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CO reduction by calcium and ytterbium hydride complexes with a bulky monodentate carbazolyl ligand†

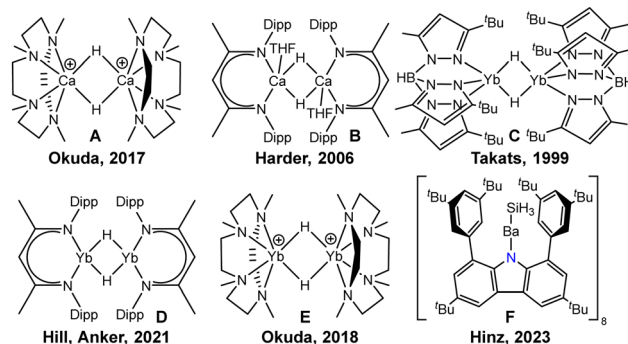
 Alexander Hinz, * Lucas Winkler and Xiaofei Sun

The bulky monodentate carbazolyl ligand 1,8-bis(3,5-ditertbutylphenyl)-3,6-ditertbutylcarbazole (dtbpCbz) was employed in the synthesis of monomeric heteroleptic amido carbazolyl complexes of Ca and Yb. For both central metal atoms, dimeric hydride complexes [(dtbpCbz)Ca(benzene)H]₂, [(dtbpCbz)Ca(THF)H]₂, [(dtbpCbz)-Yb(benzene)H]₂ and [(dtbpCbz)Yb(THF)H]₂ were obtained, which show remarkably poor solubility in organic solvents. The characteristic hydride ¹H NMR resonance of [(dtbpCbz)Ca(benzene)H]₂ was observed at 2.07 ppm, and for the first time, characteristic vibrational modes of the Ca₂H₂ and Yb₂H₂ moiety are discussed. Despite their poor solubility, the hydride complexes could be reacted with CO to yield the corresponding ethenediolate complexes.

Recent years have seen increased interest in the development of group 2 metal hydrides because of the high abundance and low toxicity of alkaline earth elements, in particular with calcium.^{1,2} Due to their similarity in ionic radii, Yb(II) frequently shows similar coordination behaviour. However, difficulties arise from the tendency of these compounds to disproportionate, and therefore, stabilisation by specific ligand systems is required. The addition of multidentate neutral ligands and use of sterically demanding monoanionic ligands was demonstrated by Okuda who employed the TACD (1,4,7,10-tetramethyl-1,4,7,10-tetraaminocyclododecane) to obtain the cationic dinuclear calcium hydrides [(TACD)₂Ca₂H₂]²⁺ (Scheme 1A) and [(TACD)₂Ca₂H₃]⁺.³ The most frequently used approach to access heavy alkaline earth hydrides is the utilisation of multidentate monoanionic ligands such as β-diketiminates (BDI). After Harder's seminal report on the dimeric complex [(BDI)Ca(THF)H]₂ (B),⁴ many applications for calcium hydrides were discovered, including stoichiometric and catalytic reactions in alkene hydrogenation⁵ and imine hydrosilylation⁶ as well as reduction of arenes⁷ and alkylation of

benzene.⁸ A variety of calcium hydrides with multidentate ligands are known to date.

Analogous ytterbium(II) hydrides are generally expected to show similar properties due to nearly identical ionic radii of Yb(II) and Ca(II). The development of ytterbium(II) hydrides was spearheaded by Takats, who reported on the synthesis of a tris-(pyrazolyl)borate-stabilised Yb(II) hydride complex C in 1999 with a new synthesis in 2002.^{9,10} A bulkier tris(pyrazolyl)borate ligand was introduced to the field by Cheng in 2021 who prepared the first monomeric Yb(II) hydride complex.^{11,12} Harder studied the Yb(II) analogues of the BDI complex B to elucidate similarities and differences of the two species.¹³ Remarkably, the group of Hill and Anker observed BDI-substituted Yb(II) hydrides without co-ligands (D) in the alkylation of arenes¹⁴ and subsequently investigated the reduction chemistry with arenes and cyclopentadienes.^{15,16} The groups of Xiang and Chen also employed an amine-decorated tetradentate BDI ligand to synthesise Yb(II) hydrides.¹⁷ In 2012, Trifonov prepared the first amidinate-stabilised Yb(II) hydride complex and observed double addition of the complex to diphenyl acetylene.¹⁸ Subsequently, the group studied the reactivity of the complex towards various other substrates.¹⁹ Moreover, Okuda employed neutral tetradentate amine ligands to stabilise cationic Yb(II) hydrides in 2018 (E).²⁰

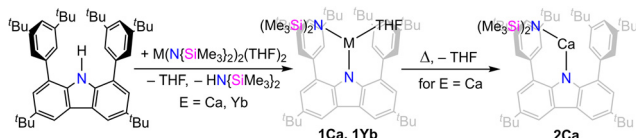


Scheme 1 Selected alkaline earth metal hydrides and bis(imino)carbazolate F (Dipp = 2,6-diisopropylphenyl, Ad = adamantyl).

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Scheme 2 Synthesis of calcium and ytterbium carbazoyl amido complexes.

Our earlier contributions include the synthesis of a bulky carbazoyl ligand to stabilise very low-coordinated environments in main group chemistry,^{21,22} and enabled efficient luminescence in non-covalently bound complexes.²³ Our previous attempts of generating a barium hydride complex with this ligand instead afforded a barium silanide complex (**F**).²⁴ In this contribution we describe the synthesis of carbazoyl hydrido complexes of calcium and ytterbium and their reactivity towards carbon monoxide.‡

The carbazoyl amido precursor complexes was prepared by treating the carbazole dtbpcbz-H with bis-amido compounds of the calcium or ytterbium. In both cases, the starting material is the THF-containing $[M(N\{SiMe_3\}_2)(THF)_2]$ ($M = Ca, Yb$). The transamination reaction proceeded readily and was complete within hours. After workup of the product, the carbazoyl amido complexes $[(dtbpcbz)Ca(N\{SiMe_3\}_2)(THF)]$ (**1Ca**, Scheme 2) and $[(dtbpcbz)Yb(N\{SiMe_3\}_2)(THF)]$ (**1Yb**) were obtained as greenish-yellow and orange material, respectively. The remaining coordinated molecule of THF was removed by prolonged drying at 120 °C in dynamic vacuum to yield $[(dtbpcbz)Ca(N\{SiMe_3\}_2)]$ (**2Ca**) which shows similar appearance as **1Ca**. However, with **1Yb** this desolvation reaction did not proceed selectively and **2Yb** was not isolated. The NMR spectra for the complexes **1Ca**, **2Ca**, and **1Yb** indicate averaged C_{2v} symmetry on the NMR time scale, which is derived from the magnetic equivalency of both aryl-*tert*butyl groups and each of the arene *ortho*-positions. The complexes were both observed exclusively as monomeric compounds in the solid state, which is in contrast to the analogous barium compound.²⁴

The molecular structures of the amido complexes **1Ca** and **1Yb** (Fig. 1) show the metal bent out of the central C_4N plane of the carbazoyl ligand by (47.4° to 56.0°). The NMN moieties themselves are bent as well, with the angle varying between 131° and 145°. Table 1 summarises bond distances of **1Ca** and **1Yb**. All $M-N$ distances in **1Ca** are shorter than the equivalent ones in **1Yb**, with the exception of the shortest $M-C_{arene}$ contact. Generally, the $M-N_{amide}$ bonds are shorter than the $M-N_{carb}$

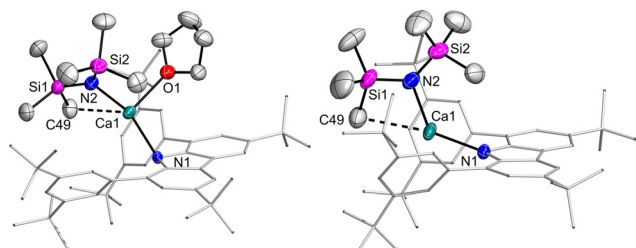


Fig. 1 Molecular structures of Ca amides **1Ca** (left) and **2Ca** (right). Thermal ellipsoids at 50% probability.

Table 1 Selected XRD data for amides **1Ca** and **1Yb**. All values are given in Å

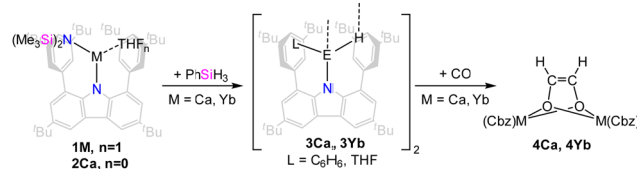
	$M-N_{carb}$	$M-N_{amide}$	$M-C_{arene}$ contacts
1Ca	2.3243(11)	2.2579(14)	C12 : 2.9072(13) C35 : 2.9286(13) C11 : 3.1278(14)
1Yb	2.383(4)	2.311(4)	C35 : 2.861(4) C12 : 2.943(4) C11 : 3.092(4)

bonds. Upon removal of the THF ligand of **1Ca**, **2Ca** was obtained. The structure changes in terms of Ca coordination sphere, as there is now a near-linear $N-Ca-C$ angle involving an agostic interaction with one of the silyl carbon atoms (Fig. 1, $N1-Ca1-C49$ 170.64(6)°) while the $N-Ca-N$ angle is still obtuse (122.80(5)°). At the same time, the $Ca-N$ contacts contract (2.2502(15), 2.2820(12) Å), while the $Ca-C_{arene}$ contacts remain largely unchanged (shortest: 2.904(2) Å).

With the goal of preparing the corresponding hydride complexes the alkaline earth metal carbazoyl amido complexes were treated with phenyl silane ($PhSiH_3$, Scheme 3).

After addition of phenyl silane, crystalline materials were obtained within one day. When **1Ca** was used for this metathesis reaction in benzene, the THF co-ligand was retained, and the dimeric hydride complex $[(dtbpcbz)Ca(THF)H]_2$ (**3Ca·THF**) was obtained. In contrast, for the synthesis of $[(dtbpcbz)Ca(C_6H_6)H]_2$ (**3Ca·C_6H_6**), the THF-free precursor **2Ca** was employed. Both of these complexes are poorly soluble in aliphatic and aromatic hydrocarbon solvents and decompose in THF. The 1H NMR resonance of the hydride of **3Ca·C_6H_6** is found at 2.07 ppm which is at higher field than known calcium hydride complexes (3.07 to 4.71 ppm) but agrees reasonably well with the computed value of 1.49 ppm (see SI 4 for details, ESI†). The strong shielding of this resonance is attributed to the interaction with the coordinated benzene molecule and, to a lesser extent, the flanking arenes of the carbazoyl ligand. Removal of the benzene molecule in the model leads to a predicted 1H NMR resonance at 3.87, while removal of the flanking arene results in a predicted 1H NMR shift of 2.00 ppm.

Both **3Ca·C_6H_6** and **3Ca·THF** comprise the dimeric, bis-hydride-bridged structural motif (Fig. 2) observed for other Ca hydrides. Each of the Ca atoms is coordinated to one additional donor, which is either THF or benzene. The molecular structures show $Ca \cdots Ca$ distances of 3.4495(6) and 3.4632(9) Å, which agree well with other Ca_2H_2 complexes. In all complexes the Ca atoms show contacts to coordinated arenes in the range of 2.8–3.0 Å.



Scheme 3 Synthesis of calcium and ytterbium(ii) hydride complexes and reaction with CO.



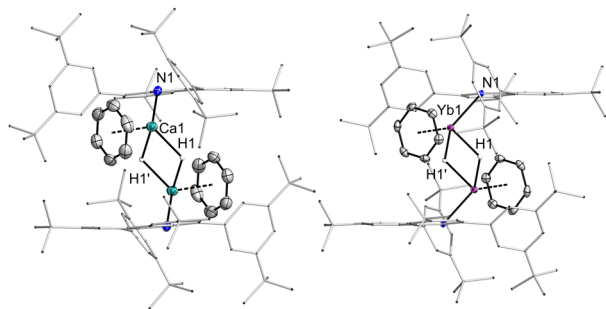


Fig. 2 Molecular structures of hydride complexes $3Ca-C_6H_6$ and $3Yb-C_6H_6$. Thermal ellipsoids at 50% probability.

In an analogous manner, ytterbium(II) hydride complexes could be prepared. However, when $1Yb$ was employed in the reaction with phenyl silane in benzene, mixed benzene and THF coordination was found. Thus, to obtain $3Yb-THF$, the metathesis reaction had to be conducted in *n*-hexane. For the preparation of $3Yb-C_6H_6$, $2Yb$ was generated *in situ* by dissolution of $1Yb$ in Et_2O and evaporation of all volatiles, and then redissolution in benzene with addition of phenyl silane but the yield was lower than for the other hydride complexes. A likely cause is partial decomposition of $1Yb$ upon removal of the THF ligand. NMR data of $3Yb-C_6H_6$ and $3Yb-THF$ could not be obtained due to the low solubility of the compounds.

The molecular structures of the ytterbium(II) hydride complexes $3Yb-C_6H_6$ and $3Yb-THF$ are similar to the calcium analogs. The $Yb \cdots Yb$ (3.4676(9), 3.4896(3) Å) and $Yb-N$ distances (2.379(2) 2.336(6) Å) are slightly longer than their Ca counterparts. In $3Yb-C_6H_6$, the Yb-benzene contacts range from 2.804 to 2.943 Å, while the corresponding contacts in $3Ca-C_6H_6$ are observed between 2.859(2) and 3.038(2) Å. Apparently, the Ca ion is slightly smaller and harder in these complexes, but for Yb the interaction with the π -scaffold of arenes is more efficient.

Three characteristic vibrations of $3Ca-C_6H_6$ and $3Yb-C_6H_6$ of high intensity were observed in the otherwise nearly identical IR spectra (Fig. 3, $3Ca-C_6H_6$ δ_1 1069, δ_2 785, δ_3 556 cm^{-1} ; $3Yb-C_6H_6$ δ_1 1073, δ_2 797, δ_3 550 cm^{-1} ; see SI 4.1, ESI[†]). Based on DFT calculations, the three vibrational bands illustrated in Fig. 3, δ_1 (symmetric in-plane deformation), δ_2 (antisymmetric in-plane deformation) and δ_3 (symmetric out-of-plane deformation) were identified and exclusively involve the Ca_2H_2 or Yb_2H_2 core of the molecule. For corresponding calcium deuteride, $3Ca-D-C_6H_6$ (see SI 2.8, ESI[†]), the three vibrations are shifted to smaller energies (obs. δ_1 774, δ_2 571, δ_3 404 cm^{-1} ; calc. δ_1 829, δ_2 601, δ_3 416 cm^{-1}). To date, similar identifications of vibrational modes were only made for a magnesium hydride complex by Jones and Stasch who assigned a $Mg-H$ stretch to a vibration at 1403 cm^{-1} .²⁹ Surprisingly, the vibrational bands of the Yb complex are observed at very similar energies as the Ca complex and no heavy atom effect is observable. Two further vibrational that involve the Ca_2H_2 or Yb_2H_2 moiety were found in the DFT model (SI 4.1, ESI[†]). However, they have only weak predicted intensity and could not be observed experimentally. In the Raman spectra, no clear assignment was possible.

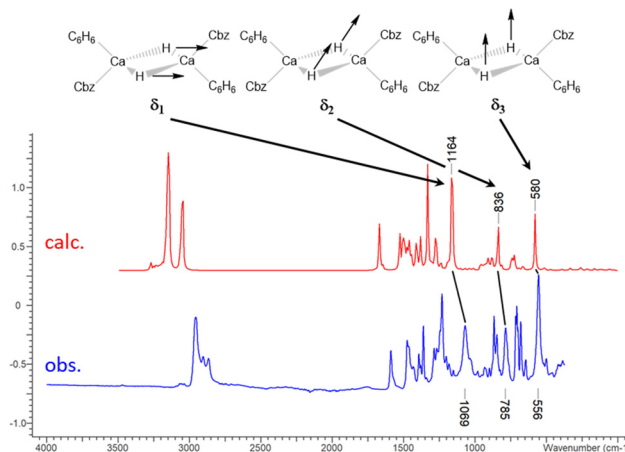


Fig. 3 Observed vibrational modes of the hydride core of $3Ca$.

Reactions of calcium hydrides with carbon monoxide as well as carbonyl complexes are well studied.^{30–32} Subsequently, the reactivity of the hydride complexes towards CO was investigated (Scheme 3). Suspensions of the hydride complexes in *n*-hexane or benzene were exposed to 1 bar of CO. The reactions proceeded and intermittently, the solution became more strongly coloured, until the crystals of the reaction product, the corresponding ethenediolate complexes $[(dtbpCbz)_2M_2L_n(O_2C_2H_2)]$ (4 , $L = THF$ or benzene, $n = 2,3$) formed. Quality of the crystals strongly depends on the solvate and solvent employed, and crystals suitable for single-crystal X-ray structure elucidation could only be obtained from $3Ca-THF$ in *n*-hexane and from $3Yb-THF$ in benzene. *In situ* NMR observation of the reaction mixture of $3Ca$ with CO allowed the identification of the ethenediolate moiety with 1H and ^{13}C NMR resonances at 2.39 and 69.46 ppm, which are both at higher field compared to the related complexes by Hill and Okuda.^{30,31} However, for the corresponding reaction with $3Yb$ only decomposition products were observed in solution which likely involve Yb(III) species as all lines were significantly broadened. However, crystallographic analysis corroborate the formation of ethenediolates in both cases (Fig. 4). IR analysis of $4b$ confirmed the disappearance of the bands assigned to the Yb_2H_2 core.

Structurally, the ethenediolate complex $4Ca$ is characterised by a Ca–Ca distance of 3.3613(7) Å. The Ca–O contacts to the bridging dianion amount to 2.2935(14) and 2.2817(13) Å, while the Ca–C contacts are found to be 2.6438(19) and 2.644(2) Å.

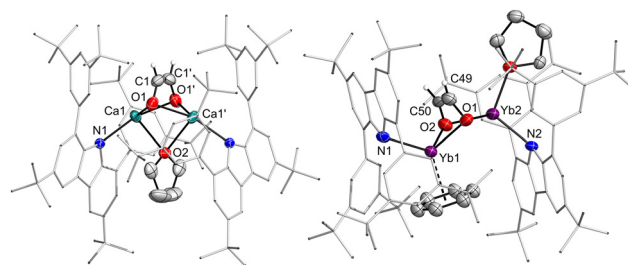


Fig. 4 Molecular structure of the ethenediolate complexes $4Ca$ and $4Yb$. Thermal ellipsoids at 50% probability.



Within the dianion, there is no bond alternation as the O–C and C–C bonds are 1.356(2) and 1.310(4) Å long, respectively. The Ca–N distance is 2.3434(12) Å. In **4Yb** the Yb–Yb distance is considerably longer (3.690(5) Å), but also, there is a second solvent molecule coordinated in the compound. The Yb–O contacts range from 2.320(7) to 2.372(7) Å, with longer Yb–C contacts between 2.628(10) and 2.680(11) Å. The Yb–arene contacts are found between 2.796(14) and 2.889(14) Å. The geometry of the dianion is again found to be without bond alternation (O–C 1.367(13), 1.370(14), C–C 1.377(16) Å). The Yb–N distances are found to be 2.360(8) and 2.378(7) Å.

In conclusion, we have demonstrated the stabilisation of dimeric calcium and ytterbium(II) hydrido complexes with monodentate carbazolyl co-ligands. For the first time, characteristic vibrations of the M₂H₂ core could be observed. The dimeric complexes are surprisingly insoluble which hampered their NMR-spectroscopic characterisation, but nonetheless, the ¹H NMR resonance of the calcium hydride complex could be detected at 2.07 ppm. Despite the poor solubility, the hydride compounds proved to be reactive towards CO to yield the corresponding ethenediolate complexes. The potential of the carbazolide ligand for the stabilisation of other hydride complexes is under investigation.

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Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data can be obtained from CCDC with deposition numbers 2145430 (**1Ca**), 2145431 (**1Ca**·C₆H₁₄), 2145432 (**2Ca**), 2145437 (**3Ca**·THF), 2145438 (**3Ca**·C₆H₆), 2372499 (**1Yb**), 2372500 (**3Yb**·THF), 2372501 (**3Yb**·C₆H₆), 2372502 (**4Ca**), 2372503 (**4Yb**).

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ During the preparation of this work, Trifonov and co-workers also reported calcium and ytterbium hydride complexes with the carbazolyl ligand and their role in pyridine hydrosilylation.

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