Heavier Group-2-Element Catalyzed Hydroamination of Carbodiimides

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The heteroleptic calcium amide [(ArNC(Me)CHC(Me)-NAr)Ca(N(SiMe3)2)(THF)] (Ar = 2,6-diisopropylphenyl) and the homoleptic heavier alkaline earth amides, [M{N(SiMe3)2}2(THF)2] (M = Ca, Sr and Ba) are reported as competent pre-catalysts for the hydroamination of 1,3-carbodiimides. Whilst the reaction scope is currently limited to reactions of aromatic amines with 1,3-dialkylcarbodiimides, in most cases preparations in hydrocarbon solvents proceed rapidly at room temperature with catalyst loadings as low as 0.2 mol-% and the guanidine reaction products crystallize directly from the reaction mixture. Initial studies are consistent with the intermediacy of heavier group-2 guanidinate complexes.

Introduction

Over the past few years a useful reaction chemistry of the organometallic compounds of the heavier alkaline earths (M = Ca, Sr and Ba) has begun to emerge.[1] Studies within our group, and elsewhere, have demonstrated the application of heavier group-2 species to the catalytic hydroamination,[2] hydrophosphination,[3] hydrosilylation,[4] and polymerization[5] of substrates containing unsaturated carbon–carbon bonds. In addition, a number of group-2 mediated catalytic reactions have been reported that employ substrates containing carbon–heteroatom multiple bonds. These include the polymerization of lactides and lactones,[6] the trimerisation of phenyl isocyanate,[7] the dimerisation of aldehydes (Tischenko reaction) [8] and the hydrophosphination of 1,3-carbodiimides.[9]

Guanidines have received considerable attention not only for use as ancillary ligands in f-block and transition-metal chemistry,[10] but also due to their appearance as functional groups in many natural products and synthetic pharmaceuticals.[11] Despite this, catalytic syntheses of these molecules remain limited to a handful of examples. These include the early transition metal,[12] lanthanide[13] and group 1[14] mediated hydroamination of carbodiimides and group 4 imido catalyzed transamination of guanidines.[12a] As part of a preliminary study toward the catalytic hydroamination of heterocumulenes, we recently reported that β-diketiminato calcium amides, [(ArNC(Me)CHC(Me)NAr)Ca{NR3}2(THF)] (Ar = 2,6-diisopropylphenyl, NR3 = NHAr, NPh2, NHCH2CH2OMe), readily undergo insertion reactions with 1,3-dialkycarbodiimides to yield the corresponding heteroleptic calcium guanidinate complexes. Furthermore, these latter complexes could be synthesized through a one-pot procedure from addition of the amine and carbodiimide to [(ArNC(Me)CHC(Me)NAr)Ca{N(SiMe3)2}(THF)] (1) in hydrocarbon solutions.[15] We now describe the extension of this work to the group-2 catalyzed synthesis of guanidines by the hydroamination of 1,3-carbodiimides.

Results and Discussion

Hydroamination Catalysis

An initial NMR experiment was conducted between 2-fluoroaniline (δ19F = −135.8 ppm), 1,3-diisopropylcarbodiimide and [Ca{N(SiMe3)2}2(THF)2] (2a) in [D6]benzene. Addition of an excess of both 2-fluoroaniline and 1,3-dialky carbodiimide to the pre-catalyst resulted in an instant crystallization of a colorless reaction product from the NMR tube. Whilst this event prevented the acquisition of satisfactory multinuclear NMR spectroscopic data on the reaction mixture, following work-up of the tube, isolation and characterization revealed the solid to be the guanidine [(2-FC6H5)N]C{NHiPr}2 (δ19F = −125.1 ppm) formed in 44% isolated yield from the catalytic hydroamination of 1,3-diisopropylcarbodiimide followed by, or concomitant with, a 1,3-proton shift. The structure of the product was confirmed by single-crystal X-ray diffraction (Figure 1). A
background experiment between 2-fluoroaniline and 1,3-diisopropylcarbodiimide demonstrated no reaction after 7 d at room temperature (Scheme 1).[16]

Figure 1. ORTEP representation (50%) of \( [(2-\text{FC}_6\text{H}_5)\text{N}]{\text{NH} \text{Pr}_2}\)]. Selected bond lengths [Å] and angles [°]: C(1)–N(1) 1.306(2), C(1)–N(2) 1.364(3), C(1)–N(3) 1.363(3), N(1)–C(1)–N(3) 118.73(19), N(1)–C(1)–N(2) 127.06(19), N(3)–C(1)–N(2) 114.15(18). Disordered fluorine atoms modelled over two sites.

Scheme 1. Group-2 catalyzed hydroamination of carbodiimides.

On the basis of this observation a series of reactions were conducted in benzene solutions. The heteroleptic calcium amide 1 and the series of homoleptic heavier alkaline earth amides \( [\text{M}\{\text{N(SiMe}_3\}_2]_{\text{2(THF)}_2}\] (\( \text{M} = \text{Ca}, \text{Sr}, \text{Ba} \)) were applied to the catalytic hydroamination of 1,3-disopropylcarbodiimide with 2-fluoroaniline. Although it has proven to be a remarkably useful prototype for the elaboration of stoichiometric calcium reactivity, in the current context, use of the \( \beta \)-diketiminato complex 1 offers no advantage over the homoleptic calcium amide 2a in terms of either activity or ease of utility. Indeed it is likely that the \( \beta \)-diketiminate ligand is protonated and effectively removed during the early stages of catalytic turnover to provide common catalytic intermediates (viz. the homoleptic guanidinate complexes 3a and 3b, vide infra). Reactions were conducted using 2 mol-% catalyst and based upon initial substrate concentrations of 0.15 M. Although, in all cases, crystallization of the product from solution was observed at room temperature, the reaction yield of the isolated guanidine was consistently low (37–68%). This latter limitation could be overcome, however, by changing the conditions for what is effectively a crystallization of the reaction product upon mixing starting materials and catalyst. In this manner, increasing the concentrations of the substrates to 0.3 M and changing the reaction solvent to hexane yielded the hydroamination product \( [(2-\text{FC}_6\text{H}_5)\text{N}]{\text{NH} \text{Pr}_2}\] in 71–84%.

Again 1 and 2a–c proved catalytically active with most reactions taking less than 5 min at room temperature (Table 1, Entries 1–4).

A number of anilines and 1,3-carbodiimides were investigated under these reaction conditions and the results of this study are presented in Table 1. The hydroamination of both symmetric and unsymmetric carbodiimides was achieved at room temperature using 2 mol-% of the calcium amide 2a. Choice of pre-catalyst was dictated by its ease of synthesis and low cost. Both electron-rich and electron-deficient anilines react readily and, in most cases, following crystallization the guanidine products could be isolated by simple filtration. Catalytic hydroamination reactions employing sterically demanding substrates, such as 1,3-di-t-tert-butylcarbodiimide (Table 1 Entries 8, 9) and 2,6-diisopropyl-aniline (Table 1, Entry 17, 18) however, could only be achieved at higher reaction temperatures. These observa-

Table 1. Group 2 catalyzed hydroamination of carbodiimides.

| Entry | \( R^1 \) | \( R^2 \) | Ar | Catalyst | Time [b] | Yield [%, c] |
|-------|----------|----------|----|---------|---------|-------------|
| 1     | \( t\text{Pr} \) | \( t\text{Pr} \) | 2-\text{FC}_6\text{H}_4 | 1 (2) | 0.1 | 84 |
| 2     | \( t\text{Pr} \) | \( t\text{Pr} \) | 2-\text{FC}_6\text{H}_4 | 2a (2) | 0.1 | 77 |
| 3     | \( t\text{Pr} \) | \( t\text{Pr} \) | 2-\text{FC}_6\text{H}_4 | 2b (2) | 0.1 | 80 |
| 4     | \( t\text{Pr} \) | \( t\text{Pr} \) | 2-\text{FC}_6\text{H}_4 | 2c (2) | 1 | 67 |
| 5     | \( \text{Cy} \) | \( \text{Cy} \) | 2-\text{FC}_6\text{H}_4 | 2a (2) | 0.1 | 79 |
| 6     | \( \text{tBu} \) | \( \text{Et} \) | 2-\text{FC}_6\text{H}_4 | 2a (2) | 12 | 91 |
| 7     | \( \text{tBu} \) | \( \text{Et} \) | 2-\text{FC}_6\text{H}_4 | 2a (2) | 0.25 | 74 |
| 8     | \( \text{tBu} \) | \( \text{tBu} \) | 2-\text{FC}_6\text{H}_4 | 2a (4) | 24 | 37 |
| 9     | \( \text{tBu} \) | \( \text{tBu} \) | 2-\text{FC}_6\text{H}_4 | 2a (4) | 24 | 46 |
| 10    | \( t\text{Pr} \) | \( t\text{Pr} \) | 4-Me-\text{C}_6\text{H}_4 | 2a (2) | 12 | 71 |
| 11    | \( \text{Cy} \) | \( \text{Cy} \) | 4-Me-\text{C}_6\text{H}_4 | 2a (4) | 4 | 81 |
| 12    | \( t\text{Pr} \) | \( t\text{Pr} \) | Ph | 2a (2) | 1 | 74 |
| 13    | \( \text{Cy} \) | \( \text{Cy} \) | Ph | 2a (2) | 0.1 | 81 |
| 14    | \( t\text{Pr} \) | \( t\text{Pr} \) | 2-\text{MeOC}_6\text{H}_4 | 2a (2) | 12 | 85 |
| 15    | \( \text{Cy} \) | \( \text{Cy} \) | 2-\text{MeOC}_6\text{H}_4 | 2a (2) | 12 | 80 |
| 16    | \( t\text{Pr} \) | \( t\text{Pr} \) | 1-naphthyl | 2a (2) | 72 | 57 |
| 17    | \( \text{Cy} \) | \( \text{Cy} \) | 2,6-PrC_6\text{H}_3 | 2a (4) | 2 | 55 |
| 18    | \( \text{Cy} \) | \( \text{Cy} \) | 2,6-PrC_6\text{H}_3 | 2a (4) | 2 | 82 |

[a] Isolated yield following crystallization of the product from hexane at 25 °C. [b] Yield determined by \(^{1}H\) NMR spectroscopy in [D\(_6\)] benzene using tetrakis(trimethylsilyl)silane as an internal standard. [c] Reaction conducted at 80 °C.
tions are consistent with those previously made in stoichiometric heavier group-2 chemistry. For example, although the calcium amide \([\text{[ArNC(Me)CHC(Me)NAr]}\text{Ca}\{\text{NHar}\}(\text{THF})]\) reacts readily with 1,3-diisopropyl- and 1,3-dicyclohexylcarbodiimide at room temperature, this latter complex does not undergo an insertion reaction with 1,3-di-tert-butylcarbodiimide even after being heated to 60 °C for 12 h.\(^{[15]}\) Initial attempts to extend the catalytic methodology to primary alkylamines proved unsuccessful. Although stoichiometric reactions using \(\mathbf{1}\) in these instances provided the expected heteroleptic calcium guanidinate complexes\(^{[15]}\); these species did not undergo catalytic turnover.

Previous catalytic syntheses of guanidines employing early transition metal, group 1 or f-block-based catalysts typically require long reaction times and/or elevated reaction temperatures to achieve the hydroamination of 1,3-carbodiimides.\(^{[13-14]}\) For instance, the reaction of aniline with 1,3-diisopropylcarbodiimide to yield \([\text{[C}_6\text{H}_5\text{N]C}{\text{NH}}\text{iPr}_2}\]) is reported to be catalyzed by \([\text{Li}\{\text{N(SiMe}_3)_2}\}] (2 mol-%, 115.81(11), N(1)–C(9)–N(3) 121.53(11), N(2)–C(9)–N(3) 122.65(11), O(1)–Ca–O(2) 89.54(4)).\(^{[17]}\) In addition, bond lengths and bond angles \([\text{Ca}–\text{N} 2.4179(10), \text{Ca}–\text{O}(2) 2.4194(10) \text{ and exception of NH protons omitted for clarity. Selected bond lengths [Å] and angles [°]. Ca–N(1) 2.4215(11), Ca–N(2) 2.4179(10), Ca–N(4) 2.4202(11), Ca–N(5) 2.4291(11), Ca–N(6) 2.4206(10), Ca–

![Figure 2. ORTEP representation (40%) of 3a. H-Atoms with \(\Delta G^\ddagger = 68 \text{kJ mol}^{-1}\) characterising one fluxional process.](image)

\(^{[15]}\) in complexes \(3a–b\).

Table 2. Selected bond lengths [Å] and bond angles [°] in complexes \(3a–b\).

|     | 3a                         | 3b                         |
|-----|---------------------------|---------------------------|
| Ca–N | 2.4215(11)                | 2.4179(10)                |
|     | (terminal)                | (terminal)                |
|     | 2.4202(11)                | 2.4291(11)                |
| Ca–N | 2.406(10)                 | 2.4269(11)                |
|     | (bridging)                | (bridging)                |
| Ca–O | 2.4106(10)                | –                          |
|     | 2.4194(10)                | –                          |
| N–C–N | 115.81(11)                | 121.24(11)                |
|     | (terminal)                | (terminal)                |
|     | 122.65(11)                | 115.97(11)                |
|     | 122.90(12)                | 122.7(12)                 |
|     | 121.37(11)                | 115.70(11)                |
| N–C–N | –                        | 123.99(12)                |
|     | (bridging)                | 116.52(11)                |
|     | –                          | 119.49(12)                |
| N–C–N | 56.13(3)                  | 57.45(4)                  |
|     | (terminal)                | (terminal)                |
|     | 55.90(4)                  | 55.08(4)                  |

In solution \(3a\) demonstrated a level of complexity that was not consistent with the solid-state data. Variable temperature NMR studies upon a [D\(_8\)]toluene solution of \(3a\) showed a number of reversible changes. At 298 K four independent isopropyl signals were observed by \(^1\)H NMR spectroscopy. In the high-temperature limit (353 K) these resonances coalesced to give only two isopropyl environments. Although coalescence of the apparent two sets of twin resonances occurred at two independent temperatures \([T_A = 318 \text{ K}; \ T_B = 338 \text{ K}]\) with two independent frequencies \([\kappa_A = 34 \text{ Hz}; \ \kappa_B = 117 \text{ Hz}]\), these data gave a single activation energy \([\Delta G^\ddagger = 68 \text{kJ mol}^{-1}]\) characterising one fluxional process. The complexity of these observations was re-
solved by the synthesis of a solvent-free analogue of 3a. Reaction of two equivalents of [(PhN)C{NH(iPr)}2]2 with [Ca{N(SiMe3)2}2(THF)2] in toluene yielded the dimeric calcium guanidinate complex 3b. An X-ray crystallographic study revealed 3b to consist, in the solid-state, of a centrosymmetric dimer in which five-coordinate calcium centers are bridged by unsymmetric Ca–N–Ca′ interactions (Figure 3 and Table 2). The N–C–N chelate rings are disposed with and anti-configuration with respect to the dimer core giving rise to an S2-symmetric tricyclic ladder structure. Further coordination at calcium is provided by terminal guanidinate ligands. As with 3a the guanidinate ligands in both terminal and bridging positions in 3b coordinate as unsymmetric κ2,N,N-chelates. The calcium–nitrogen bond lengths of the non-bridging interactions [av. 2.379 Å] are slightly shorter than those observed in 3a due to the higher coordination number at calcium in the former complex. The guanidinate bite angles within 3b [N(3)–Ca–N(1) 57.45° and N(6)–Ca–N(4) 55.08°] also differ slightly from those in the monomeric species with the terminal ligands demonstrating a more obtuse bite-angle than those in the bridging positions.

Although it has previously been reported that [(Me2Si)2N]C(NCycl)2]2Ca(OEt)2 (4) is susceptible to reversible decomposition with reformation of a carbodiimide and calcium amide[17] the attempted crossover reaction of 

\[\text{[(2-FC}_6\text{H}_5\text{N)}C{\text{NH(iPr)}}_2\text{]}_2\text{Ca(NH}_2\text{)}_2\text{]}\text{Ca(NH}_2\text{)}_2\text{]}\text{Ca(NH}_2\text{)}_2\text{]}

1,3-dicyclohexylcarbodiimide and 2 mol-% 2a yielded no new reaction products after 12 h at room temperature as monitored by 19F NMR spectroscopy. Similarly, a mixture of 

\[\text{[(2-FC}_6\text{H}_5\text{N)}C{\text{NH(iPr)}}_2\text{]}_2\text{Ca(NH}_2\text{)}_2\text{]}\text{Ca(NH}_2\text{)}_2\text{]}\text{Ca(NH}_2\text{)}_2\text{]}

4-methylaniline and 2 mol-% 2a demonstrated no signs of crossover reaction products over the same period. These experiments suggest that, under the catalytic reaction conditions, the calcium guanidinate complexes are kinetically stable and guanidine formation is non-reversible.

Proposed Catalytic Cycle

The isolated guanidinate complexes 3a and 3b were also applied to the catalytic hydroamination of 1,3-disopropylcarbodiimide with aniline. Although, both compounds proved catalytically active the isolated yields of the guanidine products (3a, 1 h, 62%; 3b, 1 h, 79%) differed slightly from those of the amide pre-catalyst [Ca(N(SiMe3)2)2−(THF)]2 (2a, 1 h, 74%), most likely due to differences in the crystallization conditions of the reaction product. This observation, and consideration of our previous studies on the hydrophosphination of carbodiimides[18] suggests that the catalytic hydroamination chemistry proceeds via fast catalyst initiation via silylamide protonation and carbodiimide insertion to form a group-2 guanidinate complex. Protonolysis of this latter species with 1 equiv. of aniline, liberates the guanidine product and reforming the transient group-2 amide complex (Scheme 2).

Although the calcium guanidinate complexes may be dimeric in solution, the nuclearity of the active catalyst species is likely to be a function of not only the substrates but also the group-2 metal employed.

Conclusions

Homoleptic group-2 amides [M{N(SiMe3)2}2(THF)2] (M = Ca, Sr and Ba) are reported as highly competent precatalysts for the catalytic hydroamination of carbodiimides with anilines. Although initial attempts to extend this reaction chemistry to primary amines has been unsuccessful, the chemistry detailed herein represents a practical and scalable synthetic approach to guanidines. Coordination...
chemistry studies upon the catalytic species (M = Ca) suggest the involvement of homoleptic dimeric guanidine complexes in solution, with catalytic turnover occurring, by analogy to our previous work, with fast Bronsted acid–Bronsted base and Lewis acid–Lewis base ligand-exchange processes at the metal center, and carbon–nitrogen bond formation proceeding by σ-bond metathesis and insertion reaction steps. We are continuing to investigate this reaction and the application of heavier group-2 species in this and related catalytic processes.

Experimental Section

General Procedures: All manipulations were carried out using standard Schlenk line and glovebox techniques under either dinitrogen or argon. All solvents were distilled under dinitrogen and dried with conventional drying agents. Anilines were purchased from Sigma–Aldrich, and 2,6-diisopropyl-phenyl, heavier alkaline earth amides [M{N(SiMe3)2}2-β-diketiminate ligand (1.584 mmol) and carbodiimide (1.584 mmol) were dissolved in [D6]benzene (2 mL). The catalyst (2 mol-%) was added and the reaction mixture was mixed thoroughly and formed a homogeneous, colorless solution. The initial concentration of reagents was measured by 1H NMR spectroscopy, followed by 19F NMR spectroscopy. Yields were calculated by 1H and 19F NMR spectroscopy. Further purification was achieved by bulb-to-bulb distillation (175 °C).

Preparative Scale Experiments: In a glovebox, the aniline (1.584 mmol) and carbodiimide (1.584 mmol) were dissolved in [D6]benzene (0.5 mL) and transferred to a Youngs tap NMR tube. The initial concentration of reagents was measured by 1H NMR spectroscopy, followed by 19F NMR spectroscopy. Yields were calculated by 1H and 19F NMR spectroscopy. Further purification was achieved by bulb-to-bulb distillation (175 °C). The catalyst was prepared by literature procedures.

Hydroamination of Carbodiimides

1,3-Dicyclohexyl-2-(2-fluorophenyl)guanidine [(2-MeOC6H5)N-C\[NHCy\]2]: The product crystallized as a colorless solid (349 mg, 80% yield) after 12 h. 1H NMR ([D6]benzene, 400 MHz, 298 K): δ = 0.85–0.97 (m, 6 H), 1.08–1.18 (m, 4 H), 1.36–1.39 (m, 2 H), 1.48–1.52 (m, 4 H), 3.46 (s, 3 H), 3.40–3.60 (apparent broad s, 2 H), 3.56 (broad s, 2 H), 6.79 (d, J = 7.8 Hz, 1 H), 6.93 (ddd, J = 7.8, 1.8 Hz, 1 H), 6.98 (dd, J = 7.5, 7.4, 1.5 Hz, 1 H), 7.21 (d, J = 7.4 Hz, 1 H) ppm. 13C NMR ([D6]benzene, 100 MHz, 298 K): δ = 25.3, 26.0, 34.1, 50.6, 55.6, 113.2, 121.1, 122.2, 125.2, 140.9, 149.5, 153.0; IR (DCM film): 1311, 1436, 1580, 2852, 2927, 3024, 3286 ppm. MS (ESI, +ve): m/z (%) = 330 (100) [M + H]+. HRMS calcd. for C19H29FN3: 330.2542 found 330.2545. M.p. (hexane) 113–114 °C. C19H29FN3O2 (329.48): calcd. C 72.91, H 9.48, N 12.75; found 72.8, 9.48, 12.7.

3-tert-Butyl-1-ethyl-2-(2-fluorophenyl)guanidine [(2-FC6H4N)-C\[NHEt\]{NH[Br] Bu]}: On a Schlenk line, a solution of 2a (16 mg, 0.032 mmol, 2 mol-%) was dissolved in toluene (2 mL) was added to a toluene (2 mL) solution of 1-tert-butyl-3-ethylcarbodiimide (200 mg, 1.58 mmol) and 2-fluorooaniline (176 mg, 1.58 mmol). The reaction mixture was stirred overnight, and then exposed to air. The solvent was removed in vacuo and the crude dissolved in diethyl ether (30 mL) and washed with water (3 x 10 mL). The organic layer was dried with magnesium sulfate, filtered and the solvent removed in vacuo. The resultant oil was deemed pure by multinuclear NMR spectroscopy and mass spectrometry. Further purification was achieved by bulb-to-bulb distillation (150 °C, 3.3 x 10 mmbar) to give the product as a yellow oil (340 mg, 1.43 mmol, 91%). The reaction monitored by 1H and 19F NMR showed a 74% yield after 15 min at room temperature. 1H NMR ([D6]benzene, 300 MHz, 298 K): δ = 0.65 (t, J = 7.2 Hz, 3 H), 1.31 (s, 9 H), 2.63 (q, J = 7.2 Hz, 3 H), 3.40 (broad m, 2 H), 6.66–6.72 (m, 1 H), 6.91 (ddd, δ = 7.6, 7.6, 1.4 Hz, 1 H), 7.00 (ddd, J = 10.8, 8.1, 1.6 Hz, 1 H), 7.08 (dd, J = 8.4, 8.1, 1.7 Hz, 1 H) ppm. 19F NMR ([D6]benzene, 298 K): δ = −125.4 ppm. 13C NMR ([D6]benzene, 100 MHz, 298 K): δ = 14.9, 29.8, 37.1, 50.8, 116.3 (d, J = 20.6 Hz, 122.0 (d, J = 7.1 Hz), 124.8 (d, J = 7.2 Hz), 126.3 (d, J = 3.2 Hz), 139.0 (d, J = 12.8 Hz), 150.6, 156.2 (d, J = 242.5 Hz) ppm. IR (DCM film): ν = 749, 1214, 1361, 1440, 1489, 1526, 1599, 1632, 2923, 2970, 3420. MS (ESI, +ve): m/z (%) = 238 (100) [M + H]+. HRMS calcd. for C11H13F2N3: 238.1719 found 238.1704.

1,3-Di-tert-butyl-2-(2-fluorophenyl)guanidine [(2-FC6H4N)-C\[NH[Br] Bu]2}: On a Schlenk line, a solution of 2a (32 mg, 0.064 mmol, 4 mol-%) in toluene (2 mL) was added to a toluene (2 mL) solution of 1,3-di-tert-butylcarbodiimide (246 mg, 1.58 mmol) and 2-fluoroaniline (176 mg, 1.58 mmol). The Schlenk tube was sealed, removed from the glovebox and heated to 80 °C for 24 h, after which point the reaction product was treated as moisture stable and the volatiles removed. Purification was achieved by bulb-to-bulb distillation (175 °C, 3.0 x 10 mmbar) to give the product as a yellow oil (156 mg, 37%). Monitoring of the reaction by 1H and 19F NMR showed a 46% yield after 24 h at 80 °C. 1H NMR ([D6]benzene, 300 MHz, 298 K): δ = 1.20 (s, 18 H), 3.66 (broad s, 2 H), 6.65–6.72 (m, 1 H), 6.88 (dd, J = 7.6, 7.6, 1.4 Hz, 1 H), 6.95–7.03 (m, 2 H) ppm. 19F NMR ([D6]benzene, 298 K): δ = 125.1 ppm. IR (DCM film): ν = 738, 1211, 1362, 1436, 1490, 1520, 1600, 1635, 2926, 3472 cm−1. MS (ESI, +ve): m/z (%) = 286 (100) [M + H]+. HRMS calcd. for C19H33FN2: 286.2346.
Calcium Guanidinate 3a: To a solution of 2a (0.253 g, 0.5 mmol) in THF (15 mL) was added a solution of 1,3-diisopropyl-2-phenylguanidine (0.219 g, 1.0 mmol) in THF (10 mL). After 12 h at room temperature the solvent was evaporated and the compound was recrystallized from hexane/THF (10 mL/1 mL) at −20 °C yielding colorless crystals of 3a (0.174 g, mmol, 60%). M.p. (10:1 hexane/THF) 158–159 °C. Multinuclear NMR spectroscopic data as below with additional resonances attributed to non-coordinated THF.

C52H80Ca2N12 (952.59): calcd. C 65.45, H 8.39, N 13.62. M.p. (hexane/THF, 10:1) 158–159 °C.

Calcium Guanidinate 3b: Toluene (10 mL) was added to a solid mixture of [Ca(NiMe2)2]2 (164 mg, 0.46 mmol) and 1,3-diisopropyl-2-phenylguanidine (200 mg, 0.92 mmol). The mixture was stirred for 30 min, filtered and the solvent volume reduced to induce crystallization. The product 3b was isolated as a colorless crystalline solid (127 mg, 0.133 mmol, 58%) by slow cooling of a hot toluene solution to 5 °C. M.p. (toluene) 153–158 °C. 1H NMR ([D8]toluene, 298 K, 400 MHz): δ = 6.71 (d, J = 6.8 Hz, 12 H), 6.76–6.81 (m, 8 H), 7.07–7.14 (m, 8 H), 7.15–7.23 (m, 8 H) ppm. 13C NMR ([D8]toluene, 298 K, 100 MHz): δ = 24.4, 24.5, 26.3, 27.1, 115.9, 118.4, 121.6, 122.7, 123.7, 130.4, 151.5, 154.9, 159.1, 163.3, 164.9 ppm. C52H80Ca2N12 (952.59): calcd. C 65.45, H 8.39, N 13.62. M.p. (hexane/THF, 10:1) 155–158 °C.

Xray Diffraction Data20 Data for [(2-FC6H5)N]2[N(HPip)]4 and 3a. 3b were collected at 150 K with a Nonius Kappa CCD diffractometer equipped with a low-temperature device, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were processed using the Nonius Software21 Structure solution, followed by full-matrix least-squares refinement was performed using either the WinGX-1.70 suite of programs22 or the programme suite X-SEED.23 Notes on refinement: 3f: Occupies both orthorhombic positions in the ratio 60:40.

C52H80Ca2N12, M = 237.32, monoclinic, P21/c, a = 8.5380(5) Å, b = 11.2920(7) Å, c = 14.0080(10) Å, β = 94.402(3), V = 1346.54(15) Å³, Z = 4, ρ = 1.711 g cm⁻³, R1 = 6.0 Hz, 12 H), 7.07–7.14 (m, 8 H), 7.15–7.23 (m, 8 H) ppm. 13C NMR ([D8]toluene, 298 K, 100 MHz): δ = 24.4, 24.5, 26.3, 27.2, 115.9, 118.4, 121.6, 122.7, 123.7, 130.4, 151.5, 154.9, 159.1, 163.3, 164.9 ppm. C52H80Ca2N12 (952.59): calcd. C 65.45, H 8.39, N 13.62, found C 65.69, H 8.97, N 13.62. M.p. (hexane/THF, 10:1) 158–159 °C.

Supporting Information (see also the footnote on the first page of this article): Complete experimental details and spectra of all isolated compounds and ¹H and ¹³C(¹H) NMR spectra of isolated guanidine compounds.

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[20] CCDC-678662 (for [(2-FC6H5)N]C[NH3Pr]2), -678663 (for 3a) and -684817 (for 3b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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