Regio- and Stereoselective Enolizations Using Calcium Bis(hexamethyldisilazide) as a Base: Synthetic, Solid-State, and Solution Studies

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The alkaline earth metal complex calcium bis(hexamethyldisilazide), $Ca(HMDS)_2$, has proven to be a useful reagent to carry out the regio- and stereoselective enolization reactions of ketones. The reactions give almost quantitative conversions to the corresponding silyl enol ethers at 0 °C using THF as solvent medium. Excellent kinetic selectivities (up to >99%) are found in the reactions of $Ca(HMDS)_2$ with a series of unsymmetrical ketones, and this base system displays high *Z*-selectivity (up to 96%) for stereoselective enolization reactions. Six new enolate-containing crystal structures have also been elucidated. The amidocalcium enolates adopt monomeric, dimeric, tetranuclear, and charge-separated constitutions. In addition, the unexpected preparation of a hexanuclear complex composed of amide, enolate, and enolized aldolate units was discovered. NMR spectroscopic studies of the amidocalcium enolate systems reveal that a common dynamic equilibrium between multiple species is established in pyridine-d_5. The solution species have been identified as amidocalcium enolates, bisenolates, bisamides, and charge-separated complexes. These studies demonstrate the structural diversity and complexity underlying these apparently straightforward calcium-mediated deprotonation reactions.

Introduction

The use of calcium complexes as reagents in synthesis is an area of rapid development.[1,2] In 2000 Ikegami described the use of a chiral calcium binolate complex as an efficient Lewis acid catalyst in the promotion of asymmetric Baylis−Hillman reactions.[3] This was followed by a report in 2001 from Noyori that a chiral hydrobenzoin calcium complex was able to catalyze asymmetric aldol reactions between ketones and aldehydes with good enantioselectivities.[4] Since then, organometallic calcium complexes have been applied to a growing number of organic transformations including intramolecular hydroaminations,[5] hydrosilylations,[6] hydrophosphinations,[7] and the Tischenko reaction.[9] Furthermore, several groups have begun to investigate the use of calcium catalysts in various polymerization reactions such as the anionic polymerization of styrene[9] and methylacrylates[10] and the ring-opening polymerization of cyclic esters.[11–13]

Our own contributions in this area have been directed toward the development of group 2 bisamides as effective Brønsted bases to conduct the enolization of ketonic substrates.[14,15] These bases are an attractive class of reagents, as they combine the properties of divalency with high reactivity.[16] Previously, we have demonstrated the utility of calcium bisamides in benchmark

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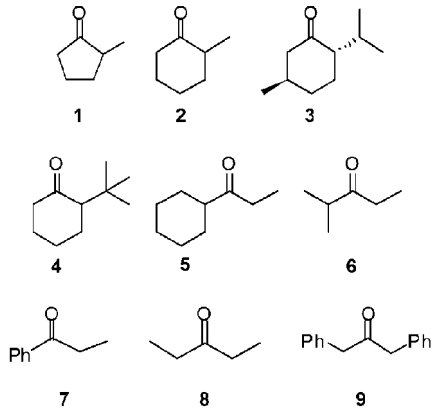
Chart 1. Ketones Used for the Enolization Studies

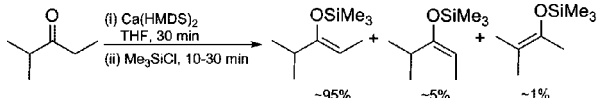


enolization reactions and detailed the crystal structures of three metal enolate products.[17–19] We now expand on our preliminary studies by reporting the use of calcium bis(hexamethyldisilazide), $Ca(HMDS)_2$, in the regio- and stereoselective enolization of ketones and also outline the structural characterization of six new enolate-containing calcium complexes.

Results and Discussion

Selectivity Studies. The nine ketones shown in Chart 1 were used for the enolization and subsequent silyl enol ether trapping studies. This set of ketones provides the opportunity to study both the regio- and stereoselectivity of the metal base system. $Ca(HMDS)_2$ was used as the reagent of choice, as it is readily prepared in a highly pure crystalline form[20] and has also been extensively studied in solution and in the solid state.[21]

A standard set of conditions was developed, and a typical reaction is shown in eq 1. Specifically, THF solutions of $Ca(HMDS)_2$ were cooled to 0 °C followed by the dropwise addition of the respective ketone (0.9 equiv). After stirring for 30 min, Me_3SiCl (4 equiv) was added, and the mixtures were stirred for a further 10−30 min, followed by quenching with saturated aqueous $NaHCO_3$. The quenched reaction mixtures were extracted with diethyl ether and analyzed by GC and NMR spectroscopic studies.



(1)

Table 1 lists the results of the reactions. All reactions proceeded smoothly with nearly quantitative conversions to the silyl enol ethers. It is notable that no significant quantities of side products, such as self-coupled aldol addition species or enones, were detected in the calcium-mediated reactions. The relatively high temperature of 0 °C chosen for the reactions contrasts with the lithium-mediated processes, where it is commonplace to carry out the reactions at very low temperatures, typically −78 °C, in order to maximize the kinetic selectivity of the enolization.[22] Initial studies of reactions carried out at −78 °C were substantially slower than those at 0 °C and showed little difference in their selectivities. For example, the reaction of ketone **1** gave a 76% conversion to the silyl enol ether after 3 h, with a k/t (kinetic/themodynamic) ratio of 88:12.

Table 1. Regio- and Stereoselective Enolizations by $Ca(HMDS)_2$ in THF Solution

ketone	conv (%)	k/t ratio[a]	*E*/*Z* ratio
1	99	80:20	
2	99	96:4	
3	97	85:15	
4	98	99:1	
5	>99	99:1	5:95
6	>99	99:1	5:95
7	>99		4:96
8	>99		12:88
9	>99		10:90

[a] k/t = kinetic/thermodynamic.

The reactions of the unsymmetrical ketones **1**−**6** all resulted in preferential removal of the more sterically accessible proton to produce the "kinetic" enolate. This selectivity is consistent with the sterically encumbered base controlling the position for the deprotonation. Reactions with ketones **5**−**9** present another level of complexity: stereoselective enolizations. In all cases good to excellent selectivities were observed for the preferential formation of the *Z*-enolates. The observed selectivity is in agreement with studies using magnesium bisamide reagents, where the use of polar solvents promotes the formation of the *Z*-enolates.[23] Switching the solvent medium from THF to toluene dramatically changes the selectivity of the reaction. Our previous studies involving the enolization of propiophenone in toluene using $Ca(HMDS)_2$ gave a 60:40 *E*/*Z* ratio.[14e] This solvent-dependent selectivity is presently under further study.

Overall, the $Ca(HMDS)_2$ reagent proves to be a competent base for both regio- and stereoselective enolization reactions. The conversions of the reactions are high, the conditions used are practical, and the selectivities of the individual benchmark reactions are comparable with or exceed existing methods.[22,24]

Solid-State Studies. Prior to this work, only three crystal structures of homometallic calcium enolates had appeared in the literature, monomeric $[(Me_3Si)_2NCaO(Ph){=}C(H)Ph \cdot pmdta]$ (where pmdta is *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine), **10**, dimeric $[(Me_3Si)_2NCaO(Mes){=}CH_2 \cdot Et_2O]_2$, **11**, and charge-separated

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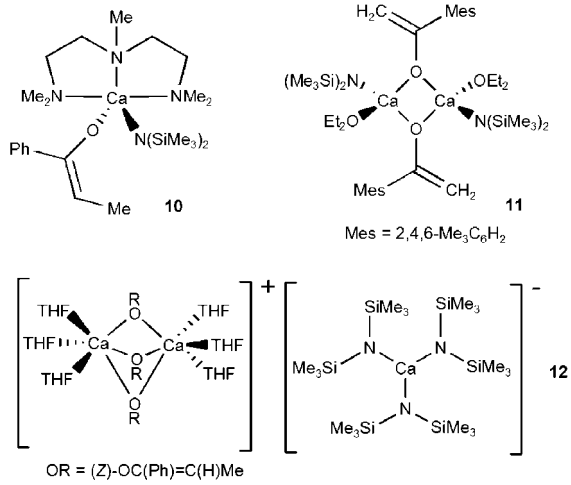
Chart 2. Structural Diagrams of the Previously Characterized Complexes 10−12



$[Ca_2\{OC(Ph)=C(H)Me\}_3\cdot 6THF]^+[Ca\{N(SiMe_3)_2\}_3]^-$, **12**. Interestingly, all three adopt quite distinct structural arrangements, as shown in Chart 2.[17,18]

In this work six new crystal structures of calcium enolates were successfully elucidated, the monomer $[(Me_3Si)_2NCa\{OC(CH_2Ph)=C(H)Ph\}\cdot 3THF]$, **13**, the two dimers $[(Me_3Si)_2NCaO\{(2S,5R)\text{-}2\text{-}^{i}Pr\text{-}5\text{-}Me\text{-}C_6H_3\}THF]_2$, **14**, and $[(Me_3Si)_2NCaO(2\text{-}^{t}Bu\text{-}C_6H_8)\cdot THF]_2$, **15**, the charge-separated species $[Ca_2\{OC(Et)=C(H)Me\}_3\cdot 6THF]^+[Ca\{N(SiMe_3)_2\}_3]^-$, **16**, the mixed enolate/aldolate/amide $[Ca_6\{OC(Et)=C(H)Me\}_6\cdot\{OC(Et)_2CH(Me)C(O)=C(H)Me\}_2\cdot\{N(SiMe_3)_2\}_2\cdot 2THF]$, **17**, and the tetranuclear complex $[\{(Me_3Si)_2N\}_2Ca_4\{O(C_6H_{11})\text{-}C=C(H)Me\}_6]$, **18** (Chart 3). With the exception of **18**, all of the compounds were prepared under conditions similar to those used for the silyl enol ether trapping studies, i.e., by the equimolar reaction of $Ca(HMDS)_2$ with the respective ketone in THF solution, followed by crystallization. The structure of each compound is presented below, and a list of comparative key bond lengths is given in Table 2.

The crystal structure of **13** is shown in Figure 1. The monomeric complex is composed of one enolate, one amide unit, and three solvating THF molecules. The gross structure is similar to complex **10**, with the replacement of the pmdta ligand by three THF molecules. C(8)−C(9) is 1.3633 Å, consistent with a localized double bond of the enolate. Overall, the pentacoordinate calcium center lies in a distorted trigonal bipyramidal geometry, with two of the THF molecules occupying the axial positions; that is, O(2)−Ca(1)−O(4) is 172.57(3)°. As expected, the two anions define the widest angle within the equatorial plane, with N(1)−Ca(1)−O(1) being 136.26(3)°, whereas the two angles O(1)−Ca(1)−O(3) and N(1)−Ca(1)−O(3) are 103.13(3)° and 120.59(3)°, respectively. The $Ca-O_{enolate}$ bond length of 2.1884(8) Å is the shortest in the series of compounds **13**−**18**. This is likely a result of its monomeric constitution, as the enolate does not bridge between multiple metals. In contrast, the Ca−N distance of 2.3522(9) Å is the longest within this set of compounds and compares well with that of 2.3283(12) Å found in **10**. The long Ca−N distances in **10** and **13** are likely a consequence of the terminal amides binding to pentacoordinate metal centers, as opposed to tetracoordinate metals for the remaining complexes. It is also notable that the enolate is in the *Z*-configuration, supporting this as the major product in the silyl enol ether trapping studies.

The two dimeric complexes **14** and **15** are shown in Figures 2 and 3. The complexes are very similar to one another and also to the previously characterized complex **11**. Each metal is tetracoordinate, binding to two bridging enolate groups, a terminal amide, and a single THF molecule. In both **14** and **15** the kinetic isomers are clearly produced, where short C−C distances arise from the double bonds on the less substituted side of the enolates, with C(1)−C(6) at 1.349(3) Å and C(11)−C(16) at 1.348(3) Å in **14** and with C(1)−C(6) at 1.354(2) Å in **15**. Again, these results are in accord with the trapping studies. The central Ca_2O_2 rings are planar and the two anions are oriented in a *transoid* fashion with respect to each other across the ring.

Complex **16** adopts an entirely different arrangement in the solid state. As seen in Figure 4, a charge-separated complex is produced consisting of a trisamide $[Ca(N(SiMe_3)_2\}_3]^-$ anion and a dinuclear $[Ca_2\{OC(Et)=C(H)Me\}_3\cdot 6THF]^+$ cation. The structure is analogous to that of the previously characterized complex **12**.[18] As expected from the trapping studies, all of the enolates are in the *Z*-configuration. It is worth noting that, as in **13**−**15**, there is a 1:1 ratio of amide to enolate present in the compound, but in this instance they are in distinct homoleptic entities. Clearly, the calcium centers in **16** are in two very different environments: trigonal planar and octahedral. The bond lengths within **16** are similar to those found in the other complexes despite the rather unusual structure adopted (Table 2). This suggests that there is relatively little steric strain imposed in either the anion or the cation.

The mixed enolate/aldolate/amide complex **17** was prepared unexpectedly using synthetic conditions similar to those for the preparation of **16**. Repeated attempts to rationally prepare this complex have thus far been unsuccessful, and its characterization is limited to the crystal structure shown in Figures 5 and 6. Nevertheless, the structure and composition of **17** are remarkable and merit attention. The complex contains six metals, two amides, six enolates, and two enolized aldolate dianions. All of the enolate groups, including those in the aldolates, are *Z*-stereoisomers. The presence of the enolized aldolate dianions in **17** is particularly notable. Such species have been utilized as intermediates in the preparation of β,β'-dihydroxyketones and β-hydroxy-β'-oxo ketones.[25,26] The identity of the enolized aldol addition product is clear from an analysis of the C−C and C−O distances. Specifically, C(9)−C(10) is 1.329(3) Å, while the remaining C−C distances of the ligand are in the range 1.504(3)−1.560(3) Å, consistent with localized double and single bonds, respectively. Also, C(9)−O(1) and C(19)−O(3) are 1.368 and 1.440 Å, respectively, in accord with single bonds and the ligand being doubly deprotonated.

The core of the structure contains a hexanuclear Ca_6O_{10} unit built from nine fused Ca_2O_2 rings. This unusual motif can be described as a quadruple open cubane, an extension of the more common double open cubane found for **18** (see later). This core structure has previously been observed for a relatively small number of hexanuclear metal complexes[27] and can be considered as structurally related to a section of the CdI_2 layer structure.[28] Only a handful of hexanuclear calcium complexes have previ-

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Chart 3. Structural Diagrams of the New Complexes 13−18

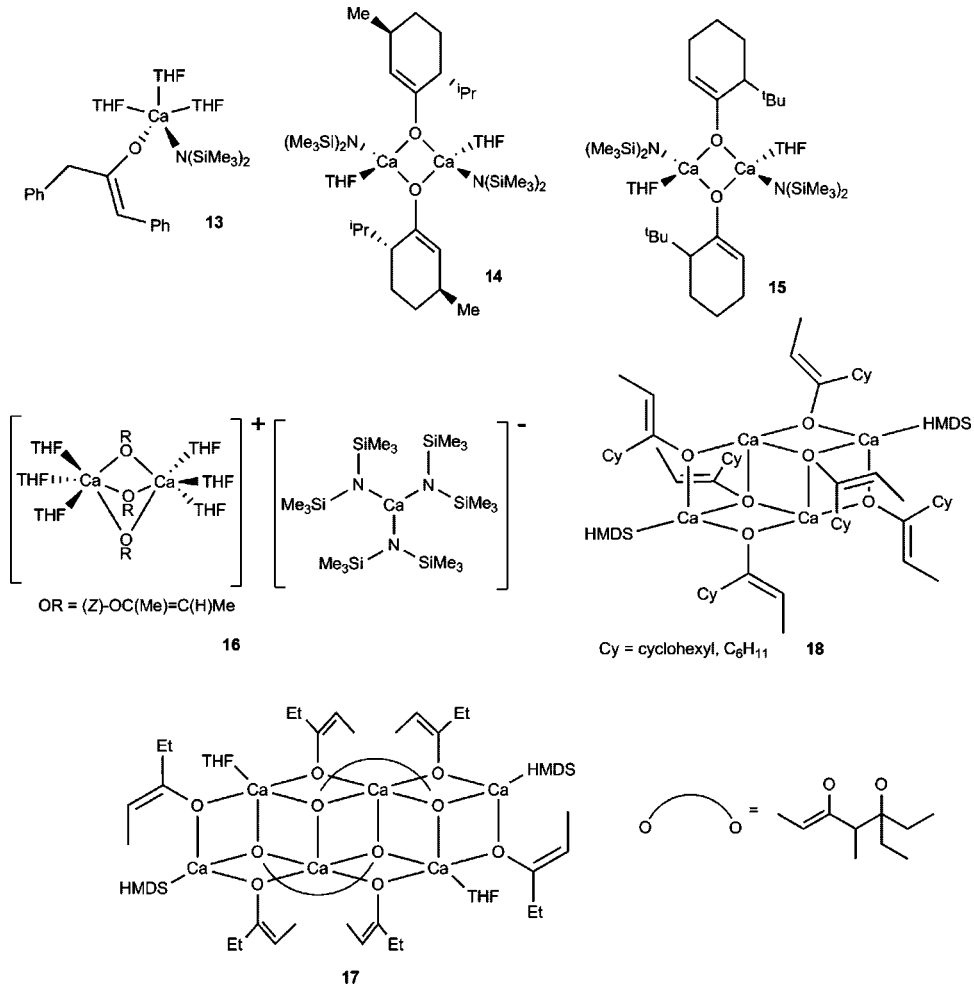

Table 2. Selected Key Bond Lengths (Å) in 13−18

	Ca−O_{anion}	Ca−O_{THF}	Ca−N	C=C
13	2.1884(8)	2.3651(8) 2.3785(8 2.3638(8)	2.3522(9)	1.3633(16)
14	2.3144(17), 2.2348(16) 2.2325(16), 2.3226(17)	2.3665(19) 2.3559(19)	2.321(2) 2.3221(19)	1.349(3) 1.348(3)
15	2.2987(13), 2.2340(14) 2.2897(6)	2.3504(14) 2.3994(7)	2.3052(15)	1.354(2)
16	2.3108(7)	2.4126(7)	2.3046(7)	1.3483(13)
17	2.4228(17), 2.2380(19) 2.2544(18), 2.3726(16) 2.2591(18), 2.3384(16) 2.3569(16), 2.2753(17) 2.2654(18), 2.4102(16) 2.2752(17), 2.3440(15)	2.4005(17)	2.298(2)	1.329(3) 1.328(4) 1.323(4)
18	2.3264(10), 2.3493(10) 2.3143(10), 2.3241(10) 2.2483(10), 2.2638(10) 2.4143(10)		2.3002(12)	1.357(2) 1.357(2) 1.3452(19)

ously been characterized, none of which adopt a structure similar to that found for **17**.[29]

Three distinct calcium environments are present in the centrosymmetric structure. The outer metal Ca(1) is tetra-

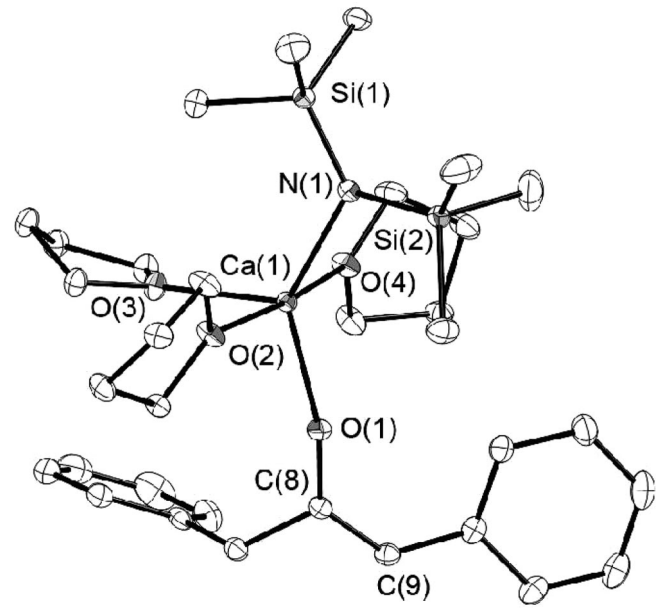

Figure 1. Molecular structure of pentacoordinate monomer **13**, with hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50% probability.

coordinate, binding to a terminal amide, two μ^2-enolates, and a μ^3-enolate section of a dianion. Ca(3) is pentacoordinate, surrounded by two μ^2-enolates, a μ^3-enolate section of a

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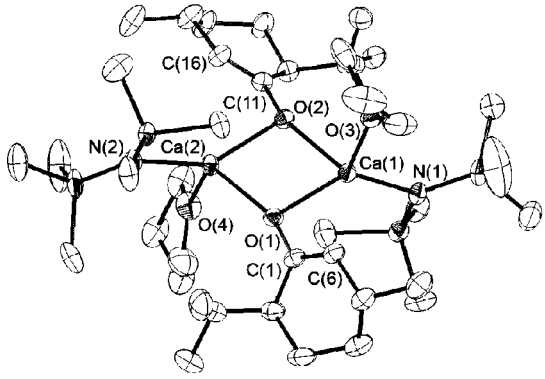


Figure 2. Molecular structure of dimer **14**, with hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50% probability.

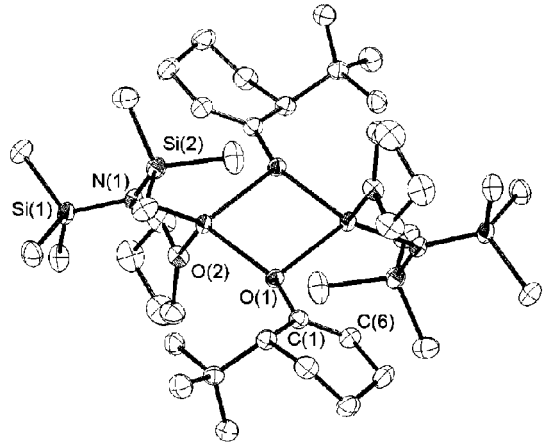


Figure 3. Molecular structure of dimer **15**, with hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50% probability.

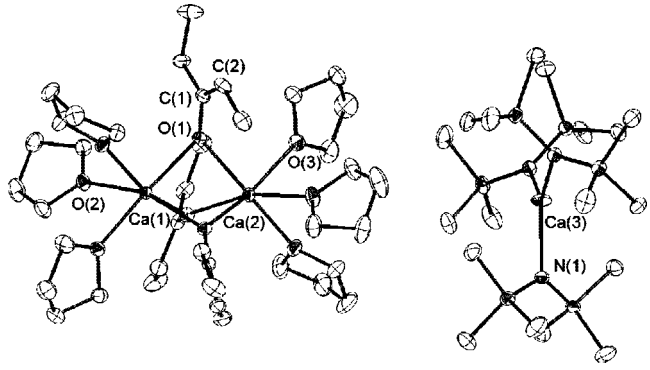


Figure 4. Molecular structure of the solvent-separated ion pair complex **16**, with hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50% probability.

dianion, a μ^3-alkoxide of a separate dianion, and a THF molecule. Finally, Ca(2) is also pentacoordinate but now binds to two μ^2-enolates, a μ^3-alkoxide of a dianion, and to both the enolate and alkoxide sections of a single dianion. The bond lengths within **17** are in accord with expectations, with the shorter M−O distances being associated with the μ^2-enolates, range 2.2383(17)−2.2755(15) Å, and longer distances for the μ^3-oxygens of the dianions, range 2.3390(14)−2.4231(15) Å.

The synthetic pathway leading to the synthesis and assembly of **17** is clearly complex. It appears that the structure represents

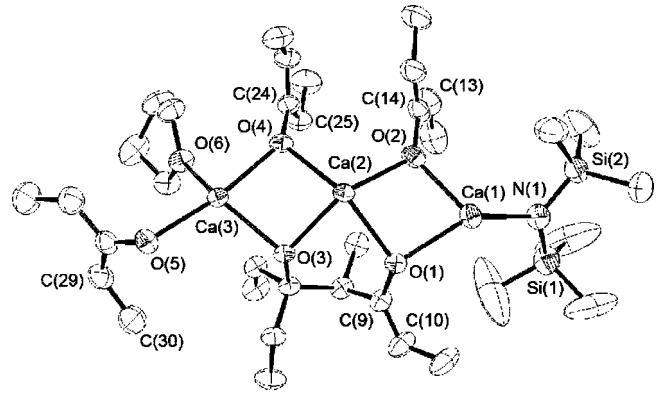


Figure 5. Asymmetric unit of **17**, with the toluene molecule of crystallization and hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability.

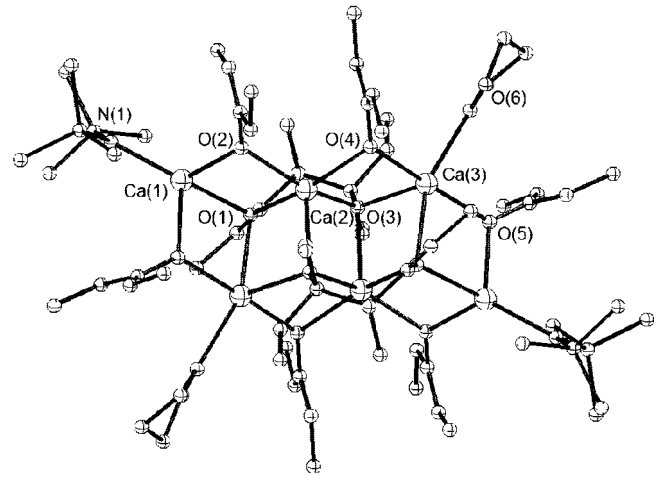
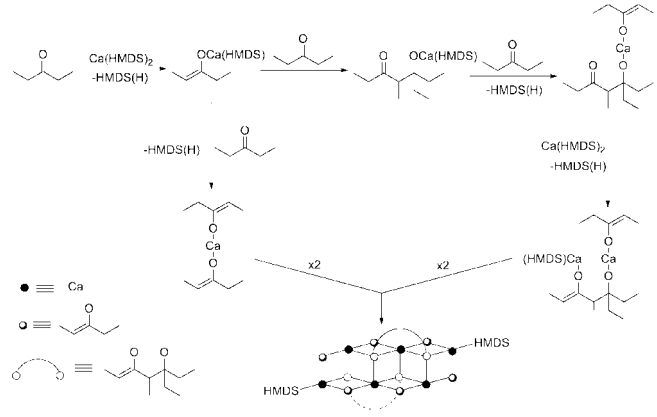


Figure 6. Molecular (simplified ball-and-stick rendition) structure of the heterotrianionic complex **17**, with the toluene molecule of crystallization and hydrogen atoms omitted for clarity.

Scheme 1. Possible Route for the Assembly of 17



a stable structural unit for aggregation by multiple, and likely independently produced, solution species. Scheme 1 outlines one possible route to produce the components present in **17**. In any event, the fortuitous characterization of **17** illustrates that multiple, but likely minor, side reactions may be occurring during these apparently straightforward calcium-mediated deprotonations.

The final structure characterized in the series is complex **18**, which was prepared from an equimolar reaction of the ketone and the base in neat hexane (Figure 7). The resulting enolates

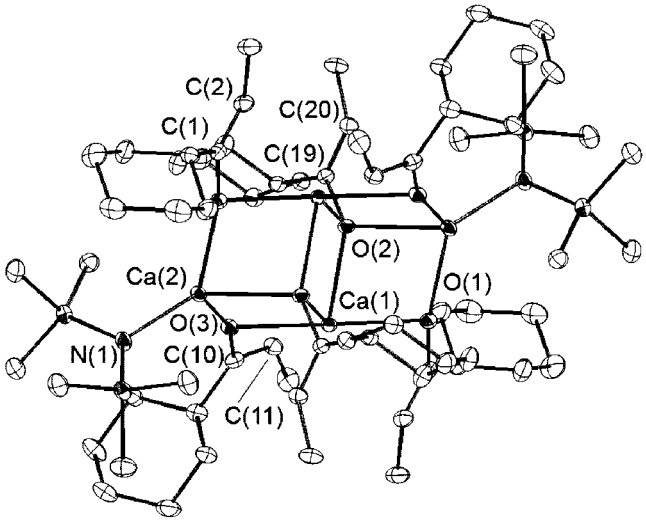


Figure 7. Molecular structure of tetranuclear **18**, with hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50% probability.

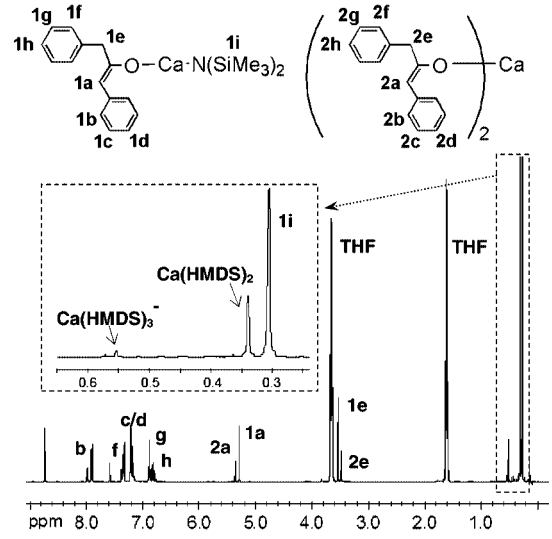


Figure 8. ^{1}H NMR spectrum upon dissolution of crystalline **13** in pyridine-d_5.

present within the complex are all *E*-stereoisomers, which contrasts with the other structures presented herein. The preference for the *E*-enolate is clearly a consequence of conducting the reaction in nonpolar solvent.[18] Nevertheless, **18** is a rare example of an organometallic *E*-enolate arising from a ketone, as the *Z*-isomer is generally more readily obtained, being the thermodynamically favored configuration.[22,24]

The structure of **18** can be described as a double open cubane, where two cubanes are fused and each is missing a single vertex. This motif is commonplace for various tetranuclear complexes and has also been previously characterized for calcium alkoxides.[30,31] All of the calcium centers in the centrosymmetric structure are tetracoordinate, but there are two distinct metal environments. The outer metal Ca(2) binds to a terminal amide, two μ^2-enolates, and a μ^3-enolate, whereas the central metal Ca(1) binds to two μ^2- and two μ^3-enolates. Again, the bond lengths fall within expected ranges relating to the coordination environment of the oxygen centers.

Another notable feature of **18** is the presence of four enolates and only two amides despite being prepared from an equimolar mixture of $Ca(HMDS)_2$ and the ketone. This composition is possibly the result of ligand redistribution, with the concomitant formation of an amide-rich counterpart such as $Ca(HMDS)_2$. It is also feasible that the reactivity of the base is altered in nonpolar solvent, such that a 1:1 amidocalcium enolate intermediate is competitive with the bis(amide) toward enolization to give the enolate-rich product **18**. The nature of the solvent clearly has a strong influence on both the stereoselectivity of the enolization and the structure of the aggregated products.

Solution Studies. A combination of ^{1}H, ^{13}C, 2D H−H COSY, and NOE NMR spectroscopic studies were undertaken to determine the nature of the complexes in d_5-pyridine solution. Our previous studies of the propiophenone derivatives **10** and **12** indicated that dissolution of crystalline amido(enolates) in d_5-pyridine resulted in the partial rearrangement to new species.[18] More specifically, these solutions contained amido(enolate), bisenolate, bisamide, and charge-separated complexes. Similar behavior was found for all of the new complexes studied here. To illustrate, a typical ^{1}H NMR spectrum obtained upon dissolution of crystalline **13** is shown in Figure 8. It should be noted that although the basic identities of the major complexes present have been established, their aggregation states and degrees of solvation are not yet known. The dominant species present is the amidocalcium enolate $(Me_3Si)_2NCa\{OC(CH_2Ph)=C(H)Ph\}$, which is identified by the 1:1 ratio of the relative integrals of the appropriate enolate and amide signals. In particular, the methine CH singlet at δ 5.30, the benzylic CH_2 at δ 3.56, and the Me_3Si signal at δ 0.31 appear in a 1:2:18 ratio, independent of sample preparation, concentration, or time. This pattern is consistent with these signals belonging to a 1:1 enolate/amide complex, as found for the solid-state structure of monomeric **13**. NOE studies confirm that the major species present are *Z*-isomers.[18]

A second smaller Me_3Si signal is apparent at δ 0.34, which is readily attributed to the bisamide $Ca(HMDS)_2$ by comparison with the ^{1}H and ^{13}C NMR spectra of the independently prepared reagent.[18] The appearance of $Ca(HMDS)_2$ suggests that the crystalline amidocalcium enolate **13** disproportionates upon dissolution. If this assertion is correct, then the remaining set of enolate signals (highlighted by the benzylic and methane singlets at δ 3.51 and 5.37, respectively) correspond to the bisenolate $Ca\{OC(CH_2Ph)=C(H)Ph\}_2$. This appears reasonable as the integrals for the $Ca(HMDS)_2$ and the bisenolate are present in an approximate 1:1 molar ratio, as required. Furthermore, the bis(enolate) was independently prepared by the in situ reaction of $Ca(HMDS)_2$ with 2 molar equiv of the ketone in d_5-pyridine. Both the ^{1}H and ^{13}C NMR spectra produced displayed a single set of signals for the bisenolate, which match those assigned as the disproportionation product. The assignments of the amido(enolate) and bisenolate are further corroborated by 2D H−H COSY experiments.

In order to determine if a charge-separated species similar to that characterized in the solid state for **16** was present in solution, the trisamide anion $[Ca(HMDS)_3]^-$ was prepared by mixing equimolar quantities of KHMDS, $Ca(HMDS)_2$, and 18-crown-6 in d_5-pyridine. We have previously shown that this mixture produces the charge-separated components and

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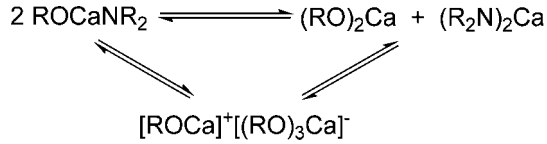
Scheme 2. Equilibria Present for the Enolate Complexes in d_5-Pyridine



have also crystallographically characterized the complex $[Ca(HMDS)_3]^-[K\cdot(18\text{-crown-}6)\cdot tol\cdot THF]$.[18] This reaction indicates that the signal for the trisamide anion $[Ca(HMDS)_3]^-$ appears δ 0.55. Analysis of the spectra of **13** reveals a small signal corresponding to this species (inset in Figure 8). In all instances in the present study the charge-separated complexes are minor components (<10%), and the enolate cations could not be detected by NMR spectroscopy because of their low abundance. Interestingly, even though complex **16** crystallizes as the charge-separated species (64% isolated yield), its ^{1}H NMR spectrum in d_5-pyridine shows a similar product distribution to **13**. Therefore, this is consistent with an equilibrium in solution (Scheme 2), where the particular product crystallized is not necessarily representative of the major species present in solution.

Conclusions

The readily prepared calcium bisamide $Ca(HMDS)_2$ has proven to be a useful reagent in the selective enolization of ketonic substrates. Moreover, this complex displays substantially increased reactivity in comparison to its magnesium analogue.[17] Reactions may be carried out under relatively mild conditions, while maintaining good selectivities and with minimal deleterious side reactions, such as self-aldol coupling or enone formation. These promising results suggest that calcium amide reagents may be useful in wide array of kinetically selective organic transformations. In particular, homochiral calcium amide reagents are excellent candidates for use in enantioselective deprotonation reactions,[32] and these studies are presently underway in our laboratories.

Although the enolization reactions appear straightforward, as judged by the silyl enol ether trapping studies, the solution chemistry taking place presents significant complexity. Multiple enolate products are present in polar solution, which leads to unexpected structural diversity for the solid-state structures that have been characterized. In comparison, the known chemistry of the magnesium analogues appears to be more straightforward.[14c] The greater complexity of the calcium system is related to the larger size of the cation and the increase in the ionic nature of the bonding involved. The presence of multiple solution species raises interesting questions regarding which aggregates are important in determining the course of further reactions.[24] Moreover, it is possible that the creation of some enolate species alters the reaction pathway as the reaction proceeds.[33] For example, the charge-separated trisamide $[Ca(HMDS)_3]^-$, one of the products of enolization, may be more reactive toward ketone than the neutral bisamide.[34] These issues are presently under further investigation.

Experimental Section

General Procedures. All operations were carried out by using Schlenk techniques or inside an argon-filled glovebox.[35,36] All glassware was flame-dried under vacuum before use. Solvents were dried by passage through copper-based catalyst and/or molecular sieve columns (Innovative Technology). $Ca(HMDS)_2$ was prepared by the transmetalation of 2 equiv of KHMDS with CaI_2 using a modified literature procedure,[20] and KHMDS was purchased from Aldrich. Ketones and trimethylsilyl chloride (Me_3SiCl) were distilled under a N_2 atmosphere before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were dried by storage over 4 Å molecular sieves. ^{1}H and ^{13}C NMR spectroscopic data were recorded at 298 K on either a Varian UnityPlus 300 MHz or a Bruker AVANCE DPX 400 MHz instrument. All ^{1}H and ^{13}C NMR spectra were referenced with respect to the residual solvent signal. Elemental analyses (C, H, N) were attempted but proved problematic due to the sensitivity of the samples and their lability to loss of lattice and/or coordinated solvents. GC experiments were performed on a Shimadzu GC-17A gas chromatograph fitted with a Rtx-5 fused Crossbond 5% diphenyl−95% dimethyl polysiloxane column (30 m, 0.25 mm i.d., 0.25 umdf), using N_2 as carrier gas. Detection was by flame ionization, and the chromatograms were interpreted using GCsolution software.

Trapping Studies. A general procedure for the trapping studies is given. A Schlenk tube was charged with 0.36 g (1 mmol) of $Ca(HMDS)_2$ inside a glovebox. The tube was then removed from the box, and further manipulations were carried out on a Schlenk line. The solid was dissolved in 5 mL of THF and the solution cooled to 0 °C. The specific ketone (**1**−**9**, 0.9 mmol) was then added to the solution dropwise, and the mixture stirred for 30 min. After this time Me_3SiCl (0.5 mL, 4 mmol) was added, the mixture was stirred for 30 min, and the resulting solution was quenched by 20 mL of saturated aqueous $NaHCO_3$. The quenched reaction mixture was extracted with ether, diluted by THF, and analyzed by NMR spectroscopy and GC. The regio- and stereochemical assignments for the silyl enol ethers were made by comparison with authentic samples.[24]

NMR Spectroscopic Studies. The crystalline compounds **13**−**18** were isolated from their respective reaction mixtures and analyzed by a combination of ^{1}H, ^{13}C, 2D H−H COSY, NOE, and C−H correlation NMR spectroscopic studies in pyridine-d_5. Pyridine-d_5 was the solvent of choice due to its relatively low cost and the absence of residual protonated signals in the areas of interest. More limited studies in THF-d_8 also showed similar dynamic behavior. In each instance, upon dissolution, the crystalline complexes were found to undergo a similar set of equilibria, containing amidocalcium enolate, calcium bisenolate, $Ca(HMDS)_2$, and charge-separated complexes (Figure 8 and Scheme 2). In each instance the major species present was the amidocalcium enolate, which was assigned from the consistent 1:1 molar ratio of the enolate and amide signals present

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Table 3. Crystallographic Data for 13−18

	13	**14**	**15**
empirical formula	$C_{33}H_{55}CaN\ O_4Si_2$	$C_{40}H_{86}Ca_2N_2O_4Si_4$	$C_{40}H_{86}Ca_2N_2O_4Si_4$
fw (g/mol)	626.04	851.63	851.63
temperature (K)	100(2)	100(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1$	$P2_12_12_1$	$P2_1/c$
a (Å)	8.5176(3)	15.269(3)	9.857(4)
b (Å)	19.9843(7)	17.846(4)	19.686(7)
c (Å)	10.2846(4)	18.960(4)	13.933(6)
α (deg)	90	90	90
β (deg)	98.502(2)	90	109.45(2)
γ (deg)	90	90	90
volume (Å^3)	1731.39(11)	5166.4(18)	2549.3(18)
Z	2	4	2
D_{calcd} (g/cm^3)	1.201	1.095	1.109
μ(Mo, Kα) (mm^{-1})	0.286	0.349	0.353
F(000)	680	1872	936
cryst size (mm^3)	0.24 × 0.19 × 0.18	0.62 × 0.50 × 0.20	0.25 × 0.30 × 0.31
θ range (deg)	2.00 to 30.51	1.57 to 31.50	1.86 to 32.63
index ranges	$-12 \le h \le 12$	$-19 \le h \le 22$	$-14 \le h \le 13$
	$-28 \le k \le 28$	$-20 \le k \le 26$	$0 \le k \le 28$
	$-14 \le l \le 14$	$-27 \le l \le 20$	$0 \le l \le 19$
no. of reflns collected	46 863	63 886	16 838
no. of independent reflns	10 281	17032	7820
GOF on F^2	1.039	1.040	1.015
R_1 [$I > 2\sigma(I)$]	0.0274	0.0532	0.0454
wR_2 (all data)	0.0686	0.1494	0.1377
largest diff peak and hole (e·Å^{-3})	0.351 and −0.197	2.042 and −0.463	0.785 and −0.519
	16	**17**	**18**
empirical formula	$C_{57}H_{129}Ca_3N_3O_9Si_6$	$C_{77}\ H_{150}\ Ca_6\ N_2\ O_{12}\ Si_4$	$C_{33}H_{63}Ca_2NO_3Si_2$
fw (g/mol)	1289.41	1650.85	658.18
temperature (K)	100(2)	293(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	trigonal	triclinic	monoclinic
space group	$R\bar{3}$	$P\bar{1}$	$P2_1/n$
a (Å)	17.8268(1)	12.9348(7)	14.9414(3)
b (Å)	17.8268(1)	13.5800(7)	13.7179(3).
c (Å)	20.7329(2)	15.0286(9)	18.2401(3)
α (deg)	90	76.942(3)	90
β (deg)	90	87.619(3)	90.379(1)
γ (deg)	120	67.419(3)	90
volume (Å^3)	5706.07(7)	2371.4(2)	3738.49(13)
Z	3	1	4
D_{calcd} (g/cm^3)	1.126	1.156	1.169
μ(Mo Kα) (mm^{-1})	0.358	0.438	0.400
F(000)	2124	900	1440
cryst size (mm^3)	0.29 × 0.29 × 0.16	0.20 × 0.21 × 0.25	0.27 × 0.25 × 0.05
θ range (deg)	1.64 to 36.30	1.39 to 26.37	1.76 to 27.88
index ranges	$-29 \le h \le 29$	$-16 \le h \le 16$	$-18 \le h \le 19$
	$-29 \le k \le 29$	$-16 \le k \le 16$	$-18 \le k \le 18$
	$-33 \le l \le 34$	$-18 \le l \le 18$	$-23 \le l \le 23$
no. of reflns collected	62 830	41 023	63 439
no. of indep reflns	12 061	9674	8907
GOF on F^2	1.043	1.032	1.031
R_1 [$I > 2\sigma(I)$]	0.0294	0.0493	0.0313
wR_2 (all data)	0.0713	0.1515	0.0808
largest diff peak and hole (e·Å^{-3})	0.558 and −0.247	0.645 and −0.525	0.739 and −0.250

in the ^{1}H NMR spectra. Also, the characteristic olefinic signals for the bisenolates were readily identified. The identities of the bisenolates were confirmed by in situ ^{1}H NMR spectroscopic studies of their independent preparation through reaction of $Ca(HMDS)_2$ with 2 molar equiv of the respective ketone. Finally, both $Ca(HMDS)_2$ and $[Ca(HMDS)_3]^-$ appear in each spectrum as characterized by the ^{1}H NMR signals at δ 0.34 and 0.56 and the ^{13}C NMR spectroscopic signals at δ 6.64 and 6.83. Due to the small concentrations of charge-separated complexes present (typically <5%), only the signals for the anionic trisamide component could be detected. The stereochemistry of the major enolate species present was determined by NOE studies to be *Z*-isomers, consistent with the solid-state studies of **13**−**17**. Compound **18** was also found to be in the *Z*-configuration, indicating that isomerization has occurred upon dissolution in pyridine-d_5.

Synthesis of [(Me$_3$Si)$_2$NCa{OC(CH$_2$Ph)═CHPh}·3THF], 13. $Ca(HMDS)_2$ (0.36 g, 1 mmol) was dissolved in 5 mL of THF at ambient temperature. 1,3-Diphenylpropan-2-one (0.18 mL, 0.9 mmol) was added dropwise, and the solution stirred for 30 min. The mixture was filtered through a sinter and the filtrate reduced to 3 mL in vacuo. Storage of the solution at −20 °C for 2 days produced colorless crystals of **13**. Yield: 0.35 g, 62%.

Amidocalcium Enolate. ^{1}H NMR (C_5D_5N): δ 0.31 (s, 18H, $SiMe_3$), 3.56 (s, 2H, $PhCH_2$), 5.30 (s, 1H, C(O)═C<u>H</u>Ph), 6.77−6.92 (m, 2H, p-H on Ar), 7.14−7.24 (m, 4H, m-H on Ar), 7.34 (d, 2H,

$^3J_{HH}$ 7.6 Hz, o-H on Ar from $PhCH_2$), 7.91 (d, 2H, $^3J_{HH}$ 7.6 Hz, o-H on Ar from C(O)=CHPh). ^{13}C NMR (C_5D_5N): δ 6.57 ($SiMe_3$), 14.06 (=CH-CH_3), 50.24 ($PhCH_2$), 97.48 (C(O)=CHPh), 121.29, 126.17, 126.20, 128.24, 128.74, 130.15, 142.71, 143.94 (Ar-C), 168.15 (C(O)).

Calcium Bisenolate. ^{1}H NMR (C_5D_5N): δ 3.51 (s, 2H, $PhCH_2$), 5.37 (s, 1H, C(O)=CHPh), 6.77−6.92 (m, 2H, *p*-H on Ar), 7.14−7.24 (m, 4H, *m*-H on Ar), 7.37 (d, 2H, $^3J_{HH}$ 7.2 Hz, *o*-H on Ar from $PhCH_2$), 7.98 (d, 2H, $^3J_{HH}$ 8.0 Hz, *o*-H on Ar from C(O)=CHPh). ^{13}C NMR (C_5D_5N): δ 50.21 ($PhCH_2$), 96.94 (C(O)=CHPh), 120.83, 126.11, 128.18, 128.76, 130.27, 143.10, 144.27 (Ar-C), 169.43 (C(O)).

Synthesis of $[(Me_3Si)_2NCaO\{(2S,5R)$-2-^{i}Pr-5-Me-$C_6H_3\}THF]_2$, 14. $Ca(HMDS)_2$ (0.36 g, 1 mmol) was dissolved in 10 mL of THF and the solution cooled to −78 °C. The ketone (2*S*,5*R*)-2-isopropyl-5-methylcyclohexanone (0.16 mL, 0.9 mmol) was added dropwise to the solution, and the mixture was warmed slowly to room temperature. The volume of the solution was reduced to 2 mL in vacuo followed by the addition of 0.5 mL of toluene and 1 mL of hexane. The reaction mixture was filtered and the filtrate stored at −20 °C. Colorless crystals of **14** were deposited over a 1 week period. Yield: 0.238 g, 62%.

Amidocalcium Enolate. ^{1}H NMR (C_5D_5N): δ 0.35 (s, 18H, $SiMe_3$), 0.90 (overlapping dd, 6H, $^3J_{HH}$ 6.4 Hz, $CH(CH_3)_2$), 1.07 (d, 3H, $^3J_{HH}$ 6.8 Hz, cyclic-$CHCH_3$), 1.53 (m, br, 1H, $CH(CH_3)_2$), 1.75−2.70 (series of overlapping broad multiplets, 6H, cyclic-H), 4.46 (m, 1H, C(O)=CH). ^{13}C NMR (C_5D_5N): δ 6.59 ($SiMe_3$), 17.41, 21.63, 23.63, 25.95, 27.79, 32.50, 34.78 (cyclic-C and CH_3), 48.04 (^{i}PrCH), 99.84 (CH=C(O)), 163.10 (C(O)).

Calcium Bisenolate. ^{1}H NMR (C_5D_5N): δ 0.88, 0.91 (dd, 6H, $^3J_{HH}$ 6.9 Hz, $CH(CH_3)_2$), 1.15 (d, 3H, $^3J_{HH}$ 6.8 Hz, cyclic-$CHCH_3$), 1.36−2.75 (series of overlapping broad multiplets, 7H, cyclic-H and $CH(CH_3)_2$), 4.59 (m, 1H, C(O)=CH).

Synthesis of $[(Me_3Si)_2NCaO(2$-^{t}Bu-$C_6H_8)THF]_2$, 15. $Ca(HMDS)_2$ (0.36 g, 1 mmol) was dissolved in 5 mL of THF and the solution cooled to −78 °C. The ketone 2-*tert*-butylcyclohexanone (0.17 mL in 2 mL of THF) was added dropwise, and the solution stirred for 2 h. The system was warmed slowly to room temperature and the solution concentrated to 3 mL. A small amount of white precipitate appeared, which was redissolved on the addition of 0.4 mL of hexane and gentle heating. Colorless crystals of **15** were deposited after storing the solution at 4 °C overnight. Yield: 0.217 g, 51%.

Amidocalcium Enolate. ^{1}H NMR (C_5D_5N): δ 0.35 (s, 18H, $SiMe_3$), 1.18 (s, 9H, ^{t}Bu), 1.60−2.32 (series of overlapping broad multiplets, 7H, cyclic-CH), 4.46 (dd, 1H, $^3J_{HH}$ 5.1 Hz, 2.4 Hz, CH=C(O)). ^{13}C NMR (C_5D_5N): δ 6.67 ($SiMe_3$), 24.87, 27.13, 28.98 (cyclic-C), 30.80 ($C(CH_3)_3$), 34.63 ($C(CH_3)_3$), 51.20 (CH^tBu), 93.05 (CH=C(O)), 164.83 (CH=C(O)).

Calcium Bisenolate. ^{1}H NMR (C_5D_5N): δ 1.30 (s, 9H, ^{t}Bu), 1.60−2.40 (series of overlapping broad multiplets, 7H, cyclic-CH), 4.42 (m, 1H, CH=C(O)).

Synthesis of $[Ca_2\{OC(Et)=CHMe\}_3\cdot 6THF]^+[Ca\{N(SiMe_3)_2\}_3]^-$, 16. $Ca(HMDS)_2$(0.36 g, 1 mmol) was dissolved in 5 mL of THF and the solution cooled to −78 °C. The ketone 3-pentanone (0.10 mL, 0.9 mmol) was added dropwise and the solution stirred for 3 h. After this time the mixture was warmed slowly to room temperature, the solution was concentrated to 3 mL, and 0.2 mL of hexane was added. The mixture was filtered and the filtrate stored at −20 °C. Clear, colorless crystals of **16** were deposited over a period of 2 days. Yield: 0.21 g, 64%.

Amidocalcium Enolate. ^{1}H NMR (C_5D_5N): δ 0.35 (s, 18H, $SiMe_3$), 1.14 (t, 3H, $^3J_{HH}$ 7.5 Hz, CH_2CH_3), 1.78 (d, 3H, $^3J_{HH}$ 6.0 Hz, *C*=CH-CH_3), 2.24 (q, 2H, $^3J_{HH}$ 7.5 Hz, CH_2CH_3), 4.19 (q, 1H, $^3J_{HH}$ 6.0 Hz, C=CH-CH_3). ^{13}C NMR (C_5D_5N): δ 6.64 ($SiMe_3$), 12.51 (CH_2CH_3), 14.06 (C=CH-CH_3), 34.30 (CH_2CH_3), 83.22 (C=CH-CH_3), 165.26 (C(O)=C(H)Me).

Calcium Bisenolate. ^{1}H NMR (C_5D_5N): δ 1.09 (br m, 3H, CH_2CH_3), 1.80 (br m, 3H, C=CH-CH_3), 2.29 (br m, 2H, $^3J_{HH}$ 7.5 Hz, CH_2CH_3), 4.28 (br m, 1H, $^3J_{HH}$ 7.2 Hz, C=CH-CH_3).

Synthesis of $[Ca_6\{OC(Et)=C(H)Me\}_6\cdot\{OC(Et)_2CH(Me)$-$C(O)=C(H)Me\}_2\cdot\{N(SiMe_3)_2\}_2\cdot 2THF]$, 17. Crystals of this complex were prepared in an identical manner to that outlined for complex **16**. Repeated attempts to reproduce the synthesis of this complex have thus far been unsuccessful, and it is likely that its fortuitous discovery was as a rogue crystal, with complex **16** being the major component present. The analysis of **17** is therefore limited to the crystal structure.

Synthesis of $[\{(Me_3Si)_2N\}_2Ca_4\{O(C_6H_{11})C=C(H)Me\}_6]$, 18. $Ca(HMDS)_2$ (0.43 g, 1.2 mmol) was dissolved in 5 mL of hexane. The ketone 1-cyclohexylpropan-1-one (0.17 mL, 1.1 mmol) was added dropwise and the solution stirred for 30 min. The mixture was filtered and the filtrate concentrated until a white precipitate appeared. The precipitate was redissolved by gentle heating and stored at 10 °C. Clear, colorless crystals of **18** were formed overnight. Yield: 0.09 g, 36%.

Amidocalcium Enolate. ^{1}H NMR (C_5D_5N): δ 0.36 (s, 18H, $SiMe_3$), 1.01−1.80 (m, 10H, cyclic-CH_2), 1.94 (d, 3H, $^3J_{HH}$ 6.8 Hz, C(O)=CHCH_3), 2.71 (m, 1H, cyclic-CHC(O)), 4.22 (q, 1H, $^3J_{HH}$ 6.8 Hz, C(O)=CHCH_3). ^{13}C NMR (C_5D_5N): δ 6.73 ($SiMe_3$), 13.84 (C(O)=CHCH_3), 27.79 ($CH_2CH_2CHC(O)$), 31.53 ($CH_2CHC(O)$), 41.45 ($CH_2CH_2CH_2CHC(O)$), 49.20 (CH_2CH_2-CHC(O)), 83.73 (C(O)=CHCH_3), 168.28 (C(O)=CHCH_3).

Calcium Bisenolate. ^{1}H NMR (C_5D_5N): δ 1.01−1.80 (m, 10H cyclic-CH_2), 1.79 (d, 3H, $^3J_{HH}$ 6.8 Hz, C(O)=CHCH_3), 2.87 (m, 1H, cyclic-CHC(O)), 4.19 (q, 1H, $^3J_{HH}$ 6.0 Hz, C(O)=CHCH_3).

X-ray Crystallography. Single crystals of **13**−**18** were grown according to the experimental procedures outlined above and were examined under Infineum V8512 oil. In each case, the datum crystal was affixed to either a thin glass fiber atop a tapered copper mounting pin or a Mitegen mounting loop and transferred to the 100 K nitrogen stream of a Bruker APEX diffractometer equipped with an Oxford Cryosystems 700 series low-temperature apparatus. Cell parameters were determined using reflections harvested from three sets of 12 0.5° φ scans. The orientation matrix derived from this was transferred to COSMO[37] to determine the optimum data collection strategy requiring a minimum of 4-fold redundancy. Final cell parameters were refined using reflections harvested from the data collection with $I \geq 10\sigma(I)$. All data were corrected for Lorentz and polarization effects, and runs were scaled using SADABS.[38]

The structures were solved and refined using SHELXTL.[39] Structure solution was by direct methods. Non-hydrogen atoms not present in the direct methods solution were located by successive cycles of full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at idealized geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2 times the equivalent isotropic *U* of the parent atom, 1.5 times for methyl hydrogens. Table 3 lists the key crystallographic parameters.

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Supporting Information Available: Crystallographic data for **13**−**18** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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