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Alkaline Earth Metal–Carbene Complexes with the Versatile Tridentate 2,6-Bis(3-mesitylimidazol-2-ylidene)pyridine Ligand

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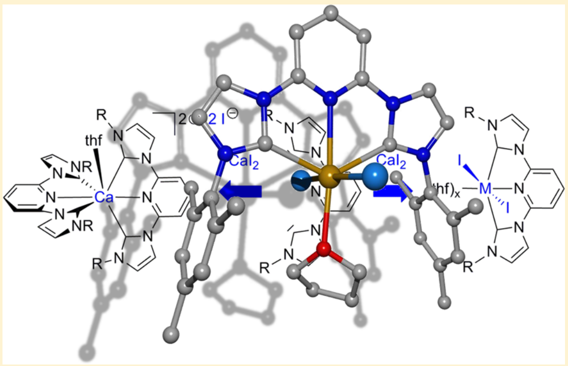
Ⓢ *Supporting Information*

ABSTRACT: Diffusion of 2,6-bis(3-mesitylimidazol-2-ylidene)pyridine ($Car^{Mes}PyCar^{Mes}$, **2**) into a solution of CaI_2 in THF leads to microcrystalline $[(Car^{Mes}PyCar^{Mes})(thf)CaI_2]$ (**3**), in one case containing a few single crystals of the unique separated ion pair $[(Car^{Mes}PyCar^{Mes})_2(thf)Ca]I_2$ (**4**) with four Ca–C bonds. However, isolation of single-crystalline $[(Car^{Mes}PyCar^{Mes})(thf)CaI_2]$ (**3**) succeeds via the addition of **2** to a solution of $[(thf)_5CaI]^+[BPh_4]^-$ due to a subsequent dismutation. Two modifications with the shapes of needles and cubes crystallize simultaneously. In contrast to this finding, the reaction of $[(thf)_5CaI]^+[AlPh_4]^-$ with **2** yields solvent separated $[(Car^{Mes}PyCar^{Mes})(thf)_2CaI]^+[AlPh_4]^-$ (**5**). The $Ca-C_{NHC}$ bond lengths lie in a typical range of $Ca-C_{Aryl}$ σ bonds and represent the shortest $Ca-C_{NHC}$ bonds known to date. Soluble $[(Car^{Mes}PyCar^{Mes})(thf)Ca(NPh_2)_2]$ (**6**) can be prepared via a metathetical approach from **4** and $KNPh_2$ as well as via the addition of **2** to $Ca(NPh_2)_2$ in tetrahydrofuran. The bulkier amido ligands lead to elongated bonds between the calcium center and the ligand **2**. Furthermore, the reactions of MI_2 (M = Sr, Ba) with **2** yield $[(Car^{Mes}PyCar^{Mes})(thf)_2MI_2]$ (M = Sr (**7**), Ba (**8**)).



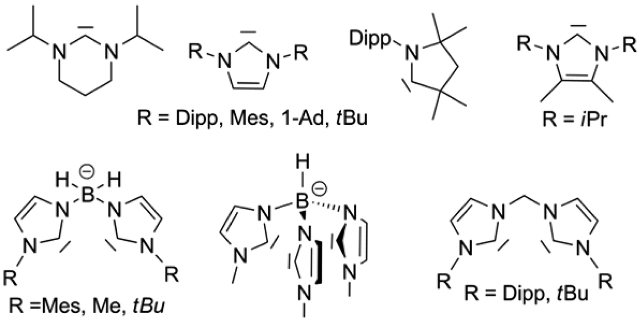
INTRODUCTION

Since the pioneering work of Wanzlick,[1] subsequently leading to the first isolation of a thermally stable, free N-heterocyclic carbene (NHC) by Arduengo and co-workers,[2] this compound class has become one of the most important Lewis bases in organometallic chemistry. These NHCs offer unique features resulting in applications in various fields of chemistry. In contrast to the fruitful and vast coordination chemistry of carbenes with transition metals, s-block metal–carbene complexes have been studied mainly with cyclopentadienyl,[3] bis(trimethylsilyl)amido (HMDS),[4] halide, and alkyl counterions.[5]

Typical carbene ligands are shown in Scheme 1. Addition of an anionic anchor group to the carbene moiety establishes another possibility to investigate s-block metal ion–carbene interactions.[6] Very recently, the metalation of NHCs with superbases has been studied.[7] However, all of these types of complexes are often indispensable intermediates in the synthesis of transition-metal complexes applying free carbenes or salt-metathetical approaches.

The strong σ-donor binding capabilities of carbenes encouraged us to reinvestigate these Lewis bases as ligands for the coordination chemistry of the alkaline earth metals. Hill and co-workers suggested a similar coordination strength of thf and monodentate NHC ligands.[4b] Schumann et al. demonstrated that ligated ethers can easily be replaced by carbenes at alkaline earth metallocenes.[3a] Consequently, enhancement of the denticity of the carbene-based Lewis base should represent a very capable class of neutral coligands in the field of s-block metal chemistry. However, to date only a few examples of such complexes are known, such as bis- and tris(imidazol-2-ylidén-1-yl)borate complexes,[8,9] which degrade in the vicinity of heavy group II metal ions, and also some lithium halide adducts of methylene-bridged bis(NHC) ligands.[10] Due to the small bite angle ($C_{NHC}\cdots C_{NHC}$ distance) of the latter Lewis base a ligation of heavier s-block metals seems to be difficult. Design of a more

Scheme 1. Representation of Commonly Used Neutral NHC Ligands in the Field of s-Block Metal Chemistry[a]



[a] Abbreviations: Ad, adamantyl; Dipp, 2,6-diisopropylphenyl; Mes, mesityl, 2,4,6-trimethylphenyl.

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suitable binding pocket and enhancement of the denticity are advantageous to stabilize such complexes. Therefore, we investigated 2,6-bis(3-mesitylimidazol-2-ylidene)pyridine (**2**, Car^{Mes}PyCar^{Mes}) as a tridentate bis(carbene)-based ligand. Here we present the results of the coordination studies with MI$_2$ of the heavy alkaline earth metals calcium, strontium, and barium.

■ RESULTS AND DISCUSSION

Structure of Car^{Mes}PyCar^{Mes}. The microcrystalline waxy solid of Car^{Mes}PyCar^{Mes} (**2**)[11,12] was recrystallized from concentrated THF/toluene mixtures, allowing structural characterization by X-ray diffraction experiments. The asymmetric unit of compound **2** contains two molecules A and B of **2** and one toluene molecule; molecule A is depicted in Figure 1.

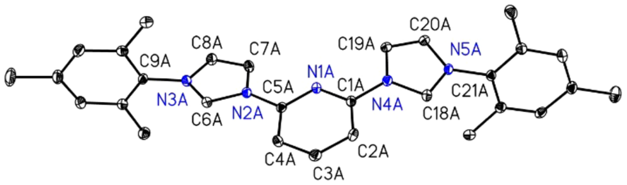
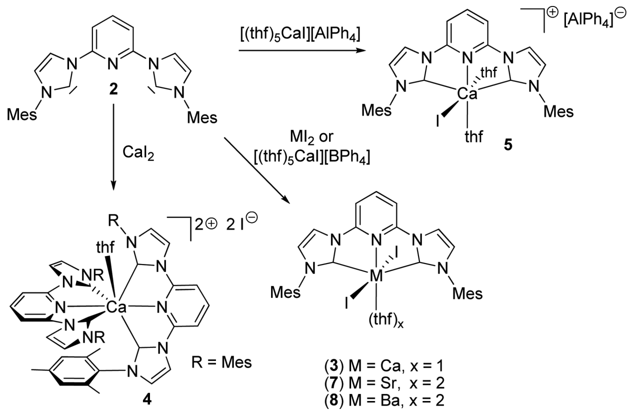


Figure 1. Molecular structure and numbering scheme of molecule A of Car^{Mes}PyCar^{Mes} (**2**). Thermal ellipsoids are shown at a probability level of 30%. H atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): C6A−N2A 1.380(3), C6A−N3A 1.363(3), C8A−C7A 1.341 (3), C18A−N4A 1.376(3), C18A−N5A 1.362(3), C19A−C20A 1.340(3), C1A−N1A 1.341(3), N1A−C5A 1.332(3); N3A−C6A−N2A 101.28(19), N5A−C18A−N4A 101.53(18), C1A−N1A−C5A 116.88(19); C18A−N4A−C1A−N1A 164.78, C6A−N2A−C5A−N1A +164.43.

The carbene moieties are twisted by 13° with respect to the central pyridine unit and show anti arrangements due to electrostatic repulsion between the C$_{NHC}$ and N$_{Py}$ lone pairs. The bond lengths and angles exhibit values comparable to those observed earlier for other unstrained carbenes.[13] This tridentate molecule attracted our attention as a potent ligand for heavy alkaline earth ions.

Coordination of Car^{Mes}PyCar^{Mes} to Group II Metals. We started our investigations with the addition of a dilute solution of anhydrous CaI$_2$ in THF to a solution of **2** in THF at room temperature. Immediately a white solid, which was collected and dried, precipitated with characteristic yields greater than 95% with respect to CaI$_2$. The white precipitate was insoluble in THF and, hence, NMR spectroscopic characterization failed. However, elementary analysis supports a composition of [(Car^{Mes}PyCar^{Mes})(thf)CaI$_2$] ([(**2**)(thf)CaI$_2$], **3**) with traces of coprecipitated [(thf)$_4$CaI$_2$]. Due to the insolubility of the material, diffusion experiments were performed and a solution of **2** in THF was layered with a dilute solution of CaI$_2$ in THF. Most commonly, microcrystalline solids of the composition [(Car^{Mes}PyCar^{Mes})(thf)CaI$_2$] were obtained, but in one case we were able to also grow a few single crystals of [(Car^{Mes}PyCar^{Mes})$_2$(thf)Ca]I$_2$ ([(**2**)$_2$(thf)Ca]I$_2$, **4**) (Scheme 2). Complex **4** represents one of the rare examples of a separated ion pair based on CaI$_2$;[14] the calcium ion has a coordination number of 7 via the coordination of two tridentate ligands **2**, in the following distinguished as **2a**^{3} and **2b**^{3}, and one THF base (according to the formulation [(**2a**^{3})(**2b**^{3})(thf)Ca]I$_2$). Both iodide ions are intercalated between the bulky [(Car^{Mes}PyCar^{Mes})$_2$(thf)Ca]$^{2+}$ cations.

Scheme 2. Reaction Diversity of Car^{Mes}PyCar^{Mes} (2) with the Iodides of the Heavy Alkaline Earth Metals Calcium, Strontium, and Barium, Yielding the Complexes 3−7



Intramolecular π stacking of the pyridyl moiety of **2a**^{3} and one mesityl group of **2b**^{3} leads to different Ca−C$_{NHC}$ bond lengths (2.565(4)/2.577(4) Å vs 2.701(4)/2.631(4) Å) as well as different Ca−N distances (2.524(3) Å vs 2.607(3) Å) of the two Car^{Mes}PyCar^{Mes} ligands (Figure 2). However, the Ca−C$_{NHC}$ bonds of **2a**^{3} are the shortest reported for the interaction of a calcium ion with carbene ligands[15] and lie in a typical range of Ca−C^{Aryl}/C^{Alkyl} σ bonds, verifying the lack of severe intramolecular strain.[16] In contrast, the Ca−C$_{NHC}$ contacts of **2b**^{3} are among the longest known.[15] Furthermore, the aforementioned π stacking opens the coordination sphere at Ca for an additional thf molecule, however, with a large Ca−O distance of 2.506(3) Å, suggesting a rather weak interaction between Ca and this ether base. The dihedral angles between the pyridyl and carbene moieties are comparable to those of free Car^{Mes}PyCar^{Mes} (**2**) (however, here a syn conformation is

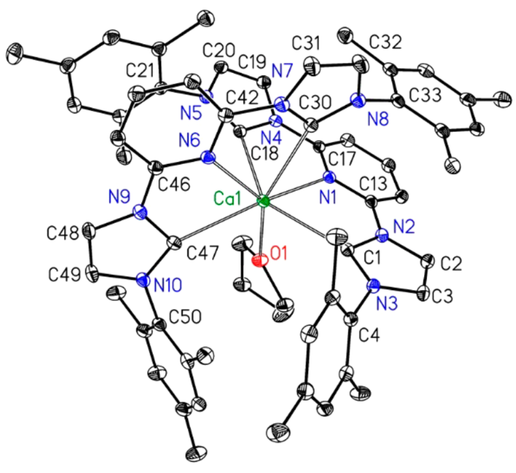


Figure 2. Molecular structure and numbering scheme of the cation of **4**. The ellipsoids represent a probability of 30%. H atoms are omitted for the sake of clarity. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): Ca1−C18 2.565(4), Ca1−C1 2.577(4), Ca1−C30 2.701(4), Ca1−C47 2.631(4), Ca1−N1 2.524(3), Ca1−N6 2.607(3), Ca1−O1 2.506(3); N3−C1−N2 102.8(3), N5−C18−N4 102.6(3), N8−C30−N7 102.1(3), N10−C47−N9 102.2(3), C13−N1−C17 117.5(3), C42−N6−C46 116.4(3), N1−Ca1−N6 138.28(10), O1−Ca1−N1 73.14(10), O1−Ca1−N6 90.38(11); C18−N4−C17−N1−11.87, C1−N2−C13−N1 + 11.41, C30−N7−C42−N6 +17.52, C47−N9−C46−N6 +3.00.

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realized), as are the other structural parameters. The finding that binding of calcium in the donor pocket of **2** leaves the geometry nearly unchanged excludes steric pressure and supports a strong bond between $\mathrm{Car^{Mes}PyCar^{Mes}}$ (**2**) and the calcium ion. This interpretation is further supported by a beneficial entropic effect, finally allowing the coordination of two molecules of **2** and leading to the formation of the separated ion pair **4**. Unfortunately, no further analytical data can be provided because the major compound consisted of $[(\mathrm{Car^{Mes}PyCar^{Mes}})(\mathrm{thf})\mathrm{CaI_2}]$.

Due to the insolubility of **4**, we attempted the substitution of one iodide anion by one noncoordinating anion such as $\mathrm{MPh_4}^-$ (M = B, Al). The heteroleptic complex $[(\mathrm{thf})_5\mathrm{CaI}]^+[\mathrm{BPh_4}]^-$ was synthesized from $\mathrm{CaBr_2}$, NaI, and $\mathrm{NaBPh_4}$ in THF and then reacted in high dilution with 1 equiv of **2**, also dissolved in THF. Due to the high dilution, NMR studies of the reaction solution failed; however, addition of a few drops of $\mathrm{Et_2O}$ initiated crystallization. Instead of the desired $[(\mathrm{Car^{Mes}PyCar^{Mes}})(\mathrm{thf})_2\mathrm{CaI}]^+[\mathrm{BPh_4}]^-$, $[(\mathrm{Car^{Mes}PyCar^{Mes}})(\mathrm{thf})\mathrm{CaI_2}]$ (**3**) was isolated in a yield of 37% with respect to calcium. This observation suggests a ligand scrambling of $[(\mathrm{Car^{Mes}PyCar^{Mes}})(\mathrm{thf})_2\mathrm{CaI}]^+[\mathrm{BPh_4}]^-$, yielding **3** and $[(\mathrm{Car^{Mes}PyCar^{Mes}})_x(\mathrm{thf})_y\mathrm{Ca}]^{2+}[\mathrm{BPh_4}]^-{}_2$, the latter forming an insoluble amorphous solid. Two modifications of **3**, appearing as long needles as well as cubes, were obtained in the same crystalline batch. The molecular structure and numbering scheme of one modification of **3** is depicted in Figure 3; the other (**3′**) is depicted in the Supporting Information. The calcium ion shows a coordination number of 6 with one tridentate molecule of **2** and two iodide anions as well as one thf base. The environment of the calcium atom is best described as a distorted octahedron with I1 and I2 in a trans arrangement with an I1−Ca1−I2 bond angle of 174.60(2)°. Due to the smaller coordination number in comparison to complex **4**, shorter $\mathrm{Ca{-}C^{NHC}}$ bonds of 2.525(3)/2.537(3) Å are found in **3** than in **4** (2.565(4)/2.577(4) and 2.701(4)/2.631(4) Å). In contrast to these smaller values, the Ca−N contact remains unchanged. The Ca−O distance is in the expected order of magnitude.[16] The insolubility of the complex may be explained by an intermolecular π stacking in the crystal involving one carbene and one pyridyl moiety of different molecules.

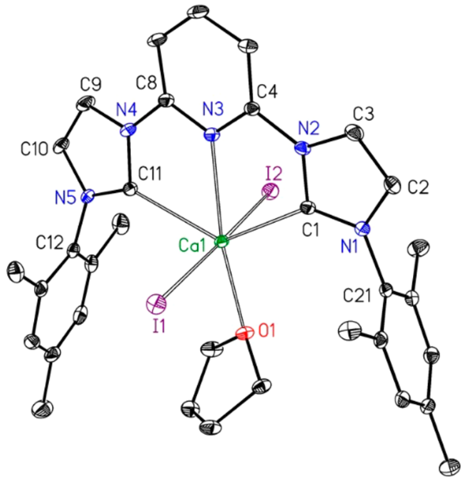

Figure 3. Molecular structure and numbering scheme of **3**. The ellipsoids represent a probability of 30%. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): Ca1−C1 2.525(3), Ca1−C11 2.537(3), Ca1−N3 2.527(3), Ca1−O1 2.349(2), Ca1−I1 3.0480(7), Ca1−I2 3.0580(7); I1−Ca1−I2 174.60(2), C1−Ca1−O1 108.07(9), O1−Ca1−N3 171.67(9); C1−N2−C4−N3 2.07, C11−N4−C8−N3 10.58.

In contrast to the reaction of **2** with $[(\mathrm{thf})_5\mathrm{CaI}]^+[\mathrm{BPh_4}]^-$, the addition of **2** to $[(\mathrm{thf})_5\mathrm{CaI}]^+[\mathrm{AlPh_4}]^-$ in THF (prepared via the addition of $[(\mathrm{thf})_4\mathrm{CaI(Ph)}]$ to $\mathrm{AlPh_3}$[17]) yielded $[(\mathrm{Car^{Mes}PyCar^{Mes}})(\mathrm{thf})_2\mathrm{CaI}]^+[\mathrm{AlPh_4}]^-$ (**5**), which was soluble enough to allow ^{1}H NMR experiments. The reaction mixture shows only a single set of resonances for **5**. However, the concentration was too low to record reliable $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra. Addition of $\mathrm{Et_2O}$ to the reaction mixture led to slow crystallization of **5** at room temperature. The hexacoordinate calcium ion of **5** (Figure 4) is in an octahedral environment which is distorted due to the constrained binding pocket of **2**. One iodide anion and a thf molecule occupy the axial positions and enclose an angle of 173.13(6)° with Ca1. Furthermore, the coordination sphere is saturated by a second thf ligand. The asymmetric unit contains two additional THF molecules and for electroneutrality reasons also the $[\mathrm{AlPh_4}]^-$ ion. Substitution of one iodide ion by a THF molecule leads to slightly elongated $\mathrm{Ca{-}C_{NHC}}$ contacts (2.525(3)/2.537(3) Å in **3** vs 2.546(2)/2.573(2) Å in **5**]. Again, the Ca1−O1/2 distances are in the characteristic range.

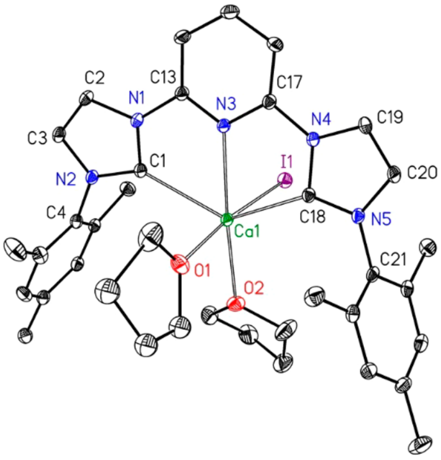

Figure 4. Molecular structure and numbering scheme of the cation of **5**. Thermal ellipsoids represent a probability of 30%. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): Ca1−C1 2.573(2), Ca1−C18 2.546(2), Ca1−N3 2.530(2), Ca1−O1 2.363(2), Ca1−O2 2.3356(19), Ca1−I1 3.0701(5); O1−Ca1−O2 83.48(7), N3−Ca1−O2 174.84(7), O1−Ca1−I1 173.13(6); C1−N1−C13−N3 −17.89, C18−N4−C17−N3 +5.07.

Extension of this method and the use of $[(\mathrm{thf})_6\mathrm{Ca}]^{2+}[\mathrm{MPh_4}]_2^-$ (M = B, synthesis by interaction of a 2:1 mixture of $\mathrm{NaBPh_4}$ and $\mathrm{CaBr_2}$ in THF; M = Al, synthesis by addition of $[(\mathrm{thf})_4\mathrm{CaPh_2}]$ to 2 equiv of $\mathrm{AlPh_3}$ in THF) in a very similar reaction with **2** yielded insoluble amorphous materials of unknown compositions.

These experiments demonstrate that purification and characterization of these calcium complexes is quite challenging, due to the fact that they are only sparingly soluble or even insoluble in common organic solvents and that reliable C, H, N analytical data are difficult to obtain because the content of solvent molecules as well as of coprecipitated $\mathrm{CaI_2}$ cannot safely

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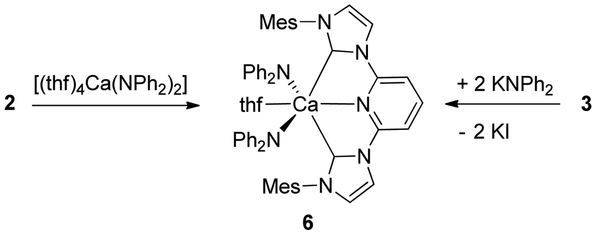
be determined. Therefore, we decided to prepare a soluble derivative, namely $[(\text{Car}^{\text{Mes}}\text{PyCar}^{\text{Mes}})_2(\text{thf})\text{Ca}(\text{NPh}_2)_2]$ ($[(\mathbf{2})_2(\text{thf})\text{Ca}(\text{NPh}_2)_2]$, **6**) (Scheme 3), to also further verify the constitution of microcrystalline **3**. Complex **6** was accessible from the reaction of **2** with $\text{Ca}(\text{NPh}_2)_2$[18] in tetrahydrofuran. Crystallization and X-ray diffraction studies verified the composition. The reaction of KNPh_2 with the amorphous and insoluble solids, described above and assigned to $[(\text{Car}^{\text{Mes}}\text{PyCar}^{\text{Mes}})(\text{thf})\text{CaI}_2]$ ($[(\mathbf{2})(\text{thf})\text{CaI}_2]$, **3**), also yielded complex **6**, as has been verified by NMR spectroscopy. The carbene resonance was observed at a characteristic shift of δ 202.9 ppm.

Scheme 3. Synthesis of Soluble $[(\text{Car}^{\text{Mes}}\text{PyCar}^{\text{Mes}})_2(\text{thf})\text{Ca}(\text{NPh}_2)_2]$ (6) via a Metathetical Approach of KNPh_2 with 3 and via Addition of 2 to $\text{Ca}(\text{NPh}_2)_2$ in THF



Compound $[(\mathbf{2})(\text{thf})\text{Ca}(\text{NPh}_2)_2]$ (**6**) crystallized with two molecules A and B in the asymmetric unit. The molecular structure and numbering scheme of molecule A is depicted in Figure 5. The hexacoordinate calcium atom is in a distorted-octahedral environment. The larger size of the amido ligands leads to an elongation of the bond lengths between Ca1 and the donor atoms of ligand **2** as well as of the ligated thf ligand. The nitrogen atoms of the diphenylamido anions are in a trigonal-planar coordination sphere due to charge back-donation from the lone pair at N into the phenyl groups.

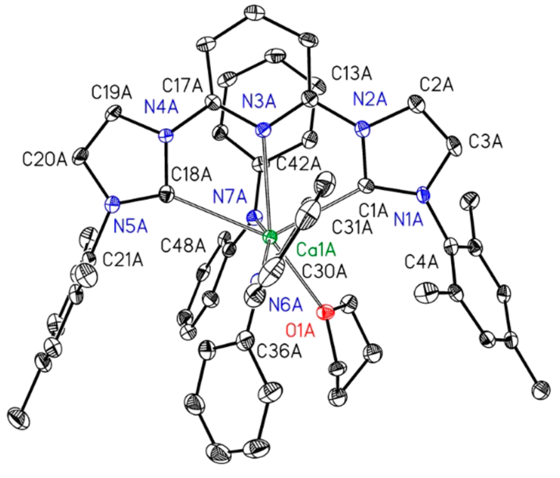


Figure 5. Molecular structure and numbering scheme of molecule A of **6**. Thermal ellipsoids represent a probability of 30%. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for molecule A [molecule B]: Ca1−C1 2.614(5) [2.664(5)], Ca1−C18 2.667(5) [2.618(5)], Ca1−N3 2.595(4) [2.616(4)], Ca1−O1 2.477(3) [2.474(3)], Ca1−N6 2.447(4) [2.428(4)], Ca1−N7 2.443(4) [2.434(4)]; N6−Ca1−N7 160.68(14) [157.43(14)], N3−Ca1−O1 147.43(12) [149.41(12)], C1−Ca1−C18 127.73(15) [127.25(15)].

The binding pocket of $\text{Car}^{\text{Mes}}\text{PyCar}^{\text{Mes}}$ (**2**) seems to be ideally suited for calcium ions and even allows binding of rather bulky diphenylamido ligands, maintaining the preferred hexacoordination of this alkaline earth ion. We were also interested in how this tridentate base adapts to larger alkaline earth ions. Therefore, we slowly combined a THF solution of MI_2 (M = Sr, Ba) with a solution of **2**, yielding single crystals with the composition $[(\text{Car}^{\text{Mes}}\text{PyCar}^{\text{Mes}})(\text{thf})_2\text{MI}_2]\cdot\text{THF}$ (M = Sr (**7**, Figure 6), Ba (**8**, see the Supporting Information)). In the crystalline state both compounds are isotypic. In both complexes the metal ions have distorted pentagonal-bipyramidal coordination spheres consisting of **2** and two thf molecules as well as two iodide counterions. The axial positions are occupied by the two halide ions, which span I1−M1−I2 angles of 177.13(1) and 175.15(1)°, respectively, for **7** and **8**. The $\text{M}{-}\text{C}_{\text{NHC}}$ bonds are in a range similar to that observed for monodentate carbene ligands at Sr (2.731−2.768 Å) and Ba (2.914−3.1209 Å).[3a,4b,19] The expected symmetry of the molecule is broken by a slight shift of the metal ion to one side of the $\kappa^2C_{\text{NHC}},\kappa^1N$ pocket of **2**, as indicated by different $\text{M}{-}\text{C}_{\text{NHC}}$ bond lengths (**7** (M = Sr), 2.779(3) and 2.808(3) Å; **8** (M = Ba), 2.888(5) and 2.925(4) Å) and dihedral angles, with one carbene ring turning out of the ligand plane.

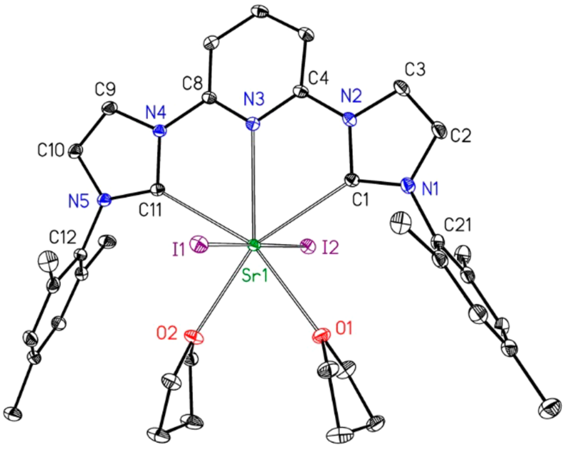


Figure 6. Molecular structure of **7** (M = Sr) [**8** (M = Ba)]. Thermal ellipsoids represent a probability of 30%. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): Sr1−C1 2.779(3) [2.888(5)], Sr1−C11 2.808(3) [2.925(4)], Sr1−N3 2.803(3) [2.962(3)], Sr1−O1 2.625(2) [2.745(3)], Sr1−O2 2.578(2) [2.713(3)], Sr1−I1 3.2302(3) [3.3696(4)], Sr1−I2 3.3493(3) [3.4855(4)]; I1−Sr1−I2 177.130(11) [175.147(11)], O1−Sr1−O2 73.14(7) [73.23(12)], C1−Sr1−N3 60.41(8) [57.63(11)], C11−Sr1−N3 60.28(8) [57.78(10)], N4−C11−N5 101.6(2) [102.5(4)], N1−C1−N2 101.6(3) [102.1(4)], C4−N3−C8 116.2 [116.8(4)]; C1−N2−C4−N3 8.84 [8.84], C11−N4−C8−N3 −15.32 [−15.45].

It is noteworthy that the M−I2 bond is significantly longer than the M−I1 bond by 11.9 pm (M = Sr1, 3.7% elongation) and 11.6 pm (M = Ba1, 3.4% elongation). In both complexes, the atom I2 shows intermolecular contacts of 3.064 Å to the hydrogen atom at C7 in the meta position of the pyridyl fragment, whereas I1 is intramolecularly more effectively shielded by the bulky aryl groups. An I···H contact of 3.064 Å is smaller than the sum of the van der Waals radii (3.5 Å)[20] and could polarize the very soft iodide, leading to a lengthening of the M−I bonds. It has been reported earlier that the Sr−I[21] and Ba−I distances[22] in complexes of strontium and barium iodides vary within the large ranges of 322−349 and 337−354 pm, respectively, depending on the coordination numbers of the alkaline earth ions and iodide as well as on the donor strength and bulkiness of the coligands.

CONCLUDING REMARKS

2,6-Bis(3-mesitylimidazol-2-ylidene)pyridine (**2**) exhibits an ideal binding pocket for heavy alkaline earth ions that has been studied by the complexation of the iodides of calcium, strontium, and barium with **2**. However, due to intermolecular π stacking of the aromatic groups most of these adducts are only sparingly soluble or even insoluble in common organic solvents. Therefore, diffusion experiments seem to be the preferred procedure to isolate crystalline complexes. Thus, CaI_2 reacts with **2** in a diffusion experiment, yielding a few crystals of the unique separated ion pair [(Car^{Mes}PyCar^{Mes})$_2$(thf)Ca]I_2 (**4**), containing two molecules of **2** which show significantly different Ca−C/N bond lengths due to intramolecular π stacking. Reaction of **2** with [(thf)$_5$CaI]$^+$[BPh$_4$]$^-$ in THF induced dismutation, leading to two modifications of [(Car^{Mes}PyCar^{Mes})(thf)CaI$_2$] (**3** and **3′**) as well as insoluble and poorly characterized [(Car^{Mes}PyCar^{Mes})$_x$(thf)$_y$Ca]$^{2+}$-[BPh$_4$]$^-{}_2$. In contrast to this finding, the reaction of **2** with [(thf)$_5$CaI]$^+$[AlPh$_4$]$^-$ in THF yields the desired complex [(Car^{Mes}PyCar^{Mes})(thf)$_2$CaI]$^+$[AlPh$_4$]$^-$ (**5**). For solubility reasons, we substituted the halide ions by diphenylamido ligands, leading to soluble [(Car^{Mes}PyCar^{Mes})$_2$(thf)Ca(NPh$_2$)$_2$] (**6**), allowing NMR spectroscopic characterization. We also investigated the coordination behavior of **2** toward the heavier alkaline earth ions. Therefore, compound **2** was added to MI$_2$, yielding isostructural [(Car^{Mes}PyCar^{Mes})(thf)$_2$MI$_2$]·THF for M = Sr (**7**), Ba (**8**).

All crystalline compounds have been characterized by X-ray diffraction studies (Table 1). These derivatives contain short Ca−C$_{NHC}$ bond lengths which are in a typical range of Ca−C σ bonds of organocalcium reagents. There are only very few complexes of strontium and barium with M−C σ bonds known, but the values for complexes **7** and **8** are also rather small. Consequently, the Lewis base **2** has verified its nature as a strong tridentate ligand for heavy alkaline earth ions being able to substitute thf ligands in the coordination spheres of heavy alkaline earth ions, whereas the halides remain bonded to the metal centers. Only for the calcium derivative **4** is substitution of the halide by a second tridentate ligand **2** observed. With the exception of this complex, rather short M−O bond lengths support the lack of severe intramolecular steric strain.

Table 1. Comparison of Average Values of Selected Bond Lengths (Å) of the Alkaline Earth Metal Complexes, Containing the Ligand Car^{Mes}PyCar^{Mes} (2)

complex	M−N$_{Py}$	M−C$_{NHC}$	M−O$_{thf}$	M−I
3	2.527	2.531	2.349	3.053
3′A[a]	2.545	2.550	2.357	3.056
3′B[a]	2.522	2.531	2.332	3.075
4	2.566	2.619	2.506	
5	2.530	2.560	2.349	3.070
6	2.606	2.641	2.476	
7	2.803	2.794	2.602	3.290
8	2.962	2.907	2.729	3.428

[a] The modification **3′** contains two crystallographically independent molecules A and B (see the Supporting Information).

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques, if not otherwise stated. The solvents were dried over KOH and subsequently distilled over sodium/benzophenone under a nitrogen atmosphere prior to use. Deuterated solvents were dried over sodium, distilled, degassed, and stored under nitrogen over sodium. If the solubility of the compounds was sufficient, ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance 400 and Avance III 600 spectrometers. Chemical shifts are reported in parts per million relative to SiMe$_4$ as an external standard referenced to the solvent's residual proton signal. All substrates were purchased from TCI or Alfa Aesar and used without further purification. KHMDS was obtained from KH and H-HMDS in toluene. The complex [(thf)$_5$CaI][AlPh$_4$] was prepared following a protocol published by Krieck et al.[17] The compound [(thf)$_5$CaI]-[BPh$_4$] was prepared from CaBr$_2$, NaBPh$_4$, and NaI in THF. The compound [(thf)$_4$Ca(NPh$_2$)$_2$] was prepared according to the procedure of Glock et al.[18] The yields given are not optimized. Ligand **2** was prepared according to literature procedures,[11,12,23] as also specified in the Supporting Information. The complexes of the heavy alkaline earth metal complexes with **2** were extremely sensitive toward air and turned dark immediately upon exposure to air. This fact together with the insolubility in common organic solvents hampered the elemental analyses. Purity and yields were verified by ^{1}H NMR spectroscopy for soluble complexes and by titration of the iodine content of an HNO$_3$ pulping of the insoluble derivatives **7** and **8**.

Synthesis of [(Car^{Mes}PyCar^{Mes})(thf)CaI$_2$] (3) and [(Car^{Mes}PyCar^{Mes})$_2$(thf)Ca]I$_2$ (4). A 254 mg portion of CaI$_2$ (0.86 mmol, 1 equiv) was suspended in 20 mL of THF, and 10.7 mL of a 0.08 M solution of Car^{Mes}PyCar^{Mes} (0.86 mmol, 1 equiv) in THF was added. The suspension was stirred for 1 day at room temperature, forming a light brown solution and a white precipitate, which was collected and dried. Yield: 664 mg (95%) of [(Car^{Mes}PyCar^{Mes})(thf)-CaI$_2$]. Single crystals suitable for X-ray diffraction were obtained by the following procedure. A dilute solution of CaI$_2$ in THF was layered with a dilute solution of Car^{Mes}PyCar^{Mes} in THF. Various attempts yielded only microcrystalline [(Car^{Mes}PyCar^{Mes})(thf)CaI$_2$], and finally a few crystals of [(Car^{Mes}PyCar^{Mes})$_2$(thf)Ca]I$_2$ (**4**) were isolated, which were suitable for X-ray diffraction studies. However, no further analytical data were accessible. Single crystals of [(Car^{Mes}PyCar^{Mes})-(thf)CaI$_2$] were obtained as follows. A 130 mg portion of [(thf)$_5$CaI][BPh$_4$] (0.15 mmol, 1 equiv) was dissolved in 30 mL of THF. To this solution was added 1.93 mL of a 0.08 M solution of Car^{Mes}PyCar^{Mes} (0.15 mmol, 1 equiv), and the mixture was filtered. Addition of Et$_2$O to the filtrate led to slow crystallization of [(Car^{Mes}PyCar^{Mes})(thf)CaI$_2$] (37%, 46 mg of **3**), suitable for X-ray diffraction experiments, as well as of an amorphous solid of the same constitution. Anal. Calcd for C$_{33}$H$_{37}$CaI$_2$N$_5$O (813.56 g mol^{-1}): C, 48.72; H, 4.58; N, 8.36; Ca, 4.93; I, 31.20. Found: C, 47.89; H, 4.50; N, 8.36; Ca, 4.87; I, 31.83. Mp: 146 °C dec. IR (ATR, cm^{-1}): ν 3053 w, 2973 w, 2945 w, 2872 w, 1610 m, 1587 m, 1461 s, 1392 m, 1270 m, 877 m, 799 m, 737 m.

Synthesis of [(Car^{Mes}PyCar^{Mes})(thf)$_2$CaI][AlPh$_4$] (5). A 162 mg portion of [(thf)$_5$CaI][AlPh$_4$] (0.18 mmol, 1 equiv) was dissolved in 15 mL of THF, and 2.35 mL of a 0.08 M solution of Car^{Mes}PyCar^{Mes} in THF was added. The mixture was stirred for 2 h and filtered. Addition of 5 mL of Et$_2$O at room temperature resulted in slow crystallization of 105 mg of [(Car^{Mes}PyCar^{Mes})(thf)$_2$CaI][AlPh$_4$] (47%). The obtained crystals were suitable for X-ray diffraction experiments. Anal. Calcd for C$_{69}$H$_{81}$CaIO$_4$AlN$_5$ (1238.35 g mol^{-1}): C, 66.92; H, 6.59; N, 5.66. Found: C, 64.60; H, 6.25; N, 5.89. The carbon content is too low most likely due to formation of Al$_4$C$_3$. Mp: 135 °C dec. IR (ATR, cm^{-1}): ν 3047 w, 2967 w, 2861 w, 1608 m, 1586 m, 1464 s, 1392 m, 1271 m, 1072 s, 705 s, 662 s, 479 s. NMR spectra were recorded of the reaction mixture due to the insolubility of the crystals. However, the concentration was too low for ^{13}C{^{1}H} NMR measurements. ^{1}H NMR (600 MHz, 25 °C, [D$_8$]THF): δ 1.82 (m, THF), 2.11 (6H,s), 2.27 (12H, s), 3.66 (m, THF), 6.91 (4H, tt, $^3J_{H-H}$ = 7.26 Hz, $^3J_{H-H}$ = 1.50 Hz), 6.97 (8H, t, $^3J_{H-H}$ = 7.26 Hz), 7.00 (4H, s), 7.31 (2H, d,

$^3J_{H-H}$ = 1.92 Hz), 7.72 (8H, bs), 7.84 (2H, d, $^3J_{H-H}$ = 8.20 Hz), 8.19 (2H, d, $^3J_{H-H}$ = 1.92 Hz), 8.24 (1H, t, $^3J_{H-H}$ = 8.20 Hz) ppm. ^{27}Al NMR (104.2 MHz, 25 °C, [D$_8$]THF): δ 133.03 ppm.

Synthesis of [(Car^{Mes}PyCar^{Mes})(thf)Ca(NPh$_2$)$_2$] (6). A 2.2 mL portion of a 0.147 M solution of [(thf)$_4$Ca(NPh$_2$)$_2$] (0.32 mmol, 1 equiv) in THF was diluted with 4 mL of THF. To this solution was added 4.1 mL of a 0.08 M solution of Car^{Mes}PyCar^{Mes} (0.32 mmol, 1 equiv) in THF. The volume was reduced by half. Storage of the solution at −40 °C led to the formation of crystals, which were suitable for X-ray diffraction ([(Car^{Mes}PyCar^{Mes})(thf)Ca(NPh$_2$)$_2$]·4THF). The product was collected, which resulted in a color change from red to orange. NMR spectra were recorded of this solid, verifying the purity of the compound and also the loss of 1.75 THF molecules during collection and drying of the crystals. Yield of [(Car^{Mes}PyCar^{Mes})(thf)-Ca(NPh$_2$)$_2$]·2.25THF: 67% (211 mg).

Due to the easy loss of cocrystallized solvent, no reliable elemental analysis data were obtained. IR (ATR, cm^{-1}): ν 3042 w, 2972 w, 2914 w, 2855 w, 1588 m, 1573 m, 1461 m, 1440m, 1342 m, 1308 m, 1269 m, 1167 m, 983 m, 743 m, 688 m, 519 m, 500 m. ^{1}H NMR (400 MHz, 25 °C, [D$_8$]THF): δ 1.81 (13H, m, THF), 1.83 (12H, s), 2.31 (6H, s), 3.65 (13H, m, THF), 6.08 (4H, bt), 6.35 (8H, bd), 6.54 (8H, bt), 6.79 (4H, s), 7.17 (2H, d, $^3J_{H-H}$ = 1.90 Hz), 7.66 (2H, d, $^3J_{H-H}$ = 8.22 Hz), 8.07 (2H, d, $^3J_{H-H}$ = 1.90 Hz), 8.11 (1H, t, $^3J_{H-H}$ = 8.22 Hz) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, 25 °C, [D$_8$]THF): δ 17.0, 20.1, 25.4, 67.2, 109.7, 112.7, 116.7, 118.6, 124.0, 127.9, 128.7, 135.4, 136.7, 137.6, 142.9, 151.3, 156.9, 202.8 ppm.

Synthesis of [(Car^{Mes}PyCar^{Mes})(thf)$_2$SrI$_2$].THF (7). A 152 mg portion of SrI$_2$ (0.44 mmol) was suspended in 20 mL of THF, and 5.61 mL of a 0.08 M solution of Car^{Mes}PyCar^{Mes} (0.44 mmol, 1 equiv) in THF was added. The suspension was stirred for 1 day at room temperature, forming a light brown solution and a white precipitate, which was collected and dried. Yield: 410 mg (93%) of [(Car^{Mes}PyCar^{Mes})(thf)$_2$SrI$_2$]. Single crystals suitable for X-ray diffraction were obtained by the following procedure. A dilute solution of SrI$_2$ in THF was layered with a dilute solution of Car^{Mes}PyCar^{Mes} (**2**) in THF. After a few days, crystals of [(Car^{Mes}PyCar^{Mes})-(thf)$_2$SrI$_2$].THF were obtained that were suitable for X-ray diffraction analysis. No reliable C, H, N analytical data were obtained. HNO$_3$ pulping: I, calcd 25.25, found 25.71. Mp: 135 °C dec. IR (ATR, cm^{-1}): ν 3023 w, 2944 w, 2859 w, 1605 m, 1592 m, 1459 s, 1390 m, 1273 s, 1258 m, 1038 m, 801 m, 735 m, 720 m.

Synthesis of [(Car^{Mes}PyCar^{Mes})(thf)$_2$BaI$_2$] (8). A 202 mg portion of BaI$_2$ (0.52 mmol) werewas suspended in 20 mL of THF, and 6.5 mL of a 0.08 M solution of Car^{Mes}PyCar^{Mes} (0.52 mmol, 1 equiv) in THF was added. The suspension was stirred for 1 day at room temperature, giving a light brown solution and a white precipitate, which was collected and dried, yielding 350 mg (70%) of [(Car^{Mes}PyCar^{Mes})(thf)$_2$BaI$_2$]. A few single crystals of [(Car^{Mes}PyCar^{Mes})(thf)$_2$BaI$_2$] were obtained by reducing the mother liquor to one-fourth of the original volume and storage at room temperature. Mp: 142 °C dec. IR (ATR, cm^{-1}): 2916 w, 2856 w, 1658 w, 1581 m, 1441 s, 1228 m, 1035 m, 851w. No reliable C, H, N analytical data were obtained. HNO$_3$ pulping: I, calcd 25.82, found 25.58.

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.[24−26]

The structures were solved by direct methods (SHELXS[27]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[26] and SHELXL-2014[28]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen, nondisordered atoms were refined anisotropically.[27,28] The crystal of **3′** was a partial-merohedral twin. The twin law was determined by PLATON[29] to (0.413, 0.000, −0.587)/(0.000, −1.000, 0.000)/(−1.413, 0.000, −0.413). The contribution of the main component was refined to 0.874(2).

Crystallographic data as well as structure solution and refinement details are summarized in the Supporting Information. XP[30] and POV-Ray[31] were used for structure representations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00914. Crystallographic data (excluding structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1519060 for **2**, CCDC-1519061 for **4**, CCDC-1519062 for **3**, CCDC-1519063 for modification **3′**, CCDC-1519064 for **5**, CCDC-1530221 for **6**, CCDC-1519065 for **7**, and CCDC-1519066 for **8**. 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).

Crystallographic data (CIF)

Synthesis of compound **2**, structure representations of modification **4′** and **7**, and crystallographic and refinement details (PDF)

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Notes

The authors declare no competing financial interest.

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