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Enhanced Fe-centered Redox Flexibility in Fe-Ti Heterobimetallic Complexes

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Abstract

Previously, we reported the synthesis of Ti[N(o-(NCH2P(Pr)2)C6H4)] and the Fe-Ti complex, FeTi[N(o-(NCH2P(Pr)2)C6H4)], abbreviated as TiL (1), and FeTiL (2), respectively. Herein, we describe the synthesis and characterization of the complete redox families of the monometallic Ti and Fe-Ti compounds. Cyclic voltammetry studies on FeTiL reveal both reduction and oxidation processes at −2.16 and −1.34 V (versus Fc/Fc⁺), respectively. Two isostructural redox members, [FeTiL]²⁺ and [FeTiL]²⁻ (2°² and 2°⁻², respectively) were synthesized and characterized, along with BrFeTiL (2-Br) and the monometallic [TiL]²⁺ complex (1°²⁺). The solid-state structures of the [FeTiL]²⁺⁻⁻ series feature short metal-metal bonds, ranging from 1.94–2.38 Å, which are all shorter than the sum of the Ti and Fe single-bond metallic radii (cf. 2.49 Å). To elucidate the bonding and electronic structures, the complexes were characterized with a host of spectroscopic methods, including NMR, EPR, ⁵⁷Fe Mossbauer, as well as Ti and Fe K-edge X-ray absorption spectroscopy (XAS). These studies, along with hybrid density functional theory (DFT) and time-dependent DFT calculations, suggest that the redox processes in the isostructural [FeTiL]²⁺⁻⁻ series are primarily Fe-based, and that the polarized Fe-Ti π-bonds play a role in delocalizing some of the additional electron density from Fe to Ti (net 13%).
Introduction

Iron is ubiquitous in a variety of catalytic transformations in biology, and is increasingly featured in synthetic processes as a viable alternative to toxic and/or precious metal catalysts. For the oxygen-activating Fe enzymes that functionalize aliphatic C-H bonds, Fe IV-oxo species are well established as key intermediates. The high-valent nature of the Fe oxo species and their synthetic models is supported by $^{57}$Fe Mössbauer spectroscopy and synchrotron-based methods. At the other extreme, sub-valent Fe species also show utility in organic transformations. For example, $[\text{Li(TMEDA)}]_2[\text{Fe(C}_2\text{H}_4)_4]$ is a precatalyst in cross-coupling reactions, and Collman’s reagent, $\text{Na}_2[\text{Fe(CO)}_4]$, is useful for a variety of organic transformations, including carbonylation, reductive coupling of two alkyl halides to form ketones, and the selective reduction of conjugated olefins. In general, the isolation of these formally Fe−II complexes requires strongly π-acidic ligands, with representative examples comprising 18-electron, homoleptic complexes supported by carbonyls, isocyanides, olefins, and trifluorophosphines. The spectroscopic, or physical, oxidation state of formally sub-valent Fe compounds, however, remains largely unstudied. In one case, a detailed investigation of the $[\text{Fe(C}_5\text{Me}_5)(\eta^4-\text{anthracene})]^+/0/−$ complexes revealed that the redox processes are primarily ligand-based and that the physical oxidation state remains FeI, thereby debunking the formal oxidation states of Fe I and Fe 0 in this series. Likewise, for Collman’s reagent, an alternative interpretation of an FeII center with reduced CO ligands has been proposed.

Another intriguing example of a formally sub-valent Fe complex is $[(\text{TPB})\text{Fe(N}_2)]^2−$, where TPB is tris((o-diisopropylphosphinophenyl)borane. The physical oxidation state assignment is complicated by the delocalization of electron density via the Z-type Fe→B σ-bonding interaction, in addition to π-back-donation from Fe to the phosphines and N2. The electronic configuration was represented by {FeB} 10, where the Feltham-Enemark notation allows for the possibility of electron delocalization across the FeB unit and reflects the ambiguity in the oxidation states at Fe and B.

We reasoned that formally sub-valent Fe centers could also be stabilized via direct bonding to an electropositive transition metal. This strategy would leverage metal-metal covalency to enhance redox flexibility at the Fe center. Specifically, the bonding between an early and late transition metal can be polarized to such an extent that the formal charges on the metals are zwitterionic. A notable example is (THF)Zr($\mu$-MesNP$i$Pr$_2$)$_3$Co(N$_2$), whose electronic structure is consistent with a Co−IZrIV core based on K-edge XAS data. Currently, we extend this concept to FeTi complexes, where the large electronegativity difference between Fe (1.80) and Ti (1.38) should also engender highly polarized Fe-Ti bonds where the electron density is mostly localized at Fe.

Previously, TiL (1) and FeTiL (2) were reported, albeit with limited characterization data. Here, we report the full synthesis and characterization of 1, 2, and their isostructural redox counterparts. Notably, the [FeTiL]$^{\text{III}}$ series exhibits a large variation in the Fe-Ti bond length between each redox member. Hence, this series makes for an interesting study because of the complex interplay between electronic structure and chemical bonding. The ambiguity of the metal oxidation states can be constrained by considering two limiting scenarios. By attributing the charge of the anionic donors solely to the bound metal, one would assign Ti$^{\text{III}}$, and hence FeI, Fe0, and Fe−I in [FeTiL]$^{\text{III}}$, respectively. On the other hand, the coordination chemistry of Ti is dominated by Ti$^{IV}$; thus, an alternative assignment is Fe0, Fe−I, and Fe−II, respectively. To obtain insights into the underlying electronic structures, a host of physical and spectroscopic studies were conducted, including CV, EPR, $^{57}$Fe Mössbauer, and multi K-edge XAS studies, as well as complementary DFT calculations.
Results and Discussion

Electrochemical Characterization of FeTiL (2)

The electrochemistry of complex 2 was probed using cyclic voltammetry (CV), as shown in Figure 1 (Fig. S1–S3). Complex 2 features a reversible reduction process at $-2.16 \text{ V versus } \text{Fc/Fc}^+$ (at 50 mV/s: $i_{pa}/i_{pc} = 0.96$, $\Delta E_p = 84 \text{ mV}$) and an oxidation event at $-1.34 \text{ V}$ (at 50 mV/s: $i_{pc}/i_{pa} = 1.02$, $\Delta E_p = 114 \text{ mV}$). As a comparison, the CV for the Ti monometallic complex, TiL (1), shows a Ti(III/IV) redox couple at $-1.57 \text{ V}$ ($i_{pc}/i_{pa} = 0.93$, $\Delta E_p = 174 \text{ mV}$ at 100 mV/s, Figure S4).

![Cyclic voltammogram of 2 in 0.4 M $[^6\text{Bu}_4\text{N}]\text{PF}_6$ in THF at a scan rate of 50 mV/s. For additional CV studies of 2, see Supporting Information Figures S1-S3.](image)

To understand the nature of the redox processes in 2, the redox potentials were compared to that of TiL (1), as well as to those of related Ti and/or bimetallic Fe–M complexes in the literature. Reports of Ti(III/IV) redox potentials are scarce, especially for complexes containing amido ligands. One notable example is the Ti(IV) complex, Ti($\kappa^2$–Me$_3$SiNCH$_2$CH$_2$NSiMe$_3$)$_2$,42 for which the Ti(III/IV) potential is estimated to be $-2.3 \text{ V versus Fc/Fc}^+$ based on the reported value of $-1.91 \text{ vs Ag/AgCl in THF}$.43-44 By comparison, the Ti(III/IV) potential for 1 is 760 mV more positive. However, this large potential difference may be ascribed to the overall anionic charge and the greater number of amide donors for $[\text{Ti}^{III}(\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{NSiMe}_3)]^-$. 

The oxidation process of 2 at $-1.34 \text{ V}$ is 230 mV more positive than that of 1. Upon incorporation of the low-valent Fe metal into 1, one might expect any localized Ti(III/IV) potential in the resulting bimetallic 2 to shift to more negative potentials compared to 1, because of the additional electron density being donated from Fe to Ti. In support, the Ti(III/IV) oxidation for the isostructural NiTiL complex occurs at $-1.90 \text{ V versus Fc/Fc}^+$ (Figure S5),45 which is 330 mV more negative than that of 1. Hence, we rule out the oxidation of 2 as being a Ti-centered redox process. We further propose that $2^{ox}$ contain an Ti(IV) center because an Fe(0)Ti(IV) assignment seems more reasonable than Fe(I)Ti(III). The case of 2 remains unclear because the $2^{ox}/2^{red}$ redox process can be either Fe-centered, e.g. Fe(0)/Fe(I/II), or delocalized across both transition metals, e.g. Fe(0)Ti(IV)/Fe(0.5)Ti(3.5).

The reduction process of 2 at $-2.16 \text{ V versus Fc/Fc}^+$ may also be considered along two limiting scenarios, where the reduction is centered on either metal, i.e. Ti(IV/III) or Fe(–I/–II). While the former may appear more plausible, the latter cannot be fully ruled out. One close analogue to 2 that has also been investigated by CV is (TPB)Fe(N$_2$), which undergoes two reductions at $-2.2$ and $-3.2 \text{ V versus Fc/Fc}^+$.23 The second reduction process, which corresponds to {FeB}, is exceedingly more negative than that observed for {FeTi}$^{10}$ $2^{red}$. However, one caveat is that {FeB}$^{10}$ is dianionic, whereas $2^{red}$ is monoanionic. Moreover, direct comparisons to (TPB)Fe(N$_2$) may have limited utility since the Fe→B dative bond is quite distinct from the multiply bonded Fe≡Ti complexes (vide infra). Another relevant
analogue is the N₂-labile Co alumatrane complex, (N₂)CoAIL, for which the “naked” [CoAIL]⁰⁻ reduction potential was measured at −2.10 V versus Fe⁺/Fe⁺⁺ under Ar.⁴⁶ This redox potential, which has a similar value to that of 2/2red, was assigned as a localized d⁹ Co(0)/d⁹ Co(−I) redox couple based on quantum chemical calculations.

Two other Fe-Ti systems have been reported in the literature: Ti(μ-XylNPPr₂)₃FeBr²⁷ and Ti(μ-NP)₃Fe / K₂[(κ¹−NP)Ti(μ-NP)₂Fe]³⁶, where Xyl is xylyl and NP is diphenylphosphinopyrrolide. Unfortunately, no CV data for these complexes were reported. However, we can draw comparisons to the isostructural FeVL and FeCrL complexes, which show [FeML]⁰⁻ reduction potentials at −2.85 V and −2.33 V, respectively. Intriguingly, the reduction potentials of the [FeML]⁰⁻ series, where M = Ti, V, and Cr, defy any periodic trend with respect to M because the potentials increase according to the order: M = V ≪ Cr < Ti. Our best explanation, so far, is that the redox potentials are strongly tied to the total d-d electron valence count, where counts of 10, i.e. {FeM}¹⁰, are strongly favored in these multiply bonded [FeML]ⁿ complexes. The energetic preference for d-d counts of 10 is sensible because it would correspond to an electronic configuration of (σ)²(2π)⁴(δx²−y², δxy)⁴,²⁹,³¹-³²,⁴⁷-⁴⁸ which maximizes the population of bonding and nonbonding molecular orbitals. Hence, the 2/2red reduction potential is the most mild because it favorably generates {FeTi}¹⁰, whereas the corresponding [FeVL]⁰⁻ reduction potential is the most harsh because generating {FeV}¹¹ from {FeV}¹⁰ is comparatively less favorable.

**Synthesis of FeTiL Redox Series**

The synthesis of the all redox members of the FeTiL family is shown in Scheme 1. As previously reported, complex 2 was prepared by mixing TiL (1), FeBr₂, and 2.1 equiv of the reductant, KC₈, in THF. Adding an additional equiv of KC₈ to 2 led to the further reduced member, [FeTiL]⁻, which was isolated as K(THF)₃[2red]. This synthetic route is preferred over the more direct reaction between FeBr₂, 1, and 3 equiv KC₈ because it avoids having to separate 2red from the KBr byproduct. In contrast, the synthesis of [FeTiL]⁺ (2ox) was less straightforward. Direct oxidation of 2 using [Fc]BArf₄ gave the desired product and a diamagnetic side product, which was independently identified as the monometallic complex, [TiL]BArf₄, or [1ox]BArf₄, where Arf = 3,5-(CF₃)₂-C₆H₃. An improved synthesis of 2ox was devised that involved the intermediacy of BrFeTiL (2-Br). The latter can be isolated from a comproportionation of 2 and “Br₂FeTiL”, which is generated in situ from mixing 1 and FeBr₂ in THF.⁴⁹-⁵₀ Next, attempts to abstract the bromide in 2-Br using NaBArf₄ in CH₂Cl₂ failed to provide 2ox, leading instead to pure 1ox. By changing the solvent to fluorobenzene, [2ox]BArf₄ was generated cleanly; however, we were unable to grow diffraction-quality single crystals. Installation of the highly crystalline dodecachlorododecaborate dianion⁵¹-⁵² (B₁₂Cl₁₂²⁻) through oxidation of complex 2 using Ag₃B₁₂Cl₁₂ allowed for the isolation of crystalline [2ox]₂B₁₂Cl₁₂.
Scheme 1. Synthetic routes to the Ti monometallic compounds (1, 1<sup>ox</sup>) and the bimetallic Fe-Ti complexes (2, 2<sub>red</sub>, 2-Br, and 2<sup>ox</sup>).

**X-ray Crystallography**

All redox members of the TiL and FeTiL series were characterized through single-crystal X-ray diffraction studies. The corresponding solid-state structures are shown in Figure 2, and relevant structural metrics are provided in Table 1 (for more bond lengths and angles, see Table S1). Additionally, the metrics for 2 are included for comparison. Comparing the structures of 1 and 1<sup>ox</sup>, the Ti−Neq bond lengths contract by ~0.05 Å upon oxidation of the Ti(III) center to Ti(IV), respectively. In addition, the Ti center moves farther above the N<sub>3</sub>-plane towards the phosphine donors with concomitant elongation of the Ti−N<sub>amine</sub> bond by 0.1 Å. The greater interaction of the Ti(IV) center with all three phosphine donors is observed in 2<sup>ox</sup> where the average Ti−P distance is 2.76 Å. On the other hand, only a single phosphine donor binds to the Ti(III) center in 1 (Ti−P = 2.7252(5) Å), while the other two Ti−P distances are greater than 3.0 Å.

In all the FeTi complexes, the Ti−Fe bond lengths are smaller than the sum of their single-bond metallic radii (2.489 Å), suggesting a strong interaction between Ti and Fe in these complexes. The formal shortness ratio (FSR), defined as the ratio of the measured intermetal distance to the sum of the metals’ single-bond radii, is useful to compare metal-metal bonding interactions between different bimetallic complexes. Typically, FSR values ≪ 1 denote metal-metal multiple bonding. The FSR values are all below unity (0.96 to 0.78) and decrease in the following order: 2-Br > 2<sup>ox</sup> > 2 > 2<sub>red</sub>. With each successive reduction, or increase in the total d-d count from 8 to 10, the Ti−Fe bond contracts. Another geometric ramification of the strengthening of the Ti−Fe bond is gleaned by comparing the distance of the Fe center to the P<sub>3</sub>-plane, in which Fe is slightly above the plane in 2<sup>ox</sup>, within the plane in 2, and below the P<sub>3</sub>-plane in 2<sub>red</sub>. Of note, 2<sub>red</sub> is among only a handful of first-row heterometallic complexes with metal-metal bond lengths shorter than 2.0 Å. Additionally, the Ti−Fe bond length of 1.9494(6) Å in 2<sub>red</sub> is close to that of K₂[(κ<sup>1</sup>−NP)Ti(μ-NP)<sub>2</sub>Fe], which currently has the shortest Ti−Fe bond in a coordination complex of 1.9474(7) Å (Table S2). Additionally, the FSR value of 0.78 for 2<sub>red</sub> is identical to that of the isostructural MnCrL complex, which formally contains a quintuply bonded Mn-Cr unit.

2<sub>red</sub> = BA<sub>F</sub>₄ or 0.5 B<sub>12</sub>C<sub>12</sub>
Figure 2. Solid-state structures of [TiL]^{0/+} (1, 1^{ox}), [FeTiL]^{0/+} (2^{red}, 2, 2^{ox}), and BrFeTiL (2-Br). Thermal ellipsoids are shown at 50% probability. Hydrogen atoms, non-coordinating solvents, and counterions are omitted for clarity. Titanium, green; iron, brick-red; phosphorus, orange; nitrogen, blue; and bromine, brown. The Ti−Fe bond distances (Å) are shown in red, while Ti−N (avg.), Ti−N_{amine}, Fe−P (avg.), and Fe−Br bond distances are shown in blue.

Table 1. Selected bond lengths (Å), bond angles (deg), and other relevant metrics for [TiL]^{0/+} (1, 1^{ox}) [FeTiL]^{0/+} (2^{red}, 2, 2^{ox}), and BrFeTiL (2-Br).

|       | 1   | 1^{ox} | 2^{red} | 2 | 2^{ox} | 2-Br |
|-------|-----|--------|---------|--|--------|------|
| Ti−Fe | N/A | N/A    | 1.9494(6)| 2.0635(6)| 2.0458(8) | 2.1613(10)| 2.3853(4) |
| FSR   | N/A | N/A    | 0.78     | 0.83     | 0.82     | 0.87 | 0.96 |
| d-count | 1  | 0      | 10       | 9         | 8        | 8    |     |
| Fe−P₃ | N/A | N/A    | 2.1234(9) | 2.2872(14) | 2.2856(16) | 2.3609(10) | 2.3888(10) |
| Fe to P₃ Plane | N/A | N/A | -0.1431(6) | -0.0373(5) | 0.0208(7) | 0.1429(9) | 0.3578(4) |
| Ti−N_{eq} | 2.0149(25) | 1.9663(7) | 2.051(3) | 2.016(3) | 2.019(5) | 1.998(3) | 1.9956(27) |
| Ti to N₃ Plane | 0.4743(8) | 0.5580(26) | 0.5231(15) | 0.4677(13) | 0.4568(15) | 0.4504(24) | 0.4888(9) |
| Ti−N_{amine} | 2.2697(13) | 2.366(2) | 2.423(3) | 2.340(2) | 2.328(2) | 2.297(4) | 2.3537(15) |
| Ti−P | 2.7252(5) | 2.7609(12) | N/A | N/A | N/A | N/A | N/A |
| P−Fe−P | N/A | N/A | 118.67(3) | 112.49(10) | 107.95(10) | 114.12(11) | 112.73(12) | 115.07(5) | 114.35(7) |
| P−Fe−P | N/A | N/A | 118.67(3) | 112.49(10) | 107.95(10) | 114.12(11) | 112.73(12) | 115.07(5) | 114.35(7) |
| Fe−Ti−N_{amine} | N/A | N/A | 179.33(7) | 178.40(7) | 179.45(7) | 180 | 178.69(4) |
| N_{eq}−Ti−N_{eq} | 115.73(6) | 112.49(10) | 107.95(10) | 114.12(11) | 112.73(12) | 115.07(5) | 114.35(7) |
In these complexes, the first coordination sphere of each metal was scrutinized to assess whether redox changes occur at Ti, Fe, or both metal sites. In the Fe-Ti bimetallic complexes, the Ti–N_{eq} bond length elongates in the order: 2-Br ≈ 2^{ox} < 2 < 2^{red}. Additionally, the average Fe–P bond length contracts in the same order, with 2^{red} possessing the shortest Fe–P bond distance in the series. In considering the isostructural complexes, the contraction of the Fe–P bond distances from 2^{ox} to 2 to 2^{red} is consistent with increasing Fe–P π-back-bonding upon reduction of the FeTi core. Interestingly, plotting both the average Ti–N_{eq} and Fe–P bond distances versus total electron count for each complex show excellent correlations ($R^2 > 0.99$; Figure S13-S14). However, the overall change in Fe–P bond distances is greater (Δ = 0.15 Å) than that of the Ti–N_{eq} bond distances (Δ = 0.05 Å), suggesting that Fe is perturbed to a larger extent than Ti upon reduction. We note that these bond length changes cannot be accounted for solely by the polarizability difference between P and N. For instance, the [FeCrL]^+/0/− complexes show the opposite trend in that the Cr–N_{eq} bond lengths vary more significantly (Δ = 0.14 Å) than the Fe–P bonds (Δ = 0.02 Å) across the series. Finally, close examination of the P–Fe–P bond angles in the solid-state structure of 2 shows a significant distortion from C_{3v}-symmetry, with one P–Fe–P angle being much larger than the rest (~128°). This suggests the complex has undergone a Jahn-Teller distortion arising from an unpaired electron that is localized at Fe in what would have otherwise been a degenerate pair of orbitals (vide infra).

**NMR and EPR Spectroscopy**

Complexes 1^{ox} and 2^{red} are diamagnetic, and the remaining complexes are paramagnetic. The $^1$H NMR spectrum of 1^{ox} and 2^{red} each show a total of 11 unique peaks for the ligand protons, including 4 aryl, 2 diastereotopic methylene, 1 methine, and 4 unique methyl protons. This is most consistent with the complex possessing $C_3$ symmetry in solution, as a fully “locked” $C_3$-symmetric complex would display a total of 12 resonances. The $^1$H NMR spectrum of 2, with 12 unique resonances, is fully consistent with $C_3v$ symmetry. In contrast, complexes 2-Br and [2^{ox}]BAr$_4^-$ only show 7 and 5 paramagnetically-shifted resonances (excluding BAr$_4^-$ protons), respectively. The fewer number of resonances may indicate an average $C_{3v}$ symmetry, which results from the fast exchange between the two propeller orientations, or that some signals are no longer observable due to paramagnetic broadening. Using Evans’s method, the solution magnetic moments of 2-Br and [2^{ox}]BAr$_4^-$ were determined to be 2.97(7) and 2.99(8) μ$_B$, respectively, which are consistent with $S = 1$ ground states (cf. spin-only $μ = 2.83$ μ$_B$).

The $S = \frac{1}{2}$ spin state of 2 was confirmed by X-band EPR spectroscopy. As shown in Figure 3, the EPR spectrum of 2 at 20 K features a pseudo axial signal with $g = (2.27, 2.05, 2.03)$, where the $g_{avg}$ of 2.12 is greater than that of a free electron ($g_e ≈ 2.002$). Similar $g$-values were observed for the related {FeM}$^9$ complexes: [(N$_2$)FeAlL], (2.20, 2.04, 2.04); [FeVL]$^+$, (2.23, 2.08, 2.04); BrFeV(μ-2-iPr$_2$NPPh$_2$)$_3$, (2.13, 2.10, 2.06). Additionally, a four-line hyperfine coupling pattern was discerned near $g_\perp$, which can be attributed to hyperfine coupling with three chemically equivalent $^{31}$P ($I = \frac{1}{2}$) nuclei, where $A_{avg}^{(31)}$P is 62 MHz (for more simulation details, see Fig. S15-S16). Unfortunately, the $^{31}$P hyperfine coupling interactions for the other {FeM}$^9$ bimetallic compounds were not resolved by X-band EPR spectroscopy. The next best comparisons are [NiAlL]$^-$ and [NiGaL]$^-$, for which $A_{avg}^{(31)}$P is 35 and 38 MHz, respectively. Of note, the unpaired spin is delocalized across both the Ni and Al/Ga centers. Hence, the larger $A_{avg}^{(31)}$P value for 2 is consistent with a localized Fe-based spin. As a control, the X-band EPR spectrum of 1 (Figure S17) shows an isotropic signal with $g_{iso} = 1.95$, which is consistent with

| 113.54(6) | 111.31(10) | 116.92(10) | 114.38(11) | 117.99(12) | 115.07(5) | 113.45(7) |
| 114.64(6) | 113.04(10) | 116.23(10) | 115.86(11) | 114.40(12) | 115.07(5) | 114.82(6) |

*Two molecules in the asymmetric unit. Average of the three values.*
other Ti(III) complexes in the literature.\textsuperscript{68-70} Overall, the $A_{avg}^{(31P)}$ value, the fact that $g_{avg} \gg g_e$, and that $g_l \gg g_\perp$ indicate that the unpaired electron is localized in an Fe-based $d$-orbital in the $xy$-plane.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{X-band EPR spectrum (9.65 GHz, 10 G, 6.33 μW) of 2 at 20 K in frozen toluene (1 mM). Experimental spectrum is shown in black, while the simulated spectrum is shown in red. Simulation parameters for 2: $g = (2.273, 2.051, 2.028)$, $A(3\times31P) = (24.0, 17.4, 21.0) \times 10^{-4}$ cm$^{-1}$, or $(71.9, 52.2, 63.0)$ MHz. For alternative EPR simulations of this spectrum, see Figure S15.}
\end{figure}

\textit{DFT calculations}

Single-point hybrid density functional theory (DFT) calculations were carried out to elucidate the electronic structures of 2$^{ox}$, 2, and 2$^{red}$ (see Experimental Section for details). The frontier molecular orbital (MO) diagrams are presented in Figure 4, and the corresponding orbital coefficients are given in Table 2. It should be noted that the selected MOs for 2$^{red}$ in Figure 4 are also representative of those for 2$^{ox}$ and 2. Complete MO lists are available in Table S4 and Figure S19. All 3 complexes display polarized Fe-Ti bonding MOs, albeit with differing Ti contributions: two π-bonds (1e) comprising the Fe and Ti $d_{xz}/d_{yz}$ orbitals, and a σ-bond (1a$_1$) between the Fe and Ti $d_{z^2}$ orbitals. The Fe $d_{xy}$ and $d_{x^2-y^2}$ (2e) orbitals, on the other hand, are localized, precluding any Fe-Ti δ-bonds. Previously, polarized triple bonds were predicted for related heterobimetallic complexes, where bond polarization increases as the two metals’ groups are further separated on the periodic table.\textsuperscript{19,22,25} Also of interest, the LUMO (2a$_1$) is similar across the series and has contributions from the Fe 4$p$, P 3$s$/3$p$, and Ti 3$d_{z^2}$ orbitals. The Fe 4$p$ and Ti 3$d_{z^2}$ contributions in the LUMO increase in the order of 2$^{red}$, 2, and 2$^{ox}$, and hence, are largest for the most oxidized Fe-Ti species, 2$^{ox}$. The presence of an energetically low-lying metal-based $p$-orbital has also been invoked in Ni$^{0}$ and Co$^{-1}$ bimetallic complexes bearing a group 13 metalloligand.\textsuperscript{71-72} In this work, the 2a$_1$ LUMO is important because it is the acceptor orbital for electronic transitions observed by Fe K-edge XAS in the pre-edge region (\textit{vide infra}).
Figure 4. (Top) DFT-predicted electronic structures of $2^{ox}$ (left), 2 (middle) and $2^{red}$ (right). See Table 2 footnotes for computational details. (Bottom) Representative molecular orbitals from $2^{red}$ represented by quasi-restricted orbitals.
Table 2. Molecular orbital composition analyses\(^a\) for \(2^{ox}\), \(2\) and \(2^{red}\).\(^b\)

| orbital     | \(2^{ox} (S = 1)\) | \(2^e (S = \frac{1}{2})\) | \(2^{red} (S = 0)\) |
|-------------|---------------------|--------------------------|---------------------|
|             | % Fe 3d | % Fe 4p | % Ti 3d | % P\(^d\) | % Fe 3d | % Fe 4p | % Ti 3d | % P\(^d\) | % Fe 3d | % Fe 4p | % Ti 3d | % P\(^d\) |
| 1e \(\pi (d_{xz},d_{yz})\) | 76 0 | 13 3 | 65/66 | 1/1 | 22/20 | 6/7 | 58 1 | 26 8 |
| 1a\(_1\) \(\sigma (d_{z^2})\) | 72 3 | 15 1 | 69 3 | 3 17 | 1 | 66 5 | 19 1 |
| 2e \(\text{Fe}(d_{x^2-y^2},d_{xy})\) | 83 4 | 0 7 | 76/75 | 4/6 | 20 14/10 | 64 5 | 3 19 |
| 2a\(_1\) LUMO | 4 28 | 13 16 | 1 24 | 9 21 | 0 19 | 9 25 |

\(^a\)Löwdin population analysis. \(^b\)Single-point calculations were performed on structures (obtained from crystallographic coordinates where only the H atom positions were optimized, see Experimental Section for details) at the B3LYP level of theory with the CP(PPP) basis set for Fe and def2-TZVP for all other atoms. The contribution of Ti 3d orbitals into bonding MOs are marked in bold. \(^c\)Due to the Jahn-Teller distortion in \(2\), the “1e” and “2e” MOs are not degenerate. Hence, two values are given. \(^d\)%P are the sum of s, p, and d contributions from phosphorus.

Complex \(2^{ox}\), with an electronic configuration of \((1e)^2(1a\(_1\))^2(2e)^2\), is best described as an Fe\(^0\) center \((S_{\text{Fe}} = 1)\) bound to a Ti\(^{IV}\) ion, due to the limited Ti participation in the 1e and 1a\(_1\) MOs (13 and 15%, respectively). Upon reduction, the additional electron(s) are predicted to occupy the Fe \(d_{xy}\) and \(d_{x^2-y^2}\) \((2e)\) orbitals. Hence, the reduction to \(2\) and \(2^{red}\) may be viewed as Fe-centered reductions, resulting in electronic structures that approach Fe\(^{IV}\) and Fe\(^{II}\), respectively. The reduced Fe centers are likely stabilized by \(\pi\)-back-bonding to the phosphine moieties as well as increasingly covalent \(\pi\)-bonding with the Ti support. These effects can be observed in the increasing contributions of P in the 2e MOs (from 7% in \(2^{ox}\) to 19% in \(2^{red}\), as well as Ti in the 1e MOs (from 13% in \(2^{ox}\) to 26% in \(2^{red}\)). The latter can be reasoned to manifest from a) electrostatic attraction of Fe bearing negative charge to the electropositive Ti center as well as b) improved energetic matching between atomic Ti and Fe 3d orbitals. These points are evidenced by the contraction of the Fe–Ti bond, which shortens by \(\sim 0.1\) Å per electron, and of the Fe-P bonds \(\sim 0.07\) Å per electron. As an aside, the presence of unequal number of electrons in the \(d_{xy}\) and \(d_{x^2-y^2}\) orbitals of \(2\) leads to a Jahn-Teller distortion manifesting in unequal P–Fe–P angles and reflected in the non-degeneracy of the \(d_{xy}/d_{yz}\) and \(d_{x^2-y^2}/d_{xy}\) pairs.
The FeTiL complexes were characterized by zero-field $^{57}\text{Fe}$ Mössbauer spectroscopy at 80 K (Figure 5). Notably, each reduction of the isostructural Fe-Ti complex is accompanied by a decrease in isomer shift ($\delta$), where there is a reasonable linear correlation between the isomer shift and the total $d$-$d$ count ($R^2 = 0.95$, Figure S22). The observed trend in the FeTiL series is also consistent with decreasing $\delta$ as the metal-metal interaction strengthens (i.e. decreasing FSR, $R^2 = 0.96$, Figure S23), which was previously noted by Thomas and co-workers for the Fe-M bimetallic families, where M is Nb, Ti, or V.\textsuperscript{27,48,73} Surprisingly, the $\delta$ trend in the [FeTiL]$^{+}/0/-$ series is different from that observed for the isostructural FeV$\text{L}$ and FeCrL series. For example, FeV$\text{L}$ and [FeV$\text{L}$]$^+$ have identical isomer shifts, despite EPR evidence supporting an Fe-based redox change (Table S7; Figure S24).\textsuperscript{31} For the FeCrL redox series, $\delta$ increases upon reduction (Figure S25).\textsuperscript{29,64} Also of relevance, 2-Br has a much higher isomer shift compared to the isoelectronic [2$^{ox}$]BArF$_4$, which demonstrates the dramatic effect on $\delta$ that a differing coordination geometry can have. The $\delta$ of 2-Br is reasonably close to that of Ti(µ-XylNPPr$_2$)$_3$FeBr (c.f. 0.51 mm/s), which shares an identical primary coordination sphere around Fe.\textsuperscript{27} Lastly, the isomer shift for 2 is identical to that observed in the [(N$_2$)FeAlL]$^-$ complex ($\delta = 0.38$ mm/s), which was shown to possess an Fe$^{-1}$ center.\textsuperscript{66} It should be noted, however, that the presence of a π-acid (N$_2$) in [(N$_2$)FeAlL]$^-$ would also influence $\delta$.

![Figure 5](image.png)

**Figure 5.** Zero-field $^{57}\text{Fe}$ Mössbauer spectra of the Fe-Ti bimetallic complexes at 80 K. Experimental data are shown using black dots, while the simulated spectra are shown in red. The asymmetry of the doublet from complex 2 was fit using a slightly different line-widths for each peak: 0.41 (left) and 0.56 (right) mm/s.

The magnitude of the quadrupole splitting parameter ($|\Delta E_Q|$) in the [FeTiL]$^{+}/0/-$ series increases with each successive reduction. Of note, this heterobimetallic series currently holds the largest variation in $|\Delta E_Q|$ across isostructural redox members, from a modest value of 0.79 mm/s for 2$^{ox}$ to a considerably large splitting of 4.32 mm/s for 2$^{red}$. To complicate matters, the isostructural Fe-Cr and Fe-V redox series consistently exhibit large quadrupole splitting (4.04 to 5.97 mm/s), whereas similar Fe-M bimetallic complexes supported by tris(phosphinoamido) ligands consistently display smaller $|\Delta E_Q|$ values (0.17 to}
2.13 mm/s). Thus, we turned to theory to gain a better understanding of how the electronic configurations of these bimetallic complexes influence the Mössbauer parameters.

$^{57}$Fe isomer shift

As tabulated in Table 3, the computed Mössbauer parameters (B3LYP; see experimental section for details) show reasonable agreement with the experimental data. More excitingly, the computations reproduce the experimental trend that the isomer shifts of $2^{ox}$, 2 and $2^{red}$ decrease upon reduction, while $|\Delta E_Q|$ increases.

| complex | $\delta$ (exp.) | $\delta$ (calc.) | $|\Delta E_Q|$ (exp.) | $|\Delta E_Q|$ (calc.) | $\eta$ (calc.) |
|---------|----------------|----------------|-----------------------|-----------------------|----------------|
| $2^{red}$ | 0.31 | 0.37 | 4.32 | +3.61 | 0 |
| 2 | 0.38 | 0.41 | 2.53 | +2.09 | 0.28 |
| $2^{ox}$ | 0.41 | 0.44 | 0.79 | +0.40 | 0 |

The $^{57}$Fe isomer shift, which is proportional to the $s$-electron density at the Fe nucleus (albeit with a negative slope), has been shown to primarily be affected by changes in the valence $4s$ electron population. The impact of an oxidation state change on the isomer shift can be understood by considering two primary effects, which have been classified as “electronic” and “geometric”. The electronic effect pertains to changes in the $d$-count, where adding 3$d$-electron(s) increasingly shields the $4s$ electrons, resulting in larger $\delta$. Geometric effects refer to structural perturbations, such as changes in metal-ligand bond lengths. For low-valent Fe complexes, contraction of metal-ligand bonds via π-back-bonding upon reduction lowers $\delta$. Hence, the electronic and geometric changes may exert opposing influences in low-valent Fe compounds, and their relative importance determines the directional change in $\delta$.

To better dissect the contribution of both factors, we devised two hypothetical molecules, $2^*$ and $2^{ox*}$. These in silico complexes were generated by removing an electron from $2^{red}$ and 2, respectively, and optimizing the wavefunction while constraining the molecular geometry. Hence, $2^*$ and $2^{ox*}$ have the $d$-count of 2 and $2^{ox}$, respectively, but have the geometry of $2^{red}$ and 2, respectively. Following this method, the isomer shifts of $2^*$ and $2^{ox*}$ should reflect only the electronic impact of removing an electron. As shown in Figure 6, the electronic and geometric effects give rise to opposing trends in $\delta$. More importantly, the geometric effect is dominant in the [FeTiL]$^{+0/-}$ series, which rationalizes the observed trend of decreasing isomer shift upon reduction.
**Figure 6.** Calculated Mössbauer isomer shift after separate electron removal (green arrow) and subsequent geometric reorganization (purple arrow) steps. $2^* (\delta = 0.32 \text{ mm/s})$ and $2^{\text{ox}*} (0.33 \text{ mm/s})$ are hypothetical complexes that are generated by removing an electron from $2^{\text{red}}$ and 2, respectively. See experimental section for details.

**Quadrupole splitting**

The quadrupole splitting, $\Delta E_Q$, reflects the interaction of the non-spherically distributed nuclear charge of the $^{57}\text{Fe}$ nuclear excited state ($I=3/2$) with the surrounding electric field gradient (EFG). The quadrupole splitting is calculated according to the equation,

$$\Delta E_Q = \frac{1}{2} eQ V_{zz} \left(1 + \frac{\eta^2}{3}\right)^{1/2},$$

where $eQ$ is the quadrupole moment of the iron nucleus, $\eta$ is the asymmetry parameter such that $\eta = \frac{v_{xx} - v_{yy}}{v_{zz}}$, and $V_{ii}$ are the eigenvalues of the EFG tensor at the nucleus. If the principal z-axis of the EFG tensor is colinear with a $C_3$ axis, then the equation simplifies to: $\Delta E_Q = \frac{1}{2} eQ V_{zz}$, since $V_{xx} = V_{yy}$ and $\eta = 0$. The trigonal symmetry of both $2^{\text{ox}}$ and $2^{\text{red}}$ motivates our focus on $V_{zz}$ in elucidating the origin of both the anomalously large quadrupole splitting measured in $2^{\text{red}}$, as well as the wide variation of $|\Delta E_Q|$ in the $[\text{FeTiL}]^{+0-}$ series (Table 3). Even in the case of 2, which displays Jahn-Teller distortion, a calculated $\eta$ value of 0.28 is still reasonably close to zero to allow for meaningful comparisons.

$V_{zz}$ can be broken down into individual multi-center interactions that contribute significantly to the EFG at the Fe nucleus:76,80

$$V_{zz}^{\text{total}} = (V_{zz}^{1\text{c,core}} + V_{zz}^{1\text{c, valence}}) + (V_{zz}^{2\text{c,bond}} + V_{zz}^{2\text{c,lattice}}) + V_{zz}^{3\text{c}}$$

The first two terms represent one-center contributions to the EFG from Fe-based electrons, where one can separately consider the contributions of the core ($1s$ to $3p$) and valence ($3d$) electrons. Smaller valence contributions to the EFG can also arise from the mixing of Fe orbitals into ligand-based MOs. The next pair of terms arise from two-center interactions with the ligand-based electrons. Again, one can segregate contributions from electrons that are directly bonded to Fe and those that act as point-charges, which are denoted as “lattice”. The last term represents three-center contributions, which typically have a negligible impact on $V_{zz}$. 
Table 4 summarizes the individual contributions of the $V_{zz}$ for the [FeTiL]$^{+0-}$ series (for the orbitals used for these calculations, see Figure S27-S29). The DFT-calculated values show three dominant terms: $V_{zz}^{1c,core}$, $V_{zz}^{1c,valence}$, and $V_{zz}^{2c,bond}$. Interestingly, the $V_{zz}^{1c,core}$ term for $2^{ox}$, $2$ and $2^{red}$ are found to be atypically large, with values ranging from 0.62–0.84 a.u. in this series. It should be noted that the polarization of core electrons is difficult to achieve, and typically requires strong metal-ligand bonding, for instance, FeIV-oxo species. Presumably, the presence of the Fe-Ti bonding is sufficient to induce distortion of the inner-shell electron density, which by proximity to the Fe nucleus, can result in a sizeable EFG. To the best of our knowledge, the polarization of core electrons has never been elucidated in complexes featuring metal-metal multiple bonds. The $V_{zz}^{2c,bond}$ term, on the other hand, is expected to be significant for low-valent Fe complexes because metal-ligand bonds are typically short and covalent. For $2^{ox}$, $2$ and $2^{red}$, this contribution is traced to the lone-pair electrons on the phosphine donors, which is reflected by the presence of Fe $p_x$, $p_y$, $d_{xy}$ and $d_{x^2-y^2}$ character in the P-based σ-bonding orbitals. Lastly, the $V_{zz}^{1c,valence}$ term is intriguing because it is largely responsible for the large variations in $V_{zz}$, and hence, $\Delta E_Q$ in this series. For the valence contributions, any charge that is localized perpendicular to $V_{zz}$ (e.g. Fe $d_{xy}$, $d_{x^2-y^2}$) yields a positive contribution to $V_{zz}$, whereas any charge parallel to $V_{zz}$ (e.g. Fe $d_x$, $d_y$, $d_z$) yields a negative contribution. Throughout the redox series from $2^{ox}$ to $2$ to $2^{red}$, the Fe $d_{xy}$ and $d_{x^2-y^2}$ orbitals become increasingly occupied. Hence, the most positive $V_{zz}^{1c,valence}$ contribution is predicted for $2^{red}$, which is consistent with $2^{red}$ having the largest $|\Delta E_Q|$ in the series. Moreover, the $V_{zz}^{1c,valence}$ term could rationalize the consistently larger $|\Delta E_Q|$ values for the isostructural FeCr and FeV redox members, for which the Fe $d_{xy}$ and $d_{x^2-y^2}$ orbitals are fully occupied in all but one case, [FeVL]$^+$. 

Table 4. Computed $V_{zz}$ values (in a.u.) for $2^{ox}$, $2$ and $2^{red}$ and the contributions from the core and 3$d$ electrons.

| Complex | $V_{zz}^{1c,core}$ | $V_{zz}^{1c,valence}$ | $V_{zz}^{2c,bond}$ | $V_{zz}^{2c,lattice}$ | $V_{zz}^{2c}$ | $V_{zz}^{total}$ |
|---------|---------------------|------------------------|-------------------|-----------------------|---------------|----------------|
| $2^{ox}$ | 0.84                | -1.18                  | 0.54              | 0.02                  | 0.02          | 0.24           |
| $2$     | 0.70                | -0.04                  | 0.57              | 0.01                  | 0.03          | 1.27           |
| $2^{red}$ | 0.62               | 0.60                   | 0.94              | 0.02                  | 0.03          | 2.21           |

XAS Studies

The Fe and Ti K-edge XAS for $2^{red}$, $2$, $2^{ox}$, and $2-Br$ (Figure 7a-b) were obtained to further unravel any ambiguities distinguishing their physical from their formal oxidation states. Because rising edge energies are often insufficient metrics of physical oxidation state, the discussion mainly focuses on the pre-edge regions. Overall, the experimental K-edge pre-edge features are well-reproduced using time dependent DFT (TD-DFT) calculations (Figures 7c, 7d and S34-S43), which serves as the bases for the interpretations provided below. The strong correlation ($R^2 = 0.95$ and 0.82 for Fe and Ti, respectively, Fig. S30) between calculated and experimental pre-edge features affords confidence in using the underlying single point calculations to assign transitions from Fe or Ti 1s to particular acceptor MOs (to compare the results from these computational methods to those presented above, see Figure S20 and Table S5). These assignments are presented in Table 5 (Table S9 and Figure S44-S51).

The Fe K-edge XAS of $2^{red}$, $2$, and $2^{ox}$ all exhibit a well-resolved pre-edge absorption feature near 7112 eV (Figure 7a). Typically, pre-edge features in first-row transition metal K-edge XAS arise from...
quadrupole-allowed 1s → 3d excitations, which can gain intensity from 4p admixture, or from excitations
to low-lying ligand-based MOs. In the present case, the substantial Fe 4p_z character in the acceptor MO
(LUMO 2a_1, Figure 4) is responsible for the high intensity of the pre-edge peaks in 2_red, 2, and 2_ox. Notably,
2-Br, which does not share this LUMO (Figure S21), lacks an intense pre-edge feature. (For more detailed
assignments, see Table S9).

Importantly, for 2 and 2_ox, an additional transition was observed (and predicted) as a lower energy
shoulder to the intense pre-edge peak, which is absent for 2_red (red trace, Figures 7a and 7c). This feature is
assigned to the Fe 1s → 2e (Fe 3d_{x^2-y^2}, 3d_{xy}) transition. Moreover, its absence in 2_red confirms the filling of
Fe-localized valence vacancies present in 2 and 2_ox, which substantiates the hypothesis that the redox
changes are Fe-based. In further support, the electronic absorption spectrum of 2_red lacks any transitions at
wavelengths longer than 900 nm, which suggests the absence of any d-d transitions, consistent with a fully
filled valence shell. In contrast, both 2 and 2_ox display band(s) in the near infrared region that can plausibly
be assigned as d-d transitions (Figure S18, Table S3).

Figure 7. Overlaid K-edge spectra of Fe (a; experimental and c; TD-DFT calculated) and Ti (b;
experimental and d; TD-DFT calculated) for complexes 2 (black), 2_red (red), 2_ox (grey) and 2-Br (blue). All
data were obtained on solid samples diluted in BN and maintained at 10 K.
Table 5. Experimental Fe and Ti pre-edge peak energies† and peak assignments for FeTi redox series. (For more detailed transition assignments, see Table S9.)

| Transitions* | Fe Pre-edge Peak Energy (eV) | Ti Pre-edge Peak Energy (eV) |
|--------------|-----------------------------|-----------------------------|
| 2_red        | Fe 1s → 2a_1                | Fe 1s → 2e                  | Ti 1s → 3e/4e               | Ti 1s → 2a_1               |
|              | 7111.8                      | N/A                         | 4967.3                     | 4969.1                     |
| 2            | 7112.2                      | 7110.1                      | 4968.3                     | 4969.3                     |
| 2_ox         | 7112.8                      | 7110.6                      | 4968.5                     | 4969.7^e                   |
| 2-Br         | 7111.0^f; 7113.1^g; 7114.3^h|                             | 4968.3^i                   |

†Pre-edge peak energies are obtained from the corresponding 2nd derivative plots of the K-edge XAS spectrum. *Primary orbital contribution. In some cases, the transitions also include additional contributions from the following MOs: ^a 3a_1; ^b 2e and 3e; ^c 3e
and aromatic π*; ^d 3a_1, 4e, and aromatic π*; ^e 3a_1, 3e, 4e, and aromatic π*.

The Ti K-edge XAS data of 2_red, 2_ox and 2-Br (Figure 7b) all exhibit two main pre-edge features with similar intensities in the range 4967.3–4969.3 eV (Table 5). On the basis of TD-DFT, the lower energy feature in the Ti XAS of the isosstructural FeTiL complexes is assigned as the Ti 1s → 3e/4e (Fe-Ti π*/Ti 3d_{x^2-y^2}, 3d_{xy}) transition, while the higher energy feature is assigned as the Ti 1s → 2a_1 (LUMO) transition. The latter feature allows a useful comparison to the Fe 1s → 2a_1 transition because they both share a common primary acceptor orbital. Notably, the energy shift of the Fe 1s → 2a_1 transition across the redox states (∆ = 1.0 eV) is greater than that of the corresponding Ti 1s → 2a_1 transition (∆ = 0.6 eV). Of note, Thomas and co-workers have observed a similar 0.5 eV variation in the Zr K-edge energies of several heterobimetallic ZrCo complexes, for which the ZrIV oxidation state is invariant and Co is the redox-active center.35 Hence, the comparison of the energy shifts for the Is → 2a_1 excitations points to Fe as the redox active site.

One counterargument is that the first pre-edge feature in the Ti XANES of the isosstructural redox series also has a sizeable shift (∆ = 1.2 eV). However, these transitions are more complex in nature, involving multiple Ti 3d-based orbitals. Also of note, the plot of the pre-edge peak energies versus the total d-electron count (Table S10, Figure S52) exhibits a strong linear correlation for both the Fe 1s → 2a_1 and Ti 1s → 2a_1 transition, with R^2 = 0.99 and 0.96, respectively. By contrast, a worse correlation (R^2 = 0.87) is found for the analogous plot of the Ti 1s → 3e/4e peak energies. At this time, we do not understand why the energies are more perturbed for the Ti 1s → 3e/4e peaks across the isosstructural redox series. Lastly, the features in the Ti XANES of 2-Br are even more complex in nature, involving multiple acceptor orbitals, including ligand-based π*-MOs (see Table 5, S9).

Summary and Conclusions

A series of Fe-Ti bimetallic complexes was investigated to better understand the nature of polarized metal-metal bonding interactions between early and late first-row transition metals. These Fe-Ti compounds add to a growing number of heterobimetallic complexes featuring short metal-metal bonds and a handful of complexes featuring direct Fe-Ti bonds. Collectively, the isosstructural Fe-Ti complexes exhibit several notable features, including one of the largest variations in both Fe-M bond lengths (where M = B, Ti, V,
Cr) and $^{57}$Fe Mössbauer quadrupole splitting ($|\Delta E_Q|$) with each redox change. Additionally, the Fe K-edge XAS for the [FeTiL]$^{+/0/−}$ series reveal an unusually intense pre-edge feature, which was attributed to the substantial Fe 4$p_z$ character present in the LUMO (the acceptor orbital). Hence, the combined theoretical and spectroscopic evidence shows that the $d$-orbitals of the early transition metal (Ti) can mix with $p$-orbitals at the late transition metal (Fe), allowing transitions to this peculiar type of LUMO to be observed. Additionally, the polarization of the core electrons on Fe can be achieved through bonding with Ti, which, to our knowledge, has not been elucidated before in any metal-metal multiply bonded system.

The collective spectroscopic and theoretical data consistently show that each redox process in the [FeTiL]$^{+/0/−}$ series is best viewed as Fe-based, albeit the Ti contribution in the Fe-Ti π-bonding MOs does increase by 13% from $2^{ox}$ to $2^{red}$. DFT calculations reveal that the additional electron(s) populate the Fe $d_{xy}/d_{x^2-y^2}$ orbitals, which is also supported by the X-band EPR spectrum of 2. In particular, the anisotropy of the $g$-values and $^{31}$P superhyperfine coupling are consistent the unpaired spin in an Fe $d$-orbital oriented in the $xy$-plane. The filling of the Fe $d_{xy}/d_{x^2-y^2}$ orbitals is also strongly supported by the Mössbauer study. More specifically, the large variation in $|\Delta E_Q|$ upon each successive reduction stems primarily from the changes in the valence-shell contribution to the electric field gradient at Fe ($V_{zz}^{1c,valence}$), for which the increasingly positive values of $V_{zz}^{1c,valence}$ with each successive reduction directly implicate the population of orbitals perpendicular to $V_{zz}$ (the $C_3$-axis), or the $d_{xy}/d_{x^2-y^2}$ orbitals. Finally, the absence of a low-intensity pre-edge feature in the Fe K-edge XAS data of $2^{red}$ indicates that $1s \rightarrow 3d$ transitions are not feasible, which is consistent with a filling of all Fe-based valence vacancies present in 2 and $2^{ox}$.

Because of the limited Ti contributions in the Fe-Ti bonding MOs, we propose that the electronic structures of $2^{ox}$ and 2 are well represented by Fe$^0$ and Fe$^{−1}$ and, hence Ti$^{IV}$. The lack of $1s \rightarrow 3d$ transitions shows that, at least spectroscopically, the polarized Fe=Ti bond in $2^{red}$ gives the appearance of an Fe$^{−II}$ center. However, the Ti support does play an important role in the enhanced redox flexibility of the Fe center. As negative charge accumulates on Fe, the Fe-Ti bond distance contracts. As elucidated by DFT, each Fe reduction results in better energy match between the Fe and Ti 3$d$ orbitals, leading to increasing Ti character in the $\sigma$- and $\pi$-symmetric MOs (up to 19 and 26% in $2^{red}$, respectively). The increased covalency in the Fe-Ti unit is also manifested in the Ti K-edge XAS, leading to lower energy pre-edge transitions with each reduction. This shows that even small covalent contributions in heterobimetallic complexes can have dramatic influences on the electronic and spectroscopic properties at each metal. In closing, the spectroscopic and structural changes across this redox series lend strong support to the unique redox flexibility of the Fe-Ti series, wherein subtle changes in the Fe-Ti covalency occur dynamically to accommodate the storage of electrons.
Experimental Section

General Considerations.

Unless otherwise stated, all manipulations were performed under an inert atmosphere in a glovebox or using standard Schlenk techniques. Standard solvents were deoxygenated by sparging with inert gas and dried by passing through activated alumina columns of a 50 ml Water solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. or Sigma-Aldrich. Fluorobenzene was purchased from Oakwood Chemicals. These solvents were dried over calcium hydride, degassed via freeze–pump–thaw cycles and stored over activated 4 Å molecular sieve. Elemental analyses were performed by Robertson Microlit Laboratories, Inc. (Ledgewood, NJ). All 1H and 31P NMR spectra were recorded on a Bruker 400 MHz spectrometer. 1H{31P} NMR spectra were recorded at ambient temperature unless otherwise stated. Cyclic voltammetry was performed using a CH instruments 600 electrochemical analyzer. The one-cell set-up used a glass carbon working electrode, Pt wire counter electrode, and Ag/AgNO₃ reference electrode in CH₂CN. Analyte solutions consisted of 0.4 M [Bu₄N]PF₆ and the voltammograms were referenced internally to the FeCp₂O⁺ (abbreviated as Fe⁺/Fe) redox couple. Evans’s method measurements were done in triplicate according to previously outlined procedures.

UV-Vis-NIR spectra were collected at room temperature on a Cary-14 spectrometer. Perpendicular-mode X-band EPR spectra were recorded at 20 K with a Bruker ESP 300 spectrometer equipped with an Oxford ESR 910 liquid-helium cryostat and an Oxford temperature controller. X-band EPR spectra were simulated using the program esimX written by Eckhard Bill. Mössbauer data were recorded on an alternating-current constant-acceleration spectrometer. The sample temperature was maintained constant at 80 K in an Oxford Instruments Variox cryostat. The 57Co/Rh source (1.8 GBq) was positioned at rt inside the gap of the magnet system at a zero-field position. Isomer shifts are quoted relative to Fe metal at 300 K. All metal halides were purchased either from Strem or Sigma Aldrich and used without further purification. The protio-ligand, N(o-(NHC₆H₄PPr₂)C₆H₄)₂ (abbreviated as LH₂), FeTiL (abbreviated as 2), Ag[BArF₄], Na[B(3,5-(CF₃)₂-C₆H₃)₄] (NaBArF₄) were synthesized according to literature procedures. TiL (abbreviated as 1) was also synthesized from literature procedures with an additional step: after isolation of crude TiL, the solid was washed with cold (−30°C) Et₂O, then extracted using CH₂Cl₂, yielding TiL as a bright yellow/orange powder.

Synthesis of [Ti(N(o-(NHC₆H₄PPr₂)C₆H₄))₂]BArF₄, 1ox.

A solution of Fe[BArF₄]₂ (28.9 mg, 0.0276 mmol) in CH₂Cl₂ (2 mL) was added dropwise to a stirred solution of 1 (20 mg, 0.0276 mmol) in Et₂O (2 mL) and stirred for 10 min. The solvent was removed in vacuo, and the solid was washed with pentane (3 x 5 mL), then placed in vacuo to yield 1ox as a green powder (40.2 mg, 92% yield). Alternatively, a solution of 2-Br (30 mg, 0.0332 mmol) in CH₂Cl₂ (3 mL) was added to a solution of NaBArF₄ (29.4 mg, 0.0332 mmol) in Et₂O (4 mL), which changes to a slightly brighter shade of green. The solution is stirred for 1 h, and is then filtered through a pad of Celite. The solution is then concentrated in vacuo to yield 1ox as a green powder (52.9 mg, 97% yield). Crystals suitable for X-ray diffraction were obtained from a concentrated PhF solution of 1ox layered with hexanes. 1H{31P} NMR (400 MHz, THF-d₈): δ 7.83 (s, 8H, BArF₄ aryl), 7.61 (s, 8H, BArF₄ aryl), 7.23 (d, J = 7.7 Hz, 3H, aryl), 7.15 (app t, J = 7.4 Hz, 3H, aryl), 6.74 (app t, J = 7.7 Hz, 3H, aryl), 6.33 (d, J = 7.4 Hz, 3H, aryl), 4.23 (d, J = 13.1 Hz, 3H, CH₃), 3.79 (d, J = 13.1 Hz, 3H, CH₃), 2.49 (sept, J = 7.3 Hz, 6H, P(CH(CH₃))₂), 1.49 (d, J = 7.3 Hz, 9H, P(CH(CH₃))₂), 1.23 (d, J = 7.0 Hz, 9H, P(CH(CH₃))₂), 0.76 (d, J = 7.0 Hz, 9H, P(CH(CH₃))₂), 31P{1H} NMR (162 MHz, THF-d₈): δ −23.8. Attempts to obtain satisfactory elemental analysis for 1ox reproducibly yielded values consistent with the addition of 1 O atom, either through reaction with water or oxygen. Anal. Calcd for C₇₁H₇₂BN₄F₂₄P₃Ti-0: C, 53.13; H, 4.52; N, 3.49. Found: C, 52.96; H, 4.28; N, 3.44.

Synthesis of BrFeTi(N(o-(NHC₆H₄PPr₂)C₆H₄)), 2-Br.

A solution of 1 (57.9 mg, 0.0798 mmol) in THF (4 mL) was added to FeBr₂ (17.2 mg, 0.0798 mmol) and stirred for 1 h, upon which the solution changes from orange/brown to dark brown. Next, a solution of 2 (62.4 mg, 0.0798 mmol) was added to the reaction solution, which immediately turns forest green. The solution is stirred overnight, which immediately consumes all of the added FeBr₂. The solution is then concentrated in vacuo, and the solid is then dissolved in benzene (8 mL) and filtered through a pad of Celite to yield 2-Br as a green powder (128.0 mg, 93% yield). Single crystals suitable for X-ray diffraction were obtained from growth of hexanes through diffusion of hexanes into a concentrated benzene solution of 2-Br. 1H NMR (400 MHz, C₆D₆): δ 4.77, 9.2, 7.8, 4.8, 4.0, −0.6, −9.6. Evans’s method (THF-d₈): 2.97 μB. UV-Vis-NIR [THF, λmax, nm (ε, M⁻¹ cm⁻¹)]: 1268 (650), 610 (890), 320 (sh) (15900), 292 (sh) (18600). Anal. Calcd for C₇₃H₇₂BN₄P₃TiFeBr-0.5(C₆H₆) (%): C, 56.02; H, 7.05; N, 6.22. Found: C, 56.13; H, 7.01; N, 5.95.

Synthesis of [FeTi(N(o-(NHC₆H₄PPr₂)C₆H₄))₂]BArF₄, 2ox/BArF₄.

A solution of 2-Br (82.2 mg, 0.0990 mmol) in fluorobenzene (4 mL) was added to a solution of NaBArF₄ (84.2 mg, 0.0999 mmol) in fluorobenzene (2 mL), which immediately changes from forest green to dark red/brown. The solution
is stirred for 2 h, and is then filtered through a pad of Celite. After removing the solvent in vacuo, the brown solid was extracted using toluene cooled to −78 °C (5 mL), and filtered through another pad of Celite. The filtrate was then concentrated in vacuo to yield 2 red as a brown powder (128.2 mg, 90% yield). 1H NMR (400 MHz, C6D6): δ 47.7, 9.2, 7.8, 4.8, 4.0, −0.6, −9.6. Evans’s method (THF-d8): 2.99 μmol. UV-Vis-NIR [THF, λmax, nm (ε, M⁻¹ cm⁻¹)]: 1279 (370), 1100 (310), 416 (3750), 304 (22900). Attempts to obtain satisfactory elemental analysis for [2 red]BArf4 reproducibly yielded values consistent with the addition of 3 O atoms, either through reaction of 2 red with water or oxygen. Anal. Calcd for C39H60N4P3TiFe: C, 50.38; H, 4.29; N, 3.31. Found: C, 50.42; H, 4.51; N, 3.30.

**Synthesis of K(THF)3[FeTi(N(CH2PPr2)C6H4)]**, 2 red.

A solution of FeTiL (100.3 mg, 0.1283 mmol) in THF (8 mL) was added to a slurry of KC8 (36.4 mg, 0.2695 mmol) cooled to −25°C overnight, yielding dark brown crystals (128.1 mg, 45% yield). Single crystals suitable for X-ray diffraction were grown by cooling a concentrated solution of 1 in diethyl ether to −25°C. Single crystals of [2 red][B12Cl12] were grown by layering 2 over a solution of 0.5 equiv of Ag2B12Cl12 in THF. A plate of 1 (0.27 × 0.20 × 0.10 mm), a plate of [1H][31P] NMR (400 MHz, THF-d8): δ 6.61 (app t, J = 7.3 Hz, 3H, aryl), 6.38 (d, J = 7.2 Hz, 3H, aryl), 6.07 (d, J = 7.3 Hz, 3H, aryl), 5.68 (app t, J = 7.2 Hz, 3H, aryl), 5.31 (br, 2H, CH2), 4.88 (br, 2H, CH2), 3.61 (AA'BB', THF CH2), 2.87 (br, 4H, P(CH2CH3)), 1.77 (AA'BB', THF CH3) 1.69 (br, 9H, P(CH2CH3)), 1.48 (br, 9H, P(CH2CH3)), 1.08 (br, 9H, P(CH2CH3)), 0.35 (br, 9H, P(CH2CH3)). 31P[1H} NMR (162 MHz, THF-d8, −83°C): δ 41.3 (s). UV-Vis-NIR [THF, λmax, nm (ε, M⁻¹ cm⁻¹)]: 690(sh) (650), 447(sh) (6430), 375(sh) (9400), 318 (37600). Elemental analysis of 2 red consistently yielded values that were too low in C and H. The closest result to theory is shown. Anal. Calcd for [C39H60N4P3TiFeK]: C, 57.08; H, 7.37; N, 6.83. Found: C, 54.49; H, 7.29; N, 6.11.

**X-ray crystallography and structure refinement details**

Single crystals of 1 suitable for X-ray diffraction were grown by cooling a concentrated solution of 1 in diethyl ether to −25°C. Single crystals of [2 red][B12Cl12] were grown by layering 2 over a solution of 0.5 equiv of Ag2B12Cl12 in THF. A plate of 1 (0.27 × 0.20 × 0.10 mm), a plate of [1H][31P] NMR (400 MHz, THF-d8): δ 6.61 (app t, J = 7.3 Hz, 3H, aryl), 6.38 (d, J = 7.2 Hz, 3H, aryl), 6.07 (d, J = 7.3 Hz, 3H, aryl), 5.68 (app t, J = 7.2 Hz, 3H, aryl), 5.31 (br, 2H, CH2), 4.88 (br, 2H, CH2), 3.61 (AA'BB', THF CH2), 2.87 (br, 4H, P(CH2CH3)), 1.77 (AA'BB', THF CH3) 1.69 (br, 9H, P(CH2CH3)), 1.48 (br, 9H, P(CH2CH3)), 1.08 (br, 9H, P(CH2CH3)), 0.35 (br, 9H, P(CH2CH3)). 31P[1H} NMR (162 MHz, THF-d8, −83°C): δ 41.3 (s). UV-Vis-NIR [THF, λmax, nm (ε, M⁻¹ cm⁻¹)]: 690(sh) (650), 447(sh) (6430), 375(sh) (9400), 318 (37600). Elemental analysis of 2 red consistently yielded values that were too low in C and H. The closest result to theory is shown. Anal. Calcd for [C39H60N4P3TiFeK]: C, 57.08; H, 7.37; N, 6.83. Found: C, 54.49; H, 7.29; N, 6.11.

| chemical formula | C39H60N4P3TiFeO3K | C39H60N4P3TiFeO3K | C39H60N4P3TiFe0.5(B12Cl12) | C39H60N4P3TiFeBr |
|------------------|-------------------|-------------------|-----------------------------|------------------|
| Fw               | 725.72            | 1718.20           | 2218.16                     | 1119.18          |
| cryst syst       | monoclinic        | monoclinic        | monoclinic                  | monoclinic       |
| space group      | P21/n             | P1               | Pn                          | P3c1             |
| a (Å)            | 11.4570(2)        | 14.3310(4)        | 12.4492(7)                  | 14.9687(4)       |
| b (Å)            | 19.5908(4)        | 14.5231(4)        | 14.8815(8)                  | 14.9687(4)       |
| c (Å)            | 17.4173(3)        | 21.7918(6)        | 16.5942(8)                  | 26.3435(7)       |

**Table 6. Crystallographic details for 1, 1H, [K(THF)3]2 red, 2-Br, and [2 red][B12Cl12].**

- **Fw**: Crystallographic data are summarized in Table 6.
- **cryst syst**: Single crystals of 1 were suitable for X-ray diffraction.
- **space group**: Single crystals of 1 were suitable for X-ray diffraction.
- **a**, **b**, **c**: Single crystals of 1 were suitable for X-ray diffraction.
X-Ray Absorption Spectroscopy (XAS)

Sample preparation, measurements and data analysis

Solid samples for X-ray spectroscopic analysis were prepared in an inert-atmosphere glove box. For Fe and Ti K-edge XAS measurements, the solid samples were finely ground using an agate mortar and pestle with boron nitride (BN) into a homogeneous mixture comprising 5% w/w photoabsorbing metal. These mixtures were pressed into 1 mm Al spacers and sealed with 38 µm Kapton tape. Fe and Ti K-edge XAS spectra were obtained at the Stanford Synchrotron Radiation Lightsource (SSRL) at beamline 9-3 under ring conditions of 3 GeV and 500 mA. A Si(220) double-crystal monochromator was used for energy selection. For Fe, a Rh-coated mirror (set to an energy cutoff of 9 keV) was used for harmonic rejection. Incident energy calibrations were performed by assigning the first inflection points of Fe and Ti foil spectra to 7111.2 eV and 4966 eV, respectively. Data were collected in fluorescence mode using a Canberra 100-element Ge array detector. Samples were maintained at 10 K in an Oxford liquid He flow cryostat. For spectra measured by fluorescence detection, elastic scatter into the detector was attenuated using a Soller slit with upstream Co or Sc filters. Data were collected from 6784 to 7510 eV for Fe and 4734 to 5360 eV for Ti. Multiple scans were measured and averaged with SIXPACK software package. No spectral changes due to photo-damage were observed after multiple scans for these complexes. Data were normalized to post-edge jumps of 1.0 (Ti: 4985 eV, Fe: 7130 eV) in SIXPACK by applying a Gaussian normalization for the pre-edge and a quadratic normalization for the post-edge to produce the final spectra. The final processed spectra were plotted using Igor Pro 6.37.

Computational details

Density functional theory (DFT) calculations were conducted to understand the electronic structures of 2ox, 2 and 2red, and to calculate their Mössbauer parameters and Fe/Ti K-edge XAS spectra. Different DFT methods were employed for the Mössbauer and XAS calculations, as detailed below. Specifically, the electronic structures shown in Figure 4 and Table 5 (also Figure S19 and Table S4) were obtained from the Mössbauer study, whereas the electronic structures derived from the XAS study are shown in Figure S20 and Table S5 of note, the different DFT methods all yielded highly similar electronic structures.

Mössbauer spectroscopy. DFT calculations on Mössbauer parameters were performed using the ORCA 4.0 package. Starting from the crystal structure coordinates, all hydrogen atoms were optimized while the positions of all the other atoms were constrained, using the functional BP86 and the basis set def2-SVP for all atoms. For estimation of the Mössbauer parameters, single-point calculations were then carried out on the resulting geometries at the B3LYP level of theory, where the basis set CP(PPP) having an uncontracted core-region was used for iron, and the basis set def2-TZVP was used for all other atoms. Of note, the use of the B3LYP functional and CP(PPP) basis set have previously been shown to satisfactorily reproduce Mössbauer parameters. All calculations were carried out in gas phase. The RIJCOSX algorithm was used to speed up the Hartree-Fock exchange. The quasi-restricted-orbitals (QROs) generated by the above single-point calculations were localized using Piek-Mezey algorithm for the Löwdin population analysis and quadrupole splitting contribution breakdown.

The isomer shift (δ) was computed from the electron density at the iron nucleus (ρ0) by using the following equation,
\[ \delta = \alpha (\rho_0 - C) + \beta \]

Parameters \( \alpha \), \( \beta \) and \( C \) were determined by a linear progression for a series of iron complexes with different oxidation states and spin multiplicities. Specifically, one first computes the electron density at the iron nucleus for each complex and then set up a linear correlation between the isomer shift measured experimentally and the calculated density. Consequently, the linear equation obtained can only be used to predict the isomer shifts of iron complexes that feature similar bonding to the preselected complexes. In the present case, the calculated isomer shifts using the parameters reported were systematically underestimated. Note that no bimetallic iron complexes that involve metal-metal bonding are included in this training set. The same situation was found for isomer shift calculations on seven related bimetallic complexes. Based on these observations, we decided to design a new calibration curve from the calculated density and experimental isomer shifts of these seven complexes, which was used for isomer shift calculations in the present study. The new set of the parameters were \( \alpha = -0.316 \), \( \beta = 2.661 \) and \( C = 11810 \). The details are shown in supporting information (Table S8 and Figure S26).

**XAS spectroscopy.** DFT calculations were performed to directly correlate X-ray spectroscopy to electronic structure. All electronic structure and spectroscopic calculations were performed using the ORCA 3.03 package. Starting from crystal structure coordinates, the structures were fully geometry-optimized using the BP86 functional, the zeroth-order regular approximation for relativistic effects (ZORA) as implemented by van Wüllen, and scalar relativistically recontracted Ahlrich's def2-TZVP(-f)(def2-TZVP(-f)-ZORA) basis set, followed by frequency calculations to ensure that no imaginary vibrational modes were present. Solvation was modelled with the conductor like screening model (COSMO) using an infinite dielectric. Fe and Ti K-edge XAS spectra were calculated using TD-DFT calculations with both geometry optimized and crystallographic coordinates utilizing B3LYP functional, the CP(PPP) basis set on the transition metals (Ti and Fe) using an integration grid accuracy of 7, and the def2-TZVP(-f)-ZORA basis set on all other atoms. Calculations with hybrid functionals used the RIJCOSX algorithm to speed the calculation of Hartree-Fock exchange. Error in core potential energetics were evaluated by plotting the calculated XAS peak energies against experimental peak energies (Figure S30). Of note, the use of B3LYP and the CP(PPP) basis set have previously been shown to satisfactorily reproduce Fe K-edge XAS data.

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**Author Information**

● These authors contributed equally.

**Notes**

The authors declare no competing financial interest.

The cif files for these structures have been deposited at the Cambridge Crystallographic Data Centre as CCDC 1863841-1863845.

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