Regiodivergent hydrosilylation, hydrogenation, \([2\pi + 2\pi]\)-cycloaddition and C–H borylation using counterion activated earth-abundant metal catalysis†

Riaz Agahi,‡a Amy J. Challinor,‡a Joanne Dunne,a Jamie H. Docherty,a Neil B. Carterb and Stephen P. Thomas‡a

The widespread adoption of earth-abundant metal catalysis lags behind that of the second- and third-row transition metals due to the often challenging practical requirements needed to generate the active low oxidation-state catalysts. Here we report the development of a single endogenous activation protocol across five reaction classes using both iron- and cobalt pre-catalysts. This simple catalytic manifold uses commercially available, bench-stable iron- or cobalt tetrafluoroborate salts to perform regiodivergent alkene and alkyne hydrosilylation, 1,3-diene hydrosilylation, hydrogenation, \([2\pi + 2\pi]\)-cycloaddition and C–H borylation. The activation protocol proceeds by fluoride dissociation from the counterion, in situ formation of a hydridic activator and generation of a low oxidation-state catalyst.

Introduction

The ubiquity of catalytic protocols using precious metals such as platinum, palladium and rhodium can be ascribed to the highly robust and reliable nature of these methods and widespread commercial availability of the catalyst precursors. Operational simplicity has made reaction screening and optimisation routine using these metals. However, beyond high value applications the low natural abundance, volatile cost and toxicity of these metals remains problematic. Earth-abundant transition metals offer an alternative, sustainable platform for catalysis, particularly for bulk and dispersive technologies, but are yet to achieve widespread adoption even though excellent catalytic activity has been achieved in exemplar industrial reactions.‡ Thus, the operational simplicity of earth-abundant-metal-catalysed reactions must be addressed to enable the widespread use and development of these powerful methodologies.

The global silicone industry is forecast to be worth $18.3 billion in 2021 and finds applications in areas as diverse as soft materials, cosmetics and food additives.3 Alkene and alkyne hydrosilylation reactions underpin this industry and the homogenous nature of these processes results in the loss of over 5 tonnes of platinum annually.3 Thus a transition to earth-abundant metal catalysis would be beneficial both environmentally and economically. Seminal studies using isolated, low oxidation-state iron- and cobalt pre-catalysts have shown the potential of these metals for alkene hydrosilylation,4 and in situ activation of metal(II/III) pre-catalysts using organometallic reagents5,6 has decreased the operational barrier to use. Methods have also been developed using bench-stable reductants such as alkoxide reagents6 or amines7 (Scheme 1a). However, an additional, external reagent is still required for pre-catalyst activation. Iron- and cobalt carboxylate salts have been shown to act as pre-catalysts for alkene hydrosilylation that do not require an external activator (Scheme 1b).8 Similarly, Huang showed that a tridentate PNN-cobalt(n) dichloride pre-catalyst could be activated thermally for alkene hydrosilylation.9 However, these are limited to a single reaction class and the carboxylate counterions are pre-catalyst specific.

The alkoxide activation of iron- and cobalt pre-catalysts (Scheme 1a) was proposed to proceed by reaction of the alkoxide and silane to form a hydridic silicon ‘ate’ complex which reduces the pre-catalyst by a hydride transfer.6a In contrast, the carboxylate and thermal activation methods were proposed to proceed by a σ-bond metathesis reaction between the metal carboxylate and silane (Scheme 1b).8 We postulated that using a counterion which is known to dissociate a nucleophile would allow an activation method that combined the operational simplicity of carboxylate activation and the broad scope of alkoxide activation. The tetrafluoroborate counterion is known to dissociate to BF3 and fluoride.9 The fluoride could react with the silane to give a hydridic silicon ‘ate’ complex,10 and activate a pre-catalyst by hydride transfer (Scheme 1c).11

† These authors contributed equally.

‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/c8sc05391j

References

1.化进程的均一性质导致了这些过程的损失，以及这些过程的产物结果在损失的5吨以上的铂金。因此，向地球丰富金属催化转变将是环保和经济上都有益的。孤立的、低氧化态的金属(II/III)前催化剂通过使用有机金属试剂在反应中使用，可以减少操作的障碍。方法也被开发出来使用bench-stable还原剂，如氧化物试剂或胺类（Scheme 1a）。然而，还需要一个外部试剂来激活预催化剂（Scheme 1b）。同样地，黄展示了三dentate PNN-钴(n)二氯化物预催化剂可以通过热激活来实现。然而，这些是局限于单一反应类的和羧酸酯的反离子是前催化剂特定的。

铁和钴的氧化物激活（Scheme 1a）被提出是通过反应的氧化物和硅烷形成一个带氢的硅‘ate’复杂来降低前催化剂通过外键转移。在相反的，羧酸酯和热激活的方法被提出是通过π键的互变反应之间金属羧酸酯和硅烷（Scheme 1b）。我们假设通过一个反离子是已知会解离的亲核物会允许一个激活方法，该方法结合了羧酸酯激活的简单性和广谱的硅烷激活。带四氟硼酸酯反离子的前催化剂是已知可以解离到BF3和氟化物。氟化物可以与硅烷反应生成一个带氢的硅‘ate’复杂，并且通过外键转移激活前催化剂（Scheme 1c）。

† 这些作者等贡献了。

‡ 电子补充信息（ESI）可用。见DOI：10.1039/c8sc05391j
Results and discussion

In order to establish the utility of the tetrafluoroborate counterion for activation of iron(i) pre-catalysts we selected alkene hydrosilylation as a model reaction. Baseline reactivity was determined by the use of iron pre-catalysts bearing strongly coordinating chloride anions \( [{\text{BIPFeCl}}_2] \) (Table 1, entry 1) and weakly coordinating triflate anions \( [{\text{BIPFe(OTf)}}_2] \) (entry 2). Both reactions showed no catalytic activity. The tetrafluoroborate pre-catalyst, formed \textit{in situ} by the reaction of the commercially available hydrate salt \( \text{Fe(BF}_4)_2 \cdot \text{H}_2\text{O} \) with bisiminopyridine ligand \( \text{BIP} \), showed excellent catalytic activity without an external activator, giving the linear silane product \( 2a \) in excellent yield and regioselectivity (Table 1, entry 3). Lower catalyst loadings showed good, but reduced, reactivity in the production of \( 2a \) (Table 1, entries 4–5). Using iron(i) tetrafluoroborate, with less hindered bisiminopyridine ligands \( \text{BIP}, \text{BIP}, \text{BIP} \) led to low reactivity, with only the \( N \)-mesityl ligand giving good yield, with similar linear:branched selectivity to that observed with \( \text{BIP} \), while the more hindered \( N \)-isopropyl ligand gave only trace reactivity (Table 1, entries 6–9). Control reactions showed the need for both iron and ligand to achieve catalysis (see ESI, Table SI 1.1).

Having established the tetrafluoroborate activation for iron-catalysed hydrosilylation, we next attempted to apply the same protocol to cobalt-catalysed alkene hydrosilylation. Using commercially available cobalt(iii) tetrafluoroborate and the \( N \)-dimethylphenyl bisiminopyridine ligand gave the linear silane \( 3a \) in excellent yield and good regioselectivity (Table 1, entry 11), the opposite to that observed under iron catalysis. Variation of the ligand \( N \)-aryl substituent showed that all cobalt catalysed systems selectively gave the branched silane, with the more hindered catalysts giving reduced yields of silane \( 3a \) (Table 1, entries 10–14). Notably, and to the best of our knowledge, this is the first example of a regiodivergent alkene hydrosilylation where high levels of regioselectivity are observed using an identical ligand and the same reaction conditions, but only varying the metal used.\(^{3a} \)

Use of a lower catalyst loading of 1 mol% gave the branched silane product in excellent yield and selectivity (Table 1, entry 15). Having established optimal conditions for olefin hydrosilylation, we set out to investigate the scope and limitations of these reactions (Scheme 2). A variety of alkyl- and alkoxysilane reagents were successfully used for alkene hydrosilylation with both iron- (anti-Markovnikov) and cobalt (Markovnikov) pre-catalysts providing the linear- \( 2 \text{a–p} \) and branched alkyl silanes \( 3 \text{a–l} \) in excellent yield and regioselectivity, respectively. Iron-catalysed hydrosilylation of 1-octene with a tertiary silane (triethoxysilane) gave the linear silane \( 2d \) with a turnover number of 425 and a turnover frequency of 5100 h\(^{−1} \). In the cobalt-catalysed system, using only 110 ppm cobalt with phenylsilane gave the branched silane \( 3a \) with an overall turnover number of 5940, and turnover frequency of 2970 h\(^{−1} \). As all reaction components are air- and moisture stable the reactions can be set up without the need for specialist equipment. Therefore the iron- and cobalt catalysed hydrosilylation of 1-octene \( 1a \) was carried out in air with only a limited loss of catalyst activity and regioselectivity (Scheme 2, \( 2a \) and \( 3a \)). Alkyl- and aryl substituted alkenes underwent hydrosilylation in

![Scheme 1](https://example.com/scheme1.png)

**Scheme 1** Overview of prior alkene hydrosilylation reactions using iron- and cobalt catalysts. (a) Pre-catalyst activation using additives. (b) Catalyst activity facilitated by carboxylate ligands or thermal activation. (c) This work: catalyst activation through use of weakly coordinating tetrafluoroborate counterions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[M] Loading (mol%)</th>
<th>Ligand</th>
<th>Yield (%) (2a : 3a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl(_2)</td>
<td>2</td>
<td>\text{BIP} 0</td>
</tr>
<tr>
<td>2</td>
<td>Fe(OTf)(_2)</td>
<td>2</td>
<td>\text{BIP} 0</td>
</tr>
<tr>
<td>3</td>
<td>Fe(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{BIP} 87 (93 : 7)</td>
</tr>
<tr>
<td>4</td>
<td>Fe(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>0.5</td>
<td>\text{BIP} 87</td>
</tr>
<tr>
<td>5</td>
<td>Fe(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{BIP} 87</td>
</tr>
<tr>
<td>6</td>
<td>Fe(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{BIP} 87</td>
</tr>
<tr>
<td>7</td>
<td>Fe(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{BIP} 87</td>
</tr>
<tr>
<td>8</td>
<td>Fe(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{BIP} 87</td>
</tr>
<tr>
<td>9</td>
<td>Fe(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{BIP} 87</td>
</tr>
<tr>
<td>10</td>
<td>Co(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{iPrBIP} 84 (86 : 14)</td>
</tr>
<tr>
<td>11</td>
<td>Co(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{iPrBIP} 84 (86 : 14)</td>
</tr>
<tr>
<td>12</td>
<td>Co(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{iPrBIP} 84 (86 : 14)</td>
</tr>
<tr>
<td>13</td>
<td>Co(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{iPrBIP} 84 (86 : 14)</td>
</tr>
<tr>
<td>14</td>
<td>Co(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>2</td>
<td>\text{iPrBIP} 84 (86 : 14)</td>
</tr>
<tr>
<td>15</td>
<td>Co(BF}_4(_2) \cdot \text{H}_2\text{O}</td>
<td>1</td>
<td>\text{EtBIP} 90 (98 : 2)</td>
</tr>
</tbody>
</table>

\(^{a}\) Reaction conditions: 1-octene (1.00 equiv.), phenylsilane (1.10 equiv.) and metal tetrafluoroborate (n mol%), THF (1 M), r.t., 1 h. Yields determined by \(^1\)H NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.
excellent yield and regioselectivity for both the iron-2e–p and cobalt-catalysed 3d–l systems. The iron-catalysed system was found to tolerate electron-withdrawing substituents and substituted alkenes such as β-pinene, norbornene, α-methylstyrene and limonene without detriment to yield or regioselectivity. The lower oxophilicity of cobalt was exemplified by chemoselective alkene hydrosilylation in the presence of ketone, ester, epoxy and amido functionalities.

Divergent diastereoselectivity was observed for the hydrosilylation of terminal alkynes with cobalt catalysis preferentially giving the (E)-alkenylsilane and the iron-catalysed system giving the (Z)-alkenylsilane. Both the iron and cobalt catalysts gave the (E)-alkenylsilane, the product of syn addition, in the hydrosilylation of 4-octyne and 3n, respectively. Hydrosilylation of the 1,3-diene myrcene proceeded with 1,4-selectivity.

The potential of the developed tetrafluoroborate activated hydrosilylations for polymer crosslinking and late-stage functionalisation was demonstrated by iterative homo- and hetero- bis-hydrosilylations using two alkenes. Beyond showing that the tetrafluoroborate activation strategy can be applied across a number of unique ligand classes and metal salts, these results also demonstrate how, as a tool for reaction screening, this method can provide a facile method for uncovering new and contrasting reactivity.

To assess the generality of tetrafluoroborate iron- and cobalt-catalysed hydrosilylation reactions we opted to perform alkene hydrosilylation reactions with ligands distinct from bisiminopyridine. We initially selected bis-phosphine ligands, xantphos and dppf, as these had been used previously by Ge for cobalt-catalysed alkene hydrosilylation. Use of both of these ligands in combination with Co(BF₄)₂·6H₂O effectively catalysed the hydrosilylation of 1-octene with phenylsilane to generate linear silane in excellent yield as a single exclusive regioisomer. Adamantyl isocyanide as a ligand additionally proved effective for both iron- and cobalt-catalysed alkene hydrosilylation to generate respectively.

Scheme 2 Scope for iron- and cobalt-catalysed hydrosilylation reactions enabled by tetrafluoroborate activation. (a) Reaction conditions: olefin, PhSiH₃ (1.1 eq.), EtBIP (2 mol%) and Fe(BF₄)₂·6H₂O (2 mol%), THF, r.t., 4 h. (b) Reaction conditions: olefin, PhSiH₃ (1.1 eq.), EtBIP (2 mol%) and Co(BF₄)₂·6H₂O (2 mol%), THF, r.t., 4 h. (c) Reaction conditions: alkene (1 equiv.), PhSiH₃ (1 equiv.), EtBIP (2 mol%), THF, r.t., 30 min then a second alkene (1 equiv.) added, 3 h. Yields determined by ¹H NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard, isolated yields in parenthesis.

excellent yield and regioselectivity for both the iron-2e–p and cobalt-catalysed 3d–l systems. The iron-catalysed system was found to tolerate electron-withdrawing substituents 2k and substituted alkenes such as β-pinene 2m, norbornene 2n, α-methylstyrene 2o and limonene 2p without detriment to yield or regioselectivity. The lower oxophilicity of cobalt was exemplified by chemoselective alkene hydrosilylation in the presence of ketone 3i, ester 3j, epoxy 3k and amido 3l functionalities. Divergent diastereoselectivity was observed for the hydrosilylation of terminal alkynes with cobalt catalysis preferentially giving the (E)-alkenylsilane 3m and the iron-catalysed system giving the (Z)-alkenylsilane 2q.

Both the iron and cobalt catalysts gave the (E)-alkenylsilane, the product of syn addition, in the hydrosilylation of 4-octyne 2r and 3n, respectively. Hydrosilylation of the 1,3-diene myrcene proceeded with 1,4-selectivity 3o.

The potential of the developed tetrafluoroborate activated hydrosilylations for polymer crosslinking and late-stage functionalisation was demonstrated by iterative homo- 2s and hetero- 2t bis-hydrosilylations using two alkenes. Beyond showing that the tetrafluoroborate activation strategy can be applied across a number of unique ligand classes and metal salts, these results also demonstrate how, as a tool for reaction screening, this method can provide a facile method for uncovering new and contrasting reactivity.

To assess the generality of tetrafluoroborate iron- and cobalt-catalysed hydrosilylation reactions we opted to perform alkene hydrosilylation reactions with ligands distinct from bisiminopyridine. We initially selected bis-phosphine ligands, xantphos and dppf, as these had been used previously by Ge for cobalt-catalysed alkene hydrosilylation. Use of both of these ligands in combination with Co(BF₄)₂·6H₂O effectively catalysed the hydrosilylation of 1-octene with phenylsilane to generate linear silane in excellent yield as a single exclusive regioisomer. Adamantyl isocyanide as a ligand additionally proved effective for both iron- and cobalt-catalysed alkene hydrosilylation to generate 2u and 2v respectively. The bidentate iminopyridine ligand, used previously by Ritter for...
1,4-hydrosilylation of 1,3-dienes,\textsuperscript{14} was effective using Fe(BF\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O to give allylic silane \textsuperscript{2w} (Scheme 3c).

As we presumed the active hydrosilylation catalyst was a low oxidation-state metal species, we next explored the use of the tetrafluoroborate activation as a general platform to access these species. We postulated that mixing the tetrafluoroborate pre-catalysts with a substoichiometric amount of silane reagent would give a generic low oxidation-state catalyst that would be applicable to transformations beyond hydrosilylation. This would negate the need to isolate a catalyst with limited stability or use pyrophoric reagents in low oxidation-state iron- and cobalt catalysis.

The first reaction tested was hydrogenation of alkenes, an industrially important transformation.\textsuperscript{15,16} Using 0.5 mol% of the iron- or cobalt tetrafluoroborate salts and the MesBIP ligand in combination with substoichiometric phenylsilane gave an active catalyst for alkene reduction in both cases (Scheme 3d). 4-Phenyl-1-butene underwent hydrogenation to the alkene \textsuperscript{6a} in good yield under cobalt catalysis and reduced yield with the analogous iron system. The cobalt-catalysed hydrogenation was found to be successful for 1,1-disubstituted alkenes \textsuperscript{6b} and \textsuperscript{6c}, 1,2-disubstituted alkenes \textsuperscript{6d} and allyl silane \textsuperscript{6e} (Scheme 3d).

Another example of a reaction which has been catalysed by low oxidation-state species is the intramolecular [2+2+2] cycloaddition of 1,6-dienes to give [3.2.0] bicyclic systems.\textsuperscript{17} In this case, N-benzyl,N,N-diallylamine \textsuperscript{7a} was converted into N-benzyl-3-azabicyclo[3.2.0]heptane \textsuperscript{8a} in good yield and N-4-fluorophenyl-N,N-diallyl amine \textsuperscript{7b} cyclised to give bicyclic \textsuperscript{8b} in excellent yield (Scheme 3e). A number of procedures have been developed for cobalt-catalysed C–H borylation, and cobalt(c)}
boryl complexes have been proposed to be the key catalytic intermediate. In order to apply tetrafluoroborate activation to a range of mechanistically distinct reactions, C−H borylation of 2-methylfurran 9 was carried out using a cobalt-terpyridine teta-
rafluoroborate pre-catalyst, to give the boronic ester 10 in 67% yield (Scheme 3f).

The facile activation observed using this protocol was thought to result from pre-catalyst reduction by an in situ formed hydridic silicon ‘ate’ complex formed by reaction of the silane reagent with fluoride dissociated from the counterion. This putative ‘ate’ complex then transfers hydride to the pre-catalyst, facilitating reductive elimination of dihydrogen (Scheme 4a). Silane reagents have been shown to be hydridic reagents in the presence of suitable nucleophiles, such as fluoride, and this has been applied in the reduction of carboxyls. To examine whether similar reactivity could be obtained in this case, n-butyrammonium tetrafluoroborate (TBABF₄) was reacted with phenylsilane in the presence of 4-fluorobenzaldehyde 10 to give the primary alcohol reduction product 11 in excellent yield (Scheme 4b). This underlines the possibility of pre-catalyst reduction by a hydridic silicon ‘ate’ complex forming by reaction of fluoride and phenylsilane. Although the exact nature of the active catalyst is not known, the reaction was tested in the presence of radical inhibitors and was unaffected (Scheme 4c and Table SI 10†), suggesting that reduction occurs by a two-electron mechanism.

Conclusions

A procedure for the regiodivergent hydrosilylation of olefins, a highly valuable industrial reaction, has been developed using iron- and cobalt-tetrafluoroborate catalysts without the need for an external activator or the use of isolated low oxidation-state complexes. This has been used as an activation platform to access the low oxidation-state catalysts in a range of iron- and cobalt-catalysed reactions including hydrosilylation, 1,3-diene hydrosilylation, alkene hydrogenation, [2π + 2π]-cycloaddition and C−H borylation. The developed tetrafluoroborate activation represents a versatile platform for activation, and serves as a generic strategy for accessing low oxidation-state reactivity with both iron and cobalt. It is hoped that this work will streamline the discovery of new reactivity, development of novel synthetic methodology and, ultimately, the replacement of precious metals with their earth-abundant counterparts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

RA and SPT thank the Royal Society for funding a PhD studentship. AJC and SPT thank Syngenta for part funding a PhD studentship. SPT thanks the Royal Society for a University Research Fellowship. JD and SPT thank Prof. M. Shaver for useful discussions. All thank the University of Edinburgh, School of Chemistry and Technical Staff for generous support.

Notes and references


