

organometallic chemistry has been to develop catalysts derived from earth-abundant, less-toxic transition metals such as iron, cobalt and nickel⁵.

In the past decade or so, startling strategies for hydrogenation reactions have also been discovered. In 2006, certain molecules containing boron and phosphorus were shown to react reversibly with hydrogen⁶. It was subsequently found⁷ that reactions between boron-containing molecules known as boranes and phosphorus-containing molecules called phosphines can be frustrated electronically or through steric effects (which occur when bulky chemical groups block access to certain parts of a molecule). This allows certain combinations of boranes and phosphines to chemically activate hydrogen molecules, and, in some cases, mediate the hydrogenation of many different types of compound^{8,9}. Then, in 2008, a remarkable calcium-based catalyst was reported¹⁰ for the hydrogenation of alkenes (hydrocarbons that contain carbon–carbon double bonds). Collectively, these findings provided evidence that hydrogenation can be catalysed by systems based on elements other than the transition metals, overturning 100 years of chemical dogma.

Bauer *et al.* have now broadened the range of alkaline-earth-metal derivatives that can form the basis of hydrogenation catalysts. The new catalysts are complexes with the general formula $M[N(\text{SiMe}_3)_2]_2$ (where M can be magnesium, calcium, strontium or barium; Si is silicon; and Me represents a methyl group), and can be readily prepared. The authors used them to hydrogenate substrates known as aldimines (Fig. 1).

The researchers performed 30 reactions using different reaction conditions and several aldimines. They varied the amount of catalyst used (between 2.5% and 10% molar equivalents of the reaction substrate), the pressure of hydrogen (1–12 bar) and the temperature (80–120 °C). Most of the reactions were 99% complete in times ranging from 15 minutes to 24 hours, depending on the specific substrate, catalyst and conditions.

The authors show that the hydrogenations are slower for bulkier aldimine molecules and when the carbon atom in the aldimine's imine (C=N) group is less electrophilic (attractive to negative charges). Conversely, the catalytic activity increases with the atomic size of the metal used: the magnesium catalyst is least reactive, and the calcium, strontium and barium catalysts are increasingly reactive. That said, the calcium catalyst¹⁰ previously reported by researchers from the same group was a highly effective catalyst for aldimine hydrogenation, which suggests that the activity of the current calcium catalyst could be optimized by modifying the ligands bound to the metal atom.

Most of the aldimines tested with the catalysts

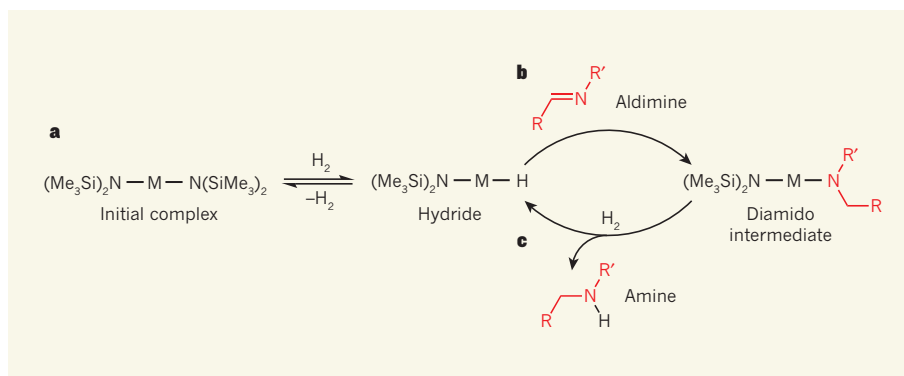


Figure 1 | Simplified hydrogenation mechanism for catalysts that contain alkaline-earth metals.

Bauer *et al.*² report that complexes containing alkaline-earth metals catalyse the reaction of aldimine compounds with hydrogen gas (H_2), and propose the following mechanism. **a**, The initial complex reacts with H_2 — probably reversibly — to generate a transient hydride intermediate. **b**, The aldimine inserts into the M–H bond of the hydride to form a diamido intermediate. **c**, This intermediate reacts with more H_2 to liberate the hydrogenation product (an amine), regenerating the hydride for further catalytic cycles. Me, methyl; Si, silicon; M, magnesium, calcium, strontium or barium; R is typically an aromatic group, such as phenyl; R' is *t*-butyl, isopropyl, phenyl or a mesityl (a bulky analogue of the phenyl group).

had a phenyl group (a benzene ring) attached to the carbon atom in the imine. Bauer *et al.* found that the catalysts still worked when electron-withdrawing or electron-donating groups were attached to the phenyl group — something that isn't always guaranteed in chemical reactions. However, the catalysts could not hydrogenate compounds known as ketimines, which are similar to aldimines but have two groups attached to the imine carbon atom, rather than just one.

Bauer and co-workers propose a mechanism for the catalytic cycle in which the catalyst first

reacts with hydrogen gas to generate a transient hydride intermediate — a process that is likely to be reversible (Fig. 1a). The aldimine inserts into the M–H bond of the hydride to generate a diamido intermediate (Fig. 1b),

which then reacts with more hydrogen gas to liberate the hydrogenation product (an amine; Fig. 1c). This last step also regenerates the hydride for further catalytic cycles.

The proposed mechanism might seem straightforward, but the authors note that the active form of the catalyst has not been unambiguously identified. When Bauer *et al.* reacted the calcium catalyst with hydrogen gas alone, the proposed hydride intermediate did form, but so, too, did aggregated forms of hydrides.

The researchers performed computational simulations of their reactions to cast further light on the reaction mechanism. The simulations revealed that the aggregation process probably releases energy, suggesting that a thermodynamic driving force could generate

a currently undefined, catalytically active complex involving an aggregated hydride. The simulations also supported the proposed stepwise mechanism for the catalytic cycle. Finally, Bauer *et al.* used a previously reported calcium hydride complex¹¹ as a model of the proposed catalytic hydride intermediate, and found that it reacts with an aldimine and hydrogen gas in a way that is consistent with the proposed catalytic cycle.

Compared with industrial reactions catalysed by transition-metal complexes, Bauer and colleagues' reactions use higher amounts of catalyst and are relatively slow. Nonetheless, the findings expand the substrate scope for hydrogenation catalysts derived from abundant alkaline-earth metals, raising the possibility that low-cost and low-toxicity catalysts could one day be used for industrial applications. Work is now needed to improve the activity of such catalysts, and to find catalysts that tolerate the presence of the impurities found in industrial-grade reagents. Perhaps most crucially, the authors' work provides further evidence that the dogma that transition metals are required for hydrogenation catalysis should be firmly relegated to the false beliefs of the past. ■

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