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Alkene Transfer Hydrogenation with Alkaline Earth Metal Catalysts

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

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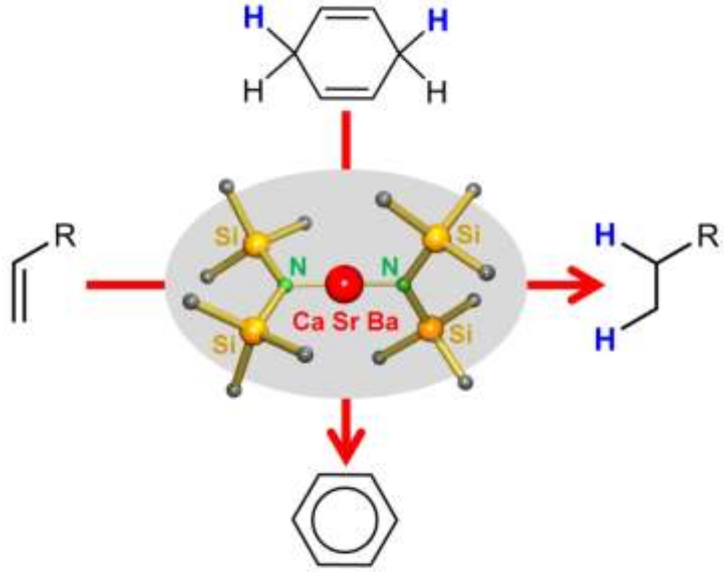

The hydrogen shuffle: Transfer of hydrogens from 1,4-cyclohexadiene to a variety of alkenes is catalyzed by simple alkaline earth metal amides. The proposed mechanism for this convenient highly selective transfer hydrogenation is supported by DFT calculations.

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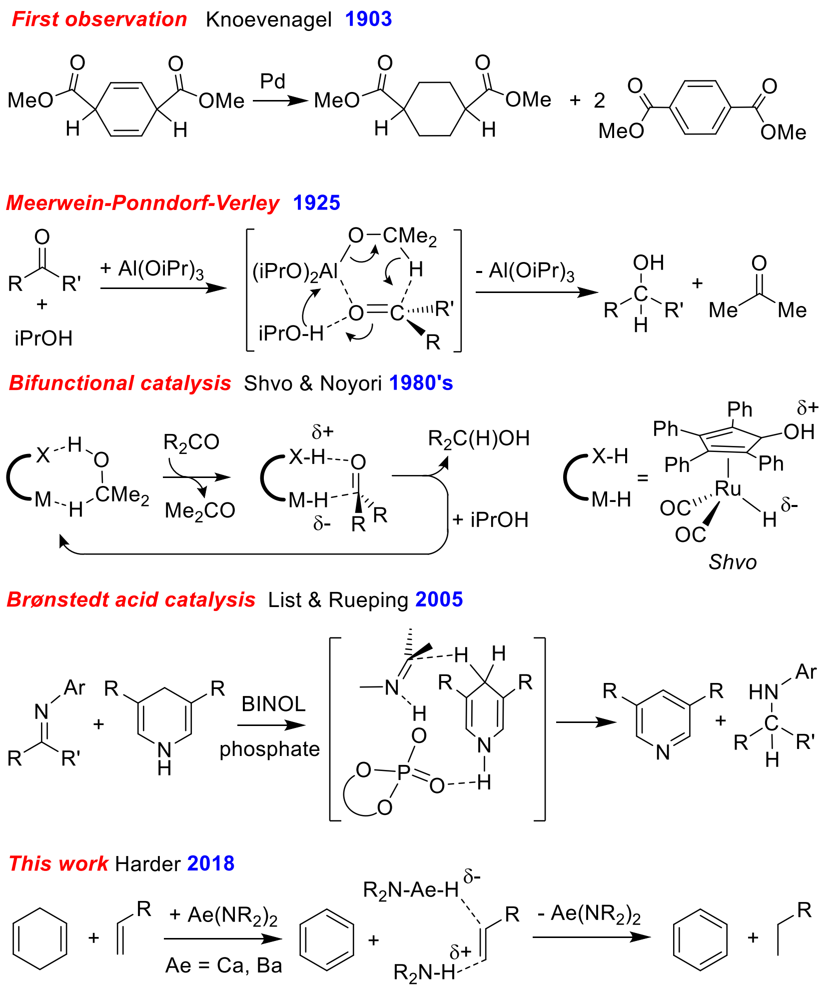
The catalytic reduction of unsaturated bonds is an integral part in the industrial production of bulk products as well as fine chemicals.[1] Whereas hydrogenation with readily available H_2 is a highly atom-efficient reaction, transfer hydrogenation (TH) is rapidly gaining popularity.[2] The latter process is defined by reduction using an alternative hydrogen source that preferentially is readily available, inexpensive and easy to handle and recycle. Avoiding use of pressurized H_2 eliminates potential safety hazards and circumvents the need for elaborate experimental set-ups and high-pressure reactors.

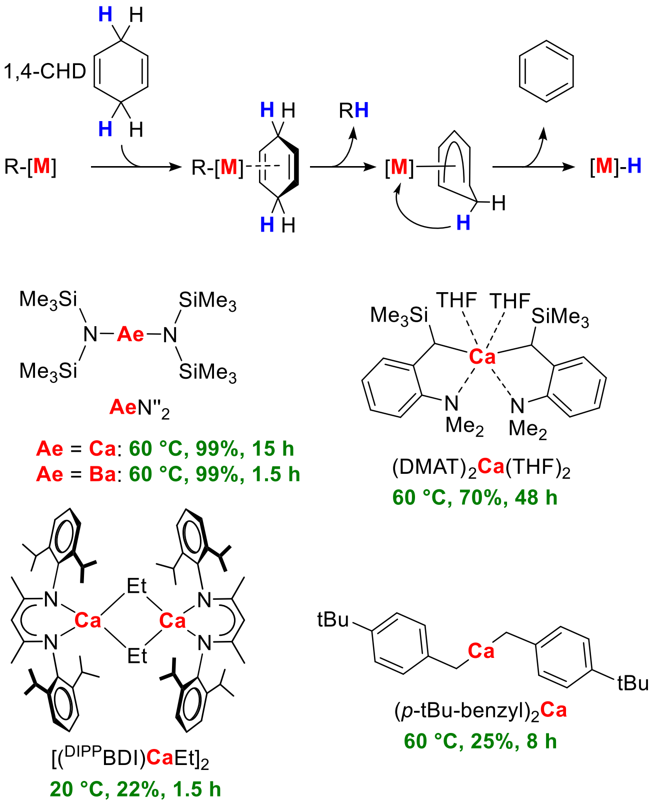
Although we are currently experiencing "the golden age of TH",[2] first observations for such reactivity already date back more than a century. In 1903, Knoevenagel described the concurrent dehydrogenation/hydrogenation of a substituted 1,4-cyclohexadiene (Scheme 1).[3] The Meerwein-Ponndorf-Verley ketone reduction is another early example of TH reactivity using a main group metal Al catalyst and *i*PrOH as the hydrogen donor.[4] Spurred on by Henbest's Ir catalysts,[5] the first well-defined Ru catalysts for TH have been introduced by Noyori[6] and Shvo.[7] These bifunctional catalysts transfer protic and hydridic H's from iPrOH to a ketone. The turn of the century witnessed major contributions in metal-free catalyzed TH. List and Rueping reported the enantioselective TH of ketones using catalytic quantities of a Brønsted acidic chiral phosphoric acid and the Hantzsch ester for hydrogen delivery.[8] Stephan and co-workers pioneered Lewis acid catalyzed imine hydrogenation using $i\mathrm{Pr_2NH}$ as H_2 substitute,[9] a process that was later extended by Oestreich *et al.* using 1,4-cyclohexadienes as a reducing agent.[10] The Stephan group reduced activated alkenes with a R_3SiH/HNR_2 combination using a Frustrated Lewis Pair (FLP) catalyst.[11] Very recently, the Melen and Morrill groups reported TH of silylenol ethers using a FLP catalyst [12] and the groups of Paradies and Hoge introduced a Lewis acidic phosphine catalyst for TH of 1,1,-diphenylethylene.[13] Interestingly, high energy "H_2 substitutes" like NH_3BH_3 or *in situ* generated HN=NH have been shown to reduce activated alkenes without using a catalyst.[14,15]

While early main group metal catalysis is a rapidly developing field,[16] TH with these metals is currently restricted to transferring hydrogen from *i*PrOH to ketones with simple bulk catalysts like NaOH or KOH.[17] Apart from this isolated example, the conversion of imines or alkenes hitherto has not been reported. During our investigation on alkene hydrogenation with H_2 using simple alkaline earth (Ae) metal amide catalysts,[18] the substrate 1,3-cyclohexadiene (1,3-CHD) showed dual reactivity and was not only hydrogenated to cyclohexene but also dehydrogenated to benzene. This striking observation implied that this diene may function as a H source offering an alternative route to formation of the metal hydride catalyst. Indeed, a mixture of 1,3-CHD and styrene could without H_2 be converted to ethylbenzene and benzene.[18] Although concomitant reduction of 1,3-CHD also gave considerable quantities of cyclohexene, this reaction suggested the feasibility of Ae metal catalyzed alkene TH. Ketone TH, and to a lesser extent imine TH, are well-studied procedures but there are hardly catalysts for the more challenging TH of the significantly less polar C=C bond.[13,19] Herein we report first comprehensive investigations towards alkene reduction by TH using easily accessible AeN''_2 catalysts ($N'' = N(SiMe_3)_2$, Scheme 1).



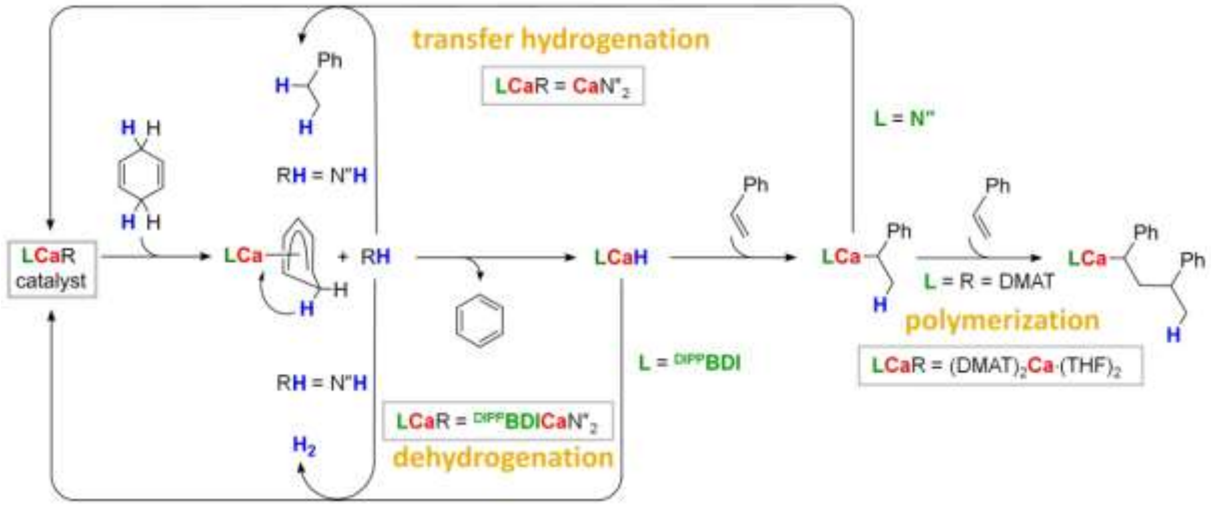
Scheme 1. Various concepts for transfer hydrogenation.

The first task was the selection of a hydrogen source that would be a convenient alternative to H_2 for the efficient generation of a metal hydride complex. Since 1,3-CHD contains conjugated double bonds, it not only delivers H but is also easily reduced to cyclohexene. The latter process does not take place using 1,4-CHD with isolated (unactivated) double bonds. The reaction of 1,4-CHD to benzene with stoichiometric quantities of a metal reagent was monitored by ^1H NMR in C_6D_6 (Scheme 2). For CaN''_2 full conversion was obtained at 60 °C within 15 hours. In line with the increasing reactivity of group 2 metal reagents with metal size, BaN''_2 was found to be considerably more reactive (99%, 1.5 h). As the THF adduct $CaN''_2{\cdot}(THF)_2$ did not react with 1,4-CHD, the presence of THF is detrimental to conversion. Based on this observation, we propose a mechanism in which 1,4-CHD forms an adduct with the metal reagent (Scheme 2). This activates 1,4-CHD for intramolecular deprotonation to give a highly unstable cyclohexadienyl anion. Such Meisenheimer anions can be stabilized by strongly electron withdrawing substituents (*e.g.* NO_2), but generally eliminate a hydride to give an aromatic product.[20,21] The dibenzyl calcium reagents $(DMAT)_2Ca{\cdot}(THF)_2$ and (4-*t*Bu-benzyl)$_2$Ca clearly underperformed (DMAT = 2-Me_2N-α-Me_3Si-benzyl). Conversion of 1,4-CHD to benzene could also be achieved by KH in THF (60 °C, >99%, 2.5 h) but not with *n*BuLi in C_6D_6 (60 °C, 5%, 48 h) whereas the superbase mixture *n*BuLi/KO*t*Bu reacted fast (20 °C, >99%, 0.25 h). The recently introduced highly reactive ethylcalcium complex $[(^{DIPP}BDI)CaEt]_2$[22] reacted already at room temperature (22%, 1.5 h) but also gave ligand exchange to homoleptic species (Figure S11-12); ^{DIPP}BDI = CH[C(Me)N-DIPP]$_2$, DIPP =2,6-di*iso*propylphenyl. Although we could not intercept the labile cyclohexadienyl intermediate, the formation of known[22] $[(^{DIPP}BDI)CaH]_2$ confirms that the reaction with 1,4-CHD is an alternative route to metal hydride species.



Scheme 2. Stoichiometric conversion of 1,4-CHD to benzene and the metal hydride catalyst (monitored by ^{1}H NMR in C_6D_6).

Using 1,4-CHD as a H source, the catalytic TH of styrene by catalyst LCaR was explored (Scheme 3; R = reactive group, L = spectator ligand). It was found that the nature of the catalyst strongly determines the course of the reaction. The simple and easily accessible Ca amide catalyst CaN’’$_2$ gave selective conversion to ethylbenzene (Table 1, Entry 1). In agreement with our earlier observations, the catalyst CaN’’$_2$ has the unique property to inhibit styrene polymerization (<1% oligomers).[18] The key to this selectivity is the presence of the relatively acidic amine N’’H (pK_a = 25.8)[23] formed during catalyst initiation. This amine quenches the reactive benzylcalcium intermediate thus preventing styrene polymerization (Scheme 3). Earlier DFT calculations confirm that reaction of N’’CaCH(Me)Ph with N’’H is a low energy escape route ($\Delta G^{\ddagger}$ = +10.2 kcal/mol) which is clearly preferred over styrene polymerization ($\Delta G^{\ddagger}$ = +14.5 kcal/mol).[18]



Scheme 3. Transfer hydrogenation of styrene using 1,4-cyclohexadiene as a H source and catalyst LCaR. Transfer hydrogenation is only observed for LCaR = CaN''_2 (N’’ = $N(SiMe_3)_2$). Catalyst (^{DIPP}BDI)CaN’’ gave exclusive dehydrogenation whereas the catalyst $(DMAT)_2Ca{\cdot}(THF)_2$ only led to polystyrene.

In contrast to Entry 1, catalyst (^{DIPP}BDI)CaN’’[24] converted 1,4-CHD into H_2 and benzene and only traces of ethylbenzene were observed (Entry 2). This implies that *in situ* formed (^{DIPP}BDI)CaH prefers deprotonation of N’’H over styrene addition (Scheme 3). Indeed, reaction of (^{DIPP}BDI)CaH with a mixture of N’’H and styrene only gave H_2 and (^{DIPP}BDI)CaN’’ leaving styrene unconverted (Figure S10). On the other hand, *in situ* formed N’’CaH (or aggregates thereof)[25] apparently prefers styrene addition over N’’H deprotonation but in case styrene is absent also slow dehydrogenation of 1,4-CHD into benzene and H_2 was observed: 5 mol% CaN''_2 in C_6D_6, 60 °C, 99% conversion after 4 days.

Using the dibenzylcalcium catalysts $(DMAT)_2Ca{\cdot}(THF)_2$ or THF-free (4-*t*Bu-benzyl)$_2$Ca changed the course of the catalytic reaction again and gave only styrene polymerization (Entries 3-4). This is due to the absence of a Brønsted acidic proton source like N’’H and implies that the benzylcalcium intermediate reacts much faster with styrene than with 1,4-CHD. The latter reaction would close the TH cycle but is not observed (Scheme 3).

This first set of experiments demonstrates that the nature of the Ca catalyst is crucial to success in alkene TH catalysis. The presence of the amide ligand N’’ is essential and bulky spectator ligands should be avoided (Scheme 3). Replacing Ca for the group 1 metals Li or K was not successful (Entries 5-6), however, using the heavier group 2 metals Sr and Ba lowered the reaction time substantially (Entries 7-8). The catalyst BaN''_2 gave even at room temperature full conversion (Entry 9). Using only one equivalent of 1,4-CHD gave also nearly quantitative conversion but clearly extended the reaction time (Entry 10). Traces of H_2 were only formed in the final stage, clearly indicating strong preference for TH over dehydrogenation. In contrast to the detrimental influence of THF in Ca-catalyzed styrene TH, THF ligands do not affect the activity of the Ba catalyst (Entry 11). This can be explained by the considerably weaker Ba···THF bond. There are cases in which Ba···arene coordination, an interaction of a large soft metal cation with a soft aromatic π-system, is competitive with THF coordination.[26] Therefore, TH of *para*-methoxystyrene by BaN′′$_2$ posed no problems (Entry 12) but *para*-chlorostyrene suffered from partial Cl/N′′ exchange (entry 13). This aromatic nucleophilic substitution is possibly facilitated by Ba···arene bonding. Higher substituted styrene substrates like 1,1-diphenylethylene, *trans*-stilbene or α-Me-styrene could be reduced quantitatively within 1-2 hours (Entries 14-16). Even the trisubstituted C=C bond in 1-Ph-cyclohexene was fully hydrogenated but only after raising the temperature to 120 °C (Entry 17). At this higher temperature, part of the reducing agent is lost due to H_2 evolution. To compensate for this undesired side-reaction, 5 equivalents of 1,4-CHD have been used.

In addition, a series of substrates with non-conjugated (isolated) double bonds could be converted. The C=C bond in $Me_3SiCH{=}CH_2$ was fully reduced at the lower temperature of 60 °C but should be regarded semi-activated by the strongly polarizing Me_3Si-substituent (Entry 18). Semi-activated norbornadiene was fully hydrogenated to norbornane and nortricyclononane (arising from intramolecular nucleophilic addition) at the higher temperature of 120 °C (Entry 19). The fact that norbornene could not be detected is in agreement with efficient reduction of norbornene to norbornane (Entry 20). The cyclic double bond in cyclohexene is somewhat less activated and could only be reduced in traces (Entry 21) whereas 3-vinyl-cylohexene gave partial reduction of the exocyclic terminal double bond (Entry 22). This is in agreement with the problematic hydrogenation of non-conjugated internal alkenes like 2-hexene, however, the truly unactivated C=C bond in 1-hexene was fully converted to hexane (Entry 23). In contrast to 1-hexene reduction with BaN′′$_2$ and H_2,[18] TH is selective and no isomerization to inert internal alkenes like 2- or 3-hexene could be observed.

Although different reaction conditions make it difficult to compare the performance of this TH method with classical alkene hydrogenation using group 2 metal catalysts, conversion rates are certainly on a par with BaN′′$_2$ catalyzed alkene hydrogenation using H_2 as a reductant.[18] Okuda's cationic Ca hydride catalysts were found to be substantially more active in alkene/H_2 reduction than neutral Ca catalysts[27] but alkene TH with BaN′′$_2$ and 1,4-CHD is in most cases significantly faster. The highly reactive THF-free Ca hydride complex $[(^{DIPP}BDI)CaH]_2$ recently reported by the Hill group,[22] hydrogenates a large range of alkene substrates (including 1-hexene) already at room temperature but full conversion generally took up to 3 weeks.[28] In the latter case, catalyst performance is clearly limited by thermal stability: slight increase in temperature led to ligand scrambling and loss of the catalyst by $(CaH_2)_\infty$ precipitation. In contrast, BaN''$_2$ is an extremely robust catalyst that can withstand operation temperatures up to 120 °C. The exact nature of the catalytic species is unclear but likely larger aggregates $N''_xBa_yH_z$ are formed.[25b]

The transfer of hydrogen from 1,4-CHD to styrene catalyzed by CaN''$_2$ was investigated by DFT methods at the M06/6-311++G(d,p)//M06/6-31++G(d,p) level of theory.[29] ΔG values at 60 °C were corrected for benzene solvent effects.[30] The energy profile given in Scheme 4 starts with a series of reactions that initiate the formation of the Ca hydride catalyst N''CaH (**CAT**, route I). The hydrogen source 1,4-CHD is deprotonated by CaN''$_2$ to an intermediate with a cyclohexadienyl anion (**I4**) which could be described as a labile hydride-Meisenheimer complex. The substantial activation energy needed for its formation (**I2***, +22.9 kcal/mol) explains the need for higher temperatures. At these temperatures, the subsequent hydride elimination through transition state **I5*** (+22.3 kcal/mol) is competitive. The activation energies for N''CaH catalyst formation from CaN''$_2$ and 1,4-CHD (via **I2*** and **I5***) are higher than the energy barrier for the reaction CaN''$_2$ + H_2 → N''CaH + N''H (+18.7 kcal/mol).[18] On the other hand, the latter reaction which formally is the deprotonation of H_2 (pK_a H_2 = 49)[31] by a weak base (pK_a N''H = 25.8)[23] was calculated to be clearly endergonic (+11.9 kcal/mol)[18] whereas generation of N''CaH from 1,4-CHD is slightly exergonic: CaN''$_2$ + 1,4-CHD → N''CaH + N''H + benzene (-1.4 kcal/mol). This is due to energy release from the conversion of the unconjugated diene 1,4-CHD to the highly stable aromatic benzene.

The subsequent hydrogenation pathway (H) starts from N''CaH (**CAT**). Styrene insertion and subsequent quenching of the benzylcalcium intermediate with N''H are clearly the lower energy processes along the reaction profile (**H5***). The activation energy for styrene polymerization (**P2***) is 4.3 kcal/mol higher and this process may only be feasible in case N''H is not present (Entries 3-4). The total energy release for transfer of hydrogen from 1,4-CHD to styrene is 34.7 kcal mol which is considerably more exergonic than styrene hydrogenation by H_2, releasing 21.4 kcal/mol. The difference of 13.3 kcal/mol is the aromatization energy for converting 1,4-CHD into benzene and H_2.

As part of our theoretical studies, we investigated an alternative route (A) that circumvents formation of the metal hydride catalyst (**CAT**). However, transferring the hydride directly from the cyclohexadienyl anion to styrene is substantially higher in energy (**A2***, 28.2 kcal/mol) and most likely not feasible.

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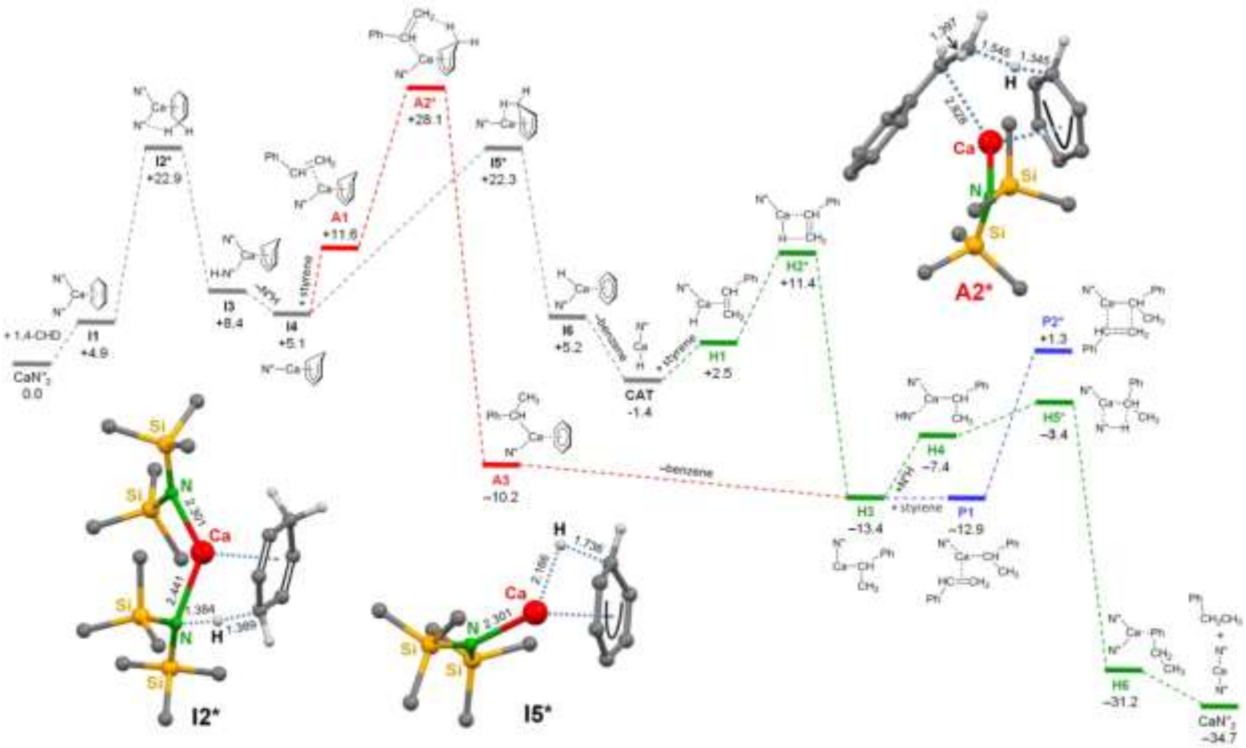

Scheme 4. Energy profile for the transfer hydrogenation of styrene with 1,4-CHD and CaN''$_2$; N'' = N(SiMe$_3$)$_2$ at the M06/6-311++G(d,p)//M06/6-31++G(d,p) level (* indicates transition state). ΔG values (60 °C, kcal/mol) were corrected for benzene solvent effects. The catalytic cycle is initiated by formation of N''CaH (I in grey), followed by styrene hydrogenation (H in green). A non-competitive alternative pathway (A) and styrene polymerization (P) are shown in red and blue, respectively. Insets show selected transition states (H's partially shown, distances in Å).

We demonstrated first successful catalytic transfer hydrogenation from 1,4-CHD, a green waste product from plant oil refinery,[32] to a variety of alkenes using group 2 metal catalysts. The choice of catalyst fully controls the course of the reaction. Amide ligands are crucial and bulky spectator ligands should be avoided for successful TH. Especially BaN''$_2$ was shown to be a highly effective and selective TH catalyst, quantitatively reducing activated double bonds (*e.g.* styrene) without oligomeric side-products and hydrogenating truly unactivated alkenes (*e.g.* 1-hexene) without double bond isomerisation. Convenient access to larger quantities of BaN''$_2$,[33] which is widely used as precursor in Ba chemistry, combined with the advantages inherent to TH (easy experimental set-up avoiding high pressure) make Ba catalyzed alkene TH a highly attractive procedure. The mechanism is different from the generally practised transition metal or acid catalyzed TH. Group 2 metal TH catalysis should therefore be considered a novel area of research, clearly demonstrating the rapidly expanding versatility of early main group metal catalysts.

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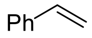
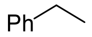
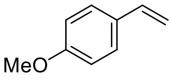
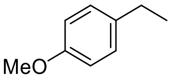
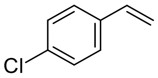
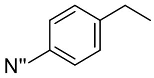
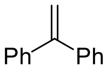
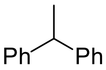
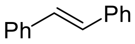
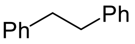
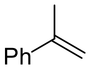
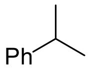
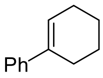
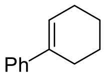
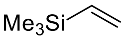
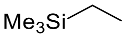
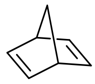
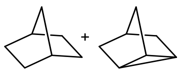
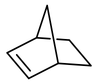
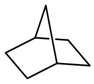
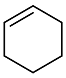
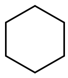
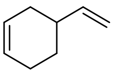
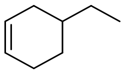
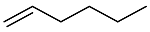
Table 1. Catalytic alkene transfer hydrogenation.[a]

Entry	Catalyst	mol%	Substrate	Eq. 1,4-CHD	T [°C]	t [h]	Product	%
1	CaN''_2	5		1.5	60	44		99
2	$(^{DIPP}BDI)CaN''$	5		1.5	60	24		traces[b]
3	$(DMAT)_2Ca\cdot(THF)_2$	5		1.5	60	20		0[c]
4	$(p\text{-tBu-benzyl})_2Ca$	5		1.5	60	20		0[c]
5	LiN''	10		1.5	60	24		30[b]
6	KN''	10		1.5	60	24		traces
7	SrN''_2	5		1.5	60	6		99
8	BaN''_2	5		1.5	60	0.75		99
9	BaN''_2	5		1.5	20	8		99
10	BaN''_2	5		1	20	21		99
11	$BaN''_2\cdot(THF)_2$	5		1.5	60	0.75		99
12	BaN''_2	5		1.5	60	1		99
13	BaN''_2	5		1.5	60	14		traces
14	BaN''_2	5		1.5	60	1.5		99
15	BaN''_2	5		1.5	60	1.5		99
16	BaN''_2	5		1.5	60	0.75		99
17	BaN''_2	10		5	120	3		99[d]
18	BaN''_2	5		1.5	60	4.25		99
19	BaN''_2	10		5	120	7		75/25[d,e]
20	BaN''_2	10		5	120	5		99[d]
21	BaN''_2	10		5	120	24		Traces[d]
22	BaN''_2	10		5	120	24		50[d]
23	BaN''_2	10		5	120	16		99[d]

[a] [Substrate] = 0.33 M in C_6D_6. Reaction times for essentially full conversion (99 %, determined by ^{1}H NMR) have been optimized in 0.25 h steps. For slower reactions the conversion after 24 h is given. GC-MS was also used for product identification. [b] 1,4-CHD is dehydrogenated to benzene and H_2; also isomerisation to 1,3-CHD observed. [c] Full conversion to polystyrene. [d] At the higher reaction temperature toluene-d_8 was used as solvent. [e] Conversion determined by GC-MS measurement.

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

Abstract:

The challenging alkene transfer hydrogenation (TH) of a variety of alkenes has been achieved with simple AeN''$_2$ catalysts (Ae = Ca, Sr, Ba; N'' = N(SiMe$_3$)$_2$) using 1,4-cyclohexadiene (1,4-CHD) as a H source. Reaction of 1,4-CHD with AeN''$_2$ gave benzene, N''H and the metal hydride species N''AeH (or aggregates thereof) which is a catalyst for alkene hydrogenation. Complex BaN''$_2$ is by far the most active catalyst. Hydrogenation of activated C=C bonds (*e.g.* styrene) proceeded already at room temperature without polymer formation. Unactivated (isolated) C=C bonds (*e.g.* 1-hexene) needed a higher temperature (120 °C) but proceeded without double bond isomerization. The choice of the catalyst is critical to successful TH. The ligands fully control the course of the catalytic reaction which can be: (*i*) alkene TH, (*ii*) 1,4-CHD dehydrogenation or (*iii*) alkene polymerization. DFT calculations support formation of a metal hydride species by deprotonation of 1,4-CHD followed by H$^-$ transfer. Convenient access to larger quantities of BaN''$_2$, its high activity and selectivity and the many advantages of TH make this a simple but attractive procedure for alkene hydrogenation.