C–F Activation

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Trifluoromethyl Coordination and C–F Bond Activation at Calcium**

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At more than 120 kcal mol^{-1} the bond dissociation energy of the C–F σ bond is larger than that of any other C–X single bond.[1] This factor, together with the reluctance of the C–F moiety to engage in coordination to metal centers, results in a notable chemical stability. As a result, the selective activation and cleavage of C–F bonds has been recognized as a great intellectual and practical challenge which, in turn, has attracted a diverse collection of workers concerned with the identification of both stoichiometric and catalytic reactivities.[2] Although the vast majority of this work has utilized reductive C–F σ-bond cleavage at low-valent transition-metal centers, more recent explorations by Andersen and co-workers have highlighted the potential for intermolecular hydrogen–fluorine exchange to be mediated by a well-defined trivalent organolanthanide complex.[3]

This latter process must necessarily occur without any adjustment of the metal oxidation state and has been reasoned to proceed through a σ-bond metathesis mechanism that is, at least superficially, similar to that employed to describe more familiar C–H and Si–H bond activations.[4] This reaction requires η^1 coordination of lanthanide to fluorine with subsequent exchange via a four-membered transition state with simultaneous Ln–H and C–F bond cleavage and Ln–F and C–H bond formation.

The work herein stems from our interest in the use of the inexpensive and environmentally benign heavier Group 2 elements (Ca, Sr, and Ba) in catalytic processes that, like the C–F exchange reaction described above, have become the domain of 4f-element chemistry. We and others have already outlined several catalytic systems that are dependent upon the heterofunctionalization of unsaturated hydrocarbon substrates and have endeavored, by stoichiometric investigations, to identify the likely course of these reactions.[5] A gratifying "lanthanide mimetic" reactivity has indeed begun to emerge from these studies to the extent that we believe that it is feasible to turn our attention to the incorporation of more challenging σ-bonded substrates into our chemistry. Herein we describe a calcium β-diketiminate complex that adopts an unprecedented N,F-chelated binding mode through a CF_3 group and C–F bond cleavage via an intermediate heteroleptic calcium fluoride complex.

The catalytic chemistry previously studied by us has utilized the β-diketiminato calcium amide **1a**. This compound was originally introduced by Chisholm et al.[6] and has proved itself as a remarkably adept and easily prepared prototype reagent for a variety of stoichiometric[7] and catalytic reactions.[5a–c] The utility of this compound is limited by the lability of less coordinatively saturated derivatives toward solution-redistribution (Schlenk-type) equilibria and the production of unreactive or insoluble homoleptic species, as well as a propensity to undergo further deprotonation and/or reductive degradation.[7e,8] With this in mind we sought to prepare the trifluoromethyl-substituted analogue of **1a**, compound **1b**, by an analogous "one-pot" reaction of the free-ligand precursor,[9] CaI_2, and two equivalents of $KN(SiMe_3)_2$ in THF, a reaction that provides excellent yields of compound **1a**. Following salt metathesis, evaporation of the solvent, and extraction into hexane, filtration and crystallization yielded colorless crystalline compound **2** in a low but reproducible yield of 20% (Scheme 1).

Compound **2** proved to be soluble in hydrocarbon solvents and, though highly moisture-sensitive and thermally unstable in solution (see below), was characterized in both solution and in the solid state. Although the ^{1}H NMR spectrum of **2** in C_6D_6 displayed a series of broad resonances consistent with a dynamic process occurring at a rate similar to that of the NMR timescale, the absence of the high-field resonance for the trimethylsilyl amide moiety expected for **1b** was clearly apparent. Similarly, ^{19}F NMR spectra of **2** in C_6D_6 at room temperature showed a number of distinct, but broad, resonances attributed to magnetically non-equivalent CF_3 groups of the ligand backbone under slow exchange (see spectrum after 15 min in Figure 2). Low-temperature ^{19}F and ^{1}H NMR experiments on a [D_8]toluene solution of **2** revealed no simplification of these complex resonances, and the fluxional process could not be resolved above 193 K. On the basis of the NMR data it appears likely that **2** undergoes facile ligand exchange in solution and, while the solid-state structure of **2** (see below) remains a probable part of such equilibria, both

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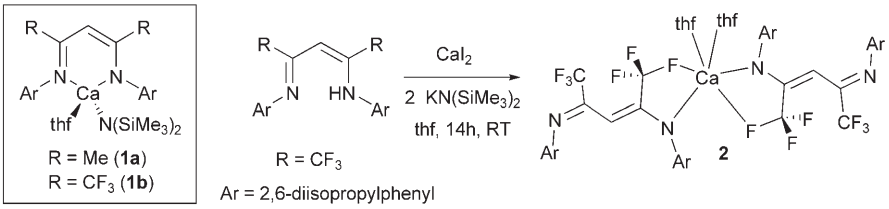


Scheme 1. Synthesis of homoleptic β-diketiminato complex **2**.

geometric isomerization of the α,β-unsaturated imine moiety and redistribution to the more familiar N,N-chelation mode of the β-diketiminate ligand can be envisaged.

The complexity of these observations was resolved by a single-crystal X-ray diffraction analysis (Figure 1), which revealed that a homoleptic complex containing a six-coordinate calcium center had been formed. The calcium coordination sphere is occupied by two *cis*-coordinated molecules of thf and two κ^2-chelated diiminate ligands, each of which are bound by what may be considered as an eneamide nitrogen donor and a fluorine atom of the adjacent (that is, α-carbon-bonded) trifluoromethyl substituent. Although the respective Ca–N (Ca–N1 2.415(3) Å versus Ca–N3 2.371(3) Å) and Ca–F bond lengths (Ca–F1 2.489(3) Å versus Ca–F9 2.468(2) Å) to each ligand are sufficiently dissimilar to imply that the N1-containing ligand is the more strongly bound; this difference is likely to have little consequence with respect to the noted lability and reactivity of compound **2** in solution (see below). Examination of the C–F bond lengths of all four trifluoromethyl substituents within the structure of **2** evidence a notable elongation of the C–F bonds to the coordinated fluorine atoms (C4–F1 1.381(5) Å, C33–F9 1.361(5) Å) in comparison to those of the uncoordinated fluorine atoms (average C–F: 1.328(5) Å) owing to the increased coordination number of these atoms.

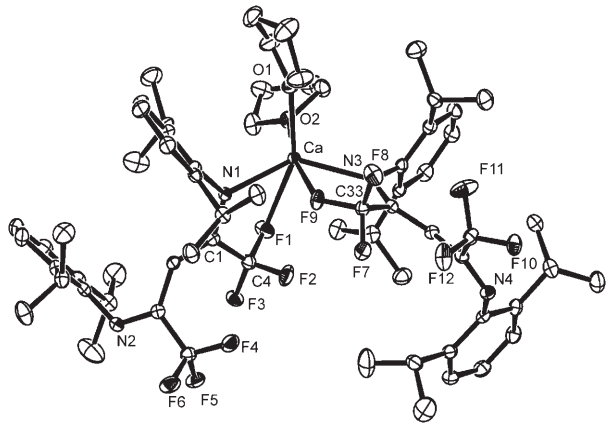


Figure 1. ORTEP representation of **2**. Thermal ellipsoids are set at 20% probability; H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ca-F1 2.489(3), Ca-F9 2.468(2), Ca-N1 2.415(3), Ca-N3 2.371(3), Ca-O1 2.311(3), Ca-O2 2.346(3), F1-C4 1.381(5), C33-F9 1.361(5), F2-C4 1.335(5), F3-C4 1.324(5), N1-C1 1.337(5), C1-C4 1.501(6); O1-Ca-O2 89.34(11), N3-Ca-F9 63.48(9), N1-Ca-F1 63.40(9), N1-Ca-F9 74,48(1), N3-Ca-F1 100.48(11), F9-Ca-F1 97.59(10).

The coordination behavior of fluorocarbon units toward Group 1 and Group 2 metal centers is surprisingly extensive and, within specially designed fluorocryptand ligands, has been investigated by Plenio and coworkers.[10] To the best our knowledge, however, the only crystallographically confirmed example of a similar C-F-Ca linkage is within the dimeric β-diketonate complex $[\{Ca(hfa)_2(OH_2)_2\}_2]$ (hfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate), in which each calcium atom engages in intermolecular bridging interactions through a CF_3 group of a neighboring hfa ligand.[11] Although the Ca–F distances in this latter, eight-coordinate species are somewhat longer (ca. 2.52 Å) than those observed in the six-coordinate complex **2**, it is notable that the possibility of more extensive fluorine bridging was implicated in the facility of the analogous unsolvated species $[Ca(hfa)_2]_x$ to decompose to CaF_2 during thermally induced chemical vapor deposition.[11]

To gain further insight into the fluxional behavior of **2** observed in solution, a series of DFT calculations were performed on the model complex $[\{PhNC(CF_3)CHC(CF_3)NPh\}K]$ using the B3LYP density functional theory and LANL2DZ pseudopotentials (and basis set) implemented in Gaussian 03.[12] Geometry optimizations were performed on N,N-, N,F-, and F,F-chelated bonding modes by selecting initial geometries with appropriate potassium–heteroatom contacts. While both N,N- and N,F-chelation modes optimized to the expected minima, the F,F-chelated species minimized to the N,N conformer. Consistent with the crystal structure of **2**, the N,F-chelation mode demonstrated several close K···F contacts (< 2.9 Å) between the metal center and the CF_3 moiety of the ligand. Although the suitability of this simple model system remains questionable because of the increased coordinative unsaturation at the metal center of $[\{PhNC(CF_3)CHC(CF_3)NPh\}K]$ relative to **2**, comparison of the overall energies of the calculated complexes revealed the N,N conformer to be about 17.2 kcal mol^{-1} lower in energy than the N,F-coordinated isomer. In conjunction with the low-temperature NMR data, suggesting the likely presence (and interconversion) of both N,N- and N,F-conformers in solution, this observation indicates that the isolation of **2** is undoubtedly dependent upon the precise conditions (solvent system, temperature) of the crystallization.[13]

Although additional high-temperature ^{19}F and ^{1}H NMR experiments on a $[D_8]$toluene solution of **2** revealed decoalescence of the broad resonances that were initially observed, this process was found to be irreversible. This observation was clearly not consistent with a fast-exchange regime but with a decomposition of **2**, which, remarkably, occurred even without heating. Storage of a C_6D_6 solution of compound **2** for 5 days at room temperature led to a slow decomposition (Figure 2), accompanied by the precipitation of a small amount of an insoluble white solid. Pulsed gradient spin echo (PGSE) NMR experiments on the decomposition

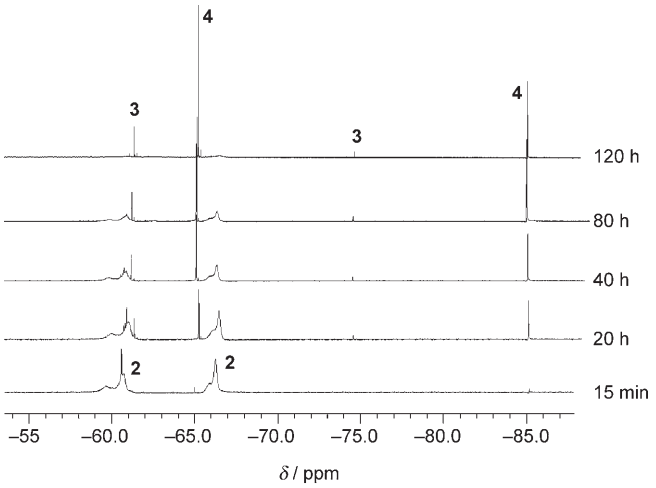


Figure 2. Stacked plot of ^{19}F NMR spectra for the solution decomposition of the homoleptic compound **2** to major (**4**) and minor (**3**) products over 120 h at room temperature.

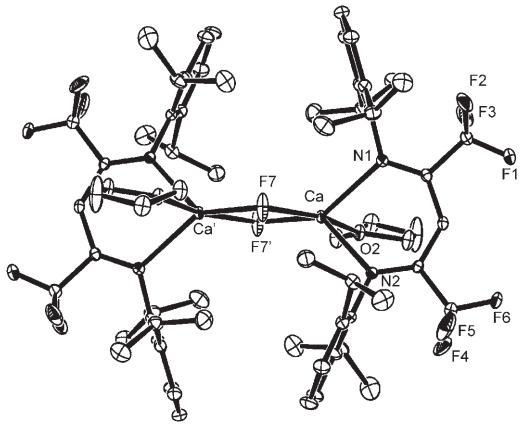
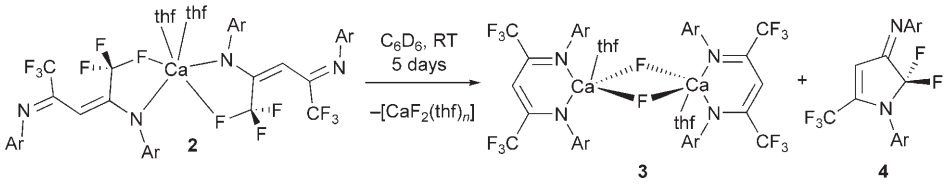


Figure 3. ORTEP representation of **3**. Thermal ellipsoids are set at 50% probability; H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ca-F7 2.168(2), Ca-N1 2.432(2), Ca-N2 2.421(2), Ca-O2 2.423(2); N1-Ca-N2 80.24(8), F7-Ca-F7′ 73.30(8), F7-Ca-N2 102.67(8), F7′-Ca-N2 136.16(9), F7-Ca-O2 157.24(7), F7′-Ca-O2 84.01(7), N2-Ca-O2 92.31(7), F7-Ca-N1 106.64(8), F7′-Ca-N1 143.44(9), O2-Ca-N1 92.59(7).

mixture demonstrated the presence of two new compounds in solution, **3** and **4** (Figure S1 in the Supporting Information). Of these, the minor product, **3**, reacted further to re-form the β-diketiminato ligand precursor [ArNC(CF_3)CHC(CF_3)-NHAr] upon exposure to an aerobic atmosphere. Although we have been unable to isolate an analytically pure bulk sample of this compound owing to its continual decomposition in solution, fractional crystallization of the crude mixture from a hexane solution allowed the isolation of this hydrolytically sensitive intermediate compound and its identification as the heteroleptic calcium fluoride **3** (Scheme 2) by ^{19}F NMR and a single-crystal X-ray diffraction analysis (Figure 3).



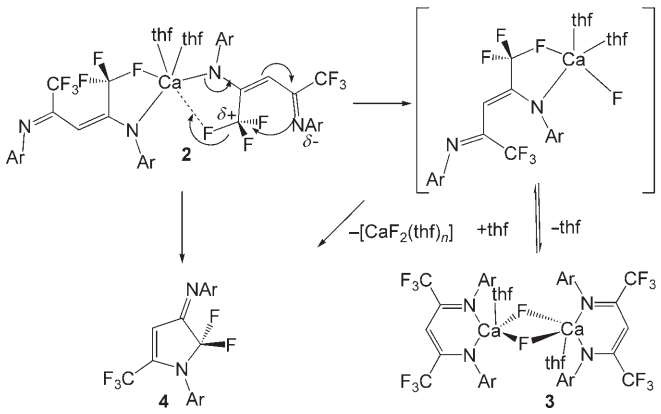
Scheme 2. Solution decomposition of **2**.

Roesky and co-workers have very recently reported the rational synthesis of an analogous (and perfectly stable) species [{LCaF(thf)}$_2$] (**5**), in which L is the nonfluorinated, but effectively isosteric, β-diketiminate ligand [ArNC-(Me)CHC(Me)NAr] (Ar = 2,6-diisopropylphenyl).[7i] Although not isostructural, the centrosymmetric dimer of **3** displays metrical parameters that differ only slightly from this previously reported species. While the Ca–N bonds are somewhat longer in compound **3** (Ca–N1: 2.432(2) Å in **3**, 2.379(2) Å in **5**), most likely as a result of charge depletion onto the nitrogen atoms owing to the trifuoromethyl substituents of the β-diketiminate ligand, and the Ca–F bond lengths (**3**: 2.168(2), 2.186(2) Å; **5**: 2.170(2), 2.189(2) Å) and F-Ca-F angles (**3**: 73.30(8)°; **5**: 74.79(7)°) are effectively identical and very similar, respectively. Furthermore, the ^{19}F NMR spectra of both heteroleptic calcium fluorides in C_6D_6 solution demonstrate distinct and comparable resonances for the bridging fluoride ion (**3**: $\delta = -74.6$ ppm; **5**: $\delta = -78.0$ ppm).[7i]

The major decomposition product, **4**, proved to be stable under aerobic conditions and could be isolated by flash column chromatography of the filtrate following the crystallization of **3**. The ^{1}H, ^{19}F, and ^{13}C NMR spectra are consistent with a heterocyclic structure and, most convincingly, display a series of ^{19}F-coupled resonances in the ^{13}C NMR spectrum, characteristic of magnetically distinct -CF_2 and -CF_3 moieties. The imine carbon atom of **4** appeared as a triplet at $\delta =$ 161.2 ppm (t, $^2J_{F,C} = 21.6$ Hz) while the CF_3-bound quaternary carbon atom appeared as a quartet at $\delta = 153.5$ ppm (q, $^2J_{F,C} =$ 36.5 Hz). Furthermore, both the -CF_3 and -CF_2 carbon nuclei were heavily deshielded and appeared at $\delta = 119.6$ (q, $^1J_{F,C} = 273.3$ Hz) and 116.4 ppm (t, $^1J_{F,C} = 254.8$ Hz), respectively. This heterocyclic connectivity was established unambiguously by a single-crystal X-ray analysis (Figure S2 in the Supporting Information) following recrystallization from benzene.

This solution decomposition represents C–F activation of the coordinated trifluoromethyl group of the homoleptic calcium complex **2**. The current evidence suggests that the decomposition proceeds by an anchimerically assisted intramolecular nucleophilic cyclization reaction. Coordination of the CF_3 group of the β-diketiminate ligand to the calcium center in **2** effectively polarizes one of the C–F bonds, resulting in an enhancement of the electrophilicity of the trifluoromethyl carbon atom, which is thus susceptible to

intramolecular attack by the nucleophilic nitrogen atom of the "free" (that is, uncoordinated) imine. This metal-assisted cyclization reaction yields, in addition to the heterocyclic product **4**, the intermediate calcium species **3**, which may arise from ligand redistrubtion and dimerization of the initial heteroleptic decomposition product (Scheme 3). Species **3**



Scheme 3. Proposed mechanism for the solution decomposition of **2**.

may further decompose to **4** and $[CaF_2(thf)_n]$, which is observed as a fine insoluble precipitate following storage of hydrocarbon solutions of **2** at room temperature for several days, by a similar cyclization mechanism.

A natural population analysis performed on the solid-state structure of **2** (using the B3LYP density functional theory and LANL2DZ pseudopotentials and basis set that are implemented in Gaussian 03)[12] provided support for this hypothesis. The analysis revealed a significant charge localization upon the terminal nitrogen atoms of the β-diketiminate ligand (average NBO charge: N_{imine} −0.469) as well as significant polarization (and therefore activation) of the metal-bound C–F bond (average NBO charges: F_{coord} −0.426, $F_{uncoord}$ −0.366) and a modest electron deficiency at the carbon atom of the metal-bound CF_3 group (average NBO charges: F_3C_{coord} +1.120, $F_3C_{uncoord}$ +1.115).

Although this C–F activation process does not proceed by a mechanism analogous to that employing trivalent lanthanide centers, the solution decomposition of **2** does set an encouraging precedent for the study of Group 2 mediated C–F σ-bond activation processes. We are continuing to investigate the reaction chemistry of well-defined heavier-alkaline-earth complexes and the potential application of **2** as a precursor for nanoparticulate CaF_2.

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