Abstract: The first “naked” (Lewis base-free) cationic Ca amidinate complex [BuAmDIPP\(\text{Ca(C}_2\text{H}_4)\)]\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) was prepared in 62 \% yield (BuAmDIPP = \text{BuC(N–DIPP)}\(_2\)). DIPP = 2,6-disopropylphenyl) by reaction of [BuAmDIPP\(\text{CaH}_2\)]\(^+\) with [Ph\(_3\)C]\([\text{B(C}_6\text{F}_5\text{)}\_4]\)]\(^-\) in chlorobenzene. The ether-free complex \(\text{BuAmDIPP}\text{CaN(SiMe}_3\text{)}\_2\) was obtained by removal of diethyl ether from its ether adduct. Crystal structures show that the amidinate ligand in both complexes is N,chelating. In this coordination mode the bulk of the amidinate ligand is comparable to that of a DIPP-substituted \(\beta\)-diketiminato ligand. Isomers with \(N,N\)-coordinating amidinate ligands are circa 15 kcal/mol higher in energy and this coordination mode is only present in case additional ether ligands compensate for energy loss or in case of space limitation at the metal, e.g. in homoleptic \(\text{BuAmDIPP}\text{Ca}\_2\). A series of four Ca amidinate complexes, \(\text{BuAmDIPP}\text{CaX}\), were tested in the catalytic hydroboration of ketones and aldehydes by pinacolborane (HBpin). Catalytic activities increase for \(X^- = \text{I}^- < \text{B(C}_6\text{F}_5\text{)}\_4\)\(^-\). For catalysts with unreactive anions, like \(\text{I}^-\) or \(\text{B(C}_6\text{F}_5\text{)}\_4\)\(^-\), catalyst performance increases with the Lewis acidity of the metal and a mechanism is proposed in which HBpin and ketone coordinate to the \(\text{Ca}^{2+}\) ion which is followed by direct hydroboration. The more active catalysts with \(X^- = \text{(Me}_3\text{Si)}\_2\text{N}^-\) or \(\text{H}^-\) likely operate through a mechanism which involves intermediate metal hydride (or borate) complexes.

Introduction

Over the last decades, research on alkaline earth metal based homogeneous catalysis gained momentum and conquered fields, which were long thought to be the exclusive domain of transition metal catalysis.\(^{[1–4]}\) Although often still not on par with their classical transition metal based counterparts, alkaline earth metals make up for lower catalytic activity of their complexes by price, availability and non-toxicity, at least in case of magnesium and calcium. Calcium catalysis reactions include \textit{inter alia} polymerizations,\(^{[5]}\) alkene hydrogenations,\(^{[6]}\) alkene and imine hydrosilylation,\(^{[7]}\) intramolecular alkene hydroamination,\(^{[8]}\) alkene and alkyne hydrophosphination,\(^{[9]}\) hydroboration,\(^{[10]}\) or Mannich-type reactions.\(^{[11]}\)

Notwithstanding those successful applications, the conceptual foundation to predict whether a calcium catalyst is highly active for a certain reaction is so far unknown. This is due to the fact that the limited number of reports in calcium catalysis often describe results with drastically different catalysts. Nevertheless, possible factors to influence the reactivity of a catalyst in a given environment are in principle well known and include, but are not limited to, steric demand, charge, donor capacity and donor atom type of spectator ligands, their number and the resulting coordination number of the metal ion, the nuclearity of the resulting complexes and the counterions present. In general, catalysts of type \(\text{LCaR}\) consist of a passive spectator \(\text{L}\) in combination with a reactive group \(\text{R}\). The catalytic reaction is based on a combination of substrate activation by the Lewis-acidic \(\text{Ca}^{2+}\) center and the high nucleophilicity or basicity of \(\text{R}\). In some cases, also catalysts that only rely on Lewis acid activation have been reported.\(^{[11,12]}\) E.g. the Sen group introduced the amidinate calcium iodide catalyst \(\text{I}\) in the hydroboration of ketones and aldehydes.\(^{[12]}\) It is unlikely that the highly stable iodide ligand actively takes part in catalysis. In an effort to address the importance of this second anionic ligand, we chose to study the hydroboration of ketones (and aldehydes) as a function of the ligands. We present here a series of catalysts with the bulky amidinate spectator ligand \(\text{BuAmDIPP}\) \(\text{BuAmDIPP} = \text{BuC(N–DIPP)}\(_2\)) by reaction of \(\text{BuAmDIPP}\text{CaI(thf)}\_2\) with \(\text{PhC(N–DIPP)}\(_2\)) that allowed for the synthesis and isolation of complexes \(\text{BuAmDIPP}\text{CaX}\) with \(X^- = \text{I}^- < \text{B(C}_6\text{F}_5\text{)}\_4\)\(^-\) (see Scheme 1). The performance of these catalysts will be directly compared with results reported earlier by Sen and co-workers for \(\text{PhC(NPr)}\text{CaI(THF)}\_2\) (\(\text{BuAmPrCaI(THF)}\_2\)). While synthetic strategies for \(\text{BuAmDIPP}\text{CaN(SiMe}_3\text{)}\_2\text{Et}_2\text{O}\)\(^{[14]}\) and \(\text{BuAmDIPP}\text{CaH}_2\) \(^{[4]}\)\(^{[14]}\) are known, synthetic routes had to be developed for \(\text{BuAmDIPP}\text{Ca(N(SiMe}_3\text{)}\_2\text{)}\) and ether-free \(\text{BuAmDIPP}\text{CaN(SiMe}_3\text{)}\_2\) used in the current investigations.

Results and Discussion

Ligand Choice and Precatalyst Synthesis

Our spectator ligand of choice for the current investigation was \(\text{BuAmDIPP}\). This chelating ligand was first reported by Westerhau-
Scheme 1. Previously used calcium based catalyst for the hydroboration of ketones (1) and calcium catalysts used in this investigation (1–4).

Scheme 2. Explored synthetic routes for \([\text{tBuAmDIPPCa(C}_6\text{H}_6]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) (2).

Figure 1. Molecular structures of \([\text{tBuAmDIPPCa(1,4-dioxane)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) (middle left; hydrogen atoms and co-crystallized 1,4-dioxane have been omitted) and of \([\text{tBuAmDIPPCa(NBO-H)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) (2) (middle right; hydrogen atoms and B(C\(_6\)F\(_5\))\(_4\)]\(^-\) have been omitted) as well as steric maps for the buried volume in these complexes (in case of \([\text{tBuAmDIPPCa(1,4-dioxane)}]\) the bulkier of two ligands was chosen).

sen and co-workers\(^{[15]}\) and previously used in our group for the stabilization of highly reactive calcium hydride complexes,\(^{[14]}\) and for Ca derivatives featuring stilbene dianions\(^{[13]}\) or novel anionic N-heterocyclic olefins.\(^{[16]}\) This ligand choice might seem counterintuitive, since \([\text{tBuAmDIPPCa(1,4-dioxane)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) has a higher steric demand and lower basicity of its nitrogen atoms when compared to \([\text{PhAm\(i\)PrCa(1,4-dioxane)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\). However, its superior adaptability to the changing needs of a bound calcium ion, which is related to a facile interconversion of its \(N,N\)- and \(N\text{,Aryl}\)-coordination mode,\(^{[15,18]}\) makes this ligand almost a requirement, when it comes to the synthesis of one of our envisioned precatalysts, namely \([\text{tBuAmDIPPCa(NBO-H)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) (2). Related cat-ionic calcium compounds were so far only accessible by the use of the sterically demanding \(\beta\)-diketiminato ligand \([\text{MeBDIDIPPCa(1,4-dioxane)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) or \([\text{MeBDIDIPPCa(NBO-H)}]\)\(^+\)[Al\(_8\)OC\(_3\)(CF\(_3\))\(_3\)]\(^-\), which has a buried volume of 49.4 % in \([\text{MeBDIDIPPCa(C}_6\text{H}_6(\text{Me})\text{H})]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) or even \(64.1 \%\) in \([\text{MeBDIDIPPCa(C}_6\text{H}_6(\text{H})\text{H})]\)\(^+\)[Al\(_8\)OC\(_3\)(CF\(_3\))\(_3\)]\(^-\). Such values seem out of reach for the amidinate \([\text{tBuAmDIPPCa(1,4-dioxane)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\), which shows \(V_B\)'s of 34.0 % to 40.1 % in \(N,N\)-coordination mode in published calcium complexes, depending on the coordination number (see Table S1, Supporting Information). For the previously unpublished structure of \([\text{tBuAmDIPPCa(1,4-dioxane)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) (see Figure 1), the so far highest value of \(V_B = 42.4 \%\) is found for one of the ligands, but the sterical shielding provided by \([\text{tBuAmDIPPCa(1,4-dioxane)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) in this compound is still significantly lower than for \([\text{MeBDIDIPPCa(1,4-dioxane)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) when it comes to sterical demand (see Scheme 2, Supporting Information).

With this knowledge at hand, the synthesis of \([\text{tBuAmDIPPCa(C}_6\text{H}_6(\text{Me})\text{H})]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) (2) was attempted in analogy to the published strategy for \([\text{MeBDIDIPPCa(C}_6\text{H}_6(\text{Me})\text{H})]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) (see Scheme 2, left side).\(^{[20,21]}\) The required salt \([\text{tBuAmDIPPCa(NBO-H)}]\)\(^+\)[B(C\(_6\)F\(_5\))\(_4\)]\(^-\) (for XRD data see Supporting Infor-
tion) was synthesized in 94 % yield by treating $^{tBu}_{Am}$DIPP$^+$ with $[HOEt_2]^+$ in chlorobenzene. Unfortunately, addition of solvent-free Ca($t$-Bu-benzyl)$_2$ to $[^{tBu}_{Am}$DIPP$^+$]$^+$-Cl$^-$ in chlorobenzene did not lead to a selective reaction, thus precluding the isolation of $[^{tBu}_{Am}$DIPP$^+$]Ca$^+$-[Cl$^-$]. Therefore we followed a strategy similar to the one successful for complexes of the type $[^{tBu}_{BDI}$M$^-$][arene]$_2$-[Cl$^-$]. Addition of $[P_3H_2]^+$-[Cl$^-$] to a suspension of the literature known, donor-free complex $[^{tBu}_{Am}$DIPP$^+$]CaH$_2$,$^{[14]}$ in chlorobenzene led overnight to a slow color change from orange-red to brown. After removal of chlorobenzene, a brown foam was obtained which formed a biphasic system upon addition of benzene. The lower phase was washed with benzene until colorless crystals in a sticky brown residue grew. These crystals were suitable for X-ray analysis, but further purification was necessary. The crude product could be crystallized by thermal diffusion in a hexane/benzene (2:1) mixture in good yield (62 %) (see Figure S11, Supporting Information).

XRD structure determination (see Figure 1, Table 1) revealed the retention of the ($N_{Aryl}$)-coordination mode of the starting material $[^{tBu}_{Am}$DIPP$^+$]CaH$_2$ in $[^{tBu}_{Am}$DIPP$^+$]Ca([Cl$^-$])$_2$,[b] as well as complete separation of cation and anion. This contrasts with the structure of the $d$- diketiminate complex $[^{tBu}_{BDI}$DIPP$^+$]Ca([Cl$^-$])$_2$,$^{[15]}$ in which a Ca–F contact to the anion persisted. Similar cation-anion separation was earlier observed when Krossing’s even weaker coordinating anion $[Al(OCCF_3)_2]^-$ was employed.$^{[19]}$ In related magnesium complexes, containing the B($C_6F_5$)$_2F^-$ anion, it was necessary to further increase the steric bulk of the BDI ligand by an exchange of $Me$ groups for $tBu$ groups in the ligand backbone, to break the Mg–F interaction.$^{[22]}$

These findings indicate that the $^{tBu}_{Am}$DIPP$^+$ ligand in $N_{Aryl}$-coordination mode is at least as bulky as the $^{tMe}_{BDI}$DIPP$^+$ ligand with $N_{N^+}$-coordination. This assumption is supported by almost identical values for the volume buried by those ligands in the three-coordinate cations of $[^{tBu}_{Am}$DIPP$^+$]Ca([Cl$^-$])$_2$,[b] 63.2 %) and $[^{tMe}_{BDI}$DIPP$^+$]Ca([Cl$^-$])$_2$,$^{[15]}$ (64.1 %).

The complete separation of cation and anion in 2 clearly leads to a much higher metal Lewis acidity and consequently shorter bonds to both, N2 and the aryl ring are observed, when compared to contact ion pair $[^{tBu}_{Am}$DIPP$^+$][Cl$^-$]. Expectedly, the effect is stronger for the negatively charged nitrogen (2: Ca–N2 2.2814(14) Å; $[^{tBu}_{Am}$DIPP$^+$][Cl$^-$]: Ca–N2 2.3841(11) Å) than for the $η^6$-coordinated aryl ring (Ca–Cav. 2.8018 Å vs. Ca–Cav. 2.839 Å) (see Table 1).

Despite the very strong metal-ligand interaction in 2, exchange between coordinated and non-coordinated DIPP substituents is not prevented. While at ambient temperature, two distinct sets of $^1H$ NMR signals for the different DIPP moieties are observed (four doublets and two heptets for the $iPr$ substituents), those signals show coalescence upon heating. The activation energy for fast exchange between the two different sides of the amidinate ligand has been estimated from the coalescence temperature of 337 K as $\Delta G^\ddagger = 16.1$ kcal/mol. This value is in the same range as observed for $[^{tBu}_{Am}$DIPP$^+$]CaH$_2$,$^4$ ($\Delta G^\ddagger = 16.8$ kcal/mol).$^{[14]}$

Dissolving complex 2 in [D$_2$]bromobenzene, led to loss of the coordinated benzene ligand and likely coordination of bromobenzene. This is evident from the benzene chemical shift of 7.21 ppm, which is the value of free benzene in this solvent.

Complex $[^{tBu}_{Am}$DIPP$^+$]Ca([SiMe$_3$]$^-$)$_2$ (3) shows similar behavior. The flexible coordination mode of the $^{tBu}_{Am}$DIPP$^+$ ligand in 3 is nicely illustrated by its synthesis from the corresponding diethyl ether adduct $[^{tBu}_{Am}$DIPP$^+$]Ca([SiMe$_3$]$^-$)$_2$([Et$_2$O]). The remarkably facile removal of ether in vacuo is accompanied by a change of the coordination mode from $NN$ to $N_{Aryl}$, as confirmed by XRD (see Figure 2). Structural features of 3 are similar to

![Molecular structure of $[^{tBu}_{Am}$DIPP$^+$]Ca([SiMe$_3$]$^-$)$_2$](image)
the additional THF ligands in co-workers (compare entries 1–2, 6–7 and 11–12, Table 2). Since between spectator ligand. This could be due to difference in ligand bulk reactivity can be solely attributed to the different amidinate and HBpin, which are present in large excess, the difference in accessibility in comparison to PhAm

**Catalyst Screening in Hydroboration**

With the four precatalysts 1–4 at hand, their performance in the hydroboration of various ketones using HBpin (4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was investigated (see Table 2). From these observations the following conclusions can be drawn.

(i) Complex \(\text{[Bu}^\text{AmDIPP} \text{Ca})_2\text{(SD)}\) (1), which exists as a iodo-bridged dimer in the solid state, already shows superior performance in comparison to \(\text{PrCa}_3\text{(THF)}_3\) used by Sen and co-workers (compare entries 1–2, 6–7 and 11–12, Table 2). Since the additional THF ligands in 1 have no influence on the catalysis, because they are rapidly replaced by the ketone substrates and HBpin, which are present in large excess, the difference in reactivity can be solely attributed to the different amidinate spectator ligand. This could be due to difference in ligand bulk between \(\text{[Bu}^\text{AmDIPP} \text{Ca})_2\text{(THF)}_3\) (1) and \(\text{PrAm}_3\text{Ca} \text{(THF)}_3\) thus making the metal center in \(\text{[Bu}^\text{AmDIPP} \text{Ca})_2\text{(THF)}_2\) (1) more electrophilic.

(ii) In case high electrophilicity of the Ca center is needed for activity, the exchange of the iodo anion for B(C\(_6\)F\(_5\))\(_4\) in 4(\(\text{MeO}\))\text{-Ca})_2\text{Me} (2) and subsequently to a change in coordination modes has been evaluated. The differences in coordination modes have been evaluated by DFT calculations (see Table S3 and S4, Supporting Information) are likely related to the increased Lewis acidity of the calcium center in the intermediate \(\text{[Bu}^\text{AmDIPP} \text{Ca})_2\text{Me} \text{(substrate)}\)\(_i\) in comparison to \(\text{[Bu}^\text{AmDIPP} \text{Ca})_2\text{Me} \text{(substrate)}\)\(_i\) (substrate = aldehyde, ketone and/or HBpin). Although the coordination mode of the amidinate differs in the precatalysts \(\text{[Bu}^\text{AmDIPP} \text{Ca})_2\text{Me} \text{(substrate)}\)\(_i\) to a symmetrical \(\text{N,Aryl}\) coordination is unlikely. It could be shown that addition of benzaldehyde (as a model substrate) led to a replacement of benzene in 2 and subsequently to a change of the initial \(\text{N,Aryl}\)-coordination mode to a symmetrical \(\text{N,N}\)-coordination, when an excess of substrate is present, as it is during catalysis (see Figure S12, Supporting Information).

(iii) The performance in catalysis of \(\text{[Bu}^\text{AmDIPP} \text{Ca})_2\text{Me} \text{(SMe)}_2\) (3) is not only clearly better than that of highly Lewis acidic 2 and an activity similar to that of previously investigated magnesium catalysts was found. For instance, the TOF of 600 h\(^{-1}\) in case of benzophenone, which often serves as benchmark substrate, is comparable to a replacement of benzene in 2 and subsequently to a change of the initial \(\text{N,Aryl}\)-coordination mode to a symmetrical \(\text{N,N}\)-coordination (see Table 2).

### Table 2. Hydroboration of ketones \((\text{R}^1\text{)}\text{(R}^2\text{)}\text{C}=\text{O})\) with HBpin at 25 °C in benzene/chlorobenzene (1:1).

| Entry | \(\text{R}^1\) | \(\text{R}^2\) | Catalyst[a,b] | Loading | \(t\) | Conv. |
|-------|----------------|----------------|-----------------|--------|-----|------|
| 1     |               |               | \(\text{PrAm}_3\text{Cal}\) | 3      | 300 | 95   |
| 2     | \(\text{Ph}\) | \(\text{Me}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 140 | 95   |
| 3     | \(\text{Ph}\) | \(\text{Me}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 40  | 97   |
| 4     | \(\text{Ph}\) | \(\text{Me}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 20  | >99  |
| 5     | \(\text{Ph}\) | \(\text{Me}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 20  | >99  |
| 6     | \(\text{Ph}\) | \(\text{Me}\)  | \(\text{PrAm}_3\text{Cal}\) | 3      | 300 | 73   |
| 7     | \(\text{Me}\) | \(\text{Ph}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 30  | >99  |
| 8     | \(\text{Me}\) | \(\text{Ph}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 20  | >99  |
| 9     | \(\text{Me}\) | \(\text{Ph}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 20  | >99  |
| 10    | \(\text{Me}\) | \(\text{Ph}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 20  | >99  |
| 11    | \(\text{Me}\) | \(\text{Ph}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 30  | >99  |
| 12    | \(\text{Me}\) | \(\text{Ph}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 30  | >99  |
| 13    | \(\text{Me}\) | \(\text{Ph}\)  | \(\text{PrAm}_3\text{Cal}\) | 0.5    | 30  | >99  |

[a] Catalysts: \(\text{[Bu}^\text{AmDIPP} \text{Ca})_2\text{Me} \text{(SMe)}_2\) \(\text{M} = \text{I} \) (1), \(\text{B}(\text{C}\(_6\)\text{F}\(_5\))_4\text{–}\) (2), (\(\text{SMe})_2\text{N}) \(\text{–}\) (3), \(\text{H}^+\) (4). [b] Determined by \(\text{H}^+\) NMR in 10 min intervals. [d] Determined by \(\text{H}^+\) NMR measurements.
(iv) Our earlier reported Ca hydride complex \( \text{[BuAmDIPP}CaH]\_2 \) (4) showed activities which are very similar to those of \( \text{[BuAmDIPP}CaN(SiMe\_2)\_2 \) (3). It is therefore likely that catalysts 3 and 4 operate through a metal hydride mechanism that is generally accepted for Mg catalysts of type LMgR (L = spectator ligand and R = active group).

The intermediacy of a hydride complex is obvious in case of 4 or Stasch’s Mg hydride catalyst, where the hydride is already present, or in case of \( \text{[MeBDIDIPP}MgBu} \) where the formation of \( \text{[MeBDIDIPP}MgH\_2} \) upon reaction with HBpin was conclusively proven. In case of Okuda’s \( \text{[Mg(thf)}\_6[HBPh\_3]_2 \) catalyst, transfer of a hydride from the boron center of the anion to magnesium (or directly to the substrate) seems feasible. In \( \text{[Mg(THF)}\_6[HB(C\_6H\_5)\_3]_2 \), however, such transfer is impeded by the higher Lewis acidity of the boron center, which is likely the reason for the inferior catalytic activity of this system. Calcium complexes containing a \( \text{(Me\_3Si)\_2N}^- \) group are also known as excellent precursors for the formation of calcium hydride complexes, e.g. by reaction with PhSiH\_3, and it may be envisioned that the well-known complex \( \text{[BuAmDIPP}CaH\_2} \) forms under catalytic conditions as well.

Alternative to a hydride cycle is a pathway in which the hydride is not transferred from the metal to the ketone but directly from the borate (Scheme 3, far left). Indications that hydroboration not necessarily proceeds through the intermediacy of a metal hydride complex come from our group’s previous studies of pyridine hydroboration. This conclusion was based on differences in regioselectivity between stoichiometric metal hydride reactions and catalytic conversions.

Catalysts 1, 2 and 2 do not contain active groups and it is a priori not clear how in this case intermediate hydride or borate species could be formed. Since the activity for this groups of catalysts increases with increasing Lewis acidity, we propose a mechanism in which the metal’s Lewis acidity plays a central role. It could be envisioned that HBpin and the ketone both bind to the Ca\(^{2+}\) metal center. Polarization of the C=O bond subsequently leads to hydride transfer and concomitant B–O bond formation. This direct B–H/C=O addition mechanism is similar to that proposed for catalyst-free ketone hydroboration. Ketone hydroboration by Lewis acidic Ca complexes could best be interpreted by considering the Ca\(^{2+}\) metal as a connector that brings both substrates in close vicinity. This compensates for the considerable entropy loss in ketone hydroboration.

Hydroboration of aldehydes was also briefly tested, but due the ease of this transformation and the resulting higher reaction rates, differences between the different catalysts are less pronounced (compare Supporting Information, Table S3).

**Conclusion**

We have prepared a series of Ca amidinate complexes with the amidinate ligand \( \text{BuAmDIPP} \). This bulky ligand is able to saturate the coordination sphere of large metal ions like Ca\(^{2+}\) by N\_Aryl- or N\_N-chelation. N\_N-coordination is typically observed when coordinating solvents are present, e.g. in \( \text{[BuAmDIPP}Ca(THF)\_2} \) (1) or \( \text{[BuAmDIPP}CaN(SiMe\_2)\_2Et\_2O} \) or when there is not enough space available for N\_ary coordination, e.g. in homoleptic \( \text{[BuAmDIPP}Ca} \). The buried volume for the ligand with N\_aryl-coordination is comparable to that of the widely known \( \beta\)-ketiminate ligand \( \text{MeBDIDIPP} \). Using \( \text{BuAmDIPP} \) we achieved the isolation of the first “naked” (Lewis base-free) cationic Ca amidinate complex \( \text{[BuAmDIPP}Ca(C\_6H\_5)\_2[BC(C\_6H\_5)\_3]} \) (2) in which the ligand is bound by N\_aryl-chelation. This coordination mode was also found in ether-free \( \text{BuAmDIPP}CaN(SiMe\_2)\_2 \) (3). In solution, the fast exchange between N\_aryl- and N\_N-coordination modes is more facile in \( \text{BuAmDIPP}CaN(SiMe\_2)\_2 \) (\( \Delta G = 14.3 \) kcal/mol) than in the cation \( \text{[BuAmDIPP}Ca(C\_6H\_5)\_2]^{+} \) (\( \Delta G = 16.1 \) kcal/mol). This likely originates from the higher Lewis acidity of the metal in the cationic complex.

We demonstrated that calcium complexes bearing the highly flexible amidinate ligand \( \text{BuAmDIPP} \) are suitable catalysts for the hydroboration of ketones and aldehydes. Since catalysts 1–4 carry the same spectator ligand the influence of the second anionic ligand or counter anion could be evaluated. The anion
or counterion X− in the catalysts [BuAmDIPP]CaX significantly influences the performance of the system and activities increase along the series I− < B(C6F5)4− < (Me3Si)2N− N− = H+. For the first two catalysts with I− or B(C6F5)4−, catalyst activities increase with the Lewis acidity of the metal. However, compared to these catalysts, Ca complexes with X− = (Me3Si)2N− or H− must operate through a reactive ligand X−, like (Me3Si)2N− or H−, in vacuum (hept, 3 Å). C6D6, C6D5Br and CDCl3 were dried with 3 Å molecular sieves. All experiments were conducted under an inert nitrogen atmosphere in vacuum (hept, 3 Å). C6D6, C6D5Br and CDCl3 were dried with 3 Å molecular sieves unless otherwise noted. Chlorobenzene was dried with activated aluminium oxide (Solvent Purification System: Pure Solv 400–4 MD). Innovative Technology) and stored over 3 Å molecular sieves unless otherwise noted. Chlorobenzene was dried with calcium hydride, distilled under N2 atmosphere and stored over molecular sieves 3 Å, C6D6, C6D5Br and CDC13 were dried with 3 Å molecular sieves. [Ph3C]+[B(C6F5)4]− (Boulder Scientific), 4′-nitroacetophenone, 4-chlorobenzaldehyde, 4-cyanoacetophenone, H3pbin, 4′-bromocetophenone, mesitylaldehyde, benzophenone, 4′-methoxyacetophenone and 4′- (trifluoromethyl)acetophenone were used as received. Benzaldehyde, cyclohexanone, pinacolone and acetoacetone were dried with molecular sieves 3 Å, distilled and stored as received. Benzaldehyde, cyclohexanone, pinacolone and acetoacetone were used.

**Experimental Section**

All experiments were conducted under an inert nitrogen atmosphere using standard Schlenk and glovebox techniques (MBraun, Labmaster SP). Benzene, toluene and hexane were degassed with nitrogen, dried with activated aluminium oxide (Solvent Purification System: Pure Solv 400–4 MD). Innovative Technology) and stored over 3 Å molecular sieves unless otherwise noted. Chlorobenzene was dried with calcium hydride, distilled under N2 atmosphere and stored over molecular sieves 3 Å, C6D6, C6D5Br and CDC13 were dried with 3 Å molecular sieves. [Ph3C]+[B(C6F5)4]− (Boulder Scientific), 4′-nitroacetophenone, 4-chlorobenzaldehyde, 4-cyanoacetophenone, H3pbin, 4′-bromocetophenone, mesitylaldehyde, benzophenone, 4′-methoxyacetophenone and 4′- (trifluoromethyl)acetophenone were used as received. Benzaldehyde, cyclohexanone, pinacolone and acetoacetone were dried with molecular sieves 3 Å, distilled and stored under N2 atmosphere. The resulting yellow suspension was stirred overnight, and all volatiles were removed in vacuo. Addition of benzene (2 mL) to the yellow foam led to the formation of two phases. The upper phase was removed, and the lower phase was washed with benzene (5 × 1 mL). Crystals could be obtained by storing the biphasic system at room temperature over several days. Crystallization can be forced by addition of seed crystals. The obtained crystals have to be further purified by thermal diffusion in an 1:4 mixture of benzene/hexane at 65 °C (see Supporting Information, Figure S11). Yield: 392.4 mg (62 %). 1H NMR (600 MHz, C6D5Br, 298 K): δ/ppm = 0.82 (d, 3JHH = 6.6 Hz, 6H, CHMe2), 1.27–1.16 (m, 27H, CMe3, 3 × CHMe), 3.03 (hept, 3JHH = 6.3 Hz, 2H, CHMe2), 6.84 (d, 3JHH = 7.6 Hz, 2H, ArH), 6.91 (1H, 3JHH = 7.6 Hz, 1H, ArH), 7.11 (1H, 3JHH = 7.5 Hz, 1H, ArH), 7.01 (partly omitted by solvent, 2H, ArH), 7.21 (1H, 6H, benzene).

**Synthesis of [{BuAmDIPP} H2][BuAmDIPP][C(C6F5)3]:** A solution of 480.9 mg (0.5214 mmol) [Ph3C]+[B(C6F5)4]− in 2 mL of chlorobenzene was added slowly to a suspension of 240.3 mg [Ph3C]+[B(C6F5)4]− in 2 mL of chloroform. The solutions were added at the respective residual signals of the deuterated solvents. Elemental analysis was performed with a Euro EA 3000 (Euro Vector) analyzer. All crystal structures have been measured on an Agilent automatic diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector.

**Catalytic Hydroboration of Aldehydes and Ketones:**

For catalysts 1–3 0.82 mmol and 8.22 mm mol stock solutions in chlorobenzene were prepared. Since catalyst 4 is insoluble in chlorobenzene, a 8.22 mm mol stock solution in THF was prepared. For catalytic runs with 0.05–1 mol-% catalyst loadings, the following quantities of stock solutions have been used: 0.05 mol-% (60 µL, 0.82 mmol), 0.5 mol-% (60 µL, 8.22 mmol), 1 mol-% (120 µL, 8.22 mmol). Catalytic experiments with catalysts 1–3 have been performed in a 2:1 chlorobenzene/

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C₆D₆ solution (400 µL chlorobenzene, 200 µL C₆D₆). Catalytic experiments with 4 were run in a THF/chlorobenzene/C₆D₆ mixture (60 µL THF, 340 µL chlorobenzene, 200 µL C₆D₆). This means that the given amount of stock solutions was filled up with chlorobenzene to a total volume of 400 µL and subsequently an additional 200 µL of C₆D₆ was added (the latter was used for D-locking during ¹H NMR monitoring). For the higher catalyst loading of 5 mol-% the catalyst was weighed in as a pure substance and dissolved in 400 µL of chlorobenzene and 200 µL of C₆D₆. After addition of 14.3 µL HBpin (98.6 µmol), the sample was thoroughly mixed and the first ¹H NMR spectrum was recorded within 10 min. The reaction was monitored by ¹H NMR in 10 min intervals. Upon completion of the reaction, the solvent was removed in vacuo and CCl₃ was added. NMR data and spectra can be found in the supporting information.

**Crystal Structure Determinations:** Using Olex2,[30] the structure was solved by Intrinsic Phasing (Shelix)[31] and refined with ShelXL[32] using Least Squares minimization. All non-hydrogen atoms were placed in ideal positions and refined as riding hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Crystal data and experimental methods can be found in the Supporting Information.

ShelXL[32] using Least Squares minimization. All non-hydrogen atoms with relative isotropic displacement parameters. Crystal data and experimental methods can be found in the Supporting Information.

Using Olex2,[30] the structure was solved by Intrinsic Phasing (Shelix) [31] and refined with ShelXL[32] using Least Squares minimization. All non-hydrogen atoms were placed in ideal positions and refined as riding hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Crystal data and experimental methods can be found in the Supporting Information.

The Cambridge Crystallographic Data Centre.

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**Keywords:** Calcium · Hydroboronation · Cationic complexes · Homogeneous catalysis · Amidinates

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