Inorg. Chem. **2008**, *47*, 7366−7376

Inorganic Chemistry
Article

Triazenide Complexes of the Heavier Alkaline Earths: Synthesis, Characterization, And Suitability for Hydroamination Catalysis

Anthony G. M. Barrett,[*,†] Mark R. Crimmin,[†] Michael S. Hill,[*,‡] Peter B. Hitchcock,[§] Gabriele Kociok-Köhn,[‡] and Panayiotis A. Procopiou[||]

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K., Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, 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 April 30, 2008

A series of triazenide complexes of the heavier alkaline earths, Ca, Sr and Ba, have been synthesized by either protonolysis or salt metathesis routes. Although complexes of the form $[\{Ar_2N_3\}M\{N(SiMe_3)_2\}(THF)_n]$ (M = Ca, *n* = 2; M = Sr, *n* = 3; Ar = 2,6-diisopropylphenyl) and $[\{Ar_2N_3\}Ca(I)(THF)_2]_2$ could be isolated and characterized by X-ray crystallography, solution studies revealed the propensity of these species to undergo Schlenk-like redistribution with the formation of $[\{Ar_2N_3\}_2M(THF)_n]$ (M = Ca, *n* = 1; M = Sr, *n* = 2). The latter compounds have been synthesized independently. In the case of the large barium dication, attempts to synthesize the heaviest analogue of the series, $[\{Ar_2N_3\}_2Ba(THF)_n]$, failed and led instead to the isolation of the potassium barate complex $[K\{Ar_2N_3\}Ba\{N(SiMe_3)_2\}_2(THF)_4]$. Single crystal X-ray diffraction studies demonstrated that, although in all the aforementioned cases the triazenide ligand binds to the electrophilic group 2 metal centers via symmetrical κ^2-*N*,*N*-chelates, in the latter compound an unprecedented bridging mode is observed in which the triazenide ligand coordinates through both terminal and internal nitrogen centers. A series of density-functional theory computational experiments have been undertaken to assist in our understanding of this phenomenon. In further experiments, the calcium and strontium amide derivatives $[\{Ar_2N_3\}M\{N(SiMe_3)_2\}(THF)_n]$ (M = Ca, *n* = 2; M = Sr, *n* = 3) proved to be catalytically active for the intramolecular hydroamination of 1-amino-2,2-diphenylpent-4-ene to form 2-methyl-4,4-diphenylpyrrolidine, with the calcium species demonstrating a higher turnover number than the strontium analogue (**2a**, TOF = 500 h^{-1}; **2b**, TOF = 75 h^{-1}). In these instances, because of ambiguities in the structural charcterization of the precatalyst in solution, such quantification holds little value and detailed catalytic studies have not been conducted.

Introduction

Recent years have witnessed considerable developments in the field of heavier group 2 homogeneous catalysis, and well-defined organometallic complexes of the heavier alkaline earths have now been reported as suitable initiators for the catalytic heterofunctionalization of unsaturated substrates,[1−3] the polymerization of styrene,[4] the polymerization of lactides and lactones,[5] the trimerization of phenylisocyanate,[6] and the dimerization of aldehydes to yield esters

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* To whom correspondence should be addressed. E-mail: msh27@bath.ac.uk.

[†] Imperial College London.

[‡] University of Bath.

[§] University of Sussex.

[||] GlaxoSmithKline Medicines Research Centre.

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10.1021/ic800789x CCC: $40.75

Chart 1. Selected Heavier Alkaline Earth Pre-Catalysts of the Form LMX

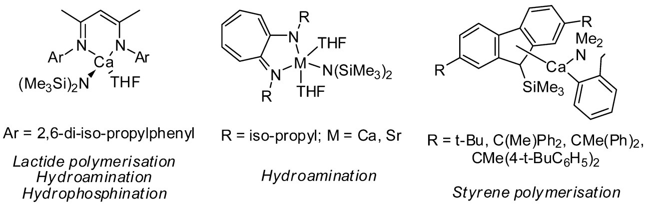
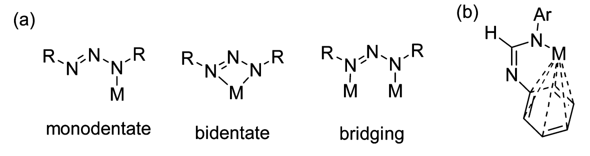


Chart 2. Examples of Bonding Modes of (a) Triazenides and (b) Formamidinates



(Tischenko reaction).[7] Studies have demonstrated that heteroleptic precatalysts of the form LMX (L = kinetically stabilizing ligand; M = Ca, Sr or Ba; X = reactive sigma-bonded substituent) may exhibit a degree of ligand control over reactivity. While comparisons may be made to the catalytic reaction chemistry of the organo(III)lanthanides, a common observation in these studies has been the propensity of group 2 species of the form LMX to undergo Schlenk-like solution equilibration to L_2M and MX_2; a pathway that may result in catalyst deactivation and/or the loss of ligand control over reactivity. On the basis of the work of Chisholm et al.,[5c,f] we have previously demonstrated that, of the series $[ArNC(Me)CHC(Me)NAr\}M\{N(SiMe_3)_2\}(THF)]$ (Ar = 2,6-di-iso-propylphenyl; M = Ca, Sr and Ba), only the derivative of the lightest congener, calcium, is stable with respect to Schlenk-like redistribution in solution.[8] This latter species has proven a vital model complex in delineating a reaction chemistry at calcium and has proven to be a useful precatalyst for the catalytic hydroamination and hydrophosphination of alkenes, alkynes, and carbodiimides.[1] Further examples of monoanionic spectator ligands employed in group 2 catalysis include the aminotropiniminates recently reported by Roesky,[2] and a number of silyl-substituted fluorenes employed by Harder in the stereocontrolled anionic polymerization of styrene (Chart 1).[4e,f]

The use of amidinate and guanidinate anions as supporting ligands in coordination chemistry has expanded dramatically in the past few years.[9] The success of these species in both applied and more fundamental research has naturally stimulated the pursuit of alternative monoanions of potentially similar denticity. As such, the readily prepared triazenides, $[R_2N_3]^-$, constitute an attractive candidate ligand class that has long been known to display comparable coordination behavior to both of the aforementioned carboxylate isosteres.[10] Although their use is not nearly so widespread, well characterized examples of triazenide complexes have been observed to contain metals coordinated via either monodentate or κ^2-*N,N*-chelated or bridged binding modes (Chart 2a).[11–13] While this behavior is also broadly typical of the majority of known amidinate and guanidinate-containing compounds, more recent studies have revealed the potential for these ligand sets to exhibit alternative chelating modes, especially upon complexation of either group 1 or heavier group 13 elements.[14,15] Of particular note, the binding of several formamidinates and 1,3-diaryl triazenides with electrophilic group 1 metals displays a preference for the formation of a polyhapto π-interaction with one (or two) of the aromatic rings (Chart 2b).[14a,b] Despite this, further studies

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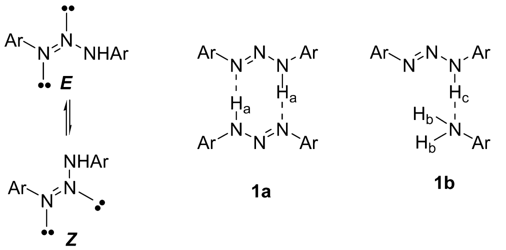
upon heavier group 2 formamidinates have demonstrated that these complexes display the more "conventional" κ^2-*N,N*-chelated binding mode in the solid state.[16]

Although the topological similarity of all three ligand classes furnishes an expectation of completely analogous coordination behavior, the addition of a central electronegative nitrogen atom provides several potentially unique features for the triazenide moiety. Thus, triazenide ligands are electron-deficient and so not only weakly σ-donating but also robust under relatively Brønstead acidic conditions. This effect has been quantified by infrared studies on late transition metal carbonyl complexes. Because of the weakly σ-donating triazenide moiety, [CpMo(CO)$_2${N$_3$Ph$_2$}] displays carbonyl stretches at higher frequency than those in an analogous amidinate complex [CpMo(CO)$_2${(Np-tol)$_2$CPh}] with ν(CO) absorptions being observed at 1978 and 1894 cm^{-1} and 1956 and 1868 cm^{-1}, respectively.[17] Perhaps more importantly, triazenide ligands may form coordination complexes involving the internal nitrogen lone-pair. Despite this clear potential, structurally characterized instances are scant and are restricted to derivatives of tetrazole-substituted triazines in which additional metal to ligand interactions provide a template to favor coordination at the internal nitrogen.[18]

A recent publication by Niemeyer et al. demonstrated the application of sterically demanding triazenide ligands to the kinetic stabilization of pentafluorophenyl complexes of the heavier alkaline earth metals of the form [{(Ar′)$_2$N$_3$}M{C$_6$F$_5$}] (Ar′ = (2,6-bis(mesityl)phenyl); M = Ca, Sr and Ba).[11d] This work, coupled with the ease of synthesis of simple symmetric triazine ligand precursors, sparked our interest in these species as possible candidates for the stabilization of catalytically relevant heteroleptic group 2 species of the form LMX. Our studies were initiated from the rationale that the weakly coordinating, electronically stable, triazenide chelate may simultaneously enhance the level of coordinative unsaturation at the electrophilic group 2 metal center while also increasing possible substrate range because of the low pK_a of the conjugate acid of the triazenide ligand, R$_2$N$_3$H.

We now report the synthesis of heteroleptic calcium and strontium complexes [{Ar$_2$N$_3$}M{N(SiMe$_3$)$_2$}(THF)$_n$] (M = Ca, $n = 2$; M = Sr, $n = 3$), [{Ar$_2$N$_3$}Ca(I)(THF)]$_2$ along with [{Ar$_2$N$_3$}$_2$M(THF)$_n$] (M = Ca, $n = 1$; M = Sr, $n = 2$) where Ar is the sterically demanding 2,6-di-iso-propylphenyl group, along with an evaluation of their solution stability and suitability as precatalysts for intramolecular hydroamination catalysis. In further work, similar attempts to synthesize the homoleptic complex [{Ar$_2$N$_3$}$_2$Ba(THF)$_n$] led instead to the isolation of the potassium barate complex [K[{Ar$_2$N$_3$}$_2$Ba{N(SiMe$_3$)$_2$}$_2$(THF)$_4$] from an otherwise intractable mixture of compounds.

Chart 3. Proposed Structures of **1**



Results and Discussion

Ligand Synthesis and Thermal Decomposition. Triazines may be synthesized by the addition of an amine or aniline to a diazonium salt.[19] Forming the latter species in situ allows for a simple one-pot synthesis and, following the recently reported procedure by Gibson and Marshall,[11c] the addition of an excess of iso-pentenyl nitrite to 2,6-di-iso-propylaniline in diethylether at 0 °C, followed by recrystallization at low temperature, yielded the triazine Ar$_2$N$_3$H (Ar = 2,6-diisopropylphenyl, **1**) as a crystalline solid. Previous solution studies upon simple symmetric triazines have demonstrated the propensity of these species to undergo thermally induced cis to trans isomerization.[20] Indeed, Gibson and Marshall reported that analytically pure samples of **1** demonstrated considerable complexity in solution and ascribed this to the formation of a 7:1 mixture of *E* and *Z* conformers in CDCl$_3$ at 298 K with isomerization occurring about a single nitrogen−nitrogen bond (Chart 3).

In accordance with this work, NMR studies upon solutions of **1** in d$_8$-toluene were consistent with the crystalline product existing as a mixture of species in solution. Pulsed-Gradient Spin−Echo studies upon a d$_8$-toluene solution of **1** demonstrated the presence of two distinct compounds at room temperature. Although variable temperature studies demonstrated no change in the ratio of these two species over a temperature range of 208−328 K, at 258 K two characteristic low field N−H environments were observed at 8.50 and 11.01 ppm. The application of nuclear Overhauser enhancement techniques demonstrated that both these N−H moieties were undergoing spin-saturation transfer not only with one another but also with a further broad resonance at 3.20 ppm, ascribed as a high field N−H environment (Chart 3 and Figure 1). Although the formation (and interconversion) of *E* and *Z* isomers of **1** in solution cannot be discounted, these observations may be attributed to 1,3-bis(2,6-di-iso-propylphenyl)triazine actually being isolated in an impure form as adducts **1a** and **1b** in an approximate 3:1 ratio (i.e., a 7:1 ratio of Ar$_2$N$_3$H to ArNH$_2$) from the reaction of 2,6-di-iso-propylaniline with iso-pentenyl nitrite.

Thus, in d$_8$-toluene the three observed N−H environments may be attributed to H$_a$ in the dimeric triazine and H$_b$ and

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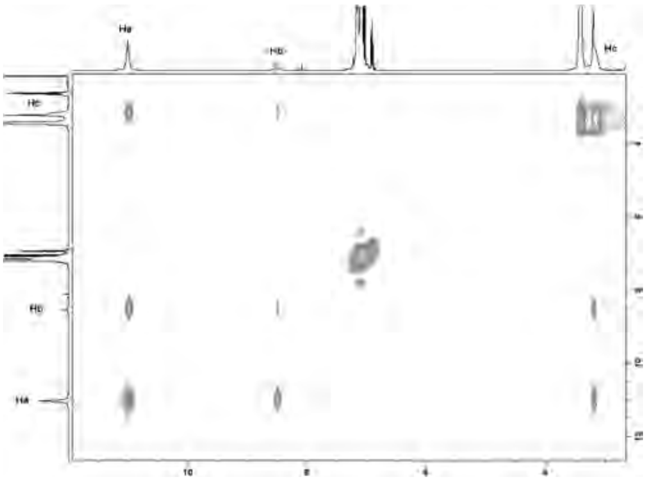
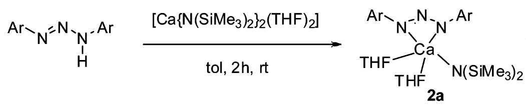


Figure 1. Selected NMR data from a nOesy experiment on **1a-b** at 258 K in d$_8$-toluene. Values quoted in ppm. Only positive contours shown.

H$_c$ in the triazine-aniline adduct, with fast proton exchange occurring between both compounds in solution. Further evidence for this hypothesis was provided by not only the literature precedent of the isolation and X-ray characterization of [{(2-MeC$_6$H$_4$)$_2$N$_3$H}.{(2-MeC$_6$H$_4$)NH$_2$}],[13a] but also the thermal decomposition of solutions of **1a** and **1b**. Heating d$_8$-toluene solutions of the latter mixture at 348 K for 14 h resulted in the decomposition of the triazine moiety to a number of new species, characterized by the nonreversible transformation of resonances attributed to the triazine to a multitude of new peaks in the ^{1}H NMR. This process occurred with no change to the resonances ascribed to 2,6-di-iso-propylaniline derived from adduct **1b**. While the mechanism of this decomposition remains open to speculation, repetition of the reaction on a preparative scale followed by distillation of the crude decomposition mixture allowed the isolation of 2,6-di-iso-propylaniline. This experiment also allowed the identification and isolation of the decomposition product, 2,2′,6,6′-iso-propyldiazobenzene, albeit in very low yield (3%).[21]

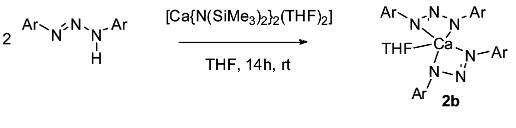
Modification of the procedure for the synthesis of **1a-b** yielded similar results. Performing the reaction neat by addition of 2 equiv of iso-pentenyl nitrite to 2,6-di-iso-propylaniline gave the product as a crystalline solid after 2 h at room temperature. After collection by filtration and washing with several portions of methanol and drying under vacuum, consistent yields of **1a-b** were achieved (52%, average of 3 experiments). Although no evidence for the significant participation of the minor aniline impurity was observed, the group 2 products derived from **1** were isolated in consistently low yields (vide infra). Previous crystallographic studies upon triazines have demonstrated the importance of two major structures in the solid state, (i) a hydrogen-bridged dimeric structure (α-modification) and (ii) infinite helical chains of hydrogen bonded molecules (*β*-modification). Furthermore, simple 1,3-diaryltriazines have been shown to form hydrogen-bonded adducts with anilines in the solid state (vide supra).[13a] X-ray analysis of single crystals within the bulk sample of **1** revealed the presence of the proposed dimeric triazine compound **1a** in the solid state (Figure 2, Table 1). Compound **1a** dimerizes via the formation of two intermolecular hydrogen bonds in which each triazine monomer acts both as a hydrogen-bond donor and hydrogen-bond acceptor. The nitrogen−nitrogen bond lengths are consistent with the resonance form required for dimerization, and localized single [N(1)−N(2) 1.333(3) and N(5)−N(6) 1.326(3)] and double [N(2)−N(3) 1.270(3) and N(4)−N(5) 1.280(3) Å] bonds can be identified. These latter values are consistent with the nitrogen−nitrogen bond lengths reported for [(C$_6$F$_5$)$_2$N$_3$H]$_2$ [1.286(3) and 1.315(3) Å].[13a] In contrast to the aforementioned triazine, which also adopts an "α-modification" in the solid state, the 8-membered supramolecular ring of **1a** displays significant deviation from planarity with the dimer being formed with a considerable torsion of two planar N$_3$H moieties about the axis bisecting N(2) and N(5). This result may be readily explained by considering that the sterically demanding 2,6-di-iso-propylphenyl groups prevent the coplanar approach of the two triazine monomers. Despite repeated sampling, crystals of **1b** could not be identified in the proposed mixture.

Synthesis of Heavier Group 2 Triazenide Complexes. Previous studies by Walsh et al. have demonstrated that triazines react with group 1 bases such as BuLi, [Li{N(SiMe$_3$)$_2$}], and [K{N(SiMe$_3$)$_2$}] to yield the corresponding lithium and potassium triazenide complexes.[11a,b] Furthermore, the same group has demonstrated that the homoleptic calcium triazenide complex [(4-MeC$_6$H$_4$)$_2$N$_3$}$_2$Ca(DME)$_2$] (DME = dimethoxyethane) may be synthesized by either (i) protonolysis of 2 equiv of the pro-ligand with [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] or by (ii) a salt metathesis reaction of 2 equiv of [{(p-tol)$_2$N$_3$}K] with CaI$_2$ in DME solvents.[11b] On the basis of this precedent, a series of reactions were conducted in which **1** was reacted either with the group 2 bis(trimethylsilyl)amide or with [K{N(SiMe$_3$)}$_2$] and the group 2 iodide, MI$_2$, in a one-pot procedure. By controlling the reaction stoichiometry attempts were made to prepare both homoleptic and heteroleptic heavier alkaline earth complexes.



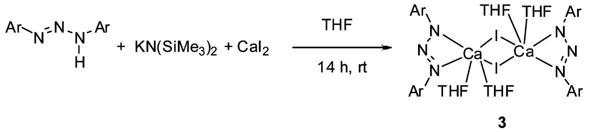
2a

(1)



2b

(2)



(3)

3

Reaction of **1** with 1 equiv of [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] in toluene at room temperature for 2 h followed by concentration of the reaction mixture yielded **2a** as a crystalline colorless solid (eq 1). Complex **2a** proved soluble in hydrocarbon solvents,

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[21] (a) Forber, C. L.; Kelusky, E. C.; Bunce, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5884. (b) Bunce, N. J.; Ferguson, G.; Forber, C. L.; Stachnyk, G. J. *J. Org. Chem.* **1987**, *52*, 394.

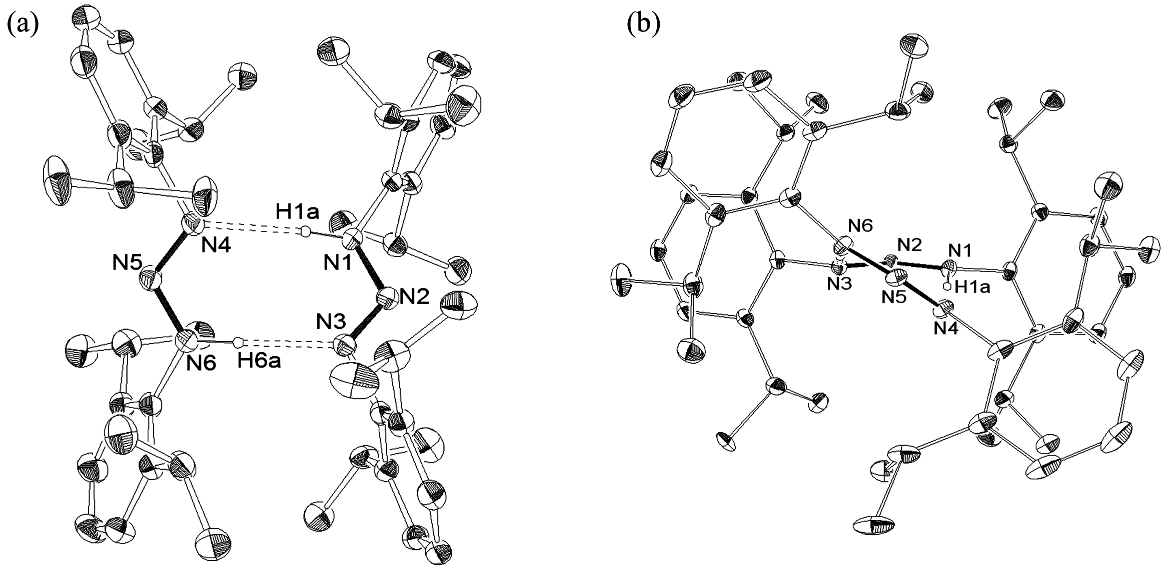

Figure 2. ORTEP (Oak Ridge Thermal Ellipsoid Plot) representations of **1a**. H-atoms, with the exception of those involved in hydrogen bonds omitted for clarity. (a) Overview of dimeric **1a** thermal ellipsoids at 40% probability. (b) View along the N(2)−N(5) axis with thermal ellipsoids at 10% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1a**

N(1)−N(2)	1.333(3)	N(4)−N(5)	1.280(3)
N(2)−N(3)	1.270(3)	N(5)−N(6)	1.326(3)
N(1)−N(2)−N(3)	111.8(2)	N(4)−N(5)−N(6)	112.1(2)

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Triazenide Complexes of Group 2

	2a	3	4a	4b
M−N(1)	2.442(2)	2.421(3)	2.683(5)	2.596(16)
M−N(3)	2.467(2)	2.431(2)	2.675(4)	2.604(2)
N(1)−N(2)	1.311(3)	1.308(3)	1.311(6)	1.307(4)
N(2)−N(3)	1.318(3)	1.321(3)	1.316(7)	1.300(4)
M−N(4)	2.307(3)		2.507(4)	
M−O(1)	2.381(2)	2.369(2)	2.582(4)	2.467(16)
M−O(2)	2.348(2)	2.348(2)	2.579(4)	
M−O(3)			2.590(3)	
M−I		3.1316(6) 3.0962(6)		
I−M−I′		87.084(16)		
N(1)−N(2)−N(3)	112.4(2)	111.3(2)	111.3(5)	111.0(3)
N(1)−M−N(3)	52.85(8)	53.13(8)	47.75(16)	48.83(8)
N(1)−M−O(1)	94.60(8)	95.10(8)	79.27(15)	129.1(4)
N(1)−M−O(2)	99.19(8)	154.89(8)	125.87(13)	
N(3)−M−O(1)	147.32(8)	88.96(8)	126.94(17)	80.5(4)
N(3)−M−O(2)	94.28(8)	102.05(8)	79.72(16)	

and X-ray quality crystals could be obtained directly from concentrated toluene solutions either at room temperature or at 0 °C. The results of a single crystal X-ray diffraction experiment are presented in Figure 3 while selected bond angles and lengths are listed in Table 2. In the solid state **2a** consists of a κ^2-chelated triazenide ligand bonded to a five-coordinate calcium center. Further coordination at the metal is provided not only by the σ-bonded hexamethyldisilazide residue but also by two molecules of THF. The complex possesses distorted trigonal-bipyramidal geometry at the metal. Although the calcium−nitrogen bond lengths to the triazenide moiety [Ca−N(1) 2.442(2) and Ca−N(3) 2.467(2) Å] are comparable to those reported in $[\{4\text{-MeC}_6\text{H}_4)_2\text{N}_3\}_2\text{Ca(DME)}_2]$,[11b] in which the triazenide demonstrates an unsymmetrical κ^2-*N,N*-chelating mode [Ca−N 2.446(2) and 2.602(2) Å], these distances are slightly longer than those reported in five-coordinate β-diketiminate and aminotropiniminate calcium amide complexes, $[\{\text{ArNC(Me)CHC(Me)NAr}\}\text{Ca}\{\eta^2\text{-NH(CH}_2)_2\text{OMe}]_2$ [Ca−N 2.413(2) and 2.398(2) Å][8] and $[(\text{iPrAT})\text{Ca}\{\text{N(SiMe}_3)_2\}(\text{THF})_2]$ [Ca−N 2.408(2) and 2.422(2) Å, iPrAT = 2-(iso-propylamino)tropiminate],[2a] consistent with the triazenide acting as a weakly coordinating ligand. By comparison, the calcium−nitrogen bond distance to the hexamethyldisilazide moiety in **2a** is considerably shorter [Ca−N(4) 2.307(2) Å] than those to the monoanionic triazenide ligand. The triazenide ligand provides an acute bite angle [N(1)−Ca−N(3) 52.85(8)°] at calcium similar to that observed in $[\{4\text{-MeC}_6\text{H}_4)_2\text{N}_3\}_2\text{Ca(DME)}_2]$ [N−Ca−N 51.46(6)°].[11b]

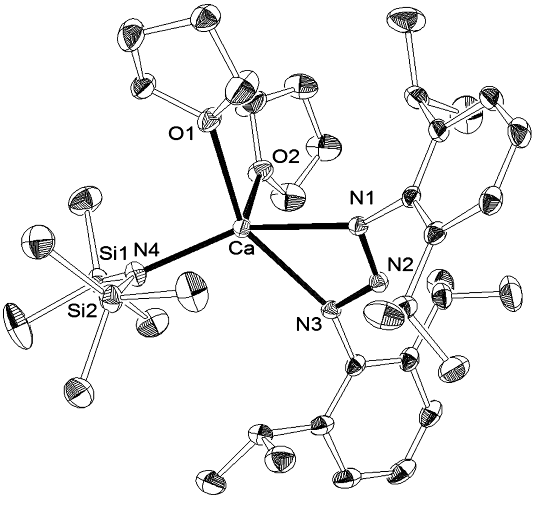

Figure 3. ORTEP representation of **2a**. Thermal ellipsoids at 30% probability. H-atoms omitted for clarity.

Although crystalline samples of **2a** provided satisfactory elemental analysis results, upon redissolving, a mixture of compounds was observed in solution. D_8-toluene solutions of **2a** demonstrated a series of resonances consistent with two magnetically nonequivalent triazenide ligands along with a further high field peak assigned to $[\text{Ca}\{\text{N(SiMe}_3)_2\}_2(\text{THF})_2]$. On the basis of these data, it is proposed that hydrocarbon solutions of **2a** (LMX) undergo deleterious Schlenk-like equilibria with the formation of the homoleptic species $[\{\text{Ar}_2\text{N}_3\}_2\text{Ca(THF)}]$ (**2b**, L_2M) and $[\text{Ca}\{\text{N(SiMe}_3)_2\}_2(\text{THF})_2]$

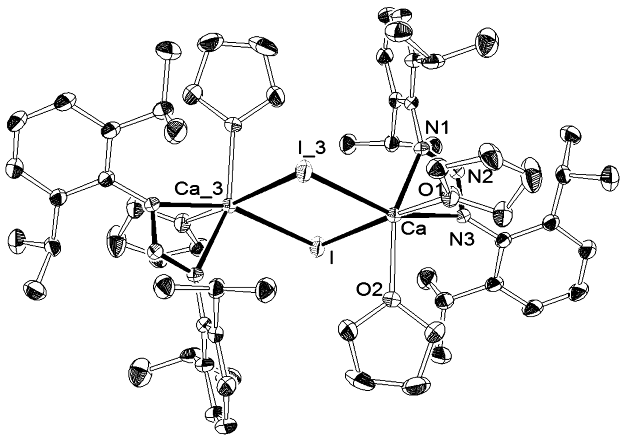

Figure 4. ORTEP representation of **3**. Thermal ellipsoids at 30% probability. H-atoms omitted for clarity.

(MX_2). While likely to be solvent dependent, further variable temperature studies demonstrated that the position of this apparent equilibrium was not dependent upon the temperature of the sample and thus suggest that the formation of **2b** is nonreversible. This observation contrasts with that made upon Chisholm's β-diketiminate calcium amide [{ArNC(Me)CHC-(Me)NAr}Ca{$N(SiMe_3)_2$}(THF)] which, although susceptible to Schlenk-like redistribution following protonolysis of the bulky trimethylsilylamide moiety, is coordinatively robust in solution at room temperature.[8]

On the basis of this solution data, attempts were made to synthesize the homoleptic calcium compound [{Ar_2N_3}$_2$Ca-(THF)] via a one-pot reaction of 2 equiv of **1** with 2 equiv of [K{$N(SiMe_3)_2$}] and 1 equiv of CaI_2 in THF. Removal of the solvent followed by extraction into toluene and crystallization by storage of concentrated solutions at −21 °C yielded the triazenide calcium iodide complex **3**. It appears that, although minor amounts of the desired product may be formed under these reaction conditions, the kinetic stability of the intermediate calcium iodide species is sufficient to prevent further reaction with [{Ar_2N_3}K] that is formed in situ. The isolated product **3** could be synthesized rationally in reproducible yield using a 1:1:1 stoichiometry of [K{$N(SiMe_3)_2$}] to CaI_2 to triazine following fractional crystallization from toluene (Figure 4).

In the solid state compound **3** dimerizes via bridging iodide ligands. The triazenide ligand again demonstrates symmetric κ^2-*N,N*-chelation, with further coordination at calcium being provided by two molecules of THF. The 6-coordinate calcium center demonstrates heavily distorted octahedral geometry because of the tight bite angle provided by the triazenide chelate [N(1)−Ca−N(3) 53.13(8)°]. It is of interest to note that both calcium−nitrogen [Ca−N(1) 2.421(3) and Ca−N(3) 2.431(2) Å] and calcium−oxygen [Ca−O(1) 2.369(2) and Ca−O(2) 2.348(2) Å] bond lengths are slightly shorter than those provided by **2a** despite the increased coordination number at the metal in **3**. While structurally characterized, hydrocarbon-soluble heterolepetic calcium iodides that are literature known remain limited to a handful of compounds,[22] the solid-state dimerization of these species has been observed previously and the calcium-iodide bond lengths in **3** [Ca−I 3.0962(6) and Ca′-I 3.1316(6) Å] are consistent with those reported in calcium iodide complexes supported by sterically demanding cyclopentadienyl, for example, [Cp*CaI(THF)$_2$]$_2$ [Ca−I 3.1356(15) and Ca−I′ 3.1980(16)],[22a] [{C_5H_2(i-Pr)$_3$}CaI(THF)]$_2$ [Ca−I 3.101(2) and Ca−I′ 3.087(2) Å][22b] and [{$C_5H_2(SiMe_3)_3$}CaI(THF)]$_2$ [Ca−I 3.066(4) and Ca′−I 3.102(4)],[22c] and β-diketiminate ligand sets, for example, [{ArNC(tBu)CHC(tBu)NAr}CaI-(THF)]$_2$ [Ca−I 3.210(1) and Ca−I′ 3.273(1) Å].[22f]

Multinuclear NMR studies upon d_8-toluene solutions of **3** again demonstrated the presence of a minor byproduct incorporating the triazenide ligand. Furthermore, attempts to acquire satisfactory elemental analysis upon crystallized samples of **3** proved unsuccessful. Again it is postulated that compound **3** is unstable with respect to Schlenk-like solution equilibria and, by analogy to the observations made by Hanusa upon the solution dynamics of cyclopentadienyl stabilized calcium iodides,[22a–d] that it is actually isolated in an impure form along with the homoleptic complex [{Ar_2N_3}$_2$Ca(THF)] (**2b**) with the alternative redistribution product [Ca(I)$_2$(THF)$_n$] being insoluble in hydrocarbon solvents. Support for the repeated occurrence of the bis-chelated compound **2b** upon dissolution of samples of **2a** and **3** was eventually provided by its rational synthesis from the addition of 2 equiv of Ar_2N_3H to [Ca{$N(SiMe_3)_2$}$_2$-(THF)$_2$] in either THF or hydrocarbon solutions. Following extraction into and crystallization from hexamethyl disiloxane, samples of **2b** provided identical multinuclear NMR data to those observed for the minor species accompanying **2a** and **3** in solution. This data heavily suggests that the 1,3-bis-(2,6-di-iso-propylphenyl)triazenide ligand provides insufficient kinetic stability to the labile calcium coordination sphere to prevent solution Schlenk-like redistribution reactions. It appears that the bulky terphenyl substituted ligand employed by Niemeyer in the isolation of pentafluoroaryl complexes of the heavier alkaline earths, [{(Ar′)$_2$-N$_3$}M{C_6F_5}] (Ar′ = 1,3-bis-(2,6-bis(mesityl)phenyl), M = Ca, Sr and Ba),[11d] provides considerably enhanced kinetic stability relative to the simpler 1,3-bis-(2,6-di-iso-propylphenyl)triazenide ligand set employed herein.

With these observations in hand, it is unsurprising therefore, that upon extension of this methodology to strontium, the heteroleptic amide complex [{Ar_2N_3}Sr{N-($SiMe_3$)$_2$}(THF)$_3$] (eq 4, **4a**), which could be isolated and characterized by X-ray crystallography, is also observed to redistribute to the homoleptic strontium complexes [{Ar_2N_3}$_2$Sr(THF)$_2$] (**4b**) and [Sr{$N(SiMe_3)_2$}$_2$(THF)$_2$] in solution. In this instance recrystallization of samples of **4a** by slow cooling of a 50 °C hexane solution also allowed for

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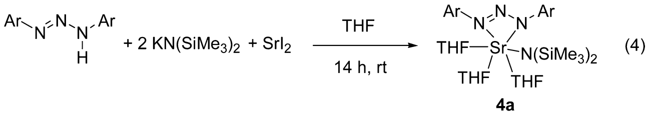
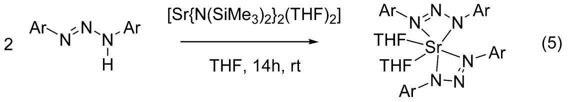
(22) (a) McCormick, M. J.; Sockwell, S. C.; Davis, C. E. H.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 2044. (b) Harvery, M. J., Jr.; Hanusa, T. P.; Young, V. G. *J. Organomet. Chem.* **2001**, *626*, 43. (c) Harvery, M. J.; Hanusa, T. P. *Organometallics* **2000**, *19*, 1556. (d) Burkey, D. J.; Alexander, E. K.; Hanusa, T. P. *Organometallics* **1994**, *13*, 2773. (f) El-Kaderi, H. M.; Heeg, M. J.; Winter, C. H. *Polyhedron* **2006**, *25*, 224. (g) Datta, S.; Gamer, M. T.; Roesky, P. W. *Dalton Trans.* [Online early access] DOI: 10.1039/b719552d. Published Online: 2008.

the isolation and characterization of **4b** by X-ray crystallography via fractional crystallization from the apparent mixture in solution. Multinuclear NMR data for the isolated compound **4b** were consistent with those assigned to this Schlenk-like redistribution product of samples of **4a** in d_8-toluene. Furthermore, the assignment of NMR resonances within this mixture to **4b** were confirmed by its independent synthesis via addition of 2 equiv of **1** to $[Sr\{N(SiMe_3)_2\}_2(THF)_2]$ (eq 5).



4a

(4)



4b

(5)

Structurally characterized triazenide complexes of strontium remain confined to a single example, the heteroleptic pentafluorophenyl strontium complex $[\{(Ar')_2N_3\}Sr\{C_6F_5\}]$ ($Ar' = 1,3$-bis-(2,6-bis(mesityl)phenyl)) reported by Niemeyer et al.[11d] Complexes **4a** and **4b** demonstrate similar structural parameters in the solid state, and results of single crystal X-ray diffraction experiments are presented in Figures 5a and 5b while important bond lengths are listed in Tables 2 and 3. In the solid state **4a** is monomeric and analogous to **2a**. Coordination at strontium is provided by the symmetric triazenide κ^2-*N,N*-chelate, a σ-bonded trimethylsilylamide moiety and three molecules of THF. Strontium–nitrogen bond lengths [Sr–N(1) 2.683(5) and Sr–N(3) 2.675(4) Å] are longer than those reported in $[\{2,5\text{-}(Mes)_2C_6H_3\}_2N_3\}Sr(C_6F_5)]$ [Sr–N 2.576(6) and 2.548(5) Å] consistent with the higher coordination number at strontium in **4a**. X-ray analysis of single crystals of **4b** revealed a similar 6-coordinate triazenide complex with the bis-trimethylsilyl amide ligand replaced by a second triazenide ligand. Metrical parameters within the triazenide ligands are similar to those not only for **4a** *but also* the homoleptic strontium formamidinate complex $[\{(2,6\text{-}^iPrC_6H_3N)_2CH\}_2Sr(THF)_2]$ reported by Junk et al., an observation exemplified by the metal–nitrogen bond lengths observed in **4a** [Sr–N(1) 2.596(16) and Sr–N(3) 2.604(2) Å] and the latter amidinate [Sr–N 2.537(3) to 2.619(3) Å].[16a] Noteworthy in these studies is that the triazenide ligand provides a much more acute bite angle to strontium [N(1)–Sr–N(3) **4a**, 47.75(16)°; **4b**, 48.83(8)°] than to calcium [N(1)–Ca–N(3) **2a**, 52.85(8)°; **3** 53.13(8)°]. We have made similar observations in relation to the coordination chemistry of group 2 β-diketiminate complexes,[8] and reason that this expected effect is due to a less efficient "fit" of the larger dication within the cavity provided by the bidentate ligand.

Attempts to synthesize the barium complex $[(Ar_2N_3)_2Ba(THF)_n]$ via the one-pot reaction of barium iodide, 2 equiv of $[K\{N(SiMe_3)_2\}]$, and 2 equiv of $[Ar_2N_3H]$ in THF led, following removal of the solvent in vacuo, extraction into hexane, and storage at −21 °C, to the isolation of a crop of pale yellow crystals in very low yield (4%). An X-ray diffraction study revealed the isolated compound to be not the expected homoleptic complex in which the triazenide ligands act as bidentate κ^2-chelates but the unusual barate complex **5** (eq 6 and Figure 6). It is worthy of note that an analogous formamidinate complex $[\{(2,6\text{-}^iPrC_6H_3N)_2CH\}_2Ba(THF)_2]$ has been synthesized by the one-pot transmetalation-protonolysis reaction of barium metal with $[Hg(C_6F_5)_2]$ and 2 equiv of $[\{(2,6\text{-}^iPrC_6H_3)N\}CH\{(2,6\text{-}iPrC_6H_3)NH)\}$ in THF.[16a]

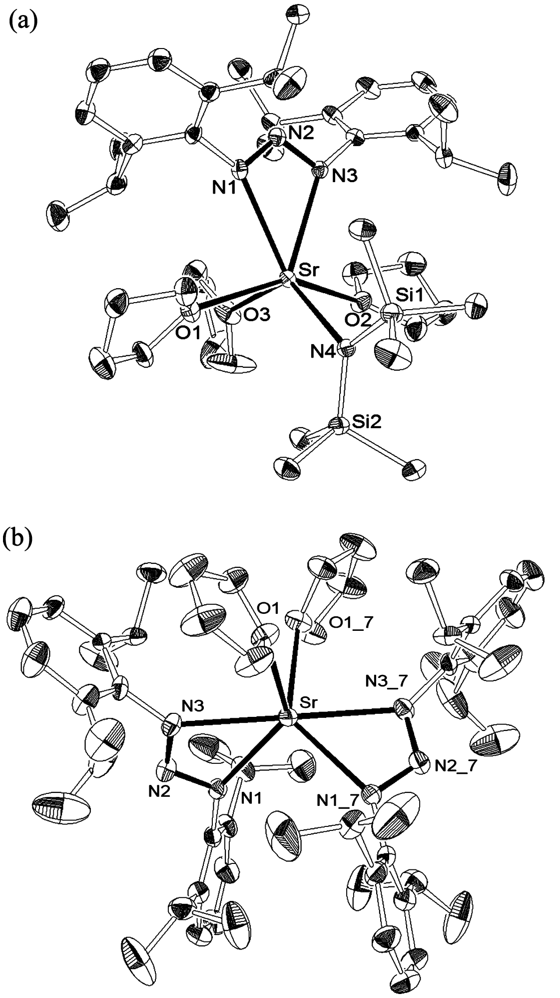
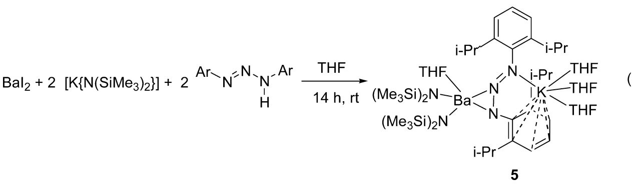


Figure 5. ORTEP representations of (a) **4a**, thermal ellipsoids at 30% probability, and (b) **4b**, thermal ellipsoids at 20% probability. H-atoms omitted for clarity.



5

(6)

In the solid state, **5** consists of a single triazenide ligand coordinated to a barium bis(trimethylsilyl)amide moiety through two adjacent nitrogen atoms and to potassium through the remaining nitrogen and an η^6-π-interaction with one of the N-Dipp aromatic groups (Figure 6 and Table 4). The triazenide is effectively tetradentate. The aryl groups are positioned *anti* with respect to one another, and the

Table 3. Crystallographic Data for Compounds **1a**, **2a**, **3**, **4a-b**, and **5**

	1a	**2a**	**3**	**4a**	**4b**	**5**
molecular formula	$C_{48}H_{70}N_6$	$C_{45}H_{76}CaN_4O_2Si_2$	$C_{76}H_{112}Ca_2I_2N_6O_4$	$C_{42}H_{76}N_4O_3Si_2Sr$	$C_{56}H_{84}N_6O_2Sr$	$C_{52}H_{99}BaKN_5O_4Si_4$
formula weight (g mol^{-1})	731.10	801.36	1507.68	828.87	960.91	1147.16
crystal system	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P\bar{1}$	Cc	$P2_1/n$	$P2_12_12_1$	$F2dd$	$P2_1/n$
a (Å)	12.2291(5)	10.8380(3)	13.3260(4)	14.2503(5)	12.0490(2)	19.7430(5)
b (Å)	13.5407(6)	24.3827(7)	20.6550(7)	17.8678(7)	24.8820(4)	16.5050(5)
c (Å)	14.9435(7)	18.8459(5)	15.1770(5)	19.0150(9)	36.7390(6)	21.2450(8)
α (deg)	88.064(2)	90	90	90	90	90
β (deg)	72.250(2)	99.391(2)	107.6310(10)	90	90	107.9340(10)
γ (deg)	80.209(2)	90	90	90	90	90
V (Å^3)	2321.95(18)	4913.5(2)	3981.2(2)	4841.6(3)	11014.5(3)	6586.5(4)
Z	2	4	2	4	8	4
μ (mm^{-1})	0.061	0.21	0.966	1.200	1.023	0.779
ρ (g cm^{-3})	1.046	1.080	1.258	1.137	1.159	1.157
È range (o)	5.55 to 27.62	3.43 to 26.02	3.36 to 27.61	3.75 to 25.07	5.40 to 27.44	2.93 to 25.10
R_1, wR_2 [$I > 2\sigma(I)$]	0.0625, 0.1317	0.044, 0.097	0.0425, 0.0980	0.060, 0.1068	0.0414, 0.0951	0.0798, 0.1818
R_1, wR_2 (all data)	0.2197, 0.1818	0.058, 0.105	0.0827, 0.1170	0.1130, 0.1247	0.0665, 0.1105	0.2108, 0.2364
measured/independent reflections/ R_{int}	22455/9759/0.1132	19331/7833/0.045	26809/9027/0.0805	27584/8388/0.1236	39917/6196/0.0692	46651/11625/0.1594

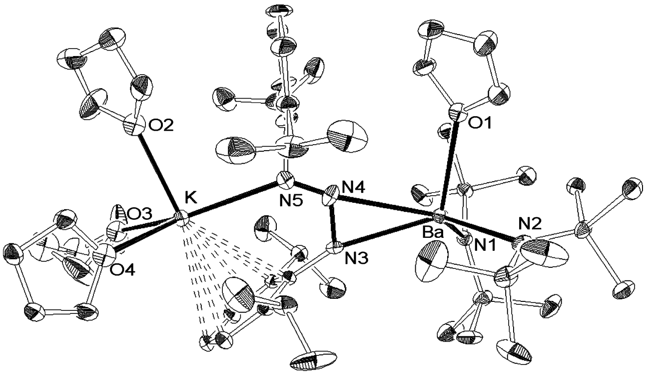


Figure 6. ORTEP representation of **5**. H-atoms omitted for clarity. Thermal ellipsoids at 10% probability.

metallic centers reside to either side of the planar N_3 residue. While the nitrogen−nitrogen bond lengths [N(3)−N(4) 1.368(10) and N(4)−N(5) 1.209(10) Å] are consistent with a localized structure of the triazenide ligand, these values differ significantly from simple κ^1-coordinated ligand sets commonly observed in late transition metal chemistry.[12g,h] Although this observation indicates that the ligand is actually polarized to allow significant charge delocalization across N(3) and the adjacent aromatic ring of **5**, the potassium−nitrogen [K−N(5) 2.851(9) Å], potassium−oxygen [K−O 2.648(9)−2.851 Å], and the potassium−carbon bond lengths [K−C 3.143(8)−3.352(11) Å] are reminiscent of those reported in the similarly coordinated potassium formamidinate complex $[\{K\{(2,6\text{-}iPr_2C_6H_3N)_2CH\}_2K(THF)_2\}_n]\cdot n$THF [K−N 2.863(4) Å; av. K−O 2.673 Å; K-arene centroid 3.034(9) Å].[14b]

Coordinative unsaturation at the large barium dication is relieved by not only two σ-bonded silylamide moieties and a single molecule of THF but also electron density from both lone-pairs of N(3) and N(4) of the triazenide ligand. While it may be argued that this unusual coordination is augmented by an interaction between the metal and the nitrogen−nitrogen π-bond, both the long N(3)−N(4) bond length (vide supra) and the short barium−nitrogen bond lengths [Ba−N(3) 2.805(7), Ba−N(4) 2.876(9) Å],[13] suggest that a Lewis-acid/Lewis-base interaction of essentially sigma character predominates. The barium−nitrogen bond lengths of the σ-bonded bis(trimethylsilyl)amides [Ba−N(1) 2.675(7), Ba−N(2) 2.671(7) Å] are slightly longer than those of the terminal ligands reported for the four-coordinate complex $[Ba\{N(SiMe_3)_2\}_2(THF)]_2$ [Ba−N 2.602(9) Å] because of the higher coordination number at barium in **5**.[23]

Our understanding of the solid-state bonding in **5** was further enhanced by undertaking density-functional theory (DFT) calculations upon the model complexes $[\{Ph_2N_3\}K]$ (**6a**), $[\{(2\text{-}MeC_6H_4)_2N_3\}K]$ (**6b**), and $[\{(2\text{-}^iPrC_6H_4)_2N_3\}K]$ (**6c**) at the B3LYP level of theory and LANDL2DZ basis set implemented in Gaussian03.[24] Considering *N,N*- versus *N,Aryl*-coordination, comparison of the relative energies of optimized structures revealed that, although the conventional κ^2-*N,N*-chelating mode is in all cases lower in energy than that utilizing a metal-π interaction [**6a**, $\Delta E = 71.4$ kJ mol^{-1}; **6b**, $\Delta E = 41.5$ kJ mol^{-1}; **6c**, $\Delta E = 26.7$ kJ mol^{-1}], this difference decreases with increasing steric demands of the triazenide aryl groups.[25] We postulate that the bonding mode observed in **5** is, in fact, an effect of the coordination to two highly electrophilic s-block elements, with the triazenide ligand undergoing significant polarization in an attempt to satisfy coordinative unsaturation at both barium and potassium centers. Furthermore, it is likely that the ease with which the triazenide ligand undergoes such polarization is dictated by the steric inhibition of the expected symmetric coordination mode.

Following crystallization, samples of compound **5** proved insoluble in hydrocarbon solvents. In d_8-THF solution, multinuclear NMR data were consistent with the triazenide ligand adopting a simple symmetric structure in which the two 2,6-di-iso-propylphenyl groups are magnetically equivalent. Although this could be explained in terms of fast dynamic exchange processes within **5**, a series of subsequent

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(23) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 121.

(24) M. J. Frisch et al. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(25) Minima were confirmed by independent frequency calculations.

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for **5**

Ba−N(1)	2.671(7)	K−O(2)	2.648(9)	N(3)−N(4)	1.368(10)
Ba−N(2)	2.675(7)	K−O(3)	2.685(9)	N(4)−N(5)	1.209(10)
Ba−N(3)	2.805(7)	K−O(4)	2.664(8)	N(5)−N(4)−N(3)	113.6(9)
Ba−O(1)	2.806(6)	K−N(5)	2.851(9)		
Ba−N(4)	2.876(9)	K−C(29)	3.143(8)		
N(1)−Ba-N(2)	110.0(2)	K−C(30)	3.219(9)		
N(1)−Ba-N(3)	104.6(2)	K−C(34)	3.223(9)		
N(2)−Ba-N(3)	125.9(2)	K−C(33)	3.293(12)		
N(3)−Ba-N(4)	27.8(2)	K−C(31)	3.320(10)		
N(5)−N(4)−Ba	171.2(7)	K−C(32)	3.352(11)		
N(3)−N(4)−Ba	73.2(5)	N(4)−N(5)−K	139.8(7)		

NMR experiments suggested that the bimetallic complex is not robust in coordinating solvent and dissociates to solvated [{Ar_2N_3}K] and [Ba{$N(SiMe_3)_2$}$_2$] derivatives. Thus, the addition of [K{$N(SiMe_3)_2$}] to Ar_2N_3H in d_8-THF gave a single product [{Ar_2N_3}K(d_8-THF)$_n$] as observed by ^1H and ^{13}C NMR spectroscopy. Removal of the solvent and reaction byproduct $HN(SiMe_3)_2$ in vacuo followed by redissolving in d_8-THF and addition of 1 equiv of [Ba{$N(SiMe_3)_2$}$_2$] yielded a reaction mixture that demonstrated near identical multinuclear NMR data to that for isolated samples of **5**. A pulsed-gradient spin−echo NMR study showed that this mixture was indeed two separate compounds in d_8-THF.

Applications in Catalysis. The fast developing field of group 2 catalysis has encouraged several research groups to develop new organometallic heavier alkaline earth species for applications as precatalysts in small molecule transformations.[1–7] In this regard, we have previously observed Chisholm's β-diketiminate-stabilized calcium amide [{ArNC(Me)CHC(Me)NAr}Ca{$N(SiMe_3)_2$}(THF)] (**7a**) and the magnesium alkyl complex [{ArNC(Me)CHC(Me)NAr}Mg(Me)(THF)] (**7b**) to be suitable precatalysts for the intramolecular hydroamination of aminoalkenes.[1] Studies have demonstrated the kinetic stability of the precatalysts in solution with respect to Schlenk-like solution redistribution.[8] A preliminary kinetic analysis has also suggested that the calcium species provides the faster reaction rates [e.g., hydroamination of ((1-allylcyclohexyl)methyl)amine [**7a**, TOF = 146 h^{-1}; **7b**, TOF = 48.5 h^{-1}],[1e] while a series of stoichiometric reaction studies suggest that both **7a** and **7b** form similar intermediates upon reactions with amines albeit via reversible and nonreversible protonolysis respectively.[8,26]

In subsequent and related work Roesky has reported that the aminotropiniminate complexes [(iPrAT)Ca{$N(SiMe_3)_2$}$(THF)_2$] and [(iPrAT)Sr{$N(SiMe_3)_2$}$(THF)_2$] may be applied to the same end.[2] Despite the observation that the calcium species is purportedly more active than the strontium, detailed solution studies are yet to be reported. It is also clear that, as yet, an homologous series of kinetically stable group 2 precatalysts of the form LMX (M = Mg, Ca, Sr, and Ba) does not exist which would allow cogent comparison of the effect of ionic radii (i.e., dication polarization and polarizability) upon reaction rate.

Although the coordination studies reported herein demonstrate the inability of the sterically demanding ligand 1,3-bis-(2,6-di-iso-propylphenyl)triazenide to stabilize heteroleptic organo-calcium and -strontium species in solution, the hydroamination cyclization of 1-amino-2,2-diphenylpent-4-ene could be achieved using just 2 mol % of either **2a** or **4a** in C_6D_6 solutions at room temperature to yield 2-methyl-4,4-diphenylpyrrolidine in greater than 99% yield as observed by ^1H NMR spectroscopy (Figures 7 and 8). Quantification of this reaction by a kinetic analysis at constant substrate and catalyst concentration ([cat] = 7−8 mM, $[sub]_o$ = 0.4 M) revealed that, in accordance with Roesky's observations, the calcium species provided faster reaction rates than observed for strontium (**2a**, TOF = 500 h^{-1}; **2b**, TOF = 75 h^{-1}). Despite this observation, the inexact nature of the precatalyst in solution does not allow a fair comparison of the effect of ionic radii as the extent of LMX, L_2M, and MX_2 equilibration upon reaction rate is not obvious and likely to be noninnocent.

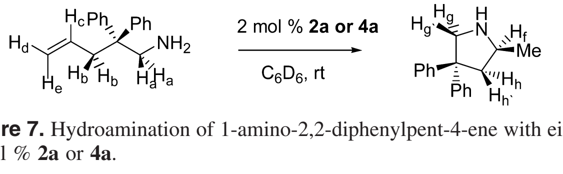

Figure 7. Hydroamination of 1-amino-2,2-diphenylpent-4-ene with either 2 mol % **2a** or **4a**.

Conclusions

A number triazenide complexes of the heavier group 2 elements (M = Ca, Sr and Ba) have been synthesized via either salt-metathesis or protonolysis (transamination) routes. Although characterization in the solid state is, in most cases, consistent with the triazenide ligand acting as a symmetric κ^2-*N,N*-chelate, solution studies have demonstrated the propensity of compounds of the form LMX (M = Ca, Sr; L = 1,3-bis-(2,6-di-iso-propylphenyl)triazenide; X = I, $N(SiMe_3)_2$) to undergo deleterious Schlenk-like solution redistribution reactions with the formation of L_2M and MX_2.

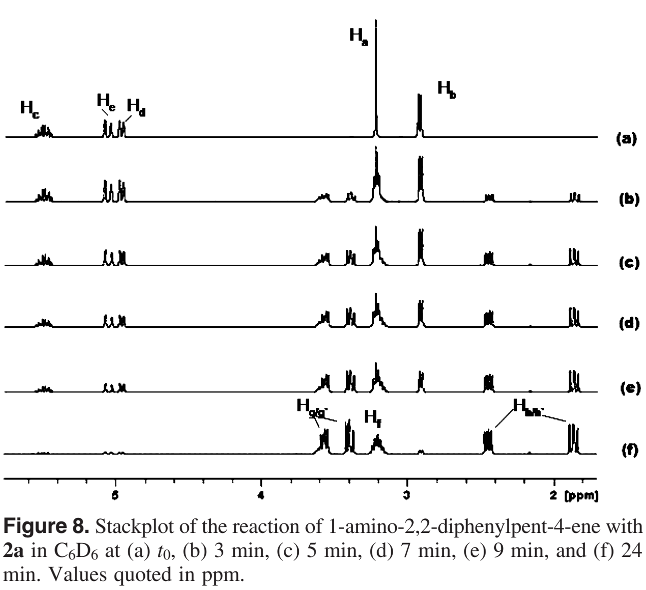

Figure 8. Stackplot of the reaction of 1-amino-2,2-diphenylpent-4-ene with **2a** in C_6D_6 at (a) t_0, (b) 3 min, (c) 5 min, (d) 7 min, (e) 9 min, and (f) 24 min. Values quoted in ppm.

In the case of barium an unusual potassium barate complex **5**, in which the triazenide bridges potassium and barium centers with coordination of both terminal and internal nitrogens of the $[Ar_2N_3]^-$ moiety, has been isolated and characterized. Although synthesized in a very low yield, **5** demonstrates the potential coordination chemistry of the internal nitrogen of the triazenide ligand set.

Strontium and calcium amide complexes $[\{Ar_2N_3\}M\{N(SiMe_3)_2\}(THF)_n]$ (M = Ca, $n = 2$; M = Sr, $n = 3$) proved catalytically active for the intramolecular hydroamination of 1-amino-2,2-diphenylpent-4-ene to yield the corresponding pyrrolidine. While, in accordance with the work of Roesky et al., kinetic analyses suggest that the calcium complex provides superior rates of reaction to the strontium species under identical reaction conditions. Any conclusions drawn from such data, however, are possibly misleading because of the inexact nature of the catalyst in solution.

Experimental Section

General Procedures. 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-500 spectrometer (^{13}C NMR 125 MHz), 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 ampoules 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. The heavier group 2 amides $[M\{N(SiMe_3)_2\}_2(THF)_2]$ (M = Ca, Sr) and the triazine **1** were prepared by literature procedures.[11c,27] Attempts to acquire satisfactory elemental analysis on both the impure triazine ligand **1** and the triazenide complexes **2a**, **3**, **4a**, and **5** were unsuccessful. Stoichiometries of the ligand precursor were calculated based upon moles of triazine considering that **1** consists of a 7:1 mixture of 1,3-bis-(2,6-di-iso-propylphenyl)triazine and 2,6-di-iso-propylaniline.

Modified Procedure for the Synthesis of 1. 2,6-Di-iso-propylaniline (9.4 g, 53.1 mmol) and iso-pentenyl nitrite (13.6 g, 116 mmol) were mixed in a large beaker (500 mL). The reaction mixture became turbid and gas evolution was observed. The reaction mixture was left, unstirred, for 2 h at room temperature, over which period the product crystallized. The solid was collected by filtration and washed with cold methanol (2 × 15 mL) to give the product as colorless crystals (5.02 g, 13.8 mmol, 52%; average of 3 experiments). Multinuclear NMR spectroscopy, elemental analysis, and mass spectrometry were consistent with the product being isolated as a 7:1 mixture of 1,3-bis-(2,6-di-iso-propylphenyl)triazine and 2,6-di-iso-propylaniline. ^1H NMR (d_8-toluene, 500 MHz, 298 K) minor 1.13 (d, $J = 6.8$ Hz, 12 H), 2.63 (hept, $J = 6.8$ Hz, 2H), 3.20 (broad s, 2H, *NH*), 6.82 (t, $J = 7.8$ Hz, 1H), 7.00 (d, $J = 7.8$ Hz, 2H), major 1.17 (d, 24H, $J = 6.9$ Hz), 3.30 (apparent hept, $J = 6.9$ Hz, 4H), 7.06−7.13 (m, 6H); ^{13}C NMR (d_8-tol, 125 MHz, 298 K) minor 23.4, 29.1, 119.8, 124.0, 133.1, 141.6, major 24.7, 29.3, 128.4, 144.2, all peaks broad remaining resonances obscured; HRMS calcd for $C_{24}H_{36}N_3$ 366.2904 found 366.2908; HRMS calcd for $C_{12}H_{20}N$ 178.1596 found 178.1591.

Thermal Decomposition of 1. A sample of **1** (1 g) was dissolved in dry toluene and heated to 80 °C for 14 h. The solvent was removed in vacuo, and the crude product purified by bulb-to-bulb distillation. Multinuclear NMR analysis of the lower boiling fraction (150 mg, 4×10^{-1} mbar at 150 °C) revealed it to contain largely 2,6-di-iso-propylaniline along with unknown impurities. Following washing with methanol, the high boiling fraction (1×10^{-1} mbar at 200 °C) yielded *cis*-2,2′,6,6′-isopropyldiazobenzene as a red solid (28 mg, 0.08 mmol, 3% based upon triazine). ^1H NMR (C_6D_6, 400 MHz, 298 K) 1.20 (d, $J = 6.8$ Hz, 24 H), 3.48 (hept, $J = 6.8$ Hz, 4H), 7.18−7.21 (m, 6H); ^{13}C NMR (C_6D_6, 100 MHz, 298 K) 24.4, 28.0, 124.3, 129.1, 141.2, 150.3 [Lit.20 13C NMR 24.2, 27.5, 123.8, 128.9, 140.9, 149.7]; HRMS calc. for $C_{24}H_{35}N_2$ 351.2800 found 351.2815; Anal. Calcd for $C_{24}H_{34}N_2$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.25; H, 9.73; N, 7.94; UV/vis ($n \rightarrow \pi^*$, nm) 463 ($\varepsilon = 770$ dm^3 mol^{-1} cm^{-1}) [Lit.[20] UV/vis ($n \rightarrow \pi^*$, nm) *trans* 467 ($\varepsilon = 910$ dm^3 mol^{-1} cm^{-1}), *cis* 462 ($\varepsilon = 1000$ dm^3 mol^{-1} cm^{-1})].

Synthesis of $[\{Ar_3N_2\}Ca\{N(SiMe_3)_2\}(THF)_2]$, 2a. In a glovebox $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (0.69 g, 1.37 mmol) and **1** (0.5 g, 1.28 mmol) were weighed into a Schlenk-tube. The Schlenk was sealed, removed from the glovebox, attached to a vacuum line, and toluene (20 mL) added to the reaction mixture. The reaction mixture was stirred for 2 h at room temperature. Upon reduction of the solvent volume to about 10 mL, crystallization of the product occurred at room temperature. The product was isolated as a colorless crystalline solid by filtration to give **2a** (0.38 g, 0.47 mmol, 37%). ^1H NMR (C_6D_6, 300 MHz, 298 K) 0.24 (s, 18H), 1.18 (m, 8H, *THF*), 1.23 (d, $J = 6.9$ Hz, 24H), 3.47 (hept, $J = 6.9$ Hz, 4H), 3.52 (m, 8H, *THF*), 7.05−7.11 (m, 5H) 7.17−7.18 (m, 1H); ^{13}C NMR (C_6D_6, 75 MHz, 298 K) 5.8, 25.0, 25.2, 28.3, 69.3, 123.5, 124.9, 142.8, 147.6; Anal. Calcd for $C_{45}H_{76}CaN_4O_2Si_2$: C, 67.39; H, 9.48; N, 6.99. Found: C, 67.39; H, 9.54; N, 6.85.

Synthesis of $[\{Ar_3N_2\}_2Ca(THF)]$, 2b. In a glovebox $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (0.22 g, 0.44 mmol) and **1** (0.4 g, 1.02 mmol) were weighed into a Schlenk-tube, which was sealed, removed from the glovebox, attached to a vacuum line, and THF (20 mL) added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo and the product extracted into hot hexamethyldisiloxane (10 mL) and filtered. The product was isolated as a colorless crystalline solid upon cooling to 5 °C to give **2b** (86 mg, 0.10 mmol, 23%). ^1H NMR (C_6D_6, 400 MHz, 298 K) 1.16 (d, $J = 6.8$ Hz, 48H), 1.17 (m, 4H, *THF*), 3.37 (hept, $J = 6.8$ Hz, 8H), 3.58 (m, 4H, *THF*), 7.10−7.17 (m, 12H); ^{13}C NMR (C_6D_6, 100 MHz, 298 K) 22.5, 24.3, 28.8, 69.3, 123.5, 125.2, 142.4, 146.7.

Synthesis of $[\{Ar_3N_2\}Ca\{I\}(THF)_2]_2$, 3. In a glovebox, CaI_2 (0.82 g, 2.74 mmol), $K\{N(SiMe_3)_2\}$ (0.55 g, 2.74 mmol) and **1** (1 g, 2.56 mmol) were weighed into a Schlenk-tube. The Schlenk was sealed, removed from the glovebox, attached to a vacuum line, and THF (20 mL) added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo and the product extracted into toluene (25 mL). The mixture was filtered and the product crystallized following concentration of the solvent to about 15 mL and storage of the solution at −21 °C. The product was isolated as a colorless crystalline solid by filtration to give **3** (0.25 g, 0.17 mmol, 13%). ^1H NMR (C_6D_6, 300 MHz, 298 K) 1.18 (m, 8H, *THF*), 1.25 (d, *J*

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= 6.8 Hz, 24 H), 3.50 (m, 8H, *THF*), 3.63 (hept, J = 6.8 Hz, 4H), 6.94−7.16 (m, 6H); ^{13}C NMR (C_6D_6, 75 MHz, 298 K) 25.3 (2 signals), 28.4, 69.8, 123.3, 124.4, 143.0, 147.9.

Synthesis of [{Ar_3N_2}Sr{N($SiMe_3$)$_2$}(THF)$_3$] 4a. In a glovebox SrI_2 (1.87 g 5.47 mmol), K{N($SiMe_3$)$_2$} (2.18 g, 5.47 mmol) and **1** (2 g, 5.12 mmol) were weighed into a Schlenk-tube. The Schlenk was sealed, removed from the glovebox, attached to a vacuum line, and THF (20 mL) added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo and the product extracted into toluene (25 mL). The mixture was filtered and the product crystallized following concentration of the solvent to about 15 mL and storage of the solution at −21 °C. The product was isolated as a colorless crystalline solid by filtration to give **4a** (0.67 g, 81 mmol, 16%). ^{1}H NMR (d_8-toluene, 400 MHz, 298 K) 0.26 (s, 18H), 1.29 (d, J = 6.9 Hz, 24H), 1.36 (m, 12H, *THF*), 3.46 (hept, J = 6.9 Hz, 4H), 3.55 (m, 12H, *THF*), 7.01−7.17 (m, 5H), 7.17−7.18 (m, 1H); ^{13}C NMR (C_6D_6, 75 MHz, 298 K) 4.3, 26.2, 26.8, 29.9, 124.7, 126.7, 143.8, 149.7;

Synthesis of [{Ar_3N_2}$_2$Sr(THF)$_2$] 4b. In a glovebox [Sr{N($SiMe_3$)$_2$}$_2$(THF)$_2$] (0.24 g, 0.44 mmol) and **1** (0.4 g, 1.02 mmol) were weighed into a Schlenk-tube. The Schlenk was sealed, removed from the glovebox, attached to a vacuum line, and THF (20 mL) added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo and the product extracted into hexane (20 mL) and filtered. The product was isolated as a colorless crystalline solid by reducing the solvent volume followed by hot recrystallization from hexane to give **4b** (0.127 g, 0.13 mmol, 30%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K) 1.16 (d, J = 6.9 Hz, 48H), 1.24 (m, 8H, *THF*), 3.40 (hept, J = 6.8 Hz, 8H), 3.55 (m, 8H, *THF*), 7.08−7.18 (m, 12H); ^{13}C NMR (C_6D_6, 75 MHz, 298 K) 24.6, 25.3, 28.6, 68.7, 123.4, 124.4, 142.2, 148.4; Anal. Calcd for $C_{56}H_{84}N_6O_2Sr$: C, 69.93; H, 8.74; N, 8.74. Found: C, 69.81; H, 8.64; N, 8.71.

Synthesis of 5. In a glovebox anhydrous barium iodide (0.535 g, 1.35 mmol), potassium hexamethyldisilazide (0.54 g, 2.7 mmol), and **1** (1 g, 2.56 mmol) were weighed into a Schlenk-tube. The tube was sealed, removed from the glovebox, and THF (20 mL) added via cannula on a vacuum line. The reaction mixture was stirred overnight, the solvent removed in vacuo, and the product extracted into hexane (15 mL). Following filtration, concentration, and storage at −21 °C for 24 h large pale yellow crystals formed, which were isolated by filtration giving **5** (0.045 g, 0.039 mmol, 4%). ^{1}H NMR (d_8-THF, 298 K, 400 MHz) 0.04 (broad s, 36H), 1.15 (d, J = 6.4 Hz, 24H), 3.56 (apparent hept, J = 6.4 Hz, 4H), 6.83 (apparent t, J = 5.2 Hz, 2H), 6.99 (d, J = 5.2 Hz, 4H); ^{13}C NMR (d_8-THF, 298 K, 100 MHz) 1.8, 24.8, 28.1, 122.8, 142.0, remaining peaks obscured.

NMR Scale Hydroamination Reactions. In a glovebox, a solution of tetrakis(trimethylsilyl)silane (2 mg, TMSS) and 1-amino-2,2-diphenylpent-4-ene (40 mg, 1.69 mmol) was made up in C_6D_6 (700 μL) and transferred to a Youngs tap NMR tube. The concentration of the substrate was determined by ^{1}H NMR spectroscopy. The catalyst (2 mol %) was added, the tube was sealed and removed from the glovebox, frozen with liquid nitrogen, and thawed just before loading into the spectrometer. ^{1}H NMR spectra were recorded at regular intervals. The reaction kinetics were monitored by integration of the methylene peak adjacent to the alkene moiety in the aminoalkene (Figure 7, H_b), and concentrations were calculated over 3 half-lives using TMSS as an internal standard. Turnover frequencies were calculated according to the procedure reported by Marks et al.[28a] fitting the data to the equation,

$$C = mt + C_0 \qquad (1)$$

The turnover frequency can be calculated thus, where E is the ratio of substrate to catalyst (accurately determined by integration of the ^{1}H NMR resonances of the catalyst against the internal standard)

$$N_t(\mathrm{h}^{-1}) = E(60m/-C_0) \qquad (2)$$

NMR data for isolated 2-methyl-4,4-diphenylpyrrolidine:[29] ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz) 1.21 (d, 3H, J = 6.4 Hz), 2.05 (dd, 1H, J = 12.7, 9.2), 2.67 (broad s, 1H), 2.74 (ddd, 1H, J = 12.7, 6.6, 1.1 Hz), 3.34 (ddd, 1H, J = 9.2, 6.6, 6.4 Hz), 3.48 (d, 1H, J = 11.4 Hz), 3.70 (dd, 1H, J = 11.4, 1.1 Hz), 7.15−7.18 (m, 2H), 7.22−7.32 (m, 8H); ^{13}C NMR ($CDCl_3$, 298K, 100 MHz) 22.1, 46.9, 53.0, 57.1, 57.6, 125.9, 125.9, 126.9, 127.0, 128.2, 128.3, 146.8, 147.5.

Crystallographic Data

Data for **1a**, **2a**, **3**, **4a-b**, and **5** 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.[30] For **2a**, **3**, and **4a** a symmetry-related (multiscan) absorption correction was employed. Structure solution, followed by full-matrix least-squares refinement, was performed using the WinGX-1.70 suite of programs.[31] Selected data are presented in Tables 1–4.

Notes on Refinement. Compound **1a** forms dimers through hydrogen bonds. Compound **3** co-crystallizes with one solvent molecule of benzene which is disordered in the ratio 60:40. Solvent atoms were refined as rigid group. Compound **4a** shows some underlying disorder in one of the THF and -$SiMe_3$ groups, however, because of the weak intensity of the data this disorder could not be resolved. The same statement applies for compound **5** which demonstrates disorder in the THF ligands. Compound **4b** crystallizes in a high symmetry which led to symmetry related disorder in one THF and one di-iso-propylphenyl group. Bond lengths in one of the di-iso-propylgroup moieties were idealized.

Acknowledgment. We thank GlaxoSmithKline for the generous endowment (to A.G.M.B.), the Royal Society for a University Research Fellowship (M.S.H.) and Royal Society Wolfson Research Merit Award (A.G.M.B.) and the Engineering and Physical Sciences Research Council and GlaxoSmithKline for generous support of our studies.

Supporting Information Available: Kinetic data from the hydroamination cyclization of 1-amino-2,2-diphenylpent-4-ene (PDF) and crystallographic information files (CIF) for **1a**, **2a**, **3**, **4a**−**b**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC800789X

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