Sterically Stabilized Terminal Hydride of a Diiron Dithiolate

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Supporting Information

ABSTRACT: The kinetically robust hydride $[\text{t-HFe}_2\text{Me}_2\text{pdt}(\text{CO})_2\text{dpv}]^+$ ($([\text{H}]^1\text{H})^+$) (Me$_2$pdta = Me$_2$C-(CH$_2$)$_2$)$_2$ dpv = cis-1,2-C$_2$H$_2$(PPh$_2$)$_2$ and related derivatives were prepared with $^{57}$Fe enrichment for characterization by NMR, FT-IR, and NRVS. The experimental results were rationalized using DFT molecular modeling and spectral simulations. The spectroscopic analysis was aimed at supporting assignments of Fe-H vibrational spectra as they relate to recent measurements on [FeFe]-hydrogenase enzymes. The combination of bulky Me$_2$pdta$^{2-}$ and dpv ligands stabilizes the terminal hydride with respect to its isomerization to the S=16 kcal/mol more stable bridging hydride ($([\mu-H]^1\text{H})^+$) with $t_{1/2}(313.3 \text{ K}) = 19.3 \text{ min}$. In agreement with the nOe experiments, the calculations predict that one methyl group in $[\text{t-H}]^1\text{H}^+$ interacts with the hydride with a computed CH···HFe distance of 1.7 Å. Although $[\text{H}^1\text{H}^1\text{H}]^+$ exhibits multiple NRVS features in the 720–800 cm$^{-1}$ region containing the bending Fe–H modes, the deuterated $[\text{D}^1\text{H}]^1\text{H}^+$ sample exhibits a unique Fe-D/CO band at ~600 cm$^{-1}$. In contrast, the NRVS spectra for $[\mu-H^1\text{H}^1\text{H}]^+$ exhibit weaker bands near 670–700 cm$^{-1}$ produced by the Fe–H–Fe wagging modes coupled to Me$_2$pdta$^{2-}$ and dpv motions.

INTRODUCTION

Currently the hydrogenases (H$_2$ases) are receiving much interest because these enzymes exhibit unusual and highly efficient pathways for activating and producing H$_2$. It has been long assumed that all hydrogenases operate via the intermediary of metal hydrides, which are otherwise elusive in nature. Such intermediates have long been directly detected for the [NiFe]-H$_2$ase.$^5$ For the [FeFe]-H$_2$ase, hydrides were initially spectroscopically implicated by the e-motion is a central in our recent direct detection of Fe–H-containing intermediates in the [FeFe]-H$_2$ase.$^{14,15}$

Biomimetic terminal hydrides participate in two reactions that complicate their analysis. When the dithiolate is the azadithiolate (adt) cofactor (or its N-substituted derivatives), the hydride can be reversibly deprotonated by amine. This effect is illustrated by the case of $[\text{term-HFe}_2\text{adt}-(\text{CO})_2\text{dpv}]^+$ (adt = azadithiolate), where the tautomerization is affected by the nature and concentration of the counterion.$^{16}$ Regardless of the nature of the dithiolate bridge, terminal Fe–H hydrides tend to isomerize irreversibly to bridging Fe–H–Fe hydrides.$^1$ We sought to suppress this reaction, since these bridging hydrides are not relevant to the biological function of [FeFe]-H$_2$ase.$^{19}$

Many studies have been reported on diiron dithiolates with “rotated structures”. The rotated motif is readily achieved with mixed-valence Fe(II)Fe(I) complexes, but Fe(I)Fe(I) compounds almost invariably adopt the $C_{2v}$ (idealized) structure...
**RESULTS AND DISCUSSION**

**Characterization of Fe\(_2\)(Me\(_2\)pdt)(CO)\(_4\)(dppv)\(_2\)** Using FT-IR and NMR Spectroscopy. UV irradiation of a solution of Fe\(_2\)(Me\(_2\)pdt)(CO)\(_4\)(dppv)\(_2\) and dppv efficiently gave Fe\(_2\)(Me\(_2\)pdt)(CO)\(_4\)(dppv)\(_2\) ([1\(^0\)])\(^\circ\). This compound was obtained as a dark green solid that is mildly sensitive to air and exhibits good solubility in several organic solvents. The FT-IR spectrum revealed intense \(\nu_{\text{CO}}\) bands at 1898 and 1865 cm\(^{-1}\) that match well with those (1888, 1868 cm\(^{-1}\)) for Fe\(_2\)(pdt)-(CO)\(_4\)(dppv)\(_2\) ([1\(^0\)])\(^\circ\). The methyl resonance, a broad singlet, is found at \(\delta = 0.15\) (Figure S3). In contrast, the two Me resonances from the apical/basal and basal/basal isomers of Fe\(_2\)(Me\(_2\)pdt)(CO)\(_4\)(dppv)\(_2\) absorb at \(\delta = 0.98\) and 1.08, and the Me resonances of Fe\(_2\)(Me\(_2\)pdt)(CO)\(_6\) absorb at \(\delta = 0.98\). The upfield shift for the methyl \(\text{^1H NMR}\) signal ([1\(^0\)])\(^\circ\) is attributed to ring current effects resulting from interactions between the methyl groups and the phenyl groups of the ligand.

The room-temperature \(\text{^31P NMR}\) spectrum of [1\(^0\)]\(^\circ\) consists of a singlet at \(\delta = 87.0\) (Figure S4). At lower temperatures, this signal splits into two singlets, and below \(-90^\circ\text{C}\) these singlets broaden further (Figure S6). However, the signal for the methyl groups remains coalesced even at \(-90^\circ\text{C}\) (Figure S5). The chemical shift difference for the \(\text{^31P NMR}\) signals in the slow exchange limit is \(\delta = 13.4\), corresponding to 2707 Hz (202 MHz observing frequency). The estimated \(^1\text{H}\) chemical shift difference between unique methyl signals is 2 ppm, corresponding to 1000 Hz (500 MHz). Therefore, the turnstile rotation of the two Fe(CO)(dppv) centers is slower than the flipping of the [Me\(_2\)pdt]\(^\circ\) ligand.

**Structure of Fe\(_2\)(Me\(_2\)pdt)(CO)\(_4\)(dppv)\(_2\)**. The structure of [1\(^0\)]\(^\circ\), which crystallizes with a disordered molecule of CH\(_2\)Cl\(_2\), was confirmed by X-ray crystallography. The overall structure was similar to that of many Fe\(_2\)(SR)\(_2\)L\(_6\) compounds with an Fe-Fe bond distance of 2.594(1) Å (Figure 1). The crystallographic analysis reveals that the coordination sphere of one Fe is highly distorted. In most compounds of the type Fe\(_2\)(SR)\(_2\)L\(_6\) terminal ligands on the two Fe centers are eclipsed (i.e., torsion angle of 0°), whereas in [1\(^0\)]\(^\circ\) the \(P_{\text{apical}}\)-Fe-Fe-

\(P_{\text{apical}}\) torsion angle is 66.43°. In the related diiron complex Fe\(_2\)(Me\(_2\)pdt)(CO)\(_4\)(dppv)\(_2\), the \(P_{\text{apical}}\)-Fe-Fe-

\(P_{\text{apical}}\) torsion angle is 28.9°, the smaller angle reflecting the diminished bulk of PMe\(_3\). Since the \(\nu_{\text{CO}}\) values for [1\(^0\)]\(^\circ\) and Fe\(_2\)(pdt)-(CO)\(_4\)(dppv)\(_2\) match well,\(^{25}\) the distortion observed in the solid state appears not to predominate in solution.

**Synthesis of Labeled \(^{57}\text{FeFe}\_2\)(Me\(_2\)pdt)(CO)\(_4\)(dppv)\(_2\)**. Also prepared in this work were \(^{57}\text{Fe}-\text{labeled}\) complexes, which are suitable for characterization by \(^{57}\text{Fe-NRVS}\) (see below). To conserve on \(^{57}\text{Fe}\), we targeted derivatives of the [H1\(^0\)]\(^\circ\) hydride species where half of the iron was \(^{57}\text{Fe}\) (Scheme 3). To prepare such “half-labeled” complexes, a \(^{57}\text{Fe}(II)\)
A dithiolate precursor was condensed with an unlabeled Fe(0) reagent. The ferrous building block $^{57}$Fe(Me$_2$pdt)(CO)$_2$(dppv) was prepared in good yield by the reaction of $^{57}$FeCl$_2$, dppv, and Li$_2$Me$_2$pdt under an atmosphere of CO. Although Fe(Me$_2$pdt)(CO)$_2$(dppv) has not been reported, the closely related Ph$_2$PC$_2$H$_4$PPh$_2$-containing analogue is known. The $^{31}$P NMR spectrum indicates a pair of isomers in a ratio of 17:1. The most abundant isomer has trans carbonyls, while the other isomer carbonyls are cis and the diphosphine exhibits two $^{31}$P NMR signals (Figure S33). The trans:cis ratio for the related but less bulky species Fe(pdt)(CO)$_2$(dppv) is 4:1. The trans isomer is apparently favored by the bulkiness of the Me$_2$pdt$^{2-}$ ligand. IR spectra for $^{57}$Fe(Me$_2$pdt)(CO)$_2$(dppv) and Fe(pdt)-(CO)$_2$(dppv) are indistinguishable (Table S1).

Treatment of $^{57}$Fe(Me$_2$pdt)(CO)$_2$(dppv) with Fe(bda)-(CO)$_3$ gave (CO)$_3$Fe(Me$_2$pdt)$^{57}$Fe(CO)(dppv) (bda = benzylideneacetone). In this diiron compound, dppv remains exclusively coordinated to $^{57}$Fe, as revealed by the observation of the doublet $^{31}$P NMR spectrum (Figure S36). This result indicates the absence of scrambling of the diphosphine. UV irradiation of a solution of this tetracarbonyl with dppv gave $^{57}$FeFe(Me$_2$pdt)(CO)$_2$(dppv)$_2$ ($[^{57}1]^0$). The $^{31}$P NMR spectrum of $[^{57}1]^0$ is characterized by a broad singlet at $\delta$ 87.2, which is similar in line shape to that of unlabeled $[^1]0$ (Figure S38).

**Electrochemistry of $[^1]0$.** Cyclic voltammetry studies on CH$_2$Cl$_2$ solutions of $[^1]0$ show a reversible oxidation at $-1.04$ V (all potentials are referenced vs Fe$^{3+/2-}$, Figure S8). With a redox couple at $-0.83$ V, Fe$_2$(pdt)(CO)$_2$(dppv)$_2$ is a poorer reductant than $[^1]0$ by $\sim210$ mV. This trend is consistent with steric stabilization of the oxidized product (see below), whose rotated geometry accommodates one of the methyl groups of the Me$_2$pdt$^{2-}$ ligand. In the case of $[^1]0$, the effect of pdt$^{2-}$ vs Me$_2$pdt$^{2-}$ is very similar: 240 mV.

**Characterization of $[^1]0$.** Oxidation of $[^1]0$ with FeBF$_4$ (Fc = [Fe(C$_5$H$_5$)$_2$]$^{+}$) gave the mixed-valence salt $[^1]BF_4$ (Figure 2). As for previously reported Fe(II)Fe(I) species, $[^1]^+$ is structurally related to the H$_{ox}$ state of [FeFe]-H$_2$ase. $[^1]BF_4$ is analogous to Fe$_2$(pdt)-(CO)$_2$(dppv)$_2$ $[^1]BF_4$. Crystallographic characterization of $[^1]BF_4$ confirmed that $[^1]BF_4$ adopts the rotated structure characteristic

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*Figure 2.* Crystal structure of Fe$_2$(Me$_2$pdt)(CO)$_2$(dppv)$_2$ $[^1]BF_4$, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and the counteranion are omitted.
of these mixed-valence species. One CO ligand is semi-bridging, with Fe$_p$–C and Fe$_d$–C distances of 2.461(2) and 1.790(6) Å, respectively. The dppv bound to the rotated iron occupies dibasal positions, whereas the dppv ligand on the second iron (Fe$_p$) occupies an apical-basal configuration, reminiscent of the location of the two donor ligands on the proximal Fe (Fe$_p$) in the enzyme. The Fe–P bonds are similar for Fe$_p$ vs Fe$_d$ (2.213(2)/2.243(2) Å vs 2.236(2)/2.254(1) Å, respectively). The crystal structure also reveals an interaction between one of the protons from a methyl group and the Fe$_d$ ($d_{C-Fe} = 2.409$ Å), consistent with an anagotic interaction. $^{58}$

EPR spectra of [I]BF$_4$ as a solution in toluene-THF were recorded at −150 and 30 °C (Figure 3). The low-temperature spectrum is characteristic of an axial symmetry with $g = 2.105$ and 2.013. For both D. desulfuricans (Dd) H$_2$ase and C. pasteurianum (Cp) H$_2$ase I, $g_1 = 2.10$ was reported, which is very similar to the $g_1$ value for [I]BF$_4$ of 2.105. However, the $g_3$ value of 2.013 for [I]BF$_4$ deviates from the $g_3$ values for Dd H$_2$ase and Cp H$_2$ase I: 1.999 and 2.00, respectively. $^{39}$ In comparison to other synthetic H$_2$ase models, [I]BF$_4$ g values match well with those of [Fe$_p$(pdt)(CO)$_3$(dppv)(P$t$_3$Pr$_3$)]$^+$-BF$_4$. $^{30}$ Hyperfine coupling, assigned to $A^{(31P)}$, is well resolved. In the isotropic spectrum, a triplet is observed at $g_{iso} = 2.045$ with $A^{(31P)} = 70$ MHz. The hyperfine splitting is consistent with the spin residing on a single Fe(dppv) center. No hyperfine coupling to the dppv on the nonrotated Fe was resolved, consistent with little delocalization.

**Characterization of [t-HFe$_{2}$(Me$_{2}$pdt)(CO)$_{3}$(dppv)$_{2}$]$^+$.** Like related diiron(I) complexes, $^{10}$ [I]$^+$ is protonated by HBF$_4$ to give a hydride complex (Scheme 3). The salt [t-HFe$_{2}$(Me$_{2}$pdt)(CO)$_{3}$(dppv)$_{2}$]BF$_4$ ([t-H1]BF$_4$) was isolated as a brown-green powder and characterized spectroscopically. Its room-temperature $^{31P}$ NMR spectrum shows four resonances (Figure S15). Consistent with the low symmetry of the complex, the four resonances indicate apical-basal dppv on the proximal iron and a dibasal dppv on the FeH (Fe$_d$) center. The locations of the four phosphine ligands are similar for [I]BF$_4$ and [t-H1]BF$_4$ consistent with a biomimetic relationship between oxidized and protonated states. Solutions of [t-H1]BF$_4$ isomerize, albeit slowly, at room temperature (see the isomerization section). The slowness of this isomerization reflects the effect of steric congestion. $^{40}$ The nature of the steric congestion was probed by 1D nuclear Overhauser effect (nOe) NMR spectroscopy (Figure 4). Irradiation of the $t$-H signal at δ $\sim-2.23$ revealed interactions between the hydride and methyl protons (δ 0.6) and between the hydride and one aryl proton (δ 7.8). Only the axial methyl interacts with the hydride. The DFT-optimized CH$_{3}$t--HFe$_{2}$ distance is $\sim$1.7 Å. Additionally, the hydride is also close to a pair of aryl protons on the distal dppv; the closest DFT-optimized CH$_{3}$t--HFe$_{2}$ distance is $\sim$2.3 Å (see Figure 6a and further details on the DFT modeling below).

**Isomerization of [t-HFe$_{2}$(Me$_{2}$pdt)(CO)$_{3}$(dppv)$_{2}$]BF$_{4}$.** As for all other examples of [t-HFe$_{2}$(SR)$_{2}$(CO)$_{3}$(dppv)$_{2}$]$^+$, [t-H1]$^+$ isomerizes irreversibly to a bridging hydride. $^{41}$ The decay rate follows first-order kinetics ($k = 6.0 \times 10^{-4}$ s$^{-1}$) with a half-life of 19.3 min at 40.3 °C (Figure 5). In contrast, the isomerization of the unmethylated analogue [t-HFe$_{2}$(pdt)(CO)$_{3}$(dppv)$_{2}$]$^+$ proceeds with a half-life of minutes at room temperature ($k = 0.001$ s$^{-1}$). $^{39}$ These disparate rates correspond to a difference in free energy of activation of about 1 kcal/mol.

The final product of the isomerization of [t-H1]$^+$ is the bridging hydride [$\mu$-H1]$^+$. Throughout the conversion a third hydride was observed, an intermediate in the isomerization. Its chemical shift at δ $\sim$3.63 indicates that this intermediate is a terminal hydride. $^{40}$ $^{42}$ It is $C_s$-symmetric, as indicated by two $^{31P}$ NMR signals (δ 79.9 and 72.7; see Figures S20 and 21). These chemical shifts are consistent with dibasal dppv ligands; in contrast, when dppv spans apical-basal sites, the apical phosphines typically absorb near δ 90. $^{40,42}$ The intermediate is only observed during isomerization but does not accumulate.
It thus appears that \([t\text{-}H1]^+\) converts to a second terminal hydride \((\text{[t-H1']})^+\), which then converts to the \(\mu\)-hydride (Scheme 4).

Scheme 4. Proposed Pathway for the Isomerization of \([t\text{-}HFe2(Me2pdt)(CO)2(dppv)2]BF4\) to \([\mu\text{-}HFe2(Me2pdt)(CO)2(dppv)2]BF4\)

Previous DFT analysis indicated that only the Fe with the hydride twists via a Ray–Dutt mechanism to form the \(\mu\)-hydride.\(^{43}\) Analysis of the isomerization of \([t\text{-}HFe2(pdt)-(CO)2(dppv)2]^+\) revealed that the symmetric terminal hydride is approximately 3 kcal/mol higher in energy than the asymmetric analogue.\(^{42}\) Thus, it is proposed that the isomerization starts with a twist at the Fe\(_d\) center to give a \(\text{C}_\text{r}\)-symmetric terminal hydride species. Subsequently, the Fe\(_d\) center rotates to give the \(\mu\)-hydride. These measurements provide evidence for involvement of the proximal (non-hydride-containing) iron in the isomerization of the hydride. The rotation of the Fe\(_d\)(CO)(dppv)H center shifts the hydride ligand to the bridging site and the dppv\(_d\) to apical-basal positions.\(^{43}\) By first forming \([t\text{-}H1']^+\), the cation is preorganized to generate the correct isomer of \([\mu\text{-}H1]^+\), wherein the hydride is trans to a CO ligand, a favored geometry.\(^{43}\) This result implies that the flexibility of Fe\(_p\) influences the isomerization of terminal to bridging hydrides. A similar sequence of events was also seen in \([t\text{-}HFe2(adt)(CO)2(PMe3)4]^+\), where the kinetically favored isomer akin to \([t\text{-}H1]^+\) converts partially to an all-basal isomer structurally analogous to \([t\text{-}H1']^+\).\(^{44}\)

For the purpose of evaluating their vibrational spectra, \([t\text{-}H57]\text{BF}_4, [t\text{-}D57]\text{O}_2\text{CF}_3, [\mu\text{-}H57]\text{O}_2\text{CF}_3, \text{and [}\mu\text{-}D57]-\text{O}_2\text{CF}_3\) were analyzed. CF\(_3\)CO\(_2\)D was selected as a convenient

Figure 6. DFT-optimized structures of the terminal (a, b) and bridging (c, d) hydride isomeric species including their d- (a and c) and p- (b and d) flippamer alternatives on the Me\(_2\)pdt\(^{2-}\) bridge conformation. Notations of the species are provided (\([t\text{-}d\text{-}H1]^+\), \([t\text{-}p\text{-}H1]^+\), \([\mu\text{-}d\text{-}H1]^+\), \([\mu\text{-}p\text{-}H1]^+\)). Important atomic labels are provided in (a and c). The H\(_{\text{t/\mu}}\) hydride site is highlighted as a blue sphere. The CH\(_X\)···H\(_{\text{t/\mu}}\) dihydrogen contacts within 3 Å are shown, with H\(_X\) highlighted as purple spheres. The relative energy ranges provided are based on the values given in Table S3.
Deuteration was incomplete but sufficient for unambiguous assignments.

**DFT Modeling of the Structures and Energies of \([t-H]^{+}\) and \([\mu-H]^{+}\).**

Density functional theory (DFT) was applied to elucidate structures and relative energies of the terminal and bridging hydride species. In the absence of their structural determinations, X-ray data on the similar complex \([t-HFe_2(adtNH_2)(CO)_(2)(dppv)(BF_4)]^{2+}\) has been used to generate

Figure 7. \(^{57}\)Fe-PVDOS vibrational spectra for the H/D variants (correspondingly in blue/red) of the terminal \([t-H/D]^{+}\) (upper panel, a, b) and bridging \([\mu-H/D]^{+}\) (lower panel, d, e) hydride species characterized by NRVS experiments (a, d) and DFT calculations (b, e). The ×10 intensity insets display the spectra >620 cm\(^{-1}\). DFT-based stick-style spectra show PVDOS for the terminal H/D (c) and bridging H/D (f) hydrides and 2 × \(^{57}\)Fe\(_{15}\) (d, e) iron nuclei. The dashed vertical line at ~600 cm\(^{-1}\) indicates the key difference between the \([t-D]^{+}\) and \([\mu-D]^{+}\) spectra as explained in the text. The labels (cm\(^{-1}\)) indicate band positions (a, b, d, e) or individual normal-mode frequencies (c, f). Mode positions marked with thick dots (c, f) correspond to significant H−D− hydride motions; arrow-style molecular representation of these modes is available in Figure 8.

See Figure S51 for alternative spectra arrangement and also DFT \(^{57}\)Fe-PVDOS for the d/p-conformers of the Me\(_2\)pd\(^{2+}\) bridge.

source of D\(^{+}\). Deuteration was incomplete but sufficient for unambiguous assignments.
erate starting structures for the models, replacing the NH$_2$ bridgehead to Me$_2$pdt$^\text{2-}$. The analysis included the two flippamers$^{30}$ for the Me$_2$pdt$^\text{2-}$ bridgehead, denoted respectively as $d/p$ depending on its orientation toward either Fe$_k$/$p$. The

Figure 8. Arrow-style molecular representation of selected normal modes having significant hydride motion character in the best-fit DFT models for the H/D variants of the terminal [t-H/D$^{57}$]$(^+$ (a, b) and bridging [μ-H/D$^{57}$]$(^+$ (c, d) hydride species. Red/blue coloring of labels and arrows corresponds to the H- or D- hydride isotope alternatives. The computed mode frequencies (cm$^{-1}$) and the H/D$_{hydride}$ nuclei displacement amplitudes (Å) are given. The same modes are marked in the H/D-PVDOS spectra in Figure 7c,f. For these and other vibrational modes animated, see the Supporting Information.
optimized structures of the 2 × 2 = 4 isomers are shown in Figure 6 and Figure S50 along with their notations used below in the text. Tables S2 and S3 provide the structural parameters of the diiron cores and relative energies.

Several computational schemes predict that the bridging hydride models (μ4-H1) are 5–16 kcal/mol more stable in comparison to the terminal hydride models (tξ-H1), regardless of the flippamer (Figure 6 and Table S3). Earlier calculations on [FeFe]-H2ase indicated 8–16 kcal/mol stabilization for the μ-H vs t-H species.\textsuperscript{15,45,46} Notably, the [tξ-H1] models yield metal–ligand distances Fe–Cα = 1.8 Å and Fe–Cγ = 2.4–2.6 Å, which reproduce the markedly asymmetric character of the semi-bridging CO binding observed in model complexes and [FeFe]-H2ase active site.\textsuperscript{12,14} Moderate Fe–H distance asymmetries within ∼0.1 Å were obtained for the bridging hydride (μ4-H1) models. For each isomer, the optimization produced two or three CHν···Hγ < 3 Å interactions involving a hydride, where X implies alternatively alkyl protons of either –CH3 (for [tξ-H1]) or –CH2– (for [tξ-H1]) at Me2pd2 and aryl protons (for all the hydride alternatives [μ4-H1]) at Ph as shown in Figure 6.

Computational analysis further revealed that the [tξ-H1] flippamer is stabilized by 3–5 kcal/mol in comparison to [tξ-H1]. This stabilization may arise in part from the CHMe···HFe distances 1.7 Å interaction (Figure 6a). Comparable interactions are invoked in isoelectronic [FeFe]-H2ase models which feature NH···HFe distances of 1.4–2.0 Å.\textsuperscript{12,15} The optimized Fe–Cγ distance is 0.2 Å shorter in [tξ-H1] vs in [tξ-H1] (Table S2). These calculations highlight the sensitivity of the Fe–Cγ interactions to subtle changes elsewhere in the molecule, as well as to the DFT methodology.\textsuperscript{12} In contrast to [tξ-H1], the bridging [μ4-H1] of the bridging hydride isomer are predicted to be essentially equal in energy with the calculated energy gaps within 1.6 kcal/mol.

**NRVS and DFT Vibrational Characterization of [t-H1]**, [t-D1], [μ-H1], and [μ-D1]. With thermally stable 57Fe-labeled terminal diiron hydride and its bridging hydride isomer in hand in the forms of [t-H/D571] and [μ-H/D571], their 57Fe–H/D vibrational signatures were characterized by 57Fe NRVS.\textsuperscript{74,75} NRVS, which is sensitive only to the motion of 57Fe nuclei, is presented as 57Fe partial vibrational density of states (PVDOS) spectra. NRVS data collected for the four samples [t-H/D571], [t-D1], [μ-H/D571], and [μ-D571]: O2CCF3, and [μ-D571] in the Supporting Information (Figure 7a,d and Figure S51a–d) were interpreted using DFT-calculation 57Fe-PVDOS spectra (Figure 7be and Figure S51a–d). The analysis is facilitated by plotting the contributions of hydride vs deuteride to the normal mode energies, provided in Figures 7cf and Figure S52b as DFT-based Hν/Dν-PVDOSs. Normal modes having significant H/D-PVDOSs are marked in Figure 7cf and shown in Figure 8 in arrow-style representations.

Weak 57Fe motion and higher frequencies make Fe–H vibrational modes particularly difficult to observe. Additional challenging factors for NRVS presently included (i) only 50% enrichment with 57Fe which effects in higher noise level and (ii) incomplete deuteration (see above). The DFT analysis considered the two Me2pd2 d/p-flippamer alternatives for both [t-H/D571] and [μ-H/D571]. Here, we restricted our attention to the ∼600–800 cm−1 “active window”, mostly exclusive to the low-intensity NRVS bands based in the δ(57Fe–H/D) bending (δ) vibrations.

As seen in NRVS studies of related complexes,\textsuperscript{12,14,15,17,49–54} the spectra exhibit intense bands associated with mixed 57Feδδ/δp/C modes <470 cm−1 and υ(Feδδ–CO) stretching (υ) and bending (δ) modes in the ∼500–600 cm−1 region. These higher intensity NRVS bands <600 cm−1, dominated by motions of the 57Fe ligands heavier than hydrides, are discussed in the Supporting Information.

NRVS spectra for [t-H1] exhibit multiple features in the 700–800 cm−1 region (Figure 7a), where our DFT calculations on [t-H/D571] predict two well-defined δ(Fe–H) modes at 749 and 789 cm−1 (Figures 7bc and 8a) and H1 moves in two perpendicular directions; these modes bear both similarity to and difference from the 57Fe–H bends characterized recently in [FeFe]-H2ase (see Figure S53 and supplementary discussions in the Supporting Information).\textsuperscript{14,15,55} However, the relative [t-H/D571] vs [t-D571] intensity levels observed in this region are indicative of the isotope sensitivity, and regional maxima at 723 (NRVS) vs 749 cm−1 (DFT) match their intensities relatively well. The situation is quite different for [t-D571], producing a band at 601 cm−1 which is missing in the spectrum of [t-H/D571] (Figure 7a). The DFT-calculated 57Fe-PVDOS for [tξ-D571] predicts a matching band at 604 cm−1 produced by modes at 599 and 606 cm−1, resulting from the coupled δ(Fe–D)/δ(Fe–CO) bending modes (Figures 7bc and 8b). The δ(Fe–D)/δ(Fe–CO) coupling is responsible for significant amplification of otherwise pure δ(Fe–D) mode intensities and is well-known to enhance the diagnostic power of NRVS on iron hydrides.\textsuperscript{14,15,54} In contrast with the 604 cm−1 band produced by [tξ-D571], DFT modeling for another [tξ-D571] flippamer produces an additional band at 621 cm−1 which does not fit the experiment (Figure S51b). Among the two flippamer alternatives, the [tξ-D571] modeling clearly provides a better fit to the observed NRVS data and therefore the d-flippamer spectra were used as representative in Figure 7b, not only is consistent with the computed [tξ-D/H571] relative energies favoring [tξ-H1] and the noe experimental results on [t-H1] (see the previous sections and Table S3). Interestingly, in spite of the tight ChMe···HFeɛ ≈ 1.7 Å dihydrogen contact achieved in [tξ-H1] (Figure 6a), this interaction does not yield any significant vibrational coupling between the HMe and Hν nuclei (see Figures S52b,c and S53 and supplementary discussions in the Supporting Information).

For the bridging hydride complex, a doublet feature is observed at 694/702 cm−1 in the spectrum of [μ-H/D571] (Figure 7d). A similar doublet feature is calculated at 670/687 cm−1 for [μ-H/D571] (Figure 7e). Mixed ω(Fe–H–Fe) out-of-plane bending, or wagging (ω), modes absorb at these energies: see e.g. the calculated modes at 670 and 692 cm−1 indicated in Figure 7f and shown in Figure 8c. In contrast, [μ-H/D571] modeling produces a relatively pure ω(Fe–H–Fe) wag at 724 cm−1 (Figure S51c), which is not consistent with the observed spectra. The DFT spectra for the bridging hydride species in Figure 7e therefore assumed the presence of the p-flippamer absorbing in the ∼600–800 cm−1 “active window” (see the Supporting Information for an extended discussion).

The [μ-D571] model produces a red-shifted ω(Fe–D–Fe) wag at 590 cm−1 (Figures 7f and 8d), having vibrational energy similar to that of the δ(Fe–D) bends from the [tξ-D571] model as discussed above. The ω(Fe–D–H/D–Fe) wags, however, contain much less H/D vibrational energy (Figure 7cf) and show smaller H/D exchange interactions only a minor perturbation of the δ(Fe–CO) bands for the bridging hydride isomer (Figure
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7d,e). DFT rationalizes this behavior as respectively stronger vs weaker involvement of the $^{57}$Fe nuclei in the $\delta$(Fe$^\text{IV}$-H/D) bending vs $\omega$(Fe$^\text{II}$H$_2$/D$_2$-Fe$^\text{II}$) wagging motion, consistent with $\sim$0.2 Å shorter Fe−H distances in $[t\text{-H}]^1$ vs $[\mu\text{-H}]^1$ (Table S2). Calculations therefore rationalize the well-defined NRVS modification between the terminal and bridging species as exposed by the H$^+$ to D$^-$ isotope exchange, which is marked by a dashed red line at $\sim$600−cm$^{-1}$ in Figure 7.

Figure 7d reveals overlapping $[\mu\text{-H}]^7$ and $[\mu\text{-D}]^7$ NRVS features at 694−702 cm$^{-1}$, consistent with the $[\mu\text{-D}^3]^{11}$O$_2$CF$_3$ sample contamination by $[\mu\text{-H}]^7$O$_2$CF$_3$, as quantified by $^1$H NMR (see above). The corresponding 670−690 cm$^{-1}$ doublet features from the DFT modeling of the pure species are however not completely eliminated by the H/D isotope exchanges regardless of the flippamers: see Figure 7be and Figure S51−d. The calculations indicate that these bands, protruding into the $\delta$(Fe−H) "active window", are produced by many mixed modes of Me$_2$pdt$^\pm$, dpv$^\pm$, and ary molecular fragments. These modes overlap with the hydride motion only in $[\mu\text{-H}]^7$ (see the 670 and 692 cm$^{-1}$ modes indicated in Figure 7f and shown in Figure 8c and also the discussion on $\omega$(Fe$_{\text{eq}}$−H$_{\text{eq}}$−Fe$_{\text{eq}}$) above).

### CONCLUSIONS

In this work, a sterically congested diron hydride complex was prepared as a model for a diferrous hydride state of the [FeFe]-hydrogenases. The steric effects were introduced by combining a pair of dpv ligands and 2,2-dimethylpropane-1,3-dithiolate. The preparative methods were adapted to allow introduction of $^{57}$Fe for NRVS analysis. The considerable steric effects are manifested at many stages in the chemistry: ring current effects are seen in the $^1$H NR spectrum of [1]$^0$, the 210 mV greater reducing power for [1]$^0$, the enhanced stability of [1]$^1$, the nOe interaction between the hydride, dithiolate, and diphosphine in $[t\text{-H}]^1$, the slow isomerization of $[t\text{-H}]^1$, and the detection of its second isomer $[t\text{-H}]^2$. The last species served as a precursor to the bridging hydride $[\mu\text{-H}]^1$ isomer, predicted by DFT to be $\sim$16 kcal/mol more stable than $[t\text{-H}]^1$.

Owing to their thermal stability, the salts of respectively $[t\text{-H}]^7$ and $[\mu\text{-H}]^7$ are well suited for their comparative assessment by NRVS spectroscopy. The Fe−H/D NRVS bands in the $\sim$600−800 cm$^{-1}$ "active window", in spite of their inherently low intensities, reveal important chemical information when they are rationalized by DFT modeling. The combined application of NRVS and DFT clearly discriminated between the terminal vs bridging hydride isomeric species that differ by the first-shell ligand arrangement in the diron core. The 720−800 cm$^{-1}$ bands produced by two perpendicular bending $\delta$(Fe−H) motions in $[t\text{-H}]^7$ are twice as intense as the 670−700 cm$^{-1}$ bands produced by wagging $\omega$(Fe−H−Fe) motion in $[\mu\text{-H}]^7$. For the deuteride samples, the higher NRVS intensity $\delta$(Fe−CO) bands at $\sim$600 cm$^{-1}$ are noticeably perturbed in $[t\text{-H}]^7$ but not in $[\mu\text{-D}]^7$. Analogous NRVS fingerprints supported our assignment of the catalytic H$_{\text{eq}}$ state in [FeFe$^\text{II}$]$_2$H$_{\text{eq}}$ to the terminal Fe$_{\text{II}}$−H hydride species (see ref 15; specifically, Figure S15). The $\delta$(Fe−H) NRVS bands around 750 cm$^{-1}$ have been indicated in H$_{\text{eq}}$ as well by an independent DFT modeling. Using techniques different from NRVS, others proposed bridging hydrides (Fe$_{\text{eq}}$−H−Fe$_{\text{eq}}$) for the H$_{\text{red}}$ and H$_{\text{red}}$ states.\textsuperscript{7,19}

Analysis of the $\delta$(Fe−H/D) and $\omega$(Fe−H/D−Fe) bands for $[t\text{-H}]^7$ and $[\mu\text{-H}]^7$ gave insights into the orientation of the Me$_2$pdt$^\pm$ bridge. The $^{57}$Fe-PV DOS spectral signatures for the terminal vs bridging hydride isomers are distinctive because of the presence or absence of H$^+$−H$_{\mu\text{eq}}$ interactions. From the NRVS data, one can infer a considerable level of structural insight. Consistent with the NRVS and nOe experiments rationalized by the DFT calculations, a closed CH$_{\mu\text{eq}}$···H$_{\text{Fe}}$ $\approx$ 1.7 Å contact is stabilized in the best-fit conformer of $[t\text{-H}]^1$. The CH$_{\mu\text{eq}}$···H$_{\text{Fe}}$ interaction is reminiscent of the NH$^+$···H$_{\text{Fe}}$ $\approx$ 2.0 Å dihydrogen interaction characterized recently for the H$_{\text{red}}$ hydride state of [FeFe$^\text{II}$]-H$_{\text{eq}}$. In contrast to $[t\text{-H}]^1$, the dihydrogen interaction in the catalytic H$_{\text{red}}$ state additionally exhibits vibrational coupling between the two H nuclei.

### EXPERIMENTAL SECTION

Reactions and manipulations were performed using standard Schlenk techniques or in a nitrogen atmosphere glovebox. HPLC-grade solvents were dried by filtration through activated alumina or distilled under nitrogen over an appropriate drying agent and then used. ESI-MS data for compounds were acquired using a Waters Micromass Quattro II spectrometer. $^1$H NMR (500 MHz) and $^1$H NMR (600 MHz) spectra were referenced to residual solvent relative to TMS. $^{31}$P($^1$H) NMR (202 and 242 MHz) spectra were referenced to external 85% H$_3$PO$_4$. Chemical shifts are reported for room temperature in the $\delta$ scale. FT-IR spectra were recorded on a PerkinElmer 100 FT-IR spectrometer. Crystallographic data for compounds [1]$^0$ and [1]$^{1}$Fe were collected using a Siemens SMART diffractometer equipped with a Mo Kα source ($\lambda = 0.71073$ Å), $\text{cis}$-1,2-Bis(diphenylphosphino)ethylene (dppe) and HBF$_4$Et$_2$O solution were purchased from Aldrich. The compounds Me$_2$pdtH$_{\text{eq}}$, Fe$_{\text{eq}}$(Me$_2$pdt)(CO)$_2$ and Fe$_{\text{eq}}$(Me$_2$pdt)(CO)$_2$ were prepared according to literature procedures.\textsuperscript{7,29}

Fe$_{\text{eq}}$(Me$_2$pdt)(CO)$_2$(dppe)$_2$ ([1]$^1$). Method 1. A mixture of Fe$_{\text{eq}}$(Me$_2$pdt)(CO)$_2$(dppe) (113 mg, 0.15 mmol) and dppe (60 mg, 0.15 mmol) was dissolved in 100 mL of toluene in a Pyrex Schlenk tube. The reaction mixture was irradiated with a 100 W UV immersion lamp (λ = 356 nm, Spectroline) until the reaction was complete ($\sim$25 h) as indicated by FT-IR spectroscopy. After the solvent was removed under vacuum, the residue was extracted into 5 mL of CH$_2$Cl$_2$. The filtered extract was layered with 50 mL of pentane, and this mixture was stored at $\sim$35 °C overnight. The product was precipitated as a greenish black solid. Yield: 105 mg (63%). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.71−7.27 (m, 44H, C$_6$H$_{14}$ and $\equiv$CH$_3$), 1.33−1.25 (m, 4H, SCH$_2$), $\sim$0.19 (br s, 6H, CH$_3$). $^{31}$P($^1$H) NMR (CD$_2$Cl$_2$): $\delta$ 8.72 FT-IR (CH$_2$Cl$_2$): $\nu$$_\text{CO}$ 1898 (vs), 1865 (vs) cm$^{-1}$. ESI-MS: m/z 1091.4 [M$^+$(calcd 1091.4)]$^0$, 1041.4 (calcld 1041.4). Anal. Calcld for C$_{59}$H$_{54}$BF$_4$Fe$_2$O$_2$P$_4$S$_2$: C, 57.93 (58.08); H, 4.62 (4.64).

Method 2. A solution of Fe$_{\text{eq}}$(Me$_2$pdt)(CO)$_2$ (83 mg, 0.20 mmol) and dppe (158 mg, 0.40 mmol) in 100 mL of dry toluene was irradiated with an LED lamp (λ = 356 nm). The reaction was complete in $\sim$7 h, as indicated by FT-IR spectroscopy. Solvent was removed under vacuum, and the residue was extracted into 5 mL of CH$_2$Cl$_2$. The filtered extract was layered with 50 mL of pentane, and this mixture was stored at $\sim$35 °C overnight. The product was precipitated as a greenish black solid. Yield: 170 mg (78%).

Fe$_{\text{eq}}$(Me$_2$pdt)(CO)$_2$(dppe)$_2$BF$_4$ ([1]$^{1}$Fe). A dark green solution of Fe$_{\text{eq}}$(Me$_2$pdt)(CO)$_2$(dppe)$_2$ (33 mg, 0.030 mmol) in 2 mL of CH$_2$Cl$_2$ was treated at $\sim$40 °C with F$_2$BF$_3$ (9 mg, 0.033 mmol) in 3 mL of CH$_2$Cl$_2$. The reaction mixture was stirred at $\sim$40 °C until the reaction was complete (5 min) as indicated by FT-IR spectroscopy. The resulting solution was then layered with 25 mL of hexane, which was allowed to stand at $\sim$35 °C overnight. The product precipitated as blue-black needle-like crystals. Yield: 170 mg ($\sim$78%).
of CH₃Cl was treated at 0 °C with HBF₄·EtOH (6.3 μL, 0.04 mmol). This species was not formed when THF was used as the solvent. The reaction mixture was stirred at 0 °C until the reaction was complete (10 min) as indicated by FT-IR spectroscopy. The resulting solution was then layered with 50 mL of hexane, which was allowed to stand at −35 °C overnight. The product, a greenish black solid, was stored at −15 °C in the glovebox. Yield: 15 mg (42%). 1H NMR (500 MHz, CDCl₃): δ 8.22–6.73 (m, 44H, CH₂ and =CH₂) 1.59–1.27 (m, 4H, SCH₂), 0.50, 0.03 (s, 6H, CH₃), −2.23 (t, JFe=H = 81 Hz, 1H, =CH₂)). 1P{1H} NMR (CDCl₃, 20): δ 95.3 (s), 87.2 (s), 80.4 (s), 68.7 (s). FT-IR (CHCl₃): νCO 1974 (vs), 1899 (s) cm⁻¹. ESI-MS: m/z 1095.1 [M − BF₄]⁺ (calcd 1095.1). Anal. Calcld for C₅₂H₅₉Fe·BF₄·H₂O: C, 52.95 (53.01); H, 4.34 (4.38).

A dark green solution of Fe₂(Me₂pdt)(CO)(dpv)₂BF₄ ([μ-H]Fe₂(Me₂pdt)(CO)(dpv)₂BF₄). A dark green solution of Fe₂(Me₂pdt)(CO)(dpv)₂, (44 mg, 0.040 mmol) in 5 mL of CH₂Cl₂ was treated at room temperature with HBF₄·Et₂O (8.4 μL, 0.060 mmol). The reaction mixture was stirred at room temperature until the reaction was complete (~41 h) as indicated by FT-IR spectroscopy. After the solvent was removed, the residue was washed with 2 × 10 mL of Et₂O and dried under vacuum. The product was obtained as a brown-red solid. Yield: 35 mg (72%). 1H NMR (500 MHz, CDCl₃): δ 8.08–6.67 (m, 44H, CH₂ and =CH₂) 2.57–1.37 (m, 4H, SCH₂), 1.15, 0.20 (s, 6H, CH₃), −14.70 (m, 1H, Fe(μ-H)Fe). 1P{1H} NMR (CDCl₃, 20): δ 86.8 (s), 81.3 (s), 78.5 (s), 72.5 (s). FT-IR (CHCl₃): νCO 1974 (broad), 1952 (vs) cm⁻¹. ESI-MS: m/z 1095.1 [M − BF₄]⁺ (1096.1). Anal. Calcld for C₅₂H₅₉Fe·BF₄·H₂O: C, 52.95 (53.01); H, 4.34 (4.38).

Fe₂(Me₂pdt)(CO)(dpv)₂BF₄ ([μ-H]Fe₂(Me₂pdt)(CO)(dpv)₂BF₄). A dark green solution of Fe₂(Me₂pdt)(CO)(dpv)₂, (55 mg, 0.050 mmol) in 5 mL of CH₂Cl₂ was treated at 0 °C with D₂O (9.0 μL, 0.050 mmol) followed by HBF₄·Et₂O (11.0 μL, 0.075 mmol). The reaction mixture was stirred at 0 °C until the reaction was complete (10 min) as indicated by FT-IR spectroscopy. The resulting solution was then layered with 50 mL of Et₂O, which was allowed to stand at −35 °C overnight. The product precipitated as a greenish black solid and was stored at −35 °C in the glovebox. Yield: 35 mg (59%). The deuterium was incomplete, as indicated by a small μ-H signal at δ −2.23. 1H NMR (500 MHz, CDCl₃): δ 8.22–6.73 (m, 44H, CH₂ and =CH₂) 1.57–1.27 (m, 4H, SCH₂), 0.49, 0.02 (s, 6H, CH₃), −2.23 (t, JFe=H = 80 Hz, 0.3H, =CH₂)). 1P{1H} NMR (600 MHz, CHCl₃): δ −2.14 (t, JFe=H = 12.4 Hz, =CH₂). 1P{1H} NMR (CDCl₃): δ 95.2 (s), 87.3 (2 × br d), 80.6 (2 × br d), 68.7 (s). FT-IR (CHCl₃): νCO 1964 (vs), 1899 (s) cm⁻¹. ESI-MS: m/z 1096.2 [M − BF₄]⁺ (1096.2).
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**Fe-Labeled [(μ-H)Fe2(Me2pdt)(CO)2(dpv)][BF4]O2CCF3 (μ-H^+1)O2CCF3 and [(μ-D)Fe2(Me2pdt)(CO)2(dpv)][O2CCF3 (μ-D^+1)O2CCF3.** Solutions of [(μ-H^+1)O2CCF3 and [(μ-D^+1)O2CCF3, respectively. The appearance of an IR band at 1855 cm⁻¹ in the spectra of [(μ-H^+1)O2CCF3 and [(μ-D^+1)O2CCF3, indicates the presence of a small amount of [(μ-D)] in these samples (Figures S44 and S47). Finally, the appearance of a signal at δ = -1.47 in the ¹H NMR spectrum of [(μ-D^+1)O2CCF3 (Figure S49) indicates only 65% deuterium, the remaining being [(μ-H^+1)O2CCF3. ¹H NMR (500 MHz, CD2Cl2) : δ 8.08−6.67 (m, 44H, C6H3), δ 1.37 (m, 4H, SC6H3). ¹H NMR (CD2Cl2), δ 8.17, 0.23 (s, s, 6H, CH3) in CH3Cl2. ¹H NMR (CD2Cl2), δ 8.17, 0.23 (s, s, 6H, CH3). FT-IR (CHCl3) : 3,2974 (902 cm⁻¹), 3,102 (793 cm⁻¹). Inorganic Chemistry

**Cyclic Voltammetry.** Electrochemical experiments were carried out in a nitrogen-filled glovebox fitted with adapters to connect to a CH Instruments Model 600D series electrochemical analyzer. These experiments were conducted in a 3 mL glass cell and a silver wire was used as a pseudoreference electrode, and experiments were conducted in a 3 mL glass cell and a silver wire was used as a pseudoreference electrode. These experiments were conducted in a glovebox, sparging was not necessary. Inorganic Chemistry

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02903.

ESI-MS, FT-IR, NMR, CV, NRVS, and DFT figures and tables; supplementary discussions on the NRVS and DFT results (PDF)

Animated vibrational normal modes (ZIP)

Coordinates of the DFT models (ZIP)

Accession Codes

CCDC 1583878–1583879 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

T.B.R. and S.P.C. planned the research and designed experiments. M.R.C., C.P.R., W.W., and P.-H.Z. carried out the LAVC3 basis set for the outermost core and valence orbitals and the quasi-relativistic Los Alamos effective core potential (ECP) for the innermost electrons. The model environment was considered using a self-consistent reaction field (SCRF) polarizable continuum model and integral equation formalism (IEF-PCM) as implemented in GAUSSIAN 09, with the static dielectric constant set to ε = 4.0 and the remaining IEF-PCM parameters at their default values for water. The calculations (i) including the two-body D3 dispersion corrections by Grimme et al.25,26 as implemented in GAUSSIAN 09 and (ii) excluding the D3 correction have been done to generate the normal modes in the (i) <470 cm⁻¹ and (ii) >470 cm⁻¹ areas, respectively; this combined approach ultimately produced DFT-based Fe-PVDSO spectra in better agreement with the experiment. The optimized structures shown in the figures are based on scheme ii, if not otherwise mentioned. On the basis of the normal mode outputs, an in-house Q-SPECTOR program successfully applied previously15,51–54 was utilized to generate the Fe-PVDSO from the normal mode composition factors. An empirical scaling of calculated frequencies has not been applied. The resolution of the observed NRVS spectra was accounted for by convolution of the computed PVDSO intensities with a full width at half-maximum (fwhm) equal to 14 cm⁻¹ Lorentzian.

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synthetic operations and preliminary characterizations. D.L.G. conducted the X-ray crystallography. C.C.P., L.B.G., and H.W. collected the NRVS data. V.P. carried out the DFT calculations and interpreted their results. T.B.R., V.P., M.R.C., and C.C.P. wrote the manuscript.

**Notes**

The authors declare no competing financial interest.

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