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Simple Alkaline-Earth Metal Catalysts for Effective Alkene Hydrogenation

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*Sjoerd Harder**[a]

Dedicated to Professor Alexander C. Filippou on the occasion of his 60th birthday.

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Keywords: Alkaline Earth Metal – Alkene – Hydrogenation – DFT calculations

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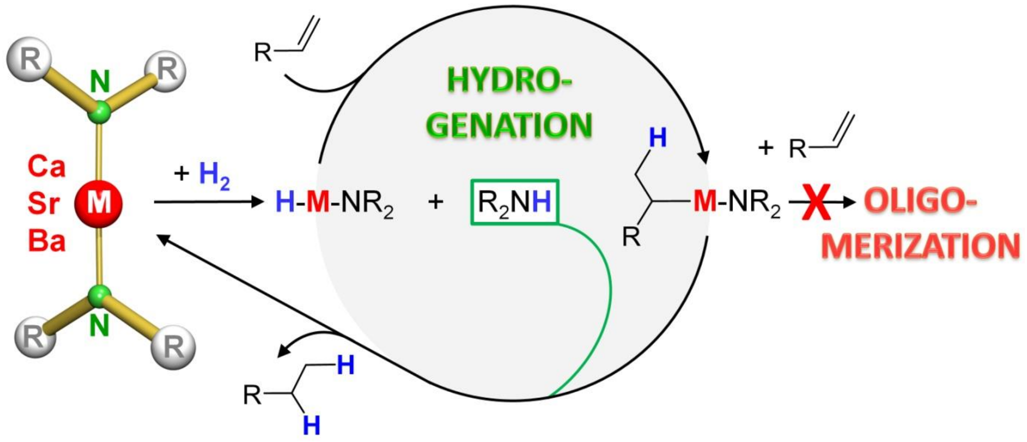
Keep it simple: The widely used, easily accessible, alkaline earth metal amides $M(NR_2)_2$ (M = Ca, Sr, Ba, R = $SiMe_3$) are highly active alkene hydrogenation catalysts. Alkene oligomerization is fully suppressed by trapping the reactive intermediate with R_2NH. A first example of group 2 metal hydrogen transfer catalysis is given.



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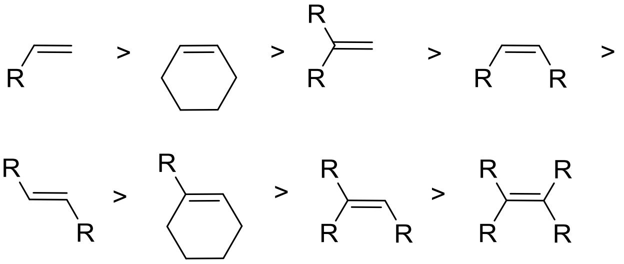
Already in 1874, von Wilde demonstrated the catalytic reduction of ethylene by Pt/H_2,[1] a ground-breaking discovery that laid the foundations for Sabatier's 1912 Nobel prize on alkene hydrogenation.[2] Despite its early roots, alkene hydrogenation is by no means old hat[3] and arguably is the chemical transformation that find most applications in industry. Although the majority of catalysts is heterogeneous, homogeneous hydrogenation catalysts contributed to the early successes of organometallic chemistry. Merits of the classical Wilkinson catalyst lie in its great selectivity that originates from a clear reactivity sequence for C=C double reduction (Scheme 1).[4] Although the most efficient catalysts are based on precious platinum group metals,[3] there is a growing awareness of the toxicity and limited availability of such metals.[5] Current research efforts focus on using earth-abundant first-row transition metals,[6] early main group metals[7] or even on metal-free routes.[8,9] Slaugh reported alkene hydrogenation mediated by main group metal hydrides under extreme conditions (150-225 °C, 150-250 bar H_2, 25 mol% cat.).[10] We introduced the first transition metal-free alkene hydrogenation under relatively mild conditions (20-60 °C, 20 bar H_2, 2.5-5 mol% cat.)[11] which broke the dogma that efficient alkene activation needs partially filled *d*-orbitals for π-backbonding.

Scheme 1. Reactivity of olefinic C=C bonds towards hydrogenation with the Wilkinson catalyst $(Ph_3P)_3RhCl$ decreases with substitution. Endocyclic bonds show a higher reactivity.



Benzyl Ca, Sr and K complexes catalyzed hydrogenation of various alkenes (Scheme 2). Stoichiometric reactions with a model catalyst and full characterization of all reaction intermediates (Scheme 2b), suggested that catalysis likely proceeds through the slow, rate-determining, formation of a metal hydride intermediate. Single reduction of cyclohexadiene or myrcene suggested that the method could be limited to activated (conjugated) alkenes like styrenes or butadienes. Preference for the reduction of conjugated bonds was explained by the stability of the intermediate: benzylic or allylic carbanions are more stable than alkyl carbanions. Since styrenes are also very sensitive towards polymerization, in most cases large quantities of oligomers were obtained as an undesired side-product (2-20%). This could to some extent be suppressed by increasing the H_2 pressure to 100 bar.

More recently, Okuda and coworkers introduced a set of cationic Ca hydride catalysts for alkene hydrogenation (Scheme 2c).[12,13] Stabilized by a neutral aza-crownether ligand, Me_4TACD, they could be pictured to consist of the fragments $(Me_4TACD)CaH_2$ and/or $(Me_4TACD)CaH^+$. Their Ph_4B^- salts are insoluble in aromatic solvents, however, in THF they were found to be highly efficient in alkene hydrogenation converting activated alkenes like styrene already at room temperature and 1 bar H_2

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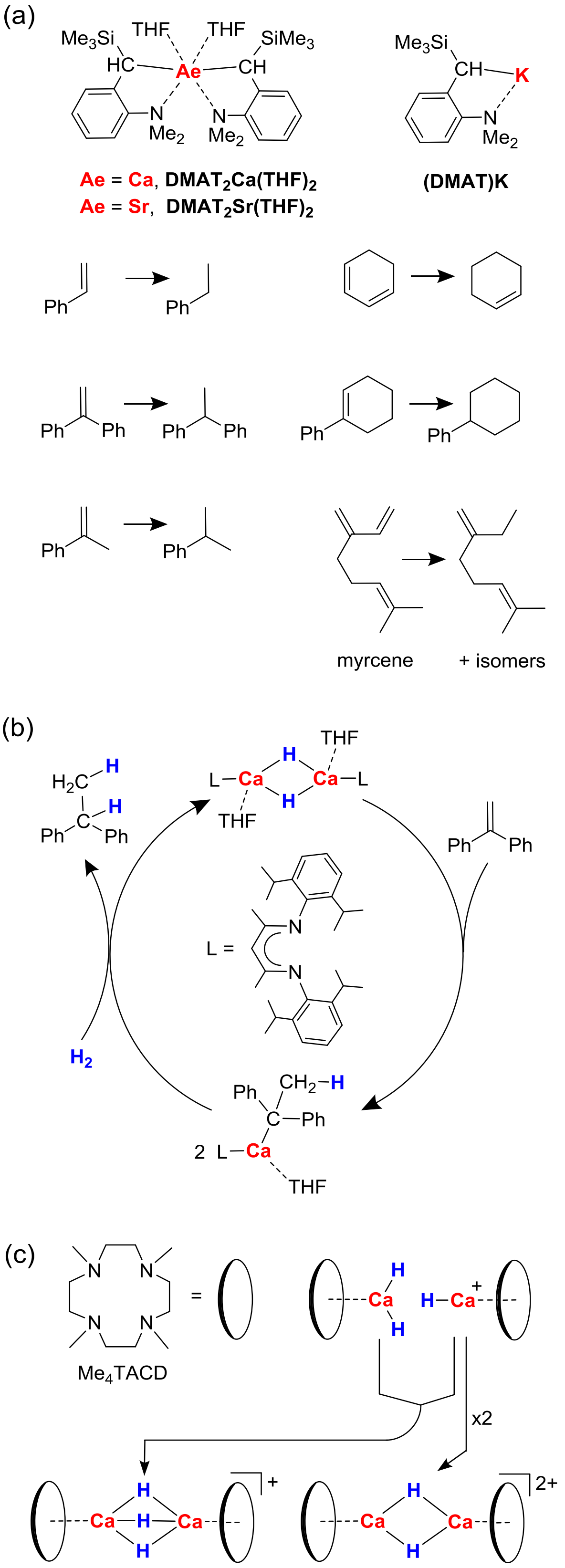
pressure. More importantly, also non-conjugated alkenes like 1-hexene could be converted albeit at higher temperatures (60 °C) and with long reaction times (24-36 h). This significant ability to react with isolated double bonds was attributed to their positive charge thought to be critical in imparting sufficient electrophilicity to the electropositive calcium center.[13] Despite their high reactivity, di-substituted unactivated double bonds were not converted. Moreover, activated substrates like styrene were prone to oligomerization as a side reaction.



Scheme 2. (a) First early main group metal catalyst for alkene hydrogenation under mild conditions.[11] (b) Proposed catalytic cycle according to stoichiometric conversions. (c) Cationic Ca hydride complexes with the Me_4TACD ligand.[13]

Notwithstanding these breakthroughs, group 2 metal alkene hydrogenation catalysis is far from being up to par with transition metal applications. Preventing oligomerization, functional group tolerance, activity improvement and hydrogen transfer protocols are important issues. Herein we present a set of simple well-known catalyst precursors, $Ae[N(SiMe_3)_2]_2$ (AeN''_2; Ae = Ca, Sr, Ba), tackling all of these goals. These common reagents can be conveniently prepared at a large scale.[14,15] Although their reaction with H_2 to form the active hydride N''AeH and N''H is unpredicted (the pK_a of 49 for H_2[16] is much higher than the 25.8 value[17] for N''H), we could recently show that these elementary reagents are converted to metal hydride catalysts for imine hydrogenation.[18] This rather unexpected amide-to-hydride conversion is supported by the very recently reported reversible activation of H_2 by similar alkali metal reagents.[19]

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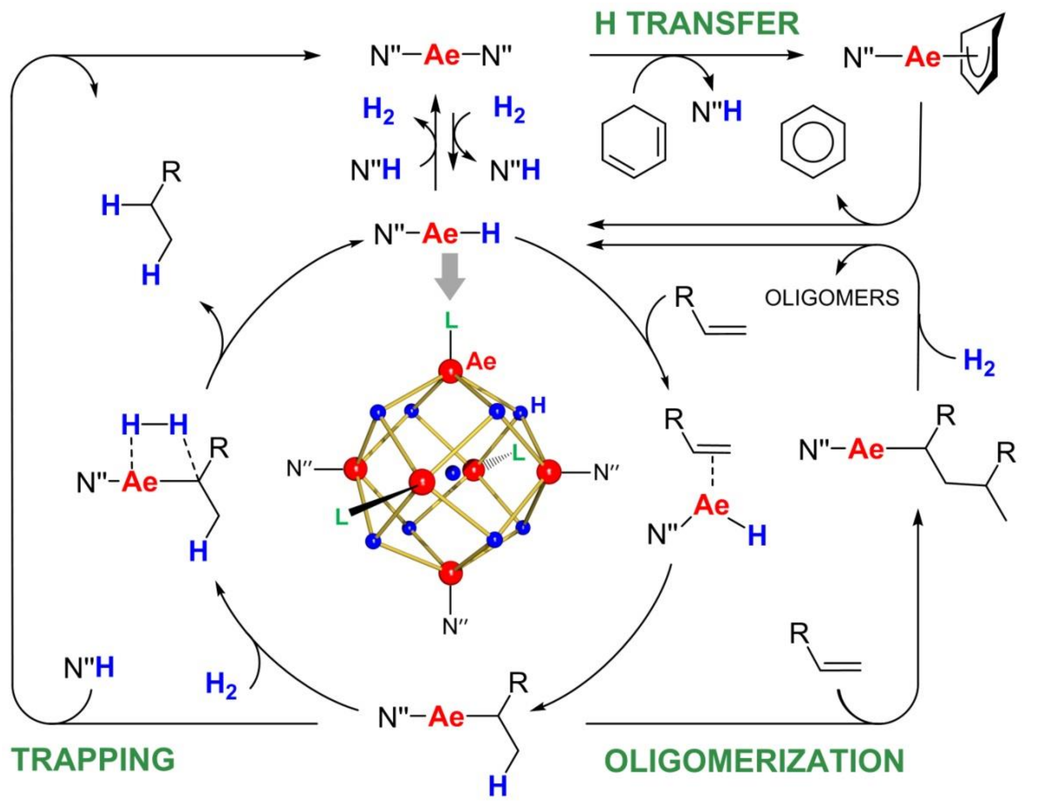
A proposed mechanism for alkene hydrogenation catalyzed by simple AeN''$_2$ reagents is shown in Scheme 3. As shown earlier,[18] precatalysts AeN''$_2$ are indeed able to deprotonate H_2, the driving force being aggregation of N''AeH to larger undefined clusters. Exemplary some of these clusters could previously be trapped and structurally characterized (Scheme 3).[20,21] Their high reactivity is the key to alkene conversion. Precatalyst CaN''$_2$ could fully convert styrene to ethylbenzene (Table 1, entries 1-5). Since increasing the temperature had a larger accelerating effect than increasing the pressure, catalysis could also conveniently be run at an ambient H_2 pressure of only 1 bar (entry 5) but room temperature conditions gave hardly conversion (entry 3). Whereas MgN''$_2$ is essentially inactive (entry 6), the heavier Ae amides show very high activity (entries 7-8). The most reactive BaN''$_2$ even allowed for full conversion at room temperature (entry 9) and, most important, enabled low catalyst loadings down to 1 mol% (entries 10-11). Alkali metal amides are hardly active (entries 12-14) suggesting that the 2+ charge of Ae is important for Lewis acidic substrate activation. The latter is supported by the complete inactivity of the system in the solvent THF. Most remarkably, polymerization sensitive styrene is converted to ethylbenzene without oligomeric side-products. We attribute this finding to the presence of the relatively acidic free amine N''H (pK_a = 25.8), which reacts much faster with the benzylmetal intermediate than H_2 ($pK_a \approx 49$) thus keeping its concentration low and preventing styrene oligomerization (Scheme 3). Only the longer runs with 1 mol% catalyst loading (entries 10-11) gave some oligostyrene on account of thermal polymerization. Addition of 9 mol% N''H, however, accelerated the trapping reaction and inhibited oligomer formation (Figure S6).

Substrate scope was investigated for precatalysts CaN''$_2$ and BaN''$_2$ using comparable reaction conditions (6 bar, 120 °C, 10 mol% cat.). Functional group tolerance was evaluated using *para*-methoxy or chloro styrene (entries 15-18). Whereas ether substituents do not pose problems the aromatic C-Cl group led to catalyst decomposition by a nucleophilic aromatic substitution of Cl for N'', a known reactivity.[22] Di-substituted conjugated alkenes like 1,1-diphenylethylene, *trans*-stilbene or α-Me-styrene react somewhat slower than styrene but gave very fast clean conversion with the highly reactive BaN''$_2$ catalyst (entries 19-24). 1,3-Cyclohexadiene, in which the double bonds are activated by conjugation, could be converted mainly to cyclohexene, leaving the remaining (isolated) double bond unaffected (entries 25-26). Interestingly, up to 23% benzene could be detected as a side-product. This formal dehydrogenation reaction can only be explained by deprotonation followed by ß-H elimination (Scheme 3, top right). This reactivity is supported by reaction of cyclohexadiene with BaN''$_2$ without H_2 pressure giving equal quantities of benzene and cyclohexene (Figure S25). Dual dehydrogenation/hydrogenation of cyclohexadiene implies that BaN''$_2$ could be used as a transfer hydrogenation catalyst. Indeed, a mixture of cyclohexadiene (used in here as a H source) and BaN''$_2$ (10 mol%) fully converted styrene into ethylbenzene (80 °C, 1.5 h, Figure S26), demonstrating first hydrogen transfer catalysis for this metal class.



Scheme 3. Postulated mechanism for alkene hydrogenation with AeN''$_2$ catalysts including trapping, oligomerization and H transfer pathways. The inset shows an isolated example of a larger aggregate (Ae = Ca or Sr and L = PMDTA).[20]

The outstanding reactivity of the Ba catalyst motivated us to investigate its performance for hydrogenation of isolated double bonds. The alkene $Me_3SiCH=CH_2$ was smoothly hydrogenated (entries 27-28). The latter, however, should be regarded semi-activated by the silyl substituent which substantially polarizes the C=C bond and stabilizes the intermediate anion $Me_3Si(Me)CH^-$ by negative hyperconjugation. Norbornadiene could be fully transformed into mixtures of norbornene, nortricyclene and norbornane (entries 29-30). Similar, its double bonds are semi-activated by homoconjugation.[23] Such a through-space interaction is demonstrated by formation of nortricyclene through an intramolecular nucleophilic addition followed by protonation. Norbornene was cleanly converted to norbornane (entries 31-33) but its double bond is semi-activated by ring strain. 1-Hexene, an alkene that is truly unactivated, was fully converted by BaN''$_2$, however, a substantial quantity of 2-hexene was observed (entry 35). Independent experiments showed that this internal alkene cannot be further hydrogenated. 1-Hexene isomerization was also observed for cationic Ca hydride catalysts.[13] This side-reaction could proceed through "wrong" addition followed by ß-H elimination (Eq. 1) or through a deprotonation/protonation protocol (Eq. 2). As the free amine N''H is likely involved in this last step, we investigated 1-hexene hydrogenation with $DMAT_2Ca·(THF)_2$. Thus, avoiding N''H formation, isomerization-free full conversion to hexane could be achieved (entry 36).

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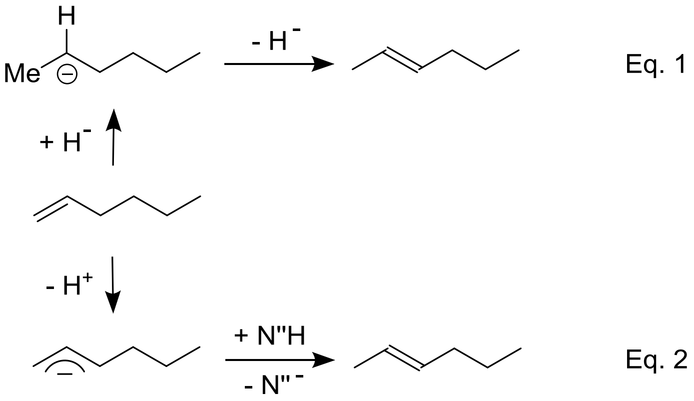
Our most active catalysts were unable to hydrogenate 1,1-diethylethylene and hydrogenation of 4-vinylcyclohexene led to reduction of the terminal alkene but not of the endocyclic C=C bond (entry 37-39). Although the scope of these catalysts could not be extended to unactivated di-substituted alkenes, the activated trisubsitituted alkene Ph-cyclohexene could be fully converted (entry 40).



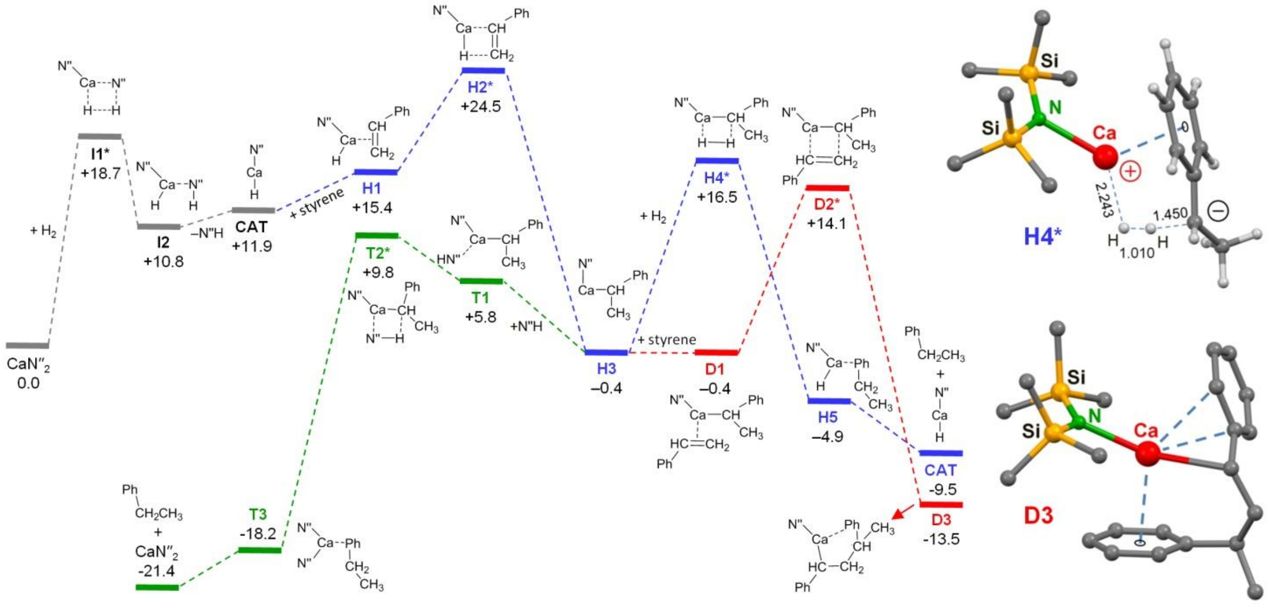
The proposed catalytic cycle for hydrogenation of styrene by CaN’’$_2$ was calculated by DFT methods at the M06/6-311++G(d,p)//M06/6-31++G(d,p) level of theory.[24] ΔG values (80 °C, 6 bar) were corrected for benzene solvent effects.[25] The energy profile (Scheme 4) consists of four parts: initiation (I), hydrogenation (H), dimerization (D) and trapping (T).

Initiation (I) of the cycle starts with precatalyst CaN’’$_2$, exchanging an amide ligand for a hydride through transition state I1* (+18.7 kcal/mol). As predicted by the large pK_a differences between H_2 (49) and N’’H (25.8), this step is clearly endothermic (I2, 10.8 kcal/mol). Release of the bulky amine N’’H to give the model catalyst (CAT) is slightly endothermic. A second amide/hydride exchange to give CaH_2 is even more endothermic (+27.3 kcal/mol)[18] and was not further considered. Note that although this initiation reaction is endothermic, further aggregation to larger cluster (*e.g.* shown in Scheme 2) will be exothermic, balancing energy loss. For simplicity, the mechanism has been modeled with the simplest Ca hydride catalyst N’’CaH (CAT).

Hydrogenation (H) follows the normal route in which styrene coordinates and inserts in the Ca-H bond (H1→H2*→H3). The benzylcalcium intermediate H3 reacts with H_2 via a σ-bond metathesis (H3→H4*→H5) to give ethylbenzene and the catalyst (CAT). Relative to the model catalyst CAT, styrene hydrogenation is exergonic by 21.4 kcal/mol. The highest point along the energy profile is the transition state for insertion (H2*, +24.5 kcal/mol). However, the activation energy for this step (CAT→H2*, +12.6 kcal/mol) is lower than that for the σ-bond metathesis step (H3→H4*, +16.9 kcal/mol). The structure of transition state H4* is reminiscent of H_2 activation by a FLP reagent (see Scheme 4). The benzyl anion in H4* is bound with its Ph ring to Ca^{2+}. The free carbanion center and Ca^{2+} span a Lewis base/acid pair that activates the H-H bond.

Dimerization (D), the first step of oligomerization, starts with benzylcalcium intermediate H3 that after styrene coordination gives insertion (H3→D1→D2*) with an activation energy of 14.5 kcal/mol, *i.e.* somewhat lower than that for hydrogenation (H4*). It is also thermodynamically favored over hydrogenation: formation of D3 is 8.6 kcal/mol more endergonic than hydrogenation (H5). The stability of D3 may be explained by its unusual structure in which Ca is sandwiched between two aromatic rings (see Scheme 4).

Trapping (T) of the benzylcalcium intermediate H3 proceeds by endergonic N’’H coordination to form T1 followed by protonolysis of the benzyl anion. Transition T2* (+9.8 kcal/mol) is significantly lower than those for either hydrogenation H4* (+16.5 kcal/mol) or dimerization D2* (+14.1 kcal/mol). This explains that even at low N’’H concentration, styrene oligomerization is prevented by trapping of the intermediate.



Scheme 4. Energy profile for the initiation (I), hydrogenation (H), dimerization (D) and trapping rection (T) at the M06/6-311++G(d,p)//M06/6-31++G(d,p) level.[24] ΔG values at 80 °C and 6 bar in kcal/mol were corrected for benzene solvent effects.[25]

We demonstrated that: (i) widely used and conveniently accessible precursors in Ae chemistry, AeN''_2, catalyze alkene hydrogenation tolerating ether functional groups, (ii) these catalysts fully suppress alkene oligomerization by trapping of the highly reactive intermediate with N’’H, (iii) especially BaN''_2 is a highly active catalyst with a broad scope, (iv) reduction of isolated, non-activated, alkenes like 1-hexene is not limited to cationic catalysts, and (v) BaN''_2 is an efficient hydrogen transfer catalyst. This study not only reveals the hidden potential of common Ae reagents in catalysis but is especially useful for further development of this rapidly growing field.

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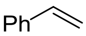
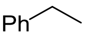
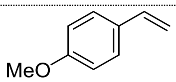
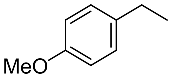
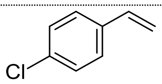
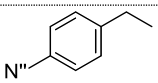
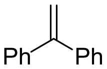
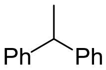
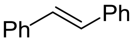
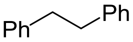
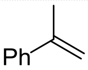
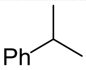
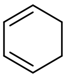
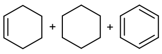
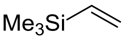
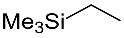
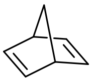
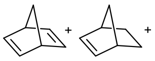
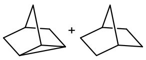
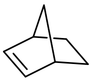
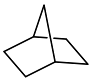
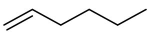
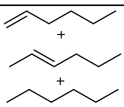
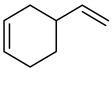
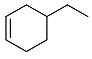
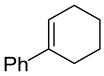
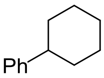
Table 1. Catalytic alkene hydrogenation.[a]

Entry	Catalyst	mol%	Substrate	H_2 (bar)	T (°C)	t (h)	Product	%Conv.
1	CaN"$_2$	10		6	80	1.5		99
2	CaN"$_2$	10		6	120	0.5		99
3	CaN"$_2$	10		6	25	24		14
4	CaN"$_2$	10		12	80	1		99
5	CaN"$_2$	10		1	80	24		97
6	MgN"$_2$	10		6	120	24		traces
7	SrN"$_2$	10		6	80	0.5		99
8	BaN"$_2$	10		6	80	0.5		99
9	BaN"$_2$	10		6	25	15		99
10	CaN"$_2$	1		6	120	24		74
11	BaN"$_2$	1		6	120	24		99
12	LiN"	10		6	120	24		traces
13	NaN"	10		6	120	24		20
14	KN"	10		6	120	24		68
15	CaN"$_2$	10		6	120	1.5		99
16	BaN"$_2$	10		6	120	0.25		99
17	CaN"$_2$	10		6	120	24		15
18	BaN"$_2$	10		6	120	24		19
19	CaN"$_2$	10		6	120	24		57
20	BaN"$_2$	10		6	120	0.75		99
21	CaN"$_2$	10		6	120	24		10
22	BaN"$_2$	10		6	120	0.5		99
23	CaN"$_2$	10		6	120	24		64
24	BaN"$_2$	10		6	120	0.25		99
25	CaN"$_2$	10		6	120	24		85/0/15[c]
26	BaN"$_2$	10		6	120	24		76/1/23[c]
27	CaN"$_2$	10		6	120	12		99
28	BaN"$_2$	10		6	120	0.5		99
29	CaN"$_2$	10		6	120	24		3/40/52/5[b]
30	BaN"$_2$	10		6	120	24		0/29/39/32[b]
31	CaN"$_2$	10		6	120	24		55
32	BaN"$_2$	10		6	120	10		99
33	(DMAT)$_2$Ca·(THF)$_2$	10		6	120	10		99
34	CaN"$_2$	10		6	120	24		70/4/26[b]
35	BaN"$_2$	10		6	120	24		1/58/42[b]
36	(DMAT)$_2$Ca·(THF)$_2$	10		6	120	20		0/0/99
37	CaN"$_2$	10		6	120	24	 + isomerization	15
38	BaN"$_2$	10		6	120	24		73
39	(DMAT)$_2$Ca·(THF)$_2$	10		6	120	24		95
40	BaN"$_2$	10		6	120	20		99

[a] [Alkene] = 0.5 M in C_6D_6. Reaction times for >99% conversion (determined by ^1H NMR) have been optimized in 15 minutes steps. For slower reactions the conversion (%) after 24 hours is given. GC-MS was also used for product identification. [b] Conversion obtained by GC-MS measurement. [c] Toluene-d_8 used as a solvent in order to detect benzene.

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Supporting Information Experimental procedures and details for the DFT investigations including XYZ coordinates for all optimized minima and transition states.

Abstract:

Alkaline earth metal amides (AeN’’$_2$: Ae = Ca, Sr, Ba, N’’ = N(SiMe$_3$)$_2$) catalyze alkene hydrogenation (80-120°C, 1-6 bar H_2, 1-10 mol% cat.), the activity increasing with metal size. Various activated C=C bonds (styrene, *p*-MeO-styrene, α-Me-styrene, $Ph_2C=CH_2$, *trans*-stilbene, cyclohexadiene, 1-Ph-cyclohexene), semi-activated C=C bonds ($Me_3SiCH=CH_2$, nornornadiene) or non-activated (isolated) C=C bonds (norbornene, 4-vinylcyclohexene, 1-hexene) could be reduced. The results show that neutral Ca or Ba catalysts are active in the challenging hydrogenation of isolated double bonds. For activated alkenes (*e.g.* styrene) polymerization is fully suppressed due to fast protonation of the highly reactive benzyl intermediate by N’’H (formed in catalyst initiation). Using cyclohexadiene as the H source, the first Ae metal catalyzed hydrogen transfer hydrogenation is reported. DFT calculations on styrene hydrogenation using CaN’’$_2$ show that styrene oligomerization competes with styrene hydrogenation. Calculations also show that protonation of the benzylcalcium intermediate with N’’H is a low-energy escape route, thus avoiding oligomerization.