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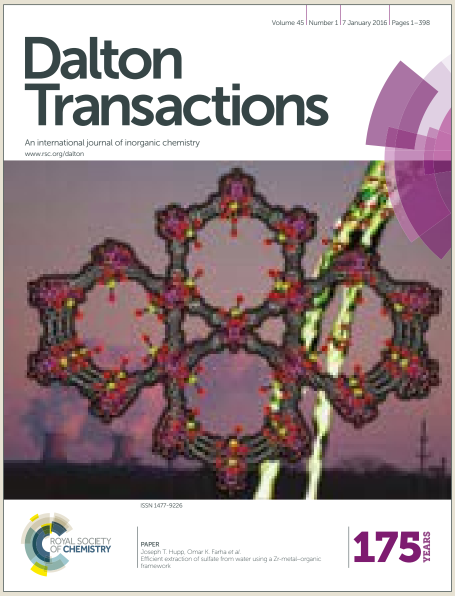

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Tethered cationic alkaline earth - olefin complexes

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Abstract

The aminofluoroalcohol *N,N,N*-(CH_2=$CHCH_2CH_2$-),($CH_3OCH_2CH_2$-),($HOC(CF_3)_2CH_2$-)N ({RO^F}H) possessing both a methoxy and an olefin dangling side arms enables the preparation of the heteroleptic charge neutral alkaline earth complexes [{μ^2-RO^F}AeN($SiMe_2H$)$_2$]$_2$ (Ae = Ca, **1**; Sr, **2**). These *O*-bridged dinuclear complexes were characterised by NMR spectroscopy and X-ray diffraction crystallography. XRD analysis of **1** and **2** showed that both complexes are stabilised by intramolecular Ae···F–C and β-agostic Ae···H–Si secondary interactions, and that the olefin does not bind to the alkaline earths while the methoxy side-arm does. The discrete ion pairs $[(\{\mu^2\text{-}RO^F\}Ae\bullet(Et_2O)_2)_2]^{2+}.2[H_2N\{B(C_6F_5)_3\}_2]^-$ (Ae = Ca, **3a**; Sr, **4a**) were synthesised upon treatment of the parent complexes **1** and **2** by $[H\bullet(Et_2O)_2]^+.[H_2N\{B(C_6F_5)_3\}_2]^-$. NMR spectroscopy showed the presence of two coordinated Et_2O molecules on each metal in these complexes. The water adduct $[(\{\mu^2\text{-}RO^F\}Sr\bullet(H_2O))_2]^{2+}.2[H_2N\{B(C_6F_5)_3\}_2]^-$ (**4b**), presumably derived from **4a** upon adventitious introduction of moisture during recrystallisation, was characterised by crystallographic methods. The dication $[(\{\mu^2\text{-}RO^F\}Sr\bullet(H_2O))_2]^{2+}$ exists as an *O*-bridged dinuclear species featuring very strong Sr···F–C interactions in the range 2.788(5)-2.997(6) Å, and no interaction with the weakly coordinating anion. Perhaps more importantly, the tethered olefins are coordinated onto the metal cations, with short Sr···Cπ interactions in the range 3.066(10)-3.092(10) Å; this represents the first example of a Sr-olefin cationic complex. Hence, cationisation of the charge neutral precursor to generate the discrete ion pair increases electron deficiency at the metal centre, resulting in the first observation of the binding of an olefin onto a well-defined cationic heavy alkaline earth. On the other hand, our attempts to produce Ae-olefin cations devoid of coordinated Lewis base with this strategy have met no success so far.

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Introduction

The coordination chemistry of the large alkaline earths (Ae) calcium, strontium and barium has enjoyed a remarkable growth in the past 15 years, in particular because these abundant metals have emerged as viable alternatives to late transition metals in homogenous catalysis.[1] Under the impulse of Westerhausen, the fundamental organometallic chemistry of calcium has proved to provide much more than just a heavier version of Grignard's magnesium reagents, and calcium alkyl and aryl compounds have instead demonstrated a reactivity of their own.[2] Some of the prominent examples include mesitylcalcium iodide,[3] diarylcalcium,[4] arylcalcium cations,[5] an exquisite inverse organocalcium(I) sandwich complex[6] or 1-alkenyl and alkyl calcium iodides.[7] By comparison, Ae-carbon bonds with stabilising electron-rich monoanionic groups, e.g. cyclopentadienyls[8] or allyls,[9] have been known for some time, while on the other hand, very little is known of the bonding between Ae metals and neutral π ligands.[2a] This situation results from the inability to establish d-π^* back donation in Ae complexes owing to their d^0 external electronic configuration, by contrast with late transition metal complexes. This paucity is best expressed for Ae-olefin complexes, for which only a handful of cases of olefin coordination are known.[10] The seminal example, Schumann's [Ae($C_5Me_4CH_2CH_2CH{=}CH_2$)$_2$] (Ae = Ca, Sr, Ba; **I** in Fig. 1),[11] was followed by Roesky's related [Ba(C_5Me_5)($C_5Me_4CH_2C_5Me_5$)].[12] More recently, we have reported on heteroleptic Ae-olefin complexes supported by fluoroalkoxides, and stabilised by a pattern of intramolecular Ae···F–C, Ae···Cπ and β-agostic Ae···H–Si secondary interactions (Fig. 1, **II-III**).[13] Ae-olefin complexes are thought to be models of putative reactive intermediates in the catalysed hydroamination and hydrophosphination of alkenes.[1,14] To our surprise, the olefin complexes **II** and **III** proved as stable as the intramolecular methoxy adducts **IV** and **V**.[15]

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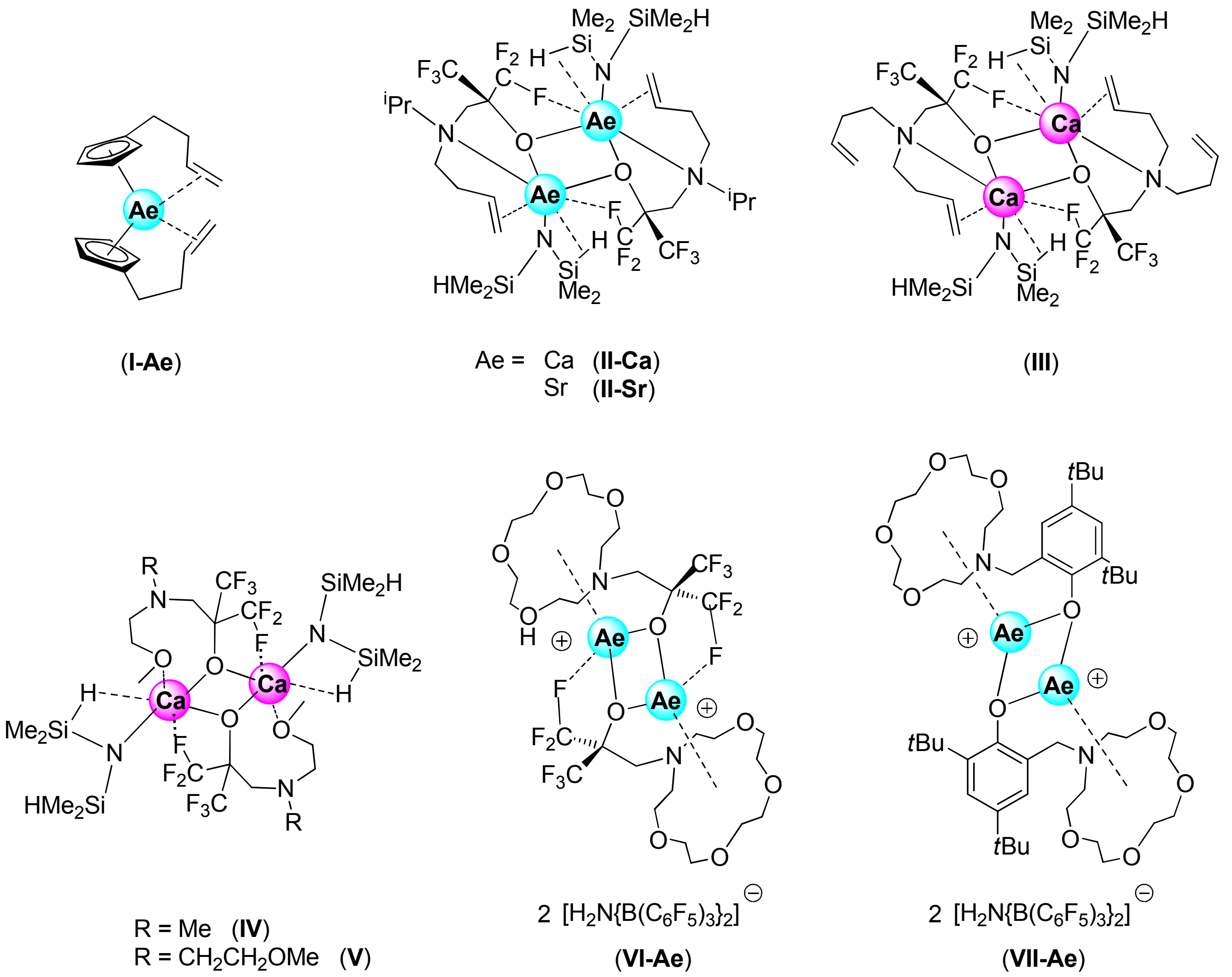

(**I-Ae**)

Ae = Ca (**II-Ca**)
Sr (**II-Sr**)

(**III**)

R = Me (**IV**)
R = CH_2CH_2OMe (**V**)

2 $[H_2N\{B(C_6F_5)_3\}_2]^{\ominus}$
(**VI-Ae**)

2 $[H_2N\{B(C_6F_5)_3\}_2]^{\ominus}$
(**VII-Ae**)

Fig. 1 Examples of Ae-olefin complexes (**I-III**), charge-neutral compounds with secondary interactions (**IV-V**), and discrete Ae cations (**VI-VII**). Ae = Ca, Sr, Ba unless otherwise stated.

Well-defined monocationic Ae complexes are another class of rare and yet useful compounds. Compared to their neutral congeners, they show greater electron-deficiency and Lewis acidity, which has been proposed to enhance their reactivity in homogenous polymerisation catalysis[1f,16] or alkene hydrogenation,[17] and, overall, to produce competent Lewis acid catalysts.[18] Yet, because of electronic depletion and high electropositivity, isolating discrete Ae cations has been tedious. Itoh and Kitagawa reported the first examples in 2001,[19] whereas we and others have more recently developed several cationic Ae polymerisation catalysts.[15,16,20]

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Multidentate aminoether-phenolato or -fluoroalkoxo ligands, owing to their low propensity to bridge multiple metal centres and generate multinuclear aggregates, have enabled substantial advances in this area, e.g by affording very reactive, solvent-free Ae complexes such as **VI** and **VII** in Fig. 1.

As part of our efforts towards implementing secondary interactions in alkaline earth chemistry, we report here on the syntheses of the first cationic calcium- and strontium-olefin complexes. It is shown how non-covalent interactions in calcium and strontium complexes[21] alone can at times fail to deliver these targets, and how this can be overcome through ligand design.

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Results and discussion

Rationale for ligand design: {RO^F}H

Following a method reported earlier to obtain Ae cations,[20] our initial attempts at preparing cationic calcium-olefin complexes consisted of the equimolar reactions between complexes **II-Ca** or **III** (see Fig. 1) with $[H\bullet(OEt_2)_2]^+.[H_2N\{B(C_6F_5)_3\}_2]^-$ (aka Bochmann's acid).[22] Even if the release of $HN(SiMe_2H)_2$ occurred, these reactions failed to yield the desired cationic Ae-olefin adducts, and only returned species which we could not authenticate. This was assumed to result from excessive electron deficiency in the expected products, leading to uncontrolled reactivity and decomposition. We therefore did not pursue this route, nor did we explore the one-step reaction of $[Ca[N(SiMe_2H)_2]_2]$ with the doubly acidic pro-ligand $[\{RO\}HH]^+.[H_2N\{B(C_6F_5)_3\}_2]^-$ which can be obtained upon protonation of the appropriate pro-ligand {RO}H with Bochmann's acid.[20,22,23]

We have shown that the coordination of a single methoxy side-arm per metal atom was sufficient to warrant the formation of the *charge neutral* calcium complex **IV**, whereas the further addition of a second pair of methoxy tethers as in **V** was superfluous as it did not interact with the calcium centres.[20c] Nonetheless, this scenario changed upon cationisation, as it was found that *all* methoxy side-arms were metal-bound in the *cationic* complexes derived from **V**.

This knowledge, combined with the apparent inability to cleanly generate cations from **II-Ca** or **III**, led us to consider the utilisation of the new mixed olefin/methoxy aminoether fluoroalcohol {RO^F}H (Scheme 1). This pro-ligand can be readily obtained (78% yield) as a colourless oil upon reaction of *N*-(2-methoxyethyl)but-3-en-1-amine with 2,2-bis(trifluoromethyl)oxirane. Its ^{19}F NMR spectrum in benzene-d_6 exhibits a single sharp singlet at

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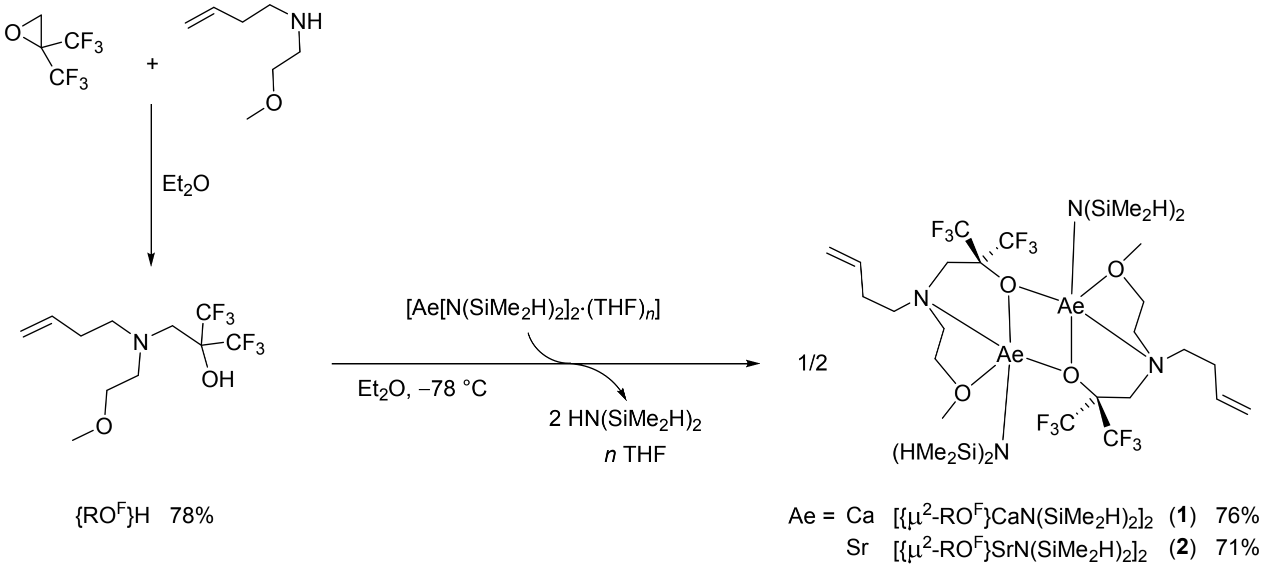
–77.51 ppm. The olefinic hydrogen atoms are characterised by clear multiplets at 5.54 ($CH{=}CH_2$) and ca. 4.95 ($CH{=}CH_2$) ppm in the ^{1}H NMR spectrum.



Scheme 1 Syntheses of $\{RO^F\}H$ and of complexes $[\{\mu^2\text{-}RO^F\}AeN(SiMe_2H)_2]_2$ (Ae = Ca, **1**; Sr, **2**). Secondary interactions are not represented.

Charge neutral heteroleptic complexes

The protonolysis reactions between $\{RO^F\}H$ and a slight (33%) excess of the alkaline earth tetramethyldisilazido precursors $[Ca[N(SiMe_2H)_2]_2\bullet(THF)]$ and $[Sr[N(SiMe_2H)_2]_2\bullet(THF)_{2/3}]$ afforded the targeted heteroleptic charge neutral complexes $[\{\mu^2\text{-}RO^F\}CaN(SiMe_2H)_2]_2$ (**1**) and $[\{\mu^2\text{-}RO^F\}SrN(SiMe_2H)_2]_2$ (**2**) upon clean release of $HN(SiMe_2H)_2$ (Scheme 1).[24] Both compounds exist as dinuclear *O*-bridged dimer in the molecular solid-sate (vide infra). They were isolated as analytically pure colourless solids after work-up in 76% and 71% yields, respectively. Their identities were established by NMR spectroscopy and X-ray diffraction crystallography, and their purity were corroborated by combustion analysis. These two complexes are soluble in ethers and hydrocarbons, including common alkanes. In their ^{1}H NMR spectra recorded in benzene-d_6, the resonance for SiH hydrogens appear as multiplets at δ 4.88 (for **1**) and 4.95 (for

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2) ppm. The corresponding $^{1}J_{\text{H-Si}}$ coupling constants of ca. 162 Hz testify to mild Ae···H–Si β-agostic interactions; such interactions are now known to contribute to the stability of electron deficient alkaline earth architectures.[25] The resonances for C*H*=CH$_2$ and CH=C*H*$_2$ hydrogens (δ 5.57 and 5.11-4.93 ppm for **1**, 5.56 and 5.09-4.97 ppm for **2**) are located in the same region as seen for the pro-ligand (5.53 and 4.98-4.91 ppm), an indication that the olefins do not bind to the metals in solution. In their ^{19}F NMR spectra, both complexes give rise to two well resolved quadruplets ($^{4}J_{\text{F-F}} \approx 9.1\text{-}9.3$ Hz) in the region between δ –76 and –78 ppm, indicating that the two geminal CF_3 groups in α position to the alkoxide lose magnetic equivalence upon coordination of the ligands to the metals. In the ^{13}C{^{1}H} NMR spectra, the *C*F$_3$ carbon atoms respectively generate a quadruplet at δ 125.99 ppm for **1** ($^{1}J_{\text{C-F}} = 288.9$ Hz) and at δ 126.60 ppm for **2** ($^{1}J_{\text{C-F}} = 288.9$ Hz). Heptets are found at δ ca. 79.31 (for **1**) or 79.87 ppm (for **2**) for the *C*(CF$_3$) atoms, with $^{2}J_{\text{C-F}} \approx 25\text{-}26$ Hz. There is hardly any change in the ^{13}C resonances for *C*H=CH$_2$ and CH=*C*H$_2$ carbon atoms compared to the pro-ligand (**1**, 134.95 and 116.91 ppm; **2**, 134.84 and 117.03 ppm; {RO$^{\text{F}}$}H, 135.61 and 116.78 ppm), another sign of the absence of significant interaction between the olefin and the metals in these two neutral complexes.

The molecular solid-state structure of **1** is depicted in Fig. 2. It shows the complex to exist as a centrosymmetric *O*-bridged dinuclear species, with coordination of the N_{amine} and O_{ether} atoms onto calcium, but without interaction between the metal cations and the olefinic tethers. There is considerable disorder in the olefinic side-arms, and only the main components of these fragments are depicted in Fig. 2. This disorder generated considerable difficulties in refining the positions of the atoms in the dangling CH$_2$CH$_2$CH=CH$_2$ tethers, and we could not manage to obtain reliable C–C and C=C bond lengths for the corresponding four carbon atoms. For this reason, a discussion of metric parameters, in particular for the C=C double bond, is inappropriate.

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Nonetheless, it is clear that there is no interaction between Ca and the C=C bonds, as indicated by the large Ca1–C21A (5.174(6) Å) and Ca1–Ca22A (6.456(11) Å) distances.

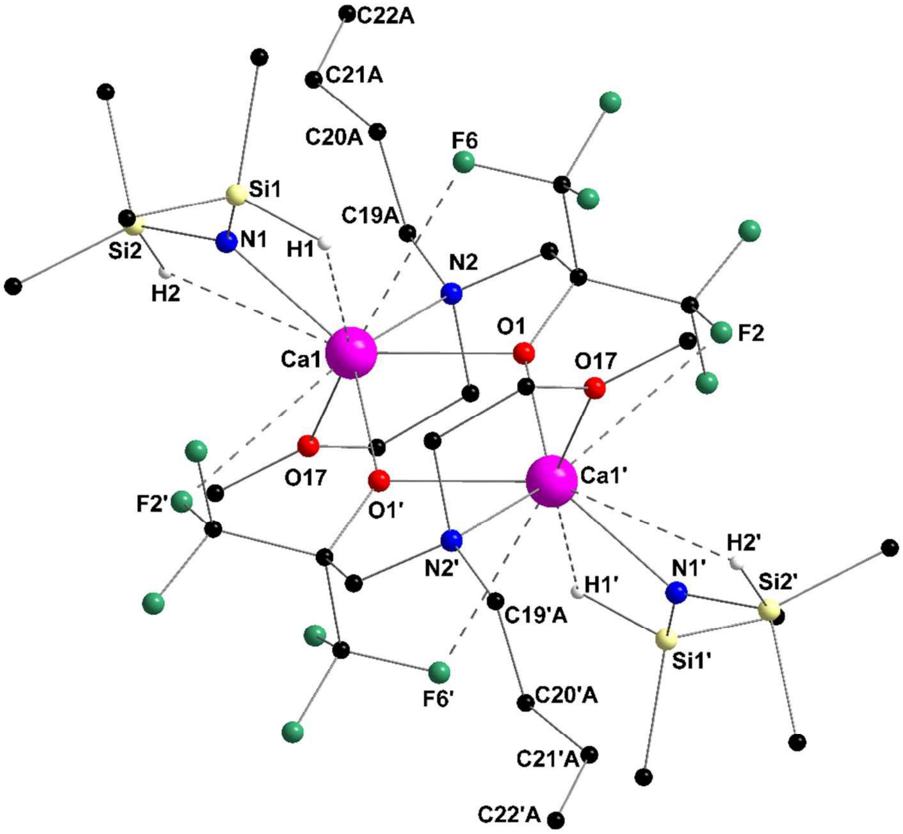

Fig. 2 Representation of the molecular solid-state structure of [{μ^2-RO^F}CaN(SiMe$_2$H)$_2$]$_2$ (**1**), showing only the main component of the disordered olefinic side-arms. Hydrogen atoms other than Si*H* are omitted for clarity. Secondary interactions are represented by dashed lines. Selected bond lengths (Å) and angles (°): Ca1–O1 = 2.3319(16), Ca1–O1' = 2.2921(17), Ca1–O17 = 2.3975(18), Ca1–N1 = 2.301(2), Ca1–N2 = 2.587(2), Ca1–F2' = 3.119(2), Ca1–F6 = 3.036(2), Ca1–H1 = 3.237(29), Ca1–H2 = 3.267(21); Si1–N1–Ca1 = 114.09(12), Si2–N1–Ca1 = 117.30(13).

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Complex **1** exhibits mild β-agostic Ca···H–Si interactions in the solid state, with for instance Ca1–H1 (3.237(29) Å) and Ca1–H2 (3.267(21) Å) distances longer than those measured in **II-Ca** or **III**, in the range 3.08(3)-3.19(3) Å.[13] This is consistent with the NMR data for this compound (vide supra). There are also two short Ca···F–C contacts per metal cation, with Ca1–F6 (3.036(2) Å) and Ca1–F2' (3.119(2) Å) both below the accepted limit for this type of interactions.[26] Again, these are on the whole weaker than those detected in **II-Ca** (3.050(2) Å) and **III** (2.931(1) Å). That both Ca···H–Si and Ca···F–C are weaker in **1** than in **II-Ca** and **III** attests reliably that the Ca–O_{ether} interactions in **1** are stronger than the Ca···Cπ interactions in the olefin adducts, as expected for an oxophilic element such as calcium. The Ca1–O17 bond length of 2.3975(18) Å is only moderately longer than the distances to the bridging anionic O_{alkoxide} atoms O1' and O1 (2.2921(17) and 2.3319(16) Å). By contrast, the Ca1–N2 interatomic distance to N_{amine} (2.587(2) Å) is much longer than Ca1–N1 to the terminal N_{amide} atom, 2.301(2) Å. Perhaps unsurprisingly, these metric parameters in **1** actually compare very well with the corresponding ones in the methoxy adducts **IV** and **V**.[15] Overall, taking the secondary interactions into consideration, each calcium centre achieves a formal coordination number of 9 in **1**, although it has been shown that these Ca···H–Si and Ca···F–C interactions are mostly electrostatic, with little or no covalent character.[13,25]

The molecular solid state structure of the strontium complex **2** resembles that of its calcium congener, but there are nonetheless some noticeable differences (Fig. 3). It also exists as an *O*-bridged dimer, with coordination of the methoxy side-arm but without interaction of the olefins onto the strontium centres (Sr1–C12A = 5.1897(77) Å, Sr1–C13A = 6.4806(98) Å). There is again considerable disorder in the olefinic side-arms, with precludes discussion of the pertaining metric parameters for these segments. The structure of **2** includes one relatively strong β-agostic Sr···H–Si interaction for each strontium, with Sr1–H1 as short as 3.0841(524) Å whereas the

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interatomic distance Sr1–H2 of 3.5090(359) is much longer. Conversely, the Sr1–N1–Si1 angle of 109.71(16) ° is substantially less obtuse than Si2–N1–Sr1 (115.83(16) °). Each strontium atom is also stabilized by two very strong Sr···F–C interactions, as testified by the very short Sr1–F1' and Sr1–F6 distances of 3.049(2) and 2.996(3) Å, respectively. Both Sr···H–Si and Sr···F–C interactions are comparatively stronger in **2** than in the related **II-Sr**, which discloses longer Sr–F (3.050(2) and 3.136(2) Å) and Sr–H (two interactions at 3.092(34) and 3.169(37) Å, by opposition to a single one in **2**) interatomic distances.[13a]

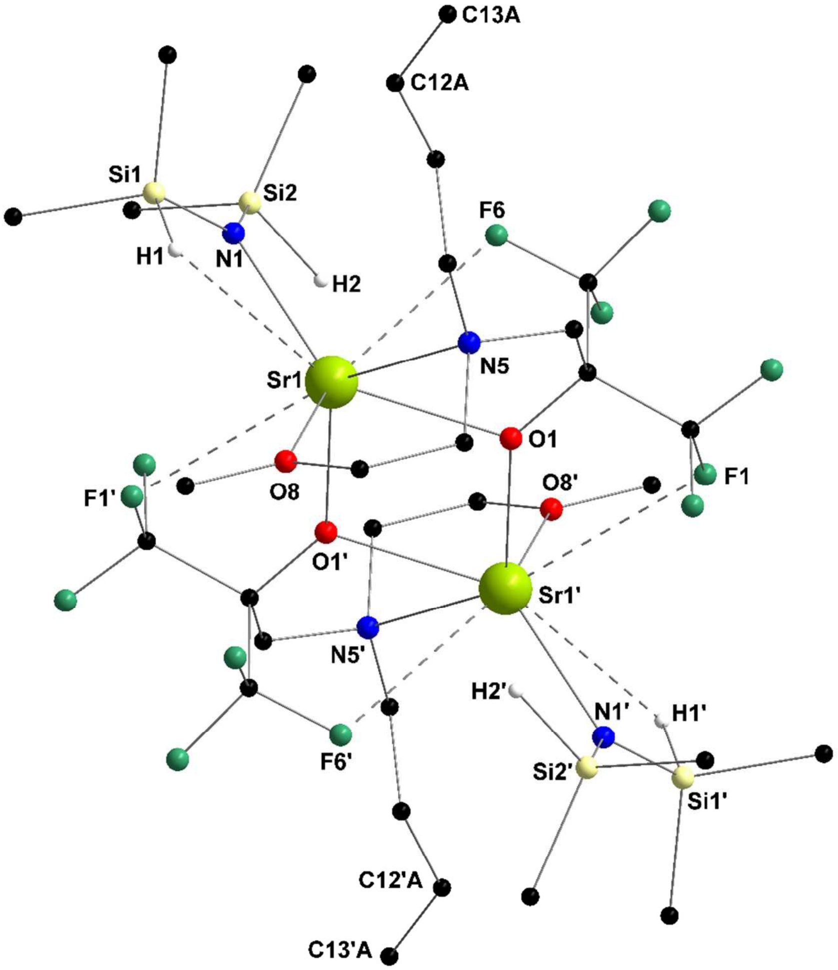

Fig. 3 Representation of the molecular solid-state structure of $[\{\mu^2\text{-RO}^F\}\text{SrN}(\text{SiMe}_2\text{H})_2]_2$ (**2**), showing only the main component of the disordered olefinic side-arms. Hydrogen atoms other

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than Si*H* are omitted for clarity. Secondary interactions are represented by dashed lines. Selected bond lengths (Å) and angles (°): Sr1–O1 = 2.466(2), Sr1–O1' = 2.432(2), Sr1–O8 = 2.535(2), Sr1–N1 = 2.450(3), Sr1–N5 = 2.759(3), Sr1–F1' = 3.049(2), Sr1–F6 = 2.996(3), Sr1–H1 = 3.0841(524); Si2–N1–Si1 = 134.1(2), Si2–N1–Sr1 = 115.83(16), Si1–N1–Sr1 = 109.71(16).

The bond lengths to bridging O_{alkoxide} (2.432(2) and 2.466(2) Å), to the terminal N_{amide} atom (Sr1–N1 = 2.450(3) Å), and to the N_{amine} atoms in **2** are very similar to those measured in **II-Sr**. Hence, the replacement of a metal-bound olefin in **II-Sr** by a coordinated methoxy in **2** only impacts the number and the strength of the non-covalent Sr···H–Si and Sr···F–C interactions, and not the bonding to the *O*- and *N*-atoms.

Cationic complexes

The treatment of **1** and **2** with one equivalent of $[H\bullet(OEt_2)_2]^+.[H_2N\{B(C_6F_5)_3\}_2]^-$ in Et_2O at room temperature resulted in the precipitation of $[(\{\mu^2\text{-}RO^F\}Ca\bullet(Et_2O)_2)_2]^{2+}.2[H_2N\{B(C_6F_5)_3\}_2]^-$ (**3a**) and $[(\{\mu^2\text{-}RO^F\}Sr\bullet(Et_2O)_2)_2]^{2+}.2[H_2N\{B(C_6F_5)_3\}_2]^-$ (**4a**), where two molecules of Et_2O are found on each metal centre. The formulation for these ion pairs was established upon examination of the NMR spectroscopic data. The two complexes were isolated as fine colourless powders in moderate yields after work-up. They are moderately soluble in ethers and dichloromethane, but they are not soluble in hydrocarbons. The compounds were repeatedly submitted to elemental analysis, but we failed to obtain reliable and reproducible results, presumably because of their extreme sensitivity.

The ^1H and $^{13}C\{^1H\}$ NMR data for **3a** and **4a** recorded in dichloromethane-d_2 at 25 °C show the presence of two molecules of diethyl ether per metal. Coordination of Et_2O is unambiguous, as all the pertaining ^1H resonances are substantially shifted towards low field in comparison with free Et_2O in the same deuterated solvent. From the ^1H and $^{13}C\{^1H\}$ NMR data, it was not possible to

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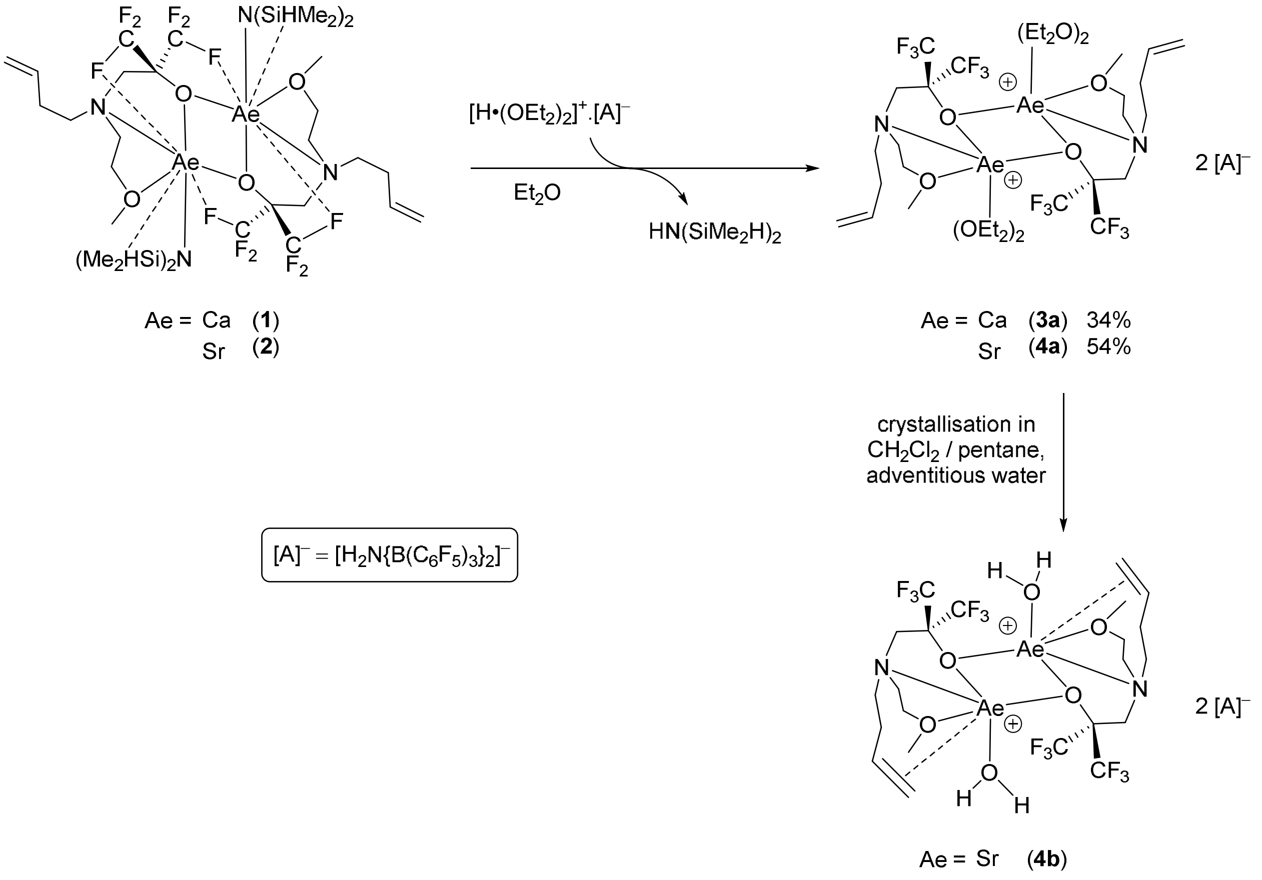
establish whether the olefin coordinates to the metal in solution. The ^{19}F NMR spectra showed the expected resonances for the weakly coordinating anion, with the typical resonances at δ –132.94, –160.26 and –165.79 ppm for **3a**, and at δ –132.89, –160.23 and –165.75 ppm for **4a**, indicating the absence of interaction between the anions and the cations in solution. The ^{19}F NMR spectra for **3a** and **4a** also exhibited three multiplets of approximate relative intensities 2:1:3 between δ –76 and –78 ppm, indicating loss of equivalence of the fluorine atoms in the CF_3 groups in the cationic components; which we interpret as a result of persistent Ae···F–C interactions. Low temperature ^{19}F NMR did not provide information about the multiplicity of these resonances. In the ^{11}B{^{1}H} spectrum of each compound, the presence of the expected single resonance at δ ca. –8.41 (in **3a**) or –8.41 (in **4a**) ppm revealed that the anion $[H_2N\{B(C_6F_5)_3\}_2]^-$ remained intact during the synthesis.



Ae = Ca (**1**)
Sr (**2**)

Ae = Ca (**3a**) 34%
Sr (**4a**) 54%

$[A]^- = [H_2N\{B(C_6F_5)_3\}_2]^-$

Ae = Sr (**4b**)

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Scheme 2 Syntheses of the ion pairs $[(\{\mu^2\text{-RO}^F\}\text{Ca}\bullet(\text{Et}_2\text{O})_2)_2]^{2+}.2[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ (**3a**) and $[(\{\mu^2\text{-RO}^F\}\text{Sr}\bullet(\text{Et}_2\text{O})_2)_2]^{2+}.2[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ (**4a**).

Recrystallisation of a concentrated solution of **4a** in dichloromethane afforded a small crop of colourless single crystals of the water adduct $[(\{\mu^2\text{-RO}^F\}\text{Sr}\bullet(\text{H}_2\text{O}))_2]^{2+}.2[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ (**4b**). Despite multiple attempts, we have not been able to obtain water-free crystals for these compounds. Although all possible care was taken to exclude the presence of moisture (including glove-box techniques and passivation of glassware with Me_3SiCl), we can only assume that the substitution of diethyl ether in **4a** by water in the single crystals of **4b** resulted from the presence of residual water during the recrystallisation procedure.

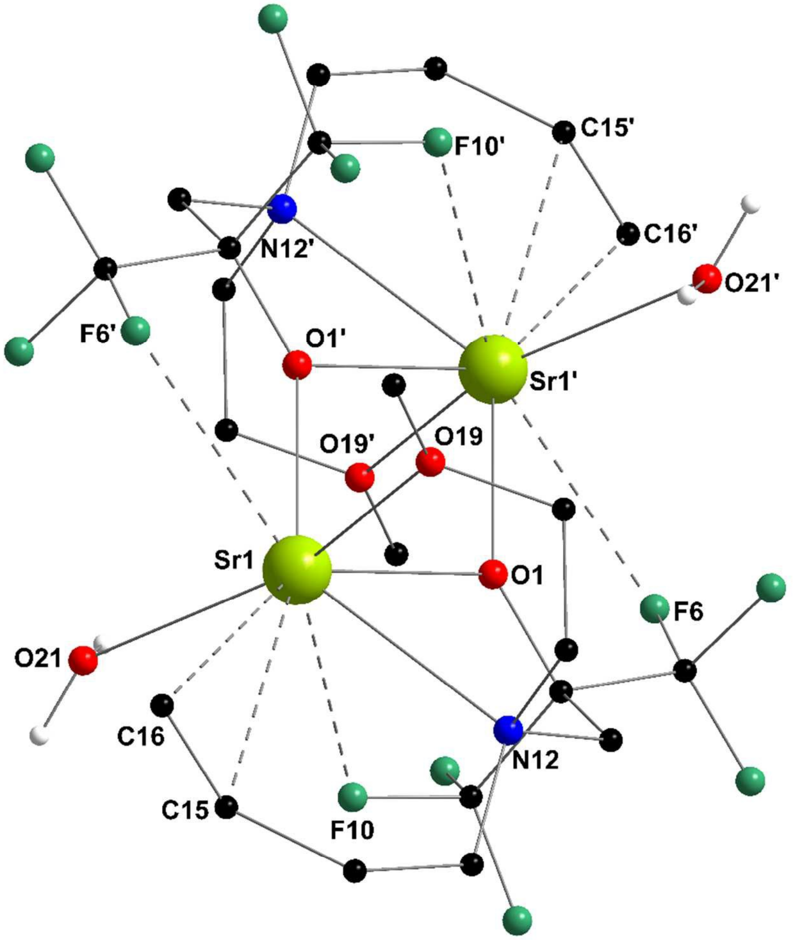

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Fig. 4 Representation of the structure of the dication **4b**$^{2+}$ from the recrystallised ion pair $[(\{\mu^2\text{-RO}^F\}\text{Sr}\bullet(\text{H}_2\text{O}))_2]^{2+}.2[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ (**4b**). Anions and non-interacting molecules of CH_2Cl_2 not represented. Hydrogen atoms other than those on water molecule omitted for clarity. Selected bond lengths (Å): Sr1–O1 = 2.417(5), Sr1–O1’ = 2.430(5), Sr1–O19 = 2.518(6), Sr1–O21 = 2.578(5), Sr1–F6’ = 2.997(6), Sr1–F10 = 2.788(5), Sr1–N12 = 2.831(6), Sr1–C15 = 3.066(10), Sr1–C16 = 3.092(10), C15–C16 = 1.358(14).

The crystal contained two molecules of non-interacting molecules of dichloromethane per asymmetric unit. As inferred from NMR data, there is no interaction in the molecular solid state between the anionic and cationic components. Hence, only the structure of the cationic component **4b**$^{2+}$ is discussed. The structure of $[(\{\mu^2\text{-RO}^F\}\text{Sr}\bullet(\text{H}_2\text{O}))_2]^{2+}$ depicted in Fig. 4 shows the dication to exist as a centrosymmetric *O*-bridged dimer, with one molecule of water coordinated on each strontium centre. More importantly, the dication is characterised by two strong Sr···F–C interactions for each strontium, as indicated by short to very short Sr1–F6’ and Sr1–F10 interatomic distances, respectively 2.997(6) and 2.788(5) Å. The latter is in particular much lower than those in the parent complex **2** (vide supra). Finally, the short Sr1–C15 (3.066(10) Å) and Sr1–C16 (3.092(10) Å) are good evidence of the coordination of the olefins to the metal atoms. To our knowledge, **4b**$^{2+}$ is the sole example of a discrete Sr-olefin cation known to date. Sr···Cπ interactions were also detected in the charge neutral complex **II-Sr**, with distances to the interacting Cπ atoms in this case (3.061(3) and 3.165(3) Å) commensurate with those in **4b**$^{2+}$. They both are also in the range of those measured in Schumann’s $[\text{Sr}(\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}{=}\text{CH}_2)_2]$, 2.99(2)-3.25(2) Å.[27] The C=C double bond in **4b**$^{2+}$ (C15–C16 = 1.358(14) Å) seems elongated with respect to that in **II-Sr** (1.316(5) Å), but the large standard deviation in **4b**$^{2+}$ precludes accurate comparison of the C=C bond lengths in the two complexes.[28]

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The Sr···F–C distances in **4b**$^{2+}$ are shorter than in **2**, with is consistent with electronic depletion at the metal ions in the dication. However, it is remarkable that the bond lengths from Sr to O_{alkoxide} (2.417(5) and 2.430(5) Å) and N_{amine} (2.831(6) Å) atoms in the dication are at best comparable, if not longer, than in the charge neutral **2**. The Sr–O_{alkoxide} bonds in **4b**$^{2+}$ are nonetheless shorter than in the strontium dicationic amino-aza-crown-ether-fluoroalkoxide in **VI-Sr** (four different Sr–O_{alkoxide} bonds in the range 2.446(7)-2.516(6) Å, average 2.486 Å),[20a] which is assumed to reflect greater electron deficiency of the metal in **4b**$^{2+}$. Although the presence of coordinated water in **4b**$^{2+}$ impacts its coordination pattern, it is also evident that the presence of strong Sr···Cπ and Sr···F–C non-covalent interactions plays is a major factor in the stability of the dication. The fate of the diethyl ether molecules during the crystallisation process is not elucidated, but one should note that the intramolecular coordination of the olefins in **4b**$^{2+}$ hence appears to be favoured over the binding of any of the four surrounding Et_2O molecules (possibly driven by favourable entropic considerations with formation of a six membered chelate).

Finally, attempts to recrystallise the calcium compound **3b** were carried out. Crystals of low quality that contained one ion pair of formula $[(\{\mu^2\text{-RO}^F\}Ca\bullet(H_2O))_2]^{2+}.2[H_2N\{B(C_6F_5)_3\}_2]^-$ and another one corresponding to $[(\{\mu^2\text{-RO}^F\}Ca\bullet(Et_2O))_2]^{2+}.2[H_2N\{B(C_6F_5)_3\}_2]^-$ in the asymmetric unit were obtained, but the quality of the best crystallographic data was insufficient and only afforded unacceptable refinement (*f*inal $R_1 > 13\%$, see the Electronic Supporting Information). This precludes any discussion of metric parameters for these two salts. Nonetheless, the connectivity unambiguously shows that the olefins do not bind to calcium in the mono-Et_2O adduct $[(\{\mu^2\text{-RO}^F\}Ca\bullet(Et_2O))_2]^{2+}$, whereas they do in the mono-water adduct $[(\{\mu^2\text{-RO}^F\}Ca\bullet(H_2O))_2]^{2+}$, suggesting that in addition to obvious electronic considerations, the binding of the olefin in these calcium cations may also be very influenced by steric factors.

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Conclusion

Our failed initial attempts at obtaining alkaline earth cations stabilised by olefins and free of coordinated solvent molecules such as THF have led us to design a fluoroalkoxy ligand possessing both a methoxy and an olefinic dangling side-arms. In the corresponding heteroleptic charge neutral calcium and strontium complexes **1** and **2**, the ether moiety binds intramolecularly to the metal, but the olefin remains fully dissociated. Olefin coordination was enforced successfully upon cationisation, yielding the bis-ether adducts **3a** and **4a**, from which crystals of the mono-water adduct $[(\{\mu^2\text{-RO}^F\}\text{Sr}\bullet(\text{H}_2\text{O}))_2]^{2+}$ (**4b**$^{2+}$) were isolated. Crystals of this dication free of coordinated water could unfortunately not be obtained, despite repeated attempts. Evidently, the complex traps even the tiniest traces of residual moisture owing to the extreme electron deficiency of **4b**$^{2+}$. We are now pursuing alternative pathways for the preparation of cationic Ae-olefin compounds devoid of coordinated solvent, a prelude for the computational analysis of the bonding by DFT methods. We should also mention that in the course of the present work, we have also prepared complexes stabilised by other π ligands, that is, where the dangling olefin groups in $\{\text{RO}^F\}\text{H}$ is replaced by a phenyl group. The neutral heteroleptic complexes akin to **1** and **2** were successfully prepared and structurally characterised, but the resulting cations were isolated and recrystallised as mono-Et_2O adducts which did not show coordination of the aromatic moiety onto the alkaline earths.

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Experimental section

General procedures. All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; $O_2 < 1$ ppm, $H_2O < 5$ ppm). CaI_2 and SrI_2 (both from Aldrich, 99.999%, anhydrous beads), and 2,2-bis(trifluoromethyl)oxirane (Apollo Scientific) were used as received. $HN(SiMe_2H)_2$ (ABCR) was dried over CaH_2 and distilled prior to use. $[Ca[N(SiMe_2H)_2]_2•(THF)]$ and $[Sr[N(SiMe_2H)_2]_2•(THF)_{2/3}]$,[25a] as well as the salt $[H(OEt_2)_2]^+•[H_2N\{B(C_6F_5)_3\}_2]^-$,[22] were prepared following the literature protocol. Solvents (THF, Et_2O, CH_2Cl_2, pentane and toluene) were purified and dried (water contents all below 10 ppm) over alumina columns (MBraun SPS). THF was further distilled under argon from sodium mirror/benzophenone ketyl. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze-thaw-vacuum cycles.

NMR spectra were recorded on a Bruker spectrometer Avance III 400 MHz equipped with a BBOF pulsed field-gradient probe or a Bruker spectrometer Avance 500 MHz equipped with a dual pulse field gradient probehead. All ^1H and ^{13}C chemicals shifts were determined using residual signals of the deuterated solvents and were calibrated *vs*. $SiMe_4$. $^{19}F\{^1H\}$ chemical shifts were determined by external reference to an aqueous solution of $NaBF_4$. Assignment of the signals was carried out using 1D (^1H, $^{13}C\{^1H\}$) and 2D (COSY, edited HSQC and HMBC) NMR experiments.

Elemental analyses were performed on a Carlo Erba 1108 Elemental Analyzer instrument at the London Metropolitan University by Stephen Boyer and were the average of two independent measurements; they were complicated by the extreme air-sensitivity of the complexes. The averaged values are reported together with the deviation. ESI mass spectra were recorded on a Bruker MicrOTOF-Q II spectrometer with a QqoaTOF geometry.

***N*-(2-methoxyethyl)but-3-en-1-amine.**

Adapting from a known procedure,[29] a mixture of 2-methoxyethylamine (8.64 g, 11.5 mmol) and 1 equiv of 4-bromo-1-butene (1.55 g, 11.5 mmol) was refluxed at 110 °C for 3 days. All volatiles were then removed under vacuum. H_2O (20 mL) was added to the reaction mixture. After separation of the two layers, the organic fraction was acidified by addition of aqueous HCl 5% to *p*H = 3. The two layers were separated and the aqueous phase was back-extracted with Et_2O (2 × 100 mL). The aqueous phase was then neutralised by slow addition of concentrated aqueous NaOH to pH = 12. To this solution, Et_2O (100 mL) was then added. The organic phase was separated and the aqueous phase was further extracted with Et_2O (3 × 50 mL). The combined organic layers were dried over $MgSO_4$. Removal of the solvent yielded the secondary amine in 74% yield (1.10 g). ^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K): δ 5.75 (ddt, 1H, $^3J_{\text{H-H}}$ (*trans*) = 17.0 Hz, $^3J_{\text{H-H}}$ (*cis*) = 10.2 Hz, $^3J_{\text{H-H}}$ = 6.8 Hz, C*H*=CH$_2$), 5.08–4.94 (m, 2H, CH=C*H*$_2$), 3.29 (t, 2H, $^3J_{\text{H-H}}$ = 5.3 Hz, C*H*$_2$OCH$_3$), 3.09 (s, 3H, OC*H*$_3$), 2.65 (t, 2H, $^3J_{\text{H-H}}$ = 5.3 Hz, C*H*$_2$CH$_2$OCH$_3$), 2.54 (t, 2H, $^3J_{\text{H-H}}$ = 6.9 Hz, NC*H*$_2$CH$_2$CH=CH$_2$), 2.16-2.07 (m, 2H, NCH$_2$C*H*$_2$CH=CH$_2$), 1.17 (br s, 1H, N*H*) ppm.

{RO$^{\text{F}}$}H.

To a solution of *N*-(2-methoxyethyl)but-3-en-1-amine (1.10 g, 8.50 mmol) in Et_2O (10 mL) was added 2,2-bis(trifluoromethyl)oxirane (1.70 g, 9.35 mmol) at room temperature. The reaction mixture was left to stir for 4 days. Removal of the volatiles followed by drying *in vacuo* afforded {RO$^{\text{F}}$}H as a colourless oil. Yield 2.03 g (78%). ^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K): 6.57 (s, 1H, O*H*), 5.53 (ddt, 1H, $^3J_{\text{H-H}}$ (*trans*) = 19.1 Hz, $^3J_{\text{H-H}}$ (*cis*) = 9.6 Hz, $^3J_{\text{H-H}}$ = 6.8 Hz,

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C*H*=CH_2), 4.98–4.91 (m, 2H, CH=C*H*$_2$), 2.96 (s, 3H, OC*H*$_3$), 2.92 (t, 2H, $^3J_{\text{H-H}}$ = 5.1 Hz, C*H*$_2$OCH_3), 2.85 (s, 2H, C*H*$_2$(CF_3)$_2$), 2.44–2.38 (m, 2H, C*H*$_2$$CH_2$CH=$CH_2$), 2.36 (t, 2H, $^3J_{\text{H-H}}$ = 5.1 Hz, C*H*$_2$$CH_2OCH_3$), 1.90 (q, 2H, $^3J_{\text{H-H}}$ = 7.5 Hz, CH_2C*H*$_2$CH=CH_2) ppm. ^{13}C{^{1}H} NMR (benzene-*d*$_6$, 100.62 MHz, 298 K): δ 135.61 (*C*H=CH_2), 124.39 (q, $^1J_{\text{C-F}}$ = 286.7 Hz, *C*F$_3$), 116.78 (CH=*C*H$_2$), 73.47 (hept, $^2J_{\text{C-F}}$ = 28.7 Hz, *C*(CF_3)$_2$), 69.73 (*C*H$_2$OCH_3), 58.38 (O*C*H$_3$), 54.71 (*C*H$_2$$CH_2OCH_3$), 54.19 (*C*H$_2$$CH_2$CH=$CH_2$), 53.49 (*C*H$_2$C($CF_3$)$_2$), 31.42 ($CH_2$*C*H$_2$CH=$CH_2$) ppm. ^{19}F{^{1}H} NMR (benzene-*d*$_6$, 376.44 MHz, 298 K): −77.51 (s, 6F, C*F*$_3$) ppm. Elemental analysis for $C_{11}H_{17}F_6NO_2$ (309.12 g mol^{-1}): theoretical, C 42.7%, H 5.5%, N 4.5%; found C 42.7%, H 5.7%, N 4.4%. Mass spectrometry ESI [M + Na$^+$] ($C_{11}H_{17}F_6NO_2Na$) *m/z* theoretical: 332.1061; found 332.1056.

[{μ^2-RO^F}CaN(SiMe$_2$H)$_2$]$_2$ (1).

A solution of {RO}H (0.24 g, 0.82 mmol) in Et_2O (10 mL) was added at −78 °C over a period of 1 h to a solution of [Ca[N(SiMe$_2$H)$_2$]$_2$•(THF)] (0.40 g, 1.06 mmol) in Et_2O (10 mL). The reaction mixture was warmed to room temperature and, after stirring for a further 1 h, the volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 × 2 mL) and washed with the same solvent (2 × 2 mL) to afford **1** as a colourless powder (0.25 g, 76%). Crystals suitable for X-ray diffractometry were obtained from a pentane solution stored at –30 °C. ^{1}H NMR (benzene-*d*$_6$, 400.13 MHz, 298 K): δ 5.57 (ddt, 1H, $^3J_{\text{H-H}}$ (*trans*) = 13.7 Hz, $^3J_{\text{H-H}}$ (*cis*) = 10.3 Hz, $^3J_{\text{H-H}}$ = 6.5 Hz, C*H*=CH_2), 5.11–4.93 (m, 2H, CH=C*H*$_2$), 4.88 (s, 2H, $^1J_{\text{Si-H}}$ = 162 Hz, Si*H*), 3.11 (s, 3H, OC*H*$_3$), 2.97–2.81 (overlapping m, 3H, C*H*$_2$OCH_3 and C(*H*)HCH_2OCH_3), 2.82–2.65 (m, 2H, C*H*$_2$$CH_2$CH=$CH_2$), 2.73 (ABq, 2H, J_{AB} = 15.1 Hz, C*H*$_2$C(CF_3)$_2$), 2.04–1.92 (m, 2H, C(H)*H*CH_2OCH_3 and CH_2C(*H*)HCH=CH_2), 1.90–1.75 (m, 1H, CH_2C(H)*H*CH=CH_2), 0.46 (d, $^3J_{\text{H-H}}$ = 2.6 Hz, 12H, SiC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (benzene-*d*$_6$, 100.63 MHz, 298 K): δ 134.95

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(*C*H=CH$_2$), 125.99 (q, $^1J_{\text{C-F}}$ = 288.9 Hz, *C*F$_3$), 125.72 (q, $^1J_{\text{C-F}}$ = 290.1 Hz, *C*F$_3$), 116.91 (CH=*C*H$_2$), 79.31 (hept, *C*(CF$_3$)$_2$, $^2J_{\text{C-F}}$ = 26.2 Hz), 69.08 (*C*H$_2$OCH$_3$), 60.36 (O*C*H$_3$), 54.79 (*C*H$_2$C(CF$_3$)$_2$), 53.97 (*C*H$_2$CH$_2$OCH$_3$), 52.01 (N*C*H$_2$CH$_2$CH=CH$_2$), 27.30 (NCH$_2$*C*H$_2$CH=CH$_2$), 5.14 (Si*C*H$_3$), 4.84 (Si*C*H$_3$) ppm. ^{19}F{^{1}H} NMR (benzene-*d*$_6$, 376.47 MHz, 298 K): δ –76.78 (q, 6F, $^4J_{\text{F–F}}$ = 9.3 Hz, C*F*$_3$), –78.02 (q, 6F, $^4J_{\text{F–F}}$ = 9.1 Hz, C*F*$_3$) ppm. Elem. Anal. for $C_{15}H_{30}CaF_6N_2O_2Si_2$ (480.66 g mol^{-1}): calcd C 37.5%, H 6.3%, N 5.8%; found C 37.3%, H 6.2%, N 5.7%.

[{μ^2-RO^F}SrN(SiMe$_2$H)$_2$]$_2$ (2).

A solution of {RO}H (0.18 g, 0.57 mmol) in Et$_2$O (10 mL) was added at −78 °C over 1 h to a solution of [Sr[N(SiMe$_2$H)$_2$]$_2$•(THF)$_{⅔}$] (0.31 g, 0.76 mmol) in Et$_2$O (10 mL). The reaction mixture was warmed to room temperature and, after stirring a further 1 h, the volatiles were pumped off. The resulting oil was stripped with pentane (3 × 3 mL) and washed with this solvent (2 × 2 mL) to afford **2** as a colourless powder (0.21 g, 71%). Crystals suitable for X-ray diffractometry were grown from a pentane solution at –30 °C. ^{1}H NMR (benzene-*d*$_6$, 400.13 MHz, 298 K): δ 5.56 (ddt, 1H, $^3J_{\text{H-H}}$ (*trans*) = 17.1 Hz, $^3J_{\text{H-H}}$ (*cis*) = 10.2 Hz, $^3J_{\text{H-H}}$ = 6.5 Hz, C*H*=CH$_2$), 5.09–4.97 (m, 2H, CH=C*H*$_2$), 4.95 (s, 2H, $^1J_{\text{Si-H}}$ = 162 Hz, Si*H*), 3.00 (s, 3H, OC*H*$_3$), 2.92–2.81 (m, 2H, C*H*$_2$OCH$_3$), 2.81–2.71 (m, 1H, C(*H*)HCH$_2$OCH$_3$), 2.70–2.57 (m, 1H, NC(*H*)HCH$_2$CH=CH$_2$), 2.65 (ABq, 2H, J_{AB} = 15.1 Hz, C*H*$_2$C(CF$_3$)$_2$), 2.55–2.42 (m, 1H, NC(H)*H*CH$_2$CH=CH$_2$), 2.12–1.80 (overlapping m, 3H, NCH$_2$C*H*$_2$CH=CH$_2$ and C(H)*H*CH$_2$OCH$_3$), 0.47 (s, 12H, SiC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (benzene-*d*$_6$, 100.63 MHz, 298 K): δ 134.84 (*C*H=CH$_2$), 126.60 (q, $^1J_{\text{C-F}}$ = 288.9 Hz, *C*F$_3$), 126.15 (q, $^1J_{\text{C-F}}$ = 290.1 Hz, *C*F$_3$), 117.03 (CH=*C*H$_2$), 79.87 (hept, *C*(CF$_3$)$_2$, $^2J_{\text{C-F}}$ = 25.3 Hz), 69.20 (*C*H$_2$OCH$_3$), 59.61 (O*C*H$_3$), 52.26 (*C*H$_2$C(CF$_3$)$_2$ and *C*H$_2$CH$_2$OCH$_3$), 52.16 (N*C*H$_2$CH$_2$CH=CH$_2$), 28.33 (NCH$_2$*C*H$_2$CH=CH$_2$), 5.02

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(Si*C*H$_3$), 4.85 (Si*C*H$_3$) ppm. ^{19}F{^{1}H} NMR (benzene-*d*$_6$, 376.47 MHz, 298 K): *δ* –77.37 (q, 6F, $^4J_{F–F}$ = 9.1 Hz, C*F*$_3$), –78.41 (q, 6F, $^4J_{F–F}$ = 9.2 Hz, C*F*$_3$) ppm. Elem. Anal. for $C_{15}H_{30}SrF_6N_2O_2Si_2$ (528.20 g mol^{-1}): calcd C 34.1%, H 5.7%, N 5.3%; found C 33.9%, H 5.6%, N 5.2%.

[({μ^2-RO^F}Ca•(Et$_2$O)$_2$)$_2$]$^{2+}$.2[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (3a).

Complex **1** (50 mg, 0.10 mmol) and [H•(OEt$_2$)$_2$]$^+$.[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (125 mg, 0.10 mmol) were dissolved in Et$_2$O (10 mL) and reacted overnight. A colourless precipitate formed immediately upon stirring. After overnight stirring, the precipitate was isolated by filtration, washed with pentane (3 × 10 mL) and dried *in vacuo* to constant weight to give **3a** as a colourless powder (54 mg, 34%). ^{1}H NMR (dichloromethane-*d*$_2$, 400.13 MHz, 298 K): *δ* 5.93-5.74 (m, 1H, C*H*=CH$_2$), 5.68 (br s, 2H, N*H*$_2$), 5.30-5.19 (m, 2H, CH=C*H*$_2$), 4.01-3.90 (m, 1H, C(*H*)HOCH$_3$), 3.82-3.75 (m, 1H, C(H)*H*OCH$_3$), 3.72-3.62 (overlapping m, 11H, OC*H*$_3$ and OC*H*$_2$CH$_3$), 3.43-3.32 (m, 1H, C(*H*)H(CF$_3$)$_2$), 3.16-2.89 (overlapping m, 3H, C(H)*H*(CF$_3$)$_2$ and C*H*$_2$CH$_2$OCH$_3$), 2.82 (t, $^3J_{H–H}$ = 7.84 Hz, 2H, NC*H*$_2$CH$_2$CH=CH$_2$), 2.48-2.21 (m, 2H, NCH$_2$C*H*$_2$CH=CH$_2$), 1.27 (t, $^3J_{H–H}$ = 7.1 Hz, 12H, OCH$_2$C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (dichloromethane-*d*$_2$, 100.63 MHz, 298 K): *δ* 149.65, 147.24, 141.03, 138.45, 138.32 (all *C*$_6$F$_5$), 136.02 (*C*H=CH$_2$), 119.63 (CH=*C*H$_2$), 71.03 (*C*H$_2$OCH$_3$), 66.58 (O*C*H$_2$CH$_3$), 61.85 (O*C*H$_3$), 52.66 (N*C*H$_2$CH$_2$CH=CH$_2$ or NC*H*$_2$CH$_2$OCH$_3$ or *C*H$_2$(CF$_3$)$_2$), 30.28 (NCH$_2$*C*H$_2$CH=CH$_2$), 14.87 (OCH$_2$*C*H$_3$) ppm. The resonances for *C*F$_3$ and *C*(CF$_3$)$_2$ were not detected. The resonances for either NC*H*$_2$CH$_2$OCH$_3$, N*C*H$_2$CH$_2$CH=CH$_2$ or *C*H$_2$(CF$_3$)$_2$ overlap with the solvent peak and therefore cannot be assigned. ^{19}F{^{1}H} NMR (dichloromethane-*d*$_2$, 376.47 MHz, 298 K): *δ* –76.87 to –77.06 (m, 3F, C*F*$_3$), –77.52 to –77.67 (m, 1F, C*F*$_3$), –77.79 to –77.98 (m, 2F, C*F*$_3$), –132.94 (d, $^3J_{F–F}$ = 18.62 Hz, 12F, *o*-C$_6$*F*$_5$), –160.26 (t, $^3J_{F–F}$ = 20.58 Hz, 6F, *p*-C$_6$*F*$_5$), –165.79 (t, $^3J_{F–F}$ = 19.06 Hz, 12F, *m*-C$_6$*F*$_5$) ppm. ^{11}B NMR

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(dichloromethane-d_2, 128.40 MHz, 298 K): δ –8.41 ppm. Satisfactory elemental analysis for **3a** could not be obtained in spite of repeated attempts.

$[(\{\mu^2\text{-RO}^F\}\text{Sr}\bullet(\text{Et}_2\text{O})_2)_2]^{2+}.2[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ (4a).

Complex **2** (80 mg, 0.15 mmol) and $[\text{H}\bullet(\text{OEt}_2)_2]^+.[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ (180 mg, 0.15 mmol) were dissolved in Et_2O (10 mL). A colourless precipitate formed immediately upon stirring. After overnight stirring, the precipitate was isolated by filtration, washed with pentane (3 × 10 mL) and dried under vacuum to give **4a** as a colourless powder (130 mg, 54%). Crystals of $[(\{\mu^2\text{-RO}^F\}\text{Sr}\bullet(\text{H}_2\text{O}))_2]^{2+}.2[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ (**4b**) suitable for X-ray diffraction were grown from a concentrated CH_2Cl_2 solution at room temperature. ^{1}H NMR (dichloromethane-d_2, 400.16 MHz, 298 K): δ 5.92-5.75 (m, 1H, C*H*=CH$_2$), 5.69 (br s, 2H, N*H*$_2$), 5.30-5.20 (m, 2H, CH=C*H*$_2$), 4.00-3.86 (m, 1H, C(*H*)HOCH$_3$), 3.78-3.65 (m, 1H, C(H)*H*OCH$_3$), 3.78-3.65 (overlapping m, 11H, OC*H*$_3$ and OC*H*$_2$CH$_3$), 3.32 (d, $^2J_{\text{H–H}}$ = 15.7 Hz, 1H, C(*H*)H(CF$_3$)$_2$), 3.13-2.63 (overlapping m, 5H, C(H)*H*(CF$_3$)$_2$, NC*H*$_2$CH$_2$CH=CH$_2$ and C*H*$_2$CH$_2$OCH$_3$), 2.50-2.21 (m, 2H, NCH$_2$C*H*$_2$CH=CH$_2$), 1.22 (t, $^3J_{\text{H–H}}$ = 7.1 Hz, 12H, OCH$_2$C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (dichloromethane-d_2, 100.63 MHz, 298 K): δ 149.67, 147.32, 140.93, 138.52, 136.14 (all *C*$_6$F$_5$), 136.67 (*C*H=CH$_2$), 120.06 (CH=*C*H$_2$), 70.80 (*C*H$_2$OCH$_3$), 66.42 (O*C*H$_2$CH$_3$), 61.14 (O*C*H$_3$), 55.66 (*C*H$_2$C(CF$_3$)$_2$), 52.44 (N*C*H$_2$CH$_2$CH=CH$_2$), 30.29 (NCH$_2$*C*H$_2$CH=CH$_2$), 15.43 (OCH$_2$*C*H$_3$) ppm. The resonances for *C*F$_3$, *C*(CF$_3$)$_2$, and N*C*H$_2$CH$_2$OCH$_3$ could not be detected; the resonance for N*C*H$_2$CH$_2$OCH$_3$ most likely overlaps with the solvent signals. ^{19}F{^{1}H} NMR (dichloromethane-d_2, 376.47 MHz, 298 K): δ –76.44 to –77.76 (m, 3F, C*F*$_3$), –76.94 to –77.16 (m, 1F, C*F*$_3$), –77.55 to –77.80 (m, 2F, C*F*$_3$), –132.89 (d, $^3J_{\text{F–F}}$ = 18.10 Hz, 12F, *o*-C$_6$*F*$_5$), –160.23 (t, $^3J_{\text{F–F}}$ = 20.10 Hz, 6F, *p*-C$_6$*F*$_5$), –165.75 (t, $^3J_{\text{F–F}}$ = 19.65 Hz, 12F, *m*-C$_6$*F*$_5$) ppm. ^{11}B NMR (dichloromethane-d_2, 128.40 MHz, 298 K): δ –8.43 ppm. Elemental analysis could not be

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performed reliably for this compound, most likely owing to its high sensitivity, or perhaps due to erratic contamination by adventitious water or other Lewis bases.

X-ray diffraction crystallography. Crystals of **1**, **2** and **4b** suitable for X-ray diffraction analysis were obtained by recrystallisation of the purified products. Diffraction data were collected at 150 K using a D8 VENTURE Bruker AXS diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Relevant collection and refinement data are summarised in Table 1. Crystal data and details of data collection and structure refinement for the three complexes (CCDC 1570851-1570853) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The structure of **1** was solved by dual-space algorithm using the SHELXT program,[30] and then refined with full-matrix least-square methods based on F2(SHELXL).[31] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except Si-linked hydrogen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. A final refinement on F2 with 5457 unique intensities and 291 parameters converged at ωR(F2) = 0.1191 (R(F) = 0.0504) for 4086 observed reflections with I > 2σ(I).

The structure of **2** was solved by dual-space algorithm using the SHELXT program,[30] and then refined with full-matrix least-square methods based on F2(SHELXL).[31] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except Si-linked hydrogen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. A final refinement on F2 with 5625 unique

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intensities and 277 parameters converged at ωR(F2) = 0.0929 (R(F) = 0.0432) for 3892 observed reflections with $I > 2\sigma(I)$.

The structure of **4b** was solved by dual-space algorithm using the SHELXT program,[30] and then refined with full-matrix least-square methods based on F2(SHELXL).[31] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except O-linked hydrogen atoms in water molecules that were introduced in the structural model from calculated positions by the method of Nardelli,[32] H atoms were finally included in their calculated positions. A final refinement on F2 with 12066 unique intensities and 824 parameters converged at ωR(F2) = 0.1961 (R(F) = 0.0880) for 6574 observed reflections with $I > 2\sigma(I)$.

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Table 1 Summary of crystallographic data for complexes **1**, **2** and **4b**.

	$[\{\mu^2\text{-RO}^F\}\text{CaN(SiMe}_2\text{H)}_2]_2$ (**1**)	$[\{\mu^2\text{-RO}^F\}\text{SrN(SiMe}_2\text{H)}_2]_2$ (**2**)	$[(\{\mu^2\text{-RO}^F\}\text{Sr}\bullet(\text{H}_2\text{O}))_2]^{2+}$ $.2[\text{H}_2\text{N}\{\text{B(C}_6\text{F}_5)_3\}_2]^-$ (**4b**)
Formula	C30 H64 Ca2 F12 N4 O4 Si4	C30 H64 F12 N4 O4 Si4 Sr2	C96 H44 B4 Cl4 F72 N4 O6 Sr2
CCDC	1570851	1570852	1570853
Mol. wt.	965.37	1056.42	3077.63
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P\ 2_1/n$	$P\ 2_1/n$	$P\ 2_1/n$
a (Å)	10.4222(3)	10.5669(6)	11.8244(12)
b (Å)	16.7411(6)	17.1007(9)	14.3892(14)
c (Å)	14.0517(5)	13.9454(8)	31.655(3)
α (°)	90	90	90
β (°)	102.7440(10)	102.799(2)	93.679(3)
γ (°)	90	90	90
V (Å^3)	2391.33(14)	2457.3(2)	5374.9(9)
Z	2	2	2
Density (g/cm^3)	1.341	1.428	1.902
Abs. coeff., (mm^{-1})	0.421	2.348	1.274
F(000)	1016	1068	3016
Crystal size, mm	0.60 × 0.40 × 0.25	0.42 × 0.26 × 0.09	0.31 × 0.21 × 0.02
θ range (°)	2.973 to 27.480	2.980 to 27.481	2.942 to 27.481
Limiting indices	$-12 < h < 13$ $-21 < k < 21$ $-18 < l < 18$	$-13 < h < 13$ $-19 < k < 22$ $-18 < l < 18$	$-15 < h < 13$ $-18 < k < 18$ $-41 < l < 41$
R(int)	0.0418	0.1001	0.1405
Reflections collected	22661	25392	39315
Refl. Unique [$I>2\sigma(I)$]	4086	5625	12066
Completeness to θ	0.995	0.999	0.978
Data/restraints/param.	5457 / 2 / 291	5625 / 0 / 277	12066 / 5 / 824
Goodness-of-fit	1.060	1.015	1.049
R_1 [$I>2\sigma(I)$] (all data)	0.0504 (0.0758)	0.0432 (0.0820)	0.0880 (0.2113)
wR_2 [$I>2\sigma(I)$] (all data)	0.1191 (0.1355)	0.0929 (0.1093)	0.1961 (0.2312)
Largest diff. (e·A^{-3})	0.325 and –0.541	0.610 and –1.018	0.889 and –1.306

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Conflicts of interest. There are no conflicts of interest to declare.

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Electronic Supporting Information. NMR spectra for **1-4**; Molecular structures of $[(\{\mu^2\text{-RO}^F\}\text{Ca}\bullet(\text{H}_2\text{O}))_2]^{2+}.2[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ and $[(\{\mu^2\text{-RO}^F\}\text{Ca}\bullet(\text{Et}_2\text{O}))_2]^{2+}.2[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$.

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Table of Contents for

Tethered cationic alkaline earth – olefin complexes

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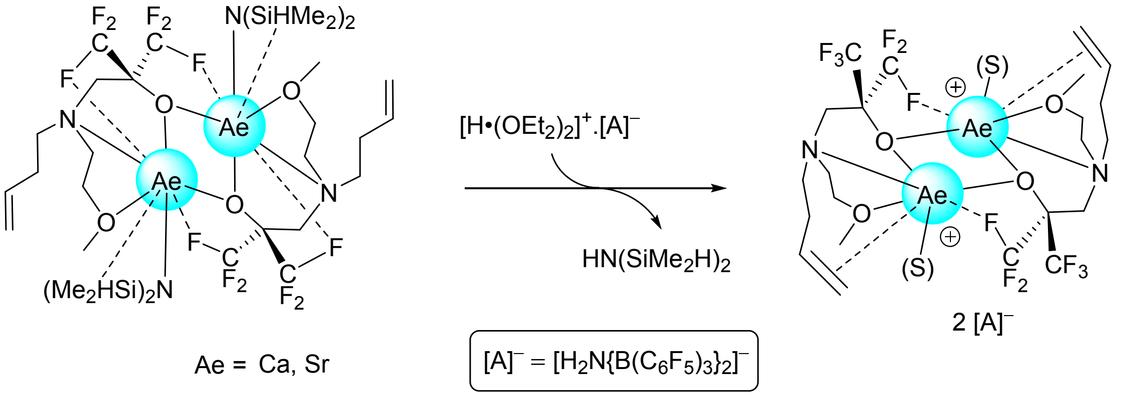

The utilisation of a specifically tailored aminofluoroalcohol possessing both a methoxy and an olefin dangling side arms enables the preparation of the first examples of a discrete calcium- and strontium-olefin cationic complexes.