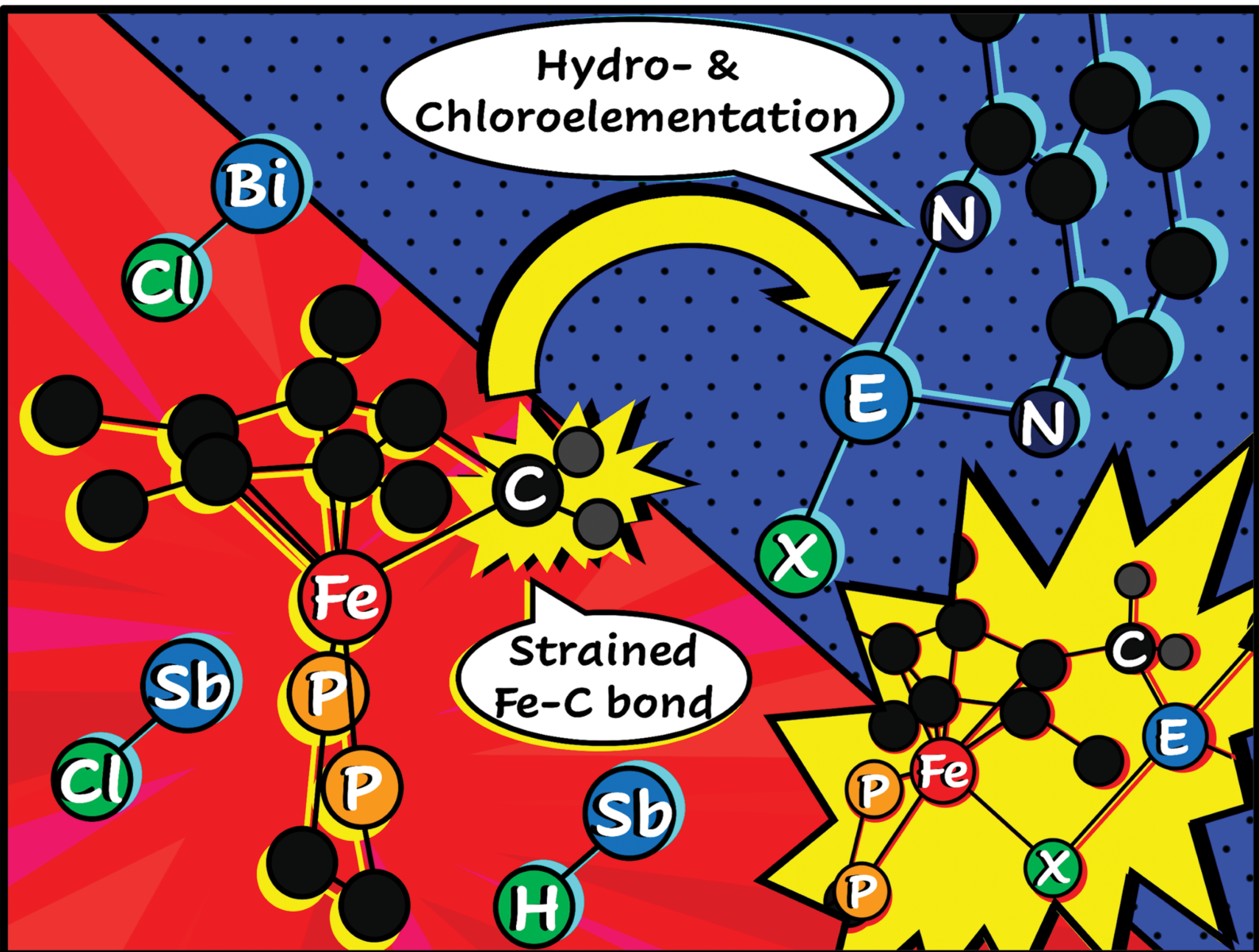


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Hydro- and chloroelementation reactions across an iron–carbon bond using heavy group 15 reagents†

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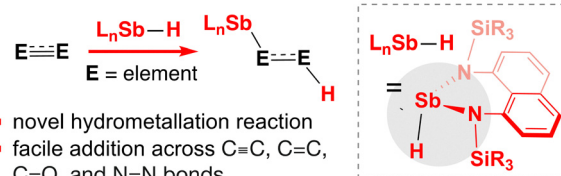
Diaminostibines ($\{\text{Sb}\}\text{-H}$) add across the iron–carbon bond of a tucked-in iron diphosphine complex, resulting in hydrostibinated iron hydride $[(\text{Cp}^*\text{-SbR}_2)\text{Fe-H}]$ complexes. The scope was broadened to include $\{\text{Sb}\}\text{-Cl}$ and $\{\text{Bi}\}\text{-Cl}$ 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.^{1–4} 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.⁵ 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.^{6–9} Alkene hydroboration, for example, has been well-established as a means to selectively install alcohol functionality following oxidation of an organoborane unit.¹⁰ 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.^{11,12} 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.^{13,14} E–H bond activations featuring heavy Group 15 E–H bonds (E = Sb or Bi) – hydrostibination and hydrobismuthation – are very rare by comparison.^{15,16} This is due to both a lack of Lewis-acidic character for Sb (by contrast to commonly employed HBR_2

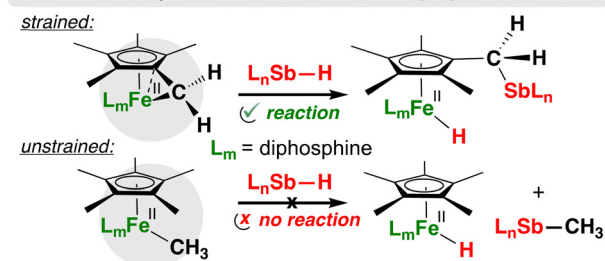
reagents), and in the case of Bi, a paucity of stable compounds that feature a $\{\text{Bi}\}\text{-H}$ bond.^{16,17}

Hydrostibination offers access to functionalized $\{\text{Sb}\}$ -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.^{18–24} 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).¹⁵ 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.²⁵ 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


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


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.^{26–29}

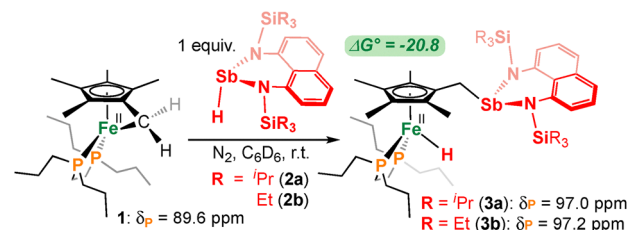
Since 2020, the Drover group has examined the role of secondary coordination sphere (SCS) Lewis acids, such as boranes and alanes, on reactivity.^{30–34} As an extension, we wondered whether hydrostibination might be used as a tool to introduce an {Sb}-based SCS, providing an entry point towards {M,Sb}-containing compounds. Previously, we reported that a strained Fe tucked-in diphosphine complex³⁵ underwent hydroboration using HBCy₂ to give a {Cp*⁻BR₂}Fe-H compound. This system was competent for catalytic CO₂ dihydroboration – a reaction sequence that requires an intramolecularly-positioned {Cp*⁻BR₂} ligand.³³ We now share a collaborative effort that exploits the ring-opening propensity of this strained {Fe}-C complex (Chart 1B)³⁵ with {Sb}-H, {Sb}-Cl, and {Bi}-Cl reagents, providing the first examples of Fe-carbon, and more generally, metal-element hydro- and chloroelementation reactions³⁶ 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.³⁷

To begin, treatment of **1**³⁵ with 1 equiv. of the iso-propylsilyl-substituted 1,8-naphthalene diamine antimony hydride **2a**¹⁵ generated an orange solution of the hydrostibinated Fe(II)-hydride, [(η⁵-C₅Me₄-CH₂-{Sb(1,8-Naphth^{1-Pr})})Fe^{II}(H)(dnppe)] (**3a**; 1,8-Naphth^{1-Pr} = 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⁻¹) across the strained {Fe}-C bond of **1**, generating a ring-opened {Cp*⁻SbR₂}Fe-H product ($\delta_{\text{H}} = -18.0$ ppm (Fe-H), $\nu[\text{Fe}-\text{H}] = 1835$ cm⁻¹). Consistent with C_s-symmetry, two resonances are observed for the dnppe *n*-Pr(CH₃) 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.

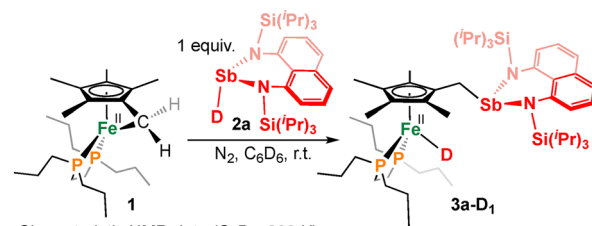
For the Sb fragment, a signal at $\delta_{\text{H}} = 2.50$ ppm is assigned to the {Sb-CH₂Cp*⁻} group, alongside appropriate signals for the coordinated 1,8-naphthalene ligand. By ³¹P{¹H} NMR spectroscopy, a singlet at $\delta_{\text{P}} = 97.0$ ppm corresponds to the dnppe ligand. Proving that the [Fe]-H unit in **3a** is derived from the Sb-hydride moiety in **2a**, reaction of **1** with the related Sb-deuteride **2a-d₁** produces **3a-d₁** (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 ³¹P{¹H} NMR spectrum. Given the similarity in NMR and IR spectroscopic features between **3a** and [Cp*⁻Fe^{II}(H)(dnppe)] ($\delta_{\text{H}} = -17.9$ ppm, $\delta_{\text{P}} = 98.1$ ppm, $\nu[\text{Fe}-\text{H}] = 1865$ cm⁻¹), the peripheral Sb and Fe-bound hydride are non-engaging.³⁸ Iron(II)-carbon bond hydrostibination was additionally expanded to a triethylsilyl-substituted 1,8-naphthalene diamine antimony hydride **2b**, giving [(η⁵-C₅Me₄-CH₂-{Sb(1,8-Naphth^{Et})})Fe^{II}(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

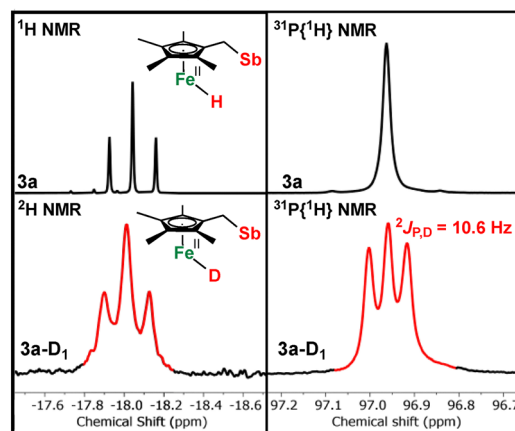
a. Hydrostibination of a strained ferra(II)cycle



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



c. Characteristic NMR data (C₆D₆, 298 K)

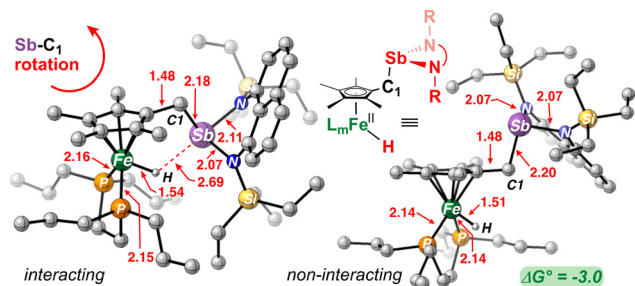


Scheme 1 (A) Hydrostibination of a strained ferra(II)cycle; (B) deuterium labelling unequivocally shows >99% [Fe]-D formation. ΔG^\ddagger in kcal mol⁻¹ calculated at the DLPNO-CCSD(T) level of theory (see ESI† for details); (C) characteristic NMR data (C₆D₆, 298 K).

(Scheme 2). For both **3a/b**, the global optimizer algorithm (GOAT)^{39–41} within ORCA 6.0.1⁴² 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)^{43–45} calculations reveal an energy difference of 6.1 kcal mol⁻¹ (**3a**) and 3.0 kcal mol⁻¹ (**3b**) in favour of the non-interacting isomer; the difference between which is attributed to the bulkier -Si(ⁱPr)₃ 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⁻¹ (X = Cl) and -3.7 kcal mol⁻¹ (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). ΔG° in kcal mol⁻¹ calculated at the DLPNO-CCSD(T) level of theory (see ESI† for details).

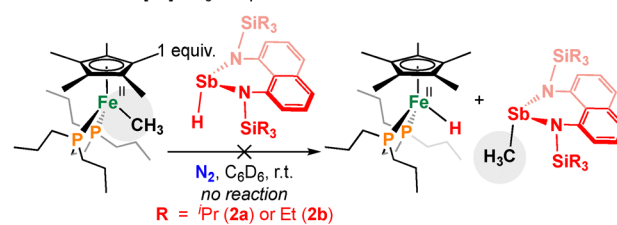
that noted for free **2b** (1.61(5) Å). This interaction, which results in some degree of $[\{Fe\}-H] \rightarrow [\{Sb\}-N](\sigma^*)$ donation, prompts slight lengthening of the *trans*-Sb-N bond (2.11 Å) *cf.*, 2.07 Å for the non-interacting isomer and an average length of 2.05 Å seen in the crystal structure of **2b** (Scheme 2).¹⁵ Thermodynamic calculations additionally revealed that hydrostibination of **1** is exergonic for both {Sb}-H compounds: $\Delta G^\circ = -20.8$ kcal mol⁻¹ 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, $[Cp^*Fe(dnppe)(CH_3)]$,³⁸ which contains an {Fe}-CH₃ 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.

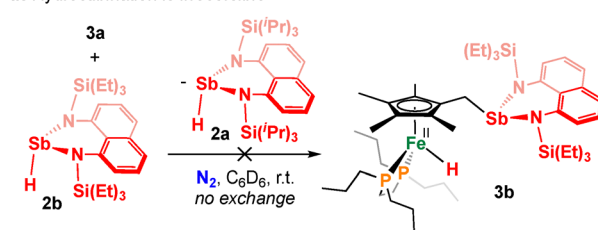
For some E-H hydroelementation reactions, retro- or dehydroelementation (the reverse) is known to readily occur.^{46–48} The reversibility of hydrostibination was accordingly probed using a cross-over experiment between **3a** and **2b**, though this reaction did not result in exchange; formation of **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**.¹⁵ 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,⁴⁹ 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 ³¹P{¹H} NMR data are similar to unfunctionalized $[Cp^*Fe(dnppe)(Cl)]$ ($\delta_P = 79.4$ ppm).³⁸ Gratifyingly, complex **5b** was amenable to analysis

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



b. Hydrostibination is irreversible



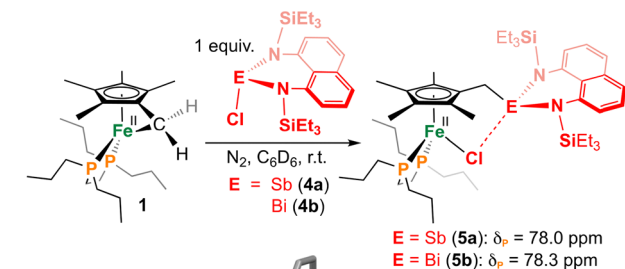
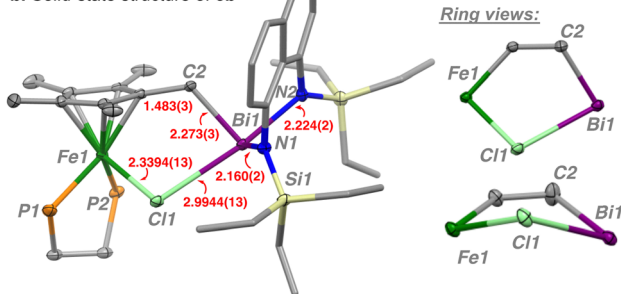
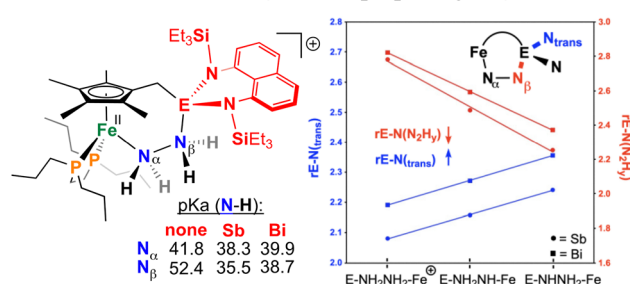
Scheme 3 (A) An unstrained $[Fe]-CH_3$ model complex shows no reaction with an $[Sb]-H$; (B) hydrostibination is irreversible.

by single-crystal X-ray diffraction, revealing a bridging μ -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).³⁸ 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⁻¹ ($X = H$), -1.6 kcal mol⁻¹ ($X = Cl$), and -6.5 kcal mol⁻¹ ($X = F$) (see ESI† for details).

Lewis acids are increasingly recognized for their role in iron-mediated N₂ fixation, particularly in systems where cooperative substrate binding facilitates activation and reduction to $[Fe]-N_xH_y$ products.^{50,51} 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 μ -NH₂NH₂ bridging mode is thermodynamically favoured by 0.7 and 2.3 kcal mol⁻¹ 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 μ -NH₂NH₂ 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).⁵² Importantly, this binding event results in a significant acidification of the N_β-H proton—by 14–17 pK_a 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-N₂H₂ 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.⁵³

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 ³¹P 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 NH_2NH_2 binding and 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 ^nPr groups have been omitted for clarity); (C) theoretical assessment of cooperative NH_2NH_2 binding and 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.⁵⁴

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-D₁**, **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-D₁** 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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