# Cationic Tetrylene-Iron(0) Complexes: Access Points for Cooperative, Reversible Bond Activation and Open-Shell Iron(-I) Ferrato-Tetrylenes

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#### Supporting Information Placeholder

ABSTRACT: The oxidative addition of catalytically relevant small molecules in molecular iron complexes poses a considerable challenge in achieving 'precious metal catalysis' utilizing this Earth abundant metal. Here, we show that noninnocent ligands based upon cationic heavier tetrylenes, E<sup>II</sup> (E = Ge, Sn), can work in synergy with a reactive iron center for the oxidative cleavage of inert bonds. Specifically, the openshell cationic stannylene-iron(0) complex 4 (4 =  $[PhiPDippSn \cdot Fe \cdot IPr]^+; PhiPDipp = {[Ph_2PCH_2Si(^iPr)_2](Dipp)N};$ Dipp =  $2,6^{-i}Pr_2C_6H_3$ ; IPr = [(Dipp)NC(H)]\_2C:) cleaves dihydrogen under very mild conditions (1.5 bar, 298K), in forming bridging hydrido-complex 6, which features a  $[Sn-(\mu-H)_2-Fe]$ core. This reaction is readily reversible, with hydrogen being entirely extruded after simple freeze-thaw degassing of reaction mixtures, regenerating 4. Computational investigation of the mechanism incites the necessity of both the Fe<sup>0</sup> and Sn<sup>II</sup> centers in the key H-H bond scission step. The related GeII system, 3, does not activate dihydrogen. However, oneelectron reduction of this species leads to clean oxidative addition of one C-P linkage of the PhiPDipp ligand in an intermediary Fe<sup>-1</sup> complex, leading to Fe<sup>1</sup> phosphide species 7. In contrast, the same one-electron reduction reaction of 4 gives facile access to the iron(-I) ferrato-stannylene, 8. This presents strong evidence for the intermediacy of such a species in the reduction of **3**, and represents an example of a covalently bound formal iron(-I) compound. EPR spectroscopy, SQUID magnetometry, and supporting computational analysis strongly indicate the high localization of electron spin density at Fe<sup>-I</sup> in this unique d<sup>9</sup>-iron complex.

## INTRODUCTION

The seminal discovery of stable carbene complexes by E. O. Fischer marked a turning point in modern organometallic chemistry,<sup>1</sup> our broader interest in the reactive capacity of carbene ligands blossoming since that time.<sup>2</sup> Carbene centers, whilst bound to a metal, can be nucleophilic, electrophilic, or indeed 'spectators', as for now ubiquitous N-heterocyclic carbenes (NHCs). Extending these concepts, bespoke pincer



Figure 1. A: Known CO-free tetrylene complexes of  $Fe^0$ ; B: a recently reported CO-free ferrato-stannylene complex; C: activation of dihydrogen by a rhodium metallo-stannylene; D: this work.

ligands incorporating nucleophilic carbene centers have the capacity to actively partake in well-defined bond scission processes across the carbene metal linkage,<sup>3</sup> in some cases reversibly.<sup>4</sup> Moving beyond the lightest element of group 14, the heavier tetrylenes also have the capacity to behave in this manner.<sup>5</sup> The past two decades have seen prolific research regarding the electronic nature of low-valent group 14 species,<sup>6</sup> and their bonding interactions with transition metals.<sup>5,7</sup> Due to the greater stability of lower oxidation states, and the decrease in electronegativity on descending group 14, their chemistry also deviates from that for carbon. Notably, the heavier tetrylenes have an amplified ambiphilicity, and are more Lewis acidic due to a lessened electronegativity. This allows such ligands to behave as electrophiles whilst simulta-

neously being strong  $\sigma$ -donors towards a transition metal,<sup>8</sup> opening up a new vista in ligand design.

Exploration of bond activation with the abundant first-row transition metals is central to the development of a sustainable chemical economy,9 given our reliance on the heavier, precious metals of the *d*-block.<sup>10</sup> Here, iron continues to be a core focus given that it is the second most abundant metal on our planet after aluminum.<sup>11</sup> Although cross-coupling catalysis is known for iron,<sup>12</sup> known systems do not operate via oxidative addition/reductive elimination (OA/RE) processes typically invoked in palladium systems, with two-electron oxidative addition processes ubiquitous in transition metal catalysis.13 Key methods in enabling two-electron chemical processes at iron have revolved almost exclusively around ligand design.14 Utilizing chemically or redox non-innocent organic ligand systems, well-defined oxidative addition of catalytically essential bonds such as C-C, C-X (X = Cl-I),<sup>13</sup> and H-H<sup>15</sup> bonds have been realized. Given the aforementioned electronically unique nature of the heavier tetrylenes, it follows that such compounds may stand as effective ligands in promoting these important bond activation processes at iron.

Heavier group 14-iron chemistry is certainly not unexplored. In pioneering work from Tilley, closely related ruthenium silvlene complexes are postulated intermediates in alkene hydrosilylation catalysis.<sup>16</sup> More recently, the same group has successfully accessed stable, base-free hydrido-silylene iron complexes via silane activation,<sup>17</sup> which may also pertain to mechanistic aspects of hydrosilylation catalysis. A small number of base-free silylene,<sup>18</sup> germylene,<sup>19</sup> and stannylene <sup>19(a),20</sup> complexes of iron(0) are now known, although it is noted that the vast majority involve the [Fe(CO)<sub>4</sub>] fragment or derivatives thereof (Fig. 1, A), rendering reactivity involving the iron centre essentially nil. Closely related ferrato-tetrylenes have also seen considerable attention. Here, base-free derivatives bearing two-coordinate group 14 centers are also rare, almost exclusively based on the monoanionic [CpFe(CO)<sub>2</sub>]<sup>-</sup> fragment (Fig. 1, **B**).<sup>21</sup> One very recent report on unique binding modes in ferrato-stannylene systems featuring the [Cp\*(<sup>i</sup>Pr<sub>2</sub>MeP)Fe] anionic fragment have been reported by Tilley et al.,<sup>22</sup> whilst a Rh-I metallo-stannylene recently reported by Wesemann et al. was shown to activate H<sub>2</sub> in the formation of a Rh<sup>I</sup> metallostannylene (Fig. 1, C),<sup>23</sup> though a mechanistic investigation into the involvement of the Sn<sup>II</sup> center was not carried out. Such systems are of interest in their relation to heavier alkylidyne congeners, which have the two resonance 'extremes' of singly bonded metallo-tetrylenes, and triply bonded tetrylidynes, poignantly displayed in both aforementioned Rh-Sn and Fe-Sn complexes, and more broadly described in the work of Fillipou and Power, who have demonstrated interchangeability between such resonance forms for a number of transition metals.<sup>24</sup>

Our own efforts have focused on the development of chelating ligands featuring a tetrylene binding center, which remains highly Lewis acidic even when bound to Ni<sup>0</sup>, due to the ligand's chelating nature.<sup>8,25</sup> Herein we describe the extension of these systems to low-valent iron chemistry, in the facile 'one-pot' synthesis of cationic germylene and stannylene complexes of iron(0). The resulting systems are electronically distinct, the Sn<sup>II</sup> complex having an open-shell ground state which allows for the facile and reversible activation of dihydrogen. The mechanism for this process is shown to involve both the Sn<sup>II</sup> and Fe<sup>0</sup> centers in the critical H-H bond activation step. These complexes are also convenient starting points for accessing hitherto unknown open-shell ferrato tetrylenes featuring Fe<sup>-I</sup> centers. Whilst the target germanium system is

unstable relative to ligand activation, the tin congener can be isolated as a stable, crystalline solid, which represents an open-shell, ferrato-stannylene featuring a  $Fe^{-I}-Sn^{II}$  covalent bond.

# **RESULTS AND DISCUSSION**

#### Cationic Tetrylene-Fe<sup>0</sup> Complexes



Figure 2. Synthesis and molecular structures of compounds **3**, and **4**. Only the cationic part is shown in molecular structures. Thermal ellipsoids at 25% probability, and hydrogen atoms omitted for clarity. Selected bond distance (Å) and angles (°) for **3**: Ge1-Fe1 2.1978(6); Ge1-C32 2.049(2); Ge1-N1 1.845(2); P1-Fe1 2.2109(9); N1-Ge1-Fe1 137.75(6); N1-Ge1-C32 119.77(7); Fe1-Ge1-C32 102.28(6); Ge1-Fe1-P1 94.17(3). For **4**: Sn1-Fe1 2.717(1); P1-Sn1 2.998(2); Fe1-C32 2.073(5); Sn1-N1 2-140(3); C1-N1 1.396(7).

Two-coordinate-tetrylene complexes of first-row transition metals are, as mentioned, very rare indeed. Furthermore, almost all low-valent group 14-iron complexes employ carbonyl ligands at iron, leading to electronic saturation and thus diminished reactivity. Our earlier reports regarding the synthesis of reactive Ni<sup>0</sup> systems bearing our cationic tetrylene ligands relied upon the use of the commonly employed Ni<sup>0</sup> synthon, Ni(cod)<sub>2</sub>. Earlier reports on similar chemistry for Fe<sup>0</sup> systems utilized the elegant, but somewhat inaccessible metal-vapor synthesis of  $bis(\eta^6$ -toluene)iron(0), used to generate the thermally labile  $(\eta^{6}-tolulene)(\eta^{2}-ethene)iron(0)$  complex.<sup>20(c),(d)</sup> More recently, a handful of closely related bis-η<sup>2</sup>alkene Fe<sup>0</sup> complexes were reported,<sup>26</sup> stabilized by bulky Nheterocyclic carbenes, which we believed may also readily undergo alkene substitution reactions.<sup>27</sup> To this end, the addition of the cationic  $E^{II}$  ligand precursors,  $[PhiPDippE][BArF_4]$  (E = Ge (1), Sn (2); PhiPDipp = {[Ph<sub>2</sub>PCH<sub>2</sub>Si(iPr)<sub>2</sub>](Dipp)N}; Dipp =  $2,6^{-i}Pr_2C_6H_3$ ; Ar<sup>F</sup> =  $3,5^{-}(CF_3)_2C_6H_3$ ),<sup>28,29</sup> to deep green solutions of IPr·Fe[ $\eta^2$ -(vtms)]<sub>2</sub> (IPr = [(Dipp)NC(H)]<sub>2</sub>C:; vtms =  $C_2H_3SiMe_3$ ) rapidly led to the formation of deep yellow-brown reaction mixtures (Fig. 2). In-situ <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic analysis already suggested differing outcomes for the two reactions, that for the Ge<sup>II</sup> system indicative of a single diamagnetic reaction product, and that for the Sn<sup>II</sup> system being silent, thus indicative of a paramagnetic reaction product. Isolation of crystalline material from the two reaction mixtures revealed considerably different structures for the two ligand systems.

The sole reaction product formed utilising the Ge<sup>II</sup> ligand system (viz. 3) shows Fe<sup>0</sup> insertion into the Ge-P bond, forming our previously observed chelating ligand motif (Fig. 2). However, presumably due to the high Lewis acidity of the cationic Gell centre, the NHC ligand has migrated from iron to germanium, the iron centre now forming an  $\eta^6$ -arene interaction with one Dipp group of this NHC ligand. The Ge-Fe distance in **3** (d<sub>GeFe</sub> = 2.1978(6) Å) is shorter than all bar one reported Ge-Fe interactions, the one shorter example being found in a remarkable (alkyl)(hydrido)germylene iron(II) complex.19(c) The Ge<sup>II</sup> center in **3** has a perfectly planar coordination geometry (sum of angles =  $359.8^{\circ}$ ), representative of a Ge $\rightarrow$ Fe dative interaction. The DFT derived HOMO (-9.16 eV) shows considerable  $\pi$ -character, which would suggest a degree of Fe $\rightarrow$ Ge back-bonding in this interaction and some degree of multiple bond character. This is further borne out by both the Mayer Bond Order (MBO) and Wiberg Bond Index (WBI) for this bond, at 1.37 and 1.35 respectively. This, together with the short Ge-Fe bond distance, would suggest that this interaction is best described as a double bond. The average of the C-C bond distances in the Fe-bound arene (d = 1.419 Å) is slightly greater than the same value for the unbound arene of the NHC ligand (d = 1.390 Å), as is known in related arene complexes of low-valent iron.<sup>30</sup> Considerable broadening of aliphatic signals in the <sup>1</sup>H NMR spectrum of **3** indicates a fluxional character in solution, which sharpen when THF-d<sub>8</sub> solutions are heated to 60 °C (Fig. S5). Notably, at low temperature (i.e. -80 °C) clear signals at  $\delta$  = 4.5, 5.4, and 6.5 ppm can be seen, pertaining to the Fe-bound Dipp group. The 57Fe Mössbauer spectrum of **3** ( $\delta$  = 0.472 mm·s<sup>-1</sup>;  $\Delta E_Q$  = 1.349 mm·s<sup>-1</sup>; Fig. S48) is in



Figure 3. Plots of  $\mu_{eff}$  vs. *T* (left) and  $\chi_{mol}$  vs. *T* (right) for paramagnetic Sn<sup>II</sup>-Fe<sup>0</sup> complex **4**.

keeping with known Fe<sup>0</sup> arene systems,<sup>30(b)</sup> aiding in confirmation of a low-spin, d<sup>8</sup> Fe<sup>0</sup> complex. This species, to the best of our knowledge, thus represents a unique example of a cationic-tetrylene Fe<sup>0</sup> complex, and indeed the first Ge<sup>II</sup>-Fe<sup>0</sup> complex absent of carbonyl ligands. The structural and electronic nature of the closely related Sn<sup>II</sup> system, 4 (Fig. 2), stands in stark contrast to the described Ge<sup>II</sup> complex. The Sn<sup>II</sup> center indeed binds the Fe<sup>0</sup> center; surprisingly, however, insertion into the Sn-P bond is not observed, but rather the Fe<sup>0</sup> center forms an  $\eta^6$ -arene interaction with the Dipp group of the stannylene ligand, generating a highly strained conformation. This strain presumably leads to a significant weakening of the P-Sn interaction, which is longer than 98% of reported Sn-P single-bonded interactions ( $d_{Sn \dots P} = 2.999(2)$  Å; sum of covalent radii = 2.51 Å). The ligand strain is exemplified by the acute Sn-Fe binding angle ( $\angle_{NSnFe}$  =81.32(1)°), and further borne out by the angles at the <sup>PhiP</sup>Dipp ligand's N-donor atom: the Sn-N-CDipp and Si-N-CDipp angles of 94.81(3)° and 142.61(3)° deviate significantly from the ideal of 120°. Finally, the Sn-Fe bond distance of 2.717(1) Å is longer than all known terminal Sn-Fe bonding interactions. The low-coordinate Sn<sup>II</sup> center appears to have some degree of stabilization from one aryl group of the NHC ligand bound to Fe<sup>0</sup>, with a distance of 3.316 Å between the Sn<sup>II</sup> center and the center of the arene plane. This is within the sum of the covalent radii for tin and carbon (3.87 Å), but considerably longer than such interactions in related low-coordinate tetrylene cations.<sup>31</sup> Electronically, Sn<sup>II</sup> complex **4** also differs significantly to the Ge<sup>II</sup> system. Solutions of redissolved crystalline 4 yield highly broadened <sup>1</sup>H NMR spectra, indicative of a paramagnetic system. This paramagnetism is rationalized best assuming a high-spin configuration for the  $d^8$  Fe<sup>0</sup> center, with S = 1. Consistent with this, complex 4 is silent when studied by X-band EPR spectroscopy, and shows the expected behavior for an S = 1 system in SQUID magnetometry measurements (Fig. 3). Here, the ambient temperature  $\mu_{eff}$  value of 3.95 B is higher than would be expected for the spin-only value for two unpaired electrons (e.g. 2.83 B), which incites a degree of spin-orbit coupling in 4. Indeed, spin-orbit coupling between heavier group 14 elements and first-row transition metals is a known phenomenon, allowing for 'tailoring' of the magnitude of these effects.<sup>32</sup> These SQUID data are also in good agreement with Curie-Weiss paramagnetism, indicative of spin-density located at iron, with no indication of spin-coupling e.g. arising from ligand reduction. Density Functional Theory (DFT) calculations also suggest a high spin density at iron (Fig. S64), further supporting the assignment of a high-spin d<sup>8</sup> Fe<sup>0</sup> complex. This spin state leads to a very narrow HOMO-LUMO gap in 4 of 0.89 eV.<sup>33</sup> Alongside the geometrically perturbed Sn-Fe interaction and low-coordination environment at the cationic Sn<sup>II</sup> center, this provides a promising platform for synergistic bond activation in this complex.

#### **Cooperative bond activation**

The differing electronic nature of the described complexes stands as an exciting point of comparison, exemplified by their reactivity. One of our key aims in the development of ambiphilic main group ligands (*e.g.* **1** and **2**) seeks to access systems whereby the ambiphilic ligand has the capacity to bind incoming nucleophiles, with a focus on ammonia.<sup>34</sup> This aims to activate ammonia in the coordination sphere of the transition metals, which is typically a highly challenging reaction.<sup>35</sup> Both complexes **3** and **4** rapidly react with ammonia. Addition of ~1.5 equiv. of ammonia to dissolved **3** led to dissipation of its characteristic deep golden-yellow color, and formation of deep red solutions. *In-situ* <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic



Figure 4. *Above*: the reactivity of **3** and **4** towards NH<sub>3</sub> and H<sub>2</sub>, respectively, showing reversibility in the latter. *Below*: the molecular structure of the cationic part in NH<sub>3</sub>-activation product **5**, and the DFT-derived structure of the cationic part in H<sub>2</sub> activation product **6**. Selected bond distance (Å) and angles (°) for **5**: Ge1-Fe1 2.219(1); Ge1-N1 1.853(5); Ge1-N2 1.870(7); Fe1-P1 2.210(3); Ge1···C32 3.520(9); N1-Ge1-N2 98.8(3); Fe1-Ge1-N1 136.2(2); Fe1-Ge1-N2 124.8(2).

analysis indicated the clean formation of a single reaction product, with a broad 2H singlet in the 1H NMR spectrum attributable to an NH<sub>2</sub> moiety ( $\delta$  = 2.26 ppm). In contrast, the same reaction for the Sn<sup>II</sup> system **4** led instead to a complex mixture of products,<sup>36</sup> giving the first indication that this latter complex is considerably more reactive than the Ge<sup>II</sup> congener. Deep red single crystals isolated from the former reaction indicated the activation of ammonia, through binding at Ge<sup>II</sup>, and proton transfer to the NHC ligand, in the formation of 5 (Fig. 4). This thus indicates that the Ge<sup>II</sup> center in 4 is indeed of high Lewis acidity, and so capable of binding the incoming nucleophilic NH<sub>3</sub>. Compound 5 represents a rare example of a 'half-parent' amido tetrylene-transition metal complex,37 and the first such complex for germanium. Remarkably, the now protonated imidazolium salt remains bound to the Fe<sup>0</sup> center through an  $\eta^6$ -arene interaction. The Ge-Fe distance of 2.219(1) Å is slightly elongated relative to starting material 3, likely due to increased N $\rightarrow$ Ge donation, so reducing Fe $\rightarrow$ Ge back-bonding. As described, the NH<sub>2</sub> ligand at Ge can be observed in the <sup>1</sup>H NMR spectrum ( $\delta$  = 2.26 ppm), as well as in the IR spectrum of the powdered compound ( $\nu = 3434$  and 3335 cm<sup>-1</sup>). Despite the persistent binding of the protonated NHC in 5, attempts to drive reversibility in this ammonia activation reaction failed, e.g. through application of heat and/or vacuum to dissolved 5. Still, this reaction demonstrates a unique cooperative ammonia activation mechanism, in which the low-valent group 14 element (e.g. Ge11) interestingly maintains its low oxidation state.

We then moved our sights to the activation of H<sub>2</sub>, expected to be more challenging given the apolar nature of this small molecule. Here, Ge<sup>II</sup> complex **3** showed no signs of reactivity, even after prolonged heating and increased H<sub>2</sub> pressures (*e.g.* up to 3 bar). Complex **4**, on the other hand, readily reacts with H<sub>2</sub> under 1.5 bar pressure, and at ambient temperature. Charging a gas-tight NMR tube containing a C<sub>6</sub>D<sub>6</sub> solution of paramagnetic **4** with H<sub>2</sub> led to the formation of a single new diamagnetic reaction product, showing a singlet in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at  $\delta$  = -24.2 ppm. More poignantly, a broad signal is



Figure 5. The DFT-derived reaction coordinate for the cooperative activation of  $H_2$  by model cationic stannylene-iron(0) complex **4'**, yielding **6'**.

observed in the <sup>1</sup>H NMR spectrum, at  $\delta$  = -13.63 ppm, integrating to 2H and bearing clear 117/119Sn satellites ( $1J_{SnH}$  = 331 Hz; Fig. S18). Conducting the same reaction with  $D_2$  gives a <sup>1</sup>H NMR spectrum identical to that described, but lacking the described high-field resonance (Fig. S26). The <sup>2</sup>D NMR spectrum of these reaction mixtures reveals a resonance at  $\delta$  = -13.97 ppm, in keeping with the activation of  $D_2$  (Fig. S28). Remarkably, degassing these reaction mixtures leads to quantitative regeneration of the starting material, thus signifying the facile reversible H<sub>2</sub> activation by **4**. This point rendered it highly challenging to attain further analytical data on this complex, and indeed to crystallize pure samples of H<sub>2</sub> activation product 6. Although crystalline material of this species could be isolated, high levels of disorder prevented refinement to levels acceptable for publication; nevertheless, this did allow us to ascertain the connectivity in 6 (Fig. S60 in ESI). Furthermore, this data could be utilized for the computationally derived lowest energy conformation of 6 (Fig. 4). Here, it is found that the hydride ligands in this complex symmetrically bridge the Sn and Fe centers, in keeping with the single resonance observed for these ligands in <sup>1</sup>H NMR spectra of reaction mixtures. Indeed, although rare, known examples of stannane-iron complexes featuring bridging hydride ligands have similar shifts and coupling constants in their respective <sup>1</sup>H NMR spectra.<sup>38</sup> At this stage, we were particularly curious as to whether the reversible activation of H<sub>2</sub> in 4 proceeds via a cooperative mechanism, that is, involving both Sn and Fe. A DFT investigation of the potential energy surface for this reaction mechanism suggests that this is indeed the case. Upon initial H<sub>2</sub> addition an intermediary  $\sigma$ -bond complex is formed at Fe<sup>0</sup> (IM1, 16.1 kcalmol<sup>-1</sup>). One H-atom can then form a bridging interaction with the cationic Sn<sup>II</sup> center (TS2, 21.2 kcalmol<sup>-1</sup>). This then proceeds by H-H bond scission, so forming bridging hydride complex 6 (-4.0 kcalmol<sup>-1</sup>). This reaction coordinate therefore provokes the involvement of both Sn and Fe centres in the cleavage of H<sub>2</sub>, giving insights into the design of heteroelemental systems for the cooperative activation of inert bonds. The small exergonic value for the overall reaction (4.0 kcalmol<sup>-1</sup>) is in keeping with the observed reversibility in this process. An additionally important point here is the oxidation state of iron in the formed hydride complex. Combined X-ray crystallographic studies and DFT calculations indicate a pseudo-octahedral iron centre in 6. This, in addition to the diamagnetic nature of this compound, would indicate a lowspin d<sup>6</sup> Fe<sup>II</sup> electronic configuration, thus making this reaction a rare example of reversible two-electron oxidative addition

at an iron centre.<sup>13-15</sup> This further highlights the utility of the novel cationic tetrylene ligands employed here, in assisting otherwise challenging bond activation processes.

#### Accessing Open-Shell Ferrato-Tetrylenes



Figure 6. Cyclic voltammograms of complexes **3** (above) and **4** (below), in THF/ $[N(n-Bu)_4]PF_6$ , at a scan rate of 100 mV·s<sup>-1</sup>.

Despite the low-valent nature of both the tetryl and transition elements in complexes 3 and 4, we hypothesized that their reduction may be possible, given that sub-valent iron systems (viz. ferrates) are known.39 The most common such species are Fe<sup>-II</sup> species, which are stable due to their d<sup>10</sup> electronic configuration.<sup>39(b)</sup> On the other hand, formal Fe<sup>-1</sup> complexes are very rare indeed. This compound class is largely represented by ion-separated alkali metal ferrates, such as Ellis's [(n<sup>4</sup>-anth)<sub>2</sub>Fe][K(L)<sub>n</sub>].<sup>39(c)</sup> A number of reduced complexes derived from or relating to this ferrate involving redox active ligands are indeed known, whereby ligand reduction occurs. forming higher valent iron species.<sup>40</sup> Further examples of saltseparated anionic complexes, potentially featuring Fe<sup>-I</sup> centers have been reported by Peters et al., although the oxidation state at iron is not entirely clear, with potential reduction of employed ligands (e.g. borane, dinitrogen, and/or cyclicalkylaminocarbene).<sup>41</sup> Covalently bound Fe<sup>-1</sup> species remain elusive. In this regard, one-electron reduction of both 3 and 4 would lead to neutral ferrato-tetrylene complexes, featuring covalently bound, open-shell Fe-I centers.

We first investigated the electrochemistry of complexes **3** and **4**, as THF solutions against the ferrocene reference electrode (Fig. 6). Both complexes show chemically reversible reductionevents (Ge:  $E_{1/2} = -1.65$  V; Sn:  $E_{1/2} = 1.44$  V). Given that these values are roughly within the reduction potential of Cp\*<sub>2</sub>Co (Cp\* = [Me<sub>5</sub>C<sub>5</sub>]-),<sup>42</sup> we sought the chemical oneelectron reduction of both **3** and **4** with this soluble reducing agent. Reduction of the Ge<sup>II</sup> system led to formation of a deep red solution, with the precipitation of a pale yellow powder presumed to be [Cp\*<sub>2</sub>Co][BArF<sub>4</sub>]. Analysis of the reaction mixture by NMR spectroscopy revealed only highly broadened spectra indicative of paramagnetism in reaction products. Good yields of a single reaction product could be isolated as Scheme 1. Reduction of complexes 3 and 4, forming ferrato-stannylene 8, and ligand-activation product 7 (*inset*: molecular structure of 7).



deep red crystals, found to be the ligand activated product 7 (Fig. 7), formally a phosphido-iron(I) compound. We hypothesise that this forms via an intermediary ferrato-germylene 7', with an Fe<sup>-I</sup> centre, which oxidatively cleaves one P-Ph bond of the flanking ligand arm (Fig. 7).43 As such, this process represents another example of a formal two-electron oxidative addition at an Fe-I center. Complex 7 contains no formal Ge-Fe interaction ( $d_{Ge}$  = 3.432(2) Å); the NHC ligand has now migrated back to the iron(I) center, which also bears an  $\eta^{6-}$ arene interaction with the phenyl group located at Ge<sup>II</sup>. The formation of this product is testament to the high reactivity of the intermediate Fe<sup>-I</sup> species. Extending this chemistry to the Sn<sup>II</sup> system, we were surprised to find that in fact the tin congener of the target ferrato-tetrylene is indeed stable. Although reduction with  $Cp^*_2Co$  also led to the formation of a yellow precipitate, again presumably [Cp\*2Co][BArF4], isolation of meaningful quantities of a pure product proved challenging from these reaction mixtures. However, direct addition of two equivalents of the Fe<sup>0</sup> precursor to the cationic stannylene 2 proved to be reducing enough to form the ferrato-stannylene



Figure 7. The molecular structure of iron(-I) ferratostannylene **8**, with ellipsoids at 25% probability, and hydrogen atoms omitted for clarity (*inset:* HOMO-1, representing the Sn-centered lone electron pair). Selected bond lengths (Å) and angles (°) for **8**: Sn1-Fe1 2.6489(9); P1-Fe1 2.238(1); Sn1-N1 2.186(2); Sn1-C32 2.444(3); Sn1-Fe1-P1 96.06(2); Fe1-Sn1-N1 107.59(6); Fe1-Sn1-C32 86.34(6); N1-Sn1-C32 115.44(8).



Figure 8. *Above*: the DFT optimized structure of **8**, and a spindensity plot of **8**, orange showing areas of positive density, and purple negative. *Below*: the EPR spectrum of **8** as a frozen THF glass at 113K, overlaid with the simulated spectrum.

8 in moderate crystalline yields, following separation from cationic by-products through extraction and crystallization from pentane. The molecular structure of compound 8 is similar to that for the cationic germylene complex 3, in that the ligand's phosphine arm now chelates the formally Fe-1 center, and the NHC is now located on Sn<sup>II</sup>, with one Dipp fragment forming an n<sup>6</sup>-arene interaction with iron. The key difference is the coordination geometry at Sn<sup>II</sup>, which is now trigonal pyramidal due to the presence of a stereo-active lone pair of electrons (sum of angles =  $309.76^\circ$ ). This contrasts with that of the Ge<sup>II</sup> center in **3**, the planarity of which indicates  $Ge \rightarrow Fe$ electron donation (sum of angles = 359.8 °), and thus the absence of a formal bonding interaction. A notable contraction of the Sn-Fe bond distance is observed on moving from cationic **4** to neutral **8**, concomitant with a considerable decrease in the calculated polarization in this bond (Table 1). These observations point towards a formal covalent Sn-Fe bonding interaction in 8. The absence of any other redox-active ligand bound to the Fe center in this complex would lead to the formal oxidation states of Sn<sup>II</sup>/Fe<sup>-1</sup>. The paramagnetic nature of 8, ascertained by its <sup>1</sup>H NMR spectrum ( $\mu_{eff}$  = 2.38  $\mu_B$  using Evans method), indicates that this species is indeed an example of an open-shell metallo-tetrylene. To the best of our knowledge this represents the first example of such a compound, and indeed a unique example of a covalently bound iron(-I) complex. To gain further insights into the electronic nature of ferrato-stannylene 8, and to ascertain the location of the free electron in this species, a combination of SQUID magnetometry, and EPR and Mössbauer spectroscopy were employed, supported by DFT calculations. The EPR spectrum of a frozen glass of 8 in toluene (5 mM) yields a rhombic spectrum (Fig. 8). Supported by the simulated spectrum, three g-values of 2.0126, 2.0410, and 2.3050 are found, giving a giso of 2.1195, fitting well for an iron-centered electron.<sup>44</sup> Hyperfine coupling to <sup>31</sup>P, <sup>117</sup>Sn, and <sup>119</sup>Sn is clearly observable, the scales of which also indicate negligible radical character at these centers (Table S10).<sup>45</sup> Calculated spin-density plots of model

Table 1. Selected metrical, analytical, and calculated parameters for 4 and 8.

	4	
dsn-Fe, Å	2.717(1)	
Mössbauer	Isomer Shift, δ	0.777
	$\Delta E_{ m Q}$ , mm·s <sup>-1</sup>	1.349
Fe-Sn Bond Polarisation	Fe/Sn	24.23/75.77
Spin popula- tion, %	Fe/Sn	70.97/11.13
NPA charge	Sn/Fe/C	0.59/0.53/0.15
WBI	Sn-Fe/Fe-C	0.52/0.57
MBO	Sn-Fe/Fe-C	0.53/0.77
	8	
dsn-Fe, Å	2.6489(9)	
Mössbauer	Isomer Shift, $\delta$	0.520
	$\Delta E_{ m Q}$ , mm·s <sup>-1</sup>	1.574
Fe-Sn Bond Polarisation	Fe/Sn	58.19/41.81
Spin popula- tion, %	Fe/Sn	77.95/16.36
NPA charge	Sn/Fe/P	0.65/-0.19/1.02
WBI	Sn-Fe/Fe-P	0.78/0.73
MDO	Sn-Fe/Fe-P	0 82/0 80

complex 8' also infer a high degree of spin density at Fe (77.95%; Fig. 8).

The zero-field 57Fe Mössbauer spectrum of 8 exhibits an unsymmetrical quadrupole doublet with an isomer shift of  $\delta$  = 0.520 mm·s<sup>-1</sup>, and a large quadrupole splitting of  $\Delta E_q = 1.574$ mm·s<sup>-1</sup>. Although the isomer shift is typically considered the key parameter for the assignment of the oxidation state, the lack of reported Fe<sup>-1</sup> compounds limits the applicability of this tool in the present case, especially given that isomer shifts have also been found to depend on various other factors (ligand properties, ligation etc.).<sup>46</sup> In this regard,  $\mathbf{8}$  is compared perhaps most reasonably with compound **3**, which features a rather similar ligand scaffold around the iron center. Lowering the oxidation state from  $Fe^0$  to  $Fe^{-1}$  on going from 3 to 8 would be expected to lead to a shift of the isomer shift into the positive region. The lengthening of the iron-tetryl element bond in 8 compared to that in 3 should also lead to a more positive isomer shift, which is indeed the case. However, even more factors change (replacement of Ge by softer Sn, and transformation of a donor/acceptor bond into a covalent bond), so that it is advisable not to overinterpret these data. The same holds true for the quadrupole splitting that is comparable for both compounds. Looking now a magnetometry data, the inverse of  $\mu_{eff}$ , derived from SQUID measurements, shows a linear increase with increasing temperature (Fig. S46), in-keeping with Curie-Weiss magnetism, and again indicative of an iron-centered electron. The SQUID-derived magnetic moment for **8** ( $\mu_{eff}^{298} = 2.33 \mu_B$ ) is in keeping with that found in the solution state using the Evans method (2.38  $\mu_B$ ), and is considerably lower than that observed for cationic complex **4** (3.95  $\mu_B$ ), as is expected following a one electron reduction. Again, as for **4**, this is greater than the spin-only value expected for an s =  $\frac{1}{2}$  system, indicative of a degree of spin-orbit coupling in this compound.<sup>32</sup> With these key data in hand, it is clear that **8** bears a single unpaired electron, which is localized at the iron center in this compound, demonstrated primarily through EPR spectroscopy, and supported by DFT studies. As such, the data discussed here strongly support the formation of a molecular, covalent Fe<sup>-1</sup> compound in **8**, which is to the best of our knowledge the first example of such a species.

# CONCLUSIONS

We have presented facile synthetic routes for gaining access to unprecedented cationic-tetrylene complexes of iron(0). Intrinsic differences in the electronic nature of the Ge<sup>II</sup> and Sn<sup>II</sup> ligands leads to considerably different electronic states in the formed complexes: the Ge<sup>II</sup> system forms a low-spin, closed shell ground state, whilst the Sn<sup>II</sup> complex is has a highspin, open shell ground state. The high reactivity of the latter open shell system is demonstrated through the activation of dihydrogen, a process which is in fact reversible, and proceeds via a cooperative mechanism involving both Sn<sup>II</sup> and Fe<sup>0</sup> in the key bond scission step. Further, the described tetrylene iron(0) complexes prove to be ideal synthons for accessing hitherto unknown iron(-I) ferrato tetrylenes. Whilst the germanium system is unstable, undergoing ligand activation presumably through a two-electron oxidative addition process at iron, the Sn<sup>II</sup>-Fe<sup>-I</sup> system is a stable, crystalline compound. Thorough analysis of this unique species suggests a high degree of spin density at Fe, and highly covalent Sn-Fe bonding interaction, opening a new vista in low-valent d-block chemistry. Further expansion of this compound class is currently underway in our laboratories, to uncover the potential reactivity of these unprecedented species, with a focus on two electron oxidative addition processes which are typically challenging in iron chemistry.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.

All crystallographic data in CIF format (CCDC numbers 2202847-2202853); All experimental details, methods and spectra, details of X-ray crystallographic methods and summary of crystallographic data, and computational methods, as a single PDF document.

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#### **Author Contributions**

T.J.H. conceived the project, carried out preliminary experiments, and wrote the manuscript. P.M.K. carried out all other experimental work. A.S. and T.S. carried out computational work. K.W. conducted Mössbauer experiments. C.L. supported Mössbauer analyses, and aided in interpreting analytical data for low-valent iron complexes.

#### Notes

The authors declare no competing financial interests.

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