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Structural Evidence of Strong Calcium−π Interactions to Aryl Substituents Stabilized by Coexistent Agostic Bonds to Alkyl Groups

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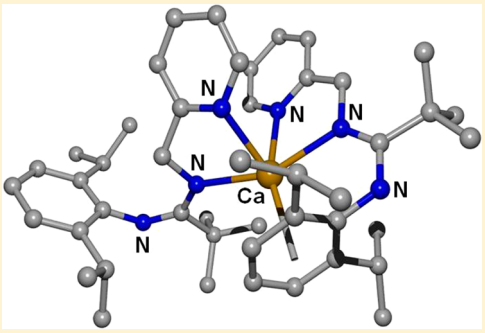
Supporting Information

ABSTRACT: Metalation of 1-(2-furanylmethyl)- (**1a**) and 1-(2-pyridylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diazaprop-2-ene (**1b**) with *n*-butyllithium and potassium bis(trimethylsilyl)amide in tetrahydrofuran (THF) yields the corresponding lithium (**2a**,**b**) and potassium derivatives (**3a**,**b**), with the alkali metals binding to the furanylmethylamido and pyridylmethylamido pockets. The calcium derivatives are accessible via a metathetical approach of the potassium complexes with calcium iodide in THF. Whereas bis[1-(2-furanylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diazaallyl]calcium (**4a**) precipitates as a thf adduct, bis[1-(2-pyridylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diazaallyl]calcium (**4b**) crystallized without solvent coligands. Instead of coordinated solvent molecules, strong calcium−π interactions to an aryl group saturate the coordination sphere. Bidentate 1,2-dimethoxyethane (DME), however, is able to replace this side-on bound aryl group, leading to the dme adduct of bis[1-(2-pyridylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diaallyl]calcium (**4c**). In all of these s-block metal complexes, strong agostic interactions between the cations and the *tert*-butyl groups stabilize these complexes.



INTRODUCTION

Interactions between metal cations and π systems play an important role in chemistry, pharmacy, and biology depending on the softness and hardness of the cations.[1] Calcium cations are considered as quite hard Lewis acids, comparable with lithium cations on the basis of the charge-to-surface ratios of the cations (electrostatic surface potential as quotient q/a of charge q and surface area a of the cation, calculated as $4\pi r^2$). Whereas cation−π interactions are common for the heavy alkali metal ions, lithium cations favor an environment of hard Lewis bases (such as ethers and amines). Nevertheless, intramolecular strain is able to restrict the accessibility of the cations for ethers such as tetrahydrofuran (THF), and complexes with a lithium−π interaction to an aryl group can be stabilized and structurally characterized.[2] Thus, the *anti* configuration of *N*,*N*′-bis(2,6-diisopropylphenyl)pivalamidinate enforces this kind of bonding, whereas in the corresponding calcium complex, this amidinate adopts a heavily strained *syn* configuration avoiding calcium−π interactions (Scheme 1). Similar observations were made for the anilides[3] and phenylphosphanides[4] of the alkaline-earth metals; whereas the barium complexes aggregate not only via bridging nitrogen and phosphorus atoms but also via barium−π interactions to phenyl groups, calcium derivatives avoid this latter kind of bonding.

Despite the challenges in identifying and verifying calcium−π interactions to aryl groups, this bonding type has been assumed in pharmacy and biology on the basis of NMR and other spectroscopic data. The calcium channel antagonist verapamil (α-isopropyl-α-(*N*-methyl-*N*-homoveratryl-γ-aminopropyl)-3,4-dimethoxyphenylacetonitrile hydrochloride) is used clinically in the treatment of several cardiovascular diseases, and on the basis of NMR experiments calcium−π interactions to the phenyl group have been proposed.[5] On the basis of vibrational spectra and as supported by DFT studies, even calcium ions sandwiched between phenyl groups of the Phe-Phe ligand (L-phenylalanyl-L-phenylalanine) have been suggested.[6]

In chemistry numerous theoretical investigations have been performed in order to clarify the interaction between calcium (in all possible oxidation states) and arenes. The interaction energy between elemental calcium and benzene in the electroneutral π complex $[Ca(\eta^6\text{-}C_6H_6)]^0$ is very small, with values of 1.30 and 3.28 kJ mol^{-1} (Table 1).[7] Kang estimated a binding energy of the calcium−benzene complex of 14.5 kJ mol^{-1}, but the formation of the bis(benzene)calcium sandwich complex $[Ca(\eta^6\text{-}C_6H_6)_2]^0$

Scheme 1. Coordination Modes of *N*,*N*′-Bis(2,6-diisopropylphenyl)pivalamidinate at Lithium, Potassium, and Calcium with *syn* (Left) and *anti* Configurations (Right)

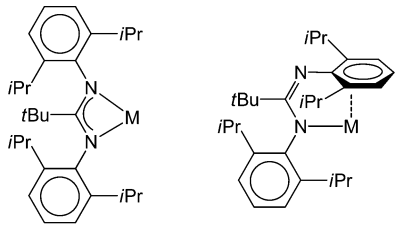


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Table 1. Interaction Energies BE between Calcium and Arene as well as Distances between the Alkaline-Earth Metal and the Side-on-Bound Arene in Complexes of the Type $[(\eta^6\text{-arene})Ae]^{n+}$ [a]

Ae^{n+}	arene	BE/kJ mol^{-1}	Ae−X/pm	method	ref
$Ca^{\pm0}$	benzene	1.30	∼500	B3LYP	7a
$Ca^{\pm0}$	benzene	3.28	378.5[b]	B3LYP	7b
$Ca^{\pm0}$	benzene	14.5	226.5	VASP[c]	8
$[(\eta^6\text{-}C_6H_6)Ca]^{\pm0}$	benzene	67.05	226.5	B3LYP	8
Ca^{+}	benzene	111.2	263.6	B3LYP	10
Ca^{+}	phenyl[d]	101.1	266.3	B3LYP	10
Ca^{2+}	benzene	308.78	247.2	MP2	12
Ca^{2+}	benzene	326.89	246.5	B3LYP	13
Ca^{2+}	benzene	330.87	283.1[b]	B3LYP	14
Ca^{2+}	benzene	340.16	235.9	B3LYP	15
$[(H_2O)Ca]^{2+}$	benzene	272.26	286.1[b,e]	B3LYP	14
$[(H_2O)_2Ca]^{2+}$	benzene	224.51	289.9[b,e]	B3LYP	14
$[(H_2O)_3Ca]^{2+}$	benzene	173.05	294.6[b,e]	B3LYP	14
$[(NC)Ca]^{+}$	benzene	167.00	254.7	MP2	12
$[ClCa]^{+}$	benzene	160.25	255.1	MP2	12
$[FCa]^{+}$	benzene	151.00	255.8	MP2	12
$[(HO)Ca]^{+}$	benzene	150.21	255.9	MP2	12
$[HCa]^{+}$	benzene	141.84	261.0	MP2	12
$[(H_2N)Ca]^{+}$	benzene	139.33	257.8	MP2	12
$[(H_3C)Ca]^{+}$	benzene	133.05	262.2	MP2	12

[a]X represents the centroid of the arene ring. [b]Ca−C distance. [c]Vienna ab initio simulation program (VASP). [d]Triplet $[(\eta^6\text{-}C_6H_5)Ca]^{+}$ complex. [e]Average value.

from calcium and two benzene molecules shows a much larger binding energy of the overall process (Ca + 2 C_6H_6) of 134.1 kJ mol^{-1}.[8] However, the reaction of calcium vapor with benzene leads to C−H activation and yields the extremely sensitive phenylcalcium hydride via insertion of a calcium atom into a C−H bond.[9] Enhancement of the positive charge on calcium also enhances the interaction energy between Ca^+ and benzene, and an interaction energy of 111.2 kJ mol^{-1} has been determined for the π complex $[Ca(\eta^6\text{-}C_6H_6)]^+$.[10] In agreement with the experimental studies of Mochida et al.[9] the σ-bond energy of 256.6 kJ mol^{-1} of Ca^+ to a phenyl radical moiety in $[Ca{-}C_6H_5]^+$ is much larger than the π interaction between Ca^+ and a phenyl unit, suggesting a preference for σ-based interactions.[10] Quantum chemical studies of the neutral dimer $[Ca{-}C_6H_5]_2$ show that the calcium−π interaction to the phenyl group of the other molecule is favored in comparison to the formation of a Ca−Ca bond.[11]

Extensive investigations have been performed on the interaction of Ca^{2+} with benzene. Depending on the basis sets and quantum chemical methods, interaction energies between 292.3 and 340.2 kJ mol^{-1} have been estimated.[12−15] Decreasing size of the alkaline-earth-metal atoms significantly enhances the interaction energy between Ae^{2+} and benzene due to smaller metal−carbon distances; thus, these energies are roughly 50% larger for the magnesium derivative. However, addition of another calcium-bound anionic Lewis base lowers the interaction energy significantly. Depending on X in complexes of the type $[(\eta^6\text{-}C_6H_6)CaX]^+$ the interaction energy between Ca^{2+} and benzene decreases to 133.1 (X = CH_3), 139.3 (X = NH_2), 151.0 (X = F), 160.3 (X = Cl), and 167.0 kJ mol^{-1} (X = CN).[12] Not only anions but also neutral Lewis bases reduce the interaction energy. In complexes of the type $[(\eta^6\text{-}C_6H_6)Ca(OH_2)_n]^{2+}$ the binding energy between calcium(II) and benzene decreases with an increasing number n of calcium-bound water molecules (n = 1, 273.3 kJ mol^{-1}; n = 2, 224.5 kJ mol^{-1}, n = 3, 173.1 kJ mol^{-1}).[14] Furthermore, methyl substituents at the arene enhance its electron density and, consequently, the calcium−π interaction energy increases as well.[16,17]

Transfer of these theoretical results into experimental chemistry requires an environment with Lewis basic reaction conditions because the highly ionic nature of calcium compounds poses solubility challenges which can only be circumvented in polar solvents such as THF. The binding energies of the Ca−O bonds in complexes lie approximately in the same order of magnitude as the calcium−π interactions. In the thf adducts $[(thf)_4CaI_2]$, $[(thf)Ca(Cp)I]$, and $[(thf)_2Ca(Cp)I]$ (Cp = cyclopentadienide) Ca−O binding energies of 108.7, 114.6, and 104.0 kJ mol^{-1}, respectively, have been calculated,[18] which again are much smaller than the Ca−O binding energy in the cationic water adduct $[Ca(OH_2)]^{2+}$ (240.0 kJ mol^{-1}).[14]

Side-on coordination of π systems to calcium(II) ions is observed for aromatic anions such as cyclopentadienyl,[19] phospha- and arsacyclopentadienyl,[20,21] cyclooctatetraenediyl,[22] benzyl,[23] and fluorenyl,[24] with the metallocenes as the most prominent compound class of this kind. The inverse sandwich complex $[\{(thf)_3Ca^I\}_2(\mu\text{-}C_6H_3\text{-}1,3,5\text{-}Ph_3)]$ represents the only isolated molecular calcium(I) complex up to now.[25] Here, the bridging 1,3,5-triphenylbenzene radical anion carries two negative charges. Neutral calcium-bound π systems are very rare; side-on-coordinated bis(trimethylsilyl)butadiyne at decamethylcalcocene exhibits Ca−C distances of 264(2) and 266 (2) pm to the butadiyne moiety.[26] In pentafluorophenylcalcium triazenide with bulky aryl groups at the triazenide anion, one side-on-oriented aryl group is observed, whereas the strontium and barium derivatives show two alkaline-earth-metal−π interactions to aryl groups. Due to steric constrictions, one aryl group acts as a cap to the calcium center with large Ca···C_{arene} contacts of more than 301 pm despite the low coordination number of 4, leading to extremely short Ca−O_{thf} and Ca−C_{C6F5} σ bonds of only 230.8(5) and 249.9(11) pm, respectively.[27] Furthermore, the product of the reaction of $Ba[P(SiMe_3)_2]_2$ with diphenylbutadiyne yields a complex with barium−π interactions to remaining alkyne moieties,[28] whereas the homologous calcium compound shows another reaction pathway.[20]

Stabilization of side-on-bound aryl groups to calcium(II) requires some preconditions. Due to the fact that organocalcium derivatives contain strongly heteropolar bonds and can be considered as ionic compounds, polar and Lewis basic solvents ensure the solubility of these saltlike complexes. Bulky substituents are mandatory in order to prevent aggregation and oligomerization via bridging Lewis bases. Suitable anions include the 1,3-diazaallyl systems with bulky N-bound aryl substituents;[29] large alkyl (amidinates) or diorganylamino groups (guanidinates) at the carbon atom in the 2-position stabilize the needed *anti* orientation of the aryl groups. Thus far, only 1,3-diazaallyl anions with a *syn* configuration have been reported in the calcium-based coordination chemistry of amidinates[30−33] and guanidinates[33−35] as well as 2-diphenylphosphanyl-1,3-diazaallyl anions.[36,37] In addition, asymmetrically substituted amidinates have already been studied as hydrophosphanylation reagents.[38] In addition to shielding substituents at the nitrogen atoms, highly electronegative donor atoms maintain a large positive charge on the calcium atom (which is required to stabilize the calcium−π interactions), whereas organyl groups show a significant covalent bond contribution and, hence, reduce the positive charge on the metal atom. On the basis of our previous work, we altered the

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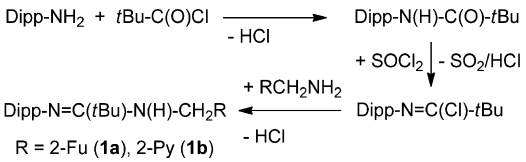
calcium bis[bis(2,6-diisopropylphenyl)amidinates][2,33] by substitution of a 2,6-diisopropylphenyl group with furanylmethyl or pyridylmethyl substituents. This alteration enhances the denticity of these bases, offers a suitable coordination pocket for calcium ions, and also allows the remaining N-bound aryl group to turn toward the cation. Furthermore, electron-donating groups (such as alkyl) at the aryl substituent enhance both the steric shielding and electron density of the π system and, due to the latter effect, additionally strengthen the calcium$-\pi$ interactions.

RESULTS AND DISCUSSION

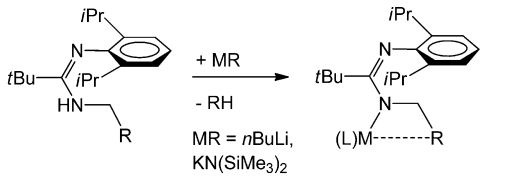
Synthesis. The preparation of bulky tridentate ligands was achieved in the style of a reported protocol.[38] 2,6-Diisopropylphenylamine (Dipp-NH_2) in anhydrous pyridine was treated with pivaloylchloride yielding Dipp-N(H)$-$C(O)*t*Bu according to eq 1. The reaction of this amide with thionyl chloride gave



(1)

nearly quantitatively Dipp-N=CCl(*t*Bu), which was treated either with 2-furanylmethylamine (H_2NCH_2-Fu) or with 2-pyridylmethylamine (H_2NCH_2-Py), leading to the formation of the desired Dipp-N=C(*t*Bu)N(H)CH_2-Fu (**1a**) and Dipp-N=C(*t*Bu)N(H)CH_2-Py (**1b**) in moderate yields of approximately 60%.

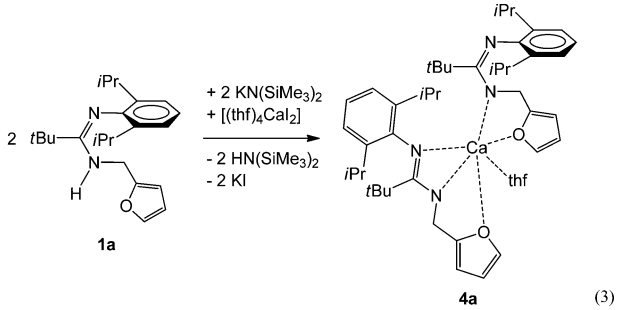
The N$-$H functionalities of these compounds **1** are very acidic, and metalation was achieved with *n*-butyllithium and potassium bis(trimethylsilyl)amide in hydrocarbons according to eq 2. The resulting alkali-metal complexes were only sparingly



(2)

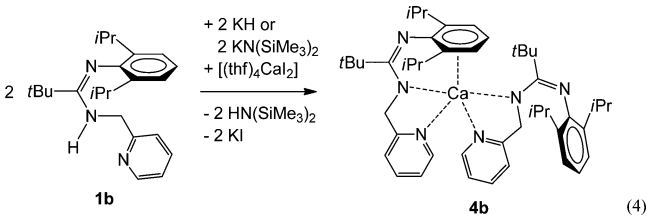
soluble in these solvents and could easily be isolated by filtration. Recrystallization from 1,2-dimethoxyethane (DME) or tetrahydrofuran yielded the crystalline lithium (R = 2-furanyl (**2a**), 64%; R = 2-pyridyl (**2b**), 82%) and potassium complexes (R = 2-furanyl (**3a**), 61%; R = 2-pyridyl (**3b**), 73%).

For the synthesis of calcium complexes a metathetical approach was chosen. The potassium derivatives **3a**,**b** were treated with calcium iodide in tetrahydrofuran (eq 3), giving **4a** with a yield of 37%. THF turned out to be the ideal solvent, because potassium iodide is insoluble in this ether whereas the thf adduct $[(thf)_4CaI_2]$ is soluble, ensuring homogeneous reaction conditions. NMR data of the isolated crystalline compound showed that a thf adduct formed during this reaction. In the $^{13}C\{^1H\}$ NMR spectrum two sets of resonances were observed for the calcium complex **4a**, already pointing toward two structurally different amidinates.



(3)

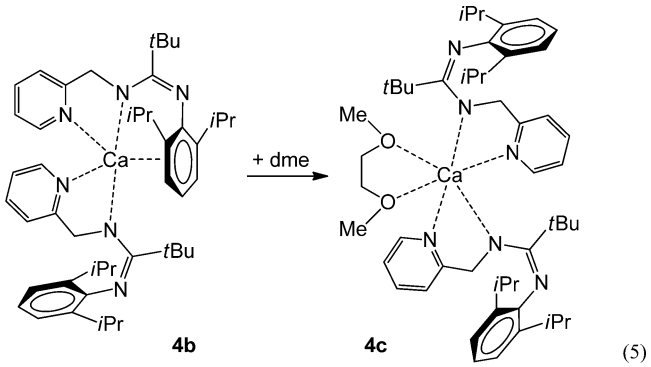
A procedure similar to that presented for the preparation of **4a** gave the calcium derivative **4b** according to eq 4 with a yield of



(4)

86%. Suitable metalation reagents are KH and $KN(SiMe_3)_2$. Surprisingly, a thf-free calcium complex was isolated after the metathesis reaction with $[(thf)_4CaI_2]$, despite the fact that this compound was synthesized in the strong Lewis base THF. Again, several carbon nuclei showed two resonances, supporting two significantly different coordination modes of the amidinate anions.

Whereas monodentate thf bases were not able to replace the calcium(II)$-\pi$ interaction to one of the Dipp groups, the reaction of bidentate dme with **4b** irreversibly yielded the corresponding adduct **4c** with hexacoordinate calcium atoms (eq 5).



(5)

This observation nicely underlines the results of the quantum chemical investigations summarized in the Introduction. The calcium(II)$-\pi$ interaction is favored if only one Ca$-$O bond to an ether molecule can be realized (due to steric shielding of the calcium ion). However, a small bidentate ether forms two Ca$-$O bonds, and hence, this complex rearranges and offers a coordination site for the dme molecule. The formation of the π complex **4b** requires an *anti* configuration of the amidinate anion, which is facilitated by the bulky *tert*-butyl group at the 2-position of the 1,3-diazaallyl moiety.

Molecular Structures. The anions (deprotonated **1a**,**b**) offer three donor atoms for coordination chemistry to cations. Former investigations of the coordination behavior of the 3-(2-furanyl)-5-(2-pyridyl)pyrazolate anion toward mono- and divalent cations showed that the pyridyl-involving coordination site is

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favored.[39] The neutral 3-(2-furanyl)-5-(2-pyridyl)pyrazole forms tetramers in the solid state via hydrogen bridges between pyrazole and pyridyl aza bases, whereas the furanyl group is not involved in the hydrogen bridge network.[40] Due to the bulkiness of the substituents monomeric molecules of **1a**,**b** crystallize without formation of intermolecular hydrogen bridges. The molecular structures and numbering schemes of **1a**,**b** are shown in Figure 1. The N-bound substituents show a *syn* configuration

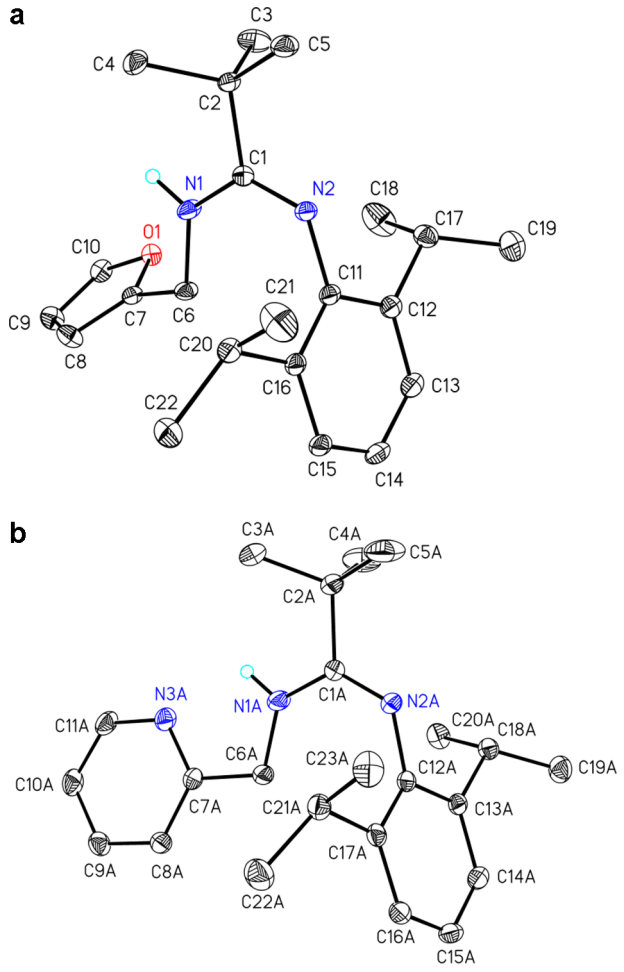

Figure 1. Molecular structures and numbering schemes of (a) **1a** and (b) **1b**. Compound **1b** contains two molecules in the asymmetric unit, but only molecule A is depicted. The ellipsoids represent a probability of 40%; C-bound H atoms are omitted for the sake of clarity.

due to steric repulsion with the *tert*-butyl group. This orientation leads to severe distortions of the coordination spheres of the atoms of the 1,3-diazapropene fragment, and all bond angles within the C_{Dipp}−N−C−N−C_{CH_2} units are significantly widened. The 1,3-diazapropene clearly shows N−C single and double bonds with values of approximately 136 and 128 pm, whereas the N−C distances to the external N-bound groups are greater than 141 pm.

The furanyl and pyridyl bases function as donors, and deprotonated **1a**,**b** act as bidentate chelate ligands toward the alkali metals lithium (**2a**,**b**) and potassium (**3a**,**b**). In Tables 2 and 3, structural parameters of the 1-(2-furanylmethyl)- and the 1-(2-pyridylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diazaallyl anions, respectively, are compared in order to study the influence of the metal atom on these amidinates. In the lithium derivatives **2a**,**b** the amidinate anions bind in a bidentate fashion via N1 and O1, forming a five-membered ring with the lithium atom, as depicted in Figure 2. The coordination spheres of the lithium atoms is saturated by two thf molecules (**2a**) or a bidentate dme molecule (**2b**), leading to distorted-tetrahedral environments.

In complexes **3a**,**b** the amidinate anions bind in a very similar manner to the soft potassium atom; however, one-dimensional coordination polymers form via intermolecular η^6 coordination of the potassium cations to Dipp groups of neighboring molecules. A part of this strandlike structure is depicted in Figure 3. The dme ligand of **3a** shows a two-site disorder, suggesting that there is only moderate crowding at the alkali metal. In order to saturate the coordination spheres, one methyl group of the *tert*-butyl substituent points toward the potassium atom, thus forming strong agostic bonds. The K···C distances to this methyl group (**3a**, K1···C5 324.0(2) pm; **3b**, K1···C11 325.2(2) pm) lie in the same range as the intermolecular potassium−π interactions to the Dipp group (**3a**, K···C between 315.5(2) and 329.7(1) pm; **3b**, K···C between 318.5(2) and 343.4(2) pm).

In contrast to the lithium and potassium derivatives **2a**,**b** and **3a**,**b**, which show rather similar structural features, the calcium derivatives crystallize with significantly different structures. Whereas **4a** precipitates as a thf adduct, complex **4b** does not form a thf complex. The molecular structure and numbering scheme of the calcium complex **4a** is depicted in Figure 4. One amidinate anion (ligand B) acts as a tridentate base, and the other anion (ligand A) binds in a bidentate fashion via the furanylmethylamido unit. Due to rather small bite angles, the coordination sphere of the calcium atom significantly deviates from an octahedron. The different coordination modes influence the structural data. Ligand B shows characteristic features of an amidinate anion such as equal N1B−C1B and N2B−C1B bond lengths of 132.7(3) and 133.8(3) pm as well as rather similar Ca1−N1B (235.3(2) pm) and Ca1−N2B (239.1(2) pm) distances. Equalization of the N1A−C1A (135.0(3) pm) and N2A−C1A (130.6(3) pm) bond lengths is less pronounced. The Ca−O distances vary within a large, although characteristic, range and have values of 235.3(2) (thf), 253.4(2) (ligand A), and 260.8(2) pm (ligand B).

Substitution of the furanyl base by a pyridyl base strengthens the Lewis basic behavior. In the ether-free complex **4b** the ligands bind as bidentate chelates via the pyridylmethylamido functionalities, as also observed for the alkali-metal compounds. The molecular structure and the numbering scheme are depicted in Figure 5. The Ca1−N bond lengths vary within a narrow range of 239.1(2)−244.5(2) pm with only a small effect of the negative charge. The most interesting feature is the intramolecular calcium−π interaction to the Dipp group of ligand B, whereas the Dipp substituent of ligand A is turned to the periphery of the molecule. The Ca1−C_{Dipp} distances vary between 276.4(2) and 313.5(2) pm (average value 295.8 pm) with a calcium−centroid distance of 260.9 pm. The shortest distance is observed to the ipso carbon atom C12B and the longest to the meta carbon C14B. The Ca1−C12B distance is only slightly larger (approximately 5−10%) than Ca−C σ-bond lengths of arylcalcium complexes of the type $[(L)_nCa(Aryl)X]$ (250−266 pm depending on L and X, L = neutral Lewis base such as ethers and amines, X = halide or pseudohalide such as Br^-, I^-, PPh_2^-, $N(SiMe_3)_2^-$).[41] As observed also for the alkali-metal derivatives of this 3-(2,6-diisopropylphenyl)-2-*tert*-butyl-1-(2-pyridylmethyl)-1,3-diazapropenide, the *tert*-butyl group turns one methyl group

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Table 2. Structural Data (Bond Lengths in pm and Angles in deg) of the 1-(2-Furanylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diazaallyl Anions Bound at Hydrogen (1a), Lithium (2a), Potassium (3a), and Calcium (4a)[a]

	1a	2a (A)	2a (B)	3a	4a (A)	4a (B)
M	H	Li	Li	K	Ca	Ca
O1−M		213.9(5)	216.8(4)	270.3(1)	253.4(2)	260.8(2)
N1−M	87(2)	199.0(4)	199.5(4)	279.5(1)	238.8(2)	235.3(2)
N1−C1	137.2(2)	133.8(3)	133.2(2)	132.1(2)	135.0(3)	132.7(3)
N1−C6	146.5(2)	146.4(3)	146.9(3)	146.3(2)	147.3(3)	145.6(3)
N2−M						239.1(2)
N2−C1	128.0(2)	131.7(2)	131.7(2)	133.3(2)	130.6(3)	133.8(3)
N2−C11	141.2(2)	139.1(2)	138.8(2)	138.4(2)	139.6(3)	140.8(3)
C1−C2	153.7(2)	154.8(3)	154.9(3)	155.3(2)	155.4(4)	155.4(4)
N1−C6−C7	111.3(1)	109.2(2)	109.0(2)	110.6(1)	110.0(2)	109.0(2)
C1−N1−C6	128.2(1)	117.1(2)	116.8(2)	117.7(1)	116.0(2)	128.3(2)
N1−C1−N2	128.2(2)	131.9(2)	132.0(2)	132.9(1)	132.5(2)	111.4(2)
N1−C1−C2	113.8(1)	113.8(2)	114.1(2)	114.8(1)	115.4(2)	124.1(2)
N2−C1−C2	118.1(1)	114.2(2)	113.7(2)	112.1(1)	111.9(2)	124.3(2)
C1−C2−C3	108.4(1)	111.0(2)	112.5(2)	107.9(1)	106.5(2)	110.8(3)
C1−C2−C4	111.0(1)	108.1(2)	107.4(2)	110.8(1)	114.5(2)	107.1(2)
C1−C2−C5	110.3(1)	111.7(2)	111.4(2)	112.8(1)	109.8(2)	113.9(2)
C1−N2−C11	124.7(1)	126.7(2)	127.7(2)	126.7(1)	130.9(2)	131.8(2)
N2−C11−C12	118.3(1)	121.6(2)	121.8(2)	122.63(1)	122.9(2)	119.2(2)
N2−C11−C16	120.5(2)	118.8(2)	118.7(2)	119.0(1)	117.0(2)	120.6(2)
C12−C11−C16	121.0(1)	119.2(2)	119.1(2)	118.0(1)	119.3(2)	119.6(2)

[a]For compound **2a** A and B distinguish between two crystallographically independent molecules, and at divalent calcium the two ligands are distinguised by the letters A and B.

Table 3. Structural Parameters (Bond Lengths in pm and Angles in deg) of the 1-(2-Pyridylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diazaallyl Anions Bound at Hydrogen (1b), Lithium (2b), Potassium (3b), and Calcium (4b,c)[a]

	1b (A)	1b (B)	2b	3b	4b (A)	4b (B)	4c (A)	4c (B)
M	H	H	Li	K	Ca	Ca	Ca	Ca
N1−M	87(4)	89(4)	196.1(3)	283.1(1)	239.1(2)	242.9(2)	244.8(2)	244.3(2)
N3−M			200.8(3)	275.7(1)	244.5(2)	243.9(2)	248.1(2)	247.6(2)
N1−C1	135.7(4)	135.5(4)	133.6(2)	131.9(2)	134.6(2)	135.7(2)	135.6(3)	135.5(3)
N1−C6	144.3(4)	145.1(4)	145.8(2)	146.5(2)	147.6(2)	146.0(2)	146.5(3)	146.6(3)
N2−C1	128.1(4)	128.5(4)	131.6(2)	133.4(2)	131.3(2)	131.4(2)	130.9(3)	130.8(3)
N2−C12	140.8(4)	141.3(4)	138.9(2)	138.2(2)	138.8(2)	139.2(2)	139.3(3)	139.4(3)
C1−C2	154.0(4)	153.9(4)	154.9(2)	155.6(2)	155.3(2)	155.1(2)	154.9(3)	155.1(3)
N1−C6−C7	109.9(3)	109.4(2)	112.1(1)	109.3(1)	112.8(1)	114.6(1)	114.8(2)	114.8(2)
C1−N1−C6	130.0(3)	129.1(3)	116.2(1)	118.1(1)	116.2(1)	119.9(1)	114.7(2)	114.9(2)
N1−C1−N2	128.5(3)	129.0(3)	132.2(1)	133.2(2)	132.2(2)	121.5(2)	132.0(2)	132.2(2)
N1−C1−C2	114.1(3)	113.7(3)	115.9(1)	114.8(1)	116.7(1)	125.3(2)	114.4(2)	114.7(2)
N2−C1−C2	117.4(3)	117.4(3)	112.0(1)	111.7(1)	111.0(1)	113.2(1)	113.6(2)	113.1(2)
C1−C2−C3	112.1(3)	109.6(3)	113.6(1)	112.9(1)	114.6(1)	110.1(2)	108.9(2)	111.7(2)
C1−C2−C4	107.5(3)	109.1(3)	109.4(1)	110.3(1)	109.1(1)	112.8(2)	110.9(2)	110.3(2)
C1−C2−C5	110.2(3)	110.8(3)	107.9(1)	107.6(2)	108.3(1)	109.9(2)	111.9(2)	108.8(2)
C1−N2−C12	126.3(3)	128.7(3)	131.3(1)	128.6(1)	130.2(1)	119.2(1)	129.0(2)	130.3(2)
N2−C12−C13	118.4(3)	117.9(3)	122.6(1)	118.4(1)	122.7(2)	119.4(2)	121.2(2)	118.5(2)
N2−C12−C17	120.3(3)	120.7(3)	117.9(1)	123.2(1)	117.7(2)	121.1(2)	119.2(2)	121.2(2)
C13−C12−C17	120.6(3)	120.6(3)	118.7(1)	118.0(1)	119.2(2)	119.3(2)	119.1(2)	119.7(2)

[a]For compound **1b** two crystallographically independent molecules are distinguished by the letters A and B, and at divalent calcium two ligands are distinguished by A and B.

toward the calcium center (Ca1···C3A 294.3(2) pm, Ca···H3A 264(2) and Ca···H3B 247(2) pm), thus blocking the attack of an ether solvent molecule.

The attraction between the calcium atom and the side-on-bound Dipp group of ligand B clearly affects the intraligand bonding parameters. Whereas the C1A−N3A--C12A bond angle of 130.1(1)° is widened due to steric reasons, the C1B−N3B−C12B angle of ligand B shows a significantly smaller value of 119.1(1)°. The calcium−π interaction also leads to a narrowing of the N1−C1−N3 bond angles; whereas steric requirements enforce a large value of 132.3(2)° for ligand A, a much more acute angle of 121.6(2)° is observed for ligand B.

Whereas ether-free compound **4b** was crystallized from a THF solution, the availability of bidentate DME yielded the corresponding ether adduct **4c**. The molecular structure and numbering scheme of this complex is depicted in Figure 6.

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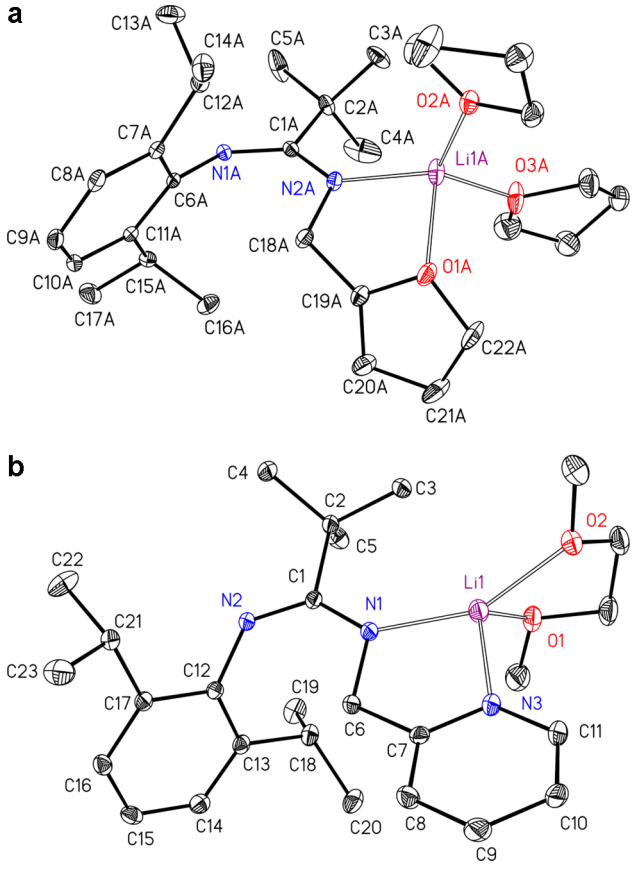

Figure 2. Molecular structures and numbering schemes of (a) **2a** and (b) **2b**. The asymmetric unit of **2a** consists of two molecules A and B; only molecule A is depicted. The ellipsoids represent a probability of 40%; H atoms are neglected for the sake of clarity.

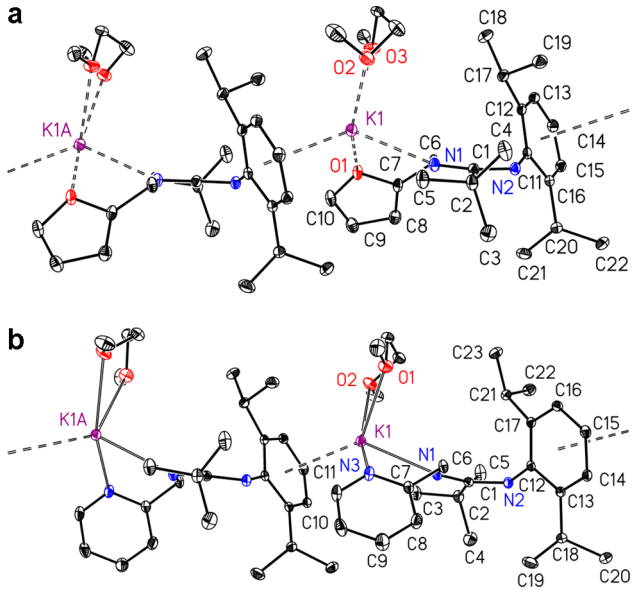

Figure 3. Cutouts of the strand-like structures of (a) **3a** and (b) **3b**. The ellipsoids represent a probability of 40%; H atoms are omitted for the sake of clarity. The intermolecular potassium−π interaction to a Dipp group is clearly shown.

Due to the crowded environment of the calcium center, rather large Ca−O (average Ca−O 252.8 pm) and Ca−N distances (average Ca−N 246.2 pm) are observed. As found for the alkali metal

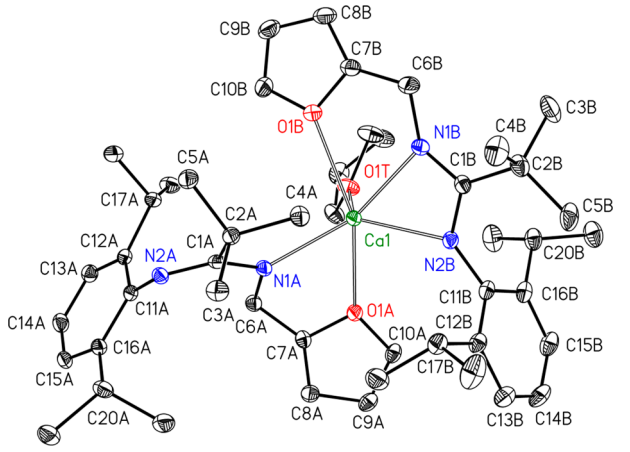

Figure 4. Molecular structure and numbering scheme of **4a**. The calcium-bound amidinate ligands are distinguished by the letters A and B. The ellipsoids represent a probability of 40%; H atoms are neglected for the sake of clarity.

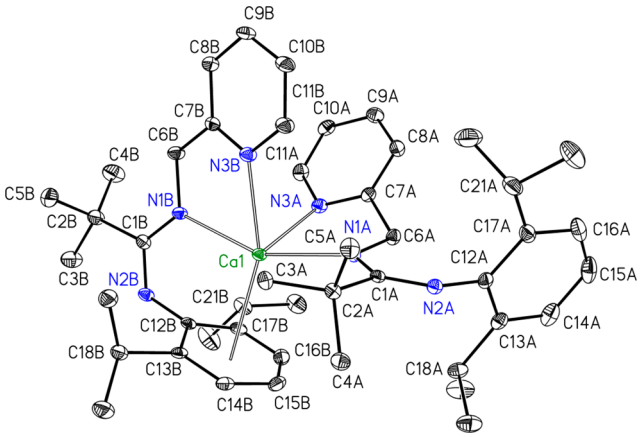

Figure 5. Molecular structure and numbering scheme of **4b**. The amidinate ligands are distinguished by the letters A and B; only ligand B shows a strong intramolecular calcium−π interaction to an aryl group. The ellipsoids represent a probability of 40%; H atoms are neglected for the sake of clarity.

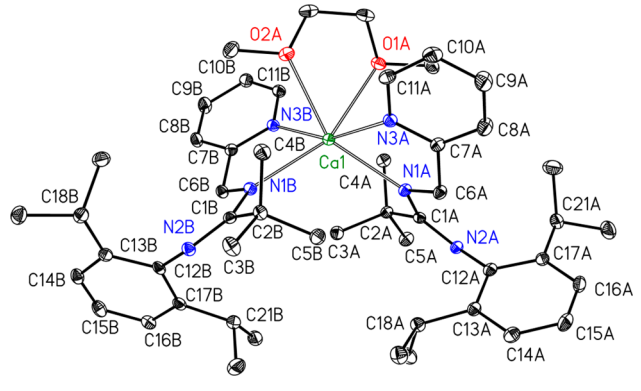

Figure 6. Molecular structure and numbering scheme of **4c**. The amidinate ligands are distinguished by the letters A and B; H atoms are not shown. The ellipsoids represent a probability of 40%. The distortion of the octahedral environment of the calcium center arising from the rather small bite angles of the bidentate ligands is clearly shown.

compounds, the bulky ligands bind via the 2-pyridylmethylamido pockets and the demanding Dipp substituents are turned to the

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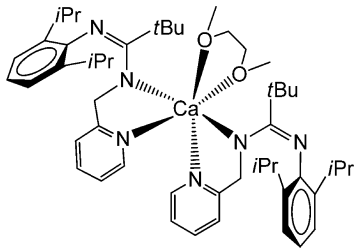
periphery of the molecule. Due to the rather small bite angles of the ligands, the octahedral environment of the calcium atom is severely distorted. On the basis of the centrosymmetric space group, the solid state consists of a racemate of Λ and Δ isomers. Scheme 2 gives a drawing of the Δ isomer.

Scheme 2. Schematic Drawing of the Δ Isomer of 4c



Agostic Bonding. The interactions of C−H, C−C, and Si−C σ bonds with metal atoms play important roles in (often catalytic) activation of those bonds. Recently, an impressive example was presented with alkane coordination at a potassium cation in a dinuclear complex with a rigid hydrophobic pocket; the shortest K···C contacts vary between 321.5(5) and 362(3) pm.[42] Depending on the nature of these bonds, agostic and anagostic bonds are distinguished.[43] The agostic bonds can be considered as a closed three-center−two-electron interaction, leading to M···H−C bond angles between 90 and 140° and short M···H distances. In contrast, the anagostic interaction is characterized by larger M···H−C bond angles of 110−170° and also by longer M···H contacts. Whereas the agostic interaction is a closed three-center bond, the anagostic interaction can be regarded as an open three-center−two-electron bond and is based on electrostatic attraction between the metal cation and slightly negative hydrogen atoms.

Due to the fact that the structure determinations were of excellent quality, the hydrogen atoms that are involved in this type of interaction were found in the electron density map and free isotropic refinement of the positional parameters of the H atoms allowed interpretation of the nature of Ca···H−C interactions of the *tert*-butyl groups. Relevant structural parameters are summarized in Table 4. A cutout of the structure of **4b** is depicted in Figure 7. The Ca···H−C bond angles adopt typical values for agostic bonds with rather short Ca···H and Ca···C bonds of 256 (average value) and 294.3(2) pm, respectively, with the Ca···C distance being comparable to the Ca−C values of the calcium−π interactions. After addition of bidentate 1,2-dimethoxyethane and formation of complex **4c**, an open three-center−two-electron Ca···H−C bond forms with characteristic parameters of an anagostic bonding situation. Thus, the obtuse Ca···H−C angle of 145° significantly elongates the Ca···C bond by 55 pm to an average value of 349.9 pm.

These calcium complexes impressively demonstrate the structural features of agostic and anagostic interactions between an alkaline-earth metal and an alkyl group. These attractive forces also have an effect on the bond angles of the *tert*-butyl group. Due to these interactions, the tetrahedral environment of the quaternary carbon atom C2 (see Table 3) is slightly distorted.

CONCLUSION

Metalation of 1-(2-furanylmethyl)- (**1a**) and 1-(2-pyridylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diazaprop-2-ene (**1b**) succeeds with good yields in tetrahydrofuran with *n*-butyllithium and potassium bis(trimethylsilyl)amide, giving the corresponding

Table 4. Structural Parameters (Bond Lengths in pm and Angles in deg) of the Intramolecular Bonds between the s-Block Metal Ions and the *tert*-Butyl Groups Based on X-ray Structure Determinations[a]

complex	M	M···C	M···H[b]	M···H−C[b]	π(M−X)
2a	Li	305.5(5) (A), 290.2(5) (B)	225 (A), 220 (B)	139.0 (A), 127.9 (B)	
2b	Li	273.6(3)	222(2)	112.2(1)	
3a	K	324.0(2)	273(2), 288(2)	112.9(4), 102.5(4)	293.3(2)
3b	K	325.2(2)	270(2), 295(2)	99.3(2), 114.8(2)	296.4(2)
4a	Ca	297.0(3)	249, 262	109.4, 100.9	
4b	Ca	294.3(2)	247(3), 264(3)	98.1(6), 108.6(6)	260.9(1)
4c	Ca	350.3(2), 352.7(2), 349.5(2), 347.2(2)	265, 268, 265, 262	145.7, 144.5, 144.8, 144.8	

[a]For comparison reasons, also the inter- (M = K) or intramolecular distances (M = Ca) between the metal atom M and the centroid X of the side-on bound Dipp group (metal−π interaction) are added (last column). [b]Values with standard deviations refer to isotropically refined hydrogen atoms, whereas values without esd values refer to H atoms which were included at ideal positions with fixed C−H bond lengths and refined with the riding model.

lithium (**2a**,**b**) and potassium derivatives (**3a**,**b**). In order to produce single-crystal material, an ether exchange proves to be advantageous and the dme adducts readily form after addition of the bidentate ether. The furanylmethyl- and pyridylmethyl-substituted amidinates exhibit coordination behavior very similar to that of the alkali metals. Treatment of calcium iodide in THF with the potassium complexes yields the thf adduct of bis[1-(2-furanylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diazaallyl]calcium (**4a**) and, unexpectedly, solvent-free bis[1-(2-pyridylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diazaallyl]calcium (**4b**). Even recrystallization of **4b** from THF does not lead to the formation of a thf adduct. However, addition of bidentate 1,2-dimethoxyethane irreversibly yields the corresponding dme adduct **4c**.

The bulky *tert*-butyl group in the 2-position compensates the preference of certain configurations (Scheme 3). Thus, in **1a**,**b**, the N-bound substituents show a *syn* configuration as a *Z* isomer. This isomeric structure is maintained in alkali-metal complexes. The hard lithium and calcium cations as well as the soft potassium cation favor the coordination to the furanylmethylamido and pyridylmethylamido pockets rather than a binding to the amidinate units. In the calcium compound **4a**, one ligand expresses the same orientation, whereas the other acts as a tridentate ligand with a syn and *E* arrangement of the substituents. In calcium derivative **4b** the *syn* and *Z* form is realized for one ligand, whereas the other prefers an *anti* and *Z* arrangement. Finally, in **4c** isomerism of the ligands is observed to be similar to that for the alkali-metal derivatives. An *anti* and *E* oriented isomer was not found in the solid state due to strong steric repulsive forces between the *tert*-butyl group and the bulky Dipp substituent.

The soft potassium ion forms intermolecular π interactions to the aryl substituent, leading to strandlike structures in the solid state. It is remarkable that in all these metal complexes one methyl group of the *tert*-butyl moiety is directed toward the metal center. This arrangement effectively shields the metal center and stabilizes low ether contents in the vicinities of the s-block metals. Due to the excellent quality of the structure determinations (which allowed localization of the hydrogen atoms in a difference

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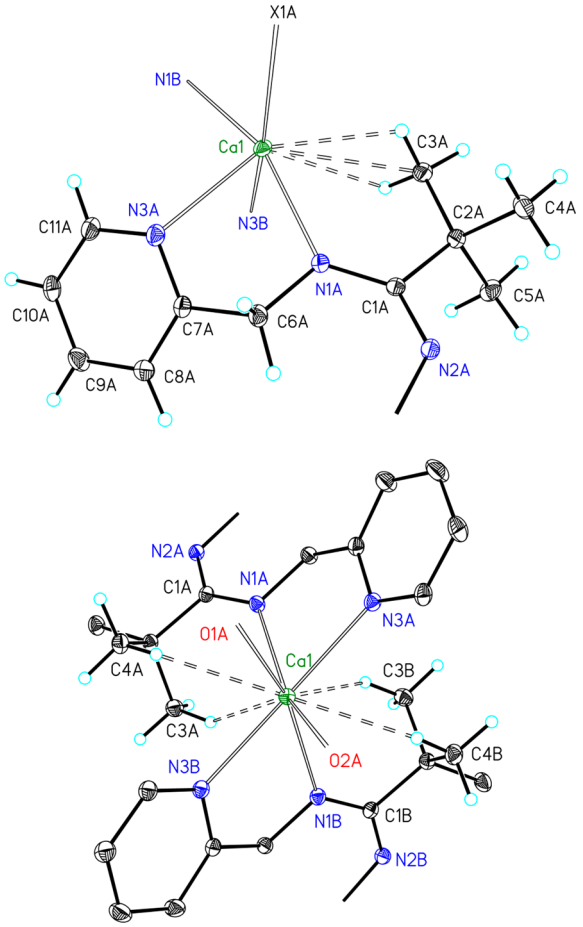
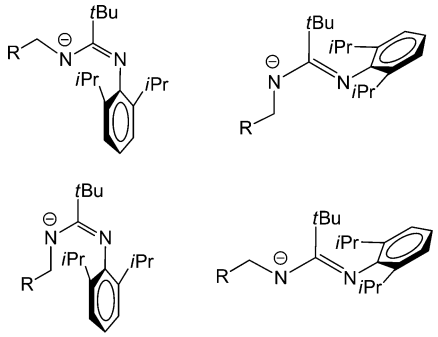


Figure 7. Clarification of the agostic interactions between the calcium atom Ca1 and the *tert*-butyl group in complex **4b** (top, dashed lines) as well as of the anagostic interactions between Ca1 and the *tert*-butyl groups in **4c** (bottom, dashed lines). The ellipsoids represent a probability of 40%; H atoms are drawn with arbitrary radii. When the centroid X1A of the Dipp group and the C3 atom of the *tert*-butyl group are considered as single ligands, the distorted-octahedral environment of Ca1 in **4b** can be recognized.

Scheme 3. Possible *anti* (Top Row) and *syn* Configurations (Bottom Row) of the Diazaallyl Anions (R = 2-Furanyl (Fu), 2-Pyridyl (Py)) as *Z* (Left Column) or *E* Isomers (Right Column) with Respect to the C═N Double Bond Shown



Fourier synthesis and their free isotropic refinement), the geometry and structural parameters of the M···H−C contacts are available, verifying the existence of strong agostic bonds.

Ether-free calcium complex **4b** is shielded by strong intramolecular calcium−π interactions to one aryl (Dipp) substituent with a distance of 260.9 pm between the alkaline-earth metal and the centroid of the arene. The structural parameters nicely correlate to quantum chemical predictions of side-on-bound benzene at calcium ions. These quantum-chemical studies of complexes of the type $[(\eta^6\text{-arene})\text{Ca(L)}_n]^{2+}$ and $[(\eta^6\text{-arene})\text{-CaX}]^+$ (L = neutral Lewis base, X = anionic Lewis base) suggest that the calcium−π interaction energy is slightly larger in comparison to Ca−O_{thf} binding energies; however, if two Ca−O bonds can be formed, the formation of an ether complex is favored as observed for **4c** after addition of bidentate dme. These considerations clarify the role of the 1-(2-pyridylmethyl)-2-*tert*-butyl-3-(2,6-diisopropylphenyl)-1,3-diazaallyl anion. The ligand has to be designed to offer an aryl moiety in the predetermined distance to the metal center in order to obtain sufficiently large metal−π interaction energy competitive with the Ca−O_{ether} binding energy. In addition, bulky groups have to limit the access of the metal center by strong and hard Lewis bases (such as ethers) because this π interaction seems to be competitive only with a single Ca−O_{ether} bond. This requirement is fulfilled by the *tert*-butyl groups in the vicinity of the calcium atom, shielding the metal center and saturating the coordination sphere by strong agostic bonds.

Returning to the initially discussed importance of s-block metal−π interactions in chemistry, pharmacy, and biology, the requirements for stabilizing such bonds might be generalized. On the one hand, soft potassium ions prefer soft π systems such as side-on-bound arene or aryl ligands, in agreement with the Pearson concept of hard and soft acids and bases. On the other hand, hard metal ions such as Ca^{2+} are able to show rather strong metal−π interactions if the competition with more than one hard Lewis base is excluded by steric factors.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over KOH and distilled over sodium/benzophenone under a nitrogen atmosphere; deuterated THF and benzene were dried over sodium, degassed, and saturated with nitrogen. The yields given are not optimized. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AC 200, AC 400, and AC 600 spectrometers. Chemical shifts are reported in parts per million relative to Me_4Si as an external standard. The residual signals of [D_8]THF, chloroform, and [D_6]benzene were used as internal standards. Due to the air and moisture sensitivity, 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.

Synthesis of Dipp-N═C(*t*Bu)N(H)CH_2-Fu (1a). Dipp-NH_2 (9.6 mL, 49.8 mmol) in 80 mL of anhydrous pyridine and pivaloyl chloride (6.2 mL, 50.4 mmol) gave 11.58 g (44.3 mmol, 89%) of Dipp-N(H)CO(*t*Bu). The purity of the product was controlled by NMR spectroscopy. The reaction of Dipp-N(H)CO(*t*Bu) (11.58 g, 44.3 mmol) with $SOCl_2$ (10 mL, 137.8 mmol) yielded 11.65 g (41.6 mmol, 94%) of pure Dipp-N═CCl(*t*Bu). The reaction of Dipp-N═CCl(*t*Bu) (11.65 g, 41.6 mmol) and NH_2CH_2-Fu (4.08 g, 42.0 mmol) led to Dipp-N═C(*t*Bu)N(H)CH_2-Fu (8.33 g, 24.5 mmol, 58%). Physical data of **1a** are as follows. Mp: 340.5 K. ^{1}H NMR ($CDCl_3$, 296.2 K, 400.075 MHz): δ 1.18 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.21 (d, $^3J_{H,H}$ = 7.2 Hz, 6H, *i*Pr CH_3), 1.32 (s, 9H, *t*Bu CH_3), 3.06 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H, *i*Pr C*H*), 3.79 (d, $^3J_{H,H}$ = 5.2 Hz, 2H, $-CH_2-$), 4.53 (broad, 1H, N*H*), 5.96 (d, $^3J_{H,H}$ = 2.8 Hz, 1H, Fu *o*-C*H*), 6.25 (dd, $^3J_{H,H}$ = 3.0 Hz, $^3J_{H,H}$ = 1.8 Hz, 1H, Fu *m*-C*H*), 6.90 (dd, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,H}$ = 7.4 Hz, 1H, Dipp *p*-C*H*), 7.00 (d, $^3J_{H,H}$ = 7.6 Hz, 2H, Dipp *m*-C*H*), 7.26 + 7.29 (m, Fu OC*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 296.8 K, 100.599 MHz): δ 22.6 + 23.2 (*i*Pr CH_3), 28.5 (*i*Pr CH), 29.2 (*t*Bu CH_3), 38.9 (*t*Bu C), 40.9 ($-CH_2-$), 106.9 (Fu *o*-C), 110.4 (Fu *m*-C), 121.3 (Dipp *p*-C), 122.2 (Dipp *m*-C),

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137.4 (Dipp *o*-C), 142.2 (Fu OCH), 146.2 (Dipp *i*-C), 152.1 (Fu *i*-C), 156.4 (^{q}C). ^{1}H NMR (C_6D_6, 296.5 K, 400.075 MHz): δ 1.19 (s, 9H, *t*Bu CH_3), 1.30 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H, *i*Pr CH_3), 3.90 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 2H, *i*Pr C*H*), 3.37 (d, $^{3}J_{H,H}$ = 4.4 Hz, 2H, $-CH_2-$), 4.36 (m, broad, 1H, N*H*), 5.68 (d, $^{3}J_{H,H}$ = 3.0 Hz, 1H, Fu *o*-C*H*), 5.92 (dd, $^{3}J_{H,H}$ = 3.0 Hz, $^{3}J_{H,H}$ = 1.8 Hz, 1H, Fu *m*-C*H*), 6.93 (d, $^{3}J_{H,H}$ = 1.2 Hz, 1H, Fu O−C*H*), 7.05 (dd, $^{3}J_{H,H}$ = 8.2 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 1H, Dipp *p*-C*H*), 7.14 (d, $^{3}J_{H,H}$ = 7.6 Hz, Dipp, 2H, *m*-C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 297.1 K, 100.599 MHz): δ 22.6 + 23.5 (*i*Pr CH_3), 29.0 (*i*Pr C*H*), 29.1 (*t*Bu CH_3), 38.9 (*t*Bu *C*), 41.0 ($-CH_2-$), 106.9 (Fu *o*-C), 110.6 (Fu *m*-C), 122.0 (Dipp *p*-C), 122.7 (Dipp *m*-C), 137.4 (Dipp *o*-C), 142.2 (Fu O-CH), 146.5 (Dipp *i*-C), 152.5 (Fu *i*-C), 156.2 (^{q}C). ^{1}H NMR ([D$_8$]THF, 297.2 K, 400.075 MHz): δ 1.13 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.17 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.31 (s, 9H, *t*Bu CH_3), 3.02 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 2H, *i*Pr C*H*), 3.85 (d, $^{3}J_{H,H}$ = 5.6 Hz, 2H, $-CH_2-$), 5.41 (m, broad, 1H, N*H*), 5.94 (d, $^{3}J_{H,H}$ = 2.8 Hz, 1H, Fu *o*-C*H*), 6.22 (dd, $^{3}J_{H,H}$ = 3.0 Hz, $^{3}J_{H,H}$ = 1.8 Hz, 1H, Fu *m*-C*H*), 6.77 (dd, $^{3}J_{H,H}$ = 7.6 Hz, $^{3}J_{H,H}$ = 7.6 Hz, 1H, Dipp *p*-C*H*), 6.92 (d, $^{3}J_{H,H}$ = 7.6 Hz, Dipp, 2H, *m*-C*H*), 7.31 (d, $^{3}J_{H,H}$ = 1.6 Hz, 1H, Fu OC*H*). ^{13}C{^{1}H} NMR ([D$_8$]THF, 297.0 K, 100.599 MHz): δ 22.6 + 23.6 (*i*Pr CH_3), 29.3 (*i*Pr C*H*), 29.4 (*t*Bu CH_3), 39.7 (*t*Bu *C*), 41.1 ($-CH_2-$), 106.9 (Fu *o*-C), 110.9 (Fu *m*-C), 121.6 (Dipp *p*-C), 122.6 (Dipp *m*-C), 137.5 (Dipp *o*-C), 142.7 (Fu OCH), 147.4 (Dipp *i*-C), 154.0 (Fu *i*-C), 157.0 (^{q}C). IR (pure): ν (cm^{-1}) 3420 vw (N−H), 2961 m, 2927 sh, 2867 w, 1650 s, 1587 w, 1503 s, 1452 m, 1431 m, 1397 w, 1381 vw, 1364 w, 1330 m, 1277 w, 1255 m, 1226 sh, 1214 m, 1163 m, 1145 m, 1077 w, 1017 m, 933 w, 912 m, 885 vw, 824 w, 797 m, 763 s, 746 vs, 715 w, 681 vw, 643 vw, 600 w. MS (Micro-ESI in $CHCl_3$ + MeOH, $C_{22}H_{32}N_2O$): calcd 341.259289, found 341.259390. Anal. Calcd for $C_{22}H_{32}N_2O$ (340.51): C, 77.60; H, 9.47; N, 8.22. Found: C, 78.25; H, 10.49; N, 8.48.

Synthesis of [(thf)$_2$Li{(Dipp-N)C(*t*Bu)NCH$_2$-Fu}] (2a). A 1.5 M solution of *n*BuLi in hexane (1.2 mL, 1.8 mmol) was added to a solution of **1a** (0.50 g, 1.5 mmol) in 20 mL of pentane at −78 °C. While it was warmed to room temperature, the solution changed from colorless via orange to red. The solution was stirred for 4 h; meanwhile, formation of a pale orange solid was observed. This precipitate was collected by filtration, consisting of the solvent-free lithium salt (0.405 g, 1.17 mmol, 87%). Recrystallization of 0.20 g (0.58 mmol) of [Li{(Dipp-N)C(*t*Bu)-NCH$_2$-Fu}] from 0.2 mL of THF and storage at −20 °C for several days gave **2a** as colorless crystals. Yield: 0.182 g (0.37 mmol, 64%). Physical data of **2a** are as follows. Dec pt: above 488 K. ^{1}H NMR (C_6D_6, 297.0 K, 400.130 MHz): δ 1.32 (m, 8H, THF CH_2), 1.46 (broad, 12H, *i*Pr CH_3), 1.60 (broad, 9H, *t*Bu CH_3), 3.38 (m, 8H, THF OCH_2), 3.74 (broad, 2H, *i*Pr C*H*), 4.41 (broad, 2H, $-CH_2-$), 5.56 (s, 1H, Fu *o*-C*H*), 5.90 (s, 1H, Fu *m*-C*H*), 6.68 (broad, 1H, Fu O−C*H*), 7.05 (m, 1H, Dipp *p*-C*H*), 7.22 (m, 2H, Dipp *m*-C*H*). ^{13}C{^{1}H} NMR (C_6D_6, 297.0 K, 100.613 MHz): δ 23.4 + 24.3 (broad, *i*Pr CH_3), 25.5 (THF CH_2), 28.7 (broad, *i*Pr C*H*), 31.3 (broad, *t*BuCH_3), 40.3 (broad, *t*Bu *C*), 47.5 (broad, $-CH_2-$), 68.1 (THF OCH_2), 104.0 (Fu *o*-C), 111.5 (Fu *m*-C), 117.7 (broad, Dipp *p*-C), 121.8 (broad, Dipp *m*-C), 138.1 (broad, Dipp *o*-C), 139.4 (broad, Fu OCH), 152.7 (broad, Dipp *i*-C), 160.2 (broad, Fu *i*-C). IR (pure): ν (cm^{-1}) 2957 s, 2869 w, 2361 vw, 1653 m, 1587 vw, 1559 vw, 1539 vw, 1492 s, 1457 m, 1428 s, 1390 w, 1357 m, 1343m, 1328 m, 1309 w, 1248 w, 1211 w, 1188 vw, 1162 vw, 1143 w, 1107 vw, 1075 w, 1012 m, 975 m, 929 w, 884 vs, 804 m, 794 m, 761 vs, 726 sv, 684 vw, 667 vw, 608 vw, 594 w, 505 w, 433 w. MS (Micro-ESI in THF + MeOH): *m*/*z* (%) 347 (4) [M + H]$^+$, 341 (100) [L + H]$^+$. Anal. Calcd for $C_{30}H_{47}N_2O_3Li$ (490.65): C, 73.44; H, 9.65; N, 5.71. Found: C, 71.52; H, 9.32; N, 5.70.

Synthesis of [(dme)K{(Dipp-N)C(*t*Bu)CH$_2$-Fu}] (3a). A solution of **1a** (0.946 g, 2.78 mmol) in 8 mL of toluene was added at room temperature to a solution of KN(SiMe$_3$)$_2$ (0.556 g, 2.79 mmol) dissolved in 15 mL of toluene. A white precipitate formed, and the solution changed from colorless to orange-brown. After the mixture was stirred overnight, the solid was collected and recrystallized from 0.5 mL of DME. Storage at 5 °C for several days gave **3a** as colorless crystals. Yield: 0.797 g (1.7 mmol, 61%). Physical data of **3a** are as follows. Dec pt: above 437 K. ^{1}H NMR ([D$_8$]THF, 297.0 K, 400.130 MHz): δ 1.10 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.16 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.26 (s, 9H, *t*Bu CH_3), 3.20 (broad, 2H, *i*Pr C*H*), 3.27 (s, 6H, DME CH_3), 3.43 (s, 4H, DME CH_2), 3.88 (s, 2H, $-CH_2-$), 5.80 (broad, 1H, Fu *o*-C*H*), 6.18 (s, 1H, Fu *m*-C*H*), 6.50 (broad, 1H, Dipp *p*-C*H*), 6.75 (broad, 2H, Dipp *m*-C*H*), 7.24 (s, 1H, Fu OC*H*). ^{13}C{^{1}H} NMR ([D$_8$]THF, 297.0 K, 100.613 MHz): δ 22.8 + 23.9 (*i*Pr CH_3), 29.1 (*i*Pr C*H*), 30.7 (broad, *t*Bu CH_3), 40.1 (broad, *t*Bu *C*), 44.6 (broad, $-CH_2-$), 59.0 (DME CH_3), 72.8 (DME CH_2), 105.9 (broad, Fu *o*-C), 110.9 (Fu *m*-C), 118.4 (broad, Dipp *p*-C), 121.8 (Dipp *m*-C), 137.4 (Dipp *o*-C), 141.6 (broad, Fu OCH), 151.0 (Dipp *i*-C), 158.4 (Fu *i*-C), 160.8 (^{q}C). IR (pure): ν (cm^{-1}) 2956 w, 2928 sh, 2868 vw, 1507 w, 1483 vs, 1446 m, 1421 vs, 1404 m, 1373 m, 1352 m, 1311 s, 1244 m, 1216 vw, 1204 vw, 1156, 1143 w, 1052 m, 1010 m, 933 w, 914 m, 796 m, 779 s, 749 w, 723 s, 597 w, 528 vw. MS (Micro-ESI in THF + MeOH): *m*/*z* (%) 379 (24) [M + H − dme]$^+$, 341 (100) [L + H]$^+$. Anal. Calcd for $C_{26}H_{41}KN_2O_3$ (468.71): C, 66.63; H, 8.81; N, 5.98. Found: C, 66.84; H, 8.25; N, 7.17.

Synthesis of [(thf)Ca{(Dipp-N)C(*t*Bu)NCH$_2$-Fu}$_2$] (4a). In 70 mL of THF, the reactants **1a** (0.379 g, 1.11 mmol), KN(SiMe$_3$)$_2$ (0.404 g, 2.02 mmol), and CaI$_2$ (0.366 g, 1.25 mmol) were combined and stirred for 24 h. Recrystallization from toluene and storage at −20 °C for several days led to the formation of **4a** as colorless crystals. Yield: 0.324 g (0.41 mmol, 37%). Physical data of **4a** are as follows. Dec pt: above 379 K. ^{1}H NMR (C_6D_6, 297.4 K, 400.075 MHz): δ 1.01 (d, $^{3}J_{H,H}$ = 6 Hz, 6H, *i*Pr CH_3), 1.16 (m, 4H, THF CH_2), 1.20−1.67 (m, broad, 36H, *i*Pr CH_3 + *t*Bu CH_3), 1.24 (s, *t*Bu CH_3), 1.35 (d, $^{3}J_{H,H}$ = 6.8 Hz, *i*Pr CH_3), 1.46 (dd, $^{3}J_{H,H}$ = 8.6 Hz, $^{3}J_{H,H}$ = 8.6 Hz, *i*Pr CH_3), 1.57 (s, *t*Bu CH_3), 3.26 (m, 4H, THF OCH_2), 3.42 + 3.62 (m, broad, 4H, *i*Pr C*H*), 4.37 + 4.71 (m, 4H, $-CH_2-$), 5.43 + 5.63 (s, broad, 2H, Fu *o*-C*H*), 5.78 + 6.08 (s, broad, 2H, Fu *m*-C*H*), 6.98−7.40(m, 8H, Dipp *p*-C*H* + Dipp *m*-C*H* + Fu OC*H*). ^{13}C{^{1}H} NMR (C_6D_6, 296.9 K, 100.599 MHz): δ 23.1 + 23.3 + 24.0 (*i*Pr CH_3), 25.3 (THF, CH_2), 28.4 + 28.9 (*i*Pr CH), 29.9 + 30.7 (*t*Bu CH_3), 40.9 + 41.9 (*t*Bu *C*), 45.4 + 46.4 ($-CH_2$-), 68.5 (THF OCH_2), 104.2 + 104.6 (Fu *o*-C), 111.3 + 112.0 (Fu *m*-C), 118.2 + 121.2 (Dipp *p*-C), 123.7 (broad, Dipp *m*-C), 137.0 + 140.3 (Dipp *o*-C), 140.1 + 140.5 (Fu OCH), 152.0 + 158.4 (broad, Dipp *i*-C), 158.2 + 158.5 (Fu *i*-C), 164.8 + 175.8 (^{q}C). IR (pure): ν (cm^{-1}) 2959 m, 2928 sh, 2869 w, 1734 vw, 1699 vw, 1680 sh, 1665 sh, 1648 vs, 1588 w, 1554 vs, 1505 vs, 1457 vs, 1429 vs, 1397 w, 1318 s, 1256 m, 1212 m, 1164 m, 1147 w, 1075 w, 1017 m, 987 w, 968 w, 935 sh, 315 s, 876 w, 803 m, 799 sh, 792 sh, 763 m, 749 vs, 732 m, 715 s, 679 vw, 601 sh, 592 w. MS (DEI): *m*/*z* (%) 719 (45) [M − dme]$^+$, 675 (25) [M − *i*Pr − dme]$^+$, 379 (100) [M − L − dme]$^+$, 340 (70) [L]$^+$, 298 (87) [L − *i*Pr]$^+$, 244 (31) [L − FMA]$^+$, 81 (97) [FMA − NH]$^+$, 42 (48) [*i*Pr]$^+$. Anal. Calcd for $C_{48}H_{70}N_4O_3Ca$ (791.184): C, 72.87; H, 8.92, 7.08. Found: C, 71.14; H, 8.61; N, 7.29.

Synthesis of Dipp-N=C(*t*Bu)N(H)CH$_2$-Py (1b). The reaction of Dipp-N=CCl(*t*Bu) (6.10 g, 21.8 mmol) with NH$_2$CH$_2$-Py (2.25 mL, 21.9 mmol) gave Dipp-N=C(*t*Bu)N(H)CH$_2$Py (4.8 g, 13.6 mmol, 62%). Physical data of **1b** are as follows. Mp: 374 K. ^{1}H NMR ($CDCl_3$, 297.2 K, 400.075 MHz): δ 1.16 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.18 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.39 (s, 9H, *t*Bu CH_3), 3.06 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 2H, *i*Pr C*H*), 3.82 (d, $^{3}J_{H,H}$ = 4 Hz, 2H, $-CH_2-$), 6.21 (broad, 1H, N*H*), 6.80 (d, $^{3}J_{H,H}$ = 7.6 Hz, 1H, Py *o*-C*H*), 6.92 (dd, $^{3}J_{H,H}$ = 8.2 Hz, $^{3}J_{H,H}$ = 7.2 Hz, 1H, Dipp *p*-C*H*), 7.01 (d, $^{3}J_{H,H}$ = 7.6 Hz, 2H, Dipp *m*-C*H*), 7.12 (dd, $^{3}J_{H,H}$ = 7.0 Hz, $^{3}J_{H,H}$ = 5.2 Hz, 1H, Py *p*-C*H*), 7.53 (ddd, $^{3}J_{H,H}$ = 7.7 Hz, $^{3}J_{H,H}$ = 7.7 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1H, Py *m*-C*H*), 8.51 (d, $^{3}J_{H,H}$ = 4.4 Hz, 1H, Py N−C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 297.0 K, 100.599 MHz): δ 22.6 + 23.2 (*i*Pr CH_3), 28.5 (*i*Pr CH), 29.4 (*t*Bu CH_3), 39.1 (*t*Bu C), 47.0 ($-CH_2-$), 121.1 (Dipp *p*-C), 121.9 (Dipp *m*-C), 122.0 (Py *o*-C), 122.1 (Py *p*-C), 136.5 (Py *m*-C), 137.9 (Dipp *o*-C), 146.9 (Dipp *i*-C), 148.9 (Py N-CH), 156.8 (Py *i*-C), 157.1 (^{q}C). ^{1}H NMR (C_6D_6, 297.2 K, 400.075 MHz): δ 1.27 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.33 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.47 (s, 9H, *t*Bu CH_3), 3.34 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 2H, *i*Pr C*H*), 3.82 (d, $^{3}J_{H,H}$ = 4 Hz, 2H, $-CH_2-$), 6.12 (d, $^{3}J_{H,H}$ = 7.8 Hz, 1H, Py *o*-C*H*), 6.46 (dd, $^{3}J_{H,H}$ = 6.8 Hz, $^{3}J_{H,H}$ = 5.2 Hz, 1H, Py *p*-C*H*), 6.69 (m, broad, 1H, NH), 6.76 (ddd, $^{3}J_{H,H}$ = 7.7 Hz, $^{3}J_{H,H}$ = 7.6 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1H, Py *m*-C*H*), 7.11−7.20 (m, 3H, Dipp *p*-C*H* + Dipp *m*-C*H*), 8.24 (d, $^{3}J_{H,H}$ = 4.8 Hz, 1H, Py NC*H*). ^{13}C{^{1}H} NMR (C_6D_6, 297.1 K, 100.599 MHz): δ 22.6 + 23.6 (*i*Pr CH_3), 29.0 (*i*Pr CH), 29.4 (*t*Bu CH_3), 39.3 (*t*Bu C), 47.1 ($-CH_2-$), 121.7 (Dipp *p*-C), 121.8 (Py *o*-C), 121.9 (Py *p*-C), 122.5 (Dipp *m*-C), 136.2 (Py *m*-C), 138.1 (Dipp *o*-C), 147.5 (Dipp *i*-C), 148.7 (Py NCH), 156.6 (Py *i*-C), 157.0 (^{q}C). ^{1}H NMR ([D$_8$]THF, 297.0 K, 400.130 MHz): δ

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1.13 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, *i*Pr CH_3), 1.38 (s, 9H, *t*Bu CH_3), 3.06 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H, *i*Pr C*H*), 3.86 (d, $^3J_{H,H}$ = 4.4 Hz, 2H, −CH_2−), 6.50 (m, broad, 1H, N*H*), 6.81−6.84 (m, 2H, Py *o*-C*H* + Dipp *p*-C*H*), 6.94 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, Dipp *m*-C*H*), 7.13 (dd, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 6.2 Hz, 1H, Py *p*-C*H*), 7.56 (ddd, $^3J_{H,H}$ = 7.6 Hz, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H Py *m*-C*H*), 8.47 (d, $^3J_{H,H}$ = 4.4 Hz, 1H, Py N−C*H*). $^{13}C\{^1H\}$ NMR ([D_8]THF, 297.1 K, 100.599 MHz): δ 22.6 + 23.6 (*i*Pr CH_3), 29.3 (*i*Pr *C*H), 29.6 (*t*Bu CH_3), 39.8 (*t*Bu *C*), 47.8 (−CH_2−), 121.7 (Dipp *p*-C), 122.4 (Py *o*-C + Py *p*-C), 122.9 (Dipp *m*-C), 137.2 (Py *m*-C), 138.1 (Dipp *o*-C), 147.9 (Dipp *i*-C), 149.6 (Py NCH), 157.5 (Py *i*-C), 157.9 (^{q}C). IR (pure): ν (cm^{-1}) 3379 w (NH), 2961 w, 2924 sh, 2866 vw, 1649 vs, 1589 w, 1570 w, 1499 m, 1479 m, 1451 w, 1432 s, 1395 vw, 1381 vw, 1357 w, 1330 w, 1258 w, 1227 vw, 1207 w, 1151 vw, 1060 vw, 1045 vw, 997 vw, 949 w, 935 sh, 802 w, 786 w, 753 vs, 730 w, 680 vw, 555 w, 529 w, 431 m, 422 sh, 414 sh. MS (Micro-ESI in MeOH, $C_{23}H_{33}N_3$): calcd 352.275273, found 352.276130. Anal. Calcd for $C_{23}H_{33}N_3$ (351.53): C, 78.58; H, 9.46; N, 11.95. Found: C, 78.04; H, 10.09; N, 11.74.

Synthesis of [(dme)Li{(Dipp-N)C(*t*Bu)NCH$_2$-Py}] (2b). A solution of *n*BuLi (0.74 mL, 1.84 mmol, 2.5 M) in hexane was added at −78 °C to a solution of **1b** (0.538 g, 1.53 mmol) dissolved in 30 mL of heptane. While it was warmed to room temperature, the solution changed to brown-red. After the mixture was stirred for 67 h, 0.56 mL of DME was added and a solid precipitated immediately. The pale yellow-green solid was collected and recrystallized from 1 mL of DME. Storage at 5 °C for several days led to **2b** as colorless crystals. Yield: 0.559 g (1.25 mmol, 82%). Physical data of **2b** are as follows. Dec pt: above 375 K. ^{1}H NMR ([D_8]THF, 297.6 K, 400.075 MHz): δ 1.09 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.10 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.30 (s, 9H, *t*Bu CH_3), 3.27 (s, 6H, DME CH_3), 3.32 (sept, $^3J_{H,H}$ = 6.8 Hz, 2H, *i*Pr C*H*), 3.43 (s, 4H, DME CH_2), 4.22 (s, 2H, −CH_2−), 6.44 (t, $^3J_{H,H}$ = 7.6 Hz, 1H, Dipp *p*-C*H*), 6.68−6.70 (broad, 1H, Py *o*-C*H*), 6.71 (d, $^3J_{H,H}$ = 7.6 Hz, 2H, Dipp *m*-C*H*), 7.05 (ddd, $^3J_{H,H}$ = 6.2 Hz $^3J_{H,H}$ = 6.2 Hz, $^4J_{H,H}$ = 0.8 Hz, 1H, Py *p*-C*H*), 7.49 (ddd, $^3J_{H,H}$ = 7.7 Hz, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.9 Hz, 1H Py *m*-C*H*), 8.31 (dd, $^3J_{H,H}$ = 5.0 Hz, $^4J_{H,H}$ = 0.8 Hz, 1H, Py N−C*H*). $^{13}C\{^1H\}$ NMR ([D_8]THF, 298.2 K, 100.599 MHz): δ 22.9 + 24.1 (*i*Pr CH_3), 29.0 (*i*Pr *C*H), 31.5 (*t*Bu CH_3), 40.4 (*t*Bu *C*), 57.4 (−CH_2), 59.0 (DME CH_3), 72.8 (DME CH_2), 116.1 (Dipp *p*-C), 120.9 (Dipp *m*-C) 121.3 (Py *o*-C), 123.3 (Py *p*-C), 137.3 (Py *m*-C), 137.4 (Dipp *o*-C), 147.8 (Py NCH), 154.1 (Dipp *i*-C), 165.4 (Py *i*-C), 167.8 (^{q}C). IR (pure): ν (cm^{-1}) 2954 w, 2865 sh, 1653 vw, 1599 w, 1571 w, 1534 vs, 1479 m, 1457 m, 1425 s, 1417 s, 1385 m, 1367 m, 1345 s, 1315 w, 1285 w, 1259, w, 1243 w, 1216 w, 1195 m, 1171 w, 1153 w, 1139 vw, 1123 m, 1106 w, 1084 vs, 1028 w, 1013 w, 977 vw, 951 m, 932 w, 885 vw, 867 m, 834 vw, 814 w, 796 w, 783 w, 7.63 m, 767 vs, 734 m, 725 m, 682 vw, 646 w, 620 w, 586 w, 561 w, 535 w, 504 m, 430 m. MS (Micro-ESI in $CHCl_3$ + MeOH): *m*/*z* (%) 358 (17) [M + H − dme]$^+$, 352 (100) [L + H]$^+$, 244 (48) [L + H − AMP]$^+$. Anal. Calcd for $C_{29}H_{47}N_3O_3Li$ (492.65): C, 70.70; H, 9.62; N, 8.53. Found: C, 70.56; H, 9.16; N, 9.11.

Synthesis of [(dme)K{(Dipp-N)C(*t*Bu)NCH$_2$-Py}] (3b). A solution of **1b** (0.51 g, 1.45 mmol) dissolved in 10 mL of toluene was added at room temperature to a solution of KN(SiMe_3)$_2$ (0.29 g, 1.45 mmol) dissolved in 10 mL of toluene. A white precipitate formed, and the solution changed from colorless via yellow to green. After the mixture was stirred overnight, the solid was collected. Recrystallization from 0.5 mL of DME and storage at 5 °C for several days gave **3b** as colorless crystals. Yield: 0.51 g (1.06 mmol, 73%). Physical data of **3b** are as follows. Dec pt: above 344 K. ^{1}H NMR ([D_8]THF, 297.0 K, 400.130 MHz): δ 1.11 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.14 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, *i*Pr CH_3), 1.28 (s, 9H, *t*Bu CH_3), 3.22−3.28 (m, 2H, *i*Pr C*H*), 3.28 (s, 6H, DME CH_3), 3.44 (s, 4H, DME CH_2), 3.98 (s, 2H, −CH_2−), 6.50 (m, broad, 1H, Py *o*-C*H*), 6.73 (d, $^3J_{H,H}$ = 7.6 Hz, 1H, Dipp *p*-C*H*), 6.77 (d, $^3J_{H,H}$ = 7.6 Hz, 2H, Dipp *m*-C*H*), 6.98 (dd, $^3J_{H,H}$ = 6.0 Hz $^3J_{H,H}$ = 6.0 Hz, 1H, Py *p*-C*H*), 7.43 (dd, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,H}$ = 7.4 Hz, 1H Py *m*-C*H*), 8.32 (d, $^3J_{H,H}$ = 4.0 Hz, 1H, Py NC*H*). $^{13}C\{^1H\}$ NMR ([D_8]THF, 297.0 K, 100.613 MHz): δ 23.0 + 24.1 (*i*Pr CH_3), 29.1 (*i*Pr *C*H), 31.2 (broad, *t*Bu CH_3), 40.4 (*t*Bu *C*), 53.9 (−CH_2), 59.0 (DME CH_3), 72.3 (DME CH_2), 116.7 (broad, Dipp *p*-C), 121.5 (Py *o*-C + Dipp *m*-C), 123.7 (Py *p*-C), 136.8 (Py *m*-C), 137.7 (Dipp *o*-C), 149.0 (Py N-CH), 153.1 (Dipp *i*-C), 162.7 (^{q}C). IR (pure): ν (cm^{-1}) 2955 w, 2866 vw, 1653 vw, 1591 w, 1570 vw, 1488 vs, 1458 m, 1434 m, 1420 vs, 1402 m, 1372 w, 1362 w, 1350 w, 1322 m, 1299 w, 1246 w, 1216 w, 1095 vw, 1049 m, 1002 w, 934 vw, 832 vw, 810 vw, 782 w, 762 vs, 746 m, 730 vw, 637 vw, 621 w, 556 vw, 534 vw, 463 w, 437 w, 425 w. MS (Micro-ESI in THF + MeOH): *m*/*z* (%) 390 (60) [M + H − dme]$^+$, 352 (37) [L + H]$^+$, 244 (100) [L + H − AMP]$^+$. Anal. Calcd for $C_{27}H_{42}KN_3O_2$ (479.74): C, 67.60; H, 8.82; N, 8.76. Found: C, 67.53; H, 8.85; N, 10.35.

Synthesis of [Ca{(Dipp-N)C(*t*Bu)NCH$_2$-Py}$_2$] (4b). The reaction of **3b** (2.8 g, 7.97 mmol), KN(SiMe_3)$_2$ (1,59 g, 7.97 mmol), and CaI_2 (1.21 g, 4.12 mmol) in 70 mL of THF led to the formation of **4b**. Storage of a saturated toluene solution at −20 °C gave the colorless crystalline product. Yield: 2.62 g (3.54 mmol, 86%). Physical data of **4b** are as follows. Dec pt: above 406 K. ^{1}H NMR (C_6D_6, 297.0 K, 600.130 MHz): δ 0.69−1.71 (m, broad, 42H, *i*Pr CH_3 + *t*Bu CH_3), 1.41 (s, *t*Bu CH_3), 1.77 (s, *t*Bu CH_3), 3.41−3.74 (m, broad, 4H, *i*Pr C*H*), 4.79−5.16 (m, broad, 4H, −CH_2−), 6.24 (dd, $^3J_{H,H}$ = 6.3 Hz, $^3J_{H,H}$ = 6.3 Hz, 2H, Py *p*-C*H*), 6.36−6.48 (m, broad, 2H, Py *o*-C*H*), 6.64−7.44 (m, broad, 8H, Py *m*-C*H* + Dipp C*H*), 7.72 + 7.79 (m, 2H, broad, Py N−C*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 297.0 K, 150.903 MHz): δ 21.75 + 22.9 + 23.7 + 24.2 (broad, *i*Pr CH_3), 28.9 (broad, *i*Pr CH), 31.1 (*t*Bu CH_3), 39.6 + 41.3 (broad, *t*Bu *C*), 54.5 + 55.7 (broad, -CH_2-), 117.7 + 120.7 + 120.9 + 121.0 + 122.0 + 122.5 + 123.7 + 125.0 + 125.7 (Dipp CH + Py *o*-CH + Py *p*-CH), 136.9 (Dipp *o*-CH), 137.7 (Py *m*-CH), 141.2 + 141.7 (broad, Dipp *o*-CH), 146.5 + 148.0 (Py N-CH), 152.6 + 156.1 (Dipp *i*-C), 164.3 (^{q}C), 165.1 + 165.7 (Py *i*-C), 172.4 (^{q}C). IR (pure): ν (cm^{-1}) 2955 m, 2919 sh, 2867 vw, 1653 w, 1603 w, 1588 vw, 1570 w, 1543 vs, 1502 s, 1479 m, 1459 m, 1435 m, 1421 m, 1359 w, 1377 w, 1345 m, 1293 w, 1257 m, 1200 w, 1158 w, 1107 w, 1083 m, 1053 w, 1012 w, 999 m, 933 vw, 879 vw, 834 vw, 804 w, 787 w, 774 m, 757 sh, 748 m, 737 m, 634 vw, 549 vw. MS (DEI): *m*/*z* (%) = 741 (17) [M]$^+$, 698 (13) [M − *i*Pr]$^+$, 389 (10) [M − L]$^+$, 351 (52) [L]$^+$, 308 (100) [L − *i*Pr]$^+$, 294 (20) [L − *t*Bu]$^+$, 244 (44) [L − AMP]$^+$, 186 (49) [Dip-NC]$^+$, 175 (42) [Dipp-N]$^+$, 92 (46) [Ph-N]$^+$. Anal. Calcd for $C_{46}H_{64}CaN_6{\cdot}C_7H_8$ (833.25): C, 76.40; H, 8.87; N, 10.10. Found: C, 76.94; H, 9.36; N, 12.01.

Synthesis of [(dme)Ca{(Dipp-N)C(*t*Bu)NCH$_2$-Py}$_2$] (4c). The reaction of **1b** (0.354 g, 1.01 mmol), KN(SiMe_3)$_2$ (0.412 g, 2.07 mmol), and CaI_2 (0.391 g, 1.33 mmol) in tetrahydrofuran led to the formation of **4b**. Recrystallization from 0.5 mL of DME and storage at 5 °C for several days gave **4c** as colorless crystals. Yield: 0.283 g (0.34 mmol, 34%). Physical data of **4c** are as follows. Dec pt: above 424 K. ^{1}H NMR (C_6D_6, 297.0 K, 600.130 MHz): δ 0.92−1.88 (m, broad, 42H, *i*Pr CH_3 + *t*Bu CH_3), 3.07 (s, 6H, DME CH_3), 3.16 (s, 4H, DME CH_2), 3.36−3.66 (m, broad, 4H, *i*Pr C*H*), 4.20−5.20 (m, broad, 4H, −CH_2−), 6.21−6.60 (m, broad, 4H, Py *o*-C*H* + Py *p*-C*H*), 6.70−6.89 (m, broad, 2H, Py *m*-C*H*), 6.97−7.37 (m, broad, 6H, Dipp C*H*), 7.63−7.91 (m, broad, Py NC*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 297.0 K, 150.903 MHz): δ 22.0 + 23.0 + 24.0 (broad, *i*Pr CH_3), 29.0 (broad, *i*Pr CH), 31.1 (*t*Bu CH_3), 39.8 + 41.2 (broad, *t*Bu *C*), 54.5 + 55.5 (broad, −CH_2−), 59.0 (DME, CH_3), 71.8 (DME, CH_2), 117.6 + 120.5 + 121.0 + 121.9 + 122.6 + 123.6 + 125.1 (Dipp CH + Py *o*-CH + Py *p*-CH), 136.8 (Dipp *o*-CH), 137.7 (Py *m*-CH), 141.4 (broad, Dipp *o*-CH), 146.6 + 147.9 (broad, Py NCH), 152.6 + 155.7 (broad, Dipp *i*-C), 164.4 (^{q}C), 165.1 + 165.6 (Py *i*-C), 172.3 (^{q}C). IR (pure): ν (cm^{-1}) 2656 m, 2920 sh, 2868 vw, 1652 s, 1590 w, 1562 w, 1534 vs, 1506 m, 1478 m, 1457 m, 1432 s, 1405 sh, 1379 w, 1356 sh, 1334 m, 1301 w, 1288 w, 1259 m, 1207 w, 1165 w, 1142 sh, 1102 w, 1061 m 998 w, 936w, 864 w, 802 w, 775 m, 754 vs, 736 sh, 718 sh, 623 w. MS (DEI): *m*/*z* (%) 741 (38) [M − dme]$^+$, 698 (22) [M − *i*Pr − dme]$^+$, 389 (14) [M − L − dme]$^+$, 351 (27) [L]$^+$, 308 (100) [L − *i*Pr]$^+$, 294 (10) [L − *t*Bu]$^+$, 244 (33) [L − AMP]$^+$, 186 (39) [Dipp-NC]$^+$, 175 (35) [Dipp-N]$^+$, 92 (91) [Ph-N]$^+$, 57 (30) [*t*Bu]$^+$. Anal. Calcd for $C_{50}H_{74}N_6O_2Ca$ (831.25): C, 72.25; H, 8.97; N, 10.11. Found: C, 70.54; H, 8.57; N, 10.50.

Structure Determinations. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo K radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[44,45] The structures were solved by direct methods (SHELXS)[46] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[46] The hydrogen atoms bound at the amine group N1 of compound **1b** and all hydrogen

atoms of compounds **1a**−**3a** (with the exception of the disordered dme molecule), **3b**, and **4b** were located by difference Fourier synthesis and refined isotropically. The hydrogen atoms of **4a** and **5b** were included at calculated positions with fixed thermal parameters. All nondisordered, non-hydrogen atoms were refined anisotropically.[46] XP (SIEMENS Analytical X-ray Instruments, Inc.)[47] was used for structure representations.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data for **1a**,**b**, **2a**,**b**, **3a**,**b**, and **4a**−**c** (excluding structure factors). This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-983887 for **1a**, CCDC-983888 for **1b**, CCDC-983889 for **2a**, CCDC-983890 for **2b**, CCDC-983891 for **3a**, CCDC-983892 for **3b**, CCDC-983893 for **4a**, CCDC-983894 for **4b**, and CCDC-983895 for **4c**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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