C–F bond activation by pentamethylcyclopentadienyl-aluminium(i): a combined experimental/computational exercise†

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The reaction of (Cp*Al)4 with a series of fluoro(hetero)arenes has been investigated and C–F bond activation was observed with perfluorotoluene, pentfluoropyridine as well as 1,2,3,4-tetrafluoro-, pentafluoro- and hexafluorobenzene. The reaction mechanism has been probed by means of DFT calculations and the computational findings are in good agreement with the experimental observations.

Since the first report about the isolation of a monovalent aluminium compound, i.e., tetrameric (Cp*Al)4 (1) by the group of Schnöckel and the isolation of the aluminium(i) β-diketiminate 2 by Roesky and co-workers in 2000,a Fig. 1, subvalent aluminium compounds and studies on their reactivity have received considerable interest. Both compounds differ from each other not only with respect to their electronic structure but also in terms of their synthetic accessibility. Although the tetramer 1 is preferred over the respective monomer 1′ by about 150 kJ mol−1,b the reactivity of dissolved (Cp*Al)4 is due to the presence of monomeric AlCp* possessing a lone pair and a vacant orbital at the aluminium atom. 2 exists as monomer in both the solid state and in solution, and is considered as an aluminium analogue of N-heterocyclic carbenes. While the synthesis of 1 has been improved from yields of 44%1 up to 93%5 and without the requirement of strong reducing agents, 2 is not as readily obtained.2,6 In distinct contrast, the reactivity of 2 is much more explored compared to 1,6 for which reports have been faded after an initial period of intense research.

The oxidative addition of strong σ-bonds has been believed to be limited to transition metals, but the last decade has witnessed that main-group elements are also able to split strong σ-bonds.9 The activation of C–F bonds is particularly challenging, due to their high bond dissociation energies and only a few examples incorporating Al(i) and Mg(i) derivatives have been reported in the last five years.7a,b,10 For aluminium, the activation of both, aliphatic and aromatic C–F bonds has been reported, but all originate from 2, which lacks access in decent yields. As the readily available pentamethylcyclopentadienyl-aluminium(i) (1) has been shown to activate Si–F bonds,11 we wondered whether it also allows for the activation of aromatic and heteroaromatic C–F bonds and our findings are reported herein.

(Cp*Al)4 (1)1 was treated with an excess of fluorobenzene, 1,2-difluorobenzene, 1,3,5-trifluorobenzene, 1,2,3,4-tetrafluorobenzene, perfluorobenzene, hexafluorobenzene, pentfluoropyridine, and perfluorotoluene, Scheme 1. While slow oxidative addition of pentfluoropyridine 3a to 1 is already observed at room temperature, as evidenced by 1H NMR spectroscopy, heating to 90 °C is desirable in order to achieve complete conversion. Here, exclusive and regioselective activation of the C–F bond in 4-position, i.e., para to the nitrogen moiety, takes place.

Activation of perfluorotoluene (3b) necessitates heating to 90 °C for 15 minutes, while for penta- (3d) and hexafluorobenzene (3c) heating for 24 hours is required. To achieve complete conversion of 1,2,3,4-tetrafluorobenzene, the reaction time has to be increased to five days. The less fluorine substituted benzenes, i.e., 1,3,5-C6H3F3, 1,2-C6H4F2, and C6H2F, do not show any reactivity despite heating to 90 °C for several days. According to the 1H NMR spectra, the conversion of 1 is quantitative in cases of 3a–e and the respective aluminium(n) complexes are obtained in crystalline yields ranging from 23 to 57%. As observed for pentfluoropyridine,
reaction of 1 with perfluorotoluene, penta- and tetrafluorobenzene occurs regioselectively by activation of the C–F bond in 4, 3, and 2 position, respectively. Such a regioselectivity has also been observed in case of the \( \text{2}/\text{C}_6\text{H}_2\text{F}_4 \) and \( \text{2}/\text{C}_6\text{HF}_5 \) couples.\(^{10a,b}\)

Single-crystals of the aluminium(III) complexes \( 4\text{a–e} \) were obtained and allowed for an X-ray diffraction analysis. The respective molecular structures in the solid state are illustrated in Fig. 2 and Fig. S1 (ESI\(^+\)). Each \( \text{Cp}^*\text{AlF}(\text{R}) \) fragment represents a part of a centrosymmetric dimer in which both distorted tetrahedral aluminium atoms are fluorine-bridged. The distances between the aluminium atom and the \( \text{Cp}^* \) plane take values between 1.876 (4a) and 1.918 (4e) Å, thus being comparable with values obtained for other \( \text{Cp}^*\text{AlXR} \)\(^2\) species as reported before.\(^{12}\) Notably, the chlorine analogue of 4c has been obtained by reacting \( \text{Cp}^*\text{2AlCl} \) with \( \text{B(C}_6\text{F}_5)\text{3} \) and possesses similar structural features.\(^{13}\) The aluminium–carbon and aluminium–fluorine bond lengths are in the range of 1.990(2) to 2.0049(14) Å and 1.8391(19) to 1.8513(19) Å, hence comparable to those found in the related \( \beta \)-diketiminate aluminium(III) complexes.\(^{10e,b}\)

The complexes 4a–e were fully characterised including \( ^1\text{H} \), \( ^{13}\text{C} \) and \( ^{19}\text{F} \) NMR as well as IR spectroscopy; \( ^{27}\text{Al-NMR} \) resonances could not been detected despite extended numbers of scans. The \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectra reveal one singlet for the \( \text{Cp}^* \) methyl resonances in the range of 1.37–1.63 ppm and 9.4–9.7 ppm, respectively. The observed steady downfield shift in going from 4a to 4e accounts for the increased deshielding due to the increasing Al–Cp* separation. The \( ^{19}\text{F} \) NMR spectra feature a broad singlet, due to \( \text{J coupling to } ^{27}\text{Al} \) \( (I = 5/2) \) at about –109 ppm, which appears downfield shifted compared to the other yet reported values of dinuclear aluminium compounds with bridging fluorine groups but more electron rich ligands.\(^{14}\) Furthermore, the additional \( ^{19}\text{F} \) resonances have the expected pattern characteristic for fluor(o)heteroarene substituents. Notably, the room temperature \( ^1\text{H} \) and \( ^{19}\text{F} \) NMR spectra of 4b, 4c, and 4d, respectively, reveal two sets of resonances in different proportions ranging from 1:4 in case of 4b to 1:12 for 4c. As the effect is most pronounced for 4b, diffusion-ordered (DOSY) NMR experiments have been performed (Fig. S30, ESI\(^+\)). Both \( ^1\text{H} \) resonances (1.4 and 1.65 ppm) show a mono-exponential and comparable diffusion behaviour, which indicates a similar hydrodynamic radius and makes a conceivable monomer–dimer equilibrium unlikely. Variable-temperature (VT) \( ^1\text{H} \) and \( ^{19}\text{F} \) NMR experiments in the 233–333 K range were also performed and a temperature dependence of the chemical shifts and incipient coalescence at 333 K was observed. Hence, we speculated that besides the dimeric species 4 observed in the solid state, an isomeric form 4’ exists in solution, in which the two fluoroaryl

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**Scheme 1** Oxidative addition of the fluoro(hetero)arenes 3a–e to 1 is observed experimentally, while 3f–h remained unreactive at 90 °C.

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**Fig. 2** Solid-state structures of 4a–d (hydrogen atoms except the aromatic protons are omitted for the sake of clarity). Selected bond lengths [Å] and angles [°] with calculated values (M06-2X/6-31G(d)//M06-2X(SMD)/6-311+G(d,p)) in square brackets: (a) 4a \( \text{Al1–C1 2.0049(14) [1.992], Al1–F1 1.8391(9) [1.849], C1–Al1–F1 99.01(5) [98.66] } \); (b) 4b \( \text{Al1–C1 1.9987(16) [1.990], Al1–F1 1.8410(9) [1.843], C1–Al1–F1 99.68(5) [99.15]} \); (c) 4c \( \text{Al1–C1 1.990(2) [1.984], Al1–F1 1.8403(12) [1.846], C1–Al1–F1 100.33(7) [99.79]} \); (d) 4d \( \text{Al1–C1 1.994(4) [1.981], Al1–F1 1.8513(19) [1.850], C1–Al1–F1 101.82(11) [100.04]} \).
substituents are located on the same instead of opposing sides of the Al₂F₂ plane. Based on the NMR data the conceivable formation of AlCp⁺R₂/AlCp⁺F₂ couples or the respective adducts by ligand redistribution is unlikely as one would not only expect two sets of ¹H resonances but also more complex ¹⁹F spectra.

In order to rationalize the experimental findings and to reveal the origin of the second set of resonances in the ¹H and ¹⁹F NMR spectra of 4b, 4c, and 4d, the oxidative addition reactions have been explored by means of density functional theory (DFT) calculations on the M06-2X/6-31G(d)//M06-2X(SMD)/6-311+G(d,p) level of theory. Notably, C–F bond activation by 2 has recently also been investigated computationally. A schematic potential-energy surface is depicted in Table 1 along with the respective energies. The calculated tetramerization enthalpy of C₆F₅ substituted aluminium cyclopentadienyls is in contrast to the experiment (−60.6 kJ mol⁻¹ at 298 K) endothermic by 20.5 kJ mol⁻¹ due to the overestimation of entropic contributions to gas-phase calculations, which has been discussed before for various substituted aluminium cyclopentadienyls. In consequence, all energies given in Table 1 are referenced to the 1/3 couples. Formation of the encounter complex Int1 is exothermic but endergonic for all substrates investigated. Int1 features weak noncovalent C–H···F–C interactions involving the fluorine atoms of the fluoro(hetero)arenes and the methyl groups of the Cp⁺ unit, with H···F distances between 2.36 and 2.50 Å. Next, C–F bond activation occurs in a concerted manner, i.e., simultaneous C–F bond breaking and Al–C as well as Al–F bond making via the three-membered transition structure TS. The transition state involves alternating electron transfer from the aluminium lone pair to the antibonding σ* orbital of the C–F bond and from the fluoride lone pair to the vacant p-type orbital at aluminium. The calculated activation energies are in good agreement with the experimental parameters and explain the non-occurring C–F bond activation in case of the substrates 3f–h, Table 1. Please note that the transition state energies reported for 2 are by 33.3 to 67.4 kJ mol⁻¹ lower, which reflects well the differences observed experimentally and attributes to the higher HOMO LUMO separation in case of 1 lower. The thus formed Lewis-acidic tricoordinated aluminium(III) species Int2 dimerises to give 4 in which the aluminium atoms are stabilised by an electron octet. The stabilisation is expressed by a gain in free energy of 90.8 to 98.7 kJ mol⁻¹. However, a second isomer 4', with almost parallel oriented fluoro(hetero)arene and adjacent Cp⁺ substituents, Fig. 3, is by only 8.0 to 14.7 kJ mol⁻¹ higher in energy compared to 4, which explains the experimental observation of the second species. Please note that according to DFT calculations the 4'...
Notes and references

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