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Mononuclear calcium complex as effective catalyst for alkenes hydrogenation†

Xianghui Shi,[a] Cuiping Hou,[ab] Lanxiao Zhao,[ac] Peng Deng[ac] and Jianhua Cheng *[ac]

Hydrogenolysis of the scorpionate-supported calcium benzyl complex [($Tp^{Ad,iPr}$)Ca(*p*-$CH_2C_6H_4$-Me)(THP)] ($Tp^{Ad,iPr}$ = hydrotris(3-adamantyl-5-isopropyl-pyrazolyl)borate, THP = tetrahydropyran) (2-THP) afforded the mononuclear calcium hydrido complex [($Tp^{Ad,iPr}$)Ca(H)(THP)] (3). Under mild conditions (40 °C, 10 atm H_2, 5 mol% cat.), complex 3 effectively catalyzed the hydrogenation of a variety of alkenes, including activated alkenes, semi-activated alkenes, non-activated terminal and internal alkenes. Mononuclear calcium unsubstituted alkyl complex [($Tp^{Ad,iPr}$)Ca{$(CH_2)_4$Ph}(THP)] (6), proposed as the catalytic hydrogenation intermediate, was isolated and structurally characterized.

Molecular alkaline-earth metal (Mg, Ca, Sr, and Ba) hydrides continue to receive growing interest,[1] as they are used as low-cost and nontoxic alternatives to transition-metal catalysts in a variety of organic transformations.[2] As two of the most abundant elements in the Earth's crust,[3] Mg and Ca based efficient catalysts are of particular attraction, due to their environmentally benign and bio-compatible nature showing potential applications in both pharmacological and medicinal fields. Among the limited number of well-defined molecular group 2 metal hydride complexes, magnesium hydrides exhibit twelve different metal hydride cores with nuclearities up to thirteen.[4] Most of the heavier complexes such as calcium,[5] strontium[5g,6] and barium[5g,7] hydrides are dimeric, and other tri-,[8] tetra-,[9] hexa-[10] and hepta-nuclear[11] metal hydrides are sporadically reported. Terminal hydrides of alkaline-earth metals, which are expected to be extremely reactive, play a key role in various catalytic cycles,[2] including hydrogenation and hydrofunctionalization.[12] Structurally characterized alkaline-earth metal terminal hydrides are limited to magnesium, with a handful of examples.[13] The more reactive calcium terminal hydride has never been observed.

Recently, we described the use of the super-bulky scorpionate ($Tp^{Ad,iPr}$) ligand to afford the dimeric barium hydrides complex [($Tp^{Ad,iPr}$)Ba(μ-H)]$_2$.[7] Under the same conditions, the expected calcium analogue [($Tp^{Ad,iPr}$)Ca(μ-H)]$_2$ was not obtained, mainly attributed to the smaller ionic radius of calcium in comparison to barium (Ca^{2+} 1.00 Å, Ba^{2+} 1.35 Å; CN = 6).[14] Neutral donor solvents play a crucial role in the stabilization of heavy alkaline-earth metal alkyl and hydride complexes, and might dissociate the aggregated metal hydrides into monomeric species.[5c,13f,15] The coordination of a donor molecule to the calcium center will lower the reactivity and provide the potential to stabilize the mononuclear species. Herein, we report the synthesis and structure of mononuclear calcium hydride complex [($Tp^{Ad,iPr}$)-Ca(H)(THP)] (**3**). We also disclose that complex **3** exhibited superior reactivity and a larger substrate scope than the previous dimeric calcium hydrides in the catalytic hydrogenation of alkenes. A series of mononuclear calcium alkyls including the *n*-alkyl derivative [($Tp^{Ad,iPr}$)Ca{$(CH_2)_4$Ph}(THP)] (**6**), regarded as the catalytic reaction intermediates, are presented as well.

Protonolysis of [Ca(*p*-$CH_2C_6H_4$-Me)$_2$(THF)$_4$] (**1**)[16] with the acid form of the scorpionate ligand ($Tp^{Ad,iPr}$)H[7] in Et_2O easily afforded the corresponding benzyl complex [($Tp^{Ad,iPr}$)Ca(*p*-$CH_2C_6H_4$-Me)-(THF)] (**2**) as a pale-yellow solid in excellent yield. Treatment of complex **2** in THP/hexane gave an almost quantitatively THP coordinated calcium benzyl complex [($Tp^{Ad,iPr}$)Ca(*p*-$CH_2C_6H_4$-Me)(THP)] (**2-THP**). Complex **2-THP** was more stable than complex **2**, in agreement with the previously reported calcium alkyl complexes.[15]

Hydrogenolysis of **2-THP** in hexane under 20 atm H_2 successfully delivered the corresponding hydride complex [($Tp^{Ad,iPr}$)Ca(H)(THP)] (**3**) as colorless crystals in 81% isolated yield (Scheme 1). The ^1H NMR spectrum of complex **3** shows the absence of the *p*-$CH_2C_6H_4$-Me group and the presence of a $Tp^{Ad,iPr}$ ligand and a THP molecule. A singlet at 5.51 ppm in d_{12}-cyclohexane, which

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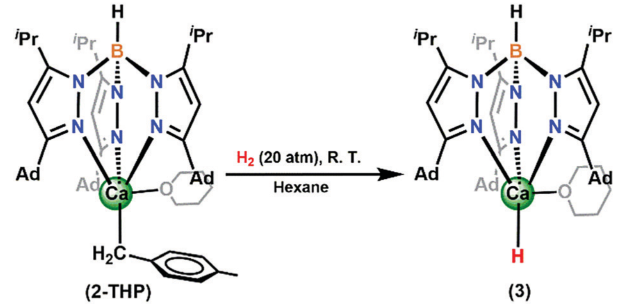
[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, No. 5625, Renmin Street, Changchun 130022, China. E-mail: jhcheng@ciac.ac.cn*
[b] *University of Chinese Academy of Sciences, Changchun Branch, Changchun 130022, China*
[c] *University of Science and Technology of China, Hefei, Anhui 230029, China*

† Electronic supplementary information (ESI) available: Selected ^1H and ^{13}C NMR spectra and crystallographic details. CCDC 1967134 (2), 1967136 (4), 1967137 (5) and 1967138 (6). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc01745k



Scheme 1 Synthesis of mononuclear calcium hydride [(Tp^{Ad,iPr})Ca(H)(THP)] (**3**).

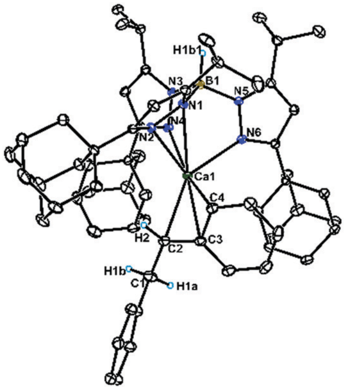


Fig. 1 ORTEP drawing of [(Tp^{Ad,iPr})Ca(PhCHCH$_2$Ph)] (**5**) with thermal ellipsoids drawn at the 20% probability level. All the hydrogen atoms in pyrazoles and phenyl groups are omitted for clarity. Selected interatomic distances [Å]: Ca1–C2 2.544(3), Ca1–C3 2.768(3), Ca1–C4 2.723(3), C1–C2 1.510(3), Ca1–N1 2.860(2), Ca1–N2 2.454(2), Ca1–N4 2.400(2), and Ca1–N6 2.401(2).

integrates as the 1H per Tp^{Ad,iPr} ligand, is assigned to the hydrido ligand, and further confirmed by deuterated analogous [(Tp^{Ad,iPr})Ca(D)(THP)] (**3-D**) in ^{2}D NMR. The hydride chemical shift in **3** is at slightly lower field than those in the dimeric calcium hydride complexes [(^{Dipp}BDI)Ca(μ-H)(THF)$_n$]$_2$ (^{Dipp}BDI = [(DippNCMe)$_2$CH]$^-$, Dipp = 2,6-iPr$_2$C$_6$H$_3$) (n = 1, 4.45 ppm;[5a] n = 0, 4.27 ppm[5e]), [(Me$_4$TACD)$_2$Ca$_2$(μ-H)$_2$]$^{2+}$ (Me$_4$TACD = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) (4.70 ppm)[5b] and [(Cp^{Ar})Ca(μ-H)(THF)]$_2$ (Cp^{Ar} = C$_5$Ar$_5$, Ar = 3,5-iPr$_2$-C$_6$H$_3$) (5.22 ppm).[5g] Complex **3** is stable in hexane and toluene at room temperature overnight without any obvious change. Owing to the co-crystallization with other calcium species and low-quality data set, only the mononuclear nature of complex **3** was verified by X-ray crystallographic analysis. A detailed discussion on bond lengths and angles is not warranted (see the ESI†).

The reaction of complex **3** with one equivalent of 1,1-diphenylethylene (DPE) in benzene at room temperature for 2 h afforded the corresponding 1,1-diphenylethyl derivative [(Tp^{Ad,iPr})Ca{CPh$_2$(Me)}] (**4**) as dark-red crystals in 56% isolated yield. The molecular structure of complex **4** (see Fig. S35, ESI†) reveals that the Ca^{2+} center is coordinated to a distorted Tp^{Ad,iPr} ligand with a side-on bound η^2-pyrazolyl ring, benzylic carbon (C2), and to a lesser extent of aromatic ring (C3 and C4). This bond pattern is different from the Ca···Ph π interaction observed previously in [(^{Dipp}BDI)Ca{(η^6-Ph)C(Ph)Me}(THF)].[17]

Treatment of complex **3** with one equivalent of *trans*-stilbene in benzene at room temperature for 2 h gave the benzyl product [(Tp^{Ad,iPr})Ca(PhCHCH$_2$Ph)] (**5**) as pale-yellow crystals in 67% isolated yield. As shown in Fig. 1, the Ca^{2+} adopts a similar coordination mode to that in complex **4**. The Ca1–C2 distance of 2.544(3) Å is slightly shorter than that of Ca–C (α-carbon of the benzylic anion) (2.608(4) Å) found in [(^{Dipp}BDI)$_2$Ca$_2$(μ-H)(PhCHCH$_2$Ph)].[18] The interatomic distances of 2.768(3) Å (Ca1–C3) and 2.723(3) Å (Ca1–C4) indicate the intense interactions between the calcium center and the *ipso* and *ortho* carbon atoms of the α-phenyl group. The C1–C2 distance of 1.510(3) Å demonstrates that the C=C bond of *trans*-stilbene has been reduced to a C–C single bond.

The reaction of complex **3** with one equivalent of CH$_2$=CHCH$_2$CH$_2$Ph (4-phenyl-1-butene) in hexane at room temperature for 0.5 h easily delivered the corresponding n-alkyl complex [(Tp^{Ad,iPr})Ca{(CH$_2$)$_4$Ph}(THP)] (**6**) as colorless crystals in 81% isolated yield. Complex **6** is stable in hydrocarbon solvents such as hexane and toluene at low temperature, but slowly decomposed at room temperature. As shown in Fig. 2, the Ca^{2+} center is five-coordinate in a trigonal-bipyramidal fashion, with distortion from ideal geometry due to the constrains imposed by the Tp^{Ad,iPr} ligand. The overall structure of complex **6** could be viewed formally by replacement of the terminal hydride in complex **3** with the (CH$_2$)$_4$Ph group. The Ca–C1 distance of 2.515(2) Å, is comparable to that of the terminal methyl moiety found in [(Tp^{tBu,Me})Ca(Me)(THP)] (2.485(2) and 2.507(2) Å),[19] and to that of the intramolecular Ca–C bonds in dimeric calcium n-alkyl complexes [(^{Dipp}BDI)Ca(CH$_2$CH$_2$R)]$_2$ (R = H, Et, *t*-Bu, *n*-Bu, *n*-Hex, CH$_2$Ph, (CH$_2$)$_2$Ph) (2.47–2.51 Å).[5e,20] As far as we know, complex **6** is the first example of the mononuclear heavier alkaline-earth metal unsubstituted n-alkyl complex.

With these well-established stoichiometric reactions in mind (Scheme 2), we then attempted the catalytic hydrogenation of a range of alkenes under mild conditions (40 °C, 10 atm H$_2$, 5 mol% cat.). Complex **2-THP** was used as the pre-catalyst, and the results of this study are summarized in Table 1.

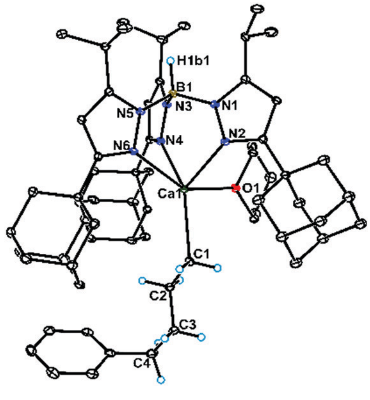
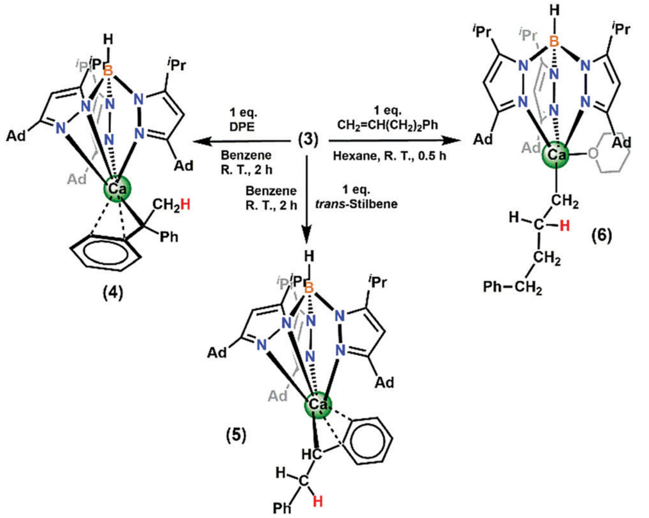
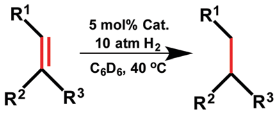


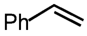
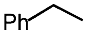
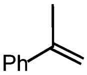
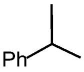
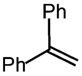
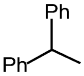
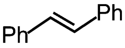
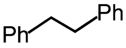
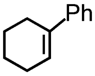
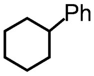
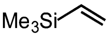
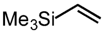
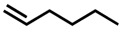
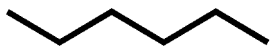
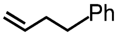
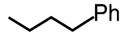
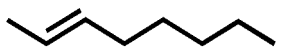
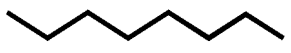
Fig. 2 ORTEP drawing of [(Tp^{Ad,iPr})Ca{(CH$_2$)$_4$Ph}(THP)] (**6**) with thermal ellipsoids drawn at the 20% probability level. All the hydrogen atoms in pyrazoles, THP and phenyl group are omitted for clarity. Selected interatomic distances [Å]: Ca1–C1 2.515(2), Ca1–O1 2.415(2), Ca1–N2 2.458(2), Ca1–N4 2.468(2), Ca1–N6 2.472(2), and C1–C2 1.527(3).



Scheme 2 Reactions of $[(Tp^{Ad,iPr})Ca(H)(THP)]$ (**3**) towards alkenes.

Table 1 Catalytic hydrogenation of alkenes with the pre-catalyst **2-THP**[a]



Entry	Substrate	t [h]	Product	% conv.[b]
1		1		99
2		3		99
3		1		99
4		4		99
5		72		53
6		1		99
7		1		99
8		1		99
9		24/72		31/90
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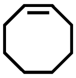
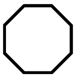
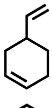
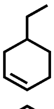
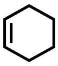
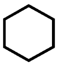
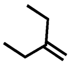
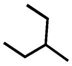
11		24		95
12		1		99[c]
13		24/120		4/22
14		24		0

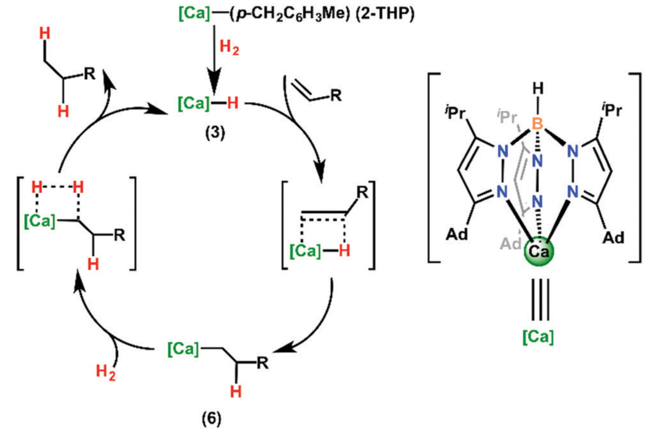
[a] Reaction conditions: 0.012 mmol of catalysts, 0.24 mmol of substrate in 1 mL of C_6D_6. [b] Determined by ^1H NMR spectroscopy. [c] Only the hydrogenation of the vinyl double bond was confirmed.

The hydrogenation of styrene and styrenic derivatives (DPE, *trans*-stilbene and α-methyl styrene) was achieved within 1–4 h, and no oligomeric by-products were observed (entries 1–4). The slow conversion of 1-phenyl-cyclohexene is mainly attributed to the steric hindrance (entry 5).

Mononuclear calcium hydride **3** also showed a remarkable performance in hydrogenation of semi-activated alkene and the non-activated alkenes. The hydrogenation of $Me_3SiCH{=}CH_2$, 1-hexene and 4-phenyl-1-butene was completed within one hour (entries 6–8). These results demonstrated that mononuclear calcium hydride exhibited superior reactivities than the previously reported dimeric calcium hydrides, including $[(^{Dipp}BDI)Ca(\mu\text{-}H)(THF)_n]_2$,[5a,e] $[(Me_4TACD)_2Ca_2(\mu\text{-}H)_2]^{2+}$,[5b] and $[(Cp^{Ar})Ca(\mu\text{-}H)(THF)]_2$.[5g]

The most striking performance of mononuclear calcium hydride is the expanded substrate scope. The internal alkenes can be hydrogenated as well. The conversion of 2-octene to octane increased gradually (entry 9), with 31% in 24 h and up to 90% over 72 h. Norbornene was reduced to norbornane in 97% conversion within 7 h (entry 10). The reaction time for hydrogenation of *cis*-cyclooctene was longer (95% in 24 h) (entry 11). In a short time, only the exocyclic C=C bond in 4-vinylcyclohexene was selectively hydrogenated to give 4-ethylcyclohexene (entry 12). It is noteworthy that the hydrogenation of cyclohexene could also be achieved, albeit the conversion was low (4%, 24 h; 22%, 120 h; entry 13). No reactivity of disubstituted 2-ethyl-1-butene was observed (entry 14).

On the basis of the above-mentioned experimental observations, a possible mechanism for terminal alkene hydrogenation is shown in Scheme 3. At first, the hydrogenation of complex **2-THP** would afford mononuclear calcium hydride **3**. The insertion of a terminal *n*-alkene into the Ca–H bond in a 1,2-fashion would give a calcium *n*-alkyl complex, such as **6**. Subsequent σ-bond metathesis with H_2 regenerated **3** and released the final product alkanes. The dissociative THP enables the Ca^{2+} center to coordinate bulky substrates. The maintenance of monomeric calcium species throughout the transformations might play a key role in the remarkable catalytic efficiency, in contrast to the dimeric structures



Scheme 3 Proposed catalytic cycle for the hydrogenation of terminal alkenes with mononuclear calcium hydride **3**.

in calcium hydrides complexes, such as $[(^{\mathrm{Dipp}}\mathrm{BDI})\mathrm{Ca}(\mu\text{-H})]_2$,[5e,18,20] $[(\mathrm{Me_4TACD})_2\mathrm{Ca_2}(\mu\text{-H})_2]^{2+}$,[5b] and $[(\mathrm{Cp^{Ar}})\mathrm{Ca}(\mu\text{-H})(\mathrm{THF})]_2$.[5g]

In summary, we have demonstrated for the first time the isolations of mononuclear calcium terminal hydride and unsubstituted *n*-alkyl complexes. Mononuclear calcium hydride shows a surprisingly outstanding performance in terms of both catalytic efficiency and substrate scope. As previous literature studies[5g,21] indicated that the activity of heavy alkaline-earth metal catalysts increases with the metal size (Ca < Sr < Ba), mononuclear strontium and barium hydride complexes are expected to exhibit higher catalytic activity and potentially have more substrate scope.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

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