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Supporting Information

Highly Ylidic Imidazolin-Based Fulvenes as Suitable Precursors for the Synthesis of Imidazolium Substituted Metallocenes

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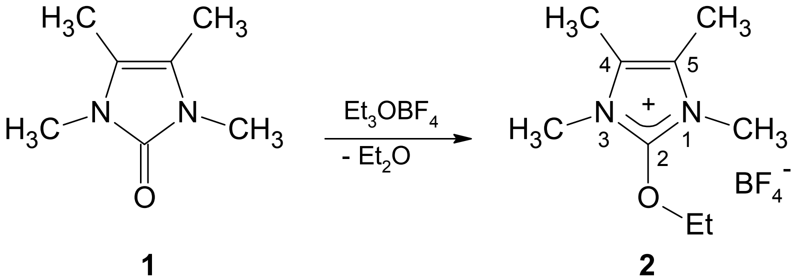
Experimental

General Comments: All manipulations were performed under a pure dry Ar or N_2 atmosphere unless otherwise noted. All reagents were obtained from commercial sources and used as received. All solvents were degassed and dried according to literature[1]. Silica gel was degassed and stored under nitrogen. 1,3,4,5-tetramethylimidazolin-2-on (**1**)[2] and *tert*-Butyl-cyclopentadienyllithium were prepared according to a literature procedure.[3]

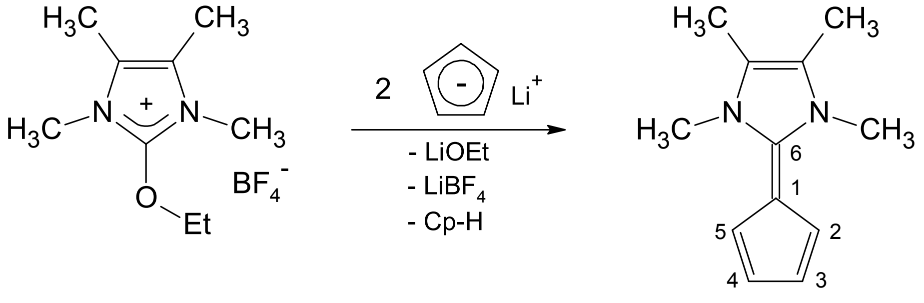
*Synthesis of 2-ethoxy-1,3,4,5-tetramethylimidazoliumtetrafluoroborate (**2**)*:



1 **2**

5.20 g (37.2 mmol) 1,3,4,5-tetramethylimidazol-2-on and 8.60 g (45.3 mmol) triethyl-oxoniumtetrafluoroborate were dissolved in 40 mL of dichloromethane. The colour changes from yellow to red within 10 min, after 2 h the solvent is evaporated in vacuo and impurities extracted with hot toluene to yield **2** (8.70 g, 92 %) as light pink crystals.[12] Mp 118.0 °C. ^{1}H NMR (250.13 MHz, CD_2Cl_2): δ = 1.53 (t, $^3J_{HH}$ = 7.1 Hz, 3H, H-12), 2.17 (s, 6H, H-8/9), 3.54 (s, 6H, H-6/7), 4.50 (q, $^3J_{HH}$ = 7.1 Hz, 2H, H-11). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ = 8.6 (C8/9), 15.7 (C12), 30.8 (C6/7), 76.3 (C11), 122.5 (C4/5), 146.6 (C2). MS (ESI$^+$): m/z (%) = 169.1 $[M-BF_4]^+$ (100.0), 140.1 $[M-BF_4-Et]^+$. Elemental analysis (%) calcd for $C_9H_{17}N_2OBF_4$: C 42.22, H 6.69, N 10.94; found: C 42.24, H 6.80, N 10.91.

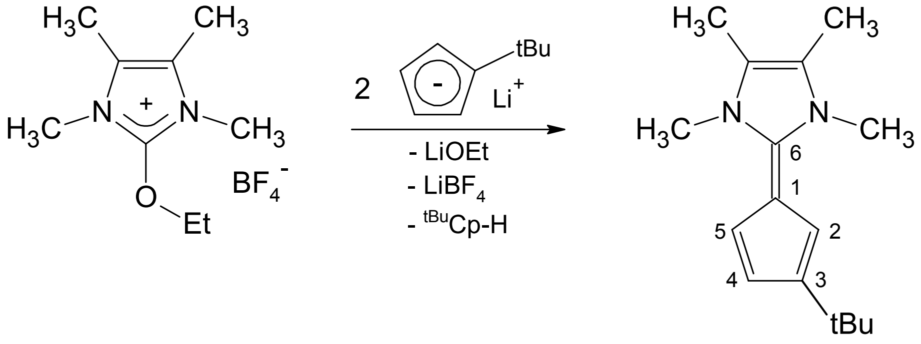
Synthesis of 2-(cyclopenta-2,4-dien-1-ylidene)-1,3,4,5-tetramethyl-2,3-dihydro-1H-imidazol (**3a**):



2 **3a**

To a suspension of 512 mg (2.00 mmol) of **2** in 6 mL of tetrahydrofuran is added a solution of 289 mg (4.00 mmol) cyclopentadienyllithium in 18 mL of tetrahydrofuran at rt and the colour changes from red to orange within a few min. After 90 min 6 mL of dichloromethane are added to quench unreacted cyclopentadienyllithium. The white solid is filtered off and extracted with tetrahydrofuran. The product is precipitated with pentane to give **3a** (253 mg 67 %) as a red solid. m.p. 148 °C (dec). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.18 (s, 6H, C-CH_3), 3.71 (s, 6H, N-CH_3), 6.04-6.06 (m, 2H, H2/5), 6.19-6.21 (m, 2H, H3/4). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 9.4 (C-CH_3), 33.8 (N-CH_3), 98.0 (C1), 110.4 (C2/5), 111.2 (C3/4), 122.1 (C8/9), 148.3 (C6). HR-MS (EI$^+$): for $C_{12}H_{16}N_2$: calcd: 188.1314; found: 188.1310. IR (KBr): $\tilde{\nu}$ = 2963 (w), 2922 (w), 1553 (vs), 1491 (w), 1339 (m), 1261(w), 1104 (m), 1053 (m), 800 (m), 712 cm^{-1} (m). UV/VIS (CH_2Cl_2): λ_1 = 254 nm (log ε = 2.71), λ_2 = 338 nm (log ε = 3.56).

*Synthesis of 2-(3-tert-butylcyclopenta-2,4-dien-1-ylidene)-1,3,4,5-tetramethyl-2,3-dihydro-1H-imidazol (**3b**)*:

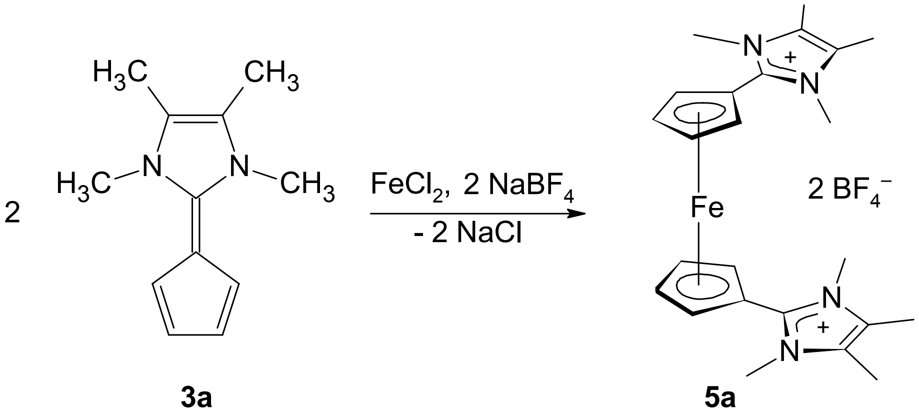


2 **3b**

384 mg (1.50 mmol) of the uronium salt **2** are suspended in 10 mL of tetrahydrofuran. A solution of 398 mg (3.10 mmol) (2.1 eq) *t*-Bu-CpLi in 6 mL of tetrahydrofuran is added dropwise within a period of ten minutes. The reaction mixture turns yellow to orange. After

48 h the solvent is evaporated in vacuo, the residue extracted with 15 mL of toluene dried in vacuo. The yellow residue is chromatographically purified with 6 mL tetrahydrofuran over neutral alumoxane. This yields 216 mg (59 %) of **3b** as pale yellow plates with a pearly shine. Mp 110 °C (dec). ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 1.23 (s, 9H, C(CH$_3$)$_3$), 2.15 (s, 6H, C-CH$_3$), 3.64 (s, 6 H, N-CH$_3$), 5.89 - 5.94 (m, 2H, H-2, H-4), 5.99 - 6.02 (m, 1H, H-5). ^{1}H NMR (250 MHz, CD$_3$CN): δ = 1.24 (s, 9H, C(CH$_3$)$_3$), 2.15 (s, 6H, C-CH$_3$), 3.64 (s, 6H, N-CH$_3$), 5.90 (dd, $^3J_{HH}$ = 3.8 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, H-4, H-5), 5.98 (dd, $^4J_{HH}$ = 2.3 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, H-2), 6.02 (dd, $^3J_{HH}$ = 3.9 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, H-4. H-5). ^{13}C{^{1}H} NMR (100 MHz, THF-d$_8$): δ = 8.8 (C-CH$_3$), 32.6 (*C*(CH$_3$)$_3$), 33.4 (C(*C*H$_3$)$_3$), 33.6 (N-CH$_3$), 96.1 (C1), 105.9 (C2), 109.8 (C4), 111.0 (C5), 121.5 (C8/9), 138.4 (C3), 149.8 (C6). IR (KBr): $\tilde{\nu}$ = 2954 (s), 1556 (vs), 1482 (w), 1433 (w), 1401 (w), 1335 (m), 1249 (w), 1073 (w), 906 (w), 783 (w), 668 cm^{-1} (w). HR-MS (EI$^+$): for $C_{16}H_{24}N_2$: calcd: 244.1939; found: 244.1937

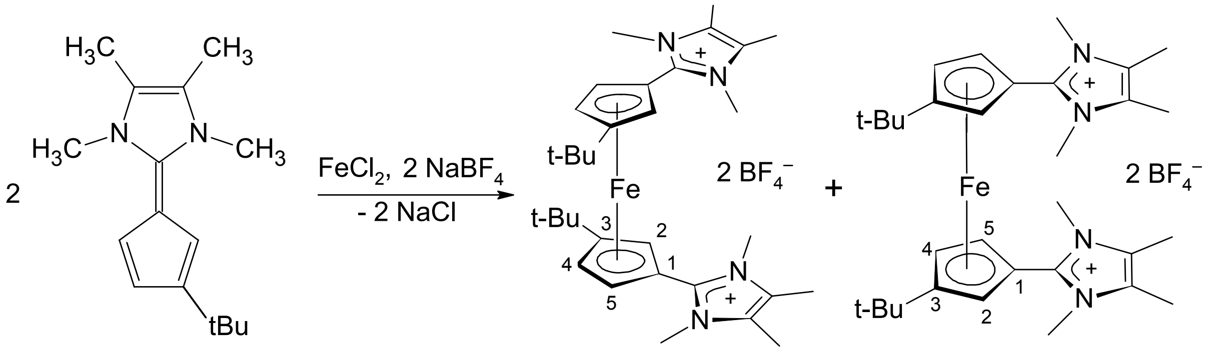
*Synthesis of 1,1-bis(1,3,4,5-tetramethylimidazolium-2-yl)ferrocene bis(tetrafluoroborate) (**5a**)*:



3a **5a**

9.8 mg (50 µmol) of fulvene **3a**, 3.5 mg (27 µmol) FeCl$_2$ and 5.8 mg (53 µmol) NaBF$_4$ are suspended in 2 mL of tetrahydrofuran and stirred for 12 h. The solvent is decanted, the residue dried in vacuo and dissolved in 0.5 mL of acetone-d$_6$. The MS (ESI$^+$) spectrum shows the product [M-BF$_4$]$^+$ signal and no formation of the complex **5a** with a [FeCl$_4$]$^{2-}$ counterion. ^{1}H NMR (300 MHz, aceton-d$_6$): δ = 2.30 (s, 12H,C-CH$_3$), 3.96 (s, 12H, N-CH$_3$), 5.03 (s, 4H, Cp-H), 5.21 (s, 4H, Cp-H). HR-MS (ESI$^+$): for $C_{24}H_{32}N_4BF_4Fe$ [M-BF$_4$+H]$^+$: calcd: 519.2048; found: 519.2017.

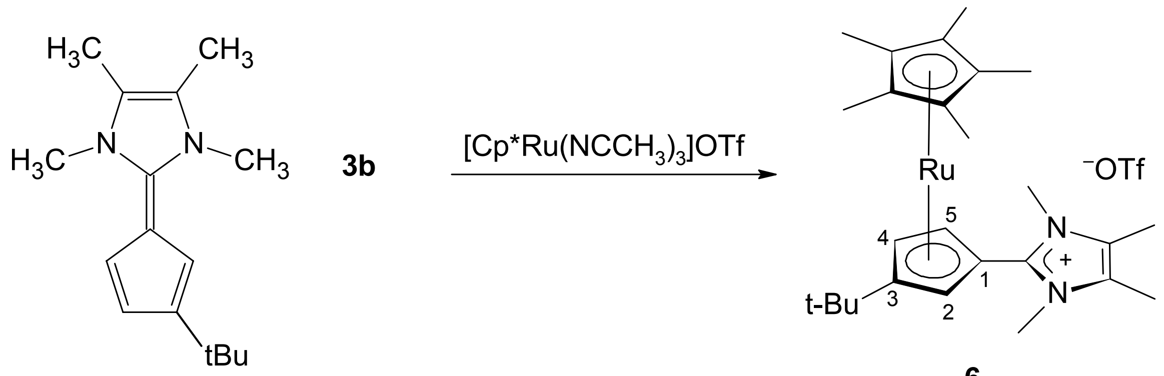
*Synthesis of 3,3'-Di-tert-butyl-1,1'-bis(1,3,4,5-tetramethylimidazolium-2-yl)ferrocene bis(tetrafluoroborate) (**5b**)*:



3b **rac-5b** **meso-5b**

To a solution of 30.0 mg (123 µmol) of fulvene **3b** in 3 mL of THF are added 7.8 mg (61 µmol) $FeCl_2$ as a solid. The reaction mixture turns red, 15.2 mg (138 µmol) sodiumtetrafluoroborate are added and stirred for 24 h. The solvent is removed in vacuo, and the residue washed with toluene and extracted with 0.5 mL of [D$_6$]acetone. ^1H NMR (250 MHz, [D$_6$]acetone, ratio 2:1): major isomer: δ = 1.28 (s, 9H, $C(CH_3)_3$), 2.38 (s, 6H, C-CH_3), 4.03 (s, 6H, N-CH_3), 4.86, 5.25, 5.43 (each br s, each 1H, Cp-H), minor isomer: δ = 1.31 (s, 9H, $C(CH_3)_3$), 2.36 (s, 6H, C-CH_3), 4.01 (s, 6H, N-CH_3), 5.05, 5.09, 5.13 (each br s, each 1H, CpH). ^1H NMR (400 MHz, CD_3CN): major isomer: δ = 1.24 (s, 9H, $C(CH_3)_3$), 2.22 (s, 6H, C-CH_3), 3.73 (s, 6H, N-CH_3), 4.58, 4.86, 5.02 (each br s, each 1H, Cp-H), minor isomer: δ = 1.21 (s, 9H, $C(CH_3)_3$), 2.26 (s, 6H, C-CH_3), 3.71 (s, 6H, N-CH_3), 4.63, 4.68, 4.86 (each br s, each 1H, Cp-H); the signal at δ = 4.86 is covered by the signal of the major isomer. ^{13}C NMR (from HSQC, 100 MHz, [D$_6$]acetone): major isomer: δ = 9.0 (C-CH_3), 31.6 (C(CH$_3$)$_3$), 34.8 (N-CH_3), 69.3, 73.1, 73.4 (CpH); minor isomer: δ = 9.0 (C-CH_3), 31.6 (C(CH$_3$)$_3$), 34.8 (N-CH_3), 69.4, 72.5, 72.8 (CpH). HR-MS (ESI$^+$) $C_{32}H_{48}BF_4FeN_4$: m/z calcd: 631.32583, found: 631.32620 [M-BF$_4$]$^+$.

*Synthesis of 1',2',3',4',5'-pentamethyl-(3-tert-butyl-1-(1,3,4,5-tetramethylimidazolium-2-yl)-ruthenocene triflate (**6**)*:



3b

6

A solution of 10.8 mg (44.2 µmol) of fulvene **3b** in 0.3 mL THF-d_8 is combined with a solution of 22.9 mg (45.0 µmol) trisacetonitril(pentamethylcyclopentadienyl)ruthenium(II)-triflat in 0.2 mL of THF-d_8. The reaction mixture turnes brownish and is characterized by NMR after 48 h and by HR-MS.

^{1}H NMR (400 MHz, [D_8]THF): $\delta = 1.21$ (s, 9H, $C(CH_3)_3$), 1.84 (s, 15H, Cp*), 2.30 (s, 6H, C-CH_3), 3.87 (s, 6H, N-CH_3), 4.50, 4.81 (br s, 1H, H4, 5), 4.83 (s, 1H, H2). ^{1}H NMR (250 MHz, [D_8]toluene): $\delta = 1.19$ (s, 9H, $C(CH_3)_3$), 1.73 (s, 15H, Cp*), 2.02 (s, 6H, C-CH_3), 3.51 (s, 6H, N-CH_3), 4.16 (br s, 1H, H2, 4, 5), 4.60 (br s, 2H, H2, 4, 5). $^{13}C\{^1H\}$ NMR (100 MHz, [D_8]THF): $\delta = 8.8$ (C-CH_3), 11.8 (Cp*), 31.2 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 34.3 (N-CH_3), 71.8 (C1), 73.1 (C2), 74.0, 74.7 (C4, C5), 87.7 (Cp*), 110.1 (C3), 127.4 (C8/9), 143.5 (C6); chemical shift of C6 taken from HMBC experiment. HR-MS (ESI^+) for $C_{26}H_{39}N_2Ru$ [M-OTf]$^+$: calcd: 481.2157; found: 481.2158

References:

[1] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, Butterworth-Heinemann, Amsterdam, **2003**.

[2] J. Akester, J. Cui, G. Fraenkel, *J. Org. Chem.* **1997**, *62*, 431-434.

[3] R. A. Howie, G. P. McQuillan, *J. Organomet. Chem.* **1986**, *303*, 213-220.