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Suppression of Schlenk Equilibration and Heavier Alkaline Earth Alkyl Catalysis: A Dearomatization Strategy

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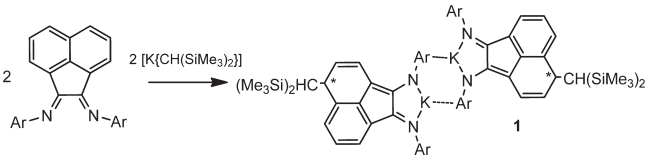
Supporting Information

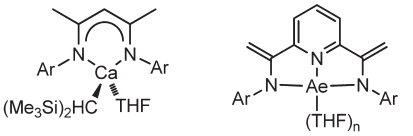
ABSTRACT: Reaction of a bis(imino)acenapthene with the heavier alkaline earth dialkyls $[Ae\{CH(SiMe_3)_2\}_2(THF)_2]$ (Ae = Mg, Ca, Sr) results in deromatization of the aromatic ligand and the isolation of heteroleptic alkyl species which show unprecedented stability toward Schlenk-type redistribution and exceptional catalytic activity toward the hydroamination of aminoalkenes.

Although alkaline earth (Ae = Mg, Ca, Sr, Ba) complexes have now been shown to catalyze a wide variety of multiple bond heterofunctionalization reactions,[1,2] a full realization of the catalytic potential of these elements will still require substantial advances in their basic coordination and organometallic chemistry. A particular problem for the larger elements below magnesium in group 2 lies in the instability of precatalytic species of the general form LAeR (L = monoanionic supporting ligand; R = reactive substituent) toward Schlenk-type redistribution to inactive or ill-defined homoleptic species.[3] Examples where R is a basic alkyl substituent are particularly limited and are restricted to a handful of calcium derivatives containing sterically demanding bis(trimethylsilyl)methyl[4] or benzyl ligands.[5] In previous work we have shown that the β-diketiminato derivative, compound **I**, may be isolated and fully characterized.[5b] The formation of **I** was, however, accompanied by a further calcium species containing a dianionic ligand produced by deprotonation of a methyl substituent bonded to an α-carbon of the imine.[5b] This observation precluded any meaningful study of **I** as a viable precatalytic species, and subsequent work has shown that pyridyl diimine ligands containing α-methyl substituents are similarly deprotonated by the well-defined dialkyl compounds $[Ae\{CH(SiMe_3)_2\}_2(THF)_2]$ (Ae = Mg, Ca, Sr, Ba)[6] to form species **IIa**−**d**.[7] This latter process occurs via dearomatized intermediates such as **III**, which, however unstable, may also be viewed as heteroleptic alkyl species conforming to the LAeR formulation. A similar dearomatization strategy has previously been employed in organolutetium chemistry, albeit with substituted terpyridine heterocycles,[8] and in this contribution we show that a selective alkylation/dearomatization process can be arrested through selection of an aromatic diimine species devoid of α-methyl substituents, providing a novel strategy to produce robust and catalytically active ligand-supported alkyl species of even the heaviest alkaline earth metals.

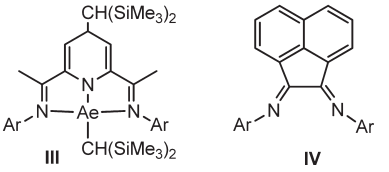
Scheme 1[a]



[a] Ar = 2,6-diisopropylphenyl.



I **II**: n = 2, **a**: Ae = Mg; **b**: Ae = Ca
Ar = 2,6-di-*iso*-propylphenyl n = 1, **c**: Ae = Sr; **d**: Ae = Ba



III **IV**

Bis(imino)acenapthene (BIAN) derivatives, such as the 2,6-diisopropylphenyl-substituted diimine **IV**, have been widely employed as neutral or mono-, di-, tri-, and tetraanionic N-donor and rigidly chelating ligands for a wide variety of transition metal and main group elements.[9] In an initial experiment, addition of the group 1 reagent $[K\{CH(SiMe_3)_2\}]$ to a suspension of **IV** in C_6D_6 caused instant solubilization of the ligand precursor, accompanied by a color change from bright orange to dark green (Scheme 1). Examination of the ^1H NMR spectrum of this solution

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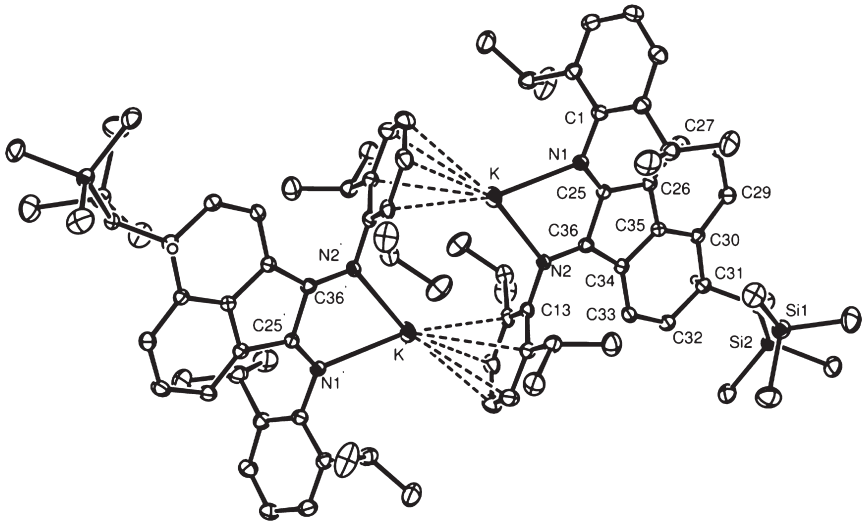
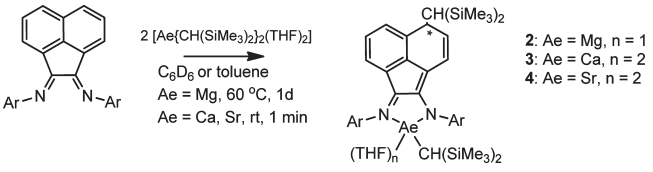


Figure 1. ORTEP representation of compound **1**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogens are omitted, except for those attached to the chiral center C(31). Selected bond lengths (Å) and angles (deg): K−N(1) = 2.694(3), K−N(2) = 2.703(3), N(1)−C(25) = 1.281(4), N(2)−C(36) = 1.335(4), C(25)−C(36) = 1.518(4), C(25)−C(26) = 1.496(4), C(34)−C(36) = 1.393(4), C(30)−C(31) = 1.533(5), C(31)−C(32) = 1.517(5), C(32)−C(33) = 1.351(5), K−centroid = 2.866(4); N(1)−K−N(2) = 63.52(8), K−N(1)−C(1) = 121.28(19), K−N(2)−C(13) = 126.18(18), K−N(1)−C(25) = 118.2(2), K−N(2)−C(36) = 117.4(2).

indicated complete consumption of both starting materials and formation of a single alkylated and dearomatized potassium BIAN species, compound **1**, characterized by six distinct multiplets in the region from 4.4 to 6.5 ppm. A COSY NMR experiment identified the alkylation of the acenaphthene backbone as having occurred on the C^5 position. As a consequence of the chiral center formed, the two magnetically inequivalent ($SiMe_3$) groups appeared as two separate 9H singlets at 0.18 and 0.04 ppm, respectively. The asymmetry of this monoalkylated species was reflected by a splitting of the isopropyl methine and methyl resonances in both the ^1H and $^{13}C\{^1H\}$ NMR spectra.

Crystallization at room temperature from toluene afforded dark green crystals of compound **1** suitable for X-ray diffraction analysis. The result of this experiment is displayed in Figure 1, while selected bond length and angle data are provided in the figure caption. In a manner similar to that observed within a radical anionic potassium complex [{**IV**}$^{\bullet-}$K],[9g] compound **1** crystallizes as a dimer in which the coordination environment about both potassium centers is provided by one of the η^6-aryl substituents of the second molecule and the bidentate imine-amido dearomatized BIAN ligand. The K−centroid and K−K′ distances of 2.866(4) and 4.5657(17) Å, respectively, are shorter than those in [{**IV**}$^{-\bullet}$K] (K−centroid = 2.904 Å; K−K′ = 4.619 Å). Despite the asymmetry of the ligand framework, the potassium−imine and potassium−amide K−N distances of 2.694(3) and 2.703(3) Å can be considered identical and are within the range of those observed in [{**IV**}$^{-\bullet}$K] and a related potassium tetrakis(imino)pyracene complex (2.653−2.757 Å).[9g] Whereas the N(1)═C(25) bond length of 1.281(4) Å falls within the range of N═C bond lengths of the ligand precursor (1.250(6) and 1.295(6) Å),[9k] the N(2)−C(36) bond of the amido fragment shows substantial elongation to 1.335(4) Å. This distance is still short for a formal N−C single bond. While the C(25)−C(36) bridge remains unaffected by the charge redistribution (**1**, 1.518(4) Å; **IV**, 1.526(3) Å), the C(36)−C(34) distance is considerably shortened compared to that in the ligand precursor

Scheme 2[a]



[a] Ar = 2,6-diisopropylphenyl.

(**1**, 1.518(4) Å; **IV**, 1.505(5) Å).[9k] The dearomatized acenaphthene ligand backbone is only slightly distorted from its original planar geometry. The C−C bond lengths and angles of the aromatic C_6H_3 ring (1.374(5)−1.410(5) Å; 116.6(3)−122.3(3)°) remain within the range of those of the ligand precursor, **IV**, while the dearomatized ring is distorted due to the presence of the pseudo-tetrahedral sp^3 C(31) carbon center (C(32)−C(31)−C(37) = 111.3(3)°; C(32)−C(31)−C(30) = 111.6(3)°; C(30)−C(31)−C(37) = 113.4(3)°).

Addition of [Ae{CH($SiMe_3$)$_2$}$_2$(THF)$_2$] (Ae = Ca, Sr) to a suspension of **IV** in C_6D_6 or toluene also resulted in the instant solubilization of the starting materials and a color change to dark green. The analogous reaction with [Mg{CH($SiMe_3$)$_2$}$_2$(THF)$_2$] required 24 h of heating at 60 °C to yield the same result (Scheme 2). In all three cases the resultant ^1H NMR spectra were reminiscent of that of **1**, showing clean formation of the alkaline earth organometallic species **2** (Mg), **3** (Ca), and **4** (Sr), with the additional 18H and 1H singlets of the metal-bound monoanionic [CH($SiMe_3$)$_2$]$^-$ coligand at ca. 0.3 and −1.7 ppm, respectively. An analogous reaction utilizing the barium dialkyl also resulted in an instant color change to dark green. ^1H NMR spectroscopic analysis of this reaction, however, indicated the formation of three dearomatized species, among which the heteroleptic barium alkyl **5** (50−70% yield) analogous to compounds **2**−**4** could be tentatively identified by a characteristic upfield Ba−CH($SiMe_3$)$_2$ proton shift at −1.73 ppm. As we have not yet completely elucidated the nature of the products of this reaction, it

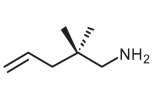
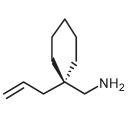
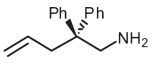
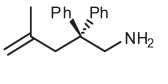
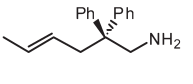
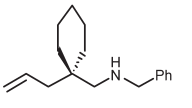
will not be discussed further here. Multiple attempts to obtain single crystals of the pure alkaline earth organometallic compounds **2**−**4** suitable for X-ray analyses were thwarted by the extreme solubility of these compounds even after months of storage at −30 °C in minimal amounts of hydrocarbon solvents such as hexane and pentane. NMR data and elemental analyses of the magnesium, calcium, and strontium products, however, left no doubt as to their formulation. Attempts to recover the alkylated amino-imine ligand by hydrolyzing the organometallic complexes initially led to a color change from green to purple, followed by a gradual change toward dark red over a period of several hours. ^{1}H NMR data and crystallization of the crude product from toluene showed quantitative conversion to the rearomatized ligand precursor **IV**, with formation of the alkane, $CH_2(SiMe_3)_2$. Although the mechanism of this reaction remains to be elucidated, we suggest that the extreme stability of the aromatic BIAN ligand in the absence of an electropositive metal center (or, conversely, the stability of $(Me_3Si)_2CH_2$) is the driving force of this dealkylation process.

DFT calculations were undertaken to investigate the regioselectivity of this BIAN alkylation process on model calcium complexes using B3LYP density functional theory and a 6-31G basis set implemented in Gaussian03.[10] Independent frequency calculations confirmed the optimized geometries as true minima. To reduce computational expense, the THF molecules within the structure of **3** were omitted and the bulky 2,6-diisopropylphenyl groups were replaced by less sterically demanding *tert*-butyl groups. The silicon atoms and methyl groups of the $CH(SiMe_3)_2$ fragments were also replaced by carbon and hydrogen atoms, respectively, and the total energy was computed for each of the C^3-, C^4-, and C^5-alkylated isomeric forms. The C^5-alkylated isomer was calculated to be the most stable product, with the C^3- and C^4-alkylated isomers 30.2 and 121.8 kJ mol^{-1} higher in energy, respectively. We propose that regio-preferential formation of the C^5-alkylated isomers arises from both electronic stabilization and minimization of the steric repulsion between the bulky alkyl substituent bonded to the acenaphthene backbone and the organic substituents bonded to the nitrogen atoms.

The kinetic stability of **2**−**4** was assessed by heating a d_8-toluene solution of these compounds at 80 °C for 1 week. Apart from a slight amount of protonolysis of the alkyl ligand to the alkane $CH_2(SiMe_3)_2$ in the case of **3** and **4** (<5%), possibly due to reaction with the solvent, the ^{1}H NMR spectra remained virtually unchanged, suggesting that the complete suppression of any Schlenk-type ligand redistribution had been achieved. Addition of 2 equiv of the ligand precursor **IV** to 1 equiv of the dialkyl species in d_8-toluene did not yield the expected homoleptic complexes at room temperature. Rather, the heteroleptic complexes **2**−**4** were formed while the excess **IV** remained unreacted. Heating of these mixtures at 90 °C over a period of several days did not result in reaction of the second equivalent of ligand but in partial protonation of the alkyl coligand, possibly due to deprotonation of the toluene solvent. We suggest that the marked stability of these compounds is a result of both the steric demands of the N-donor substituents and the rigidity of the acenapthene-based ligand structure.

The catalytic intramolecular hydroamination reaction has provided a suitable benchmark reaction for the assessment of several calcium precatalytic species.[11] Calcium complex **3** was, thus, assessed for the intramolecular hydroamination of a range of substituted aminoalkenes on an NMR scale in C_6D_6 or d_8-toluene. In all cases inspection of the ^{1}H NMR spectra showed no change suggestive of either ligand rearomatization or complex redistribution throughout the reactions. Complete disappearance of the distinctive upfield ^{1}H alkyl singlet at −1.7 ppm within the first point of analysis was indicative of rapid and irreversible catalyst initiation. Comparison of the results given in Table 1 with previous intramolecular hydroamination experiments indicated that cyclization with **3** generally occurred substantially more quickly at lower temperature and catalyst loading, an observation which may be ascribed to the irreversibility of the alkyl-based catalyst initiation step.[11] Especially remarkable was the fast cyclization of the internal olefin 1-amino-2,2-diphenyl-4-hexene at room temperature in near-quantitative yield (entry 5).

Table 1. Hydroamination Catalysis with Compound 3

Entry	Substrate	Product	Cat.[a]	t (h)	%[b]
1			**3** (2)	1	95
2			**3** (1)	0.3	99
3			**3** (0.5)	0.25	>99
4			**3** (2)	1	98
5			**3** (5)	5	95
6			**3** (5)	3.5d	92

[a] Catalyst loading (mol %) shown in parentheses; all reactions performed at 25 °C except entry 6 (60 °C). [b] NMR yields were measured against $[(Me_3Si)_4Si]$ as an internal standard in C_6D_6 or d_8-toluene.

These results reveal the potential of this new series of alkaline earth precatalysts, while the synthesis of compound **1** indicates that the dearomatized BIAN anion should also be applicable as a novel and unusual ligand in a wide range of inorganic and organometallic systems.

■ ASSOCIATED CONTENT

Supporting Information. Text, figures, tables, and a CIF file giving full experimental and instrument details, ^{1}H NMR spectra of compounds **1**−**4**, and details of the X-ray diffraction analysis of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ ACKNOWLEDGMENT

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