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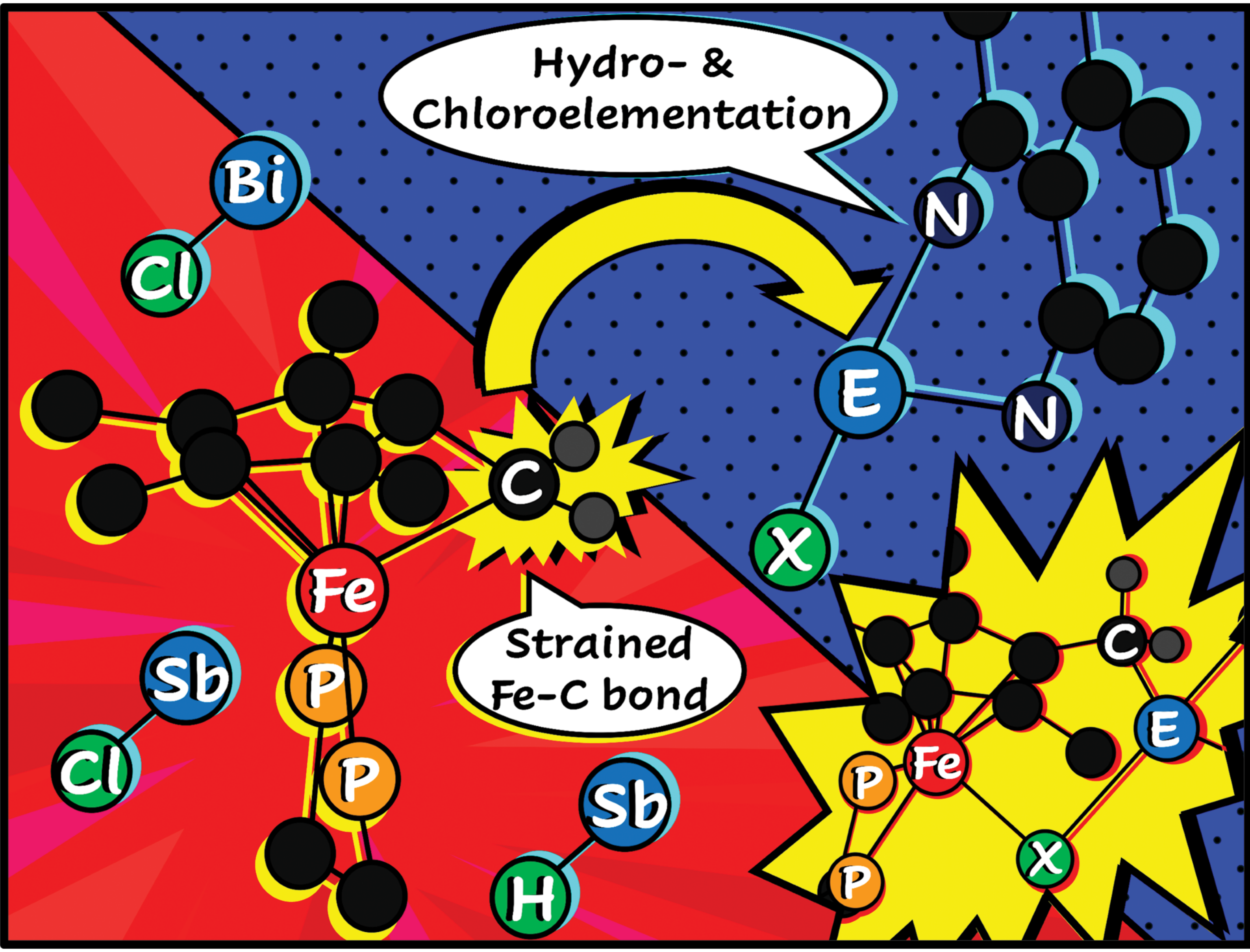

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Hydro- and chloroelementation reactions across an iron–carbon bond using heavy group 15 reagents†

Joseph A. Zurakowski,[ab] Mitchell A. Z. MacEachern,[c] Connor S. Durfy,[a] Paul D. Boyle,[a] Saurabh S. Chitnis *[c] and Marcus W. Drover *[a]

Diaminostibines ({Sb}–H) add across the iron–carbon bond of a tucked-in iron diphosphine complex, resulting in hydrostibinated iron hydride [{Cp*-SbR$_2$}Fe–H] complexes. The scope was broadened to include {Sb}–Cl and {Bi}–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 {Si}–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, {N}–H (hydroamination) and {P}–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 {Bi}–H bond.[16,17]

Hydrostibination offers access to functionalized {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 C≡C, C=C, C=O, and N=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/{Sb}–H bond interaction. For terminal C≡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

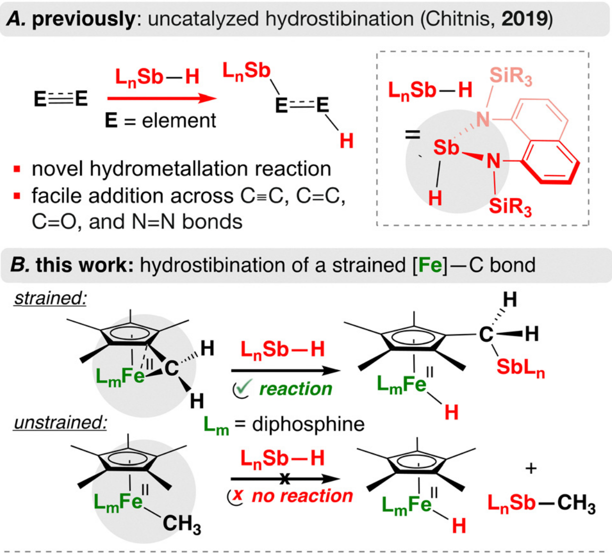

Chart 1 (A) previously: uncatalyzed hydrostibination (Chitnis, 2019); (B) this work: hydrostibination of a strained [Fe]–C bond.

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[a] Department of Chemistry, Western University, 1151 Richmond Street, London, ON, N8K 3G6, Canada. E-mail: marcus.drover@uwo.ca
[b] Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Avenue, Windsor, ON, N9B 3P4, Canada
[c] Chemistry Department, Dalhousie University, 6274 Coburg Road, Halifax, Nova Scotia, B3H 4R2, Canada. E-mail: saurabh.chitnis@dal.ca

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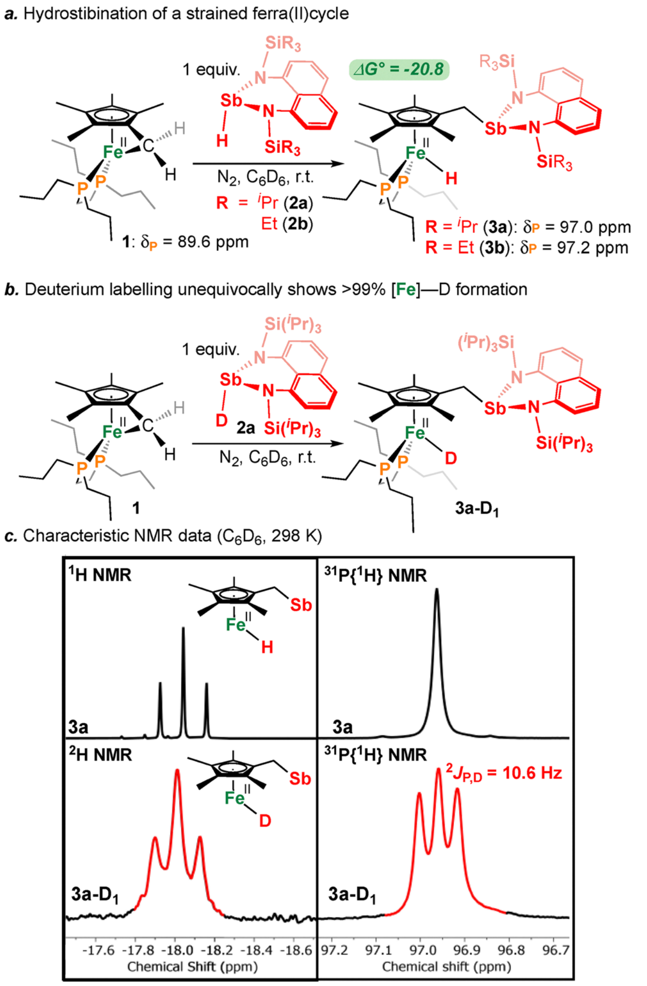
in product profile shapes a need to further develop our understanding of heavy p-block hydroelementation reactions. The scope of {Sb}–H addition reactions has been so far limited to organic substrates. There are no examples where such a functional group has been added across a metal–element bond; such products would represent interesting targets for ligand design, coordination chemistry, cooperative catalysis, and more.[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 complex[35] underwent hydroboration using $HBCy_2$ to give a {Cp*-BR_2}Fe–H compound. This system was competent for catalytic CO_2 dihydroboration – a reaction sequence that requires an intramolecularly-positioned {Cp*–BR_2} 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 reactions[36] 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, [(η^5-C_5Me_4-CH_2-{Sb(1,8-Naphth$^{i\text{-}Pr}$)})Fe^{II}(H)(d*n*ppe)] (**3a**; 1,8-Naphth$^{i\text{-}Pr}$ = 1,8-tri(i-propyl)silylamidonaphthalene, d*n*ppe = 1,2-bis(di-*n*-propylphosphino)ethane) (Scheme 1A). This process is characterized by addition of an {Sb}–H unit (δ_H = 9.88 ppm; ν[Sb–H] = 1883 cm^{-1}) across the strained {Fe}–C bond of **1**, generating a ring-opened {Cp*-SbR_2}Fe–H product (δ_H = –18.0 ppm (Fe–H), ν(Fe–H) = 1835 cm^{-1}). Consistent with C_s-symmetry, two resonances are observed for the d*n*ppe *n*-Pr(CH_3) groups at δ_H = 0.95 and 0.89 ppm (forward and backward), as well as two signals at δ_H = 1.92 and 1.86 ppm for the desymmeterized Cp*-ring.

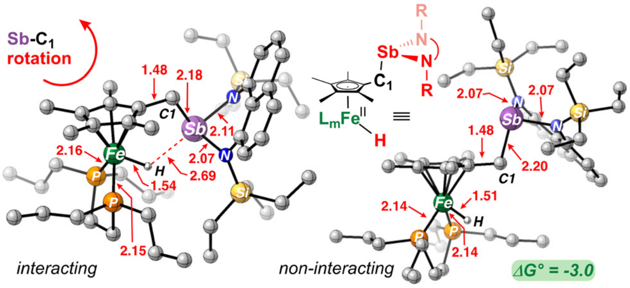
For the Sb fragment, a signal at δ_H = 2.50 ppm is assigned to the {Sb-C$\underline{H}_2$Cp*} group, alongside appropriate signals for the coordinated 1,8-naphthalene ligand. By $^{31}P\{^1H\}$ NMR spectroscopy, a singlet at δ_P = 97.0 ppm corresponds to the d*n*ppe ligand. Proving that the [Fe]–H unit in **3a** is derived from the Sb–hydride moiety in **2a**, reaction of **1** with the related Sb–deuteride **2a-d$_1$** produces **3a-d$_1$** (Scheme 1B), defined by a 1 : 1 : 1 triplet at δ_P = 97.0 ppm ($^2J_{P-D}$ = 10.6 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. Given the similarity in NMR and IR spectroscopic features between **3a** and [Cp*Fe^{II}(H)(d*n*ppe)] (δ_H = −17.9 ppm, δ_P = 98.1 ppm, ν(Fe–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 [(η^5-C_5Me_4-CH_2-{Sb(1,8-Naphth^{Et})})-Fe^{II}(H)(d*n*ppe)] (**3b**) (Scheme 1A, see ESI† for details).



Scheme 1 (A) Hydrostibination of a strained ferra(II)cycle; (B) deuterium labelling unequivocally shows >99% [Fe]–D formation. $\Delta G°$ in kcal mol^{-1} calculated at the DLPNO-CCSD(T) level of theory (see ESI† for details); (C) characteristic NMR data (C_6D_6, 298 K).

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 (Scheme 2). For both **3a/b**, the global optimizer algorithm (GOAT)[39–41] within ORCA 6.0.1[42] 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(^{i}Pr)$_3$ 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



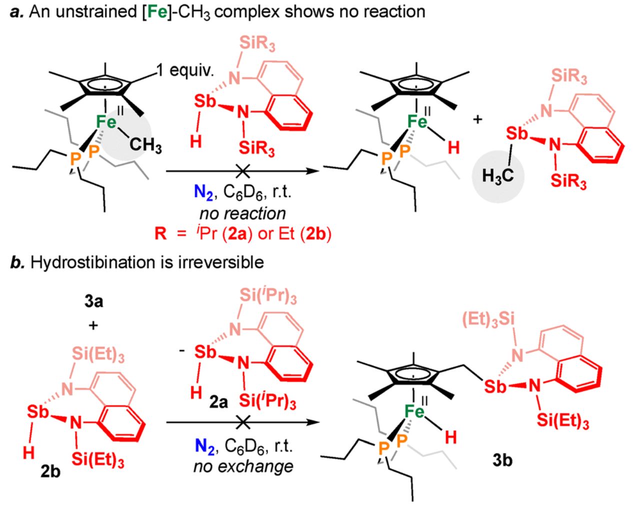
Scheme 2 Probing conformational space about the [Sb]–C bond (**3b**: R = Et). $\Delta G°$ in kcal mol^{-1} calculated at the DLPNO-CCSD(T) level of theory (see ESI† for details).

that noted for free **2b** (1.61(5) Å). This interaction, which results in some degree of [{Fe}–H] → [{Sb}–N](σ*) 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: $\Delta G° = -20.8$ 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(d*n*ppe)(CH_3)],[38] 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.[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(d*n*ppe)(CH_3)].

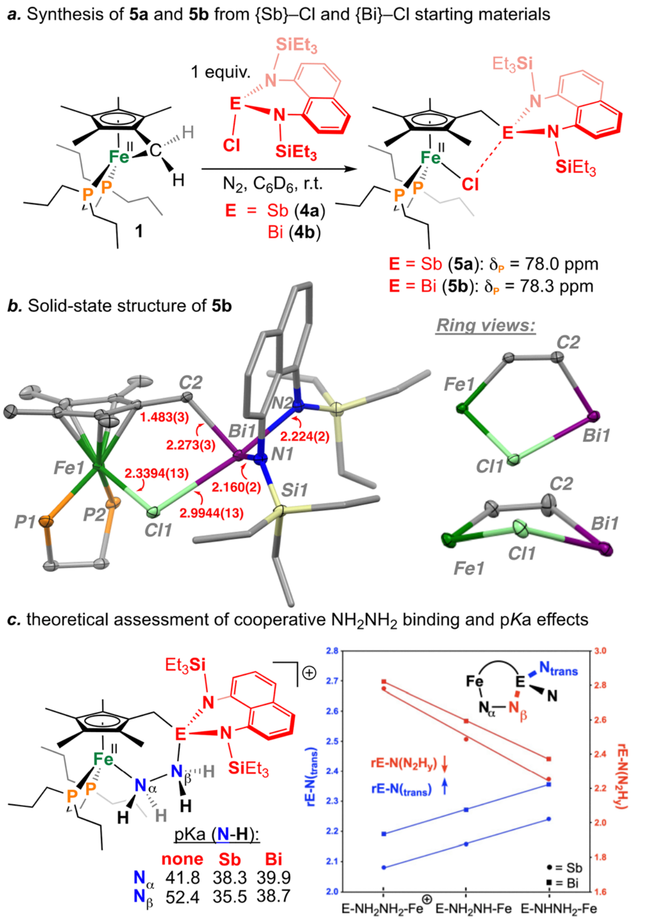
Heavy-atom addition was also expanded to include chlorostibination and -bismuthation. While scrambling of groups between EAr_3 and Ar_2ECl compounds is known to yield $ArECl_2$ derivatives,[49] the elementary chlorometallation step underlying in these reactions has not been exploited in an additive fashion 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 $^{31}P\{^1H\}$ NMR data are similar to unfunctionalized [Cp*Fe(d*n*ppe)(Cl)] (δ_P = 79.4 ppm).[38] Gratifyingly, complex **5b** was amenable to analysis 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(d*n*ppe)(Cl)] (2.349(1) Å).[38] For Bi, thermodynamic calculations of compounds (Fe–(μ-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).



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

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.[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-NH_2NH_2 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-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).[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](σ*) donation, a decrease in E–N_2H_y 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 ^{31}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



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 dnppe ^{n}Pr 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-D$_1$**, **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$_1$** 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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