Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

5-Methyl-2-thienylcalcium Iodide

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Metal-halogen exchange studies:

A) Spectroscopic investigation of the reaction of [$(Me_3SiCH_2)Ca(thp)_4I$] with 3-iodothiophene:

[$(Me_3SiCH_2)Ca(thp)_4I$] (120 mg, 0.24 mmol, 1.1 equiv.) were dissolved in 0.4 ml of [D_8]THF and cooled to –50 °C. To this solution 45 mg of 3-iodothiophene were added and the resulting solution was investigated by NMR spectroscopy. The following species have been identified: ICH_2SiMe_3 (typical product of calcium-iodine exchange reaction), 3-thienylcalcium iodide , 2-thienylcalcium iodide, 3-iodothiophene (starting material), thiophene (product of ether degradation reaction as well as of the metalation of starting 3-iodothiophene with 2- or 3-thienylcalcium iodides).

B) The diversity of the reaction of [$(Me_3SiCH_2)Ca(thp)_4I$] with 3-iodothiophene prompted us to immediately trap the initial product with chloro-trimethylsilane:

3-Iodothiophene (41.1 mg, 0.2 mmol, 1 equiv.) and 0.1 ml of $ClSiMe_3$ were dissolved in 1 ml of THF. The solution was cooled to -78 °C and then, 1 ml of a 0.242 M solution of [$(Me_3SiCH_2)Ca(thp)_4I$] (0.24 mmol, 1.2 eq) in THF was added. The reaction mixture was stirred for 30 min and then warmed to r.t. Then the reaction solution was quenched with water. The phases were separated and the aqueous phase (containing the calcium salts) was discarded. The organic layer was analyzed by GC/MS methods, yielding 3-(trimethylsilyl)-thiophene as the only product.

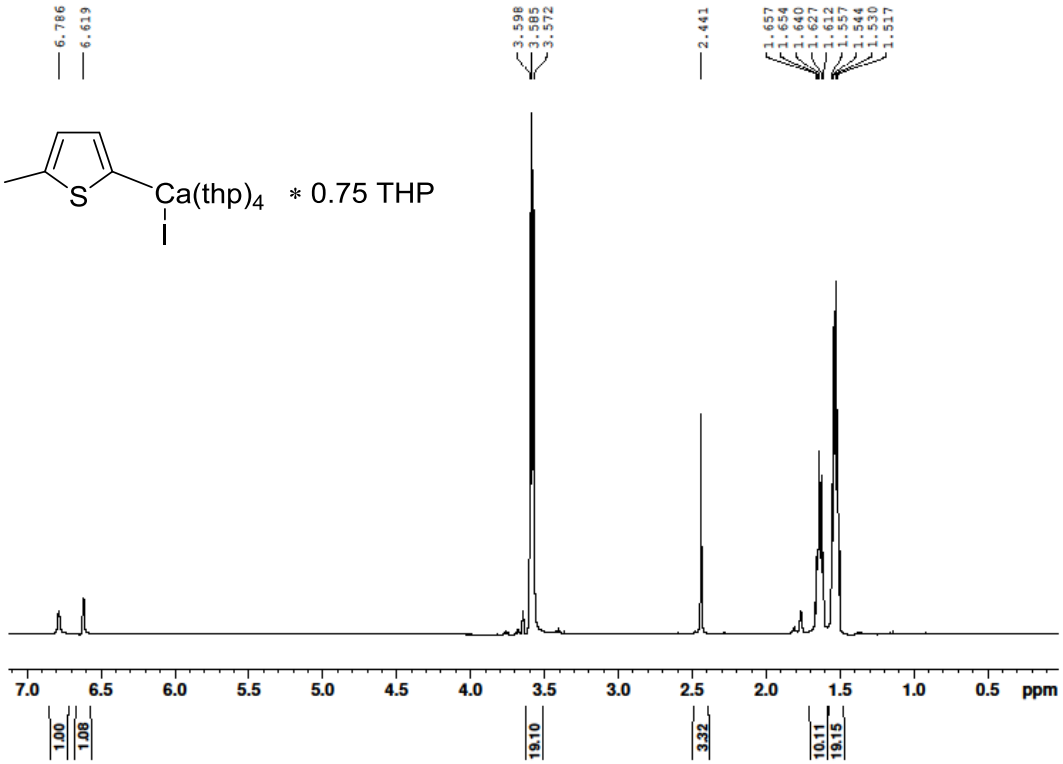

Figure S1: ^{1}H NMR spectrum ([D_8]THF, 400.13 MHz) of [5-MeThien-2-Ca(thp)$_4$I] (**2**).

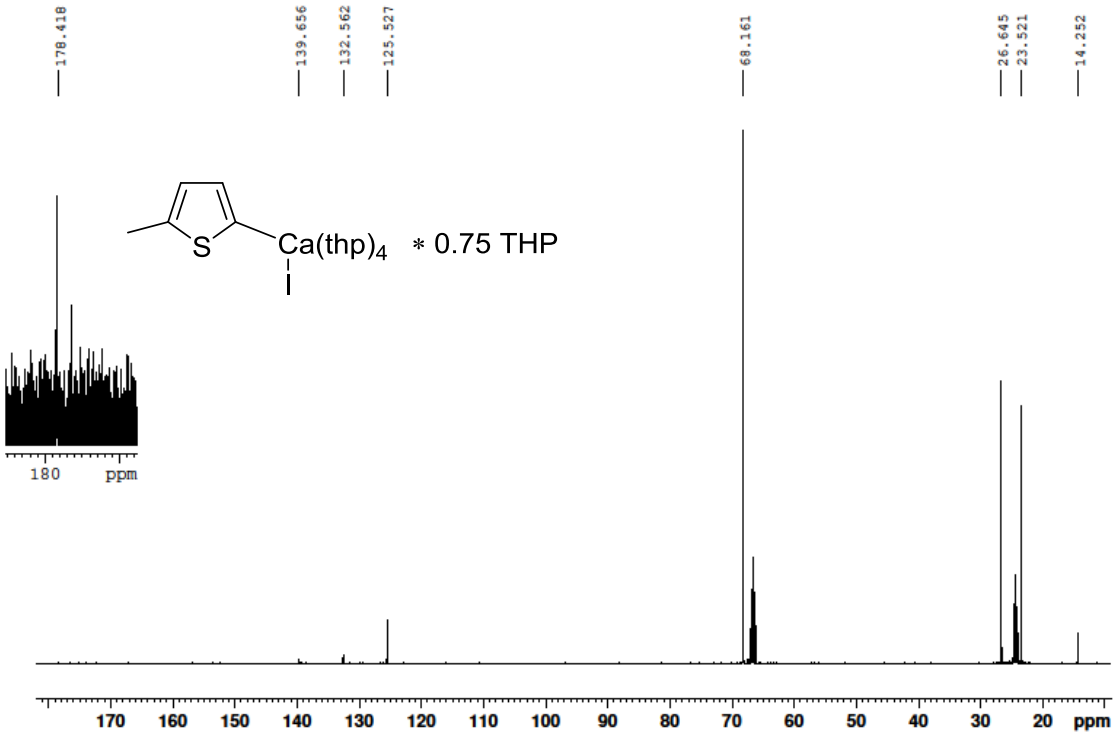

Figure S2: ^{13}C{^{1}H} NMR spectrum ([D_8]THF, 100.6 MHz) of [5-MeThien-2-Ca(thp)$_4$I] (**2**).