Synthesis, Characterization, and Solution Lability of N-Heterocyclic Carbene Adducts of the Heavier Group 2 Bis(trimethylsilyl)amides

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A series of N-heterocyclic carbene (NHC) adducts of the heavier group 2 bis(trimethylsilyl)amides, of the general formulas $[(L^1)M\{N(SiMe_3)_2\}_2]$, $[(L^2)Ca\{N(SiMe_3)_2\}_2]$, and $[(L^1)Ca\{N(SiMe_3)_2\}Cl]$ (L^1 = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene and L^2 = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, M = Ca, Sr, and Ba), have been synthesized by either the addition of the group 2 amide to the appropriate imidazolium salt or direct addition of the carbene to the solvent-free, homoleptic, metal amide. X-ray diffraction studies of the reaction products revealed the formation of monomeric three-coordinate alkaline earth metal species in which the NHC binds via conventional σ-donation of the lone pair to the electrophilic metal center. Although ^1H, ^{13}C, and NOESY NMR experiments suggest this coordination is retained in solution, reactions with protic substrates such as 2-methoxyethylamine, diphenylamine, and di-*p*-tolylphosphine demonstrate the lability of the NHC under catalytically-relevant conditions. Furthermore, a series of reactions of $[L^1Ca\{N(SiMe_3)_2\}_2]$ with Lewis bases suggest that the strength of the interaction between the metal and neutral ligand decreases across the series $Ph_3P{=}O > NHC \sim THF > PPh_3$. In the case of triphenylphosphine oxide the structure of the reaction product, $[(Ph_3P{=}O)_2Ca\{N(SiMe_3)_2\}_2]$, was confirmed by independent synthesis from addition of $Ph_3P{=}O$ to $[Ca\{N(SiMe_3)_2\}_2]$.

Introduction

Following the isolation and characterization of the first stable crystalline carbene, 1,3-diadamantylimidazol-2-ylidene, by Arduengo et al. in 1991,[1] N-heterocyclic carbenes (NHCs) have found numerous applications as ligands in coordination chemistry. NHCs typically bind as two-electron σ-donors through coordination of the filled sp^2-orbital of the singlet carbene to the metal center. Although often considered as strongly basic phosphine analogues, the utility of NHCs has been illustrated by their application in late transition metal chemistry,[2] in the stabilization of high oxidation state metal complexes,[3] and, more recently, as Lewis bases in metal-free catalytic processes.[4] Despite these studies, investigation of NHCs as ligands to electropositive s-block and f-block metals remains less widely considered.

NHC adducts of lanthanide organometallics were originally reported by Schumann in 1994 with the preparation of $[\{C_5Me_4Et\}_2Yb(C\{NRCMe\}_2)]$ (R = Me, i-Pr).[5a] In the same year, Arduengo et al. synthesized $[(Cp^*)_2Sm(C\{NMeCMe\}_2)]$ and $[Ln(thd)_3(C\{NMeCMe\}_2)]$ (Ln = Eu, Y; thd = 2,2,6,6-tetramethylheptane-3,5-dionato) through addition of the free carbene to $[Cp^*_2Sm(THF)]$ and $[Ln(thd)_3]$, respectively. In solution, the ^{13}C NMR of the yttrium(III) diketonate complex demonstrated a characteristic carbene resonance at 199 ppm (d, $^1J_{^{13}C-^{89}Y} = 33$ Hz), consistent with the NHC ligand remaining bound to the metal and not dissociating on the NMR time scale.[5b] DFT studies on the complexation of $[C\{NMeCH\}_2]$ to $SmCl_3$ are consistent with the strong binding of NHCs to electrophilic lanthanide elements, and the Gibbs' free energy of coordination of the NHC to the metal at 25 °C (−40.3 kcal mol^{-1}) has been calculated to be considerably more exothermic than that of the ethereal solvents tetrahydrofuran (−23.7 kcal

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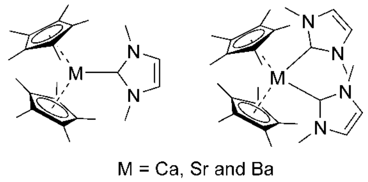
Scheme 1. Heavier Group 2 NHC Adducts



mol^{-1}) and dimethyl ether ($-$21.8 kcal mol^{-1}), suggesting such complexes should be quite stable in solution.[6]

More recently simple silylamide, $[\mathrm{Ln}\{\mathrm{N(SiMe_3)_2}\}_3(\mathrm{C}\{\mathrm{NMeCH}\}_2)]$ (Ln = Y, La),[7] and alkyl, $[\mathrm{Ln(CH_2SiMe_3)_3(C}\{\mathrm{N^iPrCMe}\}_2)_2]$ (Ln = Er, Lu),[8] NHC complexes of the lanthanide metals have been synthesized by similar solvent displacement reactions. In addition, Arnold et al. have reported the synthesis and characterization of a series of f-block N-heterocyclic complexes stabilized by chelating monoanionic ligands consisting of NHCs tethered to alkoxide or amide groups.[9] Despite these coordination studies, the applications of f-block NHC complexes in catalytic processes remains limited to only a few examples. Although $[(\mathrm{Cp^*})_2\mathrm{Sm(C}\{\mathrm{N^iPrCMe}\}_2)]$ and $[(\mathrm{Cp'})_2\mathrm{Sm}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{C}\{\mathrm{N^iPrCMe}\}_2)]$ ($\mathrm{Cp'} = {}^t\mathrm{BuC_5H_4}$) have been reported as precatalysts for the polymerization of methyl methacrylate and isoprene, respectively,[10] it is unclear whether the carbene ligand remains bound to the active catalytic species during catalytic turnover.

Our current interest lies in the application of well-defined, and similarly electropositive, heavier group 2 complexes as homogeneous catalysts for small-molecule transformations. In this regard we, and others, have demonstrated the application of heavier group 2 amides as suitable precatalysts for the heterofunctionalization of unsaturated substrates.[11] To date, the only reported NHC complexes of the heavier alkaline earth elements that have been fully characterized are adducts of group 2 metallocenes, $[(\mathrm{Cp^*})_2\mathrm{M(C}\{\mathrm{NMeCMe}\}_2)_n]$ (M = Ca, Sr, Ba; n = 1, 2).[12,13] Although additional reports have alluded to the synthesis of $[\mathrm{M}\{\mathrm{N(SiMe_3)_2}\}_2\{\mathrm{C(NRCH)_2}\}_2]$ (M = Ca, Sr, Ba; R = t-Bu, Me), full experimental details have not been forthcoming.[12] As an initial study into the suitability of NHC ligands for the kinetic stabilization of heavier group 2 organometallics, we now describe the synthesis and characterization of adducts of the bis(bis(trimethylsilyl)amides) of calcium, strontium, and barium along with initial observations of their stability in solution.

Results and Discussion

Synthesis of NHC Adducts of Group 2 Amides. Previous methods for the synthesis of s-block and f-block N-heterocyclic carbene adducts include (i) ligand exchange reactions, through addition of the free carbene to an organometallic precursor with displacement of coordinated solvent, such as $\mathrm{Et_2O}$ or THF, (ii) the deprotonation of an imidazolium salt at the C-2 position using a suitably basic organometallic species, and (iii) salt-metathesis routes in which the carbene ligand is transferred from one metal to another.[5,7–9,12–15] For group 1, representative examples include the reaction of 1,3-diisopropyl-3,4,5,6-tetrahydropyrimid-2-ylidene with $[\mathrm{M}\{\mathrm{N(SiMe_3}\}_2]$ (M = Li, Na, and K) in THF or toluene,[14e] the addition of $[\mathrm{C}\{\mathrm{Nt\text{-}BuCH_2}\}_2]$ to $[\{(\mathrm{Me_3Si})_3\mathrm{C_5H_2}\}\mathrm{Li}]$,[15b] and the reaction of a hydrotris(imidazolium)borate salt with n-BuLi at −78 °C in diethyl ether.[15d] In their original work Arduengo et al. reported the generation of noncoordinated NHCs by deprotonation of the corresponding imidazolium salts with NaH or KH in THF in the presence of dimethylsulfoxide.[1] Herrmann et al. have also reported that sodium amide in liquid ammonia/THF at −40 °C is effective for the preparation of NHCs from imidazolium salt precursors.[16]

The reaction of a 1:2 mixture of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride and calcium bis(bis(trimethylsilyl)amide) (**1a**) in toluene at room temperature, followed by removal of the solvent *in vacuo*, extraction into hexane, and crystallization at low temperature yielded the NHC adduct 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene calcium bis(bis(trimethylsilyl)amide) (Scheme 2, **2a**). The reaction is presumed to proceed via *in situ* deprotonation of the imidazolium salt to yield the mixed calcium amide−chloride NHC adduct **3** (*vide infra*) followed by either (i) carbene transfer to unreacted $[\mathrm{Ca}\{\mathrm{N(SiMe_3)_2}\}_2]$, (ii) salt metathesis of the intermediate organometallic species with a further equivalent of the amide, or (iii) Schlenk-like solution redistribution of **3**. Facile separation

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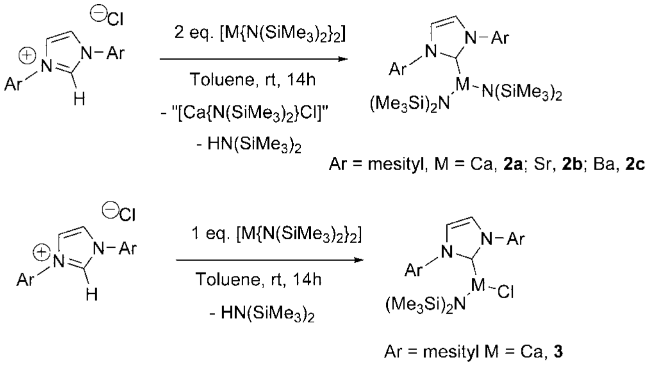
Scheme 2. Reaction of Group 2 Amides with 1,3-Bis(2,4,6-trimethylphenyl)imidazolium Chloride

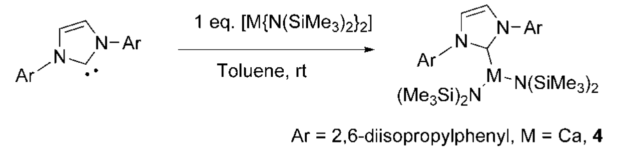


of the reaction product from the remaining calcium species could be achieved by fractional crystallization from a hexane solution.

Extension of this methodology to both strontium and barium derivatives using strontium bis(bis(trimethylsilyl)amide) (**1b**) and barium bis(bis(trimethylsilyl)amide) (**1c**) proved straightforward (Scheme 2, **2b**,**c**). In all cases the products were isolated as moisture-sensitive, colorless crystalline solids that proved highly soluble in hydrocarbon solvents such as hexane, toluene, and benzene. Varying the ratio of imidazolium salt to metal amide allowed only limited control of the product distribution. For instance, reaction of a 1:1 mixture of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride and calcium bis(bis(trimethylsilyl)amide) allowed the isolation of the mixed amide−chloride **3**. This compound proved unstable with respect to Schlenk-like solution redistribution, and heating a d_8-toluene solution of **3** for 14 h at 60 °C resulted in the production of $[L^1Ca\{N(SiMe_3)_2\}_2]$ (**2a**) and L^1, as observed by ^1H NMR spectroscopy. The latter product presumably derives from dissociation of the NHC from $CaCl_2$ in the adduct $[L^1CaCl_2]$. This hypothesis was supported by attempts to synthesize the di(chloro)calcium adduct. Reaction of a 2:1 mixture of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride and calcium bis(bis(trimethylsilyl)amide) yielded, following extraction into hexane and crystallization, the noncoordinated carbene as the only product. While the desired reaction product may be present within the reation mixture, it appears that under these crystallization conditions only the free carbene may be isolated. Attempts to isolate the product by extraction into aromatic solvents such as benzene and toluene similarly yielded the free carbene as the sole crystalline product of the reaction.

Efforts to synthesize 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene adducts of calcium bis(trimethylsilyl)amide through similar deprotonation reactions met with only partial success. Although reaction of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride with 2 equiv of $[Ca\{N(SiMe_3)_2\}_2]$ in toluene (or d_8-toluene) proceeded rapidly at room temperature to give the expected product, as monitored by ^1H NMR spectroscopy, attempts to isolate the NHC adduct by fractional crystallization were complicated by the presence of an, as yet, unidentified reaction byproduct. Analytically pure samples of **4** could, however, be obtained by the addition of the isolated NHC to 1 equiv of $[Ca\{N(SiMe_3)_2\}_2]$ in hydrocarbon solvents (Scheme 3). In these instances the product could be easily purified by crystallization from benzene or toluene in moderate yield (52%).

Scheme 3. Reaction of $[Ca\{N(SiMe_3)_2\}_2]$ with 1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene



Solid-State Structures. Compounds **2a**−**c** could all be crystallized by slow cooling of hot hexane solutions. X-ray quality crystals of **4** could be isolated by crystallization from concentrated benzene or toluene solutions following storage at 5 °C for 24 h. A series of single-crystal X-ray diffraction experiments were conducted upon these samples. The results of these experiments are presented in Figures 1–3, and selected bond angles and bond lengths are given in Table 1, while details of the analyses are listed in Table 2.

In the solid state, the group 2 NHC adducts **2a**−**c** exist as monomeric, three-coordinate, species with ligation at the metal center being provided by two amide moieties and the N-heterocyclic carbene. The latter ligand is σ-bonded through the donation of the carbene lone pair to the electrophilic metal center. In all cases the metal demonstrates a near ideal trigonal

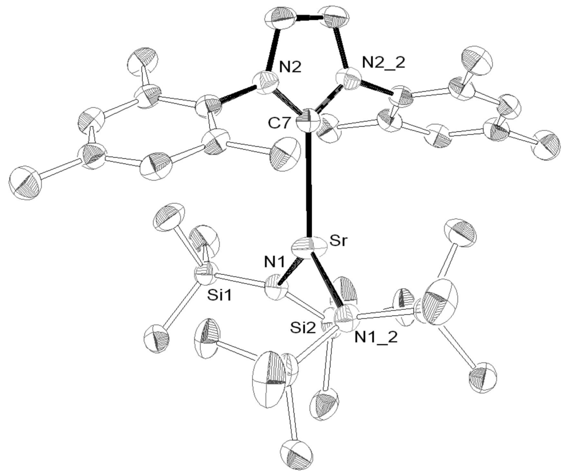


Figure 1. ORTEP representation of **2b**. Thermal ellipsoids are at 40% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg), **2b**: Sr−N(1) 2.4277(14), Sr−C(7) 2.731(3), Sr−C(6) 3.174(3), N(1)−Sr−N(1)′ 122.21(8), N(1)−Sr−C(7) 118.89(4), N(2)−C(7)−Sr 128.66(11), N(2)−C(7)−N(2)′ 102.7(2). **2a**: Ca−N(1) 2.2895(13), Ca−C(7) 2.598(2), Ca−C(6) 3.062(3), N(1)−Ca−N(1)′ 125.35(7), N(1)−Ca−C(7) 117.33(4), N(2)−C(7)−Ca 128.60(10), N(2)−C(7)−N(2)′ 102.8(2).

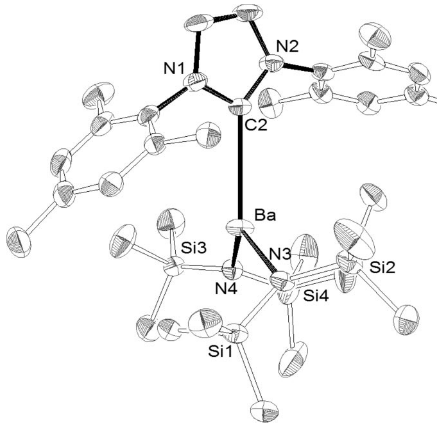


Figure 2. ORTEP representation of **2c**. Thermal ellipsoids are at 40% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ba−N(3) 2.579(3), Ba−N(4) 2.588(3), Ba−C(2) 2.915(4), N(3)−Ba−N(4) 123.88(11), N(3)−Ba−C(2) 115.67(10), N(4)−Ba−C(2) 117.11(11), N(1)−C(2)−N(2) 103.1(3), N(1)−C(2)−Ba 115.4(3), N(2)−C(2)−Ba 141.4(3).

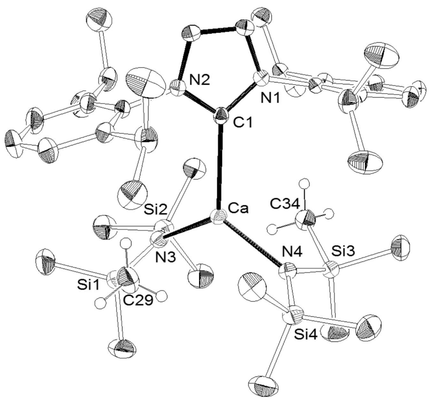


Figure 3. ORTEP representation of **4**. Thermal ellipsoids are at 40% probability. H atoms, with the exception of those attached to C34 and C29, are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ca−N(4) 2.2955(14), Ca−N(3) 2.3099(14), Ca−C(1) 2.6285(16), Ca−C(29) 2.893(2), Ca−C(34) 2.913(2), N(4)−Ca−N(3) 124.52(5), N(4)−Ca−C(1) 115.55(5), N(3)−Ca−C(1) 119.49(5), N(1)−C(1)−Ca 132.85(11), N(2)−C(1)−Ca 124.94(10), N(1)−C(1)−N(2) 102.15(13).

geometry [av X−M−X′ angles, M = Ca, 120°; Sr, 120°; Ba, 118.8°] with the NHC ring residing almost orthogonal to the plane of the N_2MC core [N−M−C−N dihedral angles, M = Ca, 75.7°; Sr, 75.6°; Ba, 68.6° and 85.5°]. While the calcium and strontium analogues are isostructural, possessing a mirror plane parallel to the N_2MC plane, the barium analogue is nonsymmetric with the carbene ligand tilting significantly in the plane orthogonal to that of the N_2MC core (Figure 2). This latter observation is characterized by the large difference in N(1)−C(2)−Ba and N(2)−C(2)−Ba bond angles of 115.4(3)° and 141.4(3)°, respectively, and although a likely effect of crystal packing, it could also be a reflection of the greater degree of freedom around the large barium dication.

Comparison of metal−nitrogen bond lengths [Ca−N 2.2895(13) Å; Sr−N 2.4277(14) Å; Ba−N(3) 2.579(3) Å, Ba−N(4) 2.588(3) Å] to the only known three-coordinate group 2 amide species, $[M\{N(SiMe_3)_2\}_2]$, reported by Westerhausen et al. reveals a good correlation between data for **2a**−**c** and the bond distances [Ca−N 2.267(7) and 2.282(6) Å; Sr−N 2.44 Å; Ba 2.576(3) Å] of the terminal amide ligands in the latter dimeric species.[17] In addition, in the case of calcium and barium, the metal−carbon bond distances of the coordinated NHC ligand in the series **2a**−**c** [Ca−C 2.598(2) Å; Sr−C 2.731(3) Å; Ba−C 2.915(4) Å] are similar to those in the series $[Cp^*_2M(C\{NMeCMe\}_2)]$ reported by Arduengo et al. [M = Ca, 2.562(2) Å; M = Ba, 2.951(3) Å].[12]

In the solid state, compound **4** demonstrates a similar structure to that described for **2a** (Figure 3). Again the calcium center is three-coordinate with trigonal geometry [av X−Ca−X′ angle 119.9°], and metal−nitrogen bond lengths [Ca−N(3) 2.2955(14) and Ca−N(4) 2.3099(14) Å] mirror those observed in **2a**. It is noteworthy, however, that both the calcium−carbon bond length [Ca−C(1) 2.6285(16) Å] and the N−M−C−N dihedral angles [46.9° and 57.6°] differ slightly from those observed in **2a** (*vide supra*). Although crystal packing effects cannot be ignored, these discrepancies may be explained by considering the more sterically demanding ligand L^2 as less nucleophilic than L^1 and, therefore, providing a weaker coordination to the electrophilic metal center. The latter statement is supported by the observation of an elongation of the M−C bond length of 1.2% in $[L^2Ca\{N(SiMe_3)_2\}_2]$ relative to that of $[L^1Ca\{N(SiMe_3)_2\}_2]$.

Complexes **2a**,**b** and **4** also demonstrate a series of close contacts between the metal and a methyl group of one (or two) of the bis(trimethylsilyl)amide ligands. Although not depicted in Figures 1–3, for **2a**,**b** the C(6)···M distances [M = Ca, 2.598(2) Å; Sr, 2.731(3) Å] lie within the range reported for agostic-type interactions in low-coordinate group 2 organometallics.[18] Eaborn et al. have reported that the two-coordinate calcium alkyl complex $[Ca\{C(SiMe_3)_3\}_2]$ demonstrated a series of Ca···Me interactions all less than 3.08 Å in the solid state.[19] Similarly Hanusa has also documented agostic-type interactions [Ca···Me 2.99(1) Å] between the metal and silyl methyl groups of the amido ligand in $[\{i\text{-}Pr_4C_5H\}Ca\{N(SiMe_3)_2\}(THF)]$.[18] Complex **4** demonstrates a series of similar close contacts in the solid state, all with Ca···C distances < 2.91(2) Å. It is also noteworthy that studies on the coordination chemistry of NHC adducts of $[Ln\{N(SiHMe_2)_2\}_3]$ (Ln = Y, La) have revealed a similar propensity for these complexes to form agostic-type interactions, albeit in this case with the Si−H bond of the amido ligand.[7]

Solution Studies. While these solid-state analyses are consistent with the NHC acting as a strong σ-donating ligand, from these studies it is not clear whether such Lewis acid/Lewis base interactions are retained in solution. To this end, a series of multinuclear NMR experiments, including nuclear Overhauser (NOESY) enhancement techniques, were conducted on C_6D_6 solutions of **2a**−**c** and **4**. Previous studies on s-block or f-block NHC adducts have demonstrated a considerable upfield shift in the ^{13}C resonance of the C-2 position of the carbene ligand upon coordination of the ligand to the electrophilic metal center ($\Delta\delta$).

Relevant ^{13}C chemical shift data for the isolated compounds, in C_6D_6 solution, along with that reported for previous heavier group 2 NHC adducts, $[(Cp^*)_2M(L^3)_n]$ (M = Ca, Sr, Ba; n = 1, 2; $L^3 = [C\{NMeCMe\}_2]$), are listed in Table 3. Although in all cases there is an upfield shift of the C-2 resonance in the organometallic species relative to that of the free carbene, consideration of these data reveals that, for a given NHC, the magnitude of $\Delta\delta$ increases with the increasing Lewis acidity of the metal (Ca > Sr > Ba). Similar observations have been made before by Hermann et al.[13a]

In all cases, a small NOE was observed between the silylmethyl resonances of the amide moieties of **2a**−**c** and those of the *ortho*-methyl protons of the NHC ligand. Similarly an experiment on a solution of **4** in C_6D_6 showed a NOE between both the isopropyl methine resonance and silylamide methyl resonance and the isopropyl methyl resonances and the silylamide methyl resonance. These findings, along with the ^{13}C NMR data, are consistent with the NHC remaining bound to the metal amide in solution and not dissociating on the NMR time scale. The NHC adducts proved stable in solution with little or no change over a period of weeks at room temperature. In addition, heating samples of **2a** or **3** for 60 °C for 24 h resulted in no obvious decomposition of the organometallic compound. A series of reactions with protic substrates, however, demonstrated the lability of the NHC in the presence of other Lewis basic donors.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds 2a−c and 4

	2a	2b	2c	4
$M-N_{amide}$	2.2895(13)	2.4277(14)	2.579(3), 2.588(3)	2.2955(14), 2.3099(14)
$M-C_{carbene}$	2.598(2)	2.731(3)	2.915(4)	2.6285(16)
$M-C_{agostic}$	3.062(3)	3.174(3)		2.893(2), 2.913(2)
$N_{amide}-M-N_{amide}$	125.35(7)	122.21(8)	123.88(11)	124.52(5)
$N_{amide}-M-C_{NHC}$	117.33(4)	118.89(4)	115.67(10), 117.11 (11)	115.55(5), 119.49(5)
$N_{NHC}-C_{NHC}-M$	128.60(10)	128.66(11)	115.4(3), 141.4(3)	124.94(10), 132.85(11)
$N_{NHC}-C-N_{NHC}$	102.8(2)	102.7(2)	103.1(3)	102.15(13)

Table 2. Crystallographic Data for Compounds 2a−c, 4, and 5

	2a	2b	2c	4	5
molecular formula	$C_{33}H_{60}CaN_4Si_4$	$C_{33}H_{60}SrN_4Si_4$	$C_{33}H_{60}BaN_4Si_4$	$C_{85}H_{152}Ca_2N_8Si_8$	$C_{48}H_{66}CaN_2O_2P_2Si_4$
fw (g mol^{-1})	665.29	712.83	762.55	1591.03	917.41
cryst system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	17.1111(4)	17.3290(3)	11.6902(2)	11.5618(2)	11.8940(1)
b (Å)	14.0257(4)	14.0360(2)	11.6877(2)	12.2760(2)	20.9365(2)
c (Å)	17.0902(4)	17.1480(3)	15.7698(3)	18.7309(3)	21.9023(2)
α (deg)	90	90	91.9310(10)	104.1990(10)	90
β (deg)	97.0430(10)	97.1870(7)	91.1140(10)	90.1600(10)	102.240(1)
γ (deg)	90	90	96.9640(10)	103.6750(10)	90
V (Å^3)	4070.62(18)	4138.13(12)	2136.94(7)	2499.03(7)	5330.10(8)
Z	4	4	2	1	4
μ (mm^{-1})	0.297	1.444	1.066	0.252	0.304
ρ (g cm^{-3})	1.086	1.144	1.185	1.057	1.143
θ range (deg)	3.77 to 27.44	4.61 to 27.52	3.51 to 27.64	3.53 to 27.37	3.57 to 27.48
no. of measd/independent reflns/R_{int}	29 424/4632/0.0601	32 531/4732/0.0419	31 009/9729/0.0580	43 885/1151/0.0579	104 722/12 205/0.0528
$R_1{}^a$, $wR_2{}^b$ $[I > 2\sigma(I)]$	0.0393, 0.0948	0.0344, 0.0836	0.0480, 0.1177	0.0422, 0.1036	0.0354, 0.0811
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0558, 0.1035	0.0430, 0.0885	0.0736, 0.1327	0.0741, 0.1172	0.0514, 0.0890

^{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. Characteristic Metrical Parameters for Synthesized and Literature Heavier Group 2 NHC Adducts

compound	$M-C_{NHC}$ (Å)	$\delta_{13}C$ C_{NHC} (ppm)^a	$\Delta\delta_{13}C$ (ppm)^a
2a	2.598(2)	193.3	26.2
3		193.0	26.5
4	2.6259(2)	195.4^b	26.3^b
$[(Cp^*)_2Ca\{L^3\}]$	2.562(2)	196.2	17.5
2b	2.731(3)	199.0	20.5
$[(Cp^*)_2Sr\{L^3\}]$		198.2	15.5
$[(Cp^*)_2Sr\{L^3\}_2]$	2.868(5), 2.854(5)	203.7	10.0
2c	2.915(4)	—^{c}	—^{c}
$[(Cp^*)_2Ba\{L^3\}]$	2.951(3)	203.5	10.2

^{a} Spectra taken in and referenced against C_6D_6. ^{b} Spectra taken in and referenced against d_8-toluene. ^{c} Carbene resonance could not be observed.

We have previously reported the β-diketiminate-stabilized calcium amide $[\{ArNC(Me)CHC(Me)NAr\}Ca\{N(SiMe_3)_2\}(THF)]$ (Ar = 2,6-diisopropylphenyl) as a useful model compound for investigating stoichiometric group 2 chemistry. This latter compound reacts readily with amines and phosphines via protonolysis to yield isolable and characterizable heteroleptic calcium amido or phosphido species, which, in turn, have proven useful in elaborating catalytic hydroamination and hydrophosphination chemistry.[11c,20]

A series of reactions were conducted upon the NHC adducts on an NMR scale in C_6D_6 solutions. The reaction of **4** with 2 equiv of either 2-methoxylethylamine, di-p-tolylphosphine, or diphenylamine did not yield well-defined, hydrocarbon-soluble, NHC adduct products. In all cases dissociation of the NHC ligand was observed by a series of resonances in the ^1H and ^{13}C NMR spectra consistent with the free carbene (δ ^{13}C = 220.9 ppm). Addition of diphenylamine to **4** was also accompanied by the precipitation of a fine white solid from solution, an assumed unsolvated analogue of the recently reported calcium bis(diphenylamide) species $[(\eta^2\text{-dme})Ca(NPh_2)_2]$.[21] Similarly, addition of 2-methoxyethylamine to **2a** yielded the free carbene (δ ^{13}C = 219.5 ppm) and no other benzene-soluble products as monitored by multinuclear NMR spectrosopy.

Although this series of experiments does not preclude the isolation and crystallographic characterization of NHC adducts of simple heavier group 2 amido or phosphido derivatives, it appears that under catalytically-relevant conditions dissociation of the carbene ligand from the metal center occurs rather readily. In order to further investigate this apparent solution lability, a series of reactions were conducted with Lewis bases. The reaction of both triphenylphosphine and triphenylphosphine oxide with the isolated compounds **2a−c** in C_6D_6 was monitored by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. In all cases addition of triphenylphosphine (δ ^{31}P = +3.2 ppm) did not result in displacement of the NHC from the coordination sphere of the group 2 organometallic species on the NMR time scale. In contrast, addition of 2 equiv of triphenylphosphine oxide (δ ^{31}P = +26.2 ppm) to **2a** in C_6D_6 resulted in quantitative displacement of the NHC from calcium with the stoichiometric formation of $[(Ph_3P{=}O)_2Ca\{N(SiMe_3)_2\}_2]$ (**5**, δ ^{31}P = +33.8 ppm) within the first point of analysis. The proposed composition of the reaction product was confirmed by an independent synthesis from the addition of 2 equiv of triphenylphosphine oxide to $[Ca\{N(SiMe_3)_2\}_2]$ in toluene.

X-ray analysis of colorless crystals grown from slow cooling of a toluene solution confirmed the 2:1 stoichiometry of triphenylphosphine oxide to calcium within **5**. In addition, this study demonstrated that **5** forms a monomeric, four-coordinate,

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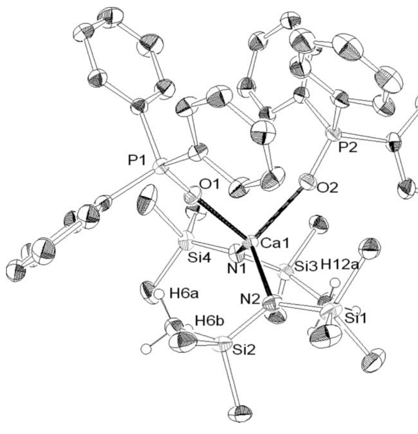

Figure 4. ORTEP representation of **5**. Thermal ellipsoids are at 40% probability. H atoms with the exception of those with agostic-type interactions are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): N(1)−Ca(1) 2.3405(13), N(2)−Ca(1) 2.3340(13), O(1)−Ca(1) 2.2670(10), O(2)−Ca(1) 2.2632(11), Ca(1)−H(6A) 2.88(2), O(1)−P(1) 1.4979(10), O(2)−P(2) 1.4962(11), O(2)−Ca(1)−O(1) 95.74(4), O(2)−Ca(1)−N(2) 112.39(5), O(1)−Ca(1)−N(2) 100.57(4), O(2)−Ca(1)−N(1) 97.23(4), O(1)−Ca(1)−N(1) 116.72(4), N(2)−Ca(1)−N(1) 129.44(5).

complex in the solid state with distorted tetrahedral geometry at calcium. The calcium−nitrogen bond lengths [N(1)−Ca(1) 2.3405(13) Å and N(2)−Ca(1) 2.3340(13) Å] are similar to those reported by Westerhausen et al. for the similarly four-coordinate bis(trimethylsilyl)amide species [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] [av Ca−N 2.30 Å].[17b] The metal−oxygen bond distances [O(1)−Ca(1) 2.2670(10) Å and O(2)−Ca(1) 2.2632(11) Å], however, are slightly longer than those reported by Harder for [{η^2-PhNCPh$_2$}Ca(HMPA)$_3$], a five-coordinate calcium complex bearing three HMPA ligands [HMPA = hexamethylphosphoramide, av M−O distance 2.254 Å],[22] most likely due to the increased Lewis basicity of the HMPA ligand relative to that of triphenylphosphine oxide. The latter Ca−O bond lengths are, however, consistent with those reported by Hanusa within the charge-separated species [{Cp*Ca(OPPh$_3$)$_3$}I] [Ca−O 2.254(2) to 2.300(2) Å].[23]

Although addition of a slight excess of d_8-tetrahydrofuran to **2a** in C$_6$D$_6$ resulted in a broadening of the resonances assigned to **2a** as monitored by ^{1}H and ^{13}C NMR spectroscopy, no obvious displacement of the NHC ligand from the metal center was observed. As fast neutral ligand exchange may be preventing the assignment of the individual components of this mixture, a further variable-temperature experiment was conducted upon a d_8-toluene solution of [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] and 2 equiv of L^1. The results of this experiment are presented in Figure 5. It should be noted that, despite the 2:1 stoichiometry of the reaction, no evidence of the formation of bis-NHC adducts of calcium was observed.

At 298 K and above a single set of ligand resonances was observed for both the NHC and the bis(trimethylsilyl)amide moiety. This time-averaged picture was resolved upon cooling of the solution, and a decoalescence of the resonances attributed to the NHC ligand to two distinct species was observed. This process was best characterized by the aromatic protons of the imidazol-2-ylidene residue, present as a singlet resonance at 6.49 ppm at 328 K. This peak split into two resonances observed at 6.10 and 6.47 ppm at 268 K attributed to coordinated and noncoordinated carbene ligands, respectively, by comparison of the chemical shift to that of the isolated compounds. At the same temperature the bis(trimethylsilyl)amide resonance resolved to two magnetically distinct environments attributed to [L^{1}Ca{N(SiMe$_3$)$_2$}$_2$] and [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$]. Further cooling shifted the position of the apparent equilibrium, depicted in Scheme 4, with lower temperatures favoring the formation of the uncoordinated NHC and THF-solvated calcium amide. While the current lack of detailed knowledge of the dynamic processes occurring in solution (e.g., the possibility of the formation of a mixed THF/L^1 adduct and/or dimeric calcium species) has left the authors reluctant to further quantify the position of the observed equilibrium, the perturbation of the system toward the reaction products (Scheme 4) at higher temperature is consistent with entropic considerations.

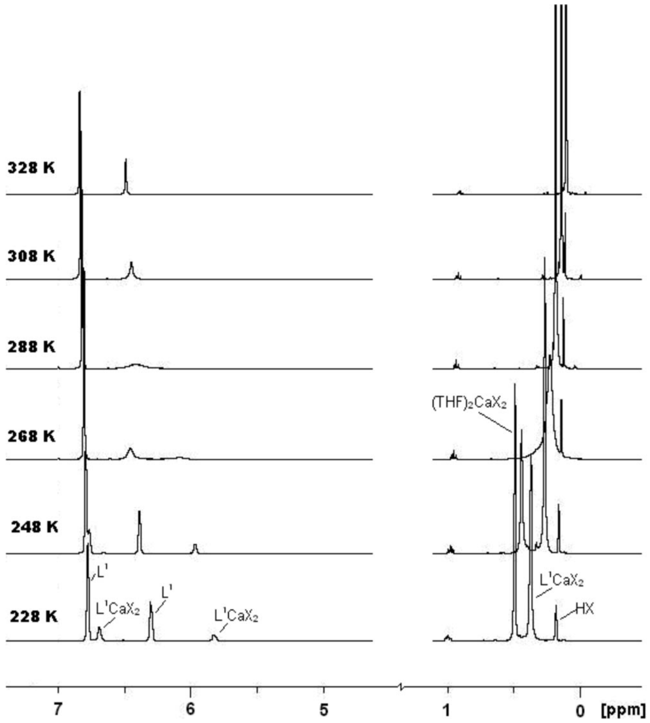

Figure 5. Variable-temperature NMR data from the reaction of [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] and 2 equiv of L^1. X = N(SiMe$_3$)$_2$. Spectra recorded in d_8-toluene; values quoted in ppm and referenced against residual solvent peaks.

Scheme 4. Postulated Equilibrium Mixture Formed upon the Addition of L^1 to [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$]

$$\mathrm{L^1 + [Ca\{N(SiMe_3)_2\}_2(THF)_2] \rightleftharpoons [L^1Ca\{N(SiMe_3)_2\}_2] + 2\ THF}$$

Conclusions

A number of heavier alkaline earth NHC complexes have been synthesized by the addition of the group 2 amide to the corresponding imidazolium salt or addition of the NHC to solvent-free group 2 amide. Solid-state studies are consistent with the formation of monomeric three-coordinate heavier alkaline earth species in which the NHC binds via donation of the lone pair to the electrophilic metal center. While multinuclear NMR experiments suggest this coordination is retained in solution, reactions with protic substrates and/or Lewis bases demonstrate the lability of the NHC ligand under catalytically relevant conditions. We are continuing to study the reaction

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chemistry of the complexes detailed herein and will report our observations in subsequent publications.

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 were collected on either a Bruker AV-500 spectrometer (^{13}C NMR 125 MHz), a Bruker AV-400 spectrometer at (^{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. 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride was purchased from Sigma-Aldrich and used as received. 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride[24] and the heavier group 2 amides $[M\{N(SiMe_3)_2\}_2]$ (M = Ca, Sr, and Ba) were prepared by literature procedures.[25]

Synthesis of NHC Adducts of Group 2 Amides. Synthesis of $[L^1M\{N(SiMe_3)_2\}_2]$: In a glovebox, $[M\{N(SiMe_3)_2\}_2]$ (1.38 mmol) and 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (236 mg, 0.69 mmol) were weighed into a Schlenk tube. The tube was removed from the glovebox and attached to a vacuum line, and toluene (20 mL) was added via cannula. The reaction mixture was stirred overnight and the toluene removed *in vacuo*. The crude product was extracted into hexane and filtered, and the solution concentrated to induce crystallization. X-ray quality crystals of samples **2a**−**c** were prepared by slow cooling of hexane solutions.

$[L^1Ca\{N(SiMe_3)_2\}_2]$ (**2a**, 243 mg, 0.37 mmol, 53%): colorless crystalline solid; ^{1}H NMR (C_6D_6, 300 MHz, 298 K) 0.17 (s, 36H), 2.02 (s, 12H), 2.12 (s, 6H), 6.04 (s, 2H), 6.81 (s, 4H); ^{13}C NMR (C_6D_6, 75 MHz, 298 K) 5.9, 18.5, 20.9, 121.9, 130.1, 135.0, 135.4, 139.7, 193.3. Anal. Calc for $C_{33}H_{60}CaN_4Si_2$: C, 59.58; H, 9.09; N, 8.42. Found: C, 59.50; H, 9.07; N, 8.47. Mp (hexane): 208−210 °C with decomposition.

$[L^1Sr\{N(SiMe_3)_2\}_2]$ (**2b**, 266 mg, 0.37 mmol, 76%): ^{1}H NMR (C_6D_6, 300 MHz, 298 K) 0.18 (s, 36H), 1.99 (s, 12H), 2.11 (s, 6H), 6.07 (s, 2H), 6.81 (s, 4H); ^{13}C NMR (C_6D_6, 75 MHz, 298 K) 5.8, 18.2, 20.9, 121.6, 130.2, 134.7, 135.5, 139.7, 199.0. Anal. Calc for $C_{33}H_{60}SrN_4Si_2$: C, 55.60; H, 8.48; N, 7.86. Found: C 55.70, H; 8.55; N, 7.76. Mp (hexane): 127−130 °C with decomposition.

$[L^1Ba\{N(SiMe_3)_2\}_2]$ (**2c**, 103 mg, 0.14 mmol, 29%): ^{1}H NMR (C_6D_6, 300 MHz, 298 K) 0.20 (s, 36H), 1.98 (s, 12H), 2.11 (s, 6H), 6.15 (s, 2H), 6.80 (s, 4H); ^{13}C NMR (C_6D_6, 75 MHz, 298 K) 5.7, 17.9, 20.9, 121.1, 129.6, 134.9, 136.6, 139.3, carbene carbon resonance could not be observed. Anal. Calc. for $C_{33}H_{60}BaN_4Si_2$: C, 51.93; H, 7.89; N, 7.34. Found: C 52.04, H; 7.82; N, 7.24.

Synthesis of $[L^1Ca\{N(SiMe_3)_2\}Cl]$ (3). In a glovebox, $[Ca\{N(SiMe_3)_2\}_2]$ (250 mg, 0.7 mmol) and 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (236 mg, 0.7 mmol) were weighed into a Schlenk. The Schlenk tube was sealed, removed from the glovebox, and attached to a vacuum line, and toluene (20 mL) was added via cannula. The reaction mixture was stirred overnight and the toluene removed *in vacuo*. The crude product was extracted into hexane and filtered, and the solution concentrated to induce crystallization. The product $[L^1Ca\{N(SiMe_3)_2\}Cl]$ (**3**, 33 mg, 0.06 mmol, 8%) was isolated as a colorless solid: ^{1}H NMR (d_8-toluene, 500 MHz, 298 K) 0.16 (s, 18H), 2.09 (s, 6H), 2.12 (s, 12H), 6.07 (s, 2H), 6.85 (s, 4H); ^{13}C NMR (C_6D_6, 125 MHz, 298 K) 6.7, 20.8, 21.8, 122.8, 130.9, 136.2, 136.6, 140.2, 194.1. The Schlenk-like solution equilibria of this compound prevented its isolation in a pure enough form to acquire satisfactory elemental analysis data (see Supporting Information).

Synthesis of $[L^2Ca\{N(SiMe_3)_2\}_2]$ (4). In a glovebox, $[Ca\{N(SiMe_3)_2\}_2]$ (508 mg, 1.38 mmol) and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (300 mg, 0.70 mmol) were weighed into separate Schlenk tubes. The tubes were sealed, removed from the glovebox, and attached to a vacuum line. Addition of toluene (10 mL) to the imidazolium salt resulted in the formation of a suspension. This mixture was cooled to −78 °C, and a toluene (10 mL) solution of $[Ca\{N(SiMe_3)_2\}_2]$ was added via cannula. Upon warming to room temperature, a homogeneous solution was formed. The reaction mixture was stirred overnight and the toluene removed *in vacuo*. The crude product was extracted into hexane (20 mL) and filtered, and the solution concentrated to ca. 5 mL. Storage of this solution at 5 °C for 48 h yielded a colorless solid, NMR analysis of which revealed both **4** and an unidentified reaction byproduct. All attempts at fractional crystallization failed. The adduct $[L^2Ca\{N(SiMe_3)_2\}_2]$ (**4**) was obtained in a pure form from addition of the NHC (53 mg, 0.14 mmol) to $[Ca\{N(SiMe_3)_2\}_2]$ (45 mg, 0.13 mol) into C_6D_6 followed by crystallization from this solvent. Following filtration, the product was isolated as large colorless crystalline blocks (51 mg, 0.07 mmol, 52%): ^{1}H NMR (C_6D_6, 300 MHz, 298 K) 0.17 (s, 36H), 0.92 (apparent d, 12H), 1.38 (d, 12H), 2.65 (apparent hept, 4H), 6.38 (s, 2H), 7.11 (d, 4H, J = 7.4 Hz), 7.22 (t, 2H, J = 7.4 Hz) all peaks broad; ^{13}C NMR (d_8-tol, 75 MHz, 298 K) 7.3, 24.8, 26.5, 29.7, 125.1, 125.9, 131.7, 136.8, 146.7, 195.4. Anal. Calc for $C_{39}H_{72}CaN_4Si_4$: C, 62.50; H, 9.68; N, 7.48. Found: C, 62.42; H, 9.64; N, 7.45. Mp (toluene): 220−223 °C.

Synthesis of $[(Ph_3P{=}O)_2Ca\{N(SiMe_3)_2\}_2]$ (5). In a glovebox, $[Ca\{N(SiMe_3)_2\}_2]$ (250 mg, 0.69 mmol) and triphenylphosphine oxide (386 mg, 1.38 mmol) were weighed into a Schlenk tube. The tube was sealed, removed from the glovebox, and attached to a vacuum line, and toluene (10 mL) was added via cannula. The solution was filtered and stored at −20 °C for 24 h. The product crystallized as a colorless solid (466 mg, 0.51 mmol, 74%): ^{1}H NMR (C_6D_6, 300 MHz, 298 K) 0.47 (s, 36H), 6.91−7.04 (m, 18H), 7.62−7.68 (s, 12H); ^{13}C NMR (C_6D_6, 75 MHz, 298 K) 6.8, 128.8 (d, J = 12.6 Hz), 130.5 (d, J = 108.1 Hz), 132.7 (d, J = 2.0 Hz), 132.9 (d, J = 10.6 Hz); ^{31}P NMR (C_6D_6, 121.5 MHz, 298 K) +33.8. Anal. Calc for $C_{48}H_{66}CaN_2O_2P_2Si_4$: C, 62.79; H, 7.69; N, 3.05. Found: C, 62.69; H, 7.08; N, 3.00. Mp (toluene): 137−138 °C (dec).

Crystallographic Data. Data for **2a**−**c**, **4**, and **5** were collected at 150 K on a Nonius Kappa CCD diffractometer equipped with a low-temperature device, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were processed using Nonius software.[27] For **2a**,**b** and **5** a symmetry-related (multiscan) absorption correction was employed. Crystal parameters and details of data collection, solution, and refinement for the complexes are provided in Tables 1 and 2. Structure solution, followed by full-matrix least-squares refinement, was performed using the WinGX-1.70 suite of programs throughout[28] and the program suite X-SEED[29] for **5**.

Notes on the refinement: 4 crystallizes along with half a molecule of toluene, which is disordered about a center of inversion. For **5**, hydrogens attached to C-6 were readily visible in the

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penultimate difference Fourier map and ultimately refined at a distance of 0.98 Å from C-6.

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Supporting Information Available: Crystallographic information files (CIF) for **2a**−**c**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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