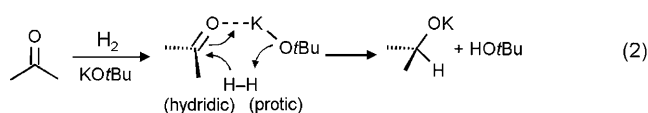


Early Main-Group Metal Catalysts for the Hydrogenation of Alkenes with H₂**

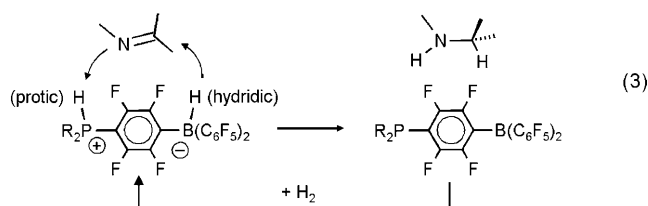
Jan Spielmann, Frank Buch, and Sjoerd Harder*

Although the catalytic hydrogenation of unsaturated compounds represents one of the earliest examples in heterogeneous^[1] as well as homogeneous^[2] catalysis, research on this particular conversion is still thriving.^[3] It boasts a myriad of industrial applications and, on account of important breakthroughs in catalytic asymmetric hydrogenation,^[4] can be a convenient key step in the production of chiral pharmaceutical products. As molecular hydrogen will potentially play a major role in future chemistry, it is anticipated that the importance of catalytic hydrogenation will further expand.^[5]

Whereas traditional homogeneous hydrogenation catalysts are based on precious metals, there is an increase in research efforts to find cheaper alternatives. This quest for "Cheap Metals for Noble Tasks"^[6] provides savings from lower catalyst cost and less-demanding requirements for catalyst recovery. In this context, especially the use of environmentally friendly metals should be promoted. New-generation catalysts for hydrogenation are based on heterolytic cleavage of molecular hydrogen into a hydridic (H⁻) and protic (H⁺) functionality. For example, the key to ionic hydrogenation of ketones is a catalyst which incorporates both functionalities [Eq. (1), M = Fe or Ru].^[7] Claims of a naturally occurring metal-free hydrogenase were recently withdrawn, as an iron-based cofactor was found.^[8] In this light, the discovery of the first non-transition-metal catalyst for ketone hydrogenation, the simple reagent KOtBu [Eq. (2)],^[9] should be regarded as a breakthrough. Recently, small organic molecules have been shown to activate hydrogen^[10] and the first metal-free catalysts for ketone and imine hydrogenation have been introduced.^[10f,11] The latter organo-

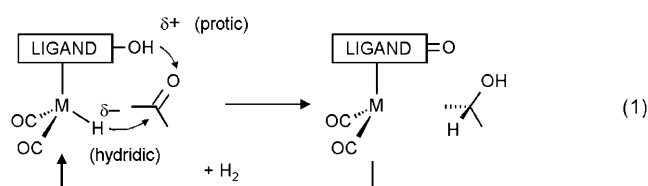


catalytic reaction is based on heterolytic cleavage of H₂ by the unique reactivity of frustrated Lewis pairs [Eq. (3)].



Hitherto, very few reports on the use of main-group metal catalysts in alkene hydrogenation have appeared. Recently, iodoboranes were introduced as Lewis acidic catalysts for the liquefaction of coal by hydrogenation (280–350 °C, 150–250 bar H₂).^[12a] Earlier reports on hydridic hydrogenation catalysts include processes mediated by soluble LiAlH₄^[12b] or by suspensions of NaH, KH, and MgH₂.^[12c] In all cases, reaction conditions are extreme (150–225 °C, 60–100 bar H₂) and various products, including oligomers and polymers, were obtained. Herein, we report on the hydrogenation of conjugated alkene functionalities with well-defined organocalcium catalysts and discuss the use of other early main-group metals.

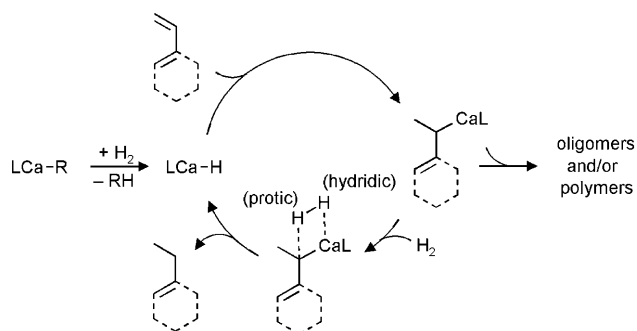
A potential mechanism for the calcium-mediated hydrogenation of alkenes (Scheme 1) is analogous to that for organolanthanide-catalyzed alkene hydrogenation.^[13] A precedent for the actual catalyst, a calcium hydride complex, has been recently reported (**1** in Scheme 2).^[14]



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Supporting information for this article (Experimental details for the catalytic experiments, product characterization, syntheses of **3**, **7**, and Ph₂CKMe, and crystal structure data for **2**, **3**, and **7**) is available on the WWW under <http://dx.doi.org/10.1002/anie.200804657>.



Scheme 1. Proposed catalytic cycle for calcium-mediated hydrogenation of conjugated alkenes. L = ligand.

The first step in the catalytic cycle, addition of **1** to an alkene, has been verified by stoichiometric reactions with conjugated alkenes (under normal conditions, **1** does not react with non-activated alkenes).^[15] 1,1-Diphenylethylene (DPE) reacts cleanly with **1** at 60 °C, to form complex **2** (Scheme 2), which has been unequivocally characterized by crystal structure determination (Figure 1). Contacts between Ca²⁺

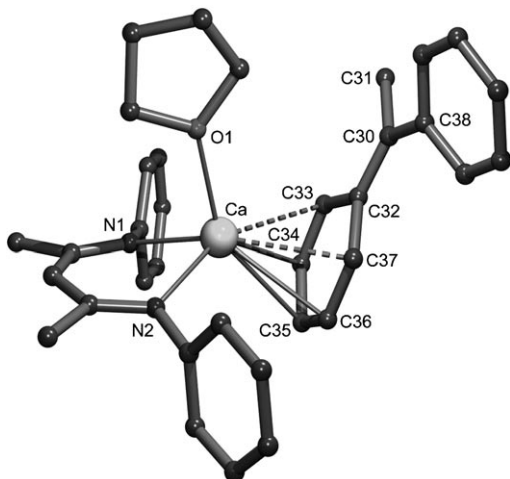


Figure 1. The crystal structure of **2**; hydrogen atoms and *i*Pr substituents have been omitted for clarity. Selected bond distances: Ca–N1 2.333(2), Ca–N2 2.350(2), Ca–O1 2.349(2), Ca–C32 3.019(2), Ca–C33 2.819(2), Ca–C34 2.754(2), Ca–C35 2.752(2), Ca–C36 2.754(2), Ca–C37 2.838(2), C30–C31 1.521(3), C30–C32 1.387(3), C30–C38 1.462(3) Å.

and the benzylic carbon atom (C30) are absent and the (Ph₂CMe)[−] ion coordinates exclusively to the metal through a Ph...Ca π interaction, inducing extensive charge delocalization in the ring, as is evident from the very short C _{α} –C_{*ipso*} bond length (C30–C32). Reaction of **1** with myrcene, a molecule incorporating three C=C bonds, indicates that addition of the calcium hydride functionality can be quite selective (Scheme 2). Hydride attack at the terminal monosubstituted double bond resulted in formation of **3**, which crystallized from solution as the *endo*-Me isomer (Figure 2). NMR spectroscopic investigations on a solution of **3** in [D₈]toluene at room temperature gave evidence for fast exchange

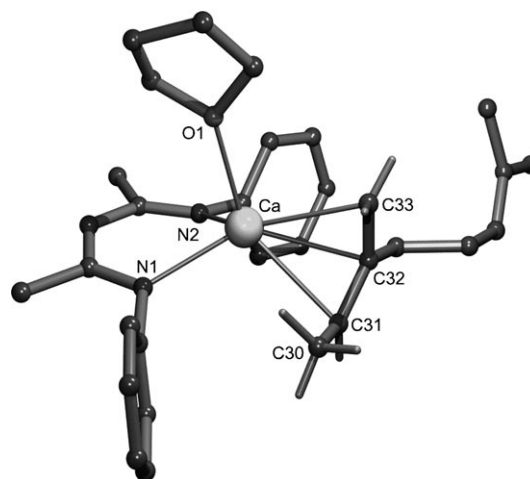


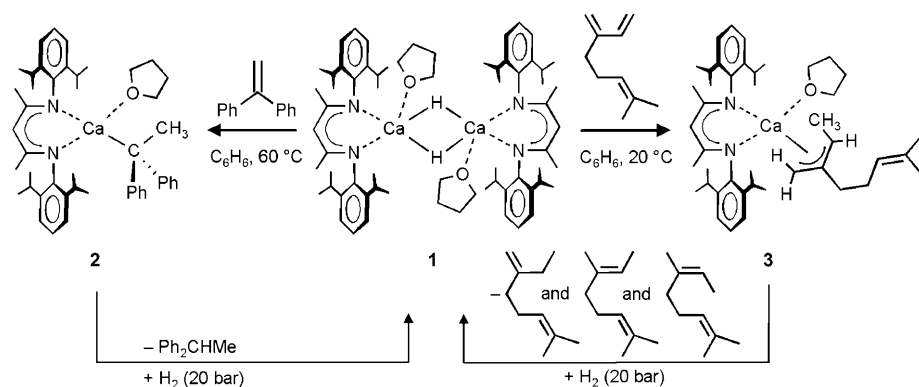
Figure 2. The crystal structure of **3**; hydrogen atoms (except those of the Me-allyl unit) and *i*Pr substituents have been omitted for clarity. Selected bond distances: Ca–N1 2.371(1), Ca–N2 2.342(1), Ca–O1 2.374(1), Ca–C31 2.658(2), Ca–C32 2.624(2), Ca–C33 2.638(2) Å.

between *endo* and *exo* isomers. However, at −50 °C, exclusively the *endo* isomer was detected.

The second step in the catalytic cycle, that is, σ -bond metathesis between the organocalcium intermediate and H₂, is in agreement with the heterolytic protocol (protic/hydridic) for activation of molecular hydrogen. This reaction, however, is unprecedented in calcium chemistry. Although it is extremely fast for alkylaluminum complexes,^[13] examples in early main-group metal chemistry are rare. The reaction of *tert*-butyllithium with H₂ yields an active form of LiH, but requires forcing conditions (200 bar H₂).^[16] Appropriate polar (co)solvents, such as tetramethylethylenediamine (TMEDA) or THF, drastically lower the energy barrier and allow conversion of *n*BuLi into LiH, even at atmospheric pressure.^[17] However, hydrogenolysis of lithium compounds can be regarded as an acid–base equilibrium, that is strongly dependent on the basicity of the carbanion, as demonstrated by calculations (MP2/6-31++G**//6-31++G**). Whereas the reaction CH₃Li + H₂ → CH₄ + LiH is exothermic (−8.3 kcal mol^{−1}), the reaction LiC≡CH + H₂ → HC≡CH + LiH is highly endothermic (+23.4 kcal mol^{−1}).^[18] As the pK_a value of H₂ is relatively high (ca. 35),^[19] it is questionable whether the resultant stabilized benzylic and allylic carbanions in Scheme 2 could undergo

efficient hydrogenolysis to regenerate a calcium hydride functionality.

First information on such σ -bond metathesis processes was obtained by saturation of a solution of the calcium deuteride [D₂]-**1** in benzene with H₂. Under very mild conditions, fast D/H exchange was detected (Table 1, entry 1).^[20] Although this thermo-neutral reaction is fast, metathesis between the benzylic calcium complex **2** and H₂ was slower and



Scheme 2. Hydrogenation of 1,1-diphenylethylene and myrcene, catalyzed by **1**.

Table 1: Reaction of various early main-group metal compounds with molecular hydrogen at 20 °C.

Entry	Substrate	Solvent	H ₂ [bar]	t [h]	conv. [%]	Product(s)
1	1-[D ₂]	C ₆ H ₆	1	0.3	90	[H ₂]-1
2	2	C ₆ H ₆	20	15	> 99	Ph ₂ CHMe
3	2	C ₆ H ₆	20	0.5	7	Ph ₂ CHMe
4	2	THF	20	0.1	> 99	Ph ₂ CHMe
5	3	THF	20	0.5	48	3 isomers ^[a]
6	3	THF	20	5	> 99	3 isomers ^[a]
7	4	THF	1	265	55	α-Me ₃ Si-2-Me ₂ N-toluene
8	4	THF	20	5	87	α-Me ₃ Si-2-Me ₂ N-toluene
9	6	THF	20	5	> 99	2-Me ₂ NC ₆ H ₇ + Me ₃ SiH
10	7	THF	20	0.5	84	2-Me ₂ NC ₆ H ₄ CH(SiMe ₃)CH ₂ CHPh ₂
11	Ph ₂ CKMe	THF	20	17	33	Ph ₂ C(H)Me

[a] See Scheme 1.

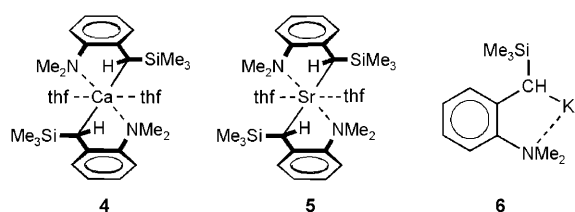
required somewhat higher hydrogen pressure (20 bar). However, the reaction was clean, and 1,1-diphenylethane and **1** were formed quantitatively (Table 1, entry 2). As has been reported for lithium chemistry,^[17] the polarity of the solvent had a strong influence on the σ-bond metathesis process (Table 1, entries 3 and 4). In THF, hydrogenolysis was complete within about 5 minutes. Hydrogenolysis of the allylcalcium complex **3** was somewhat slower and gave rise to three isomers of hydrogenated myrcene (Table 1, entries 5 and 6). Under atmospheric pressure, the homoleptic dibenzylcalcium complex **4** reacted extremely slowly with H₂ to afford α-trimethylsilyl-2-dimethylaminotoluene and presumably “CaH₂” (Table 1, entry 7).^[21] The hydrogenation of **4** occurred much faster at 20 bar of hydrogen pressure (Table 1, entry 8).

Encouragingly, all steps in the proposed catalytic cycle worked well under stoichiometric conditions, and we thus set out to test the Ca-catalyzed hydrogenation. As a substrate, we initially chose DPE, an alkene for which potential side reactions, such as alkene oligomeri-

Table 2: Summary of results for the hydrogenation of alkenes with various main-group metal catalysts.

Entry	Substrate	Solvent	Cat [mol %]	T [°C]	t [h]	conv. [%]	Product(s)
1	DPE	C ₆ H ₆	1 (5)	60	17	49	Ph ₂ CHCH ₃
2	DPE	C ₆ H ₆	4 (2.5)	60	17	41	Ph ₂ CHCH ₃
3	DPE	THF	4 (2.5)	20	3.5	94	92 % Ph ₂ CHCH ₃ 8 % dimer ^[a]
4	DPE	THF + 7.5 % HMPA	4 (2.5)	20	1.5	> 99	96 % Ph ₂ CHCH ₃ 4 % dimer ^[a]
5	DPE	THF + 20 % HMPA	CaH ₂ (30)	100	18	0	–
6	DPE	THF	5 (2.5)	20	3.5	93	92 % Ph ₂ CHCH ₃ 8 % dimer ^[a]
7	DPE	THF + 7.5 % HMPA	6 (5)	20	17	1	Ph ₂ CHCH ₃
8 ^[b]	DPE	THF	6 (5)	20	13	> 99	97 % Ph ₂ CHCH ₃ 3 % dimer ^[a]
9 ^[b]	DPE	THF	KH (10)	60	18	> 99	98 % Ph ₂ CHCH ₃ 2 % dimer ^[a]
10	DPE	C ₆ H ₆ + 5 % TMEDA	<i>n</i> BuLi (5)	20	15	21	14 % Ph ₂ CHCH ₃ 7 % dimers
11	styrene	C ₆ H ₆	1 (5)	20	15	> 99	81 % PhCH ₂ CH ₃ 19 % oligomers ^[c]
12	styrene	C ₆ H ₆	4 (2.5)	20	15	> 99	85 % PhCH ₂ CH ₃ 15 % oligomers ^[c]
13	α-methylstyrene	C ₆ H ₆	1 (5)	60	25	60	PhCH(CH ₃) ₂
14	cyclohexadiene	C ₆ H ₆	4 (2.5)	20	22	96	cyclohexene + traces of dimer
15 ^[b]	1-phenylcyclohexene	THF	6 (5)	60	18	> 99	1-phenylcyclohexane + traces of dimer

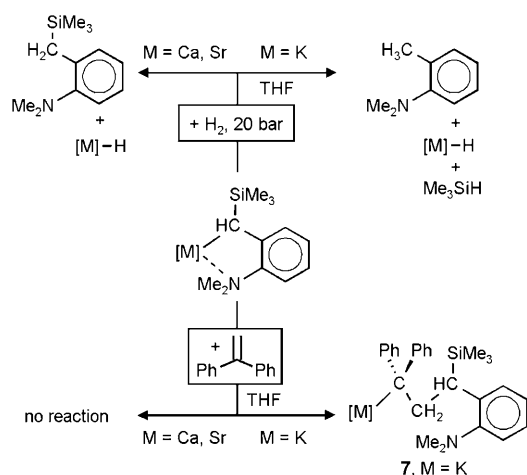
[a] The dimeric product 1,1,3,3-tetraphenylbutane is probably formed by addition of (Ph₂CMe)[–] to 1,1-diphenylethylene (DPE) followed by hydrogenation. [b] Reaction at 100 bar H₂. [c] Oligomers mainly consist of dimers and traces of trimers and tetramers. The dimer has been characterized as the cyclodimerization product 1-methyl-3-phenylindane.



significant acceleration. At 20 °C, nearly complete hydrogenation occurred within 3.5 hours (Table 2, entry 3). However, small amounts of the dimeric product 1,1,3,3-tetraphenylbutane were also found. Addition of the highly polar cosolvent hexamethylphosphoramide (HMPA) gave faster conversion and reduced formation of the dimeric by-product (Table 2, entry 4). The rate-enhancing effect of a polar reaction medium can be explained by: 1) its ability to keep

any in situ generated “CaH₂” in solution and/or 2) acceleration of the σ -bond metathesis between the alkylcalcium intermediate and H₂ (see Table 1). Finely ground commercially available CaH₂ failed to catalyze this reaction, even with 30 mol % catalyst loading and under very polar conditions (Table 2, entry 5), indicating that in situ generation of the Ca–H functionality is of major importance in Ca-mediated alkene hydrogenation.

The influence of the metal was evaluated by using similar strontium- and potassium-based catalysts. Whereas strontium catalyst **5** gave results comparable to its calcium congener (Table 2, entry 6), the potassium catalyst **6** gave essentially no conversion, even with addition of HMPA (Table 2, entry 7). The reason for this large difference in catalytic activity was investigated by a series of stoichiometric reactions (Scheme 3). The Ca and Sr catalysts, **4** and **5**, react with



Scheme 3. Stoichiometric reactions of the metal-bound benzylic group with either H₂ or DPE.

hydrogen to form α -trimethylsilyl-2-dimethylaminotoluene and, presumably, the metal hydride. However, reaction of the potassium catalyst **6** with hydrogen in THF gave 2-dimethylaminotoluene, Me_3SiH and, presumably, potassium hydride (Table 1, entry 9).^[21b] Apparently, the KH which forms initially attacks the silicon center in α -trimethylsilyl-2-dimethylaminotoluene, to give Me_3SiH and 2-dimethylaminobenzylpotassium, which hydrogenates to give 2-dimethylaminotoluene and KH. After shorter reaction times, some α -trimethylsilyl-2-dimethylaminotoluene was also isolated.

Likewise, reactions of the catalysts **4**, **5**, and **6** with DPE showed large differences. Whereas the Ca and Sr catalysts, **4** and **5**, do not react with DPE, even in THF under reflux conditions, the potassium complex **6** rapidly adds to the double bond at room temperature to give complex **7**, which crystallizes as a coordination polymer (see the Supporting Information). As complex **7** can be hydrogenated to its hydrogenolysis product and KH (Table 1, entry 10), different initiation reactions do not explain the non-activity of **6** in alkene hydrogenation. However, the slow reaction of the intermediate Ph_2CKMe with H₂, to form KH and Ph_2CHMe (Table 1, entry 11), might be responsible for this low activity.

Repeating the catalytic experiment with **6** at a H₂ pressure of 100 bar gave essentially quantitative hydrogenation (Table 2, entry 8). At 60 °C, even commercially available potassium hydride catalyzed the reaction to complete conversion (Table 2, entry 9). These experiments not only imply that the metal hydride is the catalytically active species, but also that its regeneration is the crucial step in the catalytic cycle. The reaction catalyzed by commercially available $nBuLi$ /TMEDA proceeded only to low conversion (Table 2, entry 10), suggesting that, at lower H₂ pressures, the heavier alkaline-earth metal complexes are the more efficient catalysts.

The scope of Ca-mediated alkene hydrogenation was further investigated by probing alkene substrates sensitive to polymerization. Attempted hydrogenation of styrene, under polar conditions (THF, HMPA), gave exclusively polystyrene. In benzene, however, more than 80 % of the hydrogenation product, $PhCH_2CH_3$, was formed (Table 2, entries 11 and 12). Hydrogenolysis of the intermediate α -methylbenzylcalcium species is seemingly sufficiently fast, and can compete with the polymerization side reaction. We attribute the faster hydrogenolysis to the higher basicity of $(PhCHMe)^-$ compared to $(Ph_2CMe)^-$. It is therefore fortunate that polymerization-sensitive alkenes generally produce the more reactive (least-stabilized) carbanions that can also undergo efficient hydrogenolysis under apolar conditions.

Myrcene was hydrogenated efficiently with calcium catalyst **1** to give the three expected isomers depicted in Scheme 2. As product analysis is complicated to an even greater extent by the presence of dimeric products, no further details are given. The 1,1-disubstituted alkene α -methylstyrene can be hydrogenated, albeit at significantly slower rate (Table 2, entry 13). In this case, no dimeric products were detected. Hydrogenation of the 1,2-disubstituted alkene, cyclohexadiene, gave excellent yields of cyclohexene (Table 2, entry 14). As $nBuLi$ is an extremely active initiator for the polymerization of conjugated alkenes, such as styrene, cyclohexadiene, and myrcene, no efforts were made to hydrogenate these substrates with alkali-metal-based catalysts. However, the trisubstituted alkene 1-phenylcyclohexene, which was not hydrogenated with the calcium catalysts **1** and **4**, was fully hydrogenated to phenylcyclohexane with the potassium catalyst **6** at 100 bar H₂ pressure (Table 2, entry 15). Also, the early main-group metal-mediated hydrosilylation of 1-phenylcyclohexene with $PhSiH_3$, which presumably proceeds through a catalytic cycle that involves a metal hydride, could only be achieved with **6**, but not with **1** or **4**.^[22]

In summary, we have introduced a set of well-defined early main-group metal catalysts for the hydrogenation of a variety of conjugated alkenes. Although the method could be limited to substrates with conjugated double bonds, the resultant exclusive mono-hydrogenation of these dienes is advantageous.^[23] Stoichiometric reactions and the isolation of intermediates suggest that the proposed catalytic cycle is similar to that for the lanthanide-catalyzed alkene hydrogenation. Whereas the alkaline-earth metal catalysts are effective under relatively mild conditions (20 °C, 20 bar), alkali-metal catalysts need a considerably higher H₂ pressure.

This could be due to the considerably higher Lewis acidity of the alkaline-earth metal cations. Polar conditions accelerate the hydrogenation process. However, monomers sensitive towards polymerization can only be hydrogenated in apolar solvents: polar (co)solvents and the use of more ionic alkali-metal catalysts gave exclusively polymeric products. The fine balance between alkene hydrogenation and polymerization can be controlled by choice of metal, solvent, and hydrogen pressure. The application of simple calcium and strontium complexes as catalysts in alkene hydrogenation underscores the increasing importance of the heavier alkaline-earth metals in catalysis. This study might stimulate the development of transition-metal-free heterogeneous alkene-hydrogenation catalysts that are solely based on cheap and abundant calcium.^[24]

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