β-Diketiminato Calcium Acetylides: Synthesis, Solution Dimerization, and Catalytic Carbon−Carbon Bond Formation

Anthony G. M. Barrett,*[,†] Mark R. Crimmin,[†] Michael S. Hill,*[,‡] Peter B. Hitchcock,[§] Sarah L. Lomas,[‡] Mary F. Mahon,[‡] Panayiotis A. Procopiou,[⊥] and Kogularamanan Suntharalingam[†]

Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London, SW7 2AZ, U.K., Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, U.K., The Chemistry Laboratory, University of Sussex, Falmer, Brighton, East Sussex, BN1 9QJ, U.K., and GlaxoSmithKline Medicines Research Centre, Gunnels Wood Road, Stevenage, Hertfordshire, SG1 2NY, U.K.

Received July 31, 2008

The β-diketiminate-stabilized calcium amide [{ArNC(Me)CHC(Me)NAr}Ca{N(SiMe$_3$)$_2$}(THF)] (**1**) reacts with terminal acetylenes in hydrocarbon solvents to yield the corresponding calcium acetylide complexes [{ArNC(Me)CHCN(Me)Ar}Ca{C≡CR^1}]$_2$ (R^1 = n-Bu, t-Bu, Ph, 4-MeC$_6$H$_4$, ferrocenyl, Ar = 2,6-di-isopropylphenyl, **2a**−**e**). Although in all instances solid and solution state data were consistent with the reaction products existing as dimeric species with aggregation occurring via three-center−two-electron bridging acetylide units, a further reaction of **1** with HC≡CSi(^{i}Pr)$_3$ demonstrated that both monomeric solvated [{ArNC(Me)CHC(Me)NAr}Ca{C≡CSi(^{i}Pr)$_3$}(THF)$_2$] (**3b**) or dimeric acetylide [{ArNC(Me)CHC(Me)NAr}Ca{C≡CSi(^{i}Pr)$_3$}]$_2$ (**3a**) species could be isolated from the reaction depending upon the exact conditions of the crystallization of the reaction product from solution. Further solution studies demonstrated the presence of a monomer−dimer equilibrium in solution. A van't Hoff analysis allowed Δ*G*°(298 K) for the dimerization reaction to be calculated as +27.0 kJ mol^{-1}. The reaction of these hydrocarbon-soluble kinetically stabilized calcium acetylides with 1,3-dialkylcarbodiimides gave the corresponding heteroleptic calcium C-propargyl amidinate complexes [{ArNC(Me)CHCN(Me)-Ar}Ca{(R^{2}N)$_2$CC≡CR^1}(THF)$_n$] (R^1 = 4-MeC$_6$H$_4$, *n* = 0, **4a**; 4-MeC$_6$H$_4$, *n* = 1, **4a**·THF; R^2 = ^{i}Pr; R^1 = Si(^{i}Pr$_3$), R^2 = Cy, *n* = 1, **4b**·THF) via insertion of the carbodiimide into the calcium−carbon σ-bond. The latter complexes have been characterized in both solution and the solid state including single-crystal X-ray analysis of **4a**·THF. Extension of this reactivity to catalytic systems has allowed the application of amide **1** (5 mol %) to the catalytic hydroacetylenation of 1,3-di-isopropylcarbodiimide with phenylacetylene, yielding the corresponding propargyl amidine in 59% yield following crystallization from hexane solution.

Introduction

Despite recent advancements in the coordination chemistry of the heavier alkaline earth elements,[1] well-defined heavier group 2 organometallics containing metal to carbon σ-bonds are still a relatively rare compound class. Although analogous to Grignard reagents and diorganomagnesium reagents, the synthesis of organometallic compounds of the heavier alkaline earths (M = Ca, Sr, and Ba) is complicated by the reduced reactivity of the metals and by the ill-defined nature of these compounds in solution. As a result, in initial reports, characterization was often limited to derivatization studies through reactions with electrophiles.[2] In more recent years, a number of well-defined and structurally characterized compounds have been reported. Examples include homoleptic bis(trimethylsilyl)methyl and tris(trimethylsilyl)methyl calcium complexes,[3] strontium and barium complexes of the form [{{(MeO)(Me)$_2$Si)}-(Me$_3$Si)$_2$C}M(S)$_n$] (M = Sr, S = THF, *n* = 2; M = Ba, S = DME, *n* = 1) supported by additional intramolecular coordination of pendant silyl ether groups,[4] both homoleptic and heteroleptic alkaline earth acetylides,[5] a series of heavier alkaline earth benzyl complexes,[6] and, perhaps most notably, a number of thermally labile heteroleptic "heavy Grignard" derivatives recently documented by Westerhausen et al. (Figure 1).[7] In addition, a number of heterometallic "ate" type complexes have been reported.[8]

* Corresponding author. E-mail: m.s.hill@bath.ac.uk.
† Imperial College London.
‡ University of Bath.
§ University of Sussex.
⊥ GlaxoSmithKline Medicines Research Centre.

(1) (a) Harder, S.; Feil, F.; Repo, T. *Chem.−Eur. J.* **2002**, *8*, 1992. (b) Alexander, J. S.; Ruhlandt-Senge, K. *Eur. J. Inorg. Chem.* **2002**, 2761. (c) Hanusa, T. P. *Coord. Chem. Rev.* **2000**, *210*, 329. (d) Hanusa, T. P. *Organometallics* **2002**, *21*, 2559. (e) Westerhausen, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2975. (f) Westerhausen, M. *Dalton Trans.* **2006**, 4755.

(2) (a) Beckmann, E. *Chem. Ber.* **1905**, *38*, 904. (b) Gilman, H.; Schulze, F. *J. Am. Chem. Soc.* **1926**, *48*, 2463. (c) Gilman, H.; Meals, R. N.; O'Donnell, G.; Woods, L. *J. Am. Chem. Soc.* **1943**, *65*, 268. (d) Meals, R. N. *J. Org. Chem.* **1944**, *9*, 211. (e) Gilman, H.; Woods, L. A. *J. Am. Chem. Soc.* **1945**, *67*, 520. (f) Bryce-Smith, D.; Skinner, A. C. *J. Chem. Soc.* **1963**, 577. (g) Mochida, K.; Yamanishi, T. *J. Organomet. Chem.* **1987**, *332*, 247. (h) Kawabata, N.; Matsumura, A.; Yamashita, S. *Tetrahedron* **1973**, *29*, 1069, and references therein.

(3) (a) Cloke, F. G. N.; Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1991**, 724. (b) Eaborn, C.; Hawkes, S. A.; Hitchcock, P. B.; Smith, J. D. *Chem. Commun.* **1997**, 1961.

(4) Izod, K.; Liddle, S. T.; Clegg, W. *J. Am. Chem. Soc.* **2003**, *125*, 7534.

(5) (a) Burkey, D. J.; Hanusa, T. P. *Organometallics* **1996**, *15*, 4971. (b) Green, D. C.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 354.

10.1021/om800738r CCC: $40.75
Publication on Web 11/06/2008

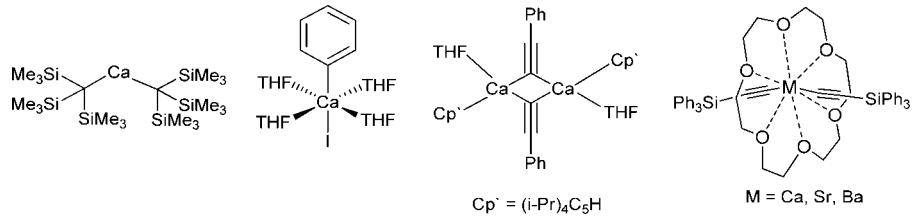


Figure 1. Examples of structurally characterized heavier group 2 complexes containing metal−carbon σ-bonds.

Metal acetylides represent a privileged member of this compound class, as the relatively low pK_a of terminal alkynes not only confers thermodynamic stability to σ-bonded group 2 complexes, through charge stabilization in the highly ionic complexes formed upon deprotonation, but also allows facile synthesis through reaction with a suitably basic group 2 precursor. The homoleptic acetylides $[M(C{\equiv}CPh)_2]_n$ (M = Ca, Sr, Ba) were originally reported in 1971 by Coles et al.[9] Coles suggested that these compounds, synthesized by the metalation of phenylacetylene with the corresponding group 2 metal in liquid ammonia, are polymeric in the solid state with slow depolymerization occurring upon dissolution in the coordinating solvent tetrahydrofuran. More recently Hanusa reported the synthesis of heteroleptic calcium acetylides $[Cp'Ca(C{\equiv}CR)(THF)]_2$ from deprotonation of RC≡CH with $[(Cp')Ca\{N(SiMe_3)_2\}(THF)_2]$ ($Cp' = {}^{i}Pr_4C_5H$).[5a] These compounds were shown to be dimeric in the solid state with acetylide units asymmetrically bridging the two calcium centers. Although stabilized by the bulky Cp′ ligand, solution studies revealed a propensity for these species to undergo undesired Schlenk-like equilibria, limiting studies of these compounds. Similarly, Ruhlandt-Senge has reported the rational synthesis of a series of homoleptic heavier alkaline earth acetylides of the formula $[(18\text{-crown-6})M(C{\equiv}CR)]_2$ (M = Ca, Sr, Ba; R = $SiPh_3$) through the deprotonation of the terminal acetylene with the appropriate group 2 bis(trimethylsilyl)amide $[M\{N(SiMe_3)_2\}_2]$ in the presence of 18-crown-6.[5b]

In contrast to these recent advancements in the appreciation in the coordination chemistry of heavier group 2 acetylides, defined reaction chemistries of these species remain limited to the series of reactions originally reported by Coles. Thus, $[Ca(C{\equiv}CPh)_2]_n$ was shown to react stoichiometrically with both benzophenone and carbon dioxide to yield, after hydrolytic workup, 1,1,3-triphenylprop-2-yn-1-ol and phenylpropynoic acid, respectively.[9] In addition, $[Ca(C{\equiv}CPh)_2]_n$ has been employed as a stoichiometric reagent in inorganic synthesis, yielding, after reaction with indene or cyclopentadiene, the corresponding group 2 sandwich compounds. We recently reported the synthesis of a series of heteroleptic β-diketiminate-stabilized calcium acetylides derived from the reaction of $[\{ArNC(Me)CHC(Me)NAr\}Ca\{N(SiMe_3)_2\}(THF)]$ (**1**, Ar = 2,6-di-isopropylphenyl)[10] with terminal acetylenes.[11] We now report a more detailed examination of these latter compounds, including studies on their solution nuclearity, a series of reactions with 1,3-dialkylcarbodiimides, and a preliminary report of their application to catalytic carbon−carbon bond formation.

Results and Discussion

The stoichiometric reaction of **1** with aromatic and alkyl terminal alkynes proceeded rapidly at room temperature to yield the corresponding heteroleptic calcium acetylides **2a**−**e**.[11] While preparations in hexane solutions resulted in near instant crystallization of the product, for the synthesis of compounds **2a**,**b**, reactions in d_6-benzene remained homogeneous and could be monitored by ^{1}H NMR spectroscopy. These latter experiments demonstrated that the deprotonation reaction occurs quantitatively within the first point of analysis (30 min) and is accompanied by the stoichiometric formation of $HN(SiMe_3)_2$, characterized by a sharp singlet resonance at 0.09 ppm in the ^{1}H NMR spectrum.

In contrast to the highly labile aryl calcium halide reagents recently reported by Westerhausen,[7] compounds **2a**−**e** are thermally stable and may be stored for prolonged periods provided they are kept under an inert atmosphere of dinitrogen or argon. With the exception of the orange ferrocenyl derivative **2e**, these compounds were isolated as colorless crystalline solids. While alkyl-substituted acetylides **2a** and **2b** were readily soluble in hexane, benzene, and toluene, those derivatives with more rigid aromatic groups on the acetylide moiety were not and became only partially soluble in hot toluene. The ferrocenyl acetylide **2e** is completely insoluble in hydrocarbon solvents and may be dissolved only in polar aprotic solvents such as tetrahydrofuran. In accordance with the observation of Coles, this action may well result in the dissociation of the dimeric acetylide to a monomeric, solvated, species in solution (*vide infra*).

The outcome of the reaction of **1** with 1 equiv of triisopropylsilylacetylene proved solvent dependent, and although in both cases a heteroleptic calcium acetylide product was synthesized, crystallization from toluene at −21 °C or hexane at room temperature allowed the isolation of the dimeric

(6) (a) Weeber, A.; Harder, S.; Brintzinger, H. H. *Organometallics* **2000**, *19*, 1325. (b) Feil, F.; Harder, S. *Organometallics* **2000**, *19*, 5010. (c) Harder, S.; Feil, F.; Weeber, A. *Organometallics* **2001**, *20*, 1044. (d) Feil, F.; Harder, S. *Organometallics* **2001**, *20*, 4616. (e) Feil, F.; Müller, C.; Harder, S. *J. Organomet. Chem.* **2003**, *683*, 56. (f) Harder, S.; Müller, S.; Hübner, E. *Organometallics* **2004**, *23*, 178.

(7) (a) Fischer, R.; Görls, H.; Westerhausen, M. *Inorg. Chem. Commun.* **2005**, *8*, 1159. (b) Fischer, R.; Gärtner, M.; Görls, H.; Westerhausen, M. *Organometallics* **2006**, *25*, 3496. (c) Fischer, R.; Gärtner, M.; Görls, H.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 609. (d) Gärtner, M.; Görls, H.; Westerhausen, M. *Organometallics* **2007**, *26*, 1077. (e) Langer, J.; Görls, H.; Westerhausen, M. *Inorg. Chem. Commun.* **2007**, *10*, 853. (f) Langer, J.; Gärtner, M.; Fischer, R.; Görls, H.; Westerhausen, M. *Inorg. Chem. Commun.* **2007**, *10*, 1001. (g) Fischer, R.; Gärtner, M.; Görls, H.; Yu, L.; Reiher, M.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1618. (h) Gärtner, M.; Görls, H.; Westerhausen, M. *J. Organomet. Chem.* **2008**, *693*, 221. (i) Gärtner, M.; Görls, H.; Westerhausen, M. *Synthesis* **2007**, 725. (j) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 1950. (k) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J.; Yu, L.; Reiher, M. *Chem.−Eur. J.* **2007**, *13*, 6292.

(8) (a) Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F. *J. Organomet. Chem.* **2002**, *663*, 263. (b) Westerhausen, M.; Birg, C.; Nöth, H.; Knizek, J.; Seifert, T. *Eur. J. Inorg. Chem.* **1999**, 2209. (c) Westerhausen, Gückel, C.; Habereder, T.; Vogt, M.; Warchhold, M.; Nöth, H. *Organometallics* **2001**, *20*, 893. See also ref 1e.[1e]

(9) Coles, M. A.; Hart, F. A. *J. Organomet. Chem.* **1971**, *32*, 279.

(10) (a) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Chem. Commun.* **2003**, 48. (b) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Inorg. Chem.* **2004**, *43*, 6717.

(11) Avent, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B. *Organometallics* **2005**, *24*, 1184.

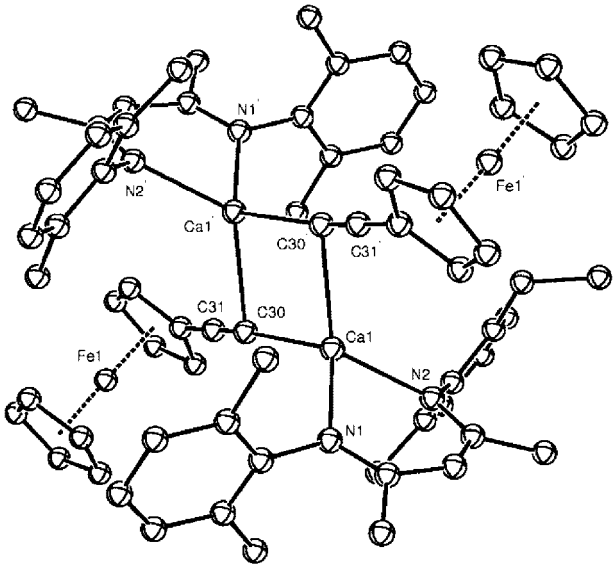


Figure 2. Ball and stick representation of the structure of **2e**. H atoms and isopropyl methyl groups are omitted for clarity.

complex **3a** and the monomeric bis-THF adduct **3b**, respectively. While these results suggest that the aggregation state of the isolated complex is dependent upon the exact conditions of the crystallization, further solution studies (*vide infra*) demonstrated that both compounds **3a** and **3b** exist in equilibrium following the initial protonolysis reaction of **1** with tri-isopropylsilylacetylene.

Solid-State Characterization. We have previously reported the results of single-crystal X-ray diffraction analyses for compounds **2b**−**d**.[11] These compounds crystallize in a dimeric form and exhibit a slightly asymmetric but essentially planar four-membered core with sp-hybridized acetylides that bridge the calcium centers via three-center−two-electron bonds. The ethynyl moieties display an apparent π-interaction with each calcium center, resulting in a series of asymmetrically bridged D_2-symmetric dimers. Although the single-crystal X-ray data collected for compounds **2e** and **3a** were unsatisfactory and preclude any detailed discussion of bond lengths and angles, the connectivity in both cases was unambiguous, and both new compounds display similar dimeric structures (Figures 2 and 3a).

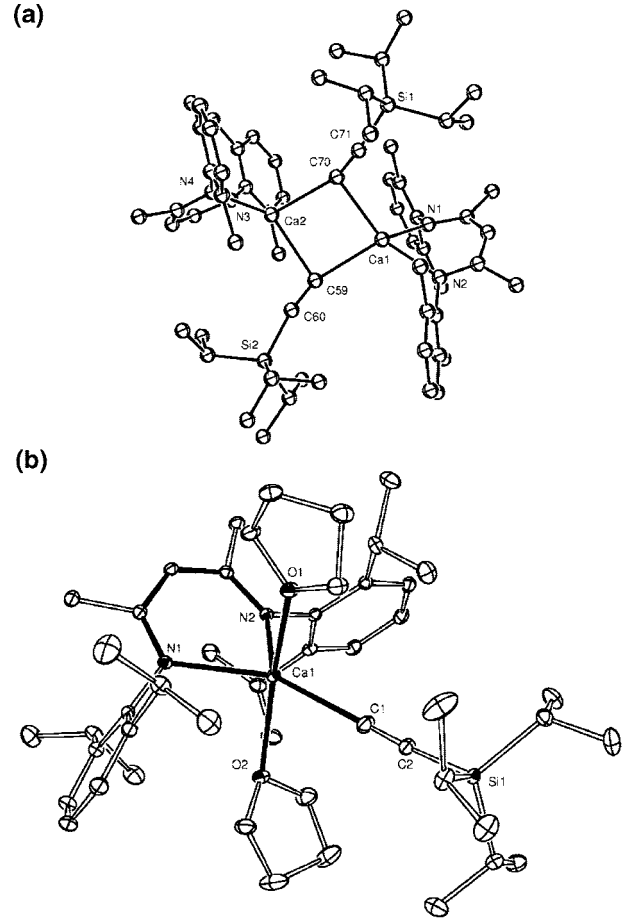


Figure 3. (a) Ball and stick representation of the structure of **3a**. H atoms and isopropyl methyl groups are omitted for clarity. (b) ORTEP representation of **3b**. H atoms are omitted for clarity. Thermal ellipsoids are at 20% probability.

Table 1. Selected Bond Length (Å) and Angles (deg) in β-Diketiminate Calcium Acetylide Complexes 2b−d and 3b

	2b	2c	2d	3b
Ca−N(1)	2.3391(10)	2.3133(13)	2.3190(14)	2.3788(14)
Ca−N(2)	2.3265(11)	2.3182(12)	2.3131(14)	2.3701(13)
N(1)−Ca−N(2)	82.89(4)	80.63(4)	80.24(5)	80.52(5)
Ca−C_α	2.4960(15)	2.5056(16)	2.492(2)	2.4703(19)
Ca′−C_α	2.5099(14)	2.5350(16)	2.530(2)	
C_α−C_β	1.216(2)	1.224(2)	1.221(2)	1.227(3)
Ca−C_α−Ca′	90.27(5)	90.30(5)	91.09(6)	
Ca′−C_β	3.1668(14)	2.9403(16)	2.895(2)	
Ca−C_α−C_β (θ)	157.99(12)	172.85(13)	174.37(15)	167.32(17)
Ca′−C_α−C_β (ϕ)	111.61(11)	96.68(11)	94.53(13)	

Compound **3b** displays a different bonding mode. X-ray analysis of single crystals of **3b** grown from hexane solutions demonstrated that, rather than existing as an asymmetric dimer, the compound is monomeric in the solid state (Figure 3b). Bond lengths and angles and details of the structural analysis are listed in Tables 1 and 2. Coordination at the pentacoordinate, trigonal-bipyramidal ($\tau = 0.7$)[13] calcium center is provided not only by the β-diketiminate ligand and two molecules of THF but also a single σ-bonded acetylide unit. To our knowledge, this is the first structurally characterized monomeric heteroleptic heavier group 2 acetylide. Both N(1)−Ca and N(2)−Ca bond lengths and the N(1)−Ca−N(2) bond angle are little altered in comparison to the dimeric analogues **2b**−**d**. Comparison of the Ca−C_α (2.4703(19) Å) and C_α−C_β bond lengths (1.227(3) Å) with those observed in the dimeric complexes reveals that, although there is little effect of coordination of an additional

(12) (a) Tsutsui, M.; Ely, N. *J. Am. Chem. Soc.* **1974**, *96*, 4042. (b) Ely, N.; Tsutsui, M. *Inorg. Chem.* **1975**, *14*, 2680. (c) Evans, W. J.; Wayda, A. L. *J. Organomet. Chem.* **1980**, *202*, C6. (d) Fischer, R. D.; Bielang, G. *J. Organomet. Chem.* **1980**, *191*, 61. (e) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115. (f) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 709. (g) Boncella, J. M.; Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 710. (h) Qian, C.; Ge, Y. *J. Organomet. Chem.* **1986**, *299*, 97. (i) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053. (j) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. *Organometallics* **1990**, *9*, 2124. (k) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1990**, *9*, 2628. (l) Shen, Q.; Zheng, D.; Lin, L.; Lin, Y. *J. Organomet. Chem.* **1990**, *391*, 307. (m) Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980. (n) Heeres, H. J.; Nijhoff, J.; Teuben, J. H. *Organometallics* **1993**, *12*, 2609. (o) Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931. (p) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618. (q) Forsyth, C. M.; Nolan, S. P.; Stern, C. L.; Marks, T. J. *Organometallics* **1993**, *12*, 3618. (r) Schaverian, C. J. *Organometallics* **1994**, *13*, 69. (s) Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **1995**, *14*, 5021. (t) Ren, J.; Hu, J.; Lin, Y.; Xing, Y.; Shen, Q. *Polyhedron* **1996**, *15*, 2165. (u) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291. (v) Lin, G.; McDonald, R.; Takats, J. *Organometallics* **2000**, *19*, 1814. (w) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 1184.

Table 2. Crystallographic Data for Compounds 3b and 4a·THF

	3b	4a·THF
molecular formula	$C_{48}H_{78}CaN_2O_2Si$	$C_{49}H_{70}CaN_4O.C_3H_7$
fw (g mol^{-1})	783.29	814.26
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$
a (Å)	13.2970(1)	11.7318(1)
b (Å)	16.6280(2)	18.3367(2)
c (Å)	21.7550(3)	23.4138(3)
α (deg)	90	90
β (deg)	90	94.186(1)
γ (deg)	90	90
V (Å^3)	4810.08(10)	5023.40(9)
Z	4	4
μ (mm^{-1})	0.192	0.16
ρ (g cm^{-3})	1.082	1.08
θ range (deg)	3.59 to 27.50	3.43 to 26.05
measd/indep reflns/R_{int}	66 668/11 025/0.0597	74 797/9878/0.046
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0367, 0.0866	0.048, 0.121
R_1[a], wR_2[b] (all data)	0.0462, 0.0913	0.063, 0.131

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^{2)2}]\}^{1/2}$.

Table 3. Comparative Infrared Spectroscopic Data for Calcium Acetylides 2 and 3[a]

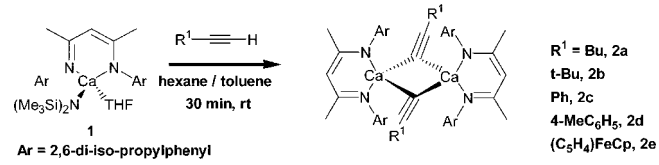
	ν(C≡C)/cm^{-1}		
compound	[LCa(C≡CR)]	HC≡CR	$\Delta\nu$/cm^{-1}
2a	2048	2118	70
2b	2029	2106	77
2c	2034	2110	76
2d	2040	2111	71
2e	2043	2110	67
3a	1978	2032	54
3b	1992	2032	41

[a] Spectra recorded from freshly pressed KBr discs.

metal upon the length of the carbon−carbon triple bond, the Ca−C_α bond length is significantly shorter in the monomeric species relative to the dimeric compounds despite the higher coordination number at calcium. This latter effect may be rationalized in terms of the bonding at C_α, with the shorter calcium−carbon bond length in the monomeric compound due to the formation two-center bonds in **3b** compared to three-center bonds in the dimeric species. Consideration of compounds in the organo(III)lanthanide literature reveals a similar trend in metal−carbon bond lengths upon dimerization, and the extension of the M−$C_\alpha$bond length in **2b**−**d** relative to **3b** (1.5−3.2%) is comparable to that observed for $[(MeC_5H_4)_2Sm(C{\equiv}C^tBu)]_2$ relative to $[(Cp^*)_2Sm(C{\equiv}CPh)(THF)]$ (2%) and $[(Cp^*)_2Sm(C{\equiv}C^tBu)]$ (5%).[12] The Ca−C_α−C_β angle of **3b** (167.32(17)°) deviates significantly from idealized linear geometry. Similar observations have been made in a series of homoleptic heavier group 2 acetylides supported by neutral crown ether ligands and may be rationalized in terms of polarization effects,[5b] such that the negative charge is dissipated across both C_α and C_β centers.

Upon deprotonation and coordination to calcium, there is a considerable red-shift in the infrared absorption of the carbon−carbon triple bond of the ethynyl moiety synchronous with a lengthening of this bond (Table 3). In agreement with the range established by the work of Coles[9] and Ruhlendt-Senge and Hanusa[5] (1985−2043 cm^{-1}) the calcium acetylide complexes documented herein display ν(C≡C) stretching frequencies between 1978 and 2048 cm^{-1} depending upon the substituent of the ethynyl group. It is of interest to note that both monomeric and dimeric compounds **3a** and **3b** provided similar

Scheme 1. Reactions of β-Diketiminate-Stabilized Amide 1 with Terminal Acetylenes



alkyne stretching frequencies (**3a**, 1978 cm^{-1}; **3b**, 1992 cm^{-1}) consistent with the similar C_α−C_β bond lengths observed in the solid state despite the differing hapticities of the acetylide ligands.

Solution Characterization. To increase our understanding of the behavior of **2a**−**e** and **3a**,**b** in solution, a series of multinuclear NMR studies were undertaken.. Although we have previously reported that compound **2b** demonstrates a temperature-dependent fluxional process ascribed to hindered rotation about the N−Ar bond of the β-diketiminate ligand set at low temperature, an attribution of this process to the retention of a dimeric formulation in solution was uncertain.[11]

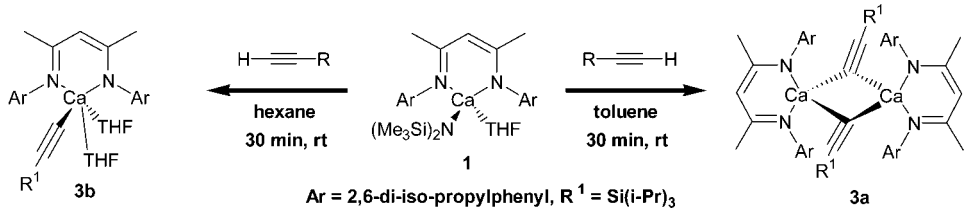
Upon dissolving pure crystalline samples of **3b** in d_8-toluene, two distinct compounds were observed in solution by ^{1}H NMR spectroscopy. At room temperature (298 K), the major component of this mixture was assigned to the solvated acetylide **3b**, while the minor component demonstrated similar ^{1}H NMR data to that displayed by isolated samples of **3a**. Further variable-temperature NMR experiments, conducted between 293 and 353 K, demonstrated that these two species are in fact in equilibrium as depicted in Scheme 3. At high temperature the equilibrium is perturbed from 2 equiv of **3b** toward the proposed dimeric reaction product along with four molecules of THF. In addition, dissolving samples of **3b** in d_8-THF led to the observation of a single compound by ^{1}H and ^{13}C NMR spectroscopy, an observation consistent with the equilibrium lying entirely toward the monomer in the presence of the coordinating solvent. A van't Hoff analysis (Figure S1) upon a d_8-toluene solution of this equilibrium mixture allowed $\Delta H°$ and $\Delta S°$ to be calculated as +91.7 kJ mol^{-1} and +214 J K^{-1} mol^{-1}, respectively. These data correspond to a value of $\Delta G°$(298 K) = +27.0 kJ mol^{-1}. The monomerization of aggregated organo(III)lanthanide acetylides by the addition of THF is well-established in the literature, and Teuben has previously reported that $[(Cp^*)_2Ce(C{\equiv}C^tBu)]_2$ readily forms $[(Cp^*)_2Ce(C{\equiv}C^tBu)(THF)]$ upon addition of THF.[12n] Similarly, bis(amidinato) yttrium acetylide complexes of the form $[\{PhC(NSiMe_3)_2\}_2Y(C{\equiv}CR)]$ (R = H, t-Bu) have been shown to dissociate in the presence of THF, as evidenced by $^1J_{Y-C}$ coupling patterns in NMR spectroscopy.[12u]

While the isolation of **3b** from hexane solution appears to be highly dependent upon the conditions of its crystallization, the observed temperature-dependent dimerization in d_8-toluene solution by ^{1}H NMR spectroscopy is consistent with the crystallization of **3a** from toluene solutions and implies that the compounds **2a**−**e** and **3a** retain their dimeric constitution in solution. Indeed, it could be expected that as the steric demands of the substituent upon the acetylide moiety are reduced from the bulky tri-isopropyl group, the activation energy of dimerization may decrease due to ease of approach of two monomer units. As such, it seems reasonable to assume that compounds **2a**−**e** readily undergo dimerization in hydrocarbon solutions under the reaction conditions of their synthesis.

Further evidence for the differing coordination chemistry, via three-center or two-center bonding modes, of the acetylide units in monomeric and dimeric samples of **3a** and **3b**, respectively, was provided by ^{13}C chemical shift data for the metal-bound

(13) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

Scheme 2. Reactions of β-Diketiminate Amide 1 with Tri-isopropylsilylacetylene



Scheme 3. Proposed Solution Equilibrium between 3a and 3b

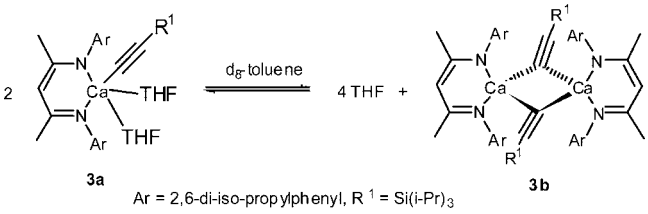


Table 4. Comparative ^{13}C Data for Heteroleptic Calcium Acetylides 3a,b and [Cp′Ca(C≡CSiR$_3$)(THF)][5a]

compound	$^{13C}\delta$/ppm[a]	
	C_α	C_β
[Cp′Ca(C≡CSiMe$_3$)(THF)]	163.3	127.4
[Cp′Ca{C≡CSi(i-Pr)$_3$}(THF)]	160.0	124.4
[Cp′Ca(C≡CSiPh$_3$)(THF)]	178.3[b]	105.4[b]
3a	163.6	123.9
3b	171.3 (171.9[b])	105.0 (103.5[b])

[a] Spectra recorded in C_6D_6. [b] Spectra recorded in d_8-THF; all spectra referenced against residual solvent peaks.

acetylide carbons C_α and C_β. In accordance with previous dimeric crystallographically characterized calcium acetylides of the form [Cp′Ca(C≡CSiR$_3$)(THF)], compound **3a** demonstrated a characteristic heavily deshielded ^{13}C resonance at 163.6 ppm consistent with C_α and a further resonance at 123.9 ppm assigned to C_β. In contrast, in both C_6D_6 and d_8-THF solutions, **3b** demonstrated ^{13}C resonances for the acetylide quaternary carbons ($^{13C}\delta$ C_6D_6: C_α = 171.3 ppm and C_β = 105.0 ppm) at distinctly different chemical shifts from those observed for the dimeric analogue (Table 4). These latter values are consistent with those reported for [Cp′Ca(C≡CSiPh$_3$)(THF)] in d_8-THF solution ($^{13C}\delta$: C_α = 178.3 ppm and C_β = 105.5 ppm), which is also presumably monomeric in this coordinating solvent.[5a] Consideration of these data suggests that upon dimerization there is an upfield shift in C_α resonance concomitant with a downfield shift of C_β. Although the precise effect of metal acetylide dimerization upon polarization of the π-cloud of the acetylide moiety remains open to debate, due to the propensity for these dimeric species to demonstrate close contacts between C_β and the second calcium center (as observed in the solid state), the effective shielding of the metal-bound carbon atom in the dimeric complex relative to the monomeric complex (**3a**,**b**; Δδ = 8 ppm) is consistent with increased negative charge residing on C_α due to the proximity of the second electrophilic calcium center.

Reactions with 1,3-Dialkylcarbodiimides. The β-diketiminato calcium acetylide **2d** reacts stoichiometrically with 1,3-di-isopropyl carbodiimide via insertion of the unsaturated carbon−nitrogen bond of the carbodiimide into the calcium carbon σ-bond of the metal acetylide. Monitoring of this reaction in C_6D_6 solution by NMR spectroscopy revealed the formation of **4a** within several hours at room temperature. Despite this, due to the low solubility of **2d** in hydrocarbon solvents, reactions were not quantitative. This drawback could be overcome, however, by performing a one-pot reaction between **1**, *p*-tolylacetylene, and 1,3-di-isopropyl carbodiimide. In this instance reaction mixtures in toluene or benzene solutions remained homogeneous, and the reaction product **4a**·THF could be isolated by recrystallization from hexane solution. The reaction was characterized by the formation of a diagnostic quaternary ^{13}C resonance at 159.2 ppm assigned to that of the central carbon of the newly formed amidinate ligand. Similarly, the reaction of **3b** with 1,3-dicyclohexyl carbodiimide in hydrocarbon solutions yielded the corresponding mono-THF-solvated insertion product within the first point of analysis. In this instance, both monomeric and dimeric components of the equilibrium mixture formed upon dissolving **3b** in C_6D_6 solution react with the 1,3-carbodiimide to yield **4b**·THF (Scheme 4).

Recrystallization of a sample of **4a**·THF from a hot hexane solution yielded a sample suitable for single-crystal X-ray diffraction analysis. This latter experiment demonstrated that **4a**·THF is monomeric in the solid state with coordination at calcium being provided by both β-diketiminate and propargyl amidinate N,N-chelating ligands (Figure 4, Table 5). Further ligation is provided by a single molecule of THF, and the five-coordinate calcium center exhibits distorted trigonal-bipyramidal geometry.[13] Both the nitrogen−calcium bond lengths (N(3)−Ca, 2.3918(14) Å; N(4)−Ca, 2.4294(14) Å) and the N(1)−Ca−N(2) bite angle of 56.65(5)° are in good agreement with those in the previously reported homoleptic calcium formamidinate complexes [{(2-MeC$_6$H$_4$N)$_2$CH}$_2$Ca(THF)$_2$] (N−Ca, 2.415(2) to 2.425(2) Å; N−Ca−N 56.41(6)° and 56.29(6)°) and [{(2,6-^{i}PrC$_6$H$_3$N)$_2$CH}$_2$Ca(THF)$_2$] (N−Ca, 2.361(3) to 2.406(3) Å; N−Ca−N 57.3(1)° and 57.8(1)°).[14]

In related studies we have demonstrated that β-diketiminato-stabilized calcium phosphides and amides undergo similar insertion reaction with 1,3-dialkyl carbodiimides and have shown that this reactivity may be extended to a catalytic

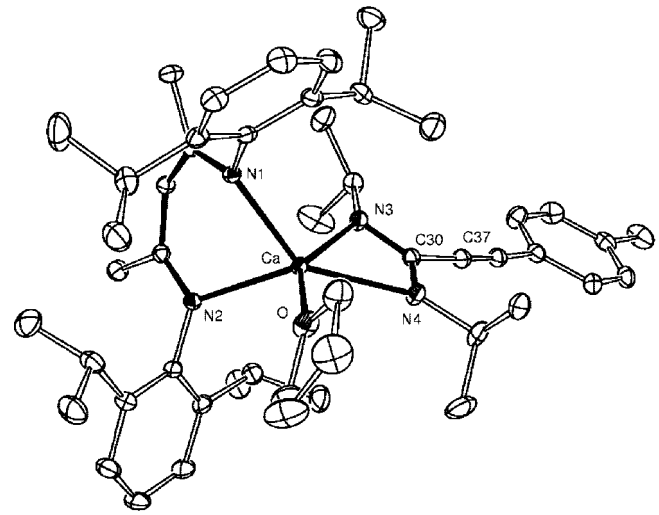
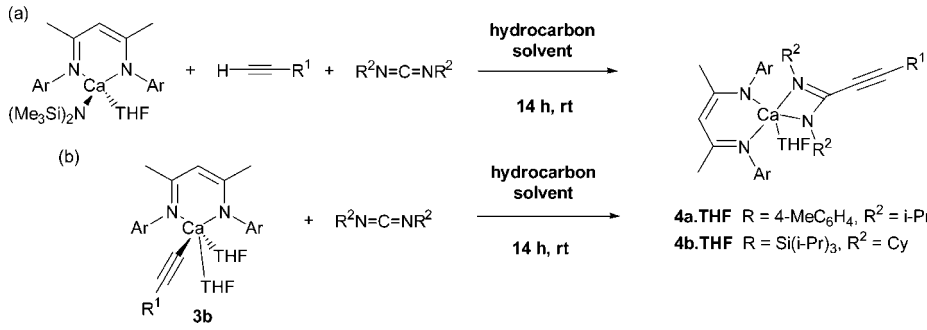
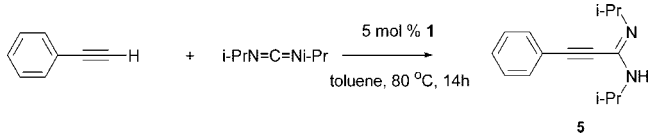


Figure 4. ORTEP representation of **4a**·THF. H atoms are omitted for clarity. Thermal ellipsoids are at 20% probability.

Scheme 4. Synthesis of β-Diketiminate-Stabilized Calcium Propargyl Amidinates



Scheme 5. Catalytic Synthesis of 5



synthesis of guanidines and phosphaguanidines via the hydroamination and hydrophosphination of carbodiimides, respectively.[15] While the precedent for catalytic carbon−carbon bond formation in heavier group 2 chemistry is essentially nonexistent, the hydroacetylenation of carbodiimides has recently been shown to be effected by similarly electropositive group 1 and f-block organometallic complexes.[16] On the basis of this work and the stoichiometric studies herein, it is unsurprising that the reaction of phenylacetylene with 1,3-di-isopropyl carbodiimide to form the corresponding propargyl amidine could be catalyzed by 5 mol % of **1** (Scheme 5). Heating a toluene reaction mixture for 14 h at 80 °C followed by removal of the volatiles and recrystallization of the product from hexane yielded **5** in 59% yield.

While we initially hypothesized that this reaction proceeded by a similar mechanism to that outlined for the analogous hydrophosphination reaction via protonolysis and insertion chemistry at well-defined β-diketiminate calcium species, a further NMR scale reaction between phenylacetylene, 1,3-di-isopropyl carbodiimide, and 5 mol % **1** demonstrated that at room temperature the β-diketiminato ligand of **1** is not stable under these reaction conditions and readily undergoes protonolysis with phenylacetylene to yield [ArNC(Me)CHC(Me)NHAr] and a new organocalcium species. We have previously reported that **1** reacts with an excess of phenylacetylene via protonolysis of the bulky ligand from the coordination sphere of calcium. Thus, it appears that under the reaction conditions neither complexes **1**, **2c**, or analogues of compounds **4a** or **4a**·THF are important as catalytically active species, rather just as intermediates to an as yet uncharacterized calcium catalyst. Despite this observation, the stoichiometric protonolysis and insertion studies detailed herein provide an important rationale for the observed catalytic chemistry.

Table 5. Selected Bond Length (Å) and Angles (deg) in β-Diketiminato Calcium Propargyl Amidinate 4a·THF

Ca−N(1)	2.3560(13)	N(1)−Ca−N(2)	80.92(5)
Ca−N(2)	2.3750(14)	N(4)−Ca−N(3)	56.65(5)
Ca−N(3)	2.3918(14)	N(2)−Ca−(N3)	108.50
Ca−N(4)	2.4294(14)	N(3)−Ca−N(4)	56.65(5)
Ca−O	2.3992(14)	N(1)−Ca−O	92.64(5)
C(37)−C(38)	1.195(3)	N(2)−Ca−O	147.21(5)
		N(3)−Ca−O	147.21(5)
		N(4)−Ca−O	92.22(5)

We are continuing to study the group 2-mediated hydroacetylenation of unsaturated substrates and a more general reaction chemistry of group 2 acetylides and will report our findings in subsequent publications.

Experimental Section

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either dinitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a glovebox. NMR spectra were collected on either a Bruker AV-400 spectrometer (^{13}C NMR 100 Hz) or a Bruker AV-300 spectrometer (^{13}C NMR 75 MHz). Solvents (toluene, benzene, THF, hexane) were dried by distillation from standard drying reagents and stored in ampules over molecular sieves. C_6D_6 and d_8-toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distillation under nitrogen and storage over molecular sieves. Compound **1** and compounds **2a**−**d** were prepared by literature procedures.[10,11] Ethynylferrocene was synthesized by the procedure documented by Polan et al.[17] and purified by sublimation (1×10^{-1} mbar, 40 °C).

Synthesis of 2e. Under an atmosphere of N_2, a solution of ethynylferrocence (78 mg, 0.37 mmol) in toluene (5 mL) was added to a solution of **1** (250 mg, 0.37 mmol) in toluene (10 mL). The reaction mixture was not stirred, and the addition was carried out so as to layer the two solutions. After 2 h at room temperature, the product crystallized from the reaction mixture as an orange solid and was isolated by filtration to give **2e** (149 mg, 0.11 mmol, 60%). Once crystalline, the product was found to be insoluble in hexane, benzene, and toluene: ^{1}H NMR (d_8-THF, 400 MHz, 298 K) 1.00 (d, 12H, J = 6.8 Hz), 1.11 (d, 12H, J = 6.8 Hz), 1.43 (s, 6H), 3.11 (hept, 2H, J = 6.8 Hz), 3.58−3.60 (m, 2H), 3.71−3.72 (m, 7H), 4.50 (s, 1H), 6.79 (t, 2H, J = 7.2 Hz), 6.90 (d, 4H, J = 7.2 Hz); ^{13}C NMR (d_8-THF, 100 MHz, 298 K) 22.1, 22.8, 25.8, 63.9, 67.2, 68.1, 72.1, 91.6, 99.4, 121.3, 121.5, 136.7, 139.9, 146.0, 162.7; IR (KBr disk, cm^{-1}) 3056, 2960, 2865, 2043, 1621, 1546, 1401, 1313, 1170, 1106. Anal. Calcd for $C_{82}H_{100}Ca_2Fe_2N_4$: C, 73.79; H, 7.50, N, 4.20. Found: C, 73.79; H, 7.56; N, 4.14.

Synthesis of 3a. Under an atmosphere of N_2, a solution of triisopropylsilylacetylene (150 μL, 0.74 mmol) in toluene (5 mL) was added to a solution of **1** (500 mg, 0.74 mmol) in toluene (10 mL). The reaction mixture was stirred for 15 min, the solvent volume

(14) (a) Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Konstas, K.; Junk, P. C. *Dalton Trans.* **2006**, 3360. (b) Cole, M. L.; Junk, P. C. *New J. Chem.* **2005**, *1*, 135.

(15) (a) Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. *Organometallics* **2008**, *27*, 497. (b) Lachs, J. R.; Barrett, A. G. M.; Crimmin, M. R.; Kociok-Köhn, G.; Hill, M. S.; Mahon, M. F.; Procopiou, P. A. *Eur. J. Inorg. Chem.* **2008**, 4173.

(16) (a) Zhang, W.-X.; Hou, Z. *Org. Biomol. Chem.* **2008**, *6*, 1720. (b) Zhang, W.-X.; Nishiura, M.; Hou, Z. *J. Am. Chem. Soc.* **2005**, *127*, 16788. (c) Zhou, S.; Wang, S.; Yang, G.; Li, Q.; Zhang, L.; Yao, Z.; Zhou, Z.; Song, H.-B. *Organometallics* **2007**, *26*, 3755. (d) Ong, T.-G.; O'Brien, J. S.; Korobkov, I.; Richeson, D. S. *Organometallics* **2006**, *25*, 4728.

reduced *in vacuo* to ca. 5 mL, and the solution stored at −21 °C for 48 h. The product crystallized from this concentrated toluene solution and isolated by filtration yielded **3a** (120 mg, 0.094 mmol, 26%) as a colorless crystalline solid: ^{1}H NMR (C_6D_6, 400 MHz, 298 K) 0.94−1.08 (m, 3H), 1.06 (d, 18H, J = 6.8 Hz), 1.20 (d, 12H, J = 6.7 Hz), 1.22 (d, 12H, J = 6.7 Hz), 3.30 (hept, 4H, J = 6.7 Hz), 4.74 (s, 1H), 7.12−7.21 (m, 6H); ^{13}C NMR (C_6D_6, 100 MHz, 298 K) 12.0, 19.2, 24.4, 25.2, 26.5, 28.1, 94.0, 123.9, 141.9, 146.6, 147.9, 163.6, 166.8; IR (KBr disk, cm^{-1}) 3057, 2865, 1966, 1654, 1622, 1516, 1316, 1170. Anal. Calcd for $C_{80}H_{124}Ca_2N_4Si_2$: C, 75.12; H, 9.70; N, 4.38. Found: C, 74.99; H, 9.82; N, 4.45.

Synthesis of 3b. Under an atmosphere of N_2, a solution of triisopropylsilylacetylene (150 μL, 0.74 mmol) in hexane (5 mL) was added to a solution of **1** (500 mg, 0.74 mmol) in hexane (20 mL). The reaction mixture was stirred for 15 min, and the solvent volume reduced *in vacuo* to induce crystallization. Following storage at 5 °C for 24 h the product was isolated by filtration, yielding **3b** (165 mg, 0.132 mmol, 36% based upon moles of THF from **1**) as a colorless crystalline solid: ^{1}H NMR (d_8-THF, 400 MHz, 298 K) 0.79−0.86 (m, 3H), 1.00 (d, 18H, J = 6.4 Hz), 1.21 (d, 12H, J = 6.8 Hz), 1.34 (d, 12H, J = 6.8 Hz), 1.68 (s, 6H), 1.79 (m, 8H, *THF*), 3.27 (hept, 4H, J = 6.8 Hz), 3.61 (m, 8H, *THF*) 4.78 (s, 1H), 7.03 (t, 2H, J = 7.2 Hz), 7.13 (d, 4H, J = 7.2 Hz); ^{13}C NMR (d_8-THF, 100 MHz, 298 K) 3.7, 11.9, 18.5, 24.0, 24.7, 25.4, 27.6, 93.6, 103.5, 123.1, 123.4, 147.5, 164.7, 171.9; IR (KBr disk, cm^{-1}) 3054, 2960, 2866, 1992, 1622, 1548, 1461, 1404, 1318, 1170, 1030. Repeated attempts to acquire satisfactory elemental analyses on this product proved unsuccessful.

Synthesis of 4a·THF. Under an atmosphere of N_2, a solution of **1** (1 g, 1.48 mmol) in hexane (10 mL) was added a solution of *p*-tolylacetylene (171 mg, 1.47 mmol) and 1,3-di-isopropyl carbodiimide (187 mg, 1.48 mmol) in hexane (10 mL). Stirring the reaction mixture overnight gave a precipitate, which could be redissolved upon gentle heating of the solution. Hot recrystallization by slow cooling of this saturated hexane solution gave the product as large colorless crystals. Compound **4a**·THF (670 mg, 0.82 mmol, 56%) was isolated by filtration: ^{1}H NMR (C_6D_6, 400 MHz, 298 K) 1.06−1.08 (m, 4H), 1.28 (d, 24H, J = 6.8 Hz), 1.32 (d, 12H, J = 6.4 Hz), 1.79 (s, 6H), 1.96 (s, 3H), 3.12−3.15 (m, 4H), 3.47 (hept, 4H, J = 6.8 Hz), 4.35 (hept, 2H, J = 6.4 Hz), 4.95 (s, 1H), 6.81 (d, 2H, J = 8.0 Hz), 7.09−7.11 (m, 2H), 7.15−7.17 (m, 4H), 7.48 (d, 2H, J = 8.0 Hz); ^{13}C NMR (C_6D_6, 100 MHz, 298 K) 24.7, 24.8, 25.2, 25.6, 26.7, 28.3, 31.9, 50.1, 68.2, 80.9, 93.6, 95.3, 123.7, 123.9, 127.4, 129.4, 132.2, 138.6, 141.7, 148.0, 159.2, 165.1; IR (KBr disk, cm^{-1}) 2961, 2867, 2209, 1620, 1550, 1463, 1278, 1175. Anal. Calcd for $C_{49}H_{70}CaN_4O$: C, 76.35; H, 9.08; N, 7.22. Found: C, 76.09; H, 9.14; N, 7.09. *In situ* ^{1}H NMR scale data for **4a**: 1.28 (12, d, J = 6.8 Hz), 1.35 (12H, d, J = 6.4 Hz), 1.37 (d, 12H, J = 6.8 Hz), 1.78 (s, 6H), 1.95 (s, 3H), 3.49 (hept, 4H, J = 6.8 Hz), 4.39 (hept, 2H, J = 6.4 Hz), 4.97 (s, 1H), 6.80 (d, 2H, J = 8.0 Hz), 7.03−7.07 (m, 2H), 7.10−7.13 (m, 4H), 7.46 (d, 2H, J = 8.0 Hz).

Synthesis of 4b·THF. To a solution of **3b** (260 mg, 0.33 mmol) in hexane (10 mL) was added a solution of 1,3-dicyclohexyl carbodiimide (68 mg, 0.33 mmol) in the same solvent (5 mL). The reaction mixture was stirred for 2 h. Upon reduction of the solvent volume to approximately 5 mL, the product crystallized as a colorless crystalline solid. Compound **4b**·THF (122 mg, 0.17 mmol, 52%) was isolated by filtration: ^{1}H NMR (C_6D_6, 400 MHz, 298 K) 1.10 (m, 4H, *THF*), 1.11−1.28 (series of m, 8H), 1.26 (d, 18H, J = 6.4 Hz), 1.29 (d, 12H, J = 6.8 Hz), 1.40 (d, 12H, J = 6.8 Hz), 1.50−1.60 (m, 5H), 1.71−1.75 (m, 2H), 1.80 (s, 6H), 1.82−1.86 (m, 4H), 1.94−1.97 (m, 4H), 3.17 (m, 4H, *THF*), 3.42 (hept, 4H, J = 6.8 Hz), 3.78−3.81 (m, 2H), 4.96 (s, 1H), 7.05−7.19 (m, 6H); ^{13}C NMR (C_6D_6, 100 MHz, 298 K) 11.7, 18.9, 24.7, 24.8, 25.2, 25.5, 26.8, 26.9, 28.2, 37.4, 58.9, 68.3, 93.7, 95.4, 98.5, 123.6, 123.9, 141.8, 148.0, 158.8, 165.1; IR (KBr disk, cm^{-1}) 2926, 2865, 2148, 1622, 1551, 1464, 1362, 1315, 1253, 1173. Anal. Calcd for $C_{44}H_{71}CaN_2OSi$: C, 74.20; H, 10.05; N, 3.93. Found: C, 74.30; H, 9.93; N, 4.07.

Catalytic Synthesis of 5. In a glovebox to a solution of phenylacetylene (0.5 g, 4.9 mmol) and 1,3-di-isopropyl carbodiimide (0.62 g, 4.9 mmol) in benzene (5 mL) in a Schlenk tube was added **1** (0.16 g, 0.24 mmol, 5 mol %). The Schlenk tube was sealed and removed from the glovebox, attached to a vacuum line, and heated at 80 °C. After 16 h, the solvent was removed *in vacuo* to yield a crystalline crude product. Recrystallization from hexanes (40−60 °C) at −21 °C yielded **5** as a colorless crystalline solid (0.65 g, 2.9 mmol, 59%): mp (hexanes) 60−61 °C; ^{1}H NMR (C_6D_6, 400 MHz, 298 K) 0.85 (br m, 6H), 1.40 (br m, 6H), 3.76 (br s, 1H, *NH*), 4.25 (hept, 2H, J = 6.4 Hz), 6.91−6.98 (m, 3H), 7.38−7.40 (m, 2H) 1.00 (d, 6H, J = 6.0 Hz), 1.40 (d, 6H, J = 6.0 Hz), 3.79 (s, 1H), 4.22−4.29 (m, 2H), 6.96−6.98 (m, 3H), 7.38−7.40 (m, 2H); ^{13}C NMR (C_6D_6, 100 MHz, 298 K) 22.9, 25.1, 42.8, 53.2, 80.8, 90.3, 122.1, 128.8, 129.3, 132.1, 140.0, 22.8, 25.6, 42.8, 53.3, 80.9, 90.3, 122.2, 128.7, 129.3, 132.1, 140.0; IR (KBr disk, cm^{-1}) 3370, 2965, 2868, 2225, 1588, 1508, 1384, 1260. Anal. Calcd for $C_{15}H_{20}N_2$: C, 78.95; H, 8.77; N, 12.28. Found: C, 79.01; H, 8.79; N, 12.34.

Crystallographic Data. Data for **3b** and **4a**·THF were collected at 150 K on a Nonius KappaCCD diffractometer equipped with a low-temperature device, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were processed using the Nonius Software.[18] In the structure of **3b** C14 was disordered over two sites in a 75:25 ratio. Hydrogens on C24 were also disordered over two sites and were included at calculated positions on this basis. An absorption correction (MULTISCAN) was applied to the structure of **4a**·THF. Structure solution, followed by full-matrix least-squares refinement, was performed using the WinGX-1.70 suite of programs.[19]

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM800738R

(17) Polan, J.; Schottenberger, H.; Anderson, B.; Martin, S. F. *Org. Synth.* **1996**, *73*, 262.

(18) DENZO-SCALEPACK. Otwinowski Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode; *Methods in Enzymology, Volume 276: Macromolecular Crystallography*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; part A, pp 307−326.

(19) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.