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Unprecedented Reaction Pathway of Sterically Crowded Calcium Complexes: Sequential C-N Bond Cleavages Induced by C-H Bond Activations

Yang Yang,[†][a] Haobing Wang,[†][a] and Haiyan Ma*[a]

Dedication ((optional))

Abstract: Five bis(quinolylmethyl)-(1*H*-indolylmethyl)amine (BQIA) compounds—{(quinol-8-yl-CH_2)$_2$$NCH_2$(3-Br-1*H*-Indol-2-yl)} (**L^{1}H**) and {[(8-R^3-quinol-2-yl)CH_2]$_2$NCH(R^2)[3-R^1-1*H*-Indol-2-yl]} (**L$^{2\text{-}5}$H**) (**L^{2}H**: R^1 = Br, R^2 = H, R^3 = H; **L^{3}H**: R^1 = Br, R^2 = H, R^3 = ^{i}Pr; **L^{4}H**: R^1 = H, R^2 = CH_3, R^3 = ^{i}Pr; **L^{5}H**: R^1 = H, R^2 = ^{n}Bu, R^3 = ^{i}Pr)—have been synthesized and used to prepare calcium complexes. The reactions of **L$^{1\text{-}5}$H** with silylamido calcium precursors (Ca[N($SiMe_2R$)$_2$]$_2$(THF)$_2$, R = Me or H) at room temperature gave heteroleptic products (L$^{1\text{-}2}$)$CaN(SiMe_3)_2$ (**1**, **2**), (L$^{3\text{-}4}$)$CaN(SiHMe_2)_2$ (**3a**, **4a**) and homoleptic complexes (L^{3,5})$_2$Ca (**D3**, **D5**). The NMR and X-ray studies proved that these calcium complexes are stabilized with Ca···C–Si, Ca···H–Si or Ca···H–C agostic interactions. Unexpectedly, calcium complexes ((L$^{3\text{-}5}$)$CaN(SiMe_3)_2$) bearing sterically more hindered ligands of the same type are extremely unstable and shortly involved in C–N bond cleavage processes induced by an intramolecular C–H bond activation, which lead to the formation of (*E*)-1,2-bis(8-isopropylquinol-2-yl)ethane exclusively.

Introduction

In contrast to the widely explored organomagnesium chemistry, organocalcium chemistry has only sprung up for the last two decades, which is to a great extent due to the challenges encountered in synthesis.[1] Recently, calcium complexes, where the metal center possesses similar oxophilic and electropositive natures as those of f-block rare earth metals, have also proved to be promising candidates for many homogeneous catalytic processes, such as catalytic polymerization of polar monomers,[2] hydroamination[3] and other miscellaneous conversions.[4] Hence, designing new ligand platforms to obtain isolable organocalcium complexes and exploiting their catalytic applications becomes a recent focus.[5]

Among various transformations, the cleavage of C–N bonds is of significant synthetic interest since such bonding is quite common in organic compounds but usually unreactive.[6] In fact, cleavages of "activated" C−N bonds (those in ammonium salts, diazonium, triazoles, aziridines) have been broadly studied.[6a, 6c-d] Based on this research, one effective strategy to promote the cleavage of an "unactivated" C–N bond is acid-assisted C–N bond activation, for example, by converting amine to ammonium salt,[6a] which however brings about many undesired limitations. Not until recently has transition-metal-catalyzed cleavage of unactivated C–N bonds been reported.[6b, 6d-e] In terms of catalysts, most of them focus on late-transition metals, especially Nickel and noble metals (e.g., Rh, Pd, Pt), where readily accessing valence variations enable an oxidative addition of unactivated C–N bonds under mild conditions. Strongly electropositive metals like rare earth metals, alkali and alkaline earth metals are still far less involved in C–N bond cleavage.[6]

In our efforts to study the chemistry of heavier alkaline earth metals—a series of inexpensive and environmentally benign metals of which organometallic compounds are showing catalytic potential, we have observed that calcium silylamido complexes supported by sterically hindered [bis(quinolylmethyl)amino]methylindol-1-ide ligands are extremely unstable and quickly decompose to give a highly specific product (*E*)-1,2-bis(8-isopropylquinol-2-yl)ethene in good yield. More importantly, mechanistic studies revealed that two types of calcium promoted C–N bond cleavages—aza-[1,2]-Wittig rearrangement and *β*-amino elimination—likely occurred in sequence, which are supposed to be induced by two times of intramolecular C–H bond activation. This unusual example not only indicates the potential of calcium species in C–N bond cleavage, but also the high specificity and nearly quantitative conversion in this first calcium involved aza-[1,2]-Wittig rearrangement provides a synthetic application of calcium reagents in promoting such a transformation, which is in contrast to the low efficiency and poor controllability of those conducted by lithium or potassium reagents.[7]

Results and Discussion

Synthesis of proligands and complexes. The bis(quinolylmethyl)-(1*H*-indolylmethyl) amines (BQIA) **L$^{1\text{-}5}$H** (Scheme 1) adopted in this work were synthesized *via* nucleophilic substitution reactions of the corresponding substituted 1*H*-indol-2-yl-alkylamines **A1**-**A3** (Scheme S1 in SI) with two equiv. of substituted bromomethylquinolines **Q1**-**Q3** (Scheme S1 in SI). Proligands **L^{1}H**-**L^{3}H** were prepared in moderate isolated yields of 41%~64%. Compared to the non-*α*-substituted amine **A1**, *α*-Me or *α*-^{n}Bu derived amines **A2** and **A3**

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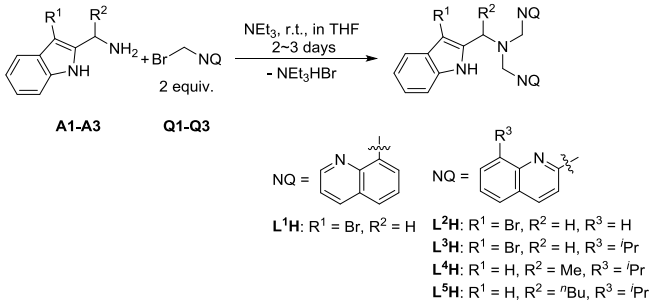
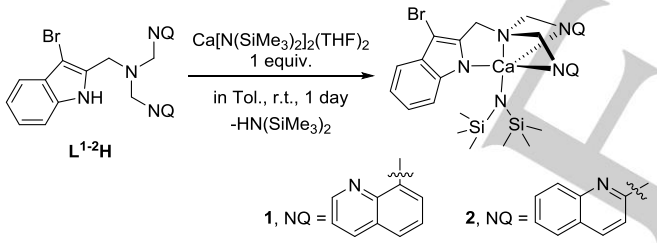
Supporting information (Preparation procedure of compounds **A1**-**A3**, **Q1**-**Q3**, proligands **L^{1}H**-**L^{5}H**, calcium and potassium complexes; X-ray data for **2**, **D3** and **BQ**; IR and NMR spectra) for this article is given via a link at the end of the document.

were found difficult to be alkylated twice. Thus, proligands **L^{4}H**-**L^{5}H** were obtained in relatively low yields (22%~23%).



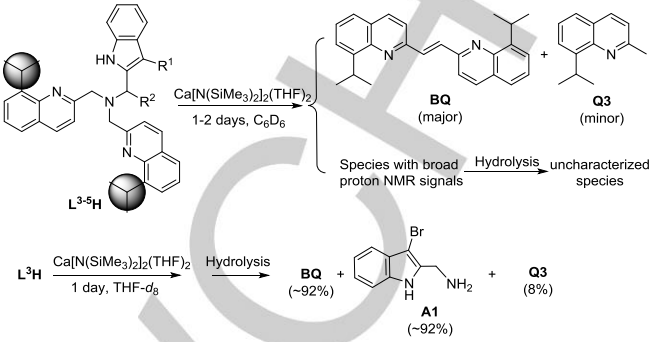
Scheme 1. Synthesis of proligands **L^{1}H**-**L^{5}H**..

Reactions of proligands **L$^{1-2}$H** with one equiv. of $Ca[N(SiMe_3)_2]_2(THF)_2$ in toluene gradually gave light yellow solutions, which after workup afforded the heteroleptic complexes **1** and **2** as pale yellow powders in 51~58% isolated yields (Scheme 2). Likely due to the presence of the sterically proper BQIA ligands, complexes **1** and **2** were found to be inert toward a Schlenk equilibrium often observed for heavy alkaline metal complexes.[1d-e] Indeed, heating a C_6D_6 solution of **1** at 50 °C over a period of 12 h did not result in any apparent decomposition or ligand redistribution.

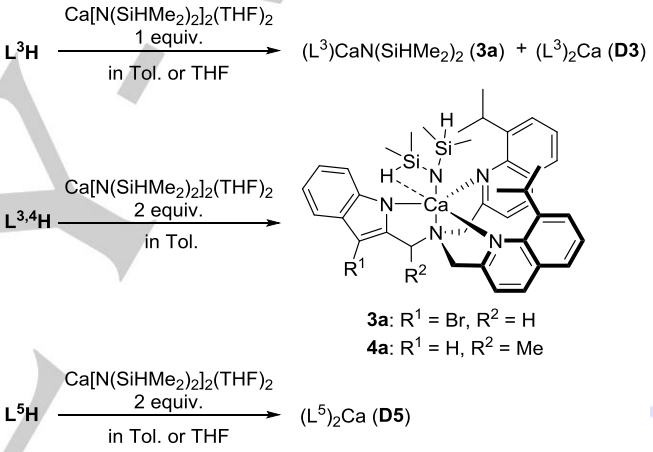


Scheme 2. Synthesis of complexes **1**-**2**.

The reactions of **L$^{3-5}$H** with one equiv. of $Ca[N(SiMe_3)_2]_2(THF)_2$ in C_6D_6 gave light brown-yellow solutions initially, which however turned to dark-green within 24 h. In each case, after cooling the green solution to −38 °C, (*E*)-1,2-bis(8-isopropylquinol-2-yl)ethene (**BQ**) was isolated unexpectedly as colorless crystals in high yield (Scheme 3), as fully characterized by ^{1}H, ^{13}C NMR, EI-MS and X-ray diffraction methods (Figure S1 in SI). Similar phenomena were observed for the reaction of **L^{3}H** and $Ca[N(SiMe_3)_2]_2(THF)_2$ carried in THF-d_8, which however afforded (3-bromo-1*H*-indol-2-yl)methanamine (**A1**) after hydrolysis in addition to **BQ** with both in about 92% isolated yields (Scheme 3). Moreover, nearly identical EPR spectra were obtained for those dark-green solutions, implying the generation of similar paramagnetic species (Figure S30 in SI). The highly symmetric EPR resonance with a *g*-value (*g* = 2.0023) close to that of the free electron in combination with the dark-green color of the reaction mixture further suggests the formation of carbon-centered radicals within delocalized aromatic systems.[8]



Scheme 3. The reactions of **L$^{3-5}$H** with one equiv. of $Ca[N(SiMe_3)_2]_2(THF)_2$.



Scheme 4. Synthesis of calcium complexes **3a**-**4a** and **D3**, **D5**.

On account of the successful synthesis of complexes **1**-**2**, the unprecedented reaction pathway of **L$^{3-5}$H** and $Ca[N(SiMe_3)_2]_2(THF)_2$ was probably triggered by the introduction of two isopropyl groups on the quinolyl rings, which caused significant repulsion between the tetradentate ligand and the silylamido group in the targeted calcium complexes. Therefore, we sought to introduce a smaller amino group -$N(SiHMe_2)_2$, which often allows the synthesis of stable heavy alkaline earth metal complexes with the help of internal metal···H–Si agostic interactions.[2b] As expected, the reaction of **L^{3}H** and $Ca[N(SiHMe_2)_2]_2(THF)_2$ in a 1:1 molar ratio in toluene did not show any sign of similar decomposition, but gave a mixture of $(L^3)CaN(SiHMe_2)_2$ (**3a**) and $(L^3)_2Ca$ (**D3**) via an amine elimination route (Scheme 4), and the homolepic complex **D3** could be isolated from the reaction mixture just by filtration. Apparently, a Schlenk equilibrium occurred due to the solubility difference of these complexes in toluene. The equimolar reaction of **L^{3}H** and $Ca[N(SiHMe_2)_2]_2(THF)_2$ in THF also failed to completely suppress the ligand resdistribution toward the

homoleptic side. Fortunately, the treatment of **L^{3}H** with two equiv. of Ca[N(SiHMe$_2$)$_2$]$_2$(THF)$_2$ gave exclusively the heteroleptic complex **3a**, and analytically pure **3a** could be isolated from a mixed solution of toluene and *n*-hexane. Complex **4a** was obtained similarly in moderate yield. The very poor solubility of the homoleptic complex (L^5)$_2$Ca (**D5**) in both toluene and THF led to its quick precipitation once mixing the proligand **L^{5}H** and Ca[N(SiHMe$_2$)$_2$]$_2$(THF)$_2$, and the corresponding heteroleptic species (L^5)CaN(SiHMe$_2$)$_2$ (**5a**) could not be obtained.

Spectroscopic and X-ray diffraction studies. Complexes **1**, **D3** and **D5** are only sparingly soluble in common organic solvents, so no reliable ^{13}C NMR or even ^{1}H NMR (**D5**) spectra could be obtained. The rest of complexes and all proligands were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as elemental analysis.

In the ^{1}H NMR spectra of complexes **1**-**2** in C_6D_6, only one set of resonances is displayed for the two quinolyl moieties of the ligand, suggesting that both quinolyl fragments are equivalent in solution and a symmetry plane that contains the metal center, the central N atom and the indole ring seems to exist. However, the X-ray diffraction study shows that in the solid state **2** is a mononuclear, six-coordinate complex without any symmetry, where the coordinative unsaturation of the calcium center is relieved by an unusual Ca···C–Si agostic interaction in addition to the coordination of the tetradentate ligand and the silylamido group (Figure 1). The Ca···C(35) distance of 2.95 Å lies within the range reported for agostic-type interactions in group 2 organometallics.[1g] The large discrepancies between two Ca–N–Si angles (Ca1–N5–Si2, 105.6(14)° and Ca1–N5–Si1, 129.0(16)°) as well as two corresponding Ca···Si distances (Ca1–Si2, 3.21 Å and Ca1–Si1, 3.63 Å) indicate undoubtedly the existence of such a Ca···C(35)–Si agostic interaction.

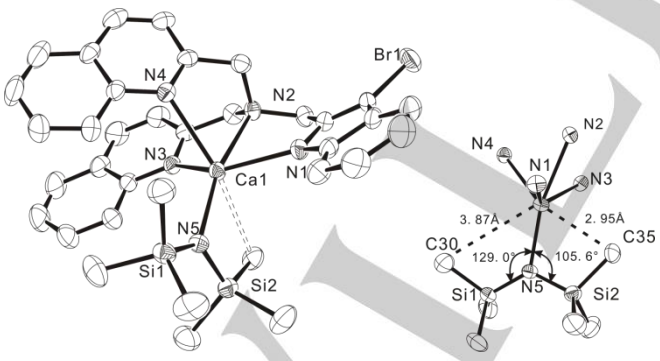


Figure 1. Molecular structure of calcium complex **2** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ca1–N5, 2.313(3); Ca1–N1, 2.398(3); Ca1–N2, 2.540(3); Ca1–N4, 2.579(3); Ca1–N3, 2.582(3); Ca1···C35, 2.950; N5–Ca1–N1, 104.72(11); N5–Ca1–N2, 164.81(11); N1–Ca1–N2, 69.26(10); N5–Ca1–N4, 125.59(11); N1–Ca1–N4, 107.48(10); N2–Ca1–N4, 69.43(10); N5–Ca1–N3, 112.61(11); N1–Ca1–N3, 134.49(11); N2–Ca1–N3, 67.93(10); N4–Ca1–N3, 70.70(9); Si2–N5–Ca1, 105.63(14); Si1–N5–Ca1, 128.99(16).[9]

The ^{1}H NMR spectral features of complex **3a** are similar to those of complexes **1**-**2**. The two equivalent quinolyl moieties also suggest the existence of an average symmetry plane in complex **3a** in solution. However, in the ^{1}H NMR spectrum of **4a**, the two quinolyl-2-methyl fragments are inequivalent, as evidenced by four doublets assigned to methylene protons of the two Quino–C*H*$_2$–N unities, as well as two septets and four doublets assigned for the two isopropyl groups. The solution-asymmetry of complex **4a** can be most probably attributed to the combination of the chirality at the *α*-position of the indolylmethyl amino group and a propeller-like conformation in such a complex with molecular helicity.[10]

The heteroleptic calcium tetramethylsilylamido complexes **3a** and **4a** were further characterized by solution ^{29}Si NMR (in C_6D_6). Representative data are collected in Table 1. The ^{29}Si resonances of complexes **3a** and **4a** appear at much higher field (−25.3~−25.8 ppm) in comparison with those of HN(SiHMe$_2$)$_2$ (*δ* ^{29}Si = −11.5 ppm) (Table 1, Figures S22-S23 in SI). The $^1J_{Si-H}$ coupling constants of 152~158 Hz detected for complexes **3a-4a** are indicative of a mild (140-160 Hz) to weak (160-170 Hz) agostic Ca···H–Si interaction in solution.[11] Moreover, one strong *ν*(Si-H) absorbance at 2121~2122 cm^{-1} and one low band at 2054~2055 cm^{-1} observed in the FT-IR spectra also confirm the presence of a Ca···H–Si agostic interaction in the solid state (Figures S28-S29 in SI). Obviously, such an agostic interaction significantly increases the stability of **3a** and **4a**.

Table 1. Selected spectroscopic data of **3a**-**4a**, {LO}CaN(SiMe$_2$)$_2$[a], HN(SiHMe$_2$)$_2$ and Ca[N(SiHMe$_2$)$_2$]$_2$(THF)$_2$ (298 K in C_6D_6)

Compound	^{1}H NMR Si-H (ppm)	^{13}C NMR Si-CH$_3$ (ppm)	^{29}Si NMR	
			Si-H (ppm)	$^1J_{Si-H}$ (Hz)
HN(SiHMe$_2$)$_2$	4.70	0.8	−11.5	194
{LO}CaN(SiMe$_2$)$_2$[a]	5.20	6.4	−25.9	165
3a	4.07	3.9	−25.3	152
4a	4.01	4.7, 4.5	−25.8	158
Ca[N(SiHMe$_2$)$_2$]$_2$(THF)$_2$	4.92	4.5	−20.5	154

[a]{LO} = 2-{(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)-methyl}-4,6-di-tert-butylphenolate[2b]

As shown in Figure 2, in the solid state the bisligated complex **D3** possesses an unusual triangulated dodecahedral geometry[2a] with the help of two short intramolecular contacts between the calcium center and hydrogens of two isopropyls (Ca1···H33 = 2.520 Å, Ca1···H68 = 2.552 Å),[12] in addition to the coordination of six N atoms of two BQIA ligands. A similar close interatomic contact (*ca.* 2.582 Å) was observed between the calcium atom and one methine C–H unit of the *ortho*-isopropyl group of the anilide ligand in [BDI]Ca{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)}(THF).[13]

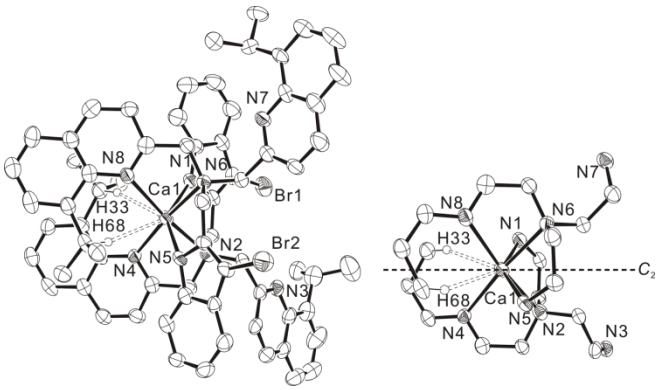


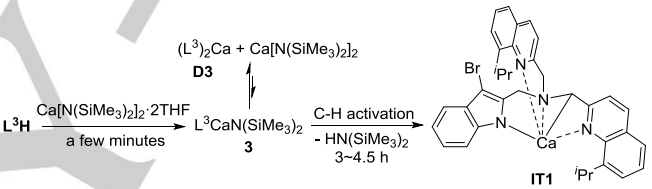
Figure 2. Molecular structure of calcium complex **D3** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ca1–N5, 2.313(3); Ca1–N1, 2.398(3); Ca1–N2, 2.540(3); Ca1–N4, 2.579(3); Ca1–N3, 2.582(3); Ca1···C35, 2.950; N5–Ca1–N1, 104.72(11); N5–Ca1–N2, 164.81(11); N1–Ca1–N2, 69.26(10); N5–Ca1–N4, 125.59(11); N1–Ca1–N4, 107.48(10); N2–Ca1–N4, 69.43(10); N5–Ca1–N3, 112.61(11); N1–Ca1–N3, 134.49(11); N2–Ca1–N3, 67.93(10); N4–Ca1–N3, 70.70(9); Si2–N5–Ca1, 105.63(14); Si1–N5–Ca1, 128.99(16).

Thus, it is clear, although different secondary agostic interactions such as Ca···*β*-Si–C, Ca···*β*-Si–H or Ca···H–C are involved in this series of heteroleptic and homoleptic calcium complexes respectively, without exception all play an important role in stablizing the calcium species.

Investigation of the reaction pathway between $L^{3\text{-}5}H$ and $Ca[N(SiMe_3)_2]_2(THF)_2$. The unprecedented and highly specific reaction pathway between $L^{3\text{-}5}H$ and $Ca[N(SiMe_3)_2]_2(THF)_2$ inspired us to further investigate this reaction. Thus, NMR scale reactions of L^3H and $Ca[N(SiMe_3)_2]_2(THF)_2$ in both C_6D_6 and THF-d_8 were monitored by ^1H NMR spectroscopy in different time intervals (Figures S34-S35 and Table S3-S4 in SI). Since the spectra detected in C_6D_6 afford better resolution for most of the involved species, herein we will mainly focus on the reaction monitored in C_6D_6.

Initially, the two reagents reacted rapidly but to give a mixture of **D3** (20%) and the targeted heteroleptic complex **3** ($(L^3)CaN(SiMe_3)_2$, 60%) (5 min after mixing) (Figure S34, Table S3 in SI). Slow decomposition of these calcium species occurred after 3 h of standing, as a set of new signals could be clearly observed although in small amount (4%). Upon further standing, the amount of **3** and **D3** decreased rapidly and the signals could not be detected soon; meanwhile the color of the mixture turned to verdant green and the signals of **BQ** appeared (4.0~4.5 h after mixing). In addition, the previously mentioned new set of resonances represented by four doublets at 5.69 ppm, 5.62 ppm (^2J = 12.6 Hz) and 5.31 ppm, 4.84 ppm (^2J = 13.4 Hz) assignable to four methylene protons of NCH_2Ar moieties became dominant at this stage, indicating the generation of a new calcium species bearing the BQIA ligand. The corresponding two sets of 8-isopropylquinolyl resonances in a 1:1 ratio further indicate an asymmetric structure of this species. Interestingly, including the singlet at 4.48 ppm, a total of five instead of six protons attributable to the three NCH_2Ar units are displayed. Besides, the same amount increase of $HN(SiMe_3)_2$ (48%) has been observed along with the generation of this new calcium species. Based on these data, we speculate that one NCH_2Ar proton in the ligand framework of this species is probably deprotonated by the Ca–$N(SiMe_3)_2$ moiety. Hydrolysis of another independent reaction mixture of L^3H and $Ca[N(SiMe_3)_2]_2(THF)_2$ after 4.5 h of mixing afforded L^3H as the main product, indicating that the formation of the new species indeed goes through a C–H bond activation of L^3 rather than other ligand rearrangement transformations.

Storage of a C_6D_6 solution of **D3** for one week gave no sign of decomposition. Addition of excess $Ca[N(SiMe_3)_2]_2(THF)_2$ to **D3** moved the Schlenk equilibrium toward the formation of the heteroleptic complex **3** exclusively (Figure S36 in SI), which started to decompose after 3 h. These rule out the possibility of an intermolecular deprotonation of **D3** by $Ca[N(SiMe_3)_2]_2(THF)_2$. Therefore, taking the final production of **BQ** into account, an intramolecular C–H activation of one Quino–CH_2–N moiety by Ca–$N(SiMe_3)_2$ is supposed to occur in **3** to generate a dianion ligated calcium intermediate **IT1** (Scheme 5).



Scheme 5. The reaction pathway of L^3H and $Ca[N(SiMe_3)_2]_2(THF)_2$ monitored by ^1H NMR spectroscopy.

Such self C–H activation was also reported by Harder's group, where a stable calcium complex supported by multiply deprotonated *β*-diketimine ligands could be isolated.[14] However, the intermediate IT1 detected in this work is not stable enough. During the period of 4.5 h to 24 h, the color of the reaction mixture turned to dark green, and the signals of IT1 gradually disappeared in the ^1H NMR spectra along with the formation of BQ (8→92%), Q3 (0→8%) and some uncharacterized species.

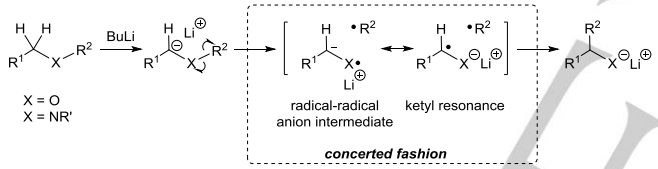
To gain insight into the relationship between the formation of **BQ** and radical species (EPR active, green color), several control experiments were carried out:

(i) TEMPO, L^3H and $Ca[N(SiMe_3)_2]_2(THF)_2$ were mixed simultaneously in C_6D_6. The ^1H NMR spectra showed that only **D3** and $Ca[N(SiMe_3)_2]_2(THF)_2$·TEMPO[15] were detected even after one week (Figure S37 in SI), implying that no decomposition would occur in the absence of the heteroleptic complex **3**.

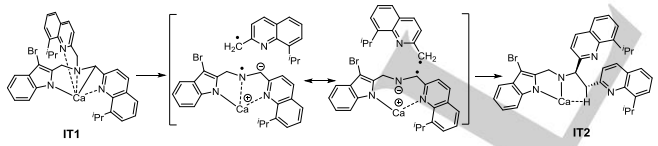
(ii) Excess TEMPO was added to another independent reaction mixture when 40% **IT1** and 2% **BQ** were detected. The green color immediately faded, suggesting that the formed radical species could be quenched instantly by TEMPO. Unexpectedly, ca. 40% **BQ** still formed after 8 h (Figure S38 in SI). These results might imply that **BQ** is not generated from the radical species detected by EPR.

We also attempted to capture the stable radical species via the addition of radical scavengers (galvinoxyl, PhSeH and BPO), however all reactions failed to give well-defined species.

It is known that, when ether or tertiary amines are treated with lithium reagents, a [1,2]-Wittig or aza-[1,2]-Wittig rearrangement would occur (Scheme 6). **IT1** possesses similar structural features as those of the intermediate in a Wittig or aza-Wittig rearrangement,[7] where the carbanion is connected directly to a heteroatom (O or N). Therefore, it is conceivable that a similar homolytic cleavage of the C–N bond between the central N and the CH_2–Quino moiety in **IT1** might occur to give a radical and a radical anion (Scheme 7). The sequential rearrangement through a radical-radical combination of the migrating group with the "ketyl resonance" form would lead to the formation of **IT2**, which bears the rudimentary structure of **BQ**. From the ^{1}H NMR spectra of C_6D_6 solution, signals of other intermediates or products could not be clearly assigned, probably due to the aggregation or insolubility of these species. But in THF-d_8, except for those species (**IT1**, **BQ** and **Q3**) observed in C_6D_6, a set of new signals appeared after 4.5 h, of which feature signals (three "dd" peaks: 5.39 ppm, ^3J = 8.0 Hz, ^3J = 9.0 Hz; 4.83 ppm, ^2J = 15.5 Hz, ^3J = 9.0 Hz; 4.77 ppm, ^2J = 15.5 Hz, ^3J = 8.0 Hz) well match the methine and methene protons of the NC*H*(Quino)C*H*$_2$(Quino) moiety in **IT2** (Figure S35). Since the coupling modes of these signals are so unique, they may serve as a direct evidence to the formation of **IT2**.

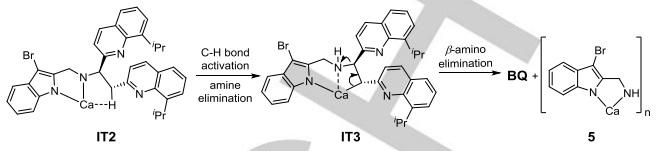


Scheme 6. The mechanism proposed for a Wittig rearrangement of ether and tertiary amine.



Scheme 7. The mechanism proposed for the aza-[1,2]-Wittig rearrangement of **IT1**.

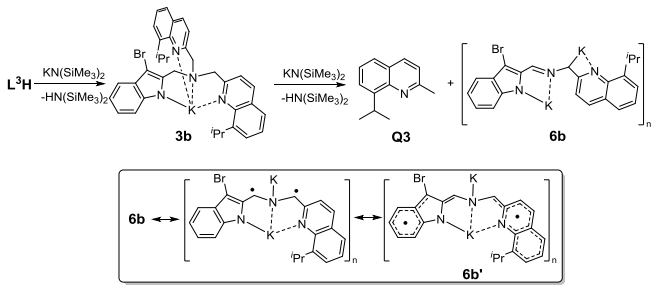
Although no other intermediates could be unambiguously assigned or captured, on the basis of the isolation of **A1** in high yield after hydrolysis of the reaction mixture in THF-d_8 (Figure S33 in SI), a mechanism involving **IT2** to form **BQ** and **5** could be hypothesized (Scheme 8). The calcium center in **IT2** is supposed to be electron deficient because of the non-coordination of quinolyl N atoms, consequently inducing the second C–H bond activation process. Thus, **IT2** undergoes *γ*-H abstraction by Ca–N bond to give a 1,3-migrated intermediate **IT3**. The coordination of the central N atom to the calcium center therefore forming a *syn*-coplanar Ca–N–C–C arrangement in **IT3** then leads to a rapid *β*-amino elimination to form **BQ** and **5**.



Scheme 8. The mechanism proposed for the formation of **BQ** and **5**.

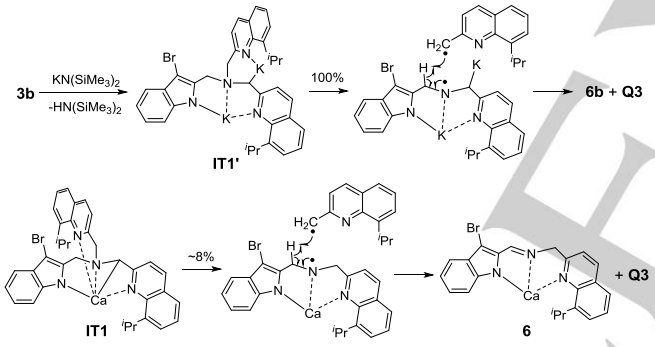
So far, the mechanism of the main decomposition pathway to form BQ and 5 has been more or less understood. However, none of the above-mentioned structures could account for the paramagnestic nature of the green solution. It is therefore conceivable there should be another minor decompositon pathway. To further explore the reaction mechanism and the role of divalent calcium center in this process, we changed the metal reagent to $KN(SiMe_3)_2$.

The potassium complex (L^3)K (**3b**) could be obtained readily as a light yellow powder from the equimolar reaction of **L^3H** and $KN(SiMe_3)_2$. However, the treatment of **3b** with $KN(SiMe_3)_2$ led to a decomposition to form **Q3** and a dipotassium complex (**6b**) nearly quantitatively (Scheme 9, Figure S39). **6b** could be isolated as air and moisture-sensitive dark-purple solids through recrystallization from a mixture of *n*-hexane and THF, and was fully characterized by ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis.[16] Being consistent with its dark-purple color, **6b** also displays a strong EPR signal (Figure S32), indicating that **6b** has a singlet-ground-state with a certain degree of biradical character.[17] The ^{1}H NMR signals of aryl protons of **6b** (7.7-6.2 ppm) are obviously downfield shifted as compared to those of **3b** (8.0-6.6 ppm), which is likely due to the shielding effect of the radical behaviour of indolyl and quinolyl rings (Figure S39 in SI). As shown in Scheme 9, when the negative charge of CH=N–CH$^-$ unit in **6b** concentrates on the nitrogen atom, the Kekulé structure of **6b** would resonate well with the biradical form **6b′**, where the two unpaired electrons can delocalize thoroughly within the indolyl or quinolyl ring, respectively. This may account for the unusual stability of **6b** as paramagnestic species.



Scheme 9. The reaction of **L^3H** with $KN(SiMe_3)_2$.

Based on the NMR scale reaction of **3b** and $KN(SiMe_3)_2$ in different time intervals (Figure S39 in SI), it is conceivable that an intermolecular amine elimination might occur between **3b** and $KN(SiMe_3)_2$ to generate a dipotassium intermediate **IT1′**, which is very unstable and decomposes rapidly in solution, just as **IT1** (Scheme 10). Although no coupling product **BQ** could be detected in the potassium case, the quantitative formation of **Q3** and **6b** does suggest a facile homolytic C–N bond cleavage of the N–CH_2–Quino moiety in these species. But why does not **IT1′** follow the same decomposition pathway as **IT1**? In this regard, we think that the lone pair on the central N atom in **IT1′** is restricted by the potassium center chelating to the indolyl group, which probably prevents one electron transfer from the C–K bond to form the "ketyl resonance". While, in the case of **IT1**, the lone pair on the central N atom and the neighboring *σ*-bonded carbanion interact with the same calcium center, which might facilitate the transformation of C–Ca to N–Ca *σ*-bonding, consequently the rearrangement. In fact, we did observe the formation of a small amount of **Q3** in the calcium case (Scheme 10),[18] which verified that such a non-rearranging decomposition pathway also occurred for **IT1** to give **Q3** and a similar calcium species **6** as minor by-products (Figure S35 in SI).[19] The biradical resonant form of **6** should account for the paramagnetic behavior of the reaction mixture of $\mathbf{L^3H}$ and $Ca[N(SiMe_3)_2]_2(THF)_2$.



Scheme 10. The mechanism proposed for the non-rearranging decomposition pathway.

Ring-opening polymerization of *rac*-lactide. The ability of the heteroleptic complexes **1**-**2**, **3a**-**4a** to promote the ring-opening polymerization (ROP) of *rac*-lactide (*rac*-LA) was evaluated preliminarily (Table S5). Calcium complex **2** showed good activities toward the ROP of *rac*-LA in toluene, and could convert 200 equiv. of *rac*-LA to 90% monomer conversion within 5 min and afford atactic PLA with a relatively broad polydispersity (PDI = 1.69) (Table S5). When the feed ratio was increased to 400:1, a monomer conversion of 74% was achieved within the same time, but further extending the reaction time did not result in a significantly increase of the conversion (76% conv. in 10 min). The activity of complex **2** is slightly lower than that of the bulky tris(pyrazolyl)borate calcium complex $[HB(3\text{-}^{t}Bupz)_3]CaN(SiMe_3)_2$ ($[LA]_0$:$[Ca]_0$ = 200:1, 90% conv. in 1 min) reported by Chisholm's group,[2d] which is also the only example that could produce heterotactic PLA almost exclusively (P_r > 90%). However, the rest complexes **1**, **3a**-**4a** were found to be extremely sensitive and showed barely any activities for lactide polymerization under identical conditions. It is suggested that, although the high electropositivity of the calcium center could usually lead to a marked increase in polymerization activity,[2a,2i] a balance between the steric protection to improve the stability, sensitivity and a precise structural design to exert stereocontrol has to be considered thoroughly.

Conclusions

A new type of monoanionic nitrogen-based ancillary ligands ($[NNNN]^-$ = {bis(quinolylmethyl)amino}methylindol-1-ide) has been synthesized and introduced to stabilize a series of heteroleptic and homoleptic calcium complexes. X-ray diffraction and NMR spectroscopic studies revealed versatile coordination modes that the BQIA ligands could form when chelating around the calcium center. Heteroleptic calcium complex **2** is stabilized in the solid state by the secondary *β*-Si–C agostic interactions. Intramolecular Ca···H–C agostic interactions were found to help the homoleptic calcium complex **D3** with adopting an unusual 8-coordinate triangulated dodecahedral geometry. Ca-*β*-Si–H agostic interactions were found to play an important role in stabilizing the tetramethylsilylamido complexes **3a**-**4a** ($(L^{3\text{-}4})CaN(SiHMe_2)_2$) both in the solid state and in solution, as indicated by FT-IR and ^{29}Si NMR spectroscopic studies.

Moreover, for bis(trimethylsilyl)amido calcium complexes bearing sterically more hindered ligands, $(L^{3\text{-}5})CaN(SiMe_3)_2$, we have observed the first example of calcium promoted C–N bond cleavages induced by intramolecular C–H bond activations. A multistep mechanism accounting for the unusual decomposition pathway of the BQIA ligand in the coordination sphere of the calcium center has been proposed, which involves a selective C(sp^3)–H bond activation step followed by a unprecedented tandem aza-[1,2]-Wittig rearrangement and a C(sp^3)–H bond activation induced *β*-amino elimination in sequence. The mechanistic studies on the contrastive potassium case gave a strong evidence to the minor radical decomposition pathway also encounted in the calcium complexes. Although this unprecedented calcium involved C–N bond cleavage occurs stoichiometrically, these findings point out that other mechanisms of C–N bond cleavage beyond those affecting the oxidation state of the metal center might also be feasible under appropriate conditions. Future work will aim at the prospective impact of this methodology for catalytic applications.

Acknowledgements

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Keywords: Calcium complex • N ligand • C-H bond activation • C-N bond cleavage • ROP of lactide

[1] a) T. P. Hanusa, *Coord. Chem. Rev.* **2000**, *210*, 329-367; b) M. Westerhausen, *Angew. Chem*. **2001**, *113*, 3063–3065; *Angew. Chem. Int. Ed.* **2001**, *40*, 2975-2977; c) A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, P. A. Procopiou, *Angew. Chem.* **2007**, *119*, 6455-6458; *Angew. Chem. Int. Ed.* **2007**, *46*, 6339-6342; d) S. Harder, *Chem. Rev.* **2010**, *110,* 3852-3876; e) A. Torvisco, A. Y. O'Brien, K. Ruhlandt-Senge, *Coord. Chem. Rev.* **2011**, *111,* 1268-1292; f) J. Penafiel, L. Maron, S. Harder, *Angew. Chem.* **2015**, *127*, 203-208; *Angew. Chem. Int. Ed.* **2015**, *54*, 201-206; g) D. J. Burkey, E. K. Alexander, T. P. Hanusa, *Organometallics* **1994**, *13*, 2773-2786; h) V. Radkov, T. Roisnel, A. Trifonov, J.-F. Carpentier, E. Kirillov, *J. Am. Chem. Soc.* **2016**, *138*, 4350-4353.

[2] a) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Inorg. Chem.* **2004**, *43*, 6717-6725; b) Y. Sarazin, D. Roşca, V. Poirier, T. Roisnel, A. Silvestru, L. Maron, J.-F. Carpentier, *Organometallics* **2010**, *29*, 6569-6577; c) Y. Sarazin, B. Liu, T. Roisnel, L. Maron, J.-F. Carpentier, *J. Am. Chem. Soc.* **2011**, *133*, 9069-9087; d) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Chem. Commun.* **2003**, 48-49; e) M. G. Cushion, P. Mountford, *Chem. Commun.* **2011**, *47*, 2276-2278; f) J-C. Buffet, J. P. Davin, T. P. Spaniol, J. Okuda, *New J. Chem.* **2011**, *35*, 2253-2257; g) J. P. Davin, J-C. Buffet, T. P. Spaniol, J. Okuda, *Dalton Trans.* **2012**, *41*, 12612-12618; h) L. Clark, G. B. Deacon, C. M. Forsyth, P. C. Junk, P. Mountford, J. P. Townley, J. Wang, *Dalton. trans.* **2013**, *42*, 9294-9312; i) C. A. Wheaton, P. G. Hayes, B. J. Ireland, *Dalton Trans.*, **2009**, 4832-4846.

[3] a) C. Brinkmann, A. G. M. Barrett, M. S. Hill, P. Procopiou, *J. Am. Chem. Soc.* **2012**, *134*, 2193-2207; b) B. Liu, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Angew. Chem.* **2012**, *124*, 5027-5030; *Angew. Chem. Int. Ed.* **2012**, *51*, 4943-4946; c) S. Datta, P. W. Roesky, S. Blechert, *Organometallics* **2007**, *26*, 4392-4394; d) S. Datta, M. T. Gamer, P. W. Roesky, *Organometallics* **2008**, *27*, 1207-1213; e) M. Arrowsmith, M. R. Crimmin, A. G. M. Barrett, M. S. Hill, G. Kociok-Köhn, P. A. Procopiou, *Organometallics* **2011**, *30*, 1493-1506; f) M. R. Crimmin, I. J. Casely, M. S. Hill, *J. Am. Chem. Soc.* **2005**, *127*, 2042-2043; g) M. R. Crimmin, M. Arrowsmith, A. G. M. Barrett, I. J. Casely, M. S. Hill, P. A. Procopiou, *J. Am. Chem. Soc.*, **2009**, *131*, 9670-9685; h) M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, *Organometallics* **2014**, *33*, 206-216; i) N. Romero, S.-C. Roșca, Y. Sarazin, J.-F. Carpentier, L. Vendier, S. Mallet-Ladeira, C. Dinoi, M. Etienne, *Chem.– Eur. J.* **2015**, *21*, 4115-4125.

[4] Hydrogen elimination: a) J. Spielmann, S. Harder, *J. Am. Chem. Soc.* **2009**, *131*, 5064-5065; C–H activation: b) P. Jochmann, T. S. Dols, T. P. Spaniol, L. Perrin, L. Maron, J. Okuda, *Angew. Chem.* **2010**, 122, 7962-7965; *Angew. Chem. Int. Ed.* **2010**, 49, 7795-7798; Hetero-dehydrocoupling: c) M. S. Hill, D. J. Liptrot, D. J. MacDougall, M. F. Mahon, T. P. Robinson, *Chem. Sci.* **2013**, *4*, 4212-4222; Mannich-type: d) T. Tsubogo, S. Shimizu, S. Kobayashi, *Chem. Asian J.* **2013**, *8*, 872-876; Cycloisomerization of enynes: e) V. J. Meyer, L. Fu, F. Marquardt, M. Niggemann, *Adv. Synth. Catal.* **2013**, *355*, 1943-1947; Metathesis reaction: f) H. Li, W-X. Zhang, Z. Xi, *Chem.– Eur. J.* **2013**, *19*, 12859-12866; Nazarov cyclization: g) J. Davies, D. Leonori, *Chem. Commun.,* **2014**, *50*, 15171-15174; Hydrothiolation of alkynes: h) M. Hut'ka, T. Tsubogo, S. Kobayashi, *Organometallics* **2014**, *33*, 5626-5629; i) M. S. Hill, D. J. Liptrot, C. Weetman, *Chem. Soc. Rev.* **2016**, *45*, 972-988.

[5] Calcium complexes supported by *α*/*β*-diketiminate ligand: a) S. Harder, *Organometallics* **2002**, *21*, 3782-3787; b) M. S. Hill, P. B. Hitchcock, *Chem. Commun.* **2003**, 1758-1759; c) S. Harder, J. Brettar, *Angew. Chem.* **2006**, *118*, 3554-3558; *Angew. Chem., Int. Ed.* **2006**, *45*, 3474-3478; d) S. P. Sarish, A. Jana, P. W. Roesky, T. Schulz, M. John, S. Datta, *Inorg. Chem.* **2010**, *49*, 3816-3820; e) S. P. Sarish, S. Nembenna, S. Nagendran, H. W. Roesky, *Acc. Chem. Res.* **2011**, *44*, 157-170; Iminopyrroles/pyridine ligands: f), M. Arrowsmith M. S. Hill, G. Kociok-Köhn, *Organometallics* **2010**, *29*, 4203-4206; g) J. Jenter, R. Köppe, P. W. Roesky, *Organometallics* **2011**, *30*, 1404-1413; h) T. K. Panda, K. Yamamoto, K. Yamamoto, H. Kaneko, Y. Yang, H. Tsurugi, K. Mashima, *Organometallics* **2012**, *31*, 2268-2274; Tris(pyrazolyl)borate ligands: i) M. H. Chisholm, *Inorg. Chim. Acta* **2009**, *362*, 4284-4290; j) M. J. Saly, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **2009**, *48*, 5303-5312; k) M. G. Cushion, J. Meyer, A. Heath, A. D. Schwarz, I. Fernández, F. Breher, P. Mountford, *Organometallics* **2010**, *29*, 1174-1190; l) O. Michel, H. M. Dietrich, R. Litlabø, K. W. Törnroos, C. Maichle-Mössmer, R. Anwander, *Organometallics* **2012**, *31*, 3119-3127. Aminophenolate ligands: m) Y. Sarazin, D. Roαşa, V. Poirier, T. Roisnel, A. Silvestru, L. Maron, J.-F. Carpentier, *Organometallics*, **2010** *29*, 6569–6577. n) B. Liu, T. Roisnel, J.-P. Guégan, J.-F. Carpentier, Y. Sarazin, *Chem.– Eur. J.* **2012**, *18*, 6289–6301. Fluorenol ligand (o) *Organometallics* **2015**, *34*, 1339−1344.

[6] a) A. Roglans, A. Pla-Quintana, M. Moreno-Mañas, *Chem. Rev.* **2006**, *106*, 4622-4643; b) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068-5083; c) C.-Y. Huang, A. G. Doyle, *Chem. Rev.* **2014**, *114*, 8153-8198; d) K. Ouyang, W. Hao, W.-X. Zhang, Z. Xi, *Chem. Rev.* **2015**, *115*, 12045-12090; e) L. Hie, N. F. F. Nathel, T. K. Shah, E. L. Baker, X. Hong, Y.-F. Yang, P. Liu, K. N. Houk, N. K. Garg, *Nature* **2015**, *524*, 79-83.

[7] a) G. Wittig, L. Löhmann, *Justus Liebigs Ann. Chem.* **1942**, 550, 260-268; b) J. Åhman, T. Jarevång, P. Somfai, *J. Org. Chem.* **1996**, 61, 8148-8159.

[8] U. Green, Z. Aizenshtat, S. Ruthsteinwc, H. Cohenw, *Phys. Chem. Chem. Phys.* **2013**, *15*, 6182-6184.

[9] CCDC numbers 1400377 (**2**), 1400378 (**D3**) and 1400381 (**BQ**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For further crystal data and details of measurements see Table S1 and S2.

[10] a) J. W. Canary, C. S. Allen, J. M. Castagnetto, Y. Wang, *J. Am. Chem. Soc.* **1995**, *117*, 8484-8485; b) C. S. Allen, C.-L. Chuang, M. Cornebise J. W. Canary, *Inorg. Chim. Acta* **1995**, *239*, 29-37; c) J. W. Canary, C. S. Allen, J. M. Castagnetto, Y.-H. Chiu, P. J. Toscano, Y. Wang, *Inorg. Chem.* **1998**, *37*, 6255-6262; d) X. D. Xu, K. J. Maresca, D. Das, S. Zahn, J. Zubieta, J. W. Canary, *Chem. – Eur. J.* **2002**, *8*, 5679-5683; e) A. E. Holmes, D. Das, J. W. Canary, *J. Am. Chem. Soc.* **2007**, *129*, 1506-1507; f) J. Liang, J. Zhang, L. Zhu, A. Duarandin, V. G. Young, N. Geacintov, J. W. Canary, *Inorg. Chem.* **2009**, *48*, 11196-11208.

[11] The $^{1}J_{SiH}$ coupling constant is generally a good probe to gauge the intensity of metal-*β*-Si-H agostic interactions.

[12] The sum of the van der Waals radii of calcium and hydrogen [$\sum(r_{wCa} + r_{wH})$] is 3.51 Å, and the cut-off value of Ca···H-C is 3.10 Å.[2e]

[13] A. G. Avent, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, *Dalton Trans.* **2005**, 278-284.

[14] S. Harder, *Angew. Chem.* **2003**, *115,* 3553-3556; *Angew. Chem. Int. Ed.* **2003**, *42*, 3430-3434.

[15] The coordination of TEMPO to $Ca[N(SiMe_3)_2]_2(THF)_2$ stabilizes this homoleptic species, and no Schlenk equlibrium towards **3** occurrs. M. P Coles, *Coord. Chem. Rev.* **2015**, 297-298, 2-23.

[16] Attempts to obtain single crystals of **6b** suitable for X-ray diffraction analysis in many solvents (benzene, THF, toluene, n-hexane or their mixtures) all failed. Given that stable potassium complexes usually need bulky coordination environment; an aggregating form of **6b** is more reasonable for stabilizing two potassium centers. On the basis of the relatively distinct ^{1}H NMR signals, a dimeric structure of **6b** is proposed.

[17] a) L. K. Montgomery, J. C. Huffman, E. A. Jurczak, M. P. Grendze, *J. Am. Chem. Soc.* **1986**, *108*, 6004-6011; b) I. de P. R. Moreira, J. M. Bofill, J. G. Solsona, J. Nebot, P. Romea, F. Urpí, *J. Am. Chem. Soc.* **2008**, *130*, 3242-3243; c) A. Konishi, Y. Hirao, M. Nakano, A. Shimizu, E. Botek, B. Champagne, D. Shiomi, K. Sato, T. Takui, K. Matsumoto,

H. Kurata, T. Kubo, *J. Am. Chem. Soc.* **2010**, *132*, 11021-11023; d) K. Takeuchi, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2011**, *133*, 12478-12481; e) T. Kubo, A. Shimizu, M. Sakamoto, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita, K. Nakasuji, *Angew. Chem.* **2005**, *44*, 6564-6568; *Angew. Chem., Int. Ed.* **2005**, *117*, 6722-6726; f) T. Kubo, A. Shimizu, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita, K. Nakasji, *Org. Lett.* **2007**, *9*, 81-84; g) A. Shimizu, M. Uruichi, K. Yakushi, H. Matsuzaki, H. Okamoto, M. Nakano, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, *Angew. Chem.* **2009**, *48*, 5482-5486; *Angew. Chem., Int. Ed.* **2009**, *121*, 5590-5594.

[18] We speculate that the non-migrated quinolyl radical rapidly grabbes one H• of the Indo–C*H*$_2$–N unit to form **Q3** and biradical species **6b**, which is the main decomposition pathway in the potassium case.

[19] The feature signals of **6** in the ^{1}H NMR spectrum, represented by two singlets at 7.54 ppm and 6.24 ppm assignable to the imine proton of C*H*=N moiety and the methine proton of C*H*–Ca unit, are quite similar to those of the potassium analogue **6b** (see Figures S35 & S39 in SI).

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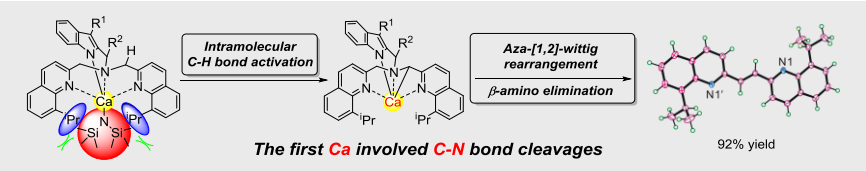

We have observed the first example of calcium involved C–N bond cleavages (*aza*-[1,2]-Wittig rearrangement and *β*-amino elimination) of the tertiary amine ligands, arising from a steric hindrance induced intramolecular C–H bond activation in calcium complexes.

*Yang Yang,[†] Haobing Wang,[†] and Haiyan Ma**

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Unprecedented Reaction Pathway of Sterically Crowded Calcium Complexes: Sequential C-N Bond Cleavages Induced by C-H Bond Activations