ORGANOMETALLICS

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pubs.acs.org/Organometallics

Directed Ortho Calciation of 1,3-Bis(3-isopropylimidazol-2-ylidene)benzene

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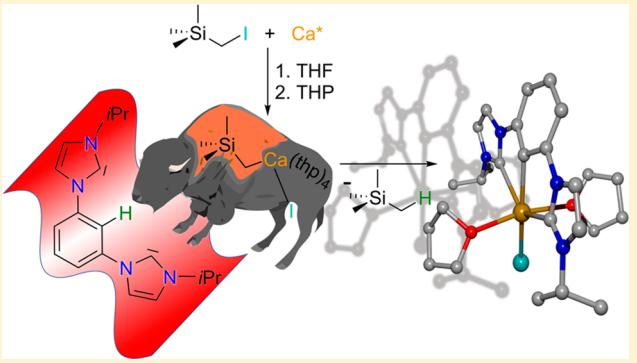
Supporting Information

ABSTRACT: The deprotonation of 1,3-bis(3-isopropylimidazol-2-ylidene)benzene with Me_3SiCH_2CaX (X = Br, I) in tetrahydrofuran (THF) yields the ether adducts of the corresponding 2,6-bis(3-isopropylimidazol-2-ylidene)-phenylcalcium halides (X = Br (**1**·2thf), I (**2**·2thf)). The crystallization behavior of **2** can be improved via substitution of ligated thf molecules by tetrahydropyran (thp) ligands, leading to **2**·2thp. These heteroleptic complexes **1**·2thf and **2**·2thp show very small $Ca-C_{ipso}$ bond lengths to the ipso-carbon atoms of the aryl groups. Calciation of 1,3-bis(3-isopropylimidazol-2-ylidene)benzene with $Ca(CH_2SiMe_3)_2$ in THP leads to the formation of ether-free homoleptic bis[2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium (**3**). Intramolecular steric strain causes an elongation of the $Ca-C_{ipso}$ bonds to the aryl groups. In all of these complexes, the $Ca-C_{carbene}$ distances are significantly larger than those to the ipso-carbon atoms of the aryl groups.

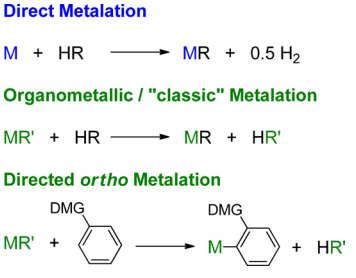


INTRODUCTION

Metalation reactions are the substitution of a hydrogen atom by a metal atom. There are two different procedures. In the direct metalation, the metal itself is employed for the deprotonation and, commonly, this reaction is a heterogeneous procedure. The "classic" metalation uses an organometallic reagent for the deprotonation, and advantageously, this reaction is performed under homogeneous conditions (Scheme 1). However, the organometallic reagent has to be prepared in an initial step if it is not commercially available.

In the form of commercially available calcium turnings, the metal itself is rather inert and only soluble in liquid ammonia, forming a deep blue solution. These solutions are extremely reactive with strongly reducing properties. Therefore, Birch-type reductions often represent the major reaction pathway if aromatic substrates are used.[1] For many direct metalations the reactivity of solid calcium turnings or calcium powders is too low. Nevertheless, undesired side reactions had been observed, leading to degradation of the substrate; thus, the reduction of 2,6-bis(diphenylphosphanylmethyl)phenyl halide with calcium led to P−C bond cleavage and formation of diphenylphosphinates in addition to other products.[2] Very acidic organic substrates such as cyclopentadienes[3] can be calciated, but less acidic compounds such as amines[4−6] and thiols[7] can only be deprotonated in the presence of anhydrous ammonia but not in common organic solvents. In these latter cases, organopotassium reagents were reacted with calcium iodide in a metathetical approach, yielding insoluble KI and organocalcium complexes. Other strategies favor transamination or metalation protocols, as achieved for the synthesis of bis(alkynyl)calcium derivatives.[8] For straightforward calciations, organocalcium reagents are required and the success of this strategy depends on the kinetic pK_a values[9] and on the availability of suitable reagents. The straightforward and multigram synthesis of bis(trimethylsilylmethyl)calcium provides such a powerful calciation reagent.[10] If a substrate contains several hydrogen atoms of comparable acidity, functional groups often serve as anchors (binding sites) for the metalation reagent and lead to directed ortho metalation (DOM), a typical domain for organolithium and to a lesser extent organomagnesium reagents.[11] Such directed metalations have already been studied using phenylcalcium complexes; these reagents deprotonated 1,3-dimethoxybenzene at the 2-position, yielding tris(2,6-

Scheme 1. Direct and "Classic" Metalation Reactions of Organic Substrates with Acidic Hydrogen Atoms (DMG = Directed Metalation Group)

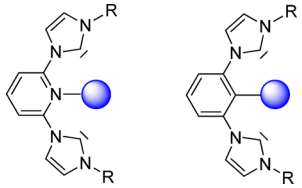


Received: April 20, 2017

DOI: 10.1021/acs.organomet.7b00303
Organometallics XXXX, XXX, XXX−XXX

dimethoxyphenyl)dicalcium iodide.[12] In another example, the deprotonation of 3-bromothiophene gave 3-bromothien-2-ylcalcium complexes which could be crystallized and structurally characterized as the 18-crown-6 adduct of bis(3-bromothien-2-yl)calcium.[13] However, in contrast to the easily achieved ortho lithiation of phenyloxazolines and *N,N*-dimethylbenzamide,[11] ortho calciation proved to be quite challenging and far from a straightforward procedure. Due to our finding that the coordination pocket of 2,6-bis(imidazol-2-ylidene)pyridine exhibits the ideal size to tightly bind calcium ions,[14] we studied the deprotonation of isoelectronic 1,3-bis(imidazol-2-ylidene)-benzene (Scheme 2) and the coordination behavior of its anion

Scheme 2. Comparison of the Isoelectronic Pyridyl and Phenyl Backbones at a Metal Center (Shown in Blue) of the Fragments Ca{NC_5H_3-2,6-$(NHC^R)_2$} (Left) and Ca{C_6H_3-2,6-$(NHC^R)_2$} (Right)



at calcium ions to elucidate the suitability of carbene side arms as directing groups. Furthermore, formation of side products should be excluded as have been reported for alkali-metal-mediated magnesiation reactions leading to metalation at various sites, introduced as normal, abnormal, and "para-normal" reactivity patterns of *N,N′*-disubstituted carbenes.[15]

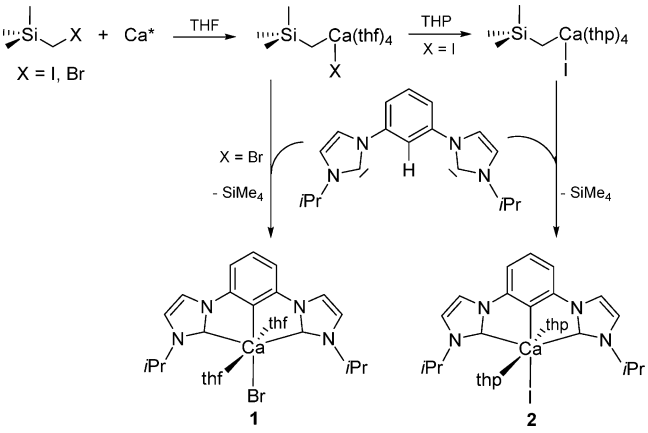
RESULTS AND DISCUSSION

The heavy Grignard reagents Me_3SiCH_2CaX (X = Br, I)[16] are easily accessible on a multigram scale with good yields according to literature procedures, and the dialkylcalcium reagent $Ca(CH_2SiMe_3)_2$[10] can be readily prepared in situ. Due to the straightforward syntheses of these reagents, isolation and purification via crystallization was not necessary. The concentrations of these alkylcalcium solutions were determined by acid−base titration of aliquots. These solutions were used for the calciation studies.

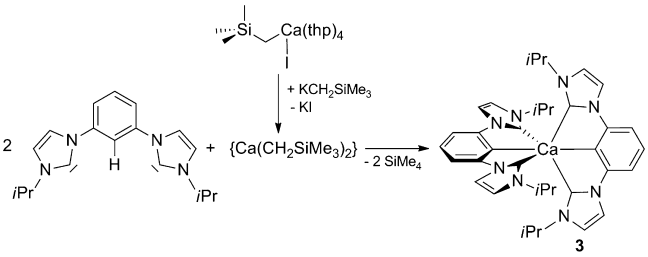
The reaction of 1,3-bis(3-isopropylimidazol-2-ylidene)-benzene, 1,3-$(NHC^{iPr})_2C_6H_4$, with a slight excess of (trimethylsilylmethyl)calcium bromide and iodide in tetrahydrofuran gave the corresponding bis(tetrahydrofuran) adducts of the [2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium halides ($[(thf)_2Ca(X)C_6H_3$-2,6-$(NHC^{iPr})_2]$; X = Br (**1**·2thf), I (**2**·2thf)) with moderate yields (Scheme 3). To improve the crystallization behavior in order to obtain single crystals, [2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium iodide was recrystallized from tetrahydropyran (THP), leading to an exchange of the ligated ether bases, and the bis(thp) complex (**2**·2thp, $[(thp)_2Ca(I)C_6H_3$-2,6-$(NHC^{iPr})_2]$) was isolated.

Calciation of 1,3-bis(3-isopropylimidazol-2-ylidene)benzene with $Ca(CH_2SiMe_3)_2$, prepared in tetrahydropyran according to a literature protocol[10] without intermediate isolation of this dialkylcalcium reagent, led to the formation of ether-free bis[2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium (**3**, $[Ca\{C_6H_3$-2,6-$(NHC^{iPr})_2\}_2]$; Scheme 4). The NMR spectroscopic monitoring of the reaction verified a complete conversion, but this diarylcalcium complex is extremely

Scheme 3. Synthesis of the [2,6-Bis(3-isopropylimidazol-2-ylidene)phenyl]calcium Halides (X = Br (1·2thf), I (2·2thp)) via Metalation of 1,3-Bis(3-isopropylimidazol-2-ylidene)benzene



Scheme 4. Synthesis of Bis[2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium (3) via Reaction of 1,3-Bis(3-isopropylimidazol-2-ylidene)benzene with $Ca(CH_2SiMe_3)_2$



sensitive toward moisture and air and very soluble, hampering a higher crystalline yield.

The NMR spectra show characteristic low-field shifts of the carbene carbons around 200 ppm (Table 1). For the starting

Table 1. Comparison of the $^{13}C\{^1H\}$ Chemical Shifts (ppm) of 1,3-Bis(3-isopropylimidazol-2-ylidene)benzene and Its Lithiated and Calciated Derivatives

compound	$\delta(C_{carbene})$	$\delta(C_{iC})$	$\delta(C_{oC})$	$\delta(C_{mC})$	$\delta(C_{pC})$
C_6H_4-1,3-$(NHC^{iPr})_2$	213.2	128.1	142.5	110.8	115.5
Li-C_6H_3-2,6-$(NHC^{iPr})_2$	200.0	169.8	153.6	112.5	124.6
$[(thf)_2Ca(Br)C_6H_3$-2,6-$(NHC^{iPr})_2]$ (**1**)	197.3	166.7	150.4	108.9	124.9
$[(thp)_2Ca(I)C_6H_3$-2,6-$(NHC^{iPr})_2]$ (**2**)	197.1	165.8	150.2	108.9	125.0
$[Ca\{C_6H_3$-2,6-$(NHC^{iPr})_2\}_2]$ (**3**)	199.9	170.2	151.3	108.7	124.3

1,3-bis(3-isopropylimidazol-2-ylidene)benzene, a chemical shift of $\delta(^{13}C_{carbene}\{^1H\})$ 213.2 ppm was observed, whereas a high-field shift of approximately 15 ppm was found upon coordination to calcium and lithium ions. The chemical shifts of the ipso-carbon atoms of the phenyl ring are again very similar for lithium and calcium complexes, and resonances around 170 ppm were detected. Furthermore, the phenyl carbon atoms, bound to the *N*-heterocyclic carbenes, also experience a significant low-field shift in comparison to 1,3-bis(3-isopropylimidazol-2-ylidene)benzene. In contrast to the phenyl group, the 4- and 5-positioned carbon atoms of the *N*-

DOI: 10.1021/acs.organomet.7b00303
Organometallics XXXX, XXX, XXX−XXX

heterocyclic carbene moieties are not affected by the coordination to these s-block metal ions.

The crystal structures of the calcium complexes **1**–**3** were determined to elucidate steric requirements and shielding of the alkaline-earth metal. The molecular structure and numbering scheme of [2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium bromide (**1**·2thf, $[(thf)_2Ca(Br)C_6H_3\text{-}2,6\text{-}(NHC^{iPr})_2]$) are depicted in Figure 1. The Ca1–$C9_{ipso}$ bond length of 247.0(4)

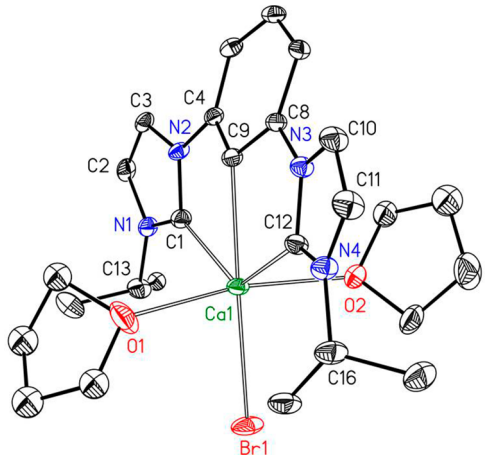


Figure 1. Molecular structure and numbering scheme of [2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium bromide (**1**·2thf). Ellipsoids represent a probability of 30%, and H atoms are neglected for the sake of clarity. Selected parameters: bond lengths (pm), Ca1–Br1 287.81(8), Ca1–O1 240.7(5), Ca1–O2 241.6(3), Ca1–C1 266.1(4), Ca1–C9 247.0(4), Ca1–C12 264.4(4), N1–C1 136.1(4), N2–C1 137.1(5), N3–C12 137.2(5), N4–C12 135.7(5); angles (deg), C1–Ca1–C9 65.76(11), C1–Ca1–C12 132.14(11), C9–Ca1–C12 66.38(11), C9–Ca1–Br1 170.34(9), Ca1–C9–C4 121.2(2), Ca1–C9–C8 119.5(2), C4–C9–C8 113.7(3).

pm is rather short and significantly shorter than the Ca–$C_{carbene}$ distances with an average value of 265.3 pm. The calcium atom is strongly pulled toward the ipso-carbon atom, leading to large N1–C1–Ca1 and N4–C12–Ca1 bond angles of 143.6(3) and 144.6(3)°, respectively. The Ca1–O_{thf} distances lie in the expected range due to lack of severe intramolecular strain. The Ca1–Br1 bond length of 287.81(8) pm is a characteristic value, as also found for other arylcalcium bromides with six-coordinate calcium atoms in distorted-octahedral environments.[13,17] A remarkable feature, however, is the fact that the calcium atom deviates from the aryl plane, leading to an angle sum around the ipso-carbon atom of only 354.4°.

The molecular structure and numbering scheme of [2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium iodide (**2**·2thp) are shown in Figure 2. In this complex, tetrahydropyran molecules are bound to the calcium atom due to an improved crystallization behavior from this ether. Due to weaker Lewis basicity, slightly larger Ca1–O_{thp} distances with an average value of 242.7 pm are observed. This weaker donor strength of the ether ligands leads to an even shorter Ca1–$C9_{ipso}$ bond length of 244.6(7) pm, among the smallest Ca–C bond lengths ever found in molecular organocalcium compounds. Even in ether-free $[Ca\{C(SiMe_3)_3\}_2]$ with a two-coordinate calcium atom and a slightly bent C–Ca–C moiety (C–Ca–C 149.7(6)°), longer Ca–C distances of 245.9(9) pm have been observed.[18] The dialkylcalcium complex $[(diox)_2Ca\{CH(SiMe_3)_2\}_2]$ with a four-coordinate calcium center also exhibits

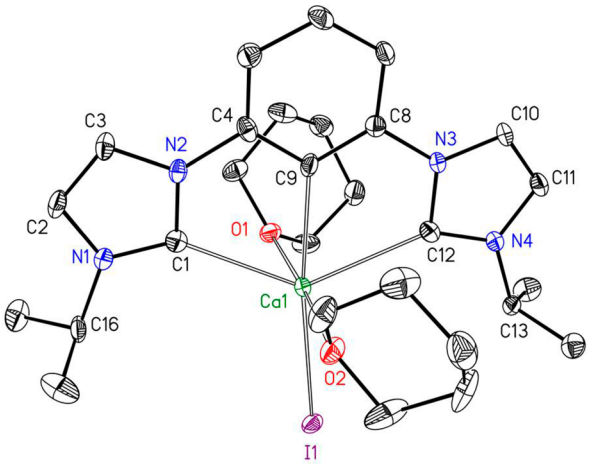


Figure 2. Molecular structure and numbering scheme of [2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium iodide (**2**·2thp). Ellipsoids represent a probability of 30%, and H atoms are omitted for clarity. Selected parameters: bond lengths (pm), Ca1–I1 308.40(13), Ca1–O1 243.4(5), Ca1–O2 242.1(6), Ca1–C1 261.3(7), Ca1–C9 244.6(7), Ca1–C12 259.1(7), N1–C1 134.6(9), N2–C1 137.5(9), N3–C12 138.6(9), N4–C12 137.0(9); angles (deg), C1–Ca1–C9 66.1(2), C1–Ca1–C12 133.2(2), C9–Ca1–C12 67.1(2), C9–Ca1–I1 172.7(2).

longer Ca–C bonds of 248.3(5) pm.[19] Furthermore, longer Ca–C bond lengths are also observed for monomeric and dimeric calcium methanediides due to the stabilization of these complexes by charge delocalization into peripheric diphenylphosphoryl substituents.[20] This short Ca1–$C9_{ipso}$ bond in **2**·2thp has the effect of pulling the calcium atom into the coordination pocket, also enforcing small Ca1–$C_{carbene}$ values (average 260.2 pm) and large N1–C1–Ca1 and N4–C12–Ca1 bond angles of 142.6(5) and 144.2(5)°, respectively. The Ca1–I1 bond length of 308.4(1) pm lies in the large range of characteristic values;[13,17,21] the quite large variation of Ca–I distances is caused by the softness of the iodide and, hence, its polarizability.

The molecular structure and numbering scheme of bis[2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium (**3**) is depicted in Figure 3. The asymmetric unit consists of two molecules A and B; due to the similarity of these molecules only molecule B is shown in this representation. Due to the rather small bite of the tridentate aryl base, the calcium is in a distorted-octahedral environment and is bound exclusively to carbon atoms. The Ca1–C_{ipso} distances are longer (average values: A, 249.3 pm; B, 251.8 pm) than those observed for the heteroleptic arylcalcium halides, verifying enhanced intramolecular strain. This finding is in agreement with elongated Ca1–$C_{carbene}$ distances with average values of 266.3 and 266.7 pm for molecules A and B, respectively. A comparison of $[Ca\{C_6H_3\text{-}2,6\text{-}(NHC^{iPr})_2\}_2]$ (**3**) with $[(thf)Ca\{NC_5H_3\text{-}2,6\text{-}(NHC^{Mes})_2\}_2]$[14] shows significant differences. The Ca–N_{Py} distances to the pyridyl backbones exhibit only slightly larger values of 252.4(3) and 260.7(3) pm (in comparison to Ca–C_{ipso} of **3**); however, intramolecular π stacking of the mesityl groups attached to the NHC fragments opens a coordination gap for an additional thf molecule. The outer N-bound isopropyl groups attached to the NHC moieties hinder such an approach between the ligands.

In Table 2, selected bond lengths of arylcalcium complexes are given. For comparison, selected alkylcalcium derivatives and

DOI: 10.1021/acs.organomet.7b00303
Organometallics XXXX, XXX, XXX–XXX

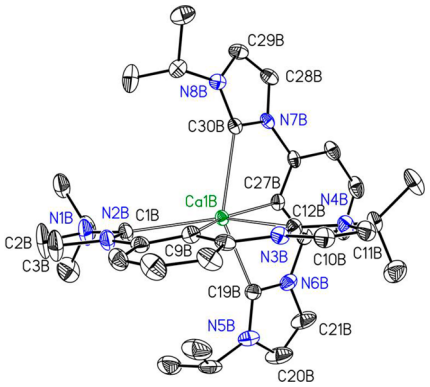


Figure 3. Molecular structure and numbering scheme of bis[2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium (**3**). Ellipsoids represent a probability of 30%, and H atoms are neglected for the sake of clarity. Selected parameters of molecule A [molecule B]: bond lengths (pm), Ca1−C1 269.6(3) [270.4(3)], Ca1−C9 248.7(3) [251.5(3)], Ca1−C12 265.6(3) [263.8(3)], Ca1−C19 265.6(3) [263.2(3)], Ca1−C27 249.8(3) [252.0(3)], Ca1−C30 264.3(3) [269.3(3)]; angles (deg), C1−Ca1−C9 65.34(10) [64.71(11)], C1−Ca1−C12 130.68(10) [129.73(10)], C9−Ca1−C12 65.35(10) [65.35(10)], C19−Ca1−C27 65.41(10) [64.84(10)], C19−Ca1−C30 130.07(10) [129.00(10)], C27−Ca1−C30 65.18(11) [64.55(10)], C9−Ca1−C27 156.45(10) [158.24(11)].

ether adducts of calcium dihalides are included. From these values the influence of the donor strength of the ether coligands is evident. Even though the Ca−O bond lengths vary in a rather narrow range, a characteristic influence on the distances between calcium and the anion (halide or aryl) is observed. The weaker Lewis basicity of thp in comparison to thf leads to a significant shortening of the corresponding Ca−X (X = Br, I) and Ca−C bond lengths. Furthermore, also the influence of the halide (Br or I) on the Ca−C bond lengths in heteroleptic Grignard-type complexes can easily be elucidated. In arylcalcium halides, the Ca−C distance is smaller for the iodides, whereas this tendency seems to be reversed for alkylcalcium halides. In addition to these electronic effects, steric requirements cannot be neglected completely. Generally, smaller coordination numbers lead to shorter Ca−C and Ca−X bonds. However, this influence is reduced because smaller coordination numbers are usually stabilized with bulky substituents at the periphery of the molecule, which also cause intramolecular strain. This intramolecular steric repulsion between the bulky ortho substituents causes an elongation of the Ca−C bonds of diarylcalcium **3**. In addition, poorly shielded calcium ions which are highly Lewis acidic often undergo agostic interactions with σ bonds of organic substituents.

CONCLUSION

In this project, we demonstrated that (trimethylsilylmethyl)-calcium halides (heavy Grignard reagents) as well as homoleptic bis(trimethylsilylmethyl)calcium are valuable metalation (calciation) reagents. The metalation force of these alkylcalcium derivatives allows efficient deprotonation of substituted arenes in a directed ortho metalation, using *N*-heterocyclic carbenes as directing groups. Side reactions, found for alkali-metal-mediated magnesiation reactions, have not been observed. In addition, ether cleavage reactions or attack of the carbene side arms does not represent a severe challenge in these deprotonation reactions. Therefore, a straightforward calciation of 1,3-bis(3-isopropylimidazol-2-ylidene)benzene in tetrahydrofuran allows the synthesis of [2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium derivatives. In all of these complexes, the calcium centers are in distorted-octahedral environments; two ether molecules (thf or thp) complete the coordination spheres of the heteroleptic arylcalcium halides **1** and **2**, whereas diarylcalcium **3** crystallizes without additional ether molecules.

The 2,6-bis(3-isopropylimidazol-2-ylidene)phenyl groups show the smallest known Ca−C_{ipso} bond lengths in the bis(ether) adducts of heteroleptic [2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium halides (**1**·2thf and **2**·2thp). In the homoleptic complex bis[2,6-bis(3-isopropylimidazol-2-ylidene)phenyl]calcium (**3**), the rather bulky 2,6-bis(3-isopropylimidazol-2-ylidene)phenyl groups induce intramolecular strain that can be recognized at the elongated Ca−C_{ipso}

Table 2. Comparison of Structural Data of Selected Aryl- And Alkylcalcium Compounds (Bond Lengths (pm) and Angles (deg); *p*Tol = 4-Methylphenyl, *p*-Tolyl)

compound	Ca−C	Ca−X	Ca−O	C−Ca−X	ref
$[(thf)_2Ca(Br)C_6H_3\text{-}2,6\text{-}(NHC^{iPr})_2]$ (**1**)	247.0	287.8	240.7, 241.6	170.3	this work
$[(thp)_2Ca(I)C_6H_3\text{-}2,6\text{-}(NHC^{iPr})_2]$ (**2**)	244.6	308.4	242.1, 243.4	172.7	this work
$[Ca\{C_6H_3\text{-}2,6\text{-}(NHC^{iPr})_2\}_2]$ (**3**)	249.3			156.5[a]	this work
$[(thf)_4Ca(Br)C_6H_5]$	258.3	289.0	238.4−239.5	178.5	22
$[(thf)_4Ca(I)C_6H_5]$	257.4	317.8	237.0−239.2	177.4	22
$[(thp)_4Ca(I)C_6H_5]$	251.0	312.1	240.2−244.7	171.8	23
$[(thf)_4Ca(I)C_6H_2\text{-}2,4,6\text{-}Me_3]$	257.4	320.8	239.3−241.9	177.4	24
$[(thf)_3Ca(I)C_6H_3\text{-}2,6\text{-}pTol_2]$	251.7	307.5	234.4−239.0	109.2	25
$[(thp)_4Ca(Br)CH_2SiMe_3]$	250.0	289.8	236.9−241.3	168.7	13
$[(thp)_4Ca(I)CH_2SiMe_3]$	252.7	319.1	238.9−241.1	170.5	16
$[(tmeda)_2Ca(CH_2SiMe_3)_2]$	258.6		261.4[b]	177.3[c]	26
$[(thf)_2Ca\{CH(SiMe_3)_2\}_2]$	249.3		233.9	135.5[c]	27
$[Ca\{C(SiMe_3)_3\}_2]$	245.9			149.7[c]	18
$[(thf)_4CaBr_2]$		288.5	236.4, 236.9	180[d]	28
$[(thp)_4CaBr_2]$		284.0	236.6−237.9	179.3[d]	21
$[(thf)_4CaI_2]$		311.3	234.9, 239.5	180[d]	29
$[(thp)_4CaI_2]$		307.8	235.7−237.5	177.7[d]	21

[a]C9−Ca1−C27 bond angle. [b]Average Ca−N bond length. [c]C−Ca−C bond angle. [d]X−Ca−X bond angle.

DOI: 10.1021/acs.organomet.7b00303
Organometallics XXXX, XXX, XXX−XXX

bonds. In summary, (trimethylsilylmethyl)calcium halides (heavy Grignard reagents) and homoleptic bis(trimethylsilylmethyl)calcium represent valuable metalation reagents with a strong deprotonation power; nevertheless, side reactions do not dominate the reactivity and, therefore, isolation of calciated complexes can be achieved in a straightforward manner. *N*-Heterocyclic carbene side arms are effective directing groups for ortho deprotonation of arenes and are not attacked by these strong metalation reagents. This class of tridentate CCC-*NHC* pincer ligands has gained more and more importance as ligands in catalytic synthesis:[30] e.g., hydroelementation reactions, paying special attention to hard Lewis acid catalyzed hydroamination reactions of unactivated alkenes.[31,32]

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques, if not otherwise noted. THF, THP, and pentane were dried over KOH and subsequently distilled over sodium/benzophenone under a nitrogen atmosphere prior to use. DMSO was dried over CaH_2. Deuterated solvents were dried over sodium, distilled, degassed, and stored under nitrogen over sodium. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance 400 and Fourier 300 spectrometers. Chemical shifts are reported in parts per million relative to $SiMe_4$ as an external standard referenced to the solvent residual proton signal. All substrates were purchased from TCI, ABCR, or Alfa Aesar and used without further purification. The yields given are not optimized. Calcium metal was activated according to a standard procedure.[17e] The starting 2,6-bis(3-isopropylimidazolium)benzene diiodide was prepared according to literature protocols,[32,33] as also described with slight variations in the Supporting Information. Purity was monitored by NMR spectroscopic measurements. Due to the air and moisture sensitivity of the compounds analytical characterizatio, e.g. combustion analyses, were challenging. Despite the fact that V_2O_5 was added, the values of the combustion analysis occasionally deviate from theoretical values, presumably due to carbonate formation and partial loss of intercalated solvent during handling and weighing.

Synthesis of 2,6-Bis(3-isopropylimidazol-2-ylidene)benzene. $KN(SiMe_3)_2$ (1.85 g, 9.25 mmol, 2.05 equiv), dissolved in THF, was added at −78 °C to a suspension of 2.48 g of 2,6-bis(3-isopropylimidazolium)benzene diiodide (4.5 mmol) in 40 mL of THF. Warming to room temperature and stirring overnight led to a light orange suspension. Depending on the quality of applied $KN(SiMe_3)_2$, a deep red suspension is sometimes observed. All solids were removed by filtration. Afterward all volatiles were removed under vacuum, leading to a cream-colored solid. In the case of a red suspension the solid was further washed with diethyl ether, finally leading to 780 mg of 2,6-bis(3-isopropylimidazol-2-ylidene)benzene (60%). ^1H NMR (400.13 MHz, 25 °C, [D$_8$]THF): δ 8.34 (1H, t, $^3J_{H-H}$ = 2.1 Hz), 7.70 (2H, dd, $^3J_{H-H}$ = 2.1 Hz, $^3J_{H-H}$ = 8.1 Hz), 7.53 (2H, d, $^3J_{H-H}$ = 1.8 Hz), 7.31 (1H, t, $^3J_{H-H}$ = 8.1 Hz), 7.11 (2H, d, $^3J_{H-H}$ = 1.8 Hz), 4.49 (2H, sept, $^3J_{H-H}$ = 6.9 Hz), 1.43 (12H, d, $^3J_{H-H}$ = 6.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, [D$_8$]THF): δ 213.2, 142.5, 128.1, 116.5, 116.0, 115.5, 110.8, 51.5, 22.4 ppm.

Synthesis of [2,6-Bis(3-isopropylimidazol-2-ylidene)phenyl]lithium. *n*BuLi solution (1.7 mL of a 1.6 M hexane solution, 2.7 mmol, 1.1 equiv) was added to a suspension of 0.73 g of 2,6-bis(3-isopropylimidazol-2-ylidene)benzene (2.45 mmol, 1 equiv) in 30 mL of pentane. The suspension was stirred for 3 days. The solid was collected and dried, yielding quantitatively 2,6-[bis(3-isopropylimidazol-2-ylidene)phenyl]lithium. ^1H NMR (300.13 MHz, 25 °C, saturated [D$_8$]THF solution): δ 7.25 (2H, d, $^3J_{H-H}$ = 1.5 Hz), 7.02 (1H, dd, $^3J_{H-H}$ = 1.6 Hz), 6.95 (2H, dd, $^3J_{H-H}$ = 1.6 Hz), 6.80 (2H, d, $^3J_{H-H}$ = 1.5 Hz), 3.96 (2H, sept, $^3J_{H-H}$ = 6.7 Hz), 1.05 (12H, d, $^3J_{H-H}$ = 6.7 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, saturated [D$_8$]THF solution): δ 200.0, 169.8, 153.6, 124.4, 116.0, 115.7, 112.4, 51.6, 23.0 ppm.

Synthesis of [2,6-Bis(3-isopropylimidazol-2-ylidene)phenyl]calcium Bromide (1·2thf). (Bromomethyl)trimethylsilane was reduced with activated calcium in THF at 0 °C. The reaction suspension was filtered, yielding a 0.11 M solution of $[(thf)_4Ca(Br)(CH_2SiMe_3)]$ in THF. From this solution, 5 mL (1.32 equiv) was added to a solution of 121 mg of 2,6-bis(3-isopropyl)imidazol-2-ylidene)benzene (0.4 mmol, 1 equiv) in 4 mL of THF at −78 °C. After it was warmed to room temperature, the reaction mixture was filtered and the volume reduced to 4 mL and a few milliliters of pentane were added. Storing of this mother liquor at −40 °C led to the crystallization of 146 mg of $[(thf)_2Ca(Br)C_6H_3\text{-}2,6\text{-}(NHC^{iPr})_2]\cdot 3THF$ ([**1**·2thf]·3THF, 47%). ^1H NMR (300.13 MHz, 25 °C, [D$_8$]THF): δ 7.62 (2H, d, $^3J_{H-H}$ = 1.6 Hz), 7.16 (2H, d, $^3J_{H-H}$ = 1.6 Hz), 6.99 (3H, m), 4.83 (2H, sept, $^3J_{H-H}$ = 6.6 Hz), 3.64 (28 H, m), 1.79 (28H, m), 1.55 (12H, d, $^3J_{H-H}$ = 6.6 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, [D$_8$]THF): δ 197.3, 166.7, 150.4, 124.9, 116.2, 115.1, 108.9, 67.2, 52.6, 25.4, 22.2 ppm. Anal. Calcd: Ca, 5.15. Found: Ca, 5.23. Single crystals were obtained by recrystallization in THF/pentane and storage at −40 °C.

Synthesis of [2,6-Bis(3-isopropylimidazol-2-ylidene)phenyl]calcium Iodide (2·2thp). A 0.14 M THP solution of $[(thp)_4Ca(I)(CH_2SiMe_3)]$ (4.5 mL, 0.65 mmol, 1.05 equiv) was added at −78 °C to a solution of 179 mg of 2,6-bis(3-isopropylimidazol-2-ylidene)-benzene (0.6 mmol, 1 equiv) in 10 mL of THF. After it was warmed to room temperature, the reaction mixture was filtered, the solvent was changed to THP, and this THP solution was stored at −40 °C, leading to crystallization of 213 mg of $[(thp)_2Ca(I)C_6H_3\text{-}2,6\text{-}(NHC^{iPr})_2]\cdot 1.5THP$ (44%) as long needles. ^1H NMR (300.13 MHz, 25 °C, [D$_8$]THF): δ 7.63 (2H, d, $^3J_{H-H}$ = 1.6 Hz), 7.18 (2H, d, $^3J_{H-H}$ = 1.6 Hz), 6.99 (3H, m), 4.91 (2H, sept, $^3J_{H-H}$ = 6.6 Hz), 3.56 (14.4 H, m), 1.62 (7.3 H, m), 1.52 (27H, m) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, [D$_8$]THF): δ 197.1, 165.8, 150.2, 125.0, 116.1, 115.2, 108.9, 68.0, 52.6, 26.6 ppm. Anal. Calcd: Ca, 5.16. Found: Ca, 5.45.

Synthesis of Bis[2,6-bis(3-isopropylimidazol-2-ylidene)-phenyl]calcium (3). KCH_2SiMe_3 (87 mg, 0.68 mmol, 1.05 equiv) was dissolved at 0 °C in 5 mL of THP. A 0.088 M THP solution of $[(thp)_4Ca(I)(CH_2SiMe_3)]$ (7.45 mL, 0.65 mmol, 1 equiv) was added to this solution, immediately forming a suspension. This mixture was stirred at 0 °C for 1 h before 370 mg of 2,6-bis(3-isopropylimidazol-2-ylidene)benzene (1.25 mmol, 1.92 equiv) was added at −40 °C. The suspension was warmed to room temperature, and all solids were removed by filtration. The volume of the filtrate was reduced to ca. 3 mL, and this mother liquor was stored at −40 °C, leading to crystallization of 38 mg of $[Ca\{C_6H_3\text{-}2,6\text{-}(NHC^{iPr})_2\}_2]\cdot 1.1THP$ (8%) in the shape of long needles. ^1H NMR (300.13 MHz, 25 °C, [D$_8$]THF): δ 7.53 (2H, d, $^3J_{H-H}$ = 1.7 Hz), 7.00 (3H, m), 6.93 (2H, d, $^3J_{H-H}$ = 1.7 Hz), 4.04 (2H, sept, $^3J_{H-H}$ = 6.5 Hz), 3.56 (7.1H, m), 1.62 (3.6H, m), 1.52 (7.1H, m), 1.06 (12H, d, $^3J_{H-H}$ = 6.5 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, 25 °C, [D$_8$]THF): δ 199.9, 170.2, 151.3, 124.3, 116.2, 114.4, 108.7, 68.8, 52.1, 26.6, 23.3, 23.1 ppm. Anal. Calcd: Ca, 5.49. Found: Ca, 5.55.

Crystal Structure Determinations. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semiempirical basis using multiple scans.[34−36] The structures were solved by direct methods (SHELXS[37]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[37] and SHELXL-2016[38]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen, nondisordered atoms were refined anisotropically.[37,38] The crystal of **3** contains large voids, filled with disordered solvent molecules. The size of the voids is 2236 Å^3/unit cell. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON,[39] resulting in 621 electrons/unit cell. Crystallographic data as well as structure solution and refinement details are summarized in Table S1 in the Supporting Information. XP[40] and POV-Ray[41] were used for structure representations.

DOI: 10.1021/acs.organomet.7b00303
Organometallics XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00303.

NMR spectra of new compounds, experimental details of the crystal structures and refinement details, and molecular representation of 2,6-bis(3-isopropylimidazolium)benzene diiodide (PDF)

Accession Codes

CCDC 1540814−1540817 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.K. thanks the Fonds der Chemischen Industrie im Verband der Chemischen Industrie e.V. (FCI/VCI, Frankfurt/Main, Germany; fund no. 510259) for a generous Ph.D. stipend and is also grateful to the Graduate Academy of the Friedrich Schiller University Jena for a concluding grant.

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