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Activation and discovery of earth-abundant metal catalysts using sodium *tert*-butoxide

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First-row, earth-abundant metals offer an inexpensive and sustainable alternative to precious-metal catalysts. As such, iron and cobalt catalysts have garnered interest as replacements for alkene and alkyne hydrofunctionalization reactions. However, these have required the use of air- and moisture-sensitive catalysts and reagents, limiting both adoption by the non-expert as well as applicability, particularly in industrial settings. Here, we report a simple method for the use of earth-abundant metal catalysts by general activation with sodium *tert*-butoxide. Using only robust air- and moisture-stable reagents and pre-catalysts, both known and, significantly, novel catalytic activities have been successfully achieved, covering hydrosilylation, hydroboration, hydrovinylation, hydrogenation and [2π+2π] alkene cycloaddition. This activation method allows for the easy use of earth-abundant metals, including iron, cobalt, nickel and manganese, and represents a generic platform for the discovery and application of non-precious metal catalysis.

Earth-abundant metal catalysis is key to the sustainable future of chemical synthesis and manufacturing. Despite this, precious-metal catalysts remain the 'go-to' for both industry and academia. Several reductive strategies have been developed to enable state-of-the-art earth-abundant metal catalysis, but the majority of these rely on the use of air- and moisture-sensitive pre-catalysts (Fig. 1a, upper)[1–8] or reagents (Fig. 1a, lower)[9–23], which are challenging to handle, store and transport, thus hindering widespread adoption of these otherwise powerful methods. In the ideal scenario, all reagents and pre-catalysts would be air- and moisture-stable solids that are easily handled and applicable in large-scale processes, with minimal associated hazards. With this in mind, we questioned whether a non-organometallic reagent could serve as a pre-catalyst activator, greatly simplifying low-oxidation-state non-precious-metal catalysis. This Article describes what promises to be a significant step along that road: the universal activation of first-row transition-metal pre-catalysts using sodium *tert*-butoxide (NaO^tBu, Fig. 1b).

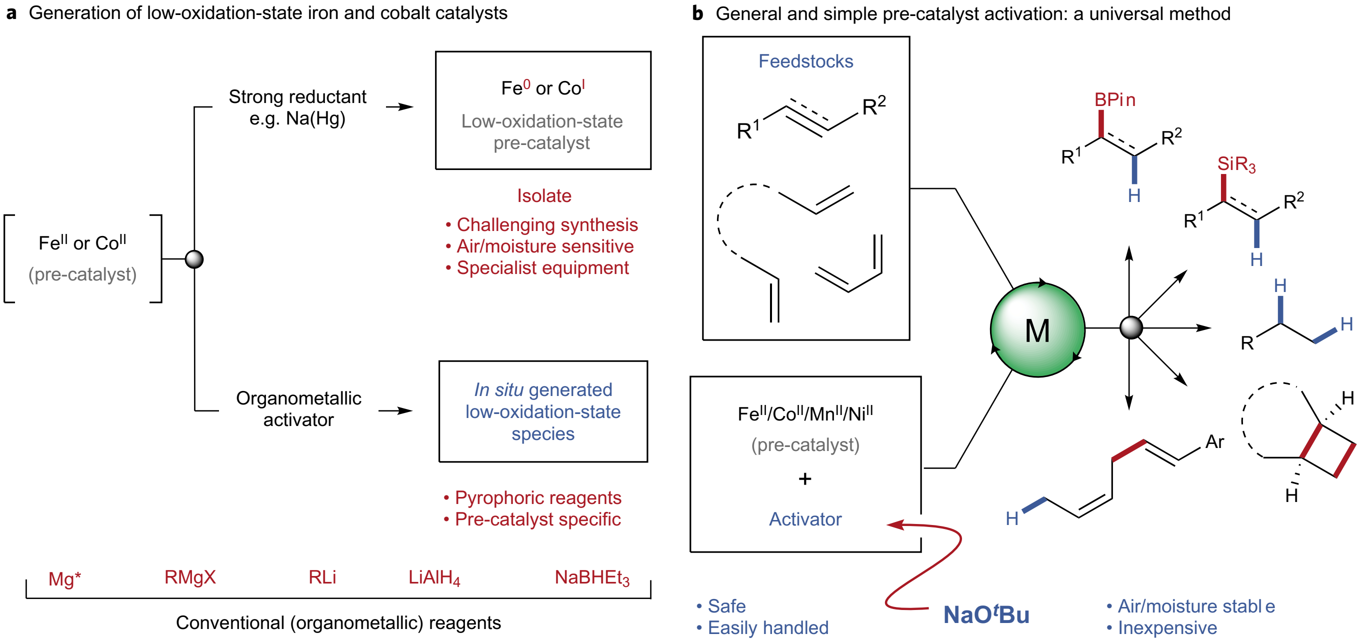

Figure 1 | Activation strategies for iron and cobalt pre-catalysts. a, Typical routes to generate catalytically active iron(0) and cobalt(I) catalysts (upper). Analogous iron(II) and cobalt(II) complexes are bench-stable surrogates for these low-oxidation-state species, which are activated using external organometallic reagents or reducing metals as *in situ* reductants (lower). **b**, Organometallic-free *in situ* pre-catalyst activation for olefin hydrofunctionalization using first-row transition metals.

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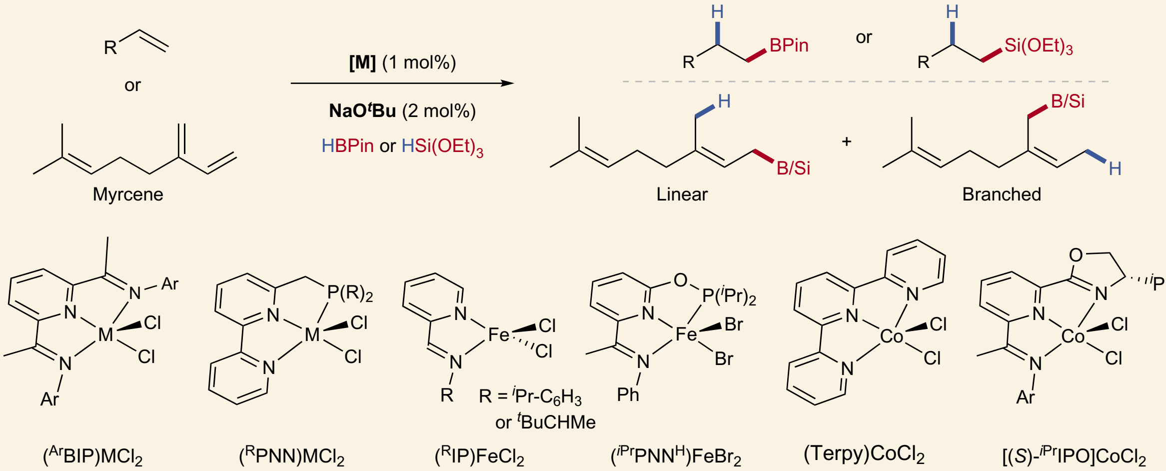
Table 1 | Iron- and cobalt-catalysed hydroboration and hydrosilylation of alkenes.



Entry	Pre-catalyst	Substrate	Previously reported		This work
			Activator	Yield (%)	Yield (%)*
Alkene hydroboration					
1a	^{Et}BIPFeCl$_2$	1-Octene	Na(Hg) (ref. 9)	>98	>95
1b			NaBHEt$_3$ (ref. 9)	47	
2	^{Et}BIPFeCl$_2$	4-Ph-1-butene	EtMgBr (ref. 18)	90	91
3	^{tBu}PNNFeCl$_2$	1-Octene	NaBHEt$_3$ (ref. 11)	90	87
4	^{iPr}IPFeCl$_2$	Myrcene	Mg* (ref. 21)	92 (18:82)	93† (20:80)
5	^{iPr}PNNCoCl$_2$	1-Octene	NaBHEt$_3$ (ref. 12)	>99	>95
6	^{Mes}BIPCoCl$_2$	1-Octene	Co(I)Me (ref. 5)	>98	>95
7	TerpyCoCl$_2$	1-Octene	Co(I)Alkyl (ref. 6)	87 (59:41)	>95 (93:7)
8	(S)-^{iPr}IPOCoCl$_2$	α-Me-Styrene	NaBHEt$_3$ (ref. 16)	85 (97% e.e.)	>95 (98% e.e.)
Alkene hydrosilylation					
9	^{Et}BIPFeCl$_2$	1-Octene	Na(Hg) (ref. 27)	>98	94‡
10	^{iPr}PNN^{H}FeBr$_2$	1-Octene	NaBHEt$_3$ (ref. 14)	90	5
11	*t*BuCHMeIPFeCl$_2$	Myrcene	(1) ArLi, (2) *t*BuCHMeIP (ref. 28)	91 (95:5)	88§ (92:8)
12	TerpyCoCl$_2$	1-Octene	–	–	68$^{\|}$ (93:7)
13	^{Et}BIPNiCl$_2$	1-Octene	–	–	48$^{\|}$
14	^{Et}BIPMnBr$_2$	1-Octene	–	–	60$^{\|,\P}$

*Reaction conditions: Alkene (0.4 mmol), HBPin (0.44 mmol) or HSi(OEt)$_3$ (0.48 mmol), [Fe] (1 mol%), NaO^{t}Bu (2 mol%), THF (0.5 ml), 25 °C, 60 min. Yield determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. Regioselectivities are reported in parentheses as a ratio of linear:branched isomers. †0.99 g product isolated. ‡8 mmol scale, neat. §1.06 g product isolated. $^{\|}$Using PhSiH$_3$. ¶Using 2 mol% [Mn] and 4 mol% NaO^{t}Bu.

In an effort to discover a practical pre-catalyst activation method, we first targeted iron-catalysed hydroboration, as there are established benchmarks using both a state-of-the-art isolated 'iron(0)' catalyst[9] and an organometallic activation method[18]. After testing several reagent classes, metal alkoxide salts proved to be exceptionally efficient activators (see Supplementary Table 1). An important series of control reactions established that the combination of an iron(II) pre-catalyst and sodium *tert*-butoxide was necessary for any catalytic activity. Stoichiometric quantities of alkoxide salt have been used previously to activate bis(pinacolato)diboron [B$_2$(Pin)$_2$] and transfer B(Pin) to iron(II) chloride, but not to trigger low-oxidation-state catalysis or a general reductive catalysis platform[19]. From a practicality perspective it is key to note that these reactions were conducted using reagents as supplied from commercial vendors, without purification, even after extended storage in air, and using a single straightforward activation protocol.

Results and discussion

The generality of any synthetic protocol is essential for widespread adoption. It was therefore important to assess whether the NaO^{t}Bu activation could be applied to a range of pre-catalyst classes (Table 1). Chirik has reported the use of iron(0) bis(imino)pyridine complexes as catalysts for the hydroboration of alkenes, where the key iron(0) species is prepared by sodium–mercury amalgam reduction of the iron(II) precursor[9]. NaO^{t}Bu activation of the bench-stable iron(II) pre-catalyst ^{Et}BIPFeCl$_2$ gave the linear alkylboronic ester product in excellent yield (>95%), with complete control of regioselectivity and, importantly, equalling the reactivity of the isolated iron(0) manifold (Table 1, entry 1a) and surpassing that using an organometallic reagent (Table 1, entry 1b). Ethyl magnesium bromide (EtMgBr) has also been used for the *in situ* activation of the iron(II) pre-catalyst ^{Et}BIPFeCl$_2$ (ref. 18). Activation using NaO^{t}Bu again gave equal reactivity to the organometallic activator, with excellent yield and regioselectivity achieved in the hydroboration of 4-phenyl-1-butene (Table 1, entry 2). Huang has reported the catalytic activity of an iron(II) pincer complex, ^{tBu}PNNFeCl$_2$, in combination with NaBHEt$_3$ as the activator for the anti-Markovnikov hydroboration of alkenes[11]. Using this iron(II) pre-catalyst and NaO^{t}Bu, in place of NaBHEt$_3$, again gave the linear alkylboronic ester in excellent yield, with exclusive regioselectivity and equal reactivity to that using NaBHEt$_3$ (87%, Table 1, entry 3). Ritter has previously used (imino)pyridine iron(II) dichloride pre-catalysts for the 1,4-hydroboration of 1,3-dienes using activated magnesium as the activator[22]. We further exemplified our activation method by successful application to six (imino)pyridine iron(II) chloride pre-catalysts (see Supplementary Table 3). Using NaO^{t}Bu, the pre-catalyst ^{iPr}IPFeCl$_2$, loading could be reduced to 1 mol% (from 4 mol%),

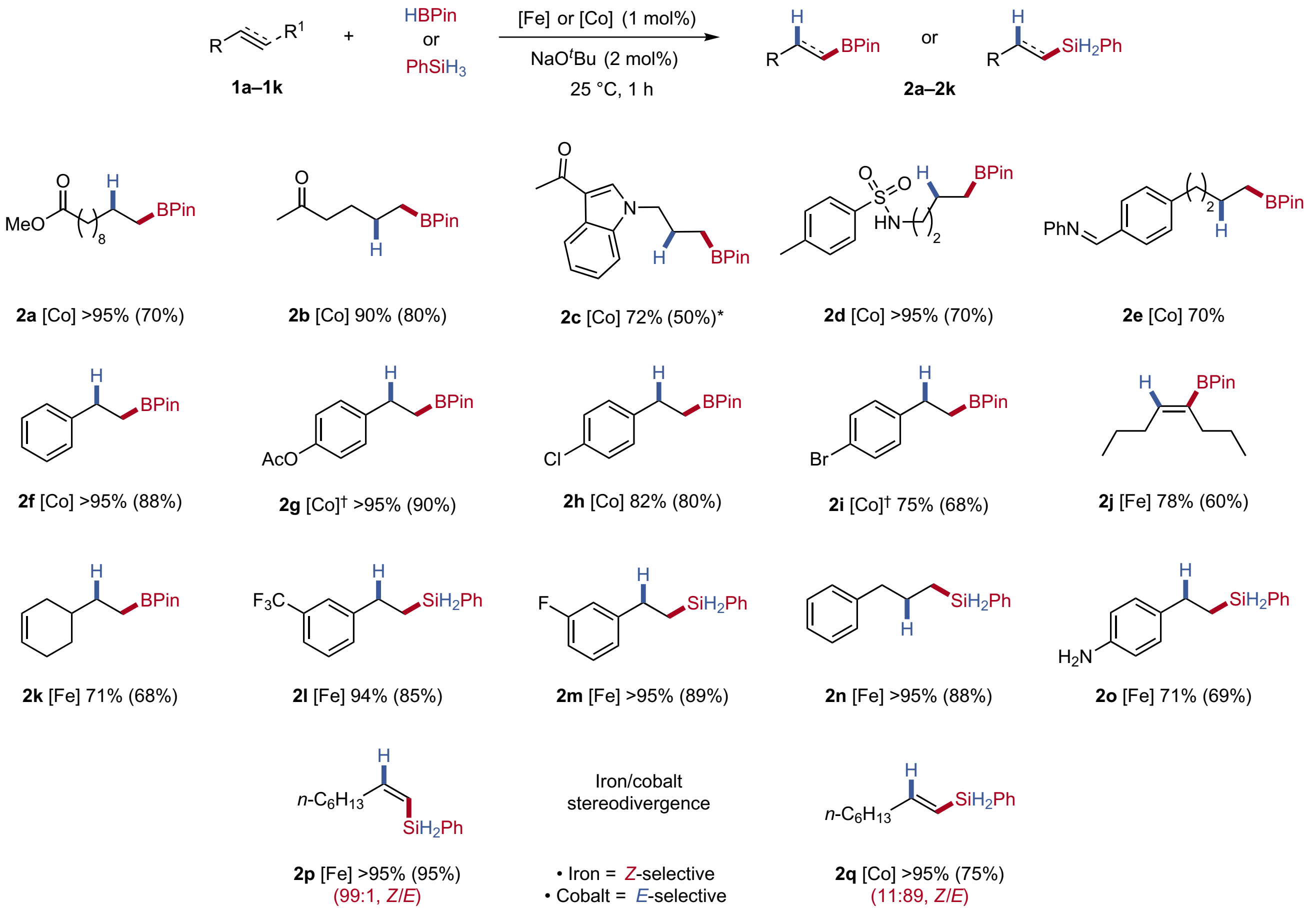


Figure 2 | Iron- and cobalt-catalysed hydroboration and hydrosilylation using NaO^{t}Bu as a pre-catalyst activator. Iron- and cobalt-catalyst substrate scope for alkene and alkyne hydroboration (**2a**–**2k**) and hydrosilylation (**2l**–**2q**). Yields determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard and isolated yields are reported in parentheses. Pre-catalyst used: [Fe] = ^{Et}BIPFeCl$_2$, [Co] = ^{Mes}BIPCoCl$_2$, [Co]† = ^{iPr}PNNCoCl$_2$. *Yield of isolated product following oxidative work-up.

and the 1,4-hydroboration products of myrcene, a naturally occurring terpene, could be synthesized in high yield (93%), on gram-scale and with equal regioselectivity to that previously reported (Table 1, entry 4).

With the successful activation of over ten iron pre-catalysts, we were curious as to whether the NaO^{t}Bu activation could be applied to other earth-abundant metals[24]. Chirik has shown that ^{Mes}BIPCo(I)Me is a highly efficient pre-catalyst for alkene hydroboration[5], and Huang similarly reported the hydroboration of alkenes using a cobalt(II)-pincer complex, ^{iPr}PNNCoCl$_2$, in combination with NaBHEt$_3$ as the activator[12]. Remarkably, NaO^{t}Bu successfully facilitated pre-catalyst activation for both structurally unique cobalt(II) pre-catalysts, ^{iPr}PNNCoCl$_2$ and ^{Mes}BIPCoCl$_2$, to give the alkyl boronic ester in equal yield to that reported previously (>95%) and with complete control of regioselectivity in both cases (Table 1, entries 5 and 6). Significantly, the activation method was extended to the activation of an enantiopure C_1-symmetric imino-pyridine-oxazoline cobalt(II) pre-catalyst ^{iPr}IPOCoCl$_2$, which enabled the hydroboration of α-methylstyrene in excellent yield (95%) and enantioselectivity (98% e.e., Table 1, entry 8), once again equalling the reported reactivity using an organometallic activator[16].

Having successfully developed a practical activation method for alkene hydroboration using different ligand structures and metals, we decided to investigate the generality of this method with respect to other reaction classes. Alkene hydrosilylation is one of the largest industrial processes currently in operation[25]. Principally, these reactions are carried out using well-established platinum catalysts, and it is estimated that the global silicone industry consumes approximately 5.6 metric tonnes of platinum annually[26]. As a consequence, several new earth-abundant metal catalysts have emerged for alkene hydrosilylation[20,27,28].

We began by testing the catalytic activity of a range of iron(II) pre-catalysts, in combination with 1-octene and silanes that were compatible with previous methods involving organometallic activators[20]. We quickly found success. A range of bis(imino)pyridine iron(II) pre-catalysts, BIPFeCl$_2$, with varying steric environments, were compatible (see Supplementary Table 6), and we could use ^{Et}BIPFeCl$_2$ to catalyse the hydrosilylation of 1-octene with triethoxysilane to give the silylated product in excellent yield (94%) with exclusive linear regioselectivity (Table 1, entry 9). Again, both the high yield and regioselectivity matched that of the analogous state-of-the-art Fe(0) complex[27]. The catalyst scope for alkene hydrosilylation was assessed by application of the activation method to a selection of pre-catalysts with literature-established low-oxidation-state catalytic activity (Table 1, entries 9–11). Ritter reported the iron-catalysed 1,4-hydrosilylation of 1,3-dienes using an (imino)pyridine iron(0) species that was formed by a ligand-induced reductive elimination (C^2_{sp}–C^2_{sp}, bond forming) from a sensitive aryl-ligated iron(II) complex[28]. We therefore applied our novel activation method to the analogous (imino)pyridine iron(II) dichloride pre-catalysts (see Supplementary Table 4). Using NaO^{t}Bu, the 1,4-hydrosilylation of myrcene was achieved on a gram scale in high yield (88%) and with equal regioselectivity to that previously reported (Table 1, entry 11).

We recognized that if NaO^{t}Bu could be used for the activation of both iron(II) and cobalt(II) pre-catalysts, then the activation of a wide range of traditionally synthetically challenging catalyst systems may also be possible. Specifically, our activation method could be used to discover novel catalytic reaction manifolds. Remarkably, we observed noteworthy reactivity from the outset. The cobalt complex TerpyCoCl$_2$, derived from the widely available terpyridine ligand, showed good hydrosilylation activity (Table 1, entry 12). To our surprise, we were unable to find literature precedent for hydrosilylation activity using any analogous terpyridine–cobalt complex. We next targeted nickel(II) and manganese(II) pre-catalysts, as there are very limited examples of alkene hydrofunctionalization reactions with these metals[29–31]. Formation of ^{Et}BIPNiCl$_2$ and ^{Et}BIPMnCl$_2$, followed by application of our NaO^{t}Bu activation method, led to the discovery of two entirely novel catalytic manifolds (Table 1, entries 13 and 14). In both cases, successful hydrosilylation to give the anti-Markovnikov silane product was achieved with complete regiocontrol in good yields. To the best of our knowledge, these are the first examples of a manganese-catalysed alkene hydrosilylation using a manganese(II) pre-catalyst and of hydrosilylation using a bis(imino)pyridine nickel species. These results illustrate the efficacy of the NaO^{t}Bu activation method, not for only the simplification of established methodologies, but also for the discovery of new catalytic processes.

Importantly, we were able to apply the NaO^{t}Bu activation to both iron and cobalt pre-catalysts for the hydroboration and hydrosilylation of a series of functionalized substrates without detriment to catalyst activity (Fig. 2). Carbonyl functionalities including ester **1a**, ketone **1b** and indole-containing ketone **1c** underwent chemoselective alkene hydroboration using ^{Mes}BIPCoCl$_2$. Sulfonamide **1d** reacted efficiently without S–N bond cleavage or reduction, and aldimine **1e** was well tolerated using these catalyst activation conditions. Styrene **1f** and derivatives bearing potentially sensitive acetoxy- **1g**, chloro- **1h** and even bromo-substituents **1i** reacted efficiently to give the expected products **2f**–**2i** in high yields and without detrimental side reactions, such as dehalogenation. Additionally, the iron pre-catalyst ^{Et}BIPFeCl$_2$ could be used for the hydroboration of internal alkyne **1j** to give (*Z*)-alkenylboronic ester **2j** in good yield. Furthermore, alkene hydrosilylation using the same catalyst, ^{Et}BIPFeCl$_2$, was successful for a number of functionalized alkenes, tolerating trifluormethyl- **1l**, fluoro- **1m** and free amine **1o** groups. We were also able to use our activation method to discover the switchable stereoselective hydrosilylation of 1-octyne to give the (*Z*)- or (*E*)-alkenylsilane, **2p** and **2q**, simply by exchanging the metal from Co to Fe, respectively. This wide functional group tolerance, even on base-sensitive substrates, demonstrates the extensive applicability of this activation method and one that should aid the general progression of base-metal catalysis.

Isolated low oxidation-state formal iron(0) complexes have been shown to offer catalytic activity that surpasses that of conventional platinium catalysts for alkene hydrosilylation[27]. Therefore, it was important to assess the effectiveness of our activation method for the generation of active catalysts in industrially relevant situations. We targeted the hydrosilylation of 1-octene with triethoxysilane, a commercially relevant silane, as there was a comparable example for this using an analogous 'iron(0)' complex. Using NaO^{t}Bu and ^{Et}BIPFeCl$_2$, we were able to achieve equal reactivity to the state-of-the-art Fe(0) complex, $\{[^{Et}BIPFe(N_2)]_2(\mu_2\text{-}N_2)\}$, with even lower catalyst loadings than have previously been reported (Fig. 3).

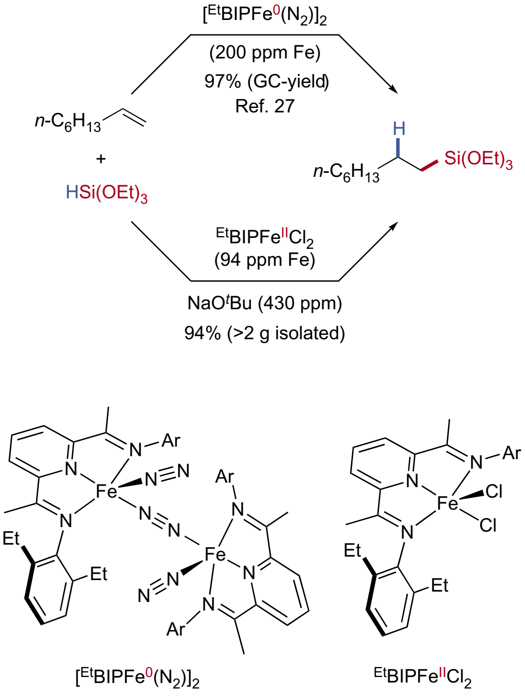


Figure 3 | Gram-scale hydrosilylation using a ppm quantity of iron pre-catalyst. Well-defined low-oxidation-state iron catalysts have been used at ppm loadings for alkene hydrosilylation in excellent yield, although these are air/moisture-sensitive and synthetically challenging. Here, we demonstrate the applicability and efficacy of the NaO^{t}Bu activation for large-scale application, matching catalytic efficiency of isolated iron(0) species.

To understand the mode of catalyst activation using NaO^{t}Bu, we carried out a series of mechanistic investigations. Initially, we recognized that the activation of these metal pre-catalysts using classical organometallic activators relied on the formation of metal-hydride or metal-alkyl intermediates that subsequently participated in a reductive elimination event to generate a low-oxidation-state active catalyst. In the NaO^{t}Bu activation process, the potential salt-metathesis with metal dichloride could lead to the generation of a metal bis-*tert*-butoxide complex (for example, ^{Et}BIPFe(O^{t}Bu)$_2$). In this scenario, however, it was difficult to propose an effective activation mechanism based on a reductive elimination event. Nonetheless, we did postulate that β-methyl-scission could potentially occur (to generate a metal–methyl complex and acetone)[32]. To assess the propensity for the formation of metal *tert*-butoxide species, we performed stoichiometric reactions between both ^{Et}BIPFeCl$_2$ and ^{Mes}BIPCoCl$_2$, and NaO^{t}Bu (that is, 2:1 alkoxide:pre-catalyst). The resulting mixtures were analysed by ^{1}H NMR spectroscopy to determine if a new species had been generated. When mixing the iron catalyst ^{Et}BIPFeCl$_2$ and sodium *tert*-butoxide in d^8-THF, we observed ligand de-metallation and formation of a catalytically inactive mixture, as had been observed previously[33]. The cobalt complex ^{Mes}BIPCoCl$_2$ showed only slight ligand de-metallation, but formed neither the alkoxide complex nor a catalytically active species.

Given that the reaction between pre-catalyst and NaO^{t}Bu led to catalytically incompetent mixtures, we postulated that the NaO^{t}Bu activation may proceed by reaction of the alkoxide with the boronic ester or silane to form a hypervalent 'ate' species. Once formed, these intermediate 'ate' complexes could then serve as hydride donors, which would facilitate the formation of metal-hydrides and allow for a dihydrogen reductive elimination event. To investigate this activation mode, we first conducted stoichiometric reactions between alkoxide and pinacolborane, which revealed a classic disproportionation by ^{11}B NMR analysis to boron 'ate' complex **3**, borane and borohydride[34]. We were able to confirm the reductive power of complex **3** by synthesis of an analogous 'ate' species in the absence of borane or borohydride (see Supplementary Section 13). Similarly, reaction of phenylsilane (PhSiH$_3$) with NaO^{t}Bu resulted in the observation of a pentacoordinate silicon 'ate' species **4** by ^{29}Si NMR spectroscopy. Addition of either of these mixtures of 'ate' complex to an iron pre-catalyst, ^{Et}BIPFeCl$_2$, resulted in the formation a mixture of

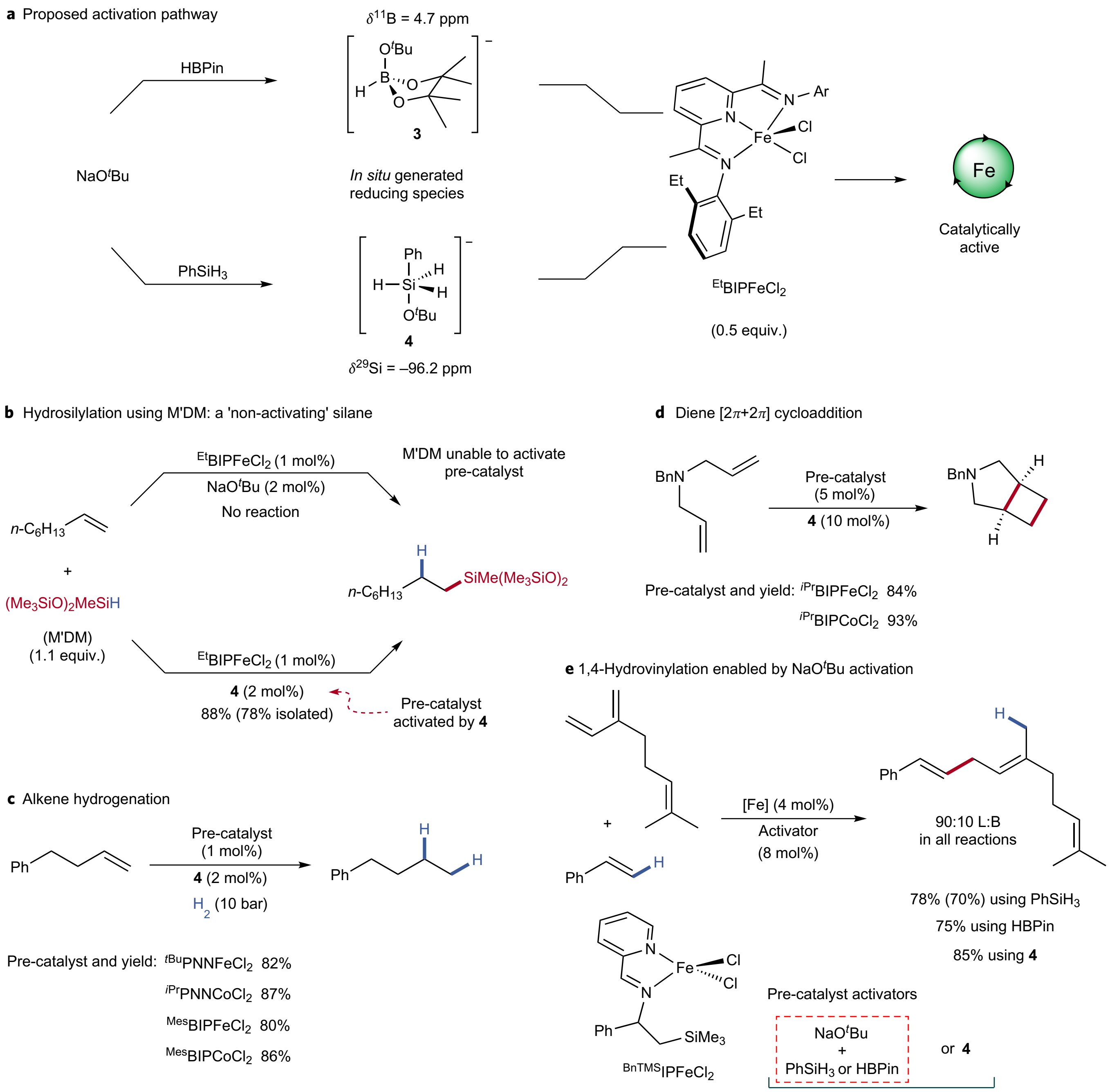


Figure 4 | Mechanistic proposal for alkoxide pre-catalyst activation and insight-driven application. a, Proposed pre-catalyst activation pathway, by formation of boron 'ate' species **3** or silicon 'ate' **4**. **b**, Alkene hydrosilylation using M'DM enabled by pre-catalyst reduction using silicon 'ate' **4**. Note that the alkoxide/M'DM fusion does not alone activate the pre-catalyst (^{Et}BIPFeCl$_2$). **c**, Alkene hydrogenation by *in situ* generated active catalysts using silicon 'ate' **4**. **d**, Alkene [2*π*+2*π*] cycloaddition, previously accessed using a low-oxidation-state pre-catalysts, enabled by *in situ* formation of active species using silicon 'ate' **4**. **e**, 1,4-Hydrovinylation of myrcene, using an iminopyridine-iron pre-catalyst activated by sub-stoichiometric quantities of either (1) phenylsilane or pinacolborane and sodium *tert*-butoxide or (2) using a solution of **4**.

paramagnetic iron species that demonstrated high catalytic activity (Fig. 4a, see Supplementary Information for experimental details). When $(Me_3SiO)_2MeSiH$, M'DM, was reacted with NaO^{t}Bu and an iron pre-catalyst, $^{Et}BIPFeCl_2$, no activation occurred, and thus catalytic hydrosilylation was unsuccessful using this substrate. However, when a pre-formed mixture of silicon 'ate' complex 4 was added to the reaction of 1-octene with M'DM with $^{Et}BIPFeCl_2$ as pre-catalyst, catalyst activity was recovered, demonstrating the role of 'ate' complex 4 in activating the pre-catalyst (Fig. 4e).

Given that we could access an active catalyst using 4, we instinctively realized that either (1) boron 'ate' complex 3, (2) silicon 'ate' complex 4, or (3) substoichiometric quantities of silane or borane and NaO^{t}Bu could potentially be used as general pre-catalyst activators to enable reactions outwith hydroboration and hydrosilylation. Therefore, we sought reactions that did not use borane or silane starting materials to unambiguously validate the role of the alkoxide in pre-catalyst activation. Specifically we targeted hydrogenation[2,17], alkene [2*π*+2*π*] cycloaddition[35,36] and hydrovinylation[21] reactions in an effort to demonstrate general accessibility to low-oxidation-state catalyst manifolds. Initially, we used 4 as an *in situ* activator for a selection of iron and cobalt pre-catalysts, which enabled alkene hydrogenation in high yield (Fig. 4c). Similarly, $^{iPr}BIPFeCl_2$ and

^{iPr}BIPCoCl$_2$ could be activated using **4** to catalyse the intramolecular [2π+2π] cycloaddition reaction, which was previously only reported using isolated low-oxidation-state (Fe^0 and Co^I) pre-catalysts (Fig. 4d). Finally, the hydrovinylation reaction of myrcene with styrene using the *in situ* generated catalyst, from ^{BnTMS}IPFeCl$_2$, produced the anticipated 1,4-functionalized products when using either substoichiometric HBPin or PhSiH$_3$ and NaO^{t}Bu, or pre-formed **4**, in excellent yields and with identical regioselectivity in every case, suggestive of a commonly generated active species (Fig. 4e).

Conclusion

In summary, an easily handled, air- and moisture-stable alkoxide salt (NaO^{t}Bu) has been used for the activation of a wide range of non-precious-metal pre-catalysts. State-of-the-art low-oxidation-state iron- and cobalt-catalysed manifolds, previously only accessible using strict air/moisture-free techniques, were realized in the simplest manner and opened to the non-expert. Notably, using the NaO^{t}Bu activation approach, novel cobalt(II)-, manganese(II)- and nickel(II)-catalysed alkene hydrofunctionalization reactions were discovered. Mechanistic investigations show that NaO^{t}Bu acts as a masked reducing agent, by forming an 'ate' species with HBPin or silanes that then serves as a pre-catalyst activator. The simplicity and generality of this method provides a platform for the development and exploitation of non-precious-metal catalysis.

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Author contributions

J.H.D. and S.P.T. conceived and discovered the NaO^{t}Bu activation. J.H.D. and J.P. conducted the experimental work. S.P.T. and A.P.D. provided advice for the investigations. J.H.D. and S.P.T. prepared the manuscript.

Additional information

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Competing financial interests

The authors declare no competing financial interests.