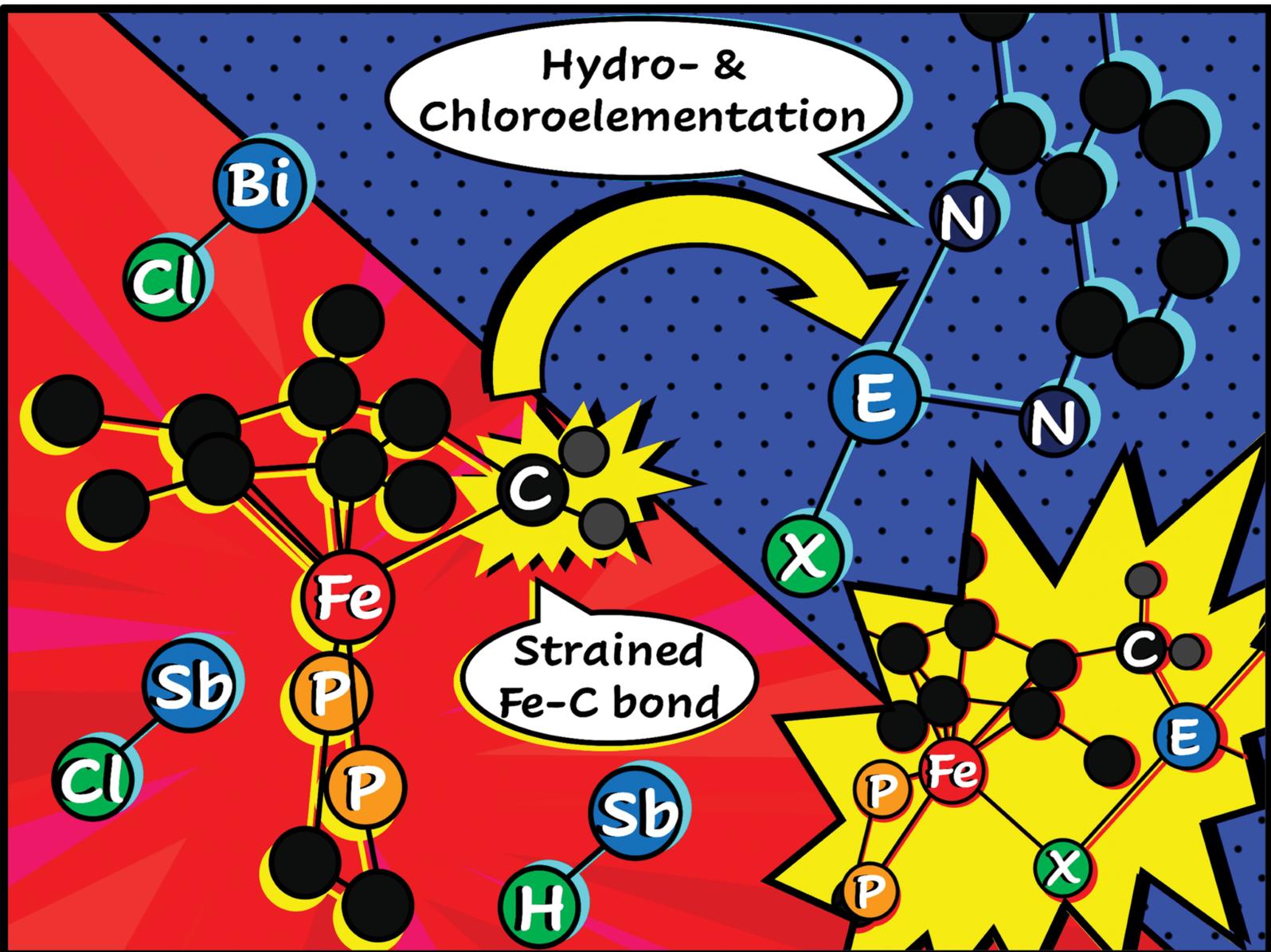


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**COMMUNICATION**

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# Hydro- and chloroelementation reactions across an iron–carbon bond using heavy group 15 reagents†

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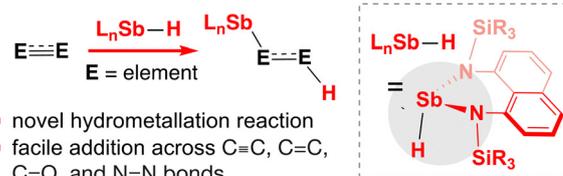
**Diaminostibines ( $\{\text{Sb}\}\text{-H}$ ) add across the iron–carbon bond of a tucked-in iron diphosphine complex, resulting in hydrostibinated iron hydride  $[(\text{Cp}^*\text{-SbR}_2)\text{Fe-H}]$  complexes. The scope was broadened to include  $\{\text{Sb}\}\text{-Cl}$  and  $\{\text{Bi}\}\text{-Cl}$  chloroelementation reactions, providing new and mild synthetic pathways to Sb- and Bi-containing heteroorganometallics.**

Hydroelementation is one of the most ubiquitous and useful reactions in synthetic chemistry.<sup>1–4</sup> The addition of an E–H (E = element) bond across an unsaturated unit *e.g.*, the C=C bond of an alkene, serves as a synthetically facile and atom economic strategy to augment molecular complexity in a single step.<sup>5</sup> Both catalytic and stoichiometric E–H (E = B, Al, Si, Ge, Sn, N, P, and S) bond addition processes are known; for many of these, stereo- and enantioselective variants have also been reported.<sup>6–9</sup> Alkene hydroboration, for example, has been well-established as a means to selectively install alcohol functionality following oxidation of an organoborane unit.<sup>10</sup> Moving to Group 14, hydrosilylation (addition of an  $\{\text{Si}\}\text{-H}$  bond) has led to significant advances in the diversification of organosilicon compounds, which find uses in lubricants, rubbers, and greases.<sup>11,12</sup> Traversing down Group 15,  $\{\text{N}\}\text{-H}$  (hydroamination) and  $\{\text{P}\}\text{-H}$  (hydrophosphination) addition reactions have also been developed, providing access to new drug candidates, ligand precursors, and more.<sup>13,14</sup> E–H bond activations featuring heavy Group 15 E–H bonds (E = Sb or Bi) – hydrostibination and hydrobismuthation – are very rare by comparison.<sup>15,16</sup> This is due to both a lack of Lewis-acidic character for Sb (by contrast to commonly employed  $\text{HBR}_2$

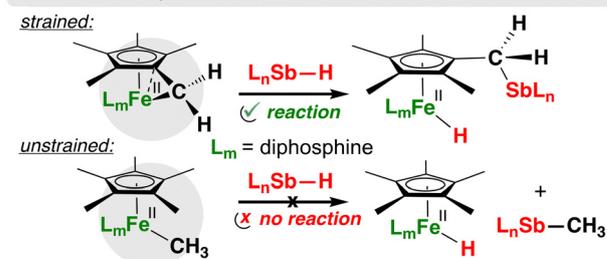
reagents), and in the case of Bi, a paucity of stable compounds that feature a  $\{\text{Bi}\}\text{-H}$  bond.<sup>16,17</sup>

Hydrostibination offers access to functionalized  $\{\text{Sb}\}\text{-}$  containing products, which have shown rich redox chemistry as well as utility as ligands for transition metals, as Lewis-acid additives for catalysis, and for organic synthesis.<sup>18–24</sup> Chitnis and colleagues previously demonstrated the first examples of catalyst- and additive-free hydrostibination of  $\text{C}\equiv\text{C}$ ,  $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ , and  $\text{N}=\text{N}$  bonds (Chart 1A).<sup>15</sup> Ligation of Sb by a rigid naphthalene diamine ligand was key to realizing this reaction, causing the compound's LUMO to resemble a vacant p-orbital, encouraging substrate/ $\{\text{Sb}\}\text{-H}$  bond interaction. For terminal  $\text{C}\equiv\text{C}$  bonds, the mechanism of hydrostibination was radical-based, generating the *anti*-addition product.<sup>25</sup> Most other hydroelementation reactions *e.g.*, hydroboration proceed *via* a two-electron pathway, giving a *syn*-addition product; this departure in mechanism and difference

### A. previously: uncatalyzed hydrostibination (Chitnis, 2019)



### B. this work: hydrostibination of a strained $[\text{Fe}]\text{-C}$ bond



**Chart 1** (A) previously: uncatalyzed hydrostibination (Chitnis, 2019); (B) this work: hydrostibination of a strained  $[\text{Fe}]\text{-C}$  bond.

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in product profile shapes a need to further develop our understanding of heavy p-block hydroelementation reactions. The scope of {Sb}-H addition reactions has been so far limited to organic substrates. There are no examples where such a functional group has been added across a metal-element bond; such products would represent interesting targets for ligand design, coordination chemistry, cooperative catalysis, and more.<sup>26–29</sup>

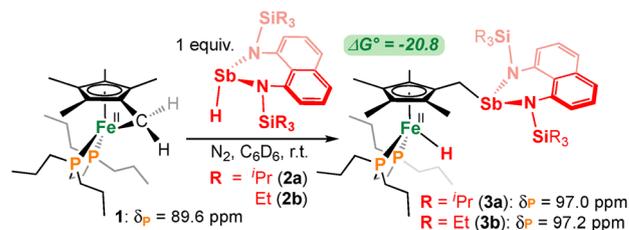
Since 2020, the Drover group has examined the role of secondary coordination sphere (SCS) Lewis acids, such as boranes and alanes, on reactivity.<sup>30–34</sup> As an extension, we wondered whether hydrostibination might be used as a tool to introduce an {Sb}-based SCS, providing an entry point towards {M,Sb}-containing compounds. Previously, we reported that a strained Fe tucked-in diphosphine complex<sup>35</sup> underwent hydroboration using HBCy<sub>2</sub> to give a {Cp\*-BR<sub>2</sub>}Fe-H compound. This system was competent for catalytic CO<sub>2</sub> dihydroboration – a reaction sequence that requires an intramolecularly-positioned {Cp\*-BR<sub>2</sub>} ligand.<sup>33</sup> We now share a collaborative effort that exploits the ring-opening propensity of this strained {Fe}-C complex (Chart 1B)<sup>35</sup> with {Sb}-H, {Sb}-Cl, and {Bi}-Cl reagents, providing the first examples of Fe-carbon, and more generally, metal-element hydro- and chloroelementation reactions<sup>36</sup> using Sb and Bi sources. To our knowledge, related {Sb}-Cl and {Bi}-Cl addition reactions – even with unfunctionalized organic substrates – are unprecedented. By contrast, haloboration has been known since the 1940s.<sup>37</sup>

To begin, treatment of **1**<sup>35</sup> with 1 equiv. of the iso-propylsilyl-substituted 1,8-naphthalene diamine antimony hydride **2a**<sup>15</sup> generated an orange solution of the hydrostibinated Fe(II)-hydride, [(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>-CH<sub>2</sub>-{Sb(1,8-Naphth<sup>1-Pr</sup>)})Fe<sup>II</sup>(H)(dnppe)] (**3a**; 1,8-Naphth<sup>i-Pr</sup> = 1,8-tri(*i*-propyl)silylamidonaphthalene, dnppe = 1,2-bis(di-*n*-propylphosphino)ethane) (Scheme 1A). This process is characterized by addition of an {Sb}-H unit ( $\delta_{\text{H}} = 9.88$  ppm;  $\nu[\text{Sb}-\text{H}] = 1883$  cm<sup>-1</sup>) across the strained {Fe}-C bond of **1**, generating a ring-opened {Cp\*-SbR<sub>2</sub>}Fe-H product ( $\delta_{\text{H}} = -18.0$  ppm (Fe-H),  $\nu[\text{Fe}-\text{H}] = 1835$  cm<sup>-1</sup>). Consistent with C<sub>s</sub>-symmetry, two resonances are observed for the dnppe *n*-Pr(CH<sub>3</sub>) groups at  $\delta_{\text{H}} = 0.95$  and 0.89 ppm (forward and backward), as well as two signals at  $\delta_{\text{H}} = 1.92$  and 1.86 ppm for the desymmetrized Cp\*-ring.

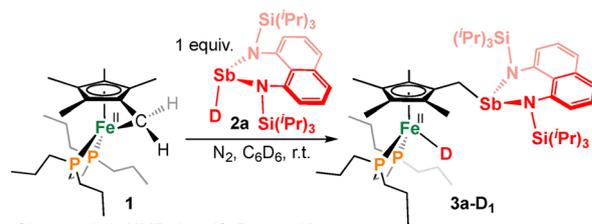
For the Sb fragment, a signal at  $\delta_{\text{H}} = 2.50$  ppm is assigned to the {Sb-CH<sub>2</sub>Cp\*} group, alongside appropriate signals for the coordinated 1,8-naphthalene ligand. By <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, a singlet at  $\delta_{\text{P}} = 97.0$  ppm corresponds to the dnppe ligand. Proving that the [Fe]-H unit in **3a** is derived from the Sb-hydride moiety in **2a**, reaction of **1** with the related Sb-deuteride **2a-d<sub>1</sub>** produces **3a-d<sub>1</sub>** (Scheme 1B), defined by a 1:1:1 triplet at  $\delta_{\text{P}} = 97.0$  ppm ( $^2J_{\text{P-D}} = 10.6$  Hz) in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. Given the similarity in NMR and IR spectroscopic features between **3a** and [Cp\*Fe<sup>II</sup>(H)(dnppe)] ( $\delta_{\text{H}} = -17.9$  ppm,  $\delta_{\text{P}} = 98.1$  ppm,  $\nu[\text{Fe}-\text{H}] = 1865$  cm<sup>-1</sup>), the peripheral Sb and Fe-bound hydride are non-engaging.<sup>38</sup> Iron(II)-carbon bond hydrostibination was additionally expanded to a triethylsilyl-substituted 1,8-naphthalene diamine antimony hydride **2b**, giving [(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>-CH<sub>2</sub>-{Sb(1,8-Naphth<sup>Et</sup>)})Fe<sup>II</sup>(H)(dnppe)] (**3b**) (Scheme 1A, see ESI† for details).

Despite our best efforts, compounds **3a/b** were not isolable in crystalline form, thwarting analysis by single crystal X-ray diffraction and motivating study by computational means

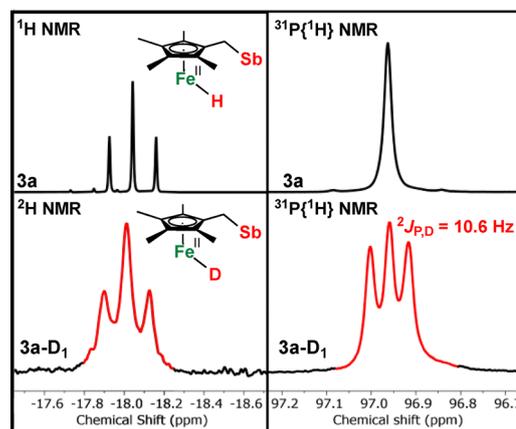
### a. Hydrostibination of a strained ferra(II)cycle



### b. Deuterium labelling unequivocally shows >99% [Fe]-D formation



### c. Characteristic NMR data (C<sub>6</sub>D<sub>6</sub>, 298 K)

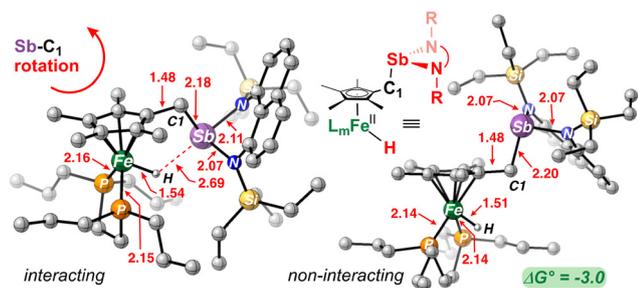


Scheme 1 (A) Hydrostibination of a strained ferra(II)cycle; (B) deuterium labelling unequivocally shows >99% [Fe]-D formation.  $\Delta G^\circ$  in kcal mol<sup>-1</sup> calculated at the DLPNO-CCSD(T) level of theory (see ESI† for details); (C) characteristic NMR data (C<sub>6</sub>D<sub>6</sub>, 298 K).

(Scheme 2). For both **3a/b**, the global optimizer algorithm (GOAT)<sup>39–41</sup> within ORCA 6.0.1<sup>42</sup> was used to locate minimum structures. This analysis provided two key geometries that differ by rotation about the Sb-C1 bond, termed ‘interacting’ where the Sb unit interacts with the Fe-bound hydride (Fe-(μ-H)-Sb) *via* a donor-acceptor interaction, and another, where no such interaction exists (‘non-interacting’) (Scheme 2). Consistent with spectroscopic observations in solution, DLPNO-CCSD(T)<sup>43–45</sup> calculations reveal an energy difference of 6.1 kcal mol<sup>-1</sup> (**3a**) and 3.0 kcal mol<sup>-1</sup> (**3b**) in favour of the non-interacting isomer; the difference between which is attributed to the bulkier -Si(<sup>i</sup>Pr)<sub>3</sub> group in **3a**. For **3b**, this small difference indicates that despite the size of the {Sb(*N,N*)} moiety, the system maintains a degree of rotational flexibility. Additional optimizations were carried out for the two halides, (Fe-(μ-X)-Sb) (X = F (**3b-F**) or Cl (**3b-Cl**)), where more favourable interaction energies of 0.4 kcal mol<sup>-1</sup> (X = Cl) and -3.7 kcal mol<sup>-1</sup> (X = F) were obtained (see ESI†).

For the μ-H complex, the interacting isomer is characterized by a lengthened {Fe}-H bond of 1.54 Å *cf.*, 1.51 Å for the non-interacting variant; an Sb-H bond length of 2.69 Å is ~1.0 Å longer than





**Scheme 2** Probing conformational space about the [Sb]-C bond (**3b**: R = Et).  $\Delta G^\circ$  in kcal mol<sup>-1</sup> calculated at the DLPNO-CCSD(T) level of theory (see ESI† for details).

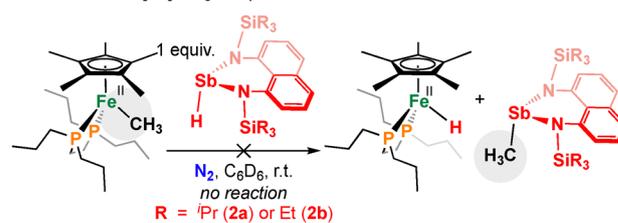
that noted for free **2b** (1.61(5) Å). This interaction, which results in some degree of  $[\{Fe\}-H] \rightarrow [\{Sb\}-N](\sigma^*)$  donation, prompts slight lengthening of the *trans*-Sb-N bond (2.11 Å) *cf.*, 2.07 Å for the non-interacting isomer and an average length of 2.05 Å seen in the crystal structure of **2b** (Scheme 2).<sup>15</sup> Thermodynamic calculations additionally revealed that hydrostibination of **1** is exergonic for both  $\{Sb\}$ -H compounds:  $\Delta G^\circ = -20.8$  kcal mol<sup>-1</sup> for both **3a** and **3b** (Scheme 1A).

To our knowledge, complexes **3** represent the first example of hydrostibination across a metal-element bond, giving access to the only known  $\{Cp^*SbR_2\}$  compounds. Seeking to expose whether a strained unit is requisite for reaction success, the iso-propyl- and ethyl-substituted antimony hydrides **2a/b** were combined with the acyclic model complex,  $[Cp^*Fe(dnppe)(CH_3)]$ ,<sup>38</sup> which contains an  $\{Fe\}-CH_3$  bond (Scheme 3A). Combination of these reagents, however, resulted in null reactivity – hydride transfer was not observed. This outcome speaks to the role of **1** as a substrate for the introduction of a secondary Sb unit *via* hydrostibination.

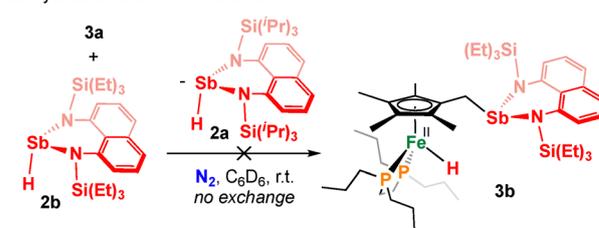
For some E-H hydroelementation reactions, retro- or dehydroelementation (the reverse) is known to readily occur.<sup>46–48</sup> The reversibility of hydrostibination was accordingly probed using a cross-over experiment between **3a** and **2b**, though this reaction did not result in exchange; formation of **3b** and **2a** was not witnessed (Scheme 3B). Further cementing lack of  $\{Sb\}$  dissociation, compounds **3a/b** do not dissociate in the presence of aldehydes *e.g.*, benzaldehyde – a known hydrostibination substrate for compounds **2**.<sup>15</sup> Together, these experiments suggest that once reacted, Sb becomes irreversibly attached to the  $\{Cp^*Fe\}$  organometallic fragment and indicates that the Sb-H bond in **2a/b** is not sufficiently basic to deprotonate the methyl group of the Cp\* ligand of  $[Cp^*Fe(dnppe)(CH_3)]$ .

Heavy-atom addition was also expanded to include chlorostibination and -bismuthation. While scrambling of groups between  $EA_3$  and  $Ar_2ECl$  compounds is known to yield  $ArECl_2$  derivatives,<sup>49</sup> the elementary chlorometallation step underlying in these reactions has not been exploited in an additive fashion to access structures of greater complexity. To this end, combination of **1** with 1 equiv. of the related diamino  $\{Sb\}$ -Cl (**4a**) or  $\{Bi\}$ -Cl (**4b**) reagent led to ring-opening, providing the  $\{Fe\}$ -Cl complex having an appended  $\{Sb\}$  (**5a**,  $\delta_P = 78.0$  ppm) or  $\{Bi\}$  (**5b**,  $\delta_P = 78.3$  ppm) unit (Scheme 4A); these <sup>31</sup>P{<sup>1</sup>H} NMR data are similar to unfunctionalized  $[Cp^*Fe(dnppe)(Cl)]$  ( $\delta_P = 79.4$  ppm).<sup>38</sup> Gratifyingly, complex **5b** was amenable to analysis

a. An unstrained  $[Fe]-CH_3$  complex shows no reaction



b. Hydrostibination is irreversible



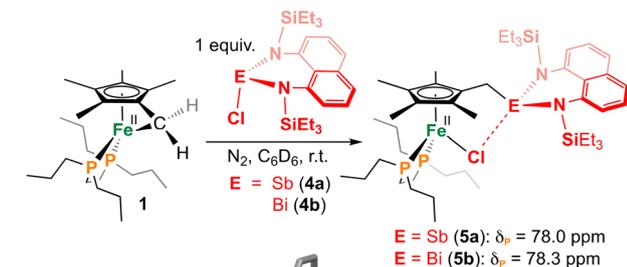
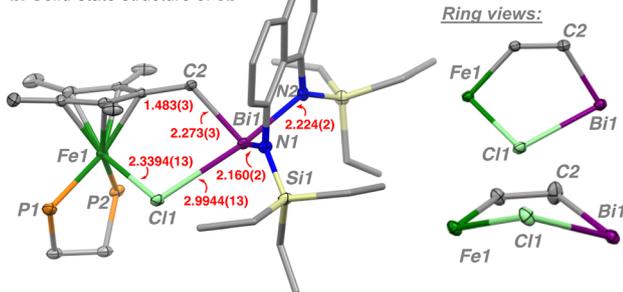
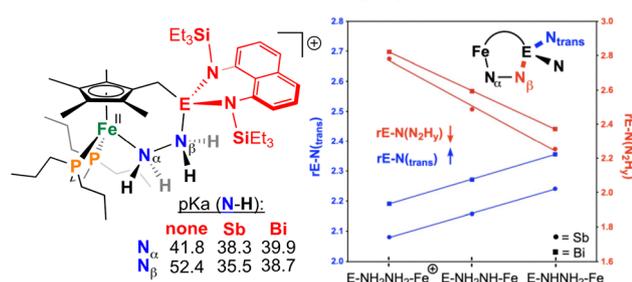
**Scheme 3** (A) An unstrained  $[Fe]-CH_3$  model complex shows no reaction with an  $[Sb]-H$ ; (B) hydrostibination is irreversible.

by single-crystal X-ray diffraction, revealing a bridging  $\mu$ -Fe-Cl-Bi unit ( $d_{Bi-Cl} = 2.9944(13)$  Å) (Scheme 4B) with an Fe-Cl bond length ( $d_{Fe-Cl} = 2.339(1)$  Å) similar to unfunctionalized  $[Cp^*Fe(dnppe)(Cl)]$  (2.349(1) Å).<sup>38</sup> For Bi, thermodynamic calculations of compounds  $(Fe-(\mu-X)-Bi)$  ( $X = H, F$  or Cl (**5b**)) revealed similarity in both magnitude and trend to the Sb analogues discussed above, with more favourable interactions being made across the series: 1.6 kcal mol<sup>-1</sup> ( $X = H$ ), -1.6 kcal mol<sup>-1</sup> ( $X = Cl$ ), and -6.5 kcal mol<sup>-1</sup> ( $X = F$ ) (see ESI† for details).

Lewis acids are increasingly recognized for their role in iron-mediated  $N_2$  fixation, particularly in systems where cooperative substrate binding facilitates activation and reduction to  $[Fe]-N_xH_y$  products.<sup>50,51</sup> To explore a model for such cooperative interactions using a heavy Group 15 element,  $\{Fe,E\}$  ( $E = Sb, Bi$ ) cations were computationally modelled using hydrazine as a substrate (Scheme 4C). These studies reveal that the  $\mu$ - $NH_2NH_2$  bridging mode is thermodynamically favoured by 0.7 and 2.3 kcal mol<sup>-1</sup> for both Sb and Bi, indicating feasibility of cooperative engagement. The optimized structures show Sb-N (2.7814 Å) or Bi-N (2.8223 Å) contacts involving the  $\mu$ - $NH_2NH_2$  unit that are significantly shorter than the sum of their respective van der Waals radii (Sb-N: 3.61 Å, Bi-N: 3.62 Å).<sup>52</sup> Importantly, this binding event results in a significant acidification of the  $N_\beta$ -H proton—by 14–17 pK<sub>a</sub> units—underscoring the ability of such heavier Group 15 elements to modulate substrate properties. Consistent with increased  $[\{Sb\}-N](\sigma^*)$  donation, a decrease in E- $N_2H_2$  bond distance correlates with an increase in E-N(*trans*) bond length (graph, Scheme 4C). This work provides, to our knowledge, the first conceptual framework for employing heavy Group 15 Lewis acids in such a role.<sup>53</sup>

Herein, we have disclosed the first example of hydro- and chloroelementation reactions across a metal-carbon bond using heavy Group 15 compounds, which occurs under ambient conditions in near-quantitative fashion (by <sup>31</sup>P NMR spectroscopy). The success of this reaction depends on the strained nature of the Fe diphosphine tucked-in complex **1**, as exemplified by null reactivity with an unstrained  $[Fe]-CH_3$  model complex. These findings



a. Synthesis of **5a** and **5b** from {Sb}–Cl and {Bi}–Cl starting materialsb. Solid-state structure of **5b**c. theoretical assessment of cooperative  $\text{NH}_2\text{NH}_2$  binding and  $\text{pK}_a$  effects

**Scheme 4** (A) Synthesis of **5a** and **5b** from chloride starting materials; (B) solid-state structure of **5b** with an enhanced view of the [Fe]–Cl–[Bi] interaction (ellipsoids drawn at 50% probability; hydrogen atoms and dnpe  $^n\text{Pr}$  groups have been omitted for clarity); (C) theoretical assessment of cooperative  $\text{NH}_2\text{NH}_2$  binding and  $\text{pK}_a$  effects.

represent an advance in main group–transition metal reactivity because they offer new and mild avenues (compared to salt metathesis or dehydrohalogenation) for designing cooperative heterobimetallic systems involving heavy p-block elements.<sup>54</sup>

J. A. Z. performed all experimental work using complex **1** and performed all computations. M. M. prepared all Sb- and Bi-containing reagents **2a**, **2a-D<sub>1</sub>**, **2b**, **4a**, and **4b**. M. W. D. and S. S. C. supervised the project. C. S. D. performed the first reaction between **1** and **2a-D<sub>1</sub>** and discovered the hydrostibination reaction. J. A. Z. collected the solid-state data for **5b**, and it was solved/refined by P. D. B. All authors were involved in writing, reviewing, and editing drafts of the paper.

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## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for **5b** has been deposited at the CCDC under 2450513.

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