Hz, 2 H, Cp-α), 7.11 (dd, $^4J_{HH}$ = 1.8 Hz, $^5J_{HH}$ = 0.9 Hz, 2 H, H-1/11), 8.53 (dd, $^3J_{HH}$ = 7.7 Hz, $^5J_{HH}$ = 0.8 Hz, 2 H, H-4/8).

^{13}C{^{1}H} NMR (toluene-d_8, 62.90 MHz): δ = 29.8 ($C(\underline{C}H_3)_3$), 34.6 ($\underline{C}(CH_3)_3$), 96.6 (C-12), 107.9 (C-14/15), 110.8 (C-1/11), 111.9 (C-13/16), 117.1 (C-3/9), 118.7 (C-11a/11b), 122.8 (C-4/8), 125.6 (C-6), 143.1 (C-2/10). A signal for the NTf_2^- anion was not detected.

^{7}Li NMR (toluene-d_8, 97.21 MHz): δ = –5.6 (s).

^{19}F{^{1}H} NMR (toluene-d_8, 376.48 MHz): δ = –84.3 (s).

The VT experiments started at 20 °C and proceeded in steps of 10 °C down to -80 °C. At around -70 °C a second signal for the *tert*-butyl groups of the dipyridoimidazolinylidene moiety begins to appear and is clearly visible at –80 °C. The other signals are very broad.

The ^{7}Li VT spectrum (194.4 MHz) was measured at 26, –50 and –80 °C. In addition, an EXSY experiment was carried out at –80 °C.

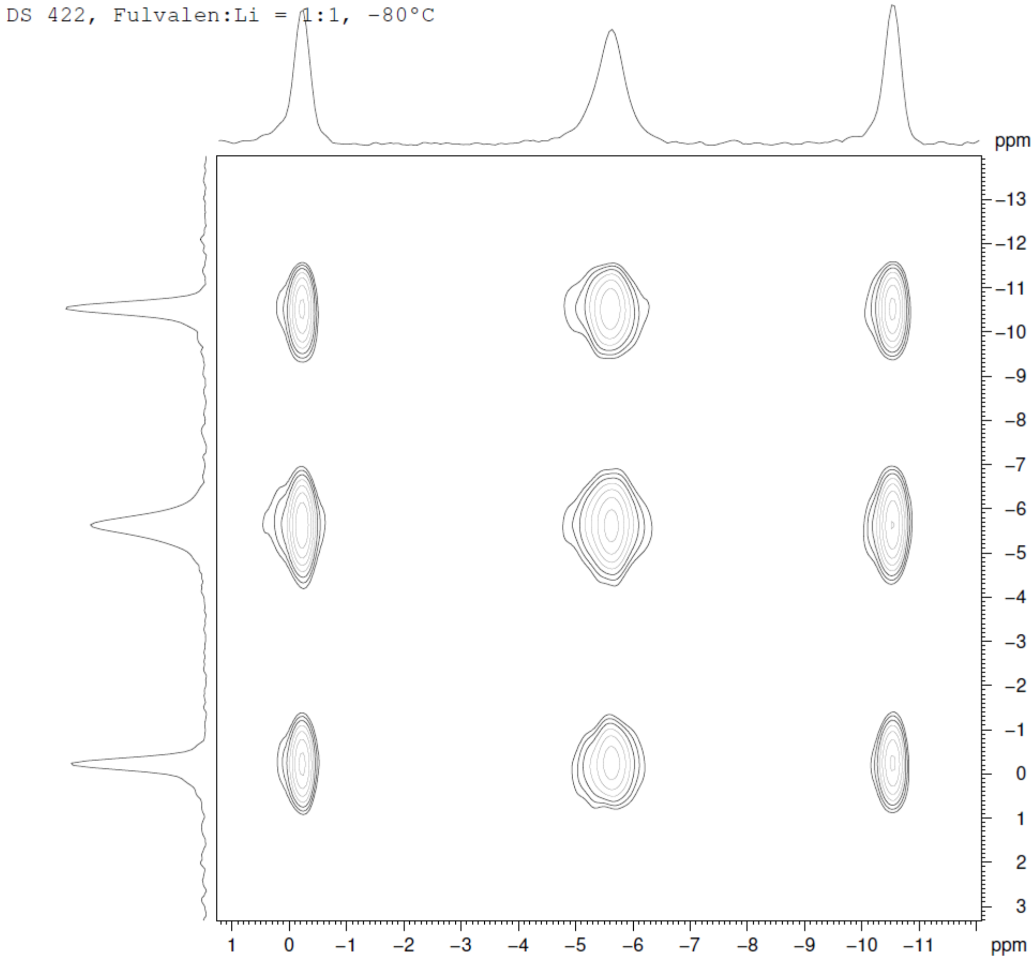


Figure 1 ^{7}Li EXSY NMR spectrum (194.4 MHz) of complex **3** recorded at –80 °C in toluene-d$_8$.

Anal. calcd for $C_{26}H_{28}F_6LiN_3O_4S_2$*0.5 C_7H_8: C, 52.29; H, 4.76; N, 6.20. Found: C, 51.88; H, 5.32; N, 5.65. The retention of aromatic lattice solvent was presumed by the fact that 1.5 eq of benzene are cocrystallised in the single crystal analysed by X-ray structure analysis of another sample.

Titration of complex 3 in C_6D_6 with tetrahydrofuran

NMR Experiment: Complex **3** was generated according to the given procedure from fulvalene **2** (12.0 mg, 34.8 µmol) and lithium bis(trifluoromethansulfonyl)imid (10.0 mg, 34.8 µmol) in 0.5 mL benzene-d_6. After confirming its formation by ^1H NMR spectroscopy, defined equivalents of THF (2.8 µL, 34 µmol) are added stepwise. The change of the chemical shifts is monitored by ^1H NMR spectroscopy.

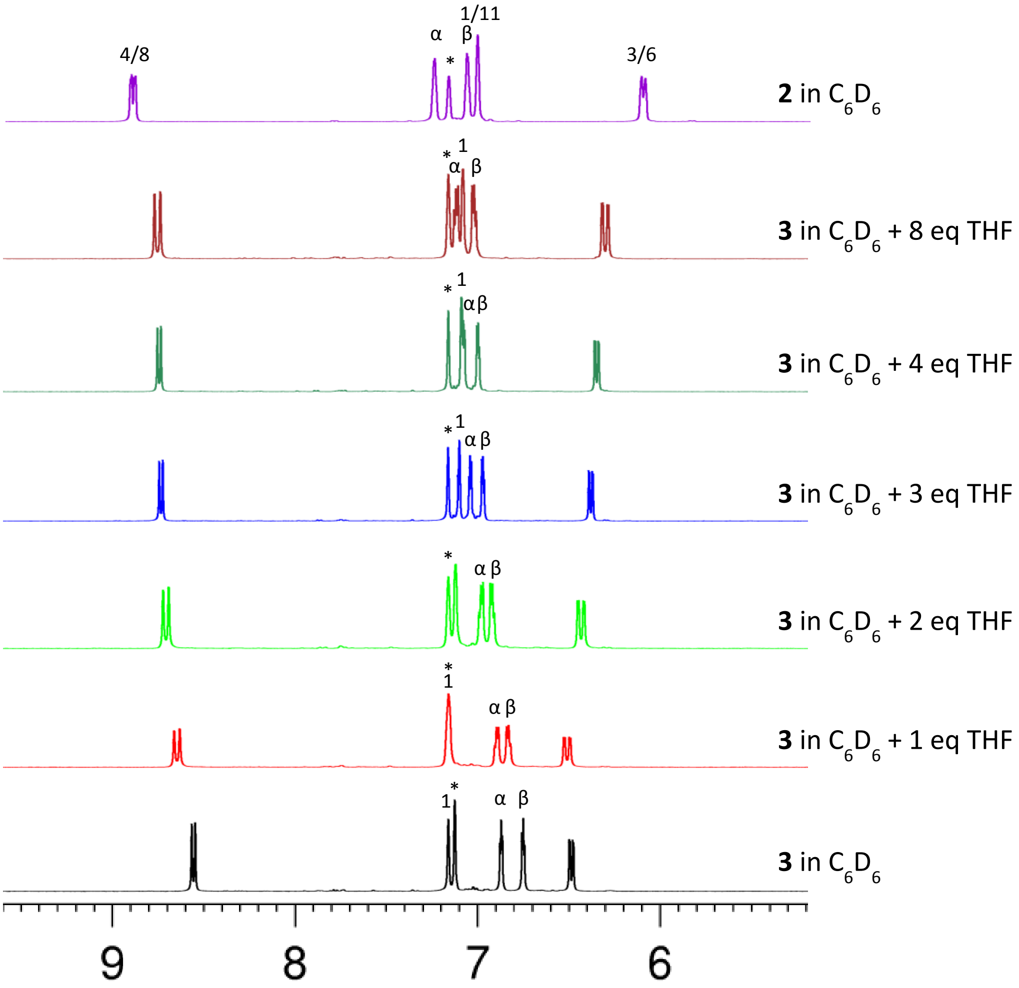
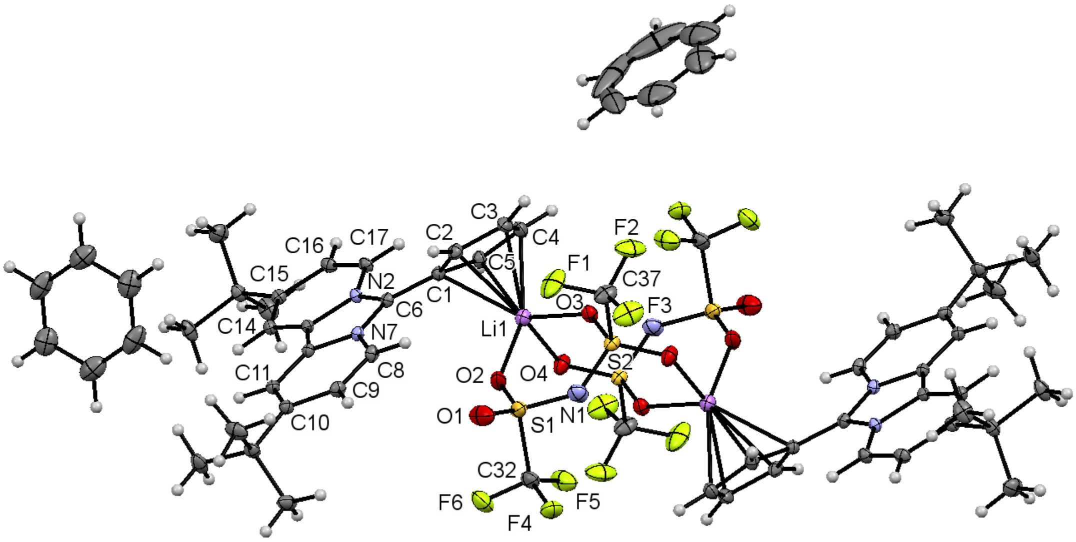


Figure 2 Detail of the ^1H NMR spectra of the titration experiment: addition of defined equivalents of THF to a solution of complex **3** in C_6D_6 (bottom) leads to a continuous shift of the signals in the direction of the free fulvalene **2** (top).

2. Crystallographic details for compound 3

Crystallographic Data collection was carried out on a Bruker APEX Duo CCD with an Incoatec IμS Microsource with a Quazar MX mirror using Mo K_α radiation (λ = 0.71073 Å) and a graphite monochromator. Corrections for absorption effects were applied using SADABS.[3] All structures were solved by direct methods using SHELXS[4] and refined using SHELXL.[5] Further details of the refinement and crystallographic data are given in the respective CIF-file. CCDC 1485216 contains the supplementary crystallographic data for **3.** These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



One molecule of benzene is missing in this view of the dimeric nature of **3** in the solid state. Anisotropic atomic displacement parameters are drawn at the 50 % probability level.

3. References

[1] W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals,* Elsevier, Oxford, 2003**.**

[2] D. Schmid, A. Seyboldt and D. Kunz, *Z. Naturforsch.* 2014, **69b**, 580–588.

[3] a) G. M. Sheldrick, University of Göttingen (Göttingen, Deutschland), 2008. b) G. M. Sheldrick, Bruker Analytical X-Ray Division (Madison), 2001.

[4] G. M. Sheldrick, University of Göttingen (Göttingen, Germany), 1997.

[5] a) G. M. Sheldrick, *Acta Crystallogr., Sect. A* 1990, **46**, 467–473. b) C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.* 2011, **44**, 1281–1284. c) G. M. Sheldrick, Bruker Analytical X-Ray Division (Madison), 2001.