β-Diketiminate C–H activation with heavier group 2 alkyls†

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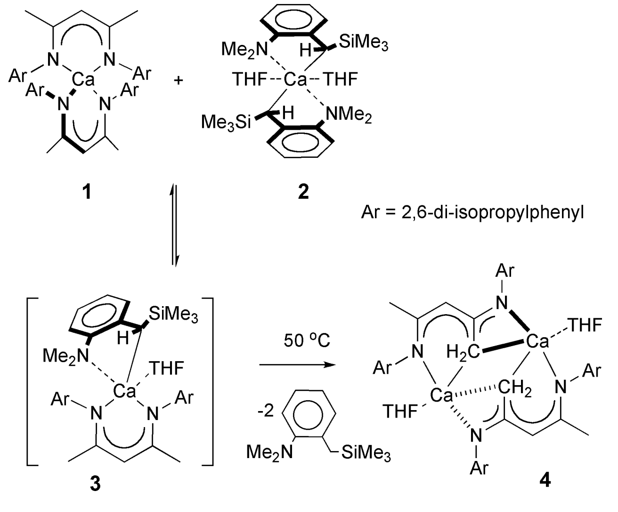
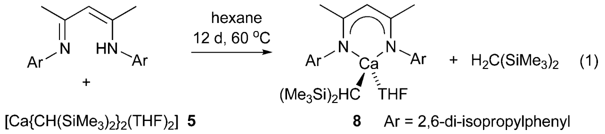
Well defined dialkyls of the heavier alkaline earth elements, [M{CH(SiMe$_3$)$_2$}$_2$(THF)$_n$] [M = Ca, n = 2; M = Sr, n = 3; M = Ba, n = 3] react to form either the heteroleptic β-diketiminato alkyl when M = Ca or unusual 'C–H activation' products in which a methyl group of the ligand is deprotonated when M = Sr or Ba.

Although examples of sp^3-C–H activation by a σ-bond metathesis pathway are scattered throughout the later d-block metals,[1] this mechanism is especially prevalent for electrophilic d^0 and d^{0}f^n complexes of the early transition elements and lanthanides in their highest oxidation states.[2] In contrast there are a vanishingly small number of authenticated examples of *intermolecular* C–H activation (sp^3-carbon deprotonation) mediated by the similarly d^0 heavier alkaline earth metals, Ca, Sr and Ba. A noteworthy reaction between the homoleptic calcium β-diketiminate, **1**, and the calcium bis-benzyl, **2**, has been reported to result in the dimeric complex, **4** (Scheme 1). It was proposed that this species was effected by "*intramolecular* C–H activation" and the intermediacy of a highly reactive heteroleptic benzyl, **3**.[3]



Scheme 1

We have recently described a series of heavier alkaline earth dialkyl derivatives [M{CH(SiMe$_3$)$_2$}$_2$(THF)$_n$] [**5**: M = Ca, n = 2; **6**: M = Sr, n = 3; **7**: M = Ba, n = 3].[4] Reaction of compound **5** with [ArNC(Me)CHC(Me)NHAr] (Ar = 2,6-di-iso-propylphenyl) in C$_6$D$_6$ proceeded slowly at 60 °C to provide the heteroleptic calcium alkyl, **8**, in a moderate isolated yield of 38% (Eq. 1). Work up yielded a crop of large colourless crystals. Although these were suitable for X-ray analysis, initial experiments have failed to provide a satisfactory refinement. The connectivity of the molecule was, however, unambiguous and the structure of **8** is illustrated as a ball and stick diagram in the ESI.†



(1)

In contrast to the proposed species **3**, once isolated, compound **8** was thermally stable at 60 °C in C$_6$D$_6$ solution for periods of up to one week and provided no evidence of ligand activation reactions. Preparative-scale reactions performed at higher concentration in *n*-hexane, however, were accompanied by the formation of the ligand activation product, compound **4**. Heating of an NMR sample of compound **8** at 60 °C with an equimolar quantity of the dialkylcalcium species **5** in C$_6$D$_6$ also resulted in the precipitation of compound **4** along with the formation of the alkane by-product [CH$_2$(SiMe$_3$)$_2$]. In view of these observations, we propose that the formation of compound **4** during these processes is, more likely, the result of inter- rather than intramolecular reactivity.

An analogous reaction of the strontium dialkyl **6** and [ArNC(Me)CHC(Me)NHAr] in C$_6$D$_6$ was monitored by ^{1}H NMR spectroscopy. Heating at 60 °C for 72 h evidenced complete consumption of the dialkyl starting material while *ca.* 50% of the ligand precursor remained unreacted. Although reaction was accompanied by the formation of a precipitate, at no point were resonances attributable to a heteroleptic species analogous to **8** observed. In a subsequent preparative scale reaction, storage of an unstirred benzene solution at 60 °C for 72 h provided a crop of large colourless crystals of compound **9** suitable for an X-ray diffraction analysis.‡The results of this experiment are illustrated in Fig. 1 and revealed that compound **9** was an isostructural strontium analogue of the previously reported calcium complex **4**. The doubly deprotonated ligand adopts a similar N,N′-*trans* conformation, which the elongated C(2)–C(3) distance suggests is best regarded as two conjoined monoanionic azaallyl fragments rather than as a delocalised dianion. Crystals of compound **9** were sufficiently soluble in D$_8$-THF to allow the acquisition of ^{1}H and ^{13}C NMR data and it was observed to display similar N,N′-*trans* to N,N′-*cis* equilibria in solution to those previously described for the calcium analogue **4**.[3]

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† Electronic supplementary information (ESI) available: Experimental details. CCDC reference numbers of **9**, **10** and **11**, 727087–727089. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b917466b

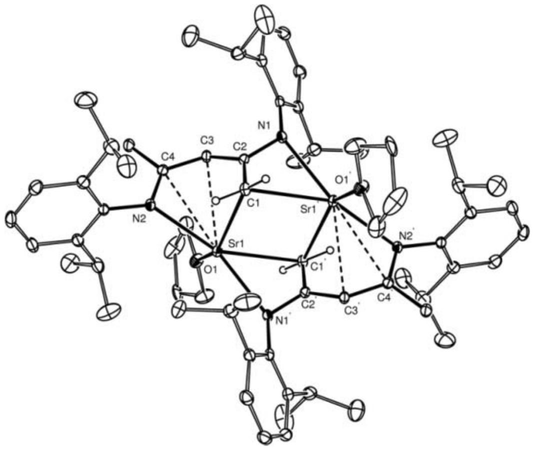

Fig. 1 ORTEP representation of compound **9** with thermal ellipsoids set at 25% probability. H atoms, except for those attached to C(1), omitted for clarity. Selected bond lengths (Å) and angles (°): Sr(1)–N(1)′ 2.5104, Sr(1)–N(2) 2.567(2), Sr(1)–C(1) 2.759(3), Sr(1)–C(2) 2.982(2), Sr(1)–C(3) 2.911(2), Sr(1)–C(1)′ 2.815(3), Sr(1)–C(2)′ 2.959(2), Sr(1)–O(1) 2.5535(18), O(1)–Sr(1)–N(2) 99.13(6), N(2)–Sr(1)–C(1) 70.50(7), N(1)′–Sr(1)–O(1) 103.17(6), N(1)′–Sr(1)–N(2) 147.38(6), C(1)–Sr(1)–C(1)′ 90.61(7).

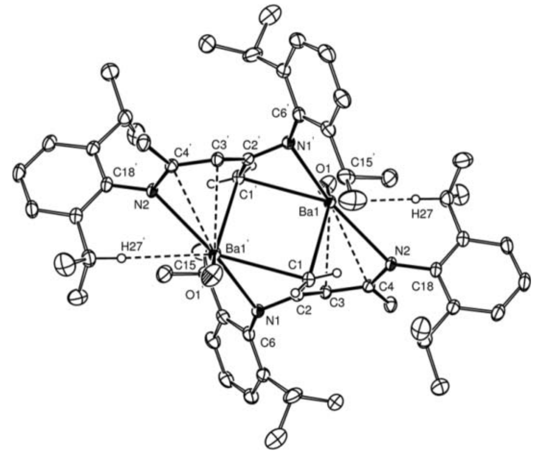

Fig. 2 ORTEP representation of compound **10** with thermal ellipsoids set at 25% probability. Carbon atoms of the coordinated THF molecules and H atoms, except for those attached to C(1) and H(27), omitted for clarity. Selected bond lengths (Å) and angles (°): Ba(1)–N(1)′ 2.6677(16), Ba(1)–N(2) 2.7576(16), Ba(1)–C(1) 2.966(2), Ba(1)–C(2)′ 3.1587(19), Ba(1)–C(1)′ 3.001(2), Ba(1)–C(2)′ 3.1587(19), Ba(1)–O(1) 2.7369(17), O(1)–Ba(1)–N(2) 100.55(5), N(2)–Ba(1)–C(1) 64.55(5), N(1)′–Ba(1)–O(1) 112.09(6), N(1)′–Ba(1)–N(2) 144.98(5), C(1)–Ba(1)–C(1)′ 89.12(6).

In contrast to the synthesis of **9**, reaction of the barium dialkyl, **7**, with [ArNC(Me)CHC(Me)NHAr] occurred smoothly at room temperature. Monitoring of the ^{1}H NMR spectrum of a reaction in C_6D_6 over a 120 h period revealed the simultaneous production of $[CH_2(SiMe_3)_2]$ and a new barium alkyl species, evidenced by broad high field methanide CH (−1.79 ppm) and $SiMe_3$ (−0.24 ppm) resonances. The emergence of these resonances coincided with the appearance of a new β-diketiminate environment and we, thus, tentatively assign this new species as the barium analogue of the heteroleptic calcium complex **8**. Although attempts to isolate this compound have been unsuccessful, it is notable that it was consumed as the reaction progressed and that this reactivity coincided with the formation of an insoluble crystalline compound **10**. A crystal structure confirmed **10** to be a C–H activation product similar, but not isostructural, to compounds **4** and **9** (Fig. 2).‡ The *pseudo* seven-coordinate barium centres within the dimeric molecule of **10** display short Ba–C distances to the $C(1)H_2$ units resulting from deprotonation of the methyl groups [Ba(1)–C(1) 2.966(2), Ba(1)–C(1)′ 3.001(2) Å] and also supplementary interactions from the isopropropyl methyl [Ba(1)–C(16)′ 3.307(3) Å] and methine residues of the Ar ligand substituents. Although the former values are somewhat longer than the Ba–C distances observed within the dialkyl compound **7** [2.879(3), 2.827(3) Å],[4] they are comparable to the $Ba–C_{methyl}$ bonds reported for the six-coordinate complex $[\{(Me_3Si)_2(MeOMe_2Si)C\}_2Ba(DME)]$ [3.049(2), 3.0363(18) Å] and thus indicative of a strong ionic organometallic interaction.[5] Once crystallised, **10** required the use of more strongly donating D_6-DMSO for the acquisition of NMR data, the resonances of which were broad and generally uninformative.

Sometimes referred to as a complex-induced proximity effect (CIPE), the *ortho*-methyl activation (deprotonation) of *ortho*-N,N-dimethyltoluidine by s-block alkyl complexes has literature precedent.[6] In an initial attempt to observe evidence for calcium-mediated intermolecular C–H reactivity, therefore, reaction of the heteroleptic species **8** with *ortho*-N,N-dimethyltoluidine was monitored in C_6D_6 at 60 °C. After 16 h a series of resonances (*ca.* 10% conversion) in the aromatic region of the ^{1}H NMR spectrum was observed [δ_H 6.11 (ddd, 1H, J = 7.9, 6.8, 1.6 Hz), 6.52 (d, 1H, J = 7.9 Hz), 6.67 (dd, 1H, J = 8.1, 1.6 Hz), 6.75 (dd, 1H, J = 8.1, 6.8 Hz)] diagnostic of an *ortho*-methyl activation of the organic substrate to form a heteroleptic calcium benzyl complex **11**. The structure of **11** was confirmed by its independent synthesis from CaI_2, [ArNC(Me)CHC(Me)NHAr] and two equivalents of $[K\{\eta^2\text{-}CH_2\text{-}2\text{-}(Me_2N)C_6H_4]$. Compound **11**, whose structure is shown in Fig. 3,‡ is an analogue of the apparently unstable species **3** and displayed identical NMR data to that observed for the reaction of **8** with *ortho*-N,N-dimethyltoluidine.

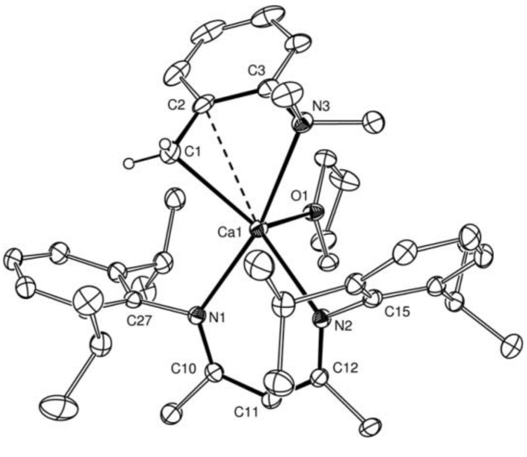

Fig. 3 ORTEP representation of compound **11** with thermal ellipsoids set at 25% probability. The Ca(1)-containing molecule only is shown. Selected bond lengths (Å) and angles (°): Ca(1)–C(1) 2.535(4), Ca(1)–N(3) 2.679(3), Ca(1)–N(1) 2.387(3), Ca(1)–N(2) 2.402(3), Ca(1)–C(2) 2.886(4), Ca(1)–C(3) 2.979(4), Ca(1)–O(1) 2.255(3), C(1)–C(2) 1.421(6), N(1)–Ca(1)–N(2) 76.84(10), N(1)–Ca(1)–N(3) 162.05(10), N(2)–Ca(1)–O(1) 95.50(9), N(2)–Ca(1)–C(1) 142.88, C(1)–Ca(1)–O(1) 121.20(13).

Although the insolubility of compounds **4**, **9** and **10** has, thus far, frustrated a meaningful quantitative analysis and it is unclear whether an intra- or intermolecular pathway is involved in their formation, it may be inferred from the relative ease of formation of compounds **4**, **9** and **10** that the heavy group 2 alkyl species display increasing reactivity toward β-diketiminate methyl group activation in the order Ca < Sr < Ba. It is noteworthy that the relative rates of reaction for degenerate methyl/methane exchange with $Cp^*_2M\text{-}CH_3$ complexes decreases in the order M = Y > Lu > Sc.[7] In DFT studies Eisenstein and Maron have also calculated that the larger, early lanthanides provide the lowest activation energies.[8] Judged by similar criteria, consideration of the lower intrinsic charge and increasing radii (6-coordinate radii: Ca^{2+}, 114: Sr^{2+} 132: Ba^{2+} 149 pm)[9] of the more electropositive alkaline earth series leads us to tentatively suggest that the relative facility of formation for compounds **4**, **9** and **10** may be underpinned by similar considerations of charge density and an interplay of polarisation effects. Irrespective of the semantics of whether the reactivity described above is termed σ-bond metathesis or deprotonation, these results provide a valuable step toward the activation and incorporation of less reactive substrates into group 2-based stoichiometric and catalytic reactivity. Future work will continue to elaborate this reactivity and to explore the apparently augmented basicity of alkyl derivatives of Sr and Ba, implied by the facile formation of compounds **9** and **10**.

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Notes and references

‡ X-ray data for **9**, **10** and **11** were collected at 150 K on a Nonius KappaCCD diffractometer, [$\lambda(Mo_{K\alpha}) = 0.71073$ Å], solved by direct methods and refined against all F^2 using SHELXL-97 with non-hydrogen atoms anisotropic and hydrogen atoms in riding mode.

Crystallographic data for **9**: ($C_{33}H_{48}N_2OSr$, $M_r = 576.35$) crystal dimensions 0.20 × 0.20 × 0.15 mm^3: orthorhombic, space group *Pcab*, $a = 13.4819(1)$, $b = 21.4266(2)$, $c = 21.6732(3)$ Å, $V = 6260.77(11)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.223$ g cm^{-3}, $\mu = 1.748$ mm^{-1}. Of 91870 reflections measured ($4.51 < \theta < 27.48$ °), 7146 were independent ($R_{int} = 0.1270$), $R1 = 0.0402$, $wR2 = 0.0827$ [for 4933 reflections with $I > 2\sigma(I)$], $R1 = 0.0774$, $wR2 = 0.0965$ (all data), GOF = 1.026. H1A, H1B, H3, H30C and H30D were located and refined at a distance of 0.98 Å from the parent atoms. 55:45 disorder modeled for C31–C33 in the THF ligand. O–C and C–C distances in the disordered solvent fragment were refined subject to similarity restraints.

Crystallographic data for **10**: ($C_{78}H_{108}Ba_2N_4O_2$, $M_r = 1408.36$) crystal dimensions 0.25 × 0.20 × 0.20 mm^3: monoclinic, space group $P2_1/c$, $a = 12.7330(2)$, $b = 24.2770(3)$, $c = 13.0420(2)$ Å, $\beta = 114.635(1)°$, $V = 3664.59(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.276$ g cm^{-3}, $\mu = 1.114$ mm^{-1}. Of 62937 reflections measured ($3.76 < \theta < 30.06°$), 10568 were independent ($R_{int} = 0.0454$), $R1 = 0.0326$, $wR2 = 0.0660$ [for 8426 reflections with $I > 2\sigma(I)$], $R1 = 0.0498$, $wR2 = 0.0723$ (all data), GOF = 1.063. The hydrogens attached to C1 and C16 were located and refined at a distance of 0.9 Å from the parent atoms. The molecule has a centre of inversion.

Crystallographic data for **11**: ($C_{42}H_{61}CaN_3O$, $M_r = 664.02$) crystal dimensions 0.20 × 0.10 × 0.10 mm^3:triclinic, space group *P*-1, $a = 12.2139(2)$, $b = 17.7982(4)$, $c = 18.2010(5)$ Å, $\alpha = 90.125(1)$, $\beta = 91.025(1)$, $\gamma = 97.899(1)°$, $V = 3918.42(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.126$ g cm^{-3}, $\mu = 0.194$ mm^{-1}. Of 65141 reflections measured ($3.84 < \theta < 25.07$ °), 13817 were independent ($R_{int} = 0.1176$), $R1 = 0.0654$, $wR2 = 0.1286$ [for 8509 reflections with $I > 2\sigma(I)$], $R1 = 0.1253$, $wR2 = 0.1575$ (all data), GOF = 1.074.

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