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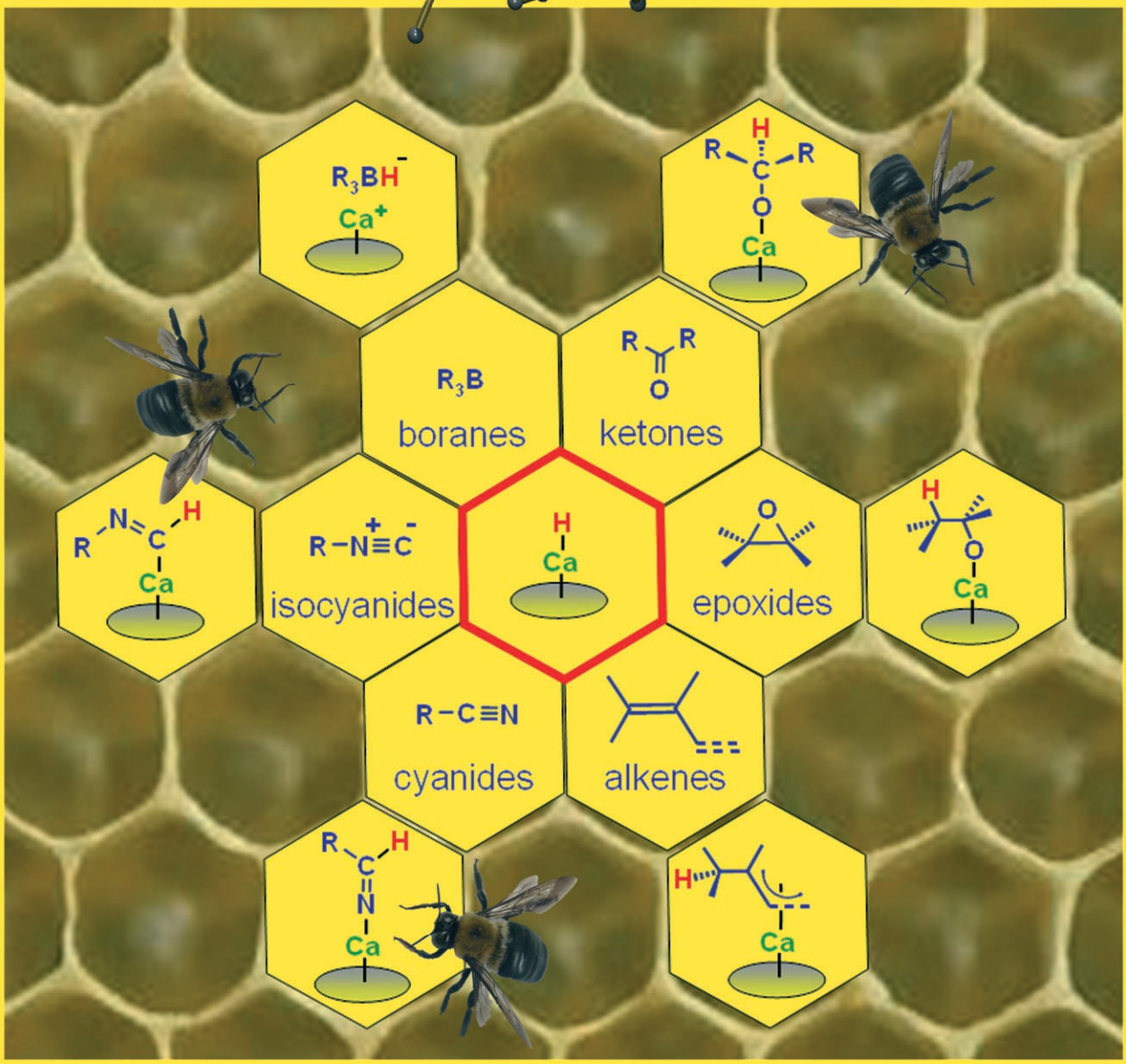

Hydrocarbon-Soluble Calcium Hydride: A "Worker-Bee" in Calcium Chemistry

Jan Spielmann and Sjoerd Harder*[a]

Abstract: The reactivity of the hydrocarbon-soluble calcium hydride complex [{CaH(dipp-nacnac)(thf)}$_2$] (**1**; dipp-nacnac = CH{(CMe)(2,6-*i*Pr$_2$-C$_6$H$_3$N)}$_2$) with a large variety of substrates has been investigated. Addition of **1** to C=O and C=N functionalities gave easy access to calcium alkoxide and amide complexes. Similarly, reduction of the C≡N bond in a cyanide or an isocyanide resulted in the first calcium aldimide complexes [Ca{N=C(H)-R}(dipp-nacnac)] and [Ca{C(H)=NR}-(dipp-nacnac)], respectively. Complexation of **1** with borane or alane Lewis acids gave the borates and alanates as contact ion pairs. In reaction with epoxides, nucleophilic ring-opening is observed as the major reaction. The high reactivity of hydrocarbon-soluble **1** with most functional groups contrasts strongly with that of insoluble CaH_2, which is essentially inert and is used as a common drying agent. Crystal structures of the following products are presented: [{Ca{OC(H)Ph$_2$}(dipp-nacnac)}$_2$], [{Ca{N=C(H)Ph}(dipp-nacnac)}$_2$], [{Ca{C(H)=NC(Me)$_2$CH$_2$C-(Me)$_3$}(dipp-nacnac)}$_2$], [{Ca{C(H)=NCy}(dipp-nacnac)}$_2$], [Ca(dipp-nacnac)(thf)]$^+$[H$_2$BC$_8$H$_{14}$]$^-$ and [{Ca-(OCy)(dipp-nacnac)}$_2$]. The generally smooth and clean conversions of **1** with a variety of substrates and the stability of most intermediates against ligand exchange make **1** a valuable key precursor in the syntheses of a wide variety of β-diketiminate calcium complexes.

Keywords: alkaline-earth metals · calcium · metal hydrides · reduction

Introduction

Complexes with the hydride ligand, the simplest functionality in chemistry, have been investigated for various metals throughout the periodic table. In particular the enormous interest in the chemistry of transition metal hydrides, expressed by numerous reviews and books, has always been fuelled by its applications in catalysis.[1] There is hardly any catalytic industrial process in which transition-metal hydrides do not play a role. As lanthanide catalysts are becoming of increasing importance, also lanthanide hydride chemistry is progressing rapidly.[2] Likewise, the considerable potential for late main-group metal hydrides as reagents in organic key transformations, material science or reduction chemistry is well established.[3]

Early main group metal hydride chemistry, however, is mainly restricted to the chemistry of their binary compounds $[MH_x]_\infty$. As these salt-like compounds, with very high lattice energies, have the ability to store and deliver hydrogen on request, they are potential key players in the hydrogen economy and research in this generously subsidised area is actively pursued.[3f,4]

This sharply contrasts with the chemistry of early main-group metal hydride complexes. With only few exceptions, this area is virtually unexplored. PhMgH and PhCaH appeared in literature already some years ago, however, no NMR spectroscopic or structural proof has been presented.[5a,b] A crystalline complex of composition [CpMgH(thf)] was characterised by NMR spectroscopy and its reduction chemistry has been investigated.[5c] Only few early main-group metal hydride complexes have been confirmed by crystallographic analysis. The hydride anion has been trapped in mixed metal clusters (Li/Al, Li/Zn or Na/Mg),[6] a larger aggregate of [(LiH)$_{17}$(*t*BuOLi)$_{16}$] has been characterised[7] and the heteroleptic scorpionate complex [tris(3-*tert*-butylpyrazolyl)hydroborato]beryllium hydride ([BeH-(*t*BuTp)]) was introduced.[8] The hydride clusters were generally prepared by self-organisation from in situ generated metal hydride and bulky anions, which in light of the complete insolubility of the binary hydrides seems the only possibility.

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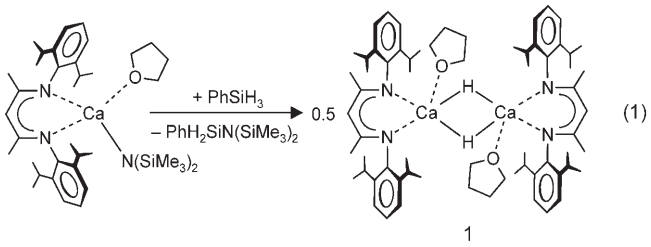
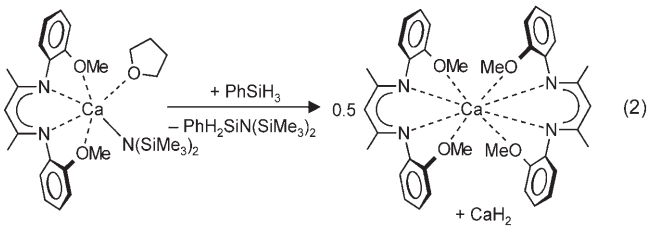
We recently introduced an efficient method for in situ generation of Group 1 and 2 metal hydrides:[9] reaction of metal–benzyl or metal–amide functionalities with $PhSiH_3$ gave clean conversion to the metal hydride and a silane (a method very common in lanthanide chemistry).[2] Thus, we prepared a calcium hydride complex [Eq. (1)], which could be characterised as a dimer by single-crystal X-ray diffraction: $[\{CaH(dipp\text{-}nacnac)(thf)\}_2]$ (**1**).[9b]



(1)



(2)

The bidentate, strongly coordinating, bulky β-diketiminate ligand dipp-nacnac (dipp-nacnac = CH{(CMe)(2,6-*i*Pr_2-C_6H_3N)}$_2$)) is of crucial importance for the stability of this hydride complex. We attempted to substitute steric shielding of the calcium coordination sphere with electronic saturation by use of a ligand recently introduced by Chisholm [Eq. (2)].[10a] Reaction of this heteroleptic calcium amide with $PhSiH_3$, however, gave complete conversion to a well-characterised homoleptic β-diketiminate calcium complex[10a] and CaH_2.

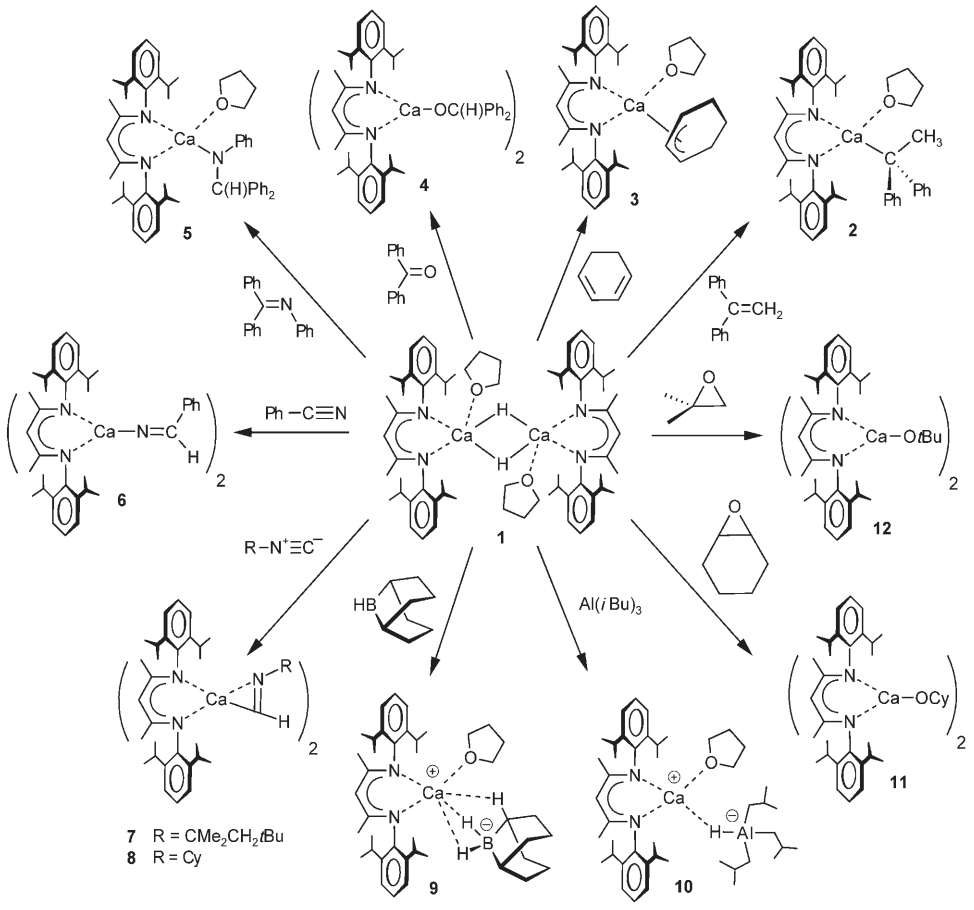
Complex **1**, however, is easily soluble in hydrocarbons and shows considerable stability against ligand disproportionation: short periods of reflux in benzene gave no significant decomposition, but longer heating gave slow ligand exchange to $[Ca(dipp\text{-}nacnac)_2]$[11] and insoluble CaH_2. The half-life time of **1** in refluxing benzene is about 24 h. This unusual stability at higher temperatures, therefore allows thorough screening on the reactivity of this well-defined calcium hydride complex. Here we present transformations with several substrates and show its importance as a convenient precursor in the syntheses of a variety of calcium complexes.

Results and Discussion

Successful transformations of **1** to isolated and characterised products are summarised in Scheme 1. These reactions can be divided in subgroups which will be discussed in the following sections.

Reactions with unsaturated CC bonds: Addition of the calcium hydride functionality to an alkene is one of the key steps in the catalytic hydrosilylation of alkenes, recently introduced by us.[9] Stoichiometric addition of **1** to alkene substrates could be a straightforward synthetic method for a wide range of alkylcalcium complexes.

Several alkenes have been screened in reaction with **1**. As expected, isolated alkenes like norbornene did not react with **1**, also not under reflux conditions. This limits the



Scheme 1.

method to styrenic and butadienic substrates and thus to benzylic and allylic products.

Addition of stoichiometric quantities of styrene to a solution of **1** in benzene gave an immediate colour change to red indicative for formation of a benzylic anion. Styrene was completely converted within 90 minutes at room temperature. However, approximately one third of **1** was unreacted, which indicates possible formation of styrene oligomers as a side reaction. This was indeed confirmed by numerous signals in the ^{1}H NMR spectrum. Attempts to isolate [Ca{CH(Me)Ph}(dipp-nacnac)] from this mixture failed and only [Ca(dipp-nacnac)$_2$] could be obtained. Similar results were obtained with α-Me-styrene. Therefore, it can be concluded that: i) the resulting benzylcalcium complexes are too reactive and further react with styrene to give oligomers, and ii) the heteroleptic benzyl and oligostyryl calcium complexes easily disproportionate in homoleptic species.

Addition of the bulkier 1,1,-diphenylethylene to a solution of **1** in benzene gave at 60 °C a clean conversion to the less nucleophilic calcium complex **2**. Although dark-red needle-like crystals could be isolated (58 %), the crystal quality was insufficient for a structure determination. ^{1}H NMR spectroscopy, however, revealed the composition [Ca{C(Ph)$_2$Me}(dipp-nacnac)(thf)] and confirmed the heteroleptic nature of the complex. Broadening of the signals for the *i*Pr-CH and part of the *i*Pr-Me groups indicate slow site-exchange of thf and the Me(Ph)$_2$C$^-$ ion, similar to the process extensively described for exchange of the *t*BuO/thf groups in [Mg(O*t*Bu)(dipp-nacnac)(thf)].[10b]

Reaction of cyclohexadiene with **1** gave at 40 °C conversion to a cyclohexenylcalcium complex (**3**), which could be crystallised as yellow plate-like crystals (34 %). The crystal structure could be solved (Figure 1); however, the refinement was hindered by poor crystal quality due to twinning problems. Therefore, no extensive discussion on bond lengths and angles can be made and only three-dimensional connectivity is presented here. The insertion product crystallises as a monomer of composition [Ca(C$_6$H$_9$)(dipp-nacnac)(thf)] in which the cyclohexenyl anion coordinates in η^3-allylic fashion to Ca^{2+}.

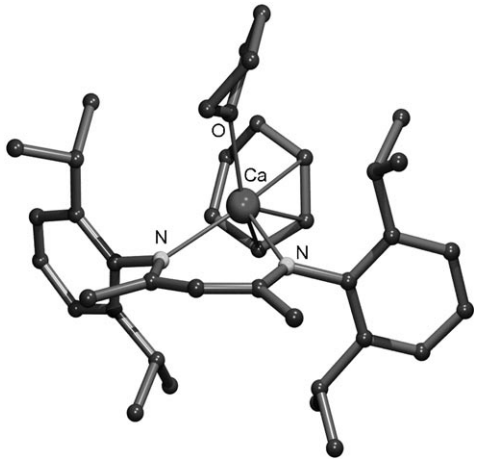


Figure 1. Crystal structure of **3**. Hydrogen atoms have been omitted for clarity. Due to poor crystal quality no geometric parameters are given.

Interestingly, the addition of the Ca–H functionality to cyclohexadiene seems reversible: a solution of **3** in benzene showed at room temperature slow decomposition in **1**, and ^{1}H NMR signals indicative for oligocyclohexadiene[12] could be observed (after 96 h 44 % of **1** is formed). This is in line with β-H elimination followed by insertion of cyclohexadiene in a Ca–C bond.

Reaction of **1** with a C≡C bond could give access to hitherto unknown alkenylcalcium complexes. Addition of diphenylacetylene to **1** dissolved in benzene gave at 40 °C a deep-red solution indicative for formation of the [Ph(H)C=(Ph)C]$^-$ ion. The ^{1}H NMR spectrum of the reaction product showed several unidentified species and broad signals suggestive of oligomerisation. Attempted crystallisation of possible reaction intermediates solely resulted in the isolation of [Ca(dipp-nacnac)$_2$]. Therefore, isolation of the intermediate alkenyl calcium complex is hindered by its high reactivity and its lability against ligand exchange.

Reactions with unsaturated CO bonds: The conversion of a carbonyl functionality in an alcohol by reduction with main-group metal hydrides is nowadays a standard reaction in organic chemistry. The solubilisation of the insoluble salts [LiH]$_\infty$ and [AlH$_3$]$_\infty$ through combination in the ether-soluble "ate" complex LiAlH$_4$ has played a pivotal role in this development.[13]

Addition of benzophenone to **1** dissolved in benzene gave immediate formation of small colourless crystals of **4**. Recrystallisation by shortly heating to 80 °C and slowly cooling to 8 °C gave the product in the form of large prisms (73 %). The crystal structure (Figure 2) shows a centrosymmetric dimeric complex in which the [Ph$_2$C(H)O]$^-$ ions bridge the

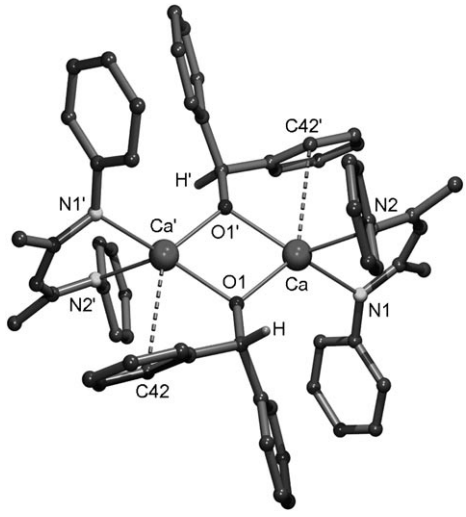


Figure 2. Crystal structure of **4**. The *i*Pr substituents and hydrogen atoms (except the hydrogen atom transferred to Ph$_2$C=O) have been omitted for clarity. Selected bond lengths (Å): Ca–O1 2.261(1), Ca–O1′ 2.317(1), Ca–N1 2.398(1), Ca–N2 2.405(1), Ca···C42′ 3.180(2).

two Ca^{2+} ions. The coordination sphere of Ca^{2+} is saturated by an additional π-Ph···Ca^{2+} interaction with one of the phenyl rings of $[Ph_2C(H)O]^-$ (the shortest Ca···C contact is 3.180(2) Å). This contact causes a slightly asymmetric bridging of the $[Ph_2C(H)O]^-$ ions: the Ca–O bond lengths are 2.261(1) Å and 2.317(1) Å.

Reactions with unsaturated CN bonds: The reduction of imines with main-group metal hydrides is a standard procedure for the syntheses of amines. Similarly, reaction of **1** with imines could give easy access to a variety of calcium amide complexes. Indeed, reaction of **1** with diphenylmethyl-*N*-phenylimine gave a fast and clean addition to the heteroleptic amide, which could be isolated as a crystalline pure product of formula [Ca{N(Ph)C(Ph)$_2$H}(dipp-nacnac)(thf)] (**5**).

Accordingly, the reduction of the cyanide functionality by $LiAlH_4$ is a well-established reaction for the syntheses of imines or amines from nitriles. Although in organic synthesis hydroalumination products are usually not isolated but quenched to the corresponding products, recently several reports appeared on the isolation and structures of the intermediate aldimide and imido complexes.[3e,14]

Reaction of **1** with benzonitrile in benzene gave at 60 °C clean conversion to the easily soluble benzaldimide complex **6**, which crystallised upon cooling a concentrated reaction mixture in 58 % yield. The crystal structure shows a centrosymmetric dimer in which benzaldimide ions bridge symmetrically between the Ca^{2+} ions (Figure 3). The Ca–N

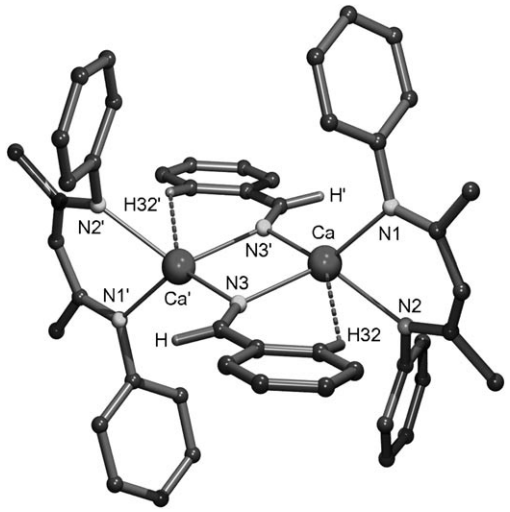


Figure 3. Crystal structure of **6**. The *i*Pr substituents and hydrogen atoms (except the hydrogen atom transferred to PhC=N and that involved in agostic interaction) have been omitted for clarity. Selected bond lengths (Å): Ca–N1 2.3357(8), Ca–N2 2.3512(8), Ca–N3 2.372(1), Ca–N3′ 2.392(1), Ca···H32 2.86(2).

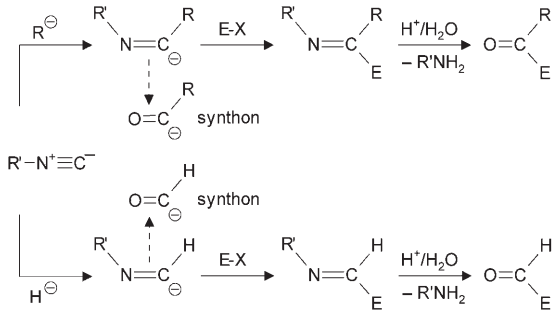
bond lengths of 2.372(1) and 2.392(1) Å are somewhat longer than those to the terminal dipp-nacnac ligand (average: 2.3435(8) Å). The nearly planar benzaldimide anions are arranged coplanar with the Ca-N3-Ca′-N3′ ring (the dihedral angle between least-squares planes is 17.6(1)°). This coplanar arrangement, which has also been observed in [{R_2Al–N=C(H)Ph}$_2$] complexes, allows for maximal interaction of the Ca^{2+} ions with the electron pairs on the sp^2-hybridised aldimide nitrogen atom. This preferred van't Hoff geometry[15] has been confirmed by calculation: the planar conformation in [(H_2C=NLi)$_2$] is 17 kcal mol^{-1} more stable than the alternative perpendicular conformation.[16] Distortion of this favourite bridging mode towards the perpendicular anti-van't Hoff geometry has been observed in the dimer [{*t*Bu$_2$C=N–Li(hmpa)$_2$}$_2$] and should be attributed to steric effects.[17] The coordination sphere of Ca^{2+} in **6** is completed by an additional agostic Ca···H interaction of 2.86(2) Å with the *ortho*-H from the benzaldimide anion (which was located and refined). This bonding interaction is an additional impetus for the coplanar van't Hoff geometry of the bridging aldimide groups.

The ^{1}H NMR spectrum of **6** exhibits a characteristic low-field signal for the H–C=N unit at 9.70 ppm, that is, slightly downfield to those in dimeric benzaldimide complexes of aluminium (range 8.82–9.13 ppm).[14] A *cis-trans* isomerisation, as observed for bridging benzaldimide ions in [R_2Al N=C(Ph)H]$_2$,[14] could not be observed for **6** and only one set of signals appeared in the ^{1}H and ^{13}C NMR spectra.

Double addition of the calcium hydride to the cyanide functionality could result in a hitherto unknown calcium imido complex: $Ca^{2+}[PhCH_2N]^{2-}$. However, this reaction could not be observed even after forcing reflux conditions. This is in contrast with the reactivity of $H_3Al{\cdot}(NMe_3)$ and [LnCp′H_2] (Ln = lanthanide), which both gave a clean double hydrometallation of benzonitrile.[3b,2d] The difference in reactivity could be attributed to the difference in Lewis acidity of the Ca^{2+} and Al^{3+} (or Ln^{3+}) ions: the stronger Lewis acid activates the intermediate Ph(H)C=N$^-$ ion for further addition of a hydride. On the other hand, reaction of [Al(alkyl)$_2$H][14] or [{Cp$_2$YH(thf)}$_2$] [18] with benzonitrile also gave exclusively single additions of the hydride to the cyanide group. The presence of more than one hydride functionality might therefore be essential for twofold addition.

Although base-catalysed polymerisation of benzonitrile has been known for quite some time, the recent publication of new domino reactions,[19,20] motivated us to react **1** also with excess benzonitrile. Reaction of **1** with three equivalents of benzonitrile at 60 °C was monitored by ^{1}H NMR spectroscopy. The initially formed product **6** reacted very slowly further and several new species could be detected. Finally, after three days 65 % of the trimerisation product (PhCN)$_3$ could be isolated. As this conversion is paralleled by formation of homoleptic [Ca(dipp-nacnac)$_2$] and presumably a fine precipitate of CaH_2, this reaction is not catalytic.

Nucleophilic addition of carbanions to the isocyanide functionality is an important reaction in the "Umpolung" concept. The intermediate metallo aldimine can be seen as an equivalent to the acyl anion (Scheme 2).[21] Similarly, addition of a metal hydride to an isocyanide function would give the synthetic equivalent to the formyl anion, an important building block for which recently also SAMP-technolo-



Scheme 2.

gy (SAMP = (*S*)-1-amino-2-methoxymethylpyrrolidine) was introduced.[22]

Reaction of the colourless calcium hydride complex **1** in benzene with 1,1,3,3-tetramethylbutylisonitrile resulted in a deep-green solution. ^{1}H NMR analysis showed that at room-temperature conversion is essentially complete after 30 minutes and several products were formed. Cooling the solution to 5 °C gave a crop of well-defined colourless crystals of the 1,1-insertion product **7** in 52 % yield. The origin of the intense deep-green colour of the mother liquor is unknown, but is likely due to intensely coloured side products. These compounds could not be ambiguously identified but could arise from oligomerisation and/or ring-closure reactions that are typical for nucleophilic attack at isonitriles (vide infra).[23] A similar reaction of **1** with cyclohexylisonitrile led to the immediate appearance of a blue colour and within minutes colourless crystals of **8** precipitated in 29 % yield.

The crystal structures of the calcium aldimide complexes **7** and **8** are shown in Figure 4. Both crystallise as centrosymmetric dimers in which the RN=(H)C$^-$ anions bridge the two Ca^{2+} ions. Whereas the Ca–C bonds in **7** are similar, 2.579(2) and 2.580(2) Å, bridging in **8** is less symmetric and Ca–C bonds of 2.556(2) and 2.625(2) Å are observed. This bridging nature of the aldimide carbon is not observed in the structure of an aluminium complex, [{Al{C(H)=N*t*Bu}-(*t*Bu)$_2$}$_2$],[14] in which the *t*BuN=(H)C$^-$ ions bridge through one Al–C and one Al–N bond. The Ca^{2+} ions in **7** and **8** are additionally bound to the N atom of the aldimide ions. The short Ca–N bond lengths of 2.332(2) (**7**) and 2.330(2) Å (**8**) are in the same range as the Ca–N bonds involving the dipp-nacnac ligands (2.327(2)–2.368(1) Å) and are indicative for the strong donor ability of the aldimide N atom. The C=N bonds in **7** (1.277(2) Å) and **8** (1.290(3) Å) are consistent with a formal C=N bond of 1.279 Å[24] and also similar to the C=N bond of 1.285(2) Å in [{Al{C(H)=N*t*Bu}-(*t*Bu)$_2$}$_2$].[14]

A colourless solution of **8** in benzene rearranged after one day at 50 °C to give complex **8′**, which is extremely soluble in hexane. Even at −80 °C, this complex could not be crystallised from highly concentrated solutions. Whereas the NMR signal for the RN=C(*H*) proton in **8** appeared at rather low field (9.97 ppm), the new complex **8′** shows a singlet at 5.29 ppm. High-resolution ESI-TOF mass spectrometry analysis of this isomerisation product unambiguously

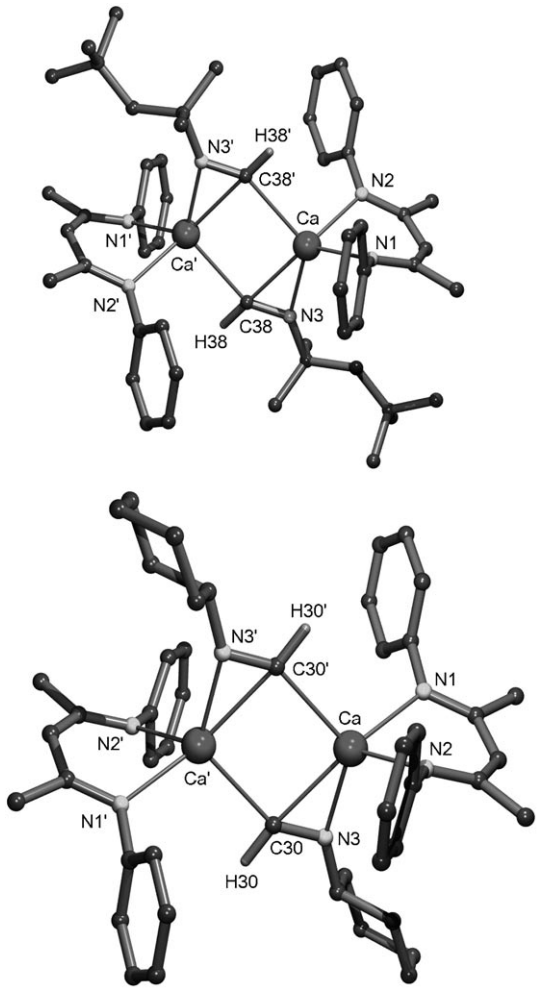
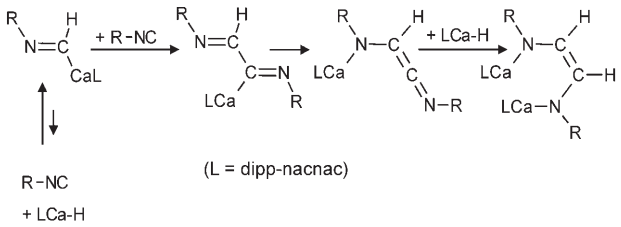


Figure 4. Crystal structures of **7** (top) and **8** (bottom). The *i*Pr substituents and hydrogen atoms (except the hydrogen atom transferred to the isonitrile) have been omitted for clarity. Selected bond lengths for **7** (Å): Ca–N1 2.327(2), Ca–N2 2.368(1), Ca–N3 2.332(2), Ca–C38 2.580(2), Ca–C38′ 2.579(2), C30–N3 1.290(3). Selected bond lengths for **8** (Å): Ca–N1 2.345(2), Ca–N2 2.341(2), Ca–N3 2.330(2), Ca–C30 2.556(2), Ca–C30′ 2.625(2), C30–N3 1.277(2).

shows C–C coupling products and we propose the isomerisation process shown in Scheme 3. It is assumed that the addition of **1** to cyclohexyl isocyanide is a reversible process. 1,1-Addition of **8** to the freed isocyanide gives a C–C coupled intermediate (comparable to the first step in the polymerisation of isonitriles) that rearranges to a ketenimine.



Scheme 3.

Subsequent addition of the hydride gives an isomer with the $[CyNCHCHNCy]^{2-}$ ion. ^{1}H and ^{13}C NMR data as well as appearance of a blue-green colour support formation of this product. Similar isomerisation processes have been observed in Ga chemistry.[23]

Reactions with Lewis acids: The R_3BH^- ion has found extensive use as a hydride source and reducing agent.[3a,25] Recently, Hanusa et al. published the synthesis and structure of a cyclopentadienylcalcium species containing a "superhydride" anion: $[Ca(HBEt_3)\{1,2,4\text{-}(Me_3Si)_3Cp\}(thf)_2]$.[26] The crystal structure shows strong bidentate Et_3BH^-–Ca^{2+} bonding through B–H···Ca^{2+} and C–H···Ca^{2+} contacts. It was reasoned that this ligation prevented the intended thermal decomposition in Et_3B and $[CaH\{(Me_3Si)_3Cp\}]$. From comparison of the Lewis acidities of Ca^{2+} and R_3B, the reverse reaction seems more likely to proceed. Reaction of **1** with borane substrates thus opens a synthetic pathway to a large variety of calcium borohydride complexes.

Addition of 9-borabicyclononane (9-BBN, $C_8H_{14}BH$) to a solution of **1** in benzene gave at 60 °C full conversion within minutes and the product **9** could be obtained as large colourless block-like crystals (67 %) by cooling a concentrated solution. The crystal structure of **9** (Figure 5) shows two monomeric calcium borohydride complexes of formula $[Ca(H_2BC_8H_{14})(dipp\text{-}nacnac)(thf)]$ in the asymmetric unit. In both, the borohydride anion binds tridentate to the Ca^{2+} ion through the BH_2 unit and an agostic C–H···Ca^{2+} interaction with very similar bond lengths. The two independent molecules differ in the relative orientation of the $[C_8H_{14}BH_2]^-$ ion towards the other ligands. The average B–H···Ca^{2+} (2.25(2) Å) and C–H···Ca^{2+} (2.42(2) Å) contacts compare well to those observed in $[Ca(HBEt_3)\{(Me_3Si)_3Cp\}(thf)_2]$ of 2.21(4) and 2.41 Å, respectively.[26] Although Ca^{2+} and Yb^{2+} have similar ionic radii and structures,[27] the borohydride ligands in $[Me_4N]_2^{2+}[Yb^{II}(C_8H_{14}BH_2)_4]^{2-}$ show much longer contacts to the metal: average B–H···Yb and C–H···Yb contacts of 2.39(4) and 2.57(4) Å have been reported, respectively.[28]

The ^{11}B NMR resonance and ^{11}B–^{1}H coupling constant in **9** dissolved in C_6D_6 ($\delta = -12.0$ ppm; $J(^{11}B,^{1}H) = 70.3$ Hz) are characteristic for a bridging B–H···metal interaction,[26] which suggests that the contact ion-pair is retained in solution. The appearance of one signal for the two primary BCH protons suggests fast exchange of the weaker agostic BCH···Ca^{2+} interaction.

Similarly, reaction of **1** with $Al(iBu)_3$ in benzene gave immediate conversion to an alanate complex. The highly soluble oily product recrystallised from hexane in the form of large well-defined colourless crystals (**10**, 25 %) of formula $[Ca(dipp\text{-}nacnac)\{HAl(iBu)_3\}(thf)]$ from which we presume its monomeric nature. As the conversion of **1** with $Al(iBu)_3$ is essentially complete, the low crystalline yield is attributed to the extreme solubility of **10** in hexanes. Despite the considerable quadrupole moment of ^{27}Al, the ^{1}H NMR signal for the aluminium hydride proton can be observed as a very broad singlet at 3.45 ppm.

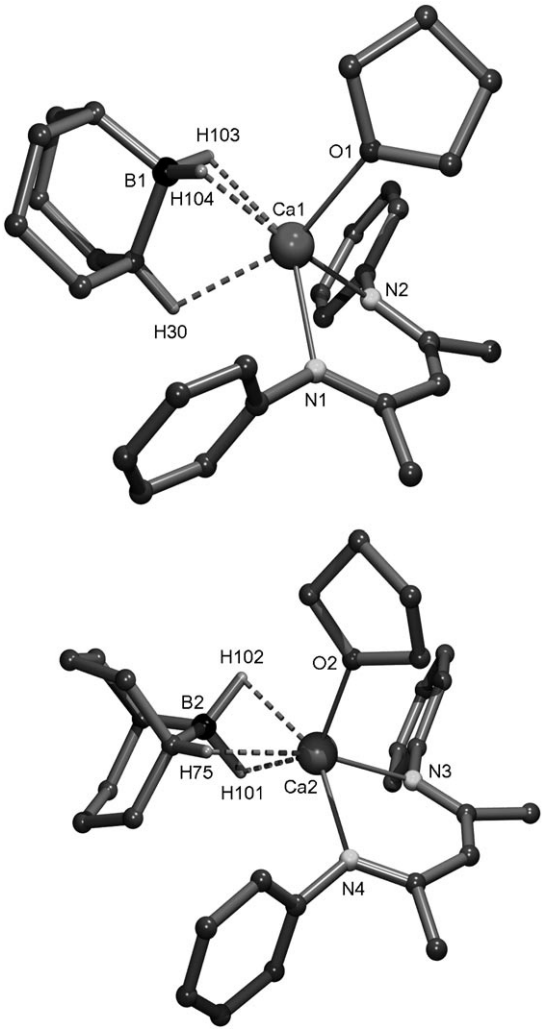


Figure 5. Crystal structure of **9**. The *i*Pr substituents and hydrogen atoms (except the hydrogen atoms involved in bonding to Ca^{2+}) have been omitted for clarity. Selected bond lengths (Å) for molecule 1 (top): Ca1–N1 2.333(1), Ca1–N2 2.334(1), Ca1–O1 2.335(1), Ca1–H103 2.36(2), Ca1–H104 2.20(2), Ca1–H30 2.41(2), Ca1···B1 2.549(2). Selected bond lengths (Å) for molecule 2 (bottom): Ca2–N3 2.320(1), Ca2–N4 2.341(1), Ca2–O2 2.324(1), Ca2–H101 2.13(2), Ca2–H102 2.31(2), Ca2–H75 2.42(2), Ca2···B2 2.550(2).

It is anticipated that a large variety of hydride-containing "ate" complexes, $[Ca(dipp\text{-}nacnac)]^+[MHL_n]^-$, are easily available by reaction of **1** with a suitable Lewis acid $[ML_n]$.

Reactions with epoxides: Reaction of **1** with cyclohexene oxide gave ring-opening of the oxirane ring. Apart from the major product, $[\{CaOCy(dipp\text{-}nacnac)\}_2]$ (**11**), other species could be detected in the ^{1}H NMR spectrum. Although repeated recrystallisation of the product gave well-defined plate-like crystals of **11**, it could never be completely freed from small amounts of a side product. GC-MS analysis of the reaction mixture showed, apart from the expected cyclohexanol, approximately 5 % of cyclohex-2-enol, indicative for ring opening by deprotonation of cyclohexene oxide.

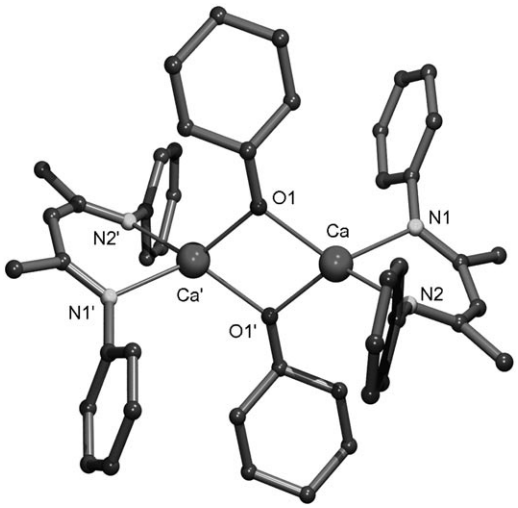


Figure 6. Crystal structure of **11**; only one of the two crystallographically independent, but very similar, dimers is shown. The *i*Pr substituents and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å; average values of both molecules): Ca–N1 2.351(3), Ca–N2 2.363(3), Ca–O1 2.226(2), Ca–O1′ 2.226(2).

The crystal structure of **11** is shown in Figure 6. The asymmetric unit contains two independent, but essentially similar, centrosymmetric dimers in which the cyclohexanolate ions bridge the Ca^{2+} ions symmetrically. The Ca^{2+} ions show a distorted tetrahedral coordination sphere and no evident agostic interactions could be detected. One of the dimers in the asymmetric unit shows disorder in cyclohexyl rings: chair and inversed chair conformations are observed. In view of the disorder problems, it is not ruled out that also a small amount of cyclohex-2-enolate, formed by proton abstraction from cyclohexene oxide followed by ring-opening, is present.

The ambiguous reaction behaviour of the calcium hydride functionality with epoxides, that is, either nucleophilic or deprotonative ring-opening, is also observed in reaction of **1** with propylene oxide. In contrast, addition of 1,1,-dimethylethylene oxide to a solution of **1** in benzene resulted in smooth ring-opening by attack of the hydride exclusively at the least substituted carbon atom. After cooling, a complex of composition [Ca(O*t*Bu)(dipp-nacnac)] (**12**) crystallised in the form of large colourless blocks (79%). The absence of THF suggests the dimeric nature of the product (similar as in **4** or **11**). Complex **12** does not react further with excess epoxide, which is in line with the observation that heteroleptic [Ca(alkoxide)(dipp-nacnac)] complexes are not active as an initiator in epoxide polymerisation.[9]

Attempts to prepare **12** by quenching [Ca{N(SiMe$_3$)$_2$}(dipp-nacnac)(thf)] with *t*BuOH gave several unidentified species and [Ca(dipp-nacnac)$_2$] as the major product.[9] Since **12** is stable towards disproportionation in homoleptic species, the appearance of the side products must be inherent to the method of preparation. It is likely that the alcohol-quench of [Ca{N(SiMe$_3$)$_2$}(dipp-nacnac)(thf)] is not selective. This would result in partial hydrolysis of the β-diketiminate ligand and formation of dipp-nacnac-H. Deprotonation of the latter by the starting material [Ca{N(SiMe$_3$)$_2$}(dipp-nacnac)(thf)] would give [Ca(dipp-nacnac)$_2$].

Alternatively, the dimeric nature of **12** could be the key to its stability. The first step in its formation is exchange of both thf ligands in **1** for 1,1,-dimethyl-ethylene oxide. Attack of these epoxide ligands by the nucleophilic hydride would give dimeric **12**. The bulkiness of the *t*BuO anion allows no further coordination of any cyclic ether, THF or epoxide, which might be important in explaining its inactivity in epoxide polymerisation. In contrast, alcoholysis of [Ca{N(SiMe$_3$)$_2$}(dipp-nacnac)(thf)] with *t*BuOH gives monomeric [Ca(O*t*Bu)(dipp-nacnac)(thf)], which could disproportionate in the homoleptic species. Reaction of **1** with 1,1,-dimethylethylene oxide thus represents a useful "alcohol-free" route for the preparation of [Ca(O*t*Bu)(dipp-nacnac)].

Conclusion

The hydrocarbon-soluble calcium hydride complex **1** reacted smoothly with a variety of unsaturated bonds (alkenes, ketones, cyanides, isocyanides), epoxides and Lewis acids. This is in striking contrast to the reactivity of homoleptic CaH_2 that is essentially inert to these functional groups. Ironically, most of the substrates used in the reactions described have been dried by extensive refluxing over a large excess of freshly ground CaH_2. This demonstrates the enormous advantage of solubilisation of the hydride functionality.

Calcium benzylide or allylide complexes have been formed in reaction of **1** with styrenic or butadienic substrates. Reaction of **1** with nitriles or isonitriles gave N- or C-metallated calcium aldimide complexes, which have not been accessible so far. Calcium alkoxide complexes could be obtained by reaction with ketones and epoxides. These reactions are in part rather clean and in some cases products could be isolated that are otherwise not accessible. Finally, clean conversion in borates or alanates is observed in reaction of **1** with boranes or alanes, respectively.

It is anticipated that the hydrocarbon-soluble calcium hydride complex **1**, which represents the first well-defined molecular Ca–H functionality, reacts smoothly with an even larger range of organic substrates. The products are generally stable against ligand exchange on account of the bulky β-diketiminate ligand: dipp-nacnac. Thus, the easily accessible calcium hydride **1** is a key intermediate in the syntheses of a wide variety of calcium complexes.

Experimental Section

General comments: All experiments were carried out under argon by using predried solvents and Schlenk techniques. The calcium hydride complex **1** was prepared as described previously.[9b] All other reagents were commercially available and dried over CaH_2 prior to use. NMR spectra have been recorded on Bruker DPX300 and DRX500 machines.

Synthesis of 2: A solution of **1** (53 mg; 0.10 mmol) and 1,1-diphenylethylene (20 mg; 0.10 mmol) in benzene (1.5 mL) was stirred for 4 h at 60 °C.

After cooling, the dark-red solution was concentrated to 20% of its original volume, layered with hexane and cooled to 8°C. Overnight dark-red needle-like crystals of **2** precipitated. Yield: 41 mg (58%); ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ = 7.15–7.10 (m, 6H; $H_{Ar,dipp}$), 6.67 (dd, ^3J(H,H) = 8.7 Hz, ^4J(H,H) = 1.3 Hz, 4H; H_{Ar}), 6.49 (dd, ^3J(H,H) = 8.7, 6.8 Hz, 4H; H_{Ar}), 5.79 (dt, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 1.3 Hz, 2H; H_{Ar}), 4.71 (s, 1H; dipp-nacnac bridge), 3.70 (m, 4H; thf), 3.02 (br m, 4H; Me_2CH), 1.69 (s, 3H; Ph_2CMe), 1.62 (s, 6H; dipp-nacnac Me), 1.31 (m, 4H; thf), 1.25–1.15 (br d, 12H; Me_2CH), 1.15 ppm (d, ^3J(H,H) = 6.8 Hz, 12H; Me_2CH); ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = 166.0, 146.7, 141.8, 141.6, 130.2, 126.3, 123.9, 117.7, 107.6, 94.0 (dipp-nacnac bridge), 88.5 (Ph_2CMe), 69.8 (thf), 28.5 (thf), 28.5 (Me_2CH), 25.3 (dipp-nacnac Me), 24.7 (Me_2CH), 24.5 (Me_2CH), 19.5 ppm (Ph_2CMe); elemental analysis calcd (%) for $C_{47}H_{62}CaN_2O$ (711.11): C 79.39, H 8.79; found: C 79.02, H 8.47.

Synthesis of 3: A solution of **1** (53 mg; 0.10 mmol) and cyclohexadiene (10 mg; 0.10 mmol) in benzene (1.5 mL) was stirred for 3.5 h at 40°C. The solvent was removed and the product crystallised from a mixture of hexane/THF at 8°C. Complex **3** was obtained in the form of yellow, rhombic crystals (yield: 16 mg, 34%). A solution of **3** in a mixture of hexane/THF slowly decomposed over a time period of a few days and colourless crystals of **1** and oligocyclohexadiene were observed. ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ = 7.17 (m, 6H; H_{Ar}), 6.42 (t, ^3J(H,H) = 7.4 Hz, 1H; $H_{cyclohexenyl}$), 4.76 (s, 1H; dipp-nacnac bridge), 3.73 (m, 4H; thf), 3.28 (br m, 4H; Me_2CH), 2.98 (t, ^3J(H,H) = 7.4 Hz, 2H; $H_{cyclohexenyl}$), 2.54–2.46 (m, 2H; $H_{cyclohexenyl}$), 1.69 (s, 6H; dipp-nacnac Me), 1.45–1.38 (m, 4H; $H_{cyclohexenyl}$), 1.35 (m, 4H; thf), 1.31 (br d, ^3J(H,H) = 6.6 Hz, 12H; Me_2CH), 1.31–1.20 (m, 2H; $H_{cyclohexenyl}$), 1.24 ppm (d, ^3J(H,H) = 6.8 Hz, 12H; Me_2CH); ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = 165.7, 147.2, 142.2, 141.6 ($C_{cyclohexenyl}$), 124.6, 123.8, 93.6 (dipp-nacnac bridge), 69.9 (thf), 68.3 ($C_{cyclohexenyl}$), 28.9 (thf), 28.5 (Me_2CH), 25.4 (dipp-nacnac Me), 24.8 (Me_2CH), 24.8 (Me_2CH), 24.5 ($C_{cyclohexenyl}$), 23.9 ppm ($C_{cyclohexenyl}$); elemental analysis calcd (%) for $C_{39}H_{58}CaN_2O$ (610.99): C 76.67, H 9.57; found: C 76.42, H 9.52.

Synthesis of 4: Addition of benzophenone (49 mg; 0.27 mmol) to a solution of **1** (134 mg; 0.25 mmol) in benzene (3.0 mL) gave immediate crystallisation of **4**. The product was dissolved again by heating to 80°C. Slowly cooling to 8°C gave large colourless prisms of **4**. Yield: 117 mg (73%); ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ = 7.23–7.12 (m, 10H; H_{Ar}), 6.96 (t, 4H; ^3J(H,H) = 7.2 Hz; H_{Ar}), 6.86 (t, 2H; ^3J(H,H) = 7.0 Hz; H_{Ar}), 5.91 (s, 1H; OCHPh$_2$), 4.62 (s, 1H; dipp-nacnac bridge), 2.90 (br sept, 4H; Me_2CH), 1.50 (s, 6H; dipp-nacnac Me), 1.06 (d, ^3J(H,H) = 6.8 Hz, 12H; Me_2CH), 0.93 ppm (br d, ^3J(H,H) = 6.7 Hz, 12H; Me_2CH). ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = 166.7, 149.5, 148.7, 142.0, 129.7, 126.4, 125.3, 124.6, 124.1, 95.0 (dipp-nacnac bridge), 79.1 (OCHPh$_2$), 28.2 (Me_2CH), 25.8 (Me_2CH), 25.3 (dipp-nacnac Me), 24.5 ppm (Me_2CH); elemental analysis calcd (%) for $C_{42}H_{52}CaN_2O$ (640.98): C 78.70, H 8.18; found: C 78.39, H 8.03.

Synthesis of 5: A solution of **1** (107 mg; 0.20 mmol) and diphenylmethyl-*N*-phenylimine (54 mg; 0.21 mmol) in benzene (2.5 mL) was stirred for two hours at 60°C and then concentrated to one-fifth of its original volume. The light-green solution was slowly cooled to 8°C to obtain light-green crystals of **5**. Yield: 99 mg (63%). ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ = 7.35 (m, 4H; H_{Ar}), 7.23–7.06 (m, 8H; H_{Ar}), 6.97–6.84 (m, 7H; H_{Ar}), 6.67 (m, 4H; H_{Ar}), 6.55 (m, 1H; H_{Ar}), 5.55 (s, 1H; CHPh$_2$), 4.97 (s, 1H; dipp-nacnac bridge), 3.48 (br m, 4H; Me_2CH), 2.64 (m, 4H; thf), 1.74 (s, 6H; dipp-nacnac Me), 1.23 (br d, 12H; Me_2CH), 1.19 (d, ^3J(H,H) = 6.7 Hz, 12H; Me_2CH), 0.84 ppm (m, 4H; thf); ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = 166.2, 158.3, 148.4, 147.3, 129.7, 128.8, 128.6, 127.6, 127.4, 126.0, 114.0, 111.3, 94.5 (dipp-nacnac bridge), 68.1 (thf), 66.6 ($CHPh_2$), 28.4 (Me_2CH), 24.7 (thf), 24.6 (dipp-nacnac Me), 24.5 (Me_2CH), 24.4 (Me_2CH); elemental analysis calcd (%) for $C_{52}H_{65}CaN_3O$ (788.20): C 79.24, H 8.31; found: C 78.96, H 8.24.

Synthesis of 6: After stirring a solution of **1** (54 mg; 0.10 mmol) and benzonitrile (10 mg; 0.10 mmol) in benzene (1.5 mL) for one hour at 60°C, the solution was concentrated to one-third of its original volume and cooled to 8°C to obtain **6** as yellow crystals. Yield: 51 mg (71%); ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ = 9.71 (s, 1H; N=CHPh), 7.53 (m, 2H; H_{ar}), 7.35 (m, 2H; H_{Ar}), 7.15–7.05 (m, 7H; H_{Ar}), 4.91 (s, 1H; dipp-nacnac bridge), 3.09 (sept, ^3J(H,H) = 6.7 Hz, 4H; Me_2CH), 1.64 (s, 6H; dipp-nacnac Me), 1.02 (d, ^3J(H,H) = 6.7 Hz, 12H; Me_2CH), 0.83 ppm (br d, 12H; Me_2CH); ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = 166.1, 165.4, 145.5, 142.1, 141.2, 129.8, 129.2, 127.0, 124.7, 124.1, 94.1 (dipp-nacnac bridge), 28.4 (Me_2CH), 25.1 (dipp-nacnac Me), 24.2 (Me_2CH), 24.2 ppm (Me_2CH); elemental analysis calcd (%) for $C_{36}H_{47}CaN_3$ (561.88): C 76.96, H 8.43; found: C 76.63, H 8.49.

Synthesis of 7: After stirring **1** (107 mg; 0.20 mmol) and 1,1,3,3-tetramethylbutylisonitrile (27 mg; 0.20 mmol) in benzene (2.0 mL) at room temperature, the resulting dark-green solution was concentrated to one-third of its original volume. By slowly cooling this solution to 8°C, complex **7** precipitated in the form of colourless crystals. Yield: 62 mg (52%); ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ = 9.95 (s, 1H; CH=N), 7.15–7.08 (m, 4H; H_{Ar}), 6.96 (m, 2H; H_{Ar}), 4.87 (s, 1H; dipp-nacnac bridge), 3.58 (sept, 2H; Me_2CH), 2.96 (sept, 2H; Me_2CH), 1.70 (s, 6H; dipp-nacnac Me), 1.65 (s, 2H; CH_2), 1.44 (d, ^3J(H,H) = 6.8 Hz, 6H; Me_2CH), 1.25 (d, ^3J(H,H) = 6.7 Hz, 6H; Me_2CH), 1.18 (d, ^3J(H,H) = 6.8 Hz, 6H; Me_2CH), 1.06 (s, 9H; CMe_3), 0.98 (s, 6H; CMe_2), 0.45 ppm (d, ^3J(H,H) = 6.7 Hz, 6H; Me_2CH); ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = 229.3 (CH=N), 165.8, 147.0, 141.7, 141.2, 124.3, 123.7, 93.0 (dipp-nacnac bridge), 64.2 (CMe_2), 57.6 (CMe_3), 32.3 (CMe_3), 31.7 (CMe_2), 28.5 (Me_2CH), 28.0 (Me_2CH), 27.2 (CH_2), 26.4 (Me_2CH), 25.0 (Me_2CH), 24.9 (dipp-nacnac Me), 24.8 (Me_2CH), 24.2 ppm (Me_2CH); elemental analysis calcd (%) for: $C_{38}H_{59}CaN_3$ (597.99): C 76.33, H 9.94; found C 75.98, H 9.64.

Synthesis of 8: Addition of cyclohexylisonitrile (35 mg; 0.36 mmol) to a solution of **1** (170 mg; 0.32 mmol) in benzene (2.8 mL) resulted in an immediate colour change to deep-blue and precipitation of **8** in the form of colourless crystals. After standing of the reaction mixture at 8°C for 90 min, complex **8** could be obtained in moderate yield (70 mg, 30%). The product is only slightly soluble in benzene. ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ = 9.97 (s, 1H; CH=N), 7.15–7.05 (m, 6H; H_{Ar}), 4.82 (s, 1H; dipp-nacnac bridge), 3.29 (br sept, 4H; Me_2CH), 2.72 (m, 1H; α-H Cy), 1.87 (m, 2H; Cy), 1.72 (m, 2H; Cy), 1.65 (s, 6H; dipp-nacnac Me), 1.46–1.20 (m, 6H; Cy) 1.16 (d, ^3J(H,H) = 6.5 Hz, 12H; Me_2CH), 0.9–0.8 ppm (br s, 12H; Me_2CH); ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = 236.3 (CH=N), 165.9, 146.5, 141.7, 124.3, 123.9, 92.7 (dipp-nacnac bridge), 74.2 (α-C Cy), 34.4 (Cy), 28.5 (Me_2CH), 27.9 (Cy), 25.6 (Cy), 25.1 (dipp-nacnac Me), 24.6 (Me_2CH), 24.5 ppm (Me_2CH); elemental analysis calcd (%) for: $C_{36}H_{53}CaN_3$ (567.92): C 76.14, H 9.41; found: C 75.87, H 9.51.

A colourless solution of **8** in benzene rearranged after one day at 50°C to give a new complex **8′** that was extremely soluble in hexane and could not be crystallised. ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ = 7.17–7.05 (m, 6H; H_{Ar}), 5.29 (s, 1H; -CHNCy), 4.69 (s, 1H; dipp-nacnac bridge), 3.20 (sept, ^3J(H,H) = 6.8 Hz, 4H; Me_2CH), 2.66 (m, 1H; α-H Cy), 1.69–1.46 (m, 4H; Cy), 1.60 (s, 6H; dipp-nacnac Me), 1.20 (d, ^3J(H,H) = 6.8 Hz, 6H; Me_2CH), 1.14 (br d, ^3J(H,H) = 6.7 Hz, 6H; Me_2CH), 1.40–0.86 ppm (m, 6H; Cy); ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = 166.5, 147.9, 141.6, 124.4, 124.0, 119.6 (CH=N), 92.7 (dipp-nacnac bridge), 61.1 (α-C Cy), 38.0 (Cy), 28.5 (Me_2CH), 27.0 (Cy), 26.4 (Cy), 25.5 (dipp-nacnac Me), 25.2 ppm (Me_2CH) 24.6(Me_2CH); ESI-TOF-MS: *m*/*z* calcd for [Cy(H)N−CH=CH−N(H)Cy+H]$^+$: 223.2174; found: 223.2183 (Δ = 0.0009); *m*/*z* calcd for [CyN=CH−CH=NCy+H]$^+$ 221.2018; found: 221.2031 (Δ = 0.0013); *m*/*z* calcd for [CyN=CH−CH=NCy+Na]$^+$ 243.1837; found: 243.1854 (Δ = 0.0017).

Synthesis of 9: A solution of **1** (107 mg; 0.20 mmol) and borabicyclononane (9-BBN) (24 mg; 0.20 mmol) in benzene (2.0 mL) was stirred for thirty minutes at 60°C and then concentrated to one-fourth of its original volume. Cooling the concentrated solution to 8°C gave precipitation of **9** in the form of colourless crystals. Yield: 88 mg (67%); ^{1}H{^{11}B} NMR (300 MHz, C_6D_6, 25°C): δ = 7.18–7.10 (m, 6H; H_{Ar}), 4.74 (s, 1H; dipp-nacnac H), 3.65 (m, 4H; thf), 3.14 (br s, 4H; Me_2CH), 2.10–2.00 (m, 2H; 9-BBN), 1.87 (m, 4H; 9-BBN), 1.77–1.67 (m, 6H; 9-BBN) 1.64 (s, 6H; dipp-nacnac Me), 1.33 (br d, ^3J(H,H) = 6.9 Hz, 12H; Me_2CH), 1.26 ppm (m, 4H; thf), 1.23 (d, ^3J(H,H) = 8.8 Hz, 12H; Me_2CH), 0.93 (s, 2H; BH_2), 0.84 ppm (br m, 2H, BCH); ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = 166.3, 150.2, 141.6, 125.1, 124.1, 93.4 (dipp-nacnac bridge), 69.8 (thf), 34.7 (9-

Table 1. Crystal data for the compounds **4**, **6**, **7**, **8**, **9** and **11**.

compound	**4**	**6**	**7**	**8**	**9**	**11**
formula	$C_{42}H_{52}CaN_2O{\cdot}C_6H_6$	$C_{36}H_{47}CaN_3$	$C_{38}H_{59}CaN_3{\cdot}C_6H_6$	$C_{36}H_{53}CaN_3{\cdot}C_6H_6$	$C_{41}H_{65}BCaN_2O_2$	$C_{70}H_{104}Ca_2N_4O_2{\cdot}C_6H_6$
M_r	719.05	561.85	676.07	646.00	652.84	1191.84
size [mm^3]	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.3	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.3	0.3 × 0.3 × 0.3
crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	12.0831(3)	15.2747(5)	25.6954(18)	12.7326(4)	12.2261(3)	22.2523(8)
b [Å]	12.9913(3)	13.1879(5)	16.7329(12)	12.7133(4)	18.5901(4)	14.8870(5)
c [Å]	15.0719(4)	16.9829(6)	19.5638(13)	12.9588(4)	18.8986(4)	23.5548(8)
α [°]	81.911(2)	90	90	90.796(2)	103.616(1)	90
β [°]	68.276(1)	100.090(2)	95.878(4)	110.699(2)	100.990(1)	113.012(2)
γ [°]	71.259(1)	90	90	89.974(2)	97.660(1)	90
V [Å^3]	2080.71(9)	3368.2(2)	8367.4(10)	1962.1(1)	4026.0(2)	7182.1(4)
Z	2	4	8	2	4	4
ρ [g cm^{-3}]	1.148	1.108	1.073	1.094	1.077	1.102
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.187	0.213	0.181	0.190	0.187	0.204
T [°C]	-80	-70	-70	-70	-70	-70
θ_{max} [°]	29.5	34.1	27.7	28.2	33.7	19.0
total reflns	68579	166441	79720	57756	169860	104598
unique reflns	11497	13763	9779	9588	30993	5801
R_{int}	0.051	0.036	0.065	0.076	0.046	0.078
obsvd reflns [$I>2\sigma(I)$]	7744	9829	7374	7141	19741	5265
parameters	677	537	437	487	1309	752
R_1	0.0468	0.0467	0.0549	0.0605	0.0553	0.0444
$wR2$	0.1139	0.1396	0.1520	0.1782	0.1630	0.1163
GOF	1.06	1.01	1.02	1.05	1.03	1.05
max/min resd [e Å^{-3}]	−0.27/0.23	−0.42/0.49	−0.33/0.59	−0.36/0.76	−0.31/0.58	−0.30/0.38

BBN), 28.6 (Me_2CH), 26.1(9-BBN), 25.2 (thf), 25.1 (9-BBN), 25.1 (Me_2CH), 24.7 (dipp-nacnac Me), 24.4 ppm (Me_2CH); ^{11}B NMR (160 MHz, C_6D_6, 25 °C): $\delta = -12.2$ ppm (t, $^1J(B,H) = 70.3$ Hz); elemental analysis calcd (%) for $C_{41}H_{65}CaN_2OB$ (652.88): C 75.43, H 10.04; found: C 75.37, H 10.39.

Synthesis of 10: A solution of triisobutylaluminium in hexane (1 M, 200 μL; 0.2 mmol) was added to a solution of **1** (107 mg; 0.20 mmol) in benzene (1.5 mL) and stirred for one hour. The solvent was evaporated under vacuum and the raw product was dissolved in a minimal amount of hexane. After cooling to −27 °C colourless needles of **10** were obtained (yield: 35 mg, 25 %). The crystals are extremely soluble in hexane. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 7.17$–7.13 (m, 6H; H_{Ar}), 4.77 (s, 1H; dipp-nacnac bridge), 3.76 (m, 4H; thf), 3.45 (br s, 1H; AlH), 3.09 (sept, $^3J(H,H) = 6.7$ Hz, 4H; Me_2CH), 1.96 (m, 3H; CH_2CHMe_2), 1.62 (s, 6H; dipp-nacnac Me), 1.33 (d, $^3J(H,H) = 6.9$ Hz, 12H; Me_2CH), 1.28 (m, 4H; thf), 1.19 (d, $^3J(H,H) = 6.8$ Hz, 12H; Me_2CH), 1.04 (d, $^3J(H,H) = 6.5$ Hz, 18H; CH_2CHMe_2), −0.11 ppm (d, $^3J(H,H) = 6.7$ Hz, 6H, CH_2CHMe_2); ^{13}C NMR (300 MHz, C_6D_6, 25 °C): $\delta = 166.6$, 145.6, 141.5, 125.3, 124.3, 94.2 (dipp-nacnac bridge), 70.0 (thf), 28.6 (CH_2CHMe_2), 28.6 (Me_2CH), 28.1(thf), 25.4 (br, CH_2CHMe_2)), 25.3(CH_2CHMe_2), 25.2 (dipp-nacnac Me), 24.7 (Me_2CH), 24.6 ppm (Me_2CH); elemental analysis calcd (%) for $C_{45}H_{77}AlCaN_2O$ (729.19): C 74.12, H 10.64; found: C 73.89, H 10.48.

Synthesis of 11: A solution of **1** (107 mg; 0.20 mmol) and cyclohexene oxide (20 mg; 0.20 mmol) in benzene (2.0 mL) was stirred for 18 h at 60 °C. After concentrating the solution to one-third of its original volume, the solution was cooled to 8 °C. Overnight a crop of well-defined colourless crystals of **11** precipitated (yield: 43 mg, 39 %). The product, however, seemed contaminated with slight amounts of much smaller crystals of different habitus. Recrystallisation of the product did not result in separation. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 7.15$–7.09 (m, 6H; H_{Ar}), 4.70 (s, 1H; dipp-nacnac bridge), 3.30 (m, 1H; α-H Cy), 3.22 (sept, $^3J(H,H) = 6.8$ Hz, 4H; Me_2CH), 1.67–1.58 (br m, 5H; Cy), 1.61 (s, 6H; dipp-nacnac Me), 1.52–1.38 (m, 2H; Cy), 1.18 (d, $^3J(H,H) = 6.8$ Hz, 12H; Me_2CH), 1.07 (d, $^3J(H,H) = 6.9$ Hz, 12H; Me_2CH), 1.01–0.87 ppm (m, 3H; Cy); ^{13}C NMR (300 MHz, C_6D_6, 25 °C): $\delta = 166.7$, 147.7, 142.2, 124.9, 124.5, 93.9 (dipp-nacnac bridge), 72.5 (α-C Cy), 40.1 (Cy), 29.2 (Me_2CH), 26.6 (Cy), 26.4 (Cy), 25.5 (dipp-nacnac Me), 25.3 (Me_2CH), 25.2 ppm (Me_2CH).

Synthesis of 12: A solution of **1** (107 mg; 0.20 mmol) and 1,1-dimethylethylene oxide (18 μL, 15 mg; 0.21 mmol) in benzene (2.0 mL) was stirred for 90 minutes at 60 °C. Cooling the yellowish solution to 8 °C gave colourless crystals of **12**. Yield: 84 mg (79 %); ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 7.20$–7.05 (m, 6H; H_{Ar}), 4.72 (s, 1H; dipp-nacnac bridge), 3.28 (sept, $^3J(H,H) = 6.8$ Hz, 4H; Me_2CH), 1.65 (s, 6H; dipp-nacnac Me), 1.17 (d, $^3J(H,H) = 6.8$ Hz, 24H; Me_2CH), 1.02 ppm (s, 9H; tBuO); ^{13}C NMR (300 MHz, C_6D_6, 25 °C): $\delta = 166.7$, 148.2, 141.9, 124.5, 124.0, 92.8 (dipp-nacnac bridge), 67.9 (CMe_3), 34.6 (CMe_3), 28.4 (Me_2CH), 25.6 (dipp-nacnac Me), 25.4 (Me_2CH), 24.8 ppm (Me_2CH); elemental analysis calcd (%) for $C_{33}H_{50}CaN_2O{\cdot}(C_6D_6)_{0.5}$ (566.89): C 76.28, H 8.89; found: C 76.19, H 8.80.

Crystal structures: Crystal diffraction data were measured on a Siemens SMART CCD diffractometer. All crystal structures were solved with SHELXS-97[29] and refined with SHELXL-97.[30] PLATON[31] was used for geometry calculations and graphics. Crystal data are given in Table 1. CCDC-649257–649262 (for **4**, **6**, **9**, **7**, **11** and **8**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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