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π Ligands in AlkalineEarth Complexes

Sorin-Claudiu Roşca, Elsa Caytan, Vincent Dorcet,

Thierry Roisnel, Jean-François Carpentier,* and Yann Sarazin*

Université de Rennes 1, CNRS, UMR 6226, Institut des Sciences Chimiques de Rennes,
Campus de Beaulieu, 35042 Rennes Cedex, France.

Graphic for the Table of Contents

Abstract

π ligands such as olefins and alkynes bind intramolecularly to the metal atom in d^0 complexes of the large alkaline earths (Ae) calcium and strontium supported by fluoroalkoxo ligands with dangling unsaturated C=C or C $\equiv$ C bonds, and having the amide N(SiMe₂H)₂[−] as the co-ligand. These *O*-bridged dinuclear complexes are further stabilized by secondary C–F→Ae and β -Si–H $\cdots$ Ae interactions. In a set of structurally related Ca-olefin complexes, the strength of these interactions gradually increases as the coordination of the olefin onto Ca²⁺ becomes weaker (from η^2 -coordinated to η^1 to fully dissociated) upon increasing steric congestion, thus ensuring that overwhelming electronic depletion does not occur at calcium. NMR data imply that the olefins are metal-bound in [D₈]toluene solutions. The Ae $\cdots$ C π , C–F→Ae and β -Si–H $\cdots$ Ae non-covalent interactions are also strong in the parent Ae-alkyne complexes, the first examples of non-acetylide Ae-alkynes compounds. Calcium-arene complexes could not be made, as the aromatic tether did not bind to the metal atom. Instead, a trinuclear complex with non-interacting C₆H₅ groups was obtained. It exhibits exceptionally strong C–F→Ca and β -Si–H $\cdots$ Ca interactions. NMR data indicate that the congeneric calcium-allene complex can be made, but it spontaneously isomerizes towards the more stable Ca-alkyne via an unusual 1,3-hydride shift intramolecular process.

Introduction

Divalent cations Ae^{2+} of the alkaline earths (Ae) calcium, strontium and barium are large (effective ionic radii: 1.00, 1.18 and 1.35 Å for C. N. = 6), polarisable and electrophilic. They form d^0 complexes that feature ionic, non-directional bonding with no propensity for π bonding due to the inability to convey $d-\pi^*$ back-donation. Following Westerhausen's syntheses of mesitylcalcium iodide,¹ diarylcalcium,² arylcalcium cations,³ and 1-alkenyl and alkyl calcium iodides,⁴ the organometallic chemistry of calcium has achieved a significant status.⁵ However, non-covalent interactions between alkaline earths and π ligands remain little explored. Hence, very few Ae-olefin complexes of Ca-Ba are known.⁶ Until recently,⁷ the only structurally authenticated Ae-olefin complexes were Schumann's $[\text{Ae}(\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2]$ (Ae = Ca-Ba)⁸ and Roesky's $[\text{Ba}(\text{C}_5\text{Me}_5)(\text{C}_5\text{Me}_4\text{CH}_2\text{C}_5\text{Me}_5)]$.⁹ Even if Ae-cyclopentadienyl and -allyl complexes are known,¹⁰ the paucity of pure Ae-olefin complexes is surprising. Similarly, although π interactions between Ae^{2+} divalent cations and charge-neutral arenes have been probed computationally,¹¹ Ae-arene adducts are rare. In the known examples, $\text{Ae}^{2+} \cdots \text{arene}$ η^6 -interactions are most often encountered, as in $[\{\text{N}_3\text{ArAr}'\}\text{AeC}_6\text{F}_5]$ (Ae = Ca-Ba) bearing aryl-substituted triazenides,¹² in bis[*N*-(2,6-diisopropylphenyl)-*N'*-(2-pyridylmethyl)pivalamidinate] and bis[*N*-diisopropylphenyl-*N'*-(8-quinolyl)pivalamidinate] calcium complexes,¹³ in the heterobimetallic $[\text{Ca}_2\text{Odpp}_3]^+ \cdot [\text{LnOdpp}_4]^-$ (Ln = Nd, Ho, Yb; Odpp = 2,6-diphenyl-phenolate),¹⁴ in $[\{\text{DippNacNac}\}\text{CaN}(\eta^2\text{-C}_6\text{H}_5)(\text{C}_6\text{H}_5) \cdot \text{THF}]$ ($\text{DippNacNac} = \text{CH}[\text{CMeN}(2,6\text{-iPr}_2\text{-C}_6\text{H}_3)]_2$),¹⁵ and in the bis(guanidinate) barium complex $[\{\text{MesN}\{\text{C}(\text{NCy}_2)\}\text{NMes}\}_2\text{Ba}]$ where Mes = 2,4,6-Me₃C₆H₂ and Cy = cyclohexyl.¹⁶ Other types of $\text{Ae}^{2+} \cdots \text{arene}$ interactions have been reported in Ae_2Odpp_4 (Ae = Ca-Ba, η^1 to η^6 interactions),¹⁷ and in the iodocalcium-cuprate(I) $[\text{ICa-}\eta^1, \eta^6\text{-(Mes}_2\text{Cu)}]_4$.¹⁸ Ae-alkyne complexes are somewhat more common. $[\{\text{C}_5\text{Me}_5\}_2\text{Ca}\{\text{MeSi}_3\text{-C}\equiv\text{C-C}\equiv\text{C-SiMe}_3\}]$ was the

first monomeric diyne complex of a main-group metal.¹⁹ Since then, “side-on” interactions between Ae metalcentres and C≡C triple bonds have been observed in dimeric acetylides²⁰ such as $[\{\text{DippNacNac}\}\text{Ca}(\mu\text{-C}\equiv\text{C-R})]_2$ (R = Ph, *p*-tol) and $[\{\text{DippNacNac}\}\text{Ca}(\mu\text{-C}\equiv\text{C-CH}_2\text{-E})]_2$ (E = OMe, OPh, NMe₂),²¹ or in the THF solvate $[\{\text{DippNacNac}\}\text{Ca}(\mu\text{-C}\equiv\text{C-Ph})\cdot(\text{THF})]_2$.²² A single side-on barium-alkyne complex, obtained by treatment of $[\text{Ba}\{\text{P}(\text{SiMe}_3)_2\}_2\cdot(\text{THF})_4]$ with diphenylbutadiyne, is known.²³ Finally, no example of π -interaction in Ae-allene complexes has appeared to date.

Following a landmark review article by Ruhlandt-Senge,²⁴ we have used secondary interactions to stabilize otherwise kinetically labile Ae heteroleptic complexes by $\beta\text{-Si-H}\cdots\text{Ae}$ agostic distortions²⁵ or by cation-dipole $\text{C-F}\rightarrow\text{Ae}$ interactions.^{26,27} We have then become keen on exploiting olefins and other π ligands to synthesize model Ae complexes which could help unravel the mechanisms of Ae-promoted olefin and alkyne hydroelementations.

We have earlier shown that the calcium- and strontium-olefin complexes $[\{\text{RO}^1\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$ (**[1-Ca]₂**) and $[\{\text{RO}^1\}\text{SrN}(\text{SiMe}_2\text{H})_2]_2$ (**[1-Sr]₂**) stabilized by intramolecular $\beta\text{-Si-H}\cdots\text{Ae}$ and $\text{C-F}\rightarrow\text{Ae}$ interactions could be synthesized upon treatment of $[\text{Ca}[\text{N}(\text{SiMe}_2\text{H})_2]_2\cdot(\text{THF})]$ or $[\text{Sr}[\text{N}(\text{SiMe}_2\text{H})_2]_2\cdot(\text{THF})_{2/3}]$ with the $\alpha,\alpha\text{-(CF}_3)_2\text{-alcohol}$ $\{\text{RO}^1\}\text{H}$ having a single dangling terminal olefinic tether (Scheme 1).⁷ The related $[\{\text{RO}^2\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$ (**[2-Ca]₂**) and $[\{\text{RO}^3\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$ (**[3-Ca]₂**), where the olefin in the ligands $\{\text{RO}^2\}^-$ and $\{\text{RO}^3\}^-$ is substituted respectively by one (*Z* configuration) and two methyl groups on the carbon atom in δ position from the N_{amine} atom, were also obtained. Coordination of the internal olefin onto the alkaline earths in **[1-Ca]₂**, **[1-Sr]₂**, **[2-Ca]₂** and **[3-Ca]₂** was evidenced by crystallographic methods. It was shown to be thermodynamically favoured over the coordination of external Lewis bases (THF). NMR data and DFT computations further attested to the existence of $\text{Ae}\cdots\text{olefin}$ interactions. Upon increasing steric hindrance about the olefin, olefin coordination switched from η^2 in **[1-Ca]₂**

and $[\mathbf{1-Sr}]_2$ to η^1 in $[\mathbf{2-Ca}]_2$ and to complete dissociation in $[\mathbf{3-Ca}]_2$. This was however compensated by the other $\beta\text{-Si-H}\cdots\text{Ae}$ and $\text{C-F}\rightarrow\text{Ae}$ interactions, which conversely became increasingly strong.

Scheme 1. Structures of complexes $[\{\text{RO}^x\}\text{AeN}(\text{SiMe}_2\text{H})_2]_2$, with secondary interactions as dashed lines. $x = 1$, Ae = Ca, $[\mathbf{1-Ca}]_2$; $x = 1$, Ae = Sr, $[\mathbf{1-Sr}]_2$; $x = 2$, Ae = Ca, $[\mathbf{2-Ca}]_2$; $x = 3$, Ae = Ca, $[\mathbf{3-Ca}]_2$; $x = 4$, Ae = Ca, $[\mathbf{4-Ca}]_2$. Positions of the C atoms labelled in the frame. For the syntheses and characterization of $[\mathbf{1-Ca}]_2$, $[\mathbf{1-Sr}]_2$, $[\mathbf{2-Ca}]_2$ and $[\mathbf{3-Ca}]_2$, see reference 7.

We report hereon related alkene, alkyne, arene and allene fluoroalkoxo calcium and strontium complexes showing interactions between the π ligands and the alkaline earths.

Results

General synthetic features

A range of calcium and strontium complexes supported by fluorinated aminoalkoxides $\{\text{RO}^x\}^-$ bearing pendant alkene, alkyne, arene or allene tethers, and incorporating the amide $\text{N}(\text{SiMe}_2\text{H})_2^-$ as a co-ligand, were synthesized (Scheme 2); specifics are given further. Typical syntheses involved the 1:1 reaction of $[\text{Ae}[\text{N}(\text{SiMe}_2\text{H})_2]_2 \cdot (\text{THF})_n]$ ($\text{Ae} = \text{Ca}$, $n = 1$; Sr , $n = 2/3$) with the proteo-ligand $\{\text{RO}^x\}\text{H}$ in diethyl ether (Ae precursor used in slight excess to avoid forming $[\{\text{RO}^x\}_2\text{Ae}]$), with temperature raising from -78 to 25°C . The heteroleptic, dinuclear complexes $[\{\text{RO}^x\}\text{AeN}(\text{SiMe}_2\text{H})_2]_2$ were generally obtained in moderate to high yields upon release of $\text{HN}(\text{SiMe}_2\text{H})_2$ and displacement of THF. All complexes were isolated as very air- and moisture-sensitive, colourless, analytically pure solids. Synthetic and characterization details for all compounds are given in the Supporting Information.

Scheme 2. General representation of the reactions between $[\text{Ae}[\text{N}(\text{SiMe}_2\text{H})_2]_2 \cdot (\text{THF})_n]$ and fluorinated aminoalcohols $\{\text{RO}^x\}\text{H}$ with tethered π ligands, yielding the heteroleptic $[\{\text{RO}^x\}\text{AeN}(\text{SiMe}_2\text{H})_2]_2$.

Olefin complexes

Elaborating on our syntheses of $[\mathbf{1}\text{-Ca}]_2$ - $[\mathbf{3}\text{-Ca}]_2$,⁷ complex $[\{\text{RO}^4\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$ ($[\mathbf{4}\text{-Ca}]_2$, see Scheme 1), where each ligand possesses *two* side-arms with terminal olefins, was obtained in 52% yield and free of coordinated THF from $[\text{Ca}[\text{N}(\text{SiMe}_2\text{H})_2]_2 \cdot (\text{THF})_2]$. It crystallized

from pentane at $-26\text{ }^{\circ}\text{C}$. Its formulation was established on the basis of crystallographic data, and its purity was confirmed by NMR spectroscopy and combustion analyses.²⁸ The proteo-ligands akin to $\{\text{RO}^2\}\text{H}$ but where the methyl group is either in γ position to the N_{amine} atom (= vinylidene end-group) or in δ position with an *E* configuration, were synthesized. However, the resulting complexes were obtained as oily materials, and although their fluxional ^1H and ^{19}F NMR data were encouraging, we could not obtain firm evidence for the formations of the desired heteroleptic complexes. Likefor $[\mathbf{1}\text{-Ca}]_2$ - $[\mathbf{3}\text{-Ca}]_2$,⁷ X-ray diffraction crystallography shows $[\mathbf{4}\text{-Ca}]_2$ to exist as an *O*-bridged dinuclear complex (Figure 1). It features η^2 -coordination of one olefinic moiety per Ca^{2+} ion ($\text{Ca1-C25}^{\#1} = 2.972(2)$ and $\text{Ca1-C26}^{\#1} = 3.121(2)$ Å). Out of the two olefinic tethers in each alkoxo ligand, only one binds to the metallic ion, in the same slightly dissymmetric η^2 -coordination mode (with a shorter distance to the internal C_{π} atom, aka C25) as that seen in $[\mathbf{1}\text{-Ca}]_2$.

Figure 1. ORTEP diagram of the molecular solid-state structure of $[\mathbf{4}\text{-Ca}]_2$. Ellipsoids at 50% probability. Only the main components of the disordered non-coordinated olefins ($\text{C29A}=\text{C30A}$) are represented. H atoms other than SiH omitted for clarity. Ca interactions with F, H and C_{π} atoms in dashed lines. Selected bond lengths (Å) and angles ($^{\circ}$): $\text{Ca1-N1} = 2.288(2)$, $\text{Ca1-O11} = 2.302(1)$, $\text{Ca1-O11}^{\#1} = 2.3127(15)$, $\text{Ca1-N22}^{\#1} = 2.597(2)$, $\text{Ca1-F15} = 2.9309(15)$, $\text{Ca1-C25}^{\#1} = 2.972(2)$, $\text{Ca1-C26}^{\#1} = 3.121(2)$, $\text{Ca1-C29A}^{\#1} = 5.780(10)$ Å, $\text{Ca1-C30A}^{\#1} = 6.707(11)$ Å, $\text{Ca1-H2} = 3.083(25)$, $\text{Ca1-H1} = 3.335(33)$; $\text{Si1-N1-Ca1} = 111.96(10)$, $\text{Si2-N1-Ca1} = 119.60(10)$.

The second olefin, which is disordered over two sites, is remote from calcium (Ca–C_π distances > 5.7 Å). The binding of this second olefin is prohibited presumably on account of excessive steric congestion about the eight-coordinate metal resulting in unfavourable entropic considerations. In addition to Ca···olefin interactions, the complex is stabilized by one intramolecular C–F→Ca interaction (Ca(1)–F(15) = 2.9309(15) Å) and one β-Si–H···Ae agostic distortion (Ca(1)–H(2) = 3.083(25) Å), by which we mean the largely electrostatic 2-electron-3-centre interaction between the electro-deficient Ae²⁺ ion and polarized ^(δ+)Si–H^(δ-) bond. The narrow Ca1–N1–Si2 (111.96(10) °), the short distances from Ca1 to H2 (3.083(25) Å; the positions of the SiH hydrogen atoms were located in the electronic density map), and the narrow Ca1–N20–Si2–H2 torsion angles (8.3 °) are reliable indications of β-Si–H···Ca agostic distortions.^{25,29} Key metric parameters for [**1**-Ca]₂ - [**4**-Ca]₂ and [**1**-Sr]₂ are given in Table 1.

Table 1. Summary of key metric parameters in Ae-olefin complexes (distances in Å, angles in °)					
	[1 -Ca] ₂	[2 -Ca] ₂ ^a	[3 -Ca] ₂	[4 -Ca] ₂	[1 -Sr] ₂
Ae–C _π (int)	2.958(3)	2.933(2)-2.978(2)	5.053(3)	2.972(2)	3.061(3)
Ae–C _π (ext)	3.102(3)	3.334(2)-3.390(2)	6.226(3)	3.121(2)	3.165(3)
Ae–F	3.050(2)	2.834(1)-2.949(1)	2.605(1)	2.9309(15)	3.050(2) 3.136(2)
Ae–HSi(1) ^b	3.12(4)	2.983(27)-3.037(27)	2.77(2)	3.083(25)	3.092(34)
Ae–HSi(2) ^b	3.19(3)				3.169(37)
∠Ca–N–Si(1)	115.22(14)	110.54(7)-112.52(7)	104.93(9)	111.96(10)	111.70(13)
∠Ca–N–Si(2)	116.69(14)	119.18(8)-122.06(8)	125.80(9)	119.60(10)	113.99(14)

^a The two metallic ions are inequivalent in this complex; only one Ca···H–Si 2e3c interaction per Ca²⁺.
Positions of H atoms located in the electronic density map, not idealized.

The geometric features in **[4-Ca]₂** combine with reasonable accuracy those seen in **[1-Ca]₂** and **[3-Ca]₂**. The metric parameters collated in Table 1 show that the strength of C–F→Ca and β-Si–H⋯Ae interactions increase when the Ca⋯olefin interactions becomes weaker, i.e. on moving from **[1-Ca]₂** (olefin η²-coordinated) to **[2-Ca]₂** (olefin η¹-coordinated) and **[3-Ca]₂** (olefin fully dissociated): stronger C–F→Ca and β-Si–H⋯Ca contacts make up for the loss of electronic density provoked by the gradual dissociation of the olefin. Such unique pattern of multiple secondary interactions ensures the stability of these heteroleptic calcium complexes by preventing aggregation, decomposition or ligand redistribution via Schlenk equilibria.

Solution NMR studies. We turned to NMR spectroscopy to inform ourselves on the solution behavior of **[1-Ca]₂**-**[4-Ca]₂** and **[1-Sr]₂**. Their NMR data were recorded in [D₆]benzene, or in [D₈]toluene for low-temperature experiments. ¹H DOSY diffusion coefficient-formula weight analyses revealed that all complexes remain dinuclear in [D₆]benzene.³⁰ Further evidence is provided by comparison of the hydrodynamic radii determined crystallographically and in solution by ¹H DOSY NMR.³¹ The ¹H and ¹⁹F VT NMR data for **[1-Ca]₂**-**[4-Ca]₂** and **[1-Sr]₂** show that in solution, the compounds are involved in complex dynamic phenomena, even at low temperatures;⁷ this was confirmed by 2D NMR, see below. As a result, ¹H and ¹⁹F spectra alone cannot demonstrate the persistence of the Ae⋯olefin interactions in aromatic solvents. Nonetheless, the deshieldings of ¹H resonances for olefinic *H*_{olefin} atoms (Table 2) on going from the proteo-ligand to the Ae complex is greater for the complexes having a coordinated olefin in the solid-state (Δδ_{1H} = 0.30-0.70 ppm) than for **[3-Ca]₂** where olefin binding is not observed in the XRD structure (Δδ_{1H} < 0.10 ppm).³² This is seen as an indication that in solution, the olefins remain coordinated in **[1-Ca]₂**, **[2-Ca]₂**, **[4-Ca]₂** and, by extrapolation, **[1-Sr]₂**.

The measurement of ^1H T_1 spin-lattice relaxation times helped our assessment of olefin coordination in solution. The participation of a small molecule or organic fragment to the coordination sphere of a large metal complex increases its rotational correlation time, which in turn results in a decrease of the relaxation time T_1 .³³ In our case, the variations of T_1 from proteo-ligands to Ae complexes are in line with the observed presence or not of a coordinated olefin in the solid state structures on the complexes. In **[1-Ca]₂**, **[1-Sr]₂** and **[2-Ca]₂**, all T_1 for olefinic hydrogens are decreased by ca. 60-80% with respect to the parent proteo-ligands, whereas no decrease or even slight increases were observed for **[3-Ca]₂** (Table 2). In each case, two conformational isomers A and B exhibited comparable values of T_1 for **[1-Ca]₂**, **[2-Ca]₂** and **[3-Ca]₂**. T_1 also diminished by 50-60% for the methyl group in **[2-Ca]₂**. The decrease of T_1 can be linked to anisotropic motion of the olefin upon coordination to Ca^{2+} , and it is an indication for the retention of olefin binding in solution in these complexes.

Table 2. Summary of key ^1H NMR data in Ae-olefin complexes ^a									
		[1-Ca]₂ ^b		[2-Ca]₂ ^c		[3-Ca]₂ ^d		[4-Ca]₂ ^e	[1-Sr]₂ ^f
		A	B	A	B	A	B		
H_{int}	δ_{H}	5.96	6.13	5.97	5.87	5.1	5.1	5.87	6.19
	$\Delta\delta_{\text{H}}^g$	0.49	0.66	0.47	0.37	0.16	0.16	0.49	0.71
	T_1^{H}	0.981	0.883	1.003	1.162	1.104	1.104	1.151	1.252
	$\Delta T_1^{\text{H}}^h$	-67%	-70%	-55%	-48%	0%	0%	-37%	-66%
<i>cis</i>		H	H	H	H	Me	Me	H	H
group ⁱ	δ_{H}	5.47	5.37	5.72	5.55	1.56	1.54	5.28	5.38
	$\Delta\delta_{\text{H}}^g$	0.52	0.42	0.54	0.37	0.06	0.04	0.37	0.43
	T_1^{H}	0.591	0.655	0.811	n.d. ^j	1.215	1.197	0.809	0.616
	$\Delta T_1^{\text{H}}^h$	-73%	-70%	-57%	n.d. ^j	+7%	+5%	-42%	-81%
<i>trans</i>		H	H	Me	Me	Me	Me	H	H
group ^k	δ_{H}	5.31	5.29	1.53	1.58	1.69	1.69	5.21	5.22
	$\Delta\delta_{\text{H}}^g$	0.34	0.32	0.04	0.09	0.02	0.02	0.33	0.28

$T_1^1\text{H}$	0.586	0.586	0.774	0.93	0.839	0.839	0.755	0.592
$\Delta T_1^1\text{H}^h$	-73%	-73%	-58%	-50%	+14%	+14%	-44%	-82%

^aAll data recorded in [D₈]toluene at the temperature of best resolution. δ_{IH} and $\Delta\delta_{\text{IH}}$ given in ppm. T_1 given in s. For complexes **[1-Ca]₂**–**[3-Ca]₂**, the data for the two distinct forms A and B are given.^b Data recorded at 263 K. ^c Data recorded at 253 K. ^d Data recorded at 233 K. ^e Data recorded at 243 K. ^f Data recorded at 298 K. ^g Variation of chemical shift compared to the resonance for the same group (H/Me) in the parent proteo-ligand. ^h Percentage of variation of T_1 compared to the same group (H/Me) in the parent proteo-ligand. ⁱ For the group (H or Me) in position *cis* with respect to H_{int}. ^j Could not be determined due to overlap. ^k For the group (H or Me) in position *trans* with respect to H_{int}.

For **[4-Ca]₂**, which features one coordinated and one dissociated olefins in the solid state and involves in a rapid equilibrium in solution (vide infra), presumably as a result of exchange between coordinated and dissociated olefin moieties, the observed T_1 relaxation times for olefinic hydrogens decrease by ca. 37-43% with respect to {RO⁴}H; it is roughly the average of the values measured for **[1-Ca]₂** (one η^2 -interacting olefin) and **[3-Ca]₂** (one non-interacting olefin). See Table 2 for details.

¹H-¹H NOESY experiments evidenced dipolar coupling (spatial proximity) between olefinic hydrogens (or terminal methyl groups) and SiH for **[1-Ca]₂**, **[2-Ca]₂**, **[4-Ca]₂** and **[1-Sr]₂** (Supporting Information S24-S30). This observation is again consistent with the retention of the Ae⋯olefin interactions in solution with these compounds. The dynamic behavior of the complexes due to conformational exchange already observed by VT experiments was confirmed by correlation cross-peaks in the ¹H-¹H NOESY spectra: (i) the rotation of ⁱPr groups is detected in each species but **[4-Ca]₂**; (ii) inversion of chiral nitrogen configuration is suggested by the following observations: at low temperature, two species are detected for **[1-Ca]₂**, **[2-Ca]₂** and **[3-Ca]₂**; conformational exchange between these two species is shown by positive correlation peaks for ⁱPr and CH₂ groups in α' position to N_{amine} atom (see Scheme 1 for labelling), and (iii) at ambient temperature, for **[1-Sr]₂**, even if only one mean resonance is observed for each site, positive correlations are seen for non-equivalent CH₂ groups. In addition, one more conformational change seems to occur for **[1-Ca]₂** and **[2-Ca]₂**: at low

temperature, two exchanging signals are seen for olefinic protons, suggesting a change of enantioface for the coordinated olefin.³⁴ All pertinent NMR spectra are given in the Supporting Information.

EXSY NMR experiments on **[1-Ca]₂** and **[2-Ca]₂** confirmed that two distinct conformational exchanges occur concomitantly. For **[1-Ca]₂** studied at 263K, the two exchange rates $k_{N,1}$ and $k_{N,-1}$ estimated for CH₂(α and α' positions vs. N_{amine}) and ⁱPr groups were in the range $0.48\text{--}0.55 \pm 0.01 \text{ s}^{-1}$, whereas the exchange rates $k_{\text{olefin},1}$ and $k_{\text{olefin},-1}$ for the olefinic protons in the range $1.41\text{--}1.55 \pm 0.01 \text{ s}^{-1}$. These different exchange rates suggest that two independent, competitive events, thought to be chiral nitrogen inversion and change of coordinated enantioface of the olefin,³⁵ take place simultaneously. The same scenario was established for **[2-Ca]₂**, albeit at different rate constants ($k_{N,1}$ and $k_{N,-1} = 0.21\text{--}0.38 \pm 0.01 \text{ s}^{-1}$, $k_{\text{olefin},1}$ and $k_{\text{olefin},-1} = 0.07\text{--}0.14 \pm 0.01 \text{ s}^{-1}$) (Supporting Information S23).

Attempts to use ¹H-¹⁵N HMBC NMR spectroscopy to establish through-metal scalar coupling between the chiral N_{amine} atom with CH_{olefin} hydrogens in **[1-Ca]₂**, or even to simply detect the N_{amine} atom, were unsuccessful; only the coupling between the terminal N_{amido} and SiH atoms was visualized. Since coupling between N_{amine} and various CH atoms was visible in {RO¹}H, this result also pleads for rapid (on the NMR time scale) inversion of the configuration at the chiral nitrogen in **[1-Ca]₂**.

Arene complexes

The syntheses of calcium complexes showing Ca $\cdots$ arene interactions were attempted by equimolar reaction of [Ca[N(SiMe₂H)₂]₂•(THF)] with the proteo-ligand {RO⁵}H bearing a pendant phenethyl substituent and a methyl substituent on the N_{amine} atom; however, this attempt only resulted in the formation of the THF-solvated complex [{RO⁵}CaN(SiMe₂H)₂•(THF)]₂ (**[5-Ca•(THF)]₂**) (Scheme 3).

Scheme 3. Synthesis and representations of the dimeric **[5-Ca•(THF)]₂** and trinuclear **[5-Ca]₃** complexes showing selected secondary interactions as dashed lines.

The molecular solid-state of this *O*-bridged dimeric complex was established by X-ray diffraction crystallography (Supporting Information). It showed there is no interaction between the calcium centre and the tethered aromatic moieties; the other expected C–F→Ca contacts and β-Si–H⋯Ca agostic distortions are seen, despite each Ca²⁺ being coordinated by a molecule of THF. Complex **[5-Ca•(THF)]₂** was characterized by NMR spectroscopy. In [D₈]toluene solution, it remains dimeric (¹H DOSY NMR, $D_t = 6.90 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) and undergoes fluxional processes (¹H, ¹⁹F NMR). The DOSY NMR data also indicated that the THF molecules ($D_t = 1.40 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) dissociate to some extent in solution, or that they engage in a fast (for the NMR time-scale) coordination-dissociation process.³⁶ It is assumed that the coordination of THF molecules instead of that of the aromatic groups in **[5-Ca•(THF)]₂** stems from unfavourable entropic factor and steric constraints associated to the folding of the CH₂–CH₂–C₆H₅ side-arm in comparison with the smaller CH₂–CH₂–CH=CH₂ in, for instance, **[1-Ca]₂**.

To alleviate the problem stemming from the presence of THF in $[\text{Ca}[\text{N}(\text{SiMe}_2\text{H})_2]_2 \cdot (\text{THF})]$ and, as a result, in $[\mathbf{5}\text{-Ca} \cdot (\text{THF})]_2$, $\{\text{RO}^5\}\text{H}$ was reacted instead with an equimolar amount of the THF-free $[\text{Ca}[\text{N}(\text{SiMe}_2\text{H})_2]_2]$.^{25c} However, instead of the expected dimeric complex $[\mathbf{5}\text{-Ca}]_2$ showing coordination of the aryl rings onto calcium, the trinuclear $[[\{\text{RO}^5\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2 \cdot \text{Ca}[\text{N}(\text{SiMe}_2\text{H})_2]_2](\mathbf{5}\text{-Ca})_3$, incorporating two alkoxo and four amido ligands and devoid of coordinated solvent, was obtained in 62% yield with respect to Ca (Scheme 3). The molecular solid-state structure of $[\mathbf{5}\text{-Ca}]_3$ exhibits a complicated pattern of strong to extremely strong $\text{C-F} \rightarrow \text{Ca}$ and $\beta\text{-Si-H} \cdots \text{Ca}$ interactions, but no $\text{Ca} \cdots \text{C}_\pi(\text{arene})$ contacts (Figure 2). The three calcium atoms are crystallographically inequivalent, even though the arrangements about the two terminal atoms Ca2 and Ca3 are very similar, hence only that around Ca2 is discussed below.

Figure 2. ORTEP diagram of the molecular solid-state structure of $[\mathbf{5}\text{-Ca}]_3$. Ellipsoids at 50% probability. H atoms other than SiH omitted for clarity. Ca interactions with F and H atoms in dashed lines. Selected bond lengths (Å) and angles (°): $\text{Ca1-O1} = 2.307(5)$, $\text{Ca1-O2} = 2.286(1)$, $\text{Ca1-N2} = 2.480(1)$, $\text{Ca1-N3} = 2.462(4)$, $\text{Ca1-F16} = 2.740(1)$, $\text{Ca1-F36} = 3.080(1)$, $\text{Ca1-F40} = 2.949(1)$, $\text{Ca1-H4} = 2.66(2)$, $\text{Ca1-H5} = 2.63(2)$, $\text{Ca2-O1} = 2.268(1)$, $\text{Ca2-N1} = 2.295(1)$, $\text{Ca2-N2} = 2.519(1)$, $\text{Ca2-N9} = 2.585(1)$, $\text{Ca2-H2} = 2.64(2)$, $\text{Ca2-H3} = 2.39(2)$, $\text{Ca3-O2} = 2.310(1)$, $\text{Ca3-N3} = 2.504(1)$, $\text{Ca3-N4} = 2.306(1)$, $\text{Ca3-N29} = 2.573(1)$, $\text{Ca3-H6} = 2.44(2)$, $\text{Ca3-H7} = 2.97(2)$; $\text{Ca1-N2-Si3} = 130.00(7)$, $\text{Ca1-N2-Si4} = 98.77(7)$, $\text{Ca1-N3-Si5} = 98.50(7)$, $\text{Ca1-N3-Si6} = 128.59(7)$, $\text{Ca2-N1-Si1} = 128.38(9)$, $\text{Ca2-N1-Si2} = 102.16(8)$, $\text{Ca2-N2-Si3} = 91.87(6)$, $\text{Ca2-N2-Si4} = 123.33(7)$, $\text{Ca3-N3-Si5} = 118.11(7)$, $\text{Ca3-N3-Si6} = 92.28(7)$, $\text{Ca3-N4-Si7} = 111.12(9)$, $\text{Ca3-N4-Si8} = 124.37(9)$.

The coordination sphere around Ca2 includes one terminal N_{amide} atom (Ca2–N1 = 2.295(1) Å), one μ^2 -bridging N_{amide} (Ca2–N2 = 2.519(1) Å) and one μ^2 -bridging $O_{alkoxide}$ (Ca2–O1 = 2.268(1)) atoms, one N_{amine} atom (Ca2–N9 = 2.585(1) Å), all with bond lengths as expected for such bonds. It is completed by two strong β -Si–H $\cdots$ Ca agostic contacts (H2 and H3), taking the coordination number to 6. Prominent features are the extremely short Ca2–H3 distance (2.39(2) Å) together with the corresponding remarkably acute Ca2–N2–Si3 angle (91.87(6) °), which both testify to a distortion of unique amplitude for a calcium complex, stronger than any of those reported to date. By comparison, although still unusually pronounced (compare for instance to the characteristic data in Table 1), the Ca2 $\cdots$ H2 agostic interaction (Ca2–H2 = 2.64(2) Å, Ca2–N1–Si2 = 102.16(8) °) looks significantly weaker. The strength of these two β -Si–H $\cdots$ Ca2 agostic contacts must stem from the absence of other secondary interactions about Ca2 with either C_π or F atoms. The geometry around the central calcium atom Ca1 differs much. It comprises two μ^2 -bridging N_{amide} (Ca1–N2 = 2.480(1) and Ca1–N3 = 2.462(4) Å) and two μ^2 -bridging $O_{alkoxide}$ (Ca1–O1 = 2.307(5), Ca1–O2 = 2.286(1) Å) atoms, and three typical C–F $\rightarrow$ Ca1 interactions (Ca1–F16 = 2.740(1), Ca1–F36 = 3.080(1) and Ca1–F40 = 2.949(1) Å); two very strong β -Si–H $\cdots$ Ca1 agostic distortions (Ca1–H4 = 2.66(2) and Ca1–H5 = 2.63(2) Å) are also detected.

^1H DOSY NMR data (diffusion - molecular weight analysis: expected mol. wt. 1278 g mol $^{-1}$, found 1201 g mol $^{-1}$; hydrodynamic radii: XRD 6.13 Å, DOSY NMR 7.42 Å) suggest that the trinuclear structure of [**5-Ca**] $_3$ is maintained in solution (Figure S22). The 1D NMR data for [**5-Ca**] $_3$ are complicated as expected in view of its structure, and in particular the multiplicity of resonances for SiH hydrogens precludes the determination of $^1J_{SiH}$ coupling constants. They were established instead by a 2D ^1H - ^{29}Si HMQC NMR experiment without broadband decoupling, which reveals the presence of four different SiH environments in solution, characterized by $^1J_{SiH}$ values of 132, 145, 161 and 161 Hz (Figure S36).³⁷ The $^1J_{SiH}$

value of 132 Hz indicates an extremely strong $\text{Ca}\cdots\text{H}-\text{Si}$ β -agostic interaction. That of 145 Hz is unusually strong for a calcium complex, whereas those of 161 Hz for mild $\text{Ca}\cdots\text{H}-\text{Si}$ contacts are more typical. These spectroscopic data are consistent with the crystallographic data.

The yield in the synthesis of **[5-Ca]₃** is improved by deliberate reaction of $[\text{Ca}[\text{N}(\text{SiMe}_2\text{H})_2]_2]$ and $\{\text{RO}^5\}\text{H}$ in the appropriate 3:2 stoichiometry. The complex can also be prepared by ligand redistribution in the 2:1 reaction of the two homoleptic precursors $[\text{Ca}[\text{N}(\text{SiMe}_2\text{H})_2]_2]$ and $\{\text{RO}^5\}_2\text{Ca}$ (a complex prepared for this purpose upon treatment of $\text{Ca}[\text{N}(\text{SiMe}_3)_2]_2\cdot(\text{THF})_2$ with 2 equiv of $\{\text{RO}^5\}\text{H}$). However, we have so far failed in obtaining complexes featuring intramolecular $\text{Ca}\cdots\text{C}_\pi(\text{arene})$ interactions with our methodology. The substitution of the nitrogen-bound Me group in $\{\text{RO}^5\}\text{H}$ by an *i*Pr one made no difference, as a trinuclear complex is returned in the same manner as that seen for **[5-Ca]₃**. The addition of 1 equiv of $\{\text{RO}^5\}\text{H}$ to **[5-Ca]₃** failed to deliver the targeted complex of expected formula $[\{\text{RO}^5\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$. Finally, the 1:1 reaction of $[\text{Ca}[\text{N}(\text{SiMe}_2\text{H})_2]_2]$ and $\{\text{RO}^5\}_2\text{Ca}$ returned **[5-Ca]₃** with another unidentified calcium complex.

Alkyne complexes

The proteo-ligand $\{\text{RO}^6\}\text{H}$ having a dangling methyl-substituted alkyne group was obtained in ca. 90% yield by reaction of *N*-isopropylpent-3-yne-1-amine³⁸ with 2,2-bis(trifluoromethyl)oxirane. The dinuclear complexes $[\{\text{RO}^6\}\text{AeN}(\text{SiMe}_2\text{H})_2]_2$ (Ae = Ca, **[6-Ca]₂**, 62%; Sr, **[6-Sr]₂**, 48%) were isolated after amine release by reacting $\{\text{RO}^6\}\text{H}$ with $[\text{Ca}[\text{N}(\text{SiMe}_2\text{H})_2]_2\cdot(\text{THF})]$ or $[\text{Sr}[\text{N}(\text{SiMe}_2\text{H})_2]_2\cdot(\text{THF})_{2/3}]$ (Scheme 4). Although they show slightly broad resonances at room temperature, their ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR data are well resolved compared to those of their congeneric olefin complexes **[1-Ca]₂** and **[1-Sr]₂**. The ^{19}F NMR spectrum for **[6-Sr]₂** in $[\text{D}_6]\text{benzene}$ (298 K) exhibits two quartets of equal intensities at

–77.98 and –77.15 ppm. The broad ^1H and ^{19}F resonances in the NMR spectra for $[\mathbf{6}\text{-Ca}]_2$ recorded at 298 K in $[\text{D}_8]\text{toluene}$ are much improved upon heating to 333 K.

Scheme 4. Synthesis and representations of the dimeric $[\mathbf{6}\text{-Ca}]_2$ and $[\mathbf{6}\text{-Sr}]_2$ Ae-alkyne complexes showing selected secondary interactions as dashed lines.

The dinuclear $[\mathbf{6}\text{-Ca}]_2$ crystallized as a centro-symmetric *O*-bridged dimer (Figure 3). Its key structural feature is the asymmetric η^2 -coordination of the alkyne groups onto the metallic ions, as indicated by short $\text{Ca}\text{--}\text{C}_\pi$ distances ($\text{Ca1}\text{--}\text{C3} = 2.875(2) \text{ \AA}$, $\text{Ca1}\text{--}\text{C2} = 3.020(2) \text{ \AA}$) both diagnostic of $\text{Ca}\cdots\text{C}_\pi$ interactions.³⁹ As in $[\mathbf{1}\text{-Ca}]_2$, the interaction is therefore substantially stronger with the internal C_π than with the external one. The $\text{Ca}\text{--}\text{C}_\pi$ distances are unsurprisingly significantly shorter in the Ca-alkyne complex than in the Ca-olefin one, but they are longer than those reported for calcium complexes containing $\text{Ca}\cdots\text{C}_\pi(\text{alkyne})$ interactions with bridging acetylides (ca. 2.53–2.82 $\text{\AA}$). The binding mode of the alkyne in $[\mathbf{6}\text{-Ca}]_2$ is unique, and this compound constitutes the only “non-acetylide” example of a calcium-alkyne complex known to date. The $\text{C2}\text{--}\text{C3}$ bond length of 1.199(3) $\text{\AA}$ is unremarkable.

Figure3. ORTEP diagram of the molecular solid-state structure of **[6-Ca]₂**. Ellipsoids at 50% probability. H atoms other than SiH omitted for clarity. Ca interactions with C_π, F and H atoms in dashed lines. Selected bond lengths (Å) and angles (°): Ca1–O20 = 2.305(1), Ca1–O20^{#1} = 2.364(1), Ca1–N1 = 2.341(1), Ca1–N6 = 2.618(1), Ca1–H1 = 2.65(3), Ca1–F15 = 2.753(1), Ca1–C2 = 3.020(2), Ca1–C3 = 2.875(2), C2–C3 = 1.199(3); Ca1–N1–Si1 = 101.37(9), Ca1–N1–Si2 = 131.6(1); Torsion angle Ca(1)–N(1)–Si(1)–H(1) = 0.6(11) °.

As with the other complexes, stabilization of **[6-Ca]₂** is further warranted by a pronounced C–F→Ca interaction (Ca1–F15 = 2.753(1) Å) and a strong β-Si–H⋯Ca distortion (Ca1–H1 = 2.65(3), Ca1–N1–Si1 = 101.37(9) ° vs. Ca1–N1–Si2 = 131.6(1) °, torsion angle Ca(1)–N(1)–Si(1)–H(1) = 0.6(11) °).

The molecular structure of the centro-symmetric **[6-Sr]₂**, the first non-acetylide strontium-alkyne complex, was also established (Figure S34). With its asymmetric Sr⋯C_πη²-coordination of the alkyne (Sr–C_π = 3.001(5) and 3.094(5) Å), strong Sr⋯H agostic (Sr–H = 2.882(49) Å to the H atom in idealized position, with corresponding Sr–N–Si angle of 103.1(3) ° and Sr–Si distance of 3.282(1) Å) and Sr⋯F–C (Sr–F = 2.806(3) Å) interactions, it resembles very closely that of its calcium parent.

Because the alkyne in **[6-Ca]₂** is more electron-donating and less hindered than the olefins in **[1-Ca]₂** and **[2-Ca]₂**, that the Ca–C_π distances in **[6-Ca]₂** are shorter than in the olefins complexes is unsurprising. However, the crystallographic data summarized in Figure 4 highlight that C–F→Ca contacts and β-Si–H⋯Ca agostic distortions are also noticeably

weaker in the calcium-olefin complexes. This is consistent with the observation that in solution, $[\mathbf{6-Ca}]_2$ (and even more so $[\mathbf{6-Sr}]_2$) undergoes fewer dynamic phenomena than in $[\mathbf{1-Ca}]_2$ and $[\mathbf{2-Ca}]_2$. The results detailed below with calcium-allene complex emphasize the particular stability of the alkyne complex $[\mathbf{6-Ca}]_2$.

Figure 4. Representation of the coordination sphere around the calcium centres in the calcium-alkyne complex $[\mathbf{6-Ca}]_2$ and calcium-olefin complexes $[\mathbf{1-Ca}]_2$ and $[\mathbf{2-Ca}]_2$. Bond distances are given in Å.

Towards allene complexes

The synthesis of a calcium-allene complex allowing $\text{Ca}\cdots\text{C}_\pi(\text{allene})$ interactions was carried out by reacting $[\text{Ca}[\text{N}(\text{SiMe}_2\text{H})_2]_2\bullet(\text{THF})]$ with one equiv of the proteo-ligand $\{\text{RO}^7\}\text{H}$ having a dangling allene tether (Scheme 5); $\{\text{RO}^7\}\text{H}$ was first prepared by the Crabbe synthesis of penta-3,4-dien-1-ol,⁴⁰ and its conversion to *N*-isopropylpenta-3,4-dien-1-amine³⁸ to ring-open 2,2-bis(trifluoromethyl)-oxirane. The protonolysis reaction afforded a colourless compound, the ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR data ($[\text{D}_6]\text{benzene}$, 298 K) of which were consistent with the formulation $[\{\text{RO}^7\}\text{CaN}(\text{SiMe}_2\text{H})_2]_n$ ($[\mathbf{7-Ca}]_n$). However, on the basis of these NMR data alone, the nuclearity n could not be clearly ascertained, and the putative structure given for $n = 2$ in Scheme 5 solely relies on a probable analogy with the other calcium complexes. The NMR data for crude $[\mathbf{7-Ca}]_n$ also unambiguously showed contamination by substantial amount of the calcium-alkyne complex $[\mathbf{6-Ca}]_2$. After 12 h, full conversion of the allene-

containing complex $[\mathbf{7-Ca}]_n$ into $[\mathbf{6-Ca}]_2$ had taken place in $[D_6]$ benzene at room temperature. We assume that isomerization of the calcium allene compound $[\mathbf{7-Ca}]_n$ into the more stable calcium alkyne complex occurs via 1,3-hydride shift as depicted in Scheme 5.

Scheme 5. Synthesis of the calcium-allene complex $[\mathbf{7-Ca}]_n$ with a putative structure for $n = 2$, and its isomerization via 1,3-hydride shift to $[\mathbf{6-Ca}]_2$.

While the isomerization of alkynes to allenes is well documented,⁴¹ reports of the conversion of allenes into alkynes are seldom. 1-Propyne can be converted to 1,2-propadiene in the presence of catalytic amounts of CaH_2 .⁴² Very recently, Mashima and co-workers employed $[\{N^{\wedge}N\}MgCH_2Ph]_2$ ($\{N^{\wedge}N\}H = N^1$ -(1,2-diphenylethyl)- N^2, N^2 -dimethylethane-1,2-diamine) to catalyze the isomerization of 3-phenyl-1-propyne to phenylallene, which was subsequently isomerized to 1-phenyl-1-propyne.⁴³ Because a pure sample of $[\mathbf{7-Ca}]_n$ could not be obtained and owing to its instability in solution, we could not obtain X-ray quality crystals to support the proposed formulation.

Conclusion

The results presented here, in conjunction with our earlier communication,⁷ show that π ligands, or at least alkenes and alkynes, can be made to work efficiently in alkaline earth chemistry.

The structures of a range of calcium- and strontium-olefin complexes supported by amino-fluoroalkoxides and bearing the $\text{N}(\text{SiMe}_2\text{H})_2^-$ amido co-ligand were established. The presence of $\text{Ae}^{2+} \cdots \text{olefin}$ interaction is clear in these complexes, although it gradually diminishes from η^2 to complete dissociation when the steric bulk around the C=C double bond increases. Since the stability of these complexes is further warranted by pattern of C–F $\rightarrow$ Ae and β -Si–H $\cdots$ Ae agostic interactions, compensation takes place and these two types of interactions become stronger as the Ae $\cdots$ olefin interaction loosens.

Considering the oxophilic nature of calcium and strontium, the absence of coordinated THF in **[1-Ca]₂**, **[2-Ca]₂**, **[4-Ca]₂** and **[1-Sr]₂** is remarkable, since they were made from the THF-containing precursor $\text{Ae}[\text{N}(\text{SiMe}_2\text{H})_2]_2 \cdot (\text{THF})_n$ or by crystallization in presence of THF.⁴⁴ The results presented here show that, against accepted wisdom, the intramolecular binding of an olefin onto calcium can be favoured over the coordination of external THF molecule(s). Related to this, we have reported before that combining C–F $\rightarrow$ Ae and β -Si–H $\cdots$ Ae interactions in aminoether–fluoroalkoxo calcium complexes was more efficient at stabilising the metal than the binding of an additional chelating methoxy arm.^{27a} This is a convincing evidence for the key role of the secondary interactions in alkalino-earth chemistry.²⁴

DFT computations have shown that the calcium $\cdots$ olefin interaction in **[1-Ca]₂** is almost purely electrostatic (like the C–F $\rightarrow$ Ae and β -Si–H $\cdots$ Ae interactions),⁷ and the solution NMR data are consistent with this interpretation. We have implemented several NMR techniques to assess whether the olefin remains metal-bound in solution in aromatic solvents. Taken collectively, the NMR spectroscopic data militate in favour of the retention of Ae $\cdots$ olefin interactions in solution. Besides, a complex pattern of fluxional processes was also demonstrated. Inversion of configuration at the chiral nitrogen atoms, reversible dissociation of the olefin, which may involve an inversion of the coordinated enantioface, or a monomer–

dimer equilibrium for which we could not however find any concrete indication, could constitute plausible reasons for these phenomena.

Non-acetylide alkaline earth-alkyne complexes were synthesized for the first time; the evidence for $\text{Ae}\cdots\text{C}_\pi(\text{alkyne})\eta^2$ -interaction is plain from crystallographic studies. The calcium-alkyne complex is particularly stable, so much so that the isomerization of the allene derivative **[7-Ca]₂** into **[6-Ca]₂**, presumably by intramolecular 1,3-hydride shift, is very facile; NMR monitoring seemed to indicate that there is no significant kinetic barrier to the isomerization. Such isomerization process is unusual, and we are endeavouring to take advantage from the stoichiometric reaction and turn it into a viable catalytic process.

Even though we have so far failed in obtaining Ae-arene complexes with our protocol, the complex **[5-Ca]₃** resulting from our attempts display a remarkably strong pattern of stabilising $\text{C-F}\rightarrow\text{Ae}$ and $\beta\text{-Si-H}\cdots\text{Ae}$ interactions to compensate for the absence of π -coordinated moieties. The existence of this complex and the trend observed upon gradual dissociation of the C=C double bonds in the Ca-olefin complexes **[1-Ca]₂**- **[4-Ca]₂** are perhaps the best illustration of the paramount importance of secondary interactions in alkaline earth chemistry, as highlighted by Ruhlandt-Senge.²⁴

■ ASSOCIATED CONTENTS

Synthetic procedures and product characterizations for all compounds; 2D NMR data; tables of NMR data; comparison of hydrodynamic radii; VT NMR data, CIF files and tables of crystallographic data for CCDC n° 1508047-1508550, 1508553 and 1508556.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail for J.-F. C.: jean-francois.carpentier@univ-rennes1.fr

*E-mail for Y. S.: yann.sarazin@univ-rennes1.fr

ORCID

Jean-François Carpentier: 0000-0002-9160-7662

Yann Sarazin: [0000-0003-1121-0292](https://orcid.org/0000-0003-1121-0292)

Notes

The authors declare no competing financial interest.

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