Teaming up main group metals with metallic iron to boost hydrogenation catalysis

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Hydrogenation of unsaturated bonds is a key step in both the fine and petrochemical industries. Homogeneous and heterogeneous catalysts are historically based on noble group 9 and 10 metals. Increasing awareness of sustainability drives the replacement of costly, and often harmful, precious metals by abundant 3d-metals or even main group metals. Although not as efficient as noble transition metals, metallic barium was recently found to be a versatile hydrogenation catalyst. Here we show that addition of finely divided Fe0, which itself is a poor hydrogenation catalyst, boosts activities of Ba0 by several orders of magnitude, enabling rapid hydrogenation of alkynes, imines, challenging multi-substituted alkenes and non-activated arenes. Metallic Fe0 also boosts the activity of soluble early main group metal hydride catalysts, or precursors thereto. This synergy originates from cooperativity between a homogeneous, highly reactive, polar main group metal hydride complex and a heterogeneous Fe0 surface that is responsible for substrate activation.
The hydrogenation of unsaturated molecules is a major achievement that pioneered the beginnings of heterogeneous\(^1\) as well as homogeneous\(^2\) catalysis. Despite its long history, hydrogenation catalysis is by no means old hat (Searching for “hydrogenation catalyst” in SciFinder gave a total of circa 33,000 hits of which nearly 11,000 date from the last decade (2010–2020) but today still a focal point of industrial as well as academic research\(^3\). Contemporary research is directed towards extending industrial applications, the conversion of biomass, and efforts to increase sustainability by replacing noble metals in classical hydrogenation catalysts with abundant metals\(^4\).

Heterogeneous alkene hydrogenation catalysts are traditionally based on late transition metals (Pd/C, Pt/C, Raney-Ni)\(^5\). Being robust, these catalysts withstand the forcing conditions needed for the reduction of highly challenging substrates such as aromatic rings. Homogenous alkene hydrogenation catalysts initially focused on the metal Rh, with Wilkinson’s catalyst RhCl(PPh\(_3\))\(_3\) as a well-known textbook example\(^6\). Further developments include Crabtree’s cationic Ir complex which still today is one of the rare catalysts that is able to reduce most challenging tetrasubstituted alkenes like Me\(_2\)C=CMMe\(_2\) (Fig. 1).\(^7\)

Although molecular catalysts are thermally sensitive and often need sophisticated ligands, the milder reaction conditions allow for higher selectivities.

Classical transition metal alkene hydrogenation follows two different routes: a dihydride pathway, which involves 2e oxidation and reduction processes, or a monohydride cycle in which the metal oxidation state is unaffected (Fig. 2a). Current research on alkene hydrogenation includes early/late heterobimetallic cooperativity\(^8\), ligand-metal cooperativity\(^9\), cooperative hydrogen-atom-transfer (HAT)\(^10\) which may be combined with photoactivation\(^11\), or Frustrated-Lewis-Pair (FLP) catalysis\(^12\).

While the latter FLP protocol is a metal-free route for alkene hydrogenation, there is also a strong drive to develop hydrogenation catalysts based on broadly available, abundant metals\(^4,13\). This development is not limited to the transition metals but also sparked the rapidly growing area of early main group metal hydride species with a transition metal surface. The Crabtree catalyst and the general rate order in alkene hydrogenation\(^5,2\) were unexpected\(^14,15\). Access to the first soluble calcium hydride complexes\(^16\) has led to a protocol for alkene hydrogenation under relatively mild conditions\(^17\). As calcium is not known for facile reversible redox reactions, this catalytic conversion follows the classical monohydride cycle (Fig. 2a). Since this initial report, there has been a considerable improvement in the performance of Ae metal catalysts\(^18–24\). Ae = alkaline earth metal. We demonstrated that common amide precursors like AeN\(_2\)\(_N\) (N\(_N\) = N(SiMe\(_3\))\(_2\)) are highly effective precatalysts for hydrogenation of imines\(^21\) and alkenes\(^22\). Catalyst initiation requires the unexpected deprotonation of H\(_2\) (pK\(_a\) = 49) by the weak AeN\(_2\) base (pK\(_a\) HN(SiMe\(_3\))\(_2\) = 25.8)\(^2\); Fig. 2b\(^25,26\). This apparent counterthermodynamic effect is enabled by subsequent exothermic aggregation of Ae(H)N\(_N\) and AeH\(_2\) species to give a variety of larger clusters for which examples have been isolated and structurally characterized, cf. [Ba(H)N\(_N\)]\(_7\) (Fig. 2b)\(^27,28\). Such mixed amide-hydride clusters of general formula Ae\(_2\)H\(_N\)N\(_N\) are thermally highly robust, enabling homogeneous catalysis in the 120–140 °C range with activities that increase going down group 2: Ca < Sr < Ba. Larger amide ligands to smaller, more reactive clusters, considerably improving catalyst activities. Using the precatalyst Ba[N(SiPr\(_2\))\(_2\)]\(_2\) extended the substrate scope to challenging tetrasubstituted alkenes and, although very slow, also benzene could be hydrogenated\(^23\).

Considering that ligand bulk is favorable for high activities, the most recent observation that barium metal alone is an even better hydrogenation catalyst was unexpected\(^24\). The metal was activated by the evaporation/condensation method (metal vapor synthesis = MVS) producing a finely divided Ba\(_0\) powder (MVS-Ba\(_0\)) which is highly reactive. This property is also utilized in radio tubes in which Ba\(_0\) mirrors serve as a getter for various gases\(^25\).

The pathway for alkene hydrogenation with MVS-Ba\(_0\) has been reported previously\(^26–28\). Although the reaction of the highly electropositive metal Ba\(_0\) with H\(_2\) normally needs a higher temperature (>80 °C)\(^30\), it was shown that MVS-activated Ba\(_0\) is already converted at room temperature\(^24\). However, full conversion to BaH\(_2\) is never achieved and generally, substoichiometric compounds are formed\(^31\). The Ba\(_0\)/BaH\(_2\) mixture is the starting point for two catalytic cycles (Fig. 2c). (1) The barium hydride cycle: alkene substrate can react with BaH\(_2\), producing soluble Ba\(_0\)(H)\(_x\) clusters with highly reactive Ba-H bonds. Further alkene insertion is followed by hydrolysis, leading to alkanes and the reformation of barium hydrides. (2) The barium metal cycle: alkenes with conjugated (activated) C=C bonds can react with Ba\(_0\) by oxidative addition, giving metallacycles. In addition to numerous examples\(^32,33\), we demonstrated the oxidative addition of MVS-activated Ba\(_0\) to Ph\(_2\)C=CPH\(_2\) or Ph\(_2\)C=NPH\(_2\).\(^24\) We also showed that the intermediates, [Ba\(_2\)\(_{2}\)] \(_{2}\) [Ph\(_2\)C-CPh\(_2\)\(_2\)]\(^–\) or [Ba\(_2\)\(_{2}\)]\(_2\) [Ph\(_2\)C-NPH\(_2\)\(_2\)]\(^–\), react with H\(_2\) to the final hydrogenation products.

The concurrent existence of Ba\(_0\) and Ba hydride species is essential for the unexpectedly high catalytic activity of MVS-Ba\(_0\). This working hypothesis is based on Wright and Weller’s early studies on ethylene hydrogenation with metallic Ca\(_0\)/CaH\(_2\) or Ba\(_0\)/BaH\(_2\) mixtures\(^34–36\). Corroborated by extensive experimental work, it was claimed that catalysis occurs at the interface between free metal and metal hydride: the Ba\(_0\) surface activates alkenes for nucleophilic attack by polar Ba hydrides (Fig. 2d). This so-called dual-site mechanism is supported by experimental verification of ethylene adsorption on a Ba\(_0\) surface\(^37\). Substrate activation by d → π* backbonding from heavier Ae metals (Ca, Sr, Ba) is gradually gaining ground, especially for metals in low oxidation states\(^38–40\). This is exemplified by several recent observations like N\(_2\) activation with Ca\(^41\), considerable red-shifting of the CO stretching frequency in Ba(CO)\(_8\)\(^38\), and benzene activation in Ba(benzene)\(_2\)\(^42\). π-Backbonding from d-orbitals on Ba\(_0\) to benzene π*-orbitals results in pronounced electron transfer from metal to benzene and an overall elongation of the C-C bonds. Although the debate on the relevance of d-orbitals for the heavier Ae metals is currently highly controversial\(^39\), it is notable that some overlap of s-, p-, and d-bands in heavier Ae metals had already been discussed by Wright and Weller in the early 1950s\(^34\).

Building upon this hypothesis, we now combine reactive main group metal hydride species with a transition metal surface. The rationale behind this idea is the fact that, in contrast to main group metals, transition metal surfaces are well known for their capability to activate unsaturated bonds. This concept of cooperative catalysis merges homogeneous catalysis, in the form of a
alkene hydrogenation.

MVS-Ba0 was obtained in a face-centered cubic (fcc) lattice typical for α-Fe. MVS-Ba0 was obtained in a face-centered cubic (fcc) lattice typical for α-Fe. MVS-Ba0 was obtained in multi-gram quantities by cocondensation of barium metal and n-heptane24. Using a similar method, multi-gram quantities of a finely divided form of Fe0 could be obtained. Cocondensation of Fe and toluene gave a red solution of the highly labile complex Fe(toluene)250. Controlled decomposition above −60 °C led to the formation of a black suspension from which a fine black Fe0 powder was isolated. 

Since no stabilizing organic capping agents were used, the MVS-activated Fe0 and Ba0 powders are extremely air-sensitive and highly pyrophoric. Elemental analysis and powder X-ray diffraction in sealed capillaries confirm their metallic state. The diffraction patterns show that both samples consist of microcrystalline nanoparticles of circa 5 nm (Fig. S1). While MVS-Fe0 crystallized in a body-centered cubic (bcc) lattice typical for α-Fe, MVS-Ba0 was obtained in a face-centered cubic (fcc) lattice. The latter β-Ba modification should be considered a metastable phase which was first observed by spraying barium vapor in a high vacuum, i.e., conditions similar to cocondensation by MVS31. 

Scanning-electron-microscope (SEM) and transmission-electron-microscope (TEM) studies show the formation of large agglomerates which are highly porous and consist of nanoparticles in the sub-10 nm regime (Figs. S2, S3). The metal particles are persistent to dispersion and extremely pyrophoric, characteristics that both prevent more accurate microscopy studies. X-ray photoelectron spectroscopy shows that the surface of these highly pyrophoric powders is partially oxidized due to sample preparation (Figs. S4–S8).

Similar to previously reported Fe0 nanoparticles47,48, the MVS-activated Fe0 powder catalyzed the hydrogenation of 1-hexene and cyclic di-substituted alkenes like cyclohexene (Fig. 3 and Table S3). It hardly reduced linear internal alkenes like 3-hexene and is inactive for the reduction of tri-substituted alkenes or arenes. In contrast, homogenous Fe complexes or clusters have been reported to reduce tetrasubstituted alkenes but are inactive in arene reduction45,46. MVS-activated Ba0, which reduced benzene very slowly24, is clearly superior to the herein obtained Fe0 but not at par with noble d-block metal hydrogenation catalysts. We now found that an equimolar Ba0/Fe0 mixture is up to three orders of magnitude more active than the most active Ba0 component alone (Fig. 3). This allows facile hydrogenation with very low catalyst loadings and further extension of the substrate scope to the most challenging arene substrates.

Using a very low catalyst loading of only 0.05 mol% BaFe0, 1-hexene was fully reduced within 15 min. The addition of Fe0 to Ba0 led to an increase in the turn-over-frequency (TOF) from 7 h−1 (Ba0) to 8000 h−1 (BaFe0), measured at full conversion. Also, internal alkenes were reduced efficiently with the expected reactivity order: cyclic alkenes > cis-alkenes > trans-alkenes > tri-substituted alkenes52. Hydrogenation of the unactivated C=C bond in 1-Me-cyclohexene is surprisingly fast (TOF =
The BaFe catalyst also hydrogenated polycyclic aromatic hydrocarbons and, depending on the conditions, selective reduction was obtained. Interestingly, whereas Ba⁰ reduces the central ring in anthracene only stoichiometrically, the BaFe combination hydrogenates the terminal rings catalytically. This demonstrates that Fe⁰ addition influences both, activity and selectivity. Naphthalene and biphenyl, both substrates in which reduction of one of the rings is facile, could be fully hydrogenated. Whereas Ba⁰ alone barely reduced the exposed double bond in acenaphthylene, the BaFe catalyst managed full conversion within minutes and, controlling the reaction conditions, all three rings could be reduced stepwise. Although ketones could not be hydrogenated, the scope of the BaFe catalyst was significantly extended, even for tetrasubstituted Ph₂C=CH₂.

400 h⁻¹). The BaFe mixture achieved even for tetrasubstituted Ph₂C=CH₂ quantitative reduction within the hour. However, the slightly higher temperature also led to traces of Ph ring reduction, indicating that the BaFe catalyst is highly efficient for benzene-to-cyclohexane conversion. Homo- or heterogeneous Fe catalysts alone are fully inactive in arene hydrogenation⁴⁵. Under the same conditions, but with only 3 mol% catalyst loading, BaFe reduced benzene quantitatively within 0.5 h. Even electron-rich, alkylated arenes like toluene and p-xylene could be fully hydrogenated, with rates decreasing with the degree of alkylation.

Fig. 3 Catalytic hydrogenation. Comparison of the activities for Ba⁰ and the mixed Ba⁰/Fe⁰ catalysts (the mixture was ground before use). P = H₂ starting pressure in bar (reactors were pressurized with H₂ and shut off from the H₂ source), T = temperature in °C, and t = time in hours which in most cases has been optimized for full conversion (99%). For comparison, TOF values (turn-over-frequency in h⁻¹) are given. The controversial use of TOF values is discussed in the Supplementary Information.
further extended to alkenes and imines in which under harsher conditions also the Ph substituents could be reduced. The heteroatom-containing ring in the Lewis base quinoline was fully reduced at room temperature (Fig. 3). The lower operation temperature allows catalytic runs in reactors even at room temperature. Full conversions can also be reached at room temperature (Table S4) and that high initial pressures are not needed. Not only the H₂ pressure but also the substrate concentration has no effect on the conversion rate (Table S5).

Investigations concerning the Ba⁰/Fe⁰ ratio revealed that the activity in benzene reduction increases linearly with Fe content, reaching an optimum at a ratio of 1/1 (Fig. S15). Mechanically grinding a mixture of both metal powders with mortar and pestle prior to catalysis, increased TOF² by a factor of 10 (Table S11). This simple method of mixing results in a rather heterogeneous Ba³Fe³ distribution (energy dispersive X-ray (EDX) mapping: Figs. S9–11). The powder X-ray diffraction (p-XRD) and X-ray photoelectron spectra (XPS) for the ground BaFe mixture is a superposition of Ba⁰ and Fe⁰ spectra (Figs. S1, S4). This is in agreement with the observation that Ba⁰ and Fe⁰ do not form alloys. Considering that Ba⁰ is soft (1.25 Mohs) and Fe⁰ is hard (4.0 Mohs), it is plausible that an intimate surface contact of both metals is beneficial for catalytic activity. Indeed, whereas a Ba³/Fe³ mixture can still be magnetically separated in its elements, the ground powder is fully magnetic and cannot be separated.

Not surprisingly, the activation of Fe⁰ is an essential requirement for catalytic activity. Commercially available iron powder is not active but pyrophoric Fe⁰, obtained by thermal decomposition of Fe-oxalate, also boosts the activity of Ba⁰. It is, however, clearly inferior to MVS-activated Fe⁰ (Table S7). The heterogeneous nature of the initial Ba⁰/Fe⁰ mixture suggests that the catalyst may be recycled. Hydrogenation of benzene to cyclohexane with BaFe gave a black suspension from which the catalyst can be removed from the mother liquor with a magnet and reused without significant loss of activity (Fig. 4). The mother liquor does not contain dissolved salts or complexes (after evaporation of all volatiles no visible products remained, see Fig. S16). As ¹H Nuclear-Magnetic-Resonance (NMR) spectra of the mother liquor do not show line-broadening, the presence of trace quantities of paramagnetic iron species is excluded.

**Catalyst variations.** The herein presented concept of cooperative main group/transition metal catalysis with a Ba⁰/Fe⁰ mixture can be extended to other Ae⁰ metals. Although BaFe is one of the most active catalysts, activities for MgFe, CaFe, and SrFe are all within a similar order of magnitude (Tables S9, 10), indicating that also abundant, biocompatible, metals like Mg⁰ and Ca⁰ can be used successfully.

Assuming that the Ae⁰ metal reacts with H₂ to form AeH₂, we investigated commercially available AeH₂ salts as a catalyst component. Whereas BaH₂ and FeH₂ are individually inactive for benzene reduction, its combination is a potent catalyst (Table 1). However, the mixtures CaH₂/FeH₂ and SrH₂/FeH₂ were essentially inactive. This may be related to the high lattice energies and poor solubilities of these commercially available metal hydrides. Metal amides, Ae₂N (Ae = Mg, Ca, Sr, Ba), which under H₂ atmosphere convert to soluble hydride clusters, are also effective cocatalysts for benzene hydrogenation. On their own, these amides cannot reduce benzene but the Ae₂N⁰/Fe⁰ combination is especially for Ba quite active (Table 1). The corresponding alkali metal amides gain activity with increasing metal size (LiN, NaN, and NaN⁺, which thus far has not shown any activity for hydrogenation of even the simplest alkenes⁴,¹⁵,²², into a very potent hydrogenation catalyst.

Table 1. Catalytic benzene hydrogenation with combined X/Fe catalysts (1.5 mol%, 150 °C, 50 bar, 2 h): X = main group metal species; N‴ = N(SiMe₂)₂; BDI = H[C(MeN)₂DIPP]₁₂ (DIPP = 2,6-disisopropylphenyl).

| X     | conv. [%] | TOF (h⁻¹) |
|-------|-----------|------------|
| Ba⁰   | >99       | >33        |
| CaH₂  | 0         | 0          |
| SrH₂  | 3         | 1          |
| BaH₂  | 82        | 21         |
| MgN₂  | 32        | 11         |
| CaN₂  | 29        | 10         |
| SrN₂  | 40        | 13         |
| BaN₂  | 86        | 29         |
| LiN‴  | 2.5       | 1          |
| NaN‴  | 10        | 3          |
| KN‴   | 40        | 13         |
| [(Ba(H)N‴)₂]⁰ | 21 | 7 |
| [(BDI)MgH]₂ | >99 | >33 |

The assumption that Ae⁰ or AeH₂ form under catalytic conditions a soluble metal hydride species is supported by the fact that BaFe in the BaFe catalyst can be replaced by the soluble hydride cluster [Ba(H)N‴]⁷ (Fig. 2b). As the fate of the [Ba(H)N‴]⁷ cluster under catalytic conditions is unclear, this is not ultimate proof for a soluble main group metal component. However, we also found that the combination of [(BDI)MgH]₂ and Fe⁰ is a highly active catalyst for benzene hydrogenation (Table 1 and Fig. 5). The robust complex [(BDI)MgH₁₂] can be seen as magnesium hydride which has been solubilized by a bulky β-diketiminate (BDI) ligand. As a stand-alone catalyst, [(BDI)MgH]₁₂ is fully inactive in benzene hydrogenation (10 mol%, 50 bar H₂, 150 °C) but in combination with MVS-Fe⁰ it is competitive with Ba⁰/Fe⁰. After magnetic separation of the Fe⁰ cocatalyst, [(BDI)MgH]₁₂ was the only complex that could be detected by ¹H NMR (Figs. S12–14). Based on these observations,
Mechanistic considerations. Although there is compelling evidence that Fe\(^0\) and Ba\(^0\) act in synergy in catalytic alkene hydrogenation, it is difficult to fully reveal the intricate details of the mechanism. Being insoluble in organics, the BaFe precatalyst is a heterogeneous system. As the catalyst can be fully recycled without loss of activity (Fig. 4), and assuming that catalytic activity is not due to undetected trace metal quantities in solution, it is also after catalysis of a heterogeneous system. A tentative mechanism for what happens during catalysis can only be postulated based on observations, reported literature and common knowledge.

\[ \text{(BDI)}\text{MgH}_2 \times 0.5 \rightarrow \text{Fe}^0 + \text{H}^2 \rightarrow \text{Fe}^+ + \text{H}_2 \]

Fig. 5 Proposed mechanism for cooperative benzene hydrogenation. Benzene, activated at a Fe\(^0\) surface, is hydrogenated by a soluble Mg hydride complex.

p-XRD and XPS investigations on the BaFe catalyst, obtained by grinding MVS-activated Ba\(^0\) and Fe\(^0\) powders, show a rather inhomogeneous element distribution. For this reason, the mechanism previously reported for Ba\(^0\)/BaH\(_2\) catalyzed alkene hydrogenation (Fig. 2c) would be a logical starting point. Indeed, as previously shown for Ba\(^0\) catalysis\(^{24}\), we here show that a spent BaFe catalyst contains metallic Ba\(^0\) and hydride functions (Figs. S17–S20). Since \(^1\)H NMR spectra of the mother liquor after catalyst separation show no sign of line broadening due to contamination with paramagnetic Fe species, it is likely that Fe\(^0\) remains heterogeneous during catalysis. Addition of liquid mercury has a poisoning effect on catalyst activity (Table S12), hinting that under catalytic conditions there is indeed a heterogeneous catalyst component\(^{56}\). Another indication of a catalytic reaction in which the key steps are heterogeneous comes from the observation that conversion rates are independent of \(H_2\) pressure and substrate concentration. This stands in strong contrast with homogeneous Ae metal-catalyzed alkene hydrogenation in which higher \(H_2\) pressure is beneficial\(^{14,17}\) and, in agreement with calculations\(^{57}\), hydrogenolysis by \(\sigma\)-bond metathesis is rate-determining (Fig. 2a). The pseudo-zero order behavior in BaFe catalyzed alkene hydrogenation is typical for a heterogeneous reaction in which substrate-active site interaction is the rate-limiting factor.

Although the catalytic reaction has a heterogeneous character, there is evidence that the main group component is during catalysis at least partially in solution. This is demonstrated by the fact that Fe\(^0\) also boosts the catalytic activity of soluble Ae metal hydrides or precursors thereto (Table 1). Although these examples may not be pertinent to the BaFe system, EDX-mapping of a fresh BaFe and a spent BaFe catalyst provide strong evidence for a soluble Ba component. While the surface of a fresh catalyst mixture shows an expected Ba/Fe ratio of circa 1/1 (Fig. S9 and Table S1), the surface of a spent BaFe catalyst is considerably enriched in Ba with a Ba/Fe ratio of circa 2/1 (Fig. S10 and Table S2). Since the catalyst is after catalysis fully recovered, this observation suggests that Ba is solubilized during catalysis and precipitates after full substrate conversion, either as Ba\(^0\) or BaH\(_2\).

Building upon the mechanism previously discussed for hydrogenation with Ba\(^0\) (Fig. 2c)\(^{24}\) and comprehensive reports by Wright and Weller on Ae\(^0\)/AeH\(_2\) catalysts\(^{34–36}\), we postulate for the Ba\(^0\)/Fe\(^0\) mixture a mechanism in which homogeneous Ba and heterogeneous Fe\(^0\) catalysts work in synergy (Fig. 6). MVS-Activated Ba\(^0\) reacts, dependent on the nature of the substrate, either first with \(H_2\) or with an alkene to give a highly reactive, solubilized Ba hydride species. The cycle is closed by alkene insertion followed by hydrogenolysis with \(H_2\). There are several steps (marked A–E in Fig. 6) in which the heterogeneous Fe\(^0\) catalyst could play an activating role:

(A) Partially filled \(d\)-orbitals on Fe\(^0\) facilitate \(H-H\) bond cleavage by backbonding in the \(\sigma^*\) orbital (LUMO). Dissociative adsorption of \(H_2\) on an Fe(110) surface has been calculated to be barrier-free\(^{58}\). This results in atomistic hydrogen which can move freely in the iron crystal lattice and is the origin of hydrogen embrittlement of steel\(^{59}\). The presence of highly reactive H radicals could facilitate the \(\text{Ba}^0 + 2 \text{H} \rightarrow \text{BaH}_2\) conversion, resulting in a salt composed of Ba\(^2+\) and \(H^-\) ions. In situ generated, unaggregated BaH\(_2\) will be a very potent reducing agent, reacting smoothly with alkenes to give an R-Ba-H species which, similar to \([\text{Ba}(\text{H})\text{N}]_7\)\(^{28}\), can go into solution in the form of a [Ba(H)]\(_n\) aggregate.

(B) The Fe\(^0\) surface can activate unsaturated substrates for hydride attack, an ability that is strongly supported by theory. It is generally agreed that in hydrogenation over a group 8 metal catalyst, benzene is adsorbed as a π-complex. Benzene adsorption energies on a Fe(110) surface have been calculated to be comparable to those for adsorption at (111)-surfaces of Ni, Pd or Pt\(^{61}\). Similar as in molecular metal-benzene complexes, the Fe\(^0\) surface accepts π-electrons from benzene’s π-HOMO and donates electrons back in the π*-LUMO\(^{62}\). Concomitant C-C bond lengthening and decrease of the HOMO-LUMO gap facilitate hydride attack.

(C) Highly reactive H radicals that are formed at the Fe\(^0\) surface could directly react with alkylbarium intermediates to form the final product. This would facilitate the hydrogenolysis step, i.e. the \(\sigma\)-bond metathesis step which under homogeneous conditions is rate-determining\(^{14,17,57}\).

(D) As previously described for Ae\(^0\)/AeH\(_2\) systems\(^{24,34–36}\), desorption of \(H_2\) from BaH\(_2\) starts at temperatures above 100 °C. Since it is well-known that Fe\(^0\) nanoparticles catalyze the hydrogen desorption kinetics for the Mg\(^0\)/MgH\(_2\) system\(^{63}\), the elimination of \(H_2\) from BaH\(_2\) could be facilitated by MVS-activated Fe\(^0\). Note that this step is only required for a full Ba\(^0\) cycle.

(E) Metal mixtures of Fe\(^0\) and Ba\(^0\) could profit from an additional activating effect. Comparable with K-promotion of the
Haber-Bosch Fe-catalyst for N₂ activation, electropositive Ba⁰ may enforce the e-transfer chain Ba⁰ → Fe⁰(d) → π*(alkene), giving substrate activation a supplementary boost. Most recently, a Cs-promoted Fe catalyst enabled N₂-to-NH₃ conversion giving substrate activation a supplementary boost. Most recently, a Cs-promoted Fe catalyst enabled N₂-to-NH₃ conversion at room temperature. It has been reported that Ba-promotion can be even more effective than Cs-promotion. Such promotion remains heterogeneous. There is currently no indication that the main group metal component can pass those of their individual components. This synergy expands the substrate scope to challenging arenes, raising the level to that known for the more noble group 9 or 10 metal catalysts. This heterobimetallic strategy could be extended to other Ae metals, including abundant, biocompatible metals like Mg⁰ and Ca⁰. A further demonstration of the sustainability of this concept is demonstrated by facile magnetic separation and recycling of the Ba⁰/Fe⁰ catalyst without significant activity loss.

The assumption that the main group component in Ae⁰/Fe⁰ forms a soluble Ae metal hydride species (or precursors thereto). A striking example of the effectiveness of this cooperative catalytic system is the facile benzene-to-cyclohexane conversion by a mixture of [(BDI)MgH]₂, a soluble well-defined Mg hydride complex, and Fe⁰.

Although it is difficult to gain insight in processes at the interface of homogeneous and heterogeneous catalysis, experimental observations suggest that the spent BaFe catalyst is a mixture of Fe⁰, Ba⁰, and hydride species. Based upon previous work and current data, we propose a mechanism in which Fe⁰ plays an activating role in H-H bond cleavage and BaH₂ formation but also activates the unsaturated substrate at its surface by π-backbonding. The Ba⁰ component is the source for soluble Ba hydride reagents and also may play a role as an electronic promoter for Fe⁰.

Boosting the activities of homogeneous main group metal catalysts by interplay with a Fe⁰ surface merges homogeneous with heterogeneous catalysis. The simplicity of this concept and the numerous possibilities for metal combinations, hold considerable potential in the future search for sustainable hydrogenation catalysts based on abundant metals.

**Data availability**

Supplementary information (general experimental procedures, experimental details for catalyst preparation and catalysis, NMR spectra, investigations towards the nature of the catalyst) is available within the Supplementary Material files, or from the corresponding author on request.

Received: 23 December 2021; Accepted: 16 May 2022; Published online: 09 June 2022

**References**

1. Sabatier, P. & Senderens, J.-B. Action du nickel sur l'éthylène. Compt. Rendus 124, 616–618 (1897).
2. Calvin, M. Homogeneous catalytic hydrogenation. Trans. Faraday Soc. 34, 1181–1191 (1938).
3. de Vries, J. G. & Elsevier, C. J. The Handbook of Homogeneous Hydrogenation (Wiley-VCH, 2007).
4. Bullock, R. M. Catalysis without Precious Metals (Wiley, 2010).
5. Wisniak, J. The history of catalysis. from the beginning to Nobel Prizes. Educ. Quim. 21, 60–69 (2010).
6. O’Connor, C. & Wilkinson, G. Selective homogeneous hydrogenation of alk-1-enes using hydridocarbonyl(trihypropylphosphine)rhodium(I) as catalyst. J. Am. Chem. Soc. 76, 5388–5390 (1954).

7. Crabtree, R. H. Iridium compounds in catalysis. Acc. Chem. Res. 12, 331–337 (1979).

8. Powers, I. G. & Uyeda, C. Metal–metal bonds in catalysis. ACS Catal. 7, 936–958 (2017).

9. Karmann, M. K. & Mankad, N. P. Cooperative strategies for catalytic hydroamination of unsaturated hydrocarbons. ACS Catal. 7, 6110–6119 (2017).

10. Kattamuri, P. V. & West, J. G. Cooperative hydrogen atom transfer: from theory to applications. Synlett 32, 1179–1186 (2001).

11. Kamei, Y. et al. Silane- and peroxide-free hydrogen atom transfer: from theory to applications. Synlett 32, 1179–1186 (2001).

12. Hounjet, L. J. & Stephan, D. W. Hydrogenation by frustrated Lewis Pairs: lessons learned and future perspectives. Science 336, 106–111 (2012).

13. Bullock, R. M. Abundant metals give precious hydrogenation performance. Science 342, 1054–1055 (2013).

14. Harder, S. From limestone to catalysis: application of calcium compounds as homogeneous catalysts. Chem. Rev. 110, 3852–3876 (2010).

15. Barrett, A. G. M., Crimmin, M. R., Hill, M. S. & Procopiou, P. A. Imine hydrogenation with simple alkaline earth metal catalysts. Proc. Roy. Soc. A, Math. Phys. Eng. Sci. 466, 973–983 (2010).

16. Harder, S. & Brettar, J. Rational design of a well-defined soluble calcium hydride complex. Angew. Chem. Int. Ed. 45, 3474–3478 (2006).

17. Spielmann, J., Buch, F. & Harder, S. Early main-group metal catalysts for the hydrogenation of alkenes with H2. Angew. Chem. Int. Ed. 47, 9434–9438 (2008).

18. Schöpf, M., Hohndorf, T., Angeliou, C., Dragoe, M., Schubert, U. Heterofunctionalization catalysis with organometallic complexes of calcium, strontium and barium. Proc. Roy. Soc. A, Math. Phys. Eng. Sci. 472, 20150261 (2016).

19. Wilson, A. S. S., Dinoi, C., Hill, M. S., Mahon, F. M. & Maron, L. Heterolysis of dihydrogen by nucleophilic calcium alkyls. Angew. Chem. Int. Ed. 57, 12367–12371 (2018).

20. Shi, X. et al. Super-bulky penta-arylcyclopentadienyl ligands: isolation of the full range of half-sandwich heavy alkaline-earth metal hydrides. Angew. Chem. Int. Ed. 58, 4356–4360 (2019).

21. Bauer, H. et al. Imine hydrogenation with simple alkaline earth metal catalysts. Nat. Catal. 1, 40–47 (2018).

22. Bauer, H. et al. Simple alkaline-earth metal catalysts for effective alkene hydroamination. Angew. Chem. Int. Ed. 57, 15177–15182 (2018).

23. Martin, J. et al. Highly active superbulky alkaline earth metal amide catalysts for hydrogenation of challenging alkenes and aromatic rings. Angew. Chem. Int. Ed. 59, 9102–9112 (2020).

24. Stephner, R. et al. Metallic barium: a versatile and efficient hydrogenation catalyst. Angew. Chem. Int. Ed. 60, 4252–4258 (2021).

25. Abdur-Raschid, K. et al. An acidity scale for phosphorus-containing compounds including metal hydrides and dihydrogen complexes in THF: toward the unification of acidity scales. J. Am. Chem. Soc. 122, 9155–9171 (2000).

26. Fraser, R. R., Mansour, T. S. & Savard, S. Acidity measurements on pyridines in tetrahydrofuran using lithiated silylamines. J. Org. Chem. 50, 3232–3234 (1985).

27. Matlind, B. et al. A simple route to calcium and strontium hydride clusters. Angew. Chem. Int. Ed. 56, 11880–11884 (2017).

28. Wissinger, M. et al. Simple access to the heaviest alkaline earth metal hydride: a strongly reducing hydrocarbon–soluble barium hydride cluster. Angew. Chem. Int. Ed. 56, 16654–16659 (2017).

29. Della Porta, P. & Orjilio, S. The sorption of hydrogen by barium getters. Vaccum 11, 26–31 (1961).

30. Richter, B., Grindel, G., Czarnecki, B., Kowald, M., Hans, H. & Jensen, T. R. From metal hydrides to metal borohydrides. Inorg. Chem. 57, 10678–10780 (2018).

31. Pedersen, A. S. Magnesium (Beryllium) and Alkaline Earth (Calcium, Strontium and Barium) Hydrides. Solid State Phenom. 49–50, 35–70 (1996).

32. Michel, O. et al. Diene dissolution of the heavier alkaline earth metals. Eur. J. Inorg. Chem. 2012, 998–1003 (2012).

33. Jiao, X. & Weller, L. The catalytic activity of barium and calcium hydrides. II. The nature of the catalyst. J. Am. Chem. Soc. 76, 5302–5305 (1954).

34. Wright, L. & Weller, L. The catalytic activity of barium and calcium hydrides. I. An exploratory study. J. Am. Chem. Soc. 76, 5305–5308 (1954).
Acknowledgements
We thank Samuel Grams for GC-MS measurement and Antigone Roth for elemental analysis. The Friedrich-Alexander-University Erlangen-Nürnberg is acknowledged for generous support.

Author contributions
C.F.: Conceptualization, investigation, validation, formal analysis, writing—original draft, and visualization. P.S., C.K., and G.B.: Investigation, validation, and formal analysis. U.Z.: Conceptualization, investigation, validation, and formal analysis. S.S.: Writing—original draft—review and editing, visualization, supervision, and project administration.

Funding
Open Access funding enabled and organized by Projekt DEAL.

Competing interests
The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-30840-4.

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Peer review information Nature Communications thanks the anonymous reviewers for their contribution to the peer review of this work. Peer reviewer reports are available.

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