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An iron-iron hydrogenase mimic with appended electron reservoir for efficient proton reduction in aqueous media

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The transition from a fossil-based economy to a hydrogen-based economy requires cheap and abundant, yet stable and efficient, hydrogen production catalysts. Nature shows the potential of iron-based catalysts such as the iron-iron hydrogenase (H2ase) enzyme, which catalyzes hydrogen evolution at rates similar to platinum with low overpotential. However, existing synthetic H2ase mimics generally suffer from low efficiency and oxygen sensitivity and generally operate in organic solvents. We report on a synthetic H2ase mimic that contains a redox-active phosphole ligand as an electron reservoir, a feature that is also crucial for the working of the natural enzyme. Using a combination of (spectro)electrochemistry and time-resolved infrared spectroscopy, we elucidate the unique redox behavior of the catalyst. We find that the electron reservoir actively partakes in the reduction of protons and that its electron-rich redox states are stabilized through ligand protonation. In dilute sulfuric acid, the catalyst has a turnover frequency of $7.0 \times 10^4$ s$^{-1}$ at an overpotential of 0.66 V. This catalyst is tolerant to the presence of oxygen, thereby paving the way for a new generation of synthetic H2ase mimics that combine the benefits of the enzyme with synthetic versatility and improved stability.

INTRODUCTION

A hydrogen-based economy is a viable alternative to our current fossil-fuel-based economy (1), but only if hydrogen is generated in a sustainable fashion. This requires technology to reversibly store sustainable (solar or wind) energy as molecular hydrogen using water as feedstock. Although these processes are technically feasible, the required catalysts for hydrogenation and oxygen evolution are currently based on platinum and iridium, respectively (2). As such, the unaffordability and unavailability of materials hamper the large-scale application of these technologies. The iron-iron hydrogenase (H2ase) enzyme catalyzes the reversible reduction of protons at rates comparable to platinum catalysts at a similar electrochemical potential (3). Although the applicability of the enzyme to commercial devices for proton reduction or oxygen oxidation is complicated by elaborate growth and isolation steps and its inherent intolerance to air (4), its high efficiency shows that iron-based complexes can, in principle, perform this crucial reaction with a performance similar to platinum. Inspired by this, numerous synthetic complexes have been prepared as structural and functional mimics for the H2ase active site (5, 6). Most of these H2ase mimics display proton reduction activity in organic solvents, but they often display low efficiency and stability and require a relatively high overpotential (7, 8). H2ase mimics that work efficiently in an aqueous environment while being tolerant to air have not yet been reported (9, 10). Clearly, certain elements around the active site in the natural H2ase are of crucial importance to its function. The incorporation of synthetic complexes into a natural apoenzyme results in H2ase enzyme hybrids that can still be fully active, further demonstrating the importance of the local environment of the active site (11, 12). One of the elements that received attention and was successfully installed in various mimics is the internal basic amine that functions as a proton relay. A similar proton relay was present in the nickel-based catalysts studied by Helm et al. (13), Bullock et al. (14), and Hou et al. (15), which resulted in the most efficient molecular catalysts for proton reduction known to date. The natural enzyme also preorganizes electrons using a [4Fe-4S] ferredoxin electron reservoir in close proximity to the active site. Adamska-Venkatesh et al. (16) recently demonstrated the active role of the electron reservoir in the catalytic cycle, via the so-called superreduced state of the H-cluster (H$_{\text{red}}$). Long before that, Tard et al. (17) published the first structural mimic with a ferredoxin-type electron reservoir. Camara and Rauchfuss (18) and Lansing et al. (19) then reported on a H2ase mimic containing a redox-active ferrocenyl phosphine that could be used for hydrogen oxidation and proton reduction catalysis. Here, we report on a synthetic H2ase mimic that contains a redox-active phosphole ligand as an electron reservoir, which actively partakes in the reduction of protons, leading to a highly efficient and oxygen-tolerant proton reduction catalyst that operates in acidic water.

RESULTS AND DISCUSSION

In view of the essential role of the electron reservoir in the proton reduction catalytic cycle in hydrogenases, we set out to synthesize functional mimics with redox-active organic ligands. We chose a redox-active phosphole ligand, a type of ligand that has been used successfully in organic light-emitting diode applications (20, 21). Various phosphole analogs can be prepared easily, including those with pyridyl moieties for improved water solubility and for supramolecular attachment of chromophores (22). The final hydrogenase mimic consists of an [2Fe-2S] cluster with a benzenedithiolato ($\mu$-bdt) bridge, with the proximal iron atom bonded to the phosphorus of the phosphole ligand. The pyridyl moieties make this complex soluble in acidic water (vide infra). Furthermore, the pyridyl functions can be used for coordination to photosensitizers such as ZnTPP.

Synthesis and characterization

The pyridyl-functionalized complex 1 and its phenyl-functionalized counterpart 1’ were prepared from the precursor complex Fe$_2$(μ-bdt)(CO)$_6$.
by displacement of one carbonyl ligand by the corresponding phosphole ligand, either through reaction in tetrahydrofuran at reflux or by treatment with trimethylamine N-oxide in dichloromethane/acetonitrile at room temperature. Both methods gave a yield of around 45%, although the first method gave a cleaner crude reaction mixture, thereby facilitating purification. Complexes 1 and 1\textsuperscript{Ph} are air-stable solids that can be prepared in gram scale from commercial starting materials in a convenient two-step synthesis. Both compounds were characterized by infrared (IR) (fig. S1), nuclear magnetic resonance (NMR) (\textsuperscript{1}H, \textsuperscript{31}P) (figs. S2 to S7), and high-resolution mass spectroscopy (figs. S8 and S9). The IR spectra of both compounds show a red shift of 25 to 30 cm\textsuperscript{-1} compared to the parent Fe\textsubscript{2}(\mu-bdt)(CO)\textsubscript{6}, as is typically observed for [2Fe-2S] carbonyl clusters (table S1).

Complex 1\textsuperscript{Ph} was crystallized from pentane at \textdegree C, and its structure was determined by x-ray diffraction analysis (fig. 1A). We were unable to crystallize complex 1, but the density functional theory (DFT)–calculated structure of 1 (fig. 1B) is in good agreement with the crystal structure of 1\textsuperscript{Ph}, with an average deviation in selected bond lengths between the structures of only 0.65% and an average deviation in selected angles of 0.76% (fig. S10).

**Redox behavior in the absence of acid**

The redox activity of the phosphole ligand in complex 1 is demonstrated by cyclic voltammetry in combination with DFT calculations and spectroelectrochemical experiments. Cyclic voltammetry in dichloromethane on a mercury electrode reveals a redox process with a cathodic peak potential of around \textminus 1.7 V (versus Fe\textsuperscript{2+/3+}) and anodic peak potentials of around \textminus 1.7 and \textminus 1.45 V (fig. 2A). Controlled potential coulometry (\textminus 2.3 V) of a solution of 1 in dichloromethane on a carbon sponge electrode shows the passage of three electrons per molecule (figs. S11 and S12). The shift in the cathodic peak potential with a scan rate \( \frac{\partial E_\text{pc}}{\partial n} \) of 8.3 mV, which is close to the 8.5 mV \( \text{[RT/3F(ln(10))]} \) expected for a three-electron process, with a rate-limiting chemical follow-up reaction after one of the electron transfers (fig. 2A, inset) (23). Fitting the voltammograms (figs. S13 and S14) by simulation (figs. S15 and S16) revealed that, during the redox process, the first reduction (\textminus 1.76 V) is followed by a chemical transformation (structural rearrangement due to electron delocalization) (24). The second electron transfer (\textminus 1.44 V) is concerted with Fe–S bond cleavage, followed by a third reduction event (\textminus 1.64 V) (table S2).

The reduced complex 1\textsuperscript{2+}, generated by chemical reduction, was further studied by electron paramagnetic resonance (EPR) at room temperature. The EPR spectrum of 1\textsuperscript{2+} in toluene shows a ligand-centered radical, as identified by a doublet from \textsuperscript{31}P coupling (\( g = 2.06; A = 47 \) G) (fig. 2B). The similarity of this signal to the reported radical on the free phosphole ligand (\( g = 2.0027; A = 28.5 \) G) indicates that one electron in 1\textsuperscript{2+} resides at the phosphole ligand (25), with the other two electrons on the other part of the di-iron complex. Spectroelectrochemical experiments (fig. 2C) reveal the IR spectrum of 1\textsuperscript{2+} in which we observed an average shift in the carbonyl stretching frequency $\Delta v_{\text{avg}}(\text{CO})$ of 75 cm\textsuperscript{-1} with respect to neutral 1.

Because of potential inversion within the reduction process, species 1\textsuperscript{−} and 1\textsuperscript{2−} cannot be characterized by conventional spectroelectrochemistry or isolated after chemical reduction. However, the mono-anion 1\textsuperscript{−} can be generated by photo-induced electron transfer from a supramolecularly anchored photosensitizer and identified by time-resolved IR spectroscopy (TR-IR) (26, 27). The 2:1 complex of ZnTPP with 1 forms through the simple mixing of these building blocks in solution, as evidenced by ultraviolet-visible (UV-vis) titration experiments (figs. S17 to S19, table S3, and accompanying text), and the coordinated ZnTPP shows quantitative static fluorescence quenching behavior (fig. S20, table S4, and accompanying text). After the excitation of a solution of the supramolecular complex 1(ZnTPP)\textsubscript{2} (fig. S21) with a 630-nm laser pulse during while probing the IR spectrum with subpicosecond resolution, a new species emerged within 5 ps (fig. 3B). Global biexponential fitting of the experimental curves at 2057, 2029, 1997, and 1970 cm\textsuperscript{-1} (Fig. 3C and fig. S22) shows that the excited state of the porphyrin leads to charge separation in 2.5 ps. The charge-separated state leads to recombination within 83 ps. The IR spectrum of the short-lived intermediate 1\textsuperscript{−} features a $\Delta v_{\text{avg}}(\text{CO})$ of 26 cm\textsuperscript{-1}, which is roughly one-third of the shift observed in 1\textsuperscript{2−}. In line with this, the DFT-calculated structure of the mono-anion 1\textsuperscript{−} (fig. 4, left) features a delocalized spin density distribution, with 0.64 e\textsuperscript{−} on the ligand and 0.33 e\textsuperscript{−} on iron. The backbone of the phosphole ligand, which is dienic in character for neutral 1, is of intermediate dienic/aromatic character in 1\textsuperscript{−}, reflecting the reduction process taking place partly on the ligand. DFT calculations on species 1\textsuperscript{2−} (fig. 4, right) reveal that diereuction of complex 1 leads to monoreduction of the di-iron complex and monoreduction of the ligand. The C–C bonds in the phosphole backbone are all 1.420 ± 0.004 Å, illustrating the aromatic character of the phosphole ligand in species 1\textsuperscript{2−}.

Comparison of the electrochemical behavior of 1 to that of the parent (\( \mu\text{-bdt} \))Fe\textsubscript{2}(CO)\textsubscript{6} clearly shows the effect of the redox behavior of the ligand on 1. Monoreduction of (\( \mu\text{-bdt} \))Fe\textsubscript{2}(CO)\textsubscript{6} leads to cleavage

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**Fig. 1. Molecular structures of 1\textsuperscript{Ph} and 1.** (A) Crystal structure of 1\textsuperscript{Ph} with displacement ellipsoids at 50% probability. (B) DFT-calculated (BP86, def2-TZVP) structure of 1.
of the Fe–S bond (28), as is evident from the DFT-calculated structure. In contrast, the [2Fe-2S] butterfly structure of 1 remains intact, with an average Fe–S bond elongation of 0.02 Å, because the electron mainly resides on the ligand. The second reduction of the complex to give 1 leads to a singly reduced ligand and singly reduced di-iron complex, which is comparable to the mono-reduced parent (μ-bdt)Fe2(CO)6. Indeed, this leads to Fe–S bond rupture to form a structure that is able to accept another electron. This suggests that, in species 1, two electrons are located on the di-iron complex and one electron is located on the ligand. These results highlight the effect of the use of redox-active ligands on this type of hydrogenase mimics and show that, as a consequence, the redox properties of 1 are similar to those of the H-cluster of the H2ase enzyme. In the natural system, one-electron reduction of the HOx state is localized on the [2Fe-2S] cluster, mediated by the [4Fe-4S] electron reservoir (29). Two-electron reduction leads to Hred with one electron on [2Fe-2S] and one on the ferredoxin [4Fe-4S] cluster (16).

Electrocatalysis in dichloromethane
In the presence of acid, complex 1 is catalytically active in the reduction of protons. Cyclic voltammetry in dichloromethane containing Et3NHBF4 on a mercury electrode shows two well-resolved reduction
waves, followed by a catalytic wave that increases in amplitude with increasing acid concentration (Fig. 5). This shows that complex 1 needs to be activated by reduction before the active species can enter the catalytic cycle.

The first redox process (1 ↔ 2) has a cathodic peak potential of around −1.4 V (versus Fc⁰/⁺), roughly 0.3 V more positive than in the absence of acid (Fig. 6A and figs. S23 to S26). This anodic shift indicates that at least one proton is involved in the redox process and that the first process involves a proton-coupled electron transfer (section S7.2) because Et₃NHBF₄ is not acidic enough to protonate 1 (fig. S27). To elucidate the operating mechanism of this first redox wave, we performed a peak potential analysis of a series of voltammograms measured at varying acid concentrations and scan rates (Fig. 6B and figs. S28 and S29). In the pure kinetic zone, the shift in the cathodic peak potential with scan rate ∂Epc/∂ln(ν) was 12.5 mV, close to the 12.9 mV [= RT/2F/ln(10)] expected for a two-electron process, with a rate-limiting chemical follow-up reaction after the first electron transfer (23). The shift in the cathodic peak potential with acid concentration ∂Epc/∂ln([Et₃NHBF₄]) was 25.2 mV, indicating that two protons are transferred after the first electron transfer. Digital simulation of the voltammograms (fig. S30) revealed an overall redox process involving two proton and two electron transfers [electrochemical, chemical, chemical, electrochemical (ECCE) process at −1.44 and −1.18 V] (table S5). The IR spectrum of the resulting species 2 was recorded using spectroelectrochemistry on a gold-amalgam working electrode (Fig. 6C) and shows CO stretching frequencies (2041, 1977, and 1915 cm⁻¹) similar to 1 [Δνavg(CO) = 15 cm⁻¹]. This relative small shift is indicative of the formation of a mono-reduced iron hydride, and the remaining electron density and proton are located on the phosphole ligand (27, 30–32). No bands belonging to a bridging carbonyl ligand were observed.
Modeling of the cyclic voltammogram in Fig. 5 reveals the nature of the second redox process (2 ↔ 3) as a two-electron and single-proton process (ECE process at −2.0 and −1.9 V), leading to the catalytic resting state 3. Spectroelectrochemical analysis of the catalytic wave (Fig. 7A) reveals the CO stretching frequencies of the resting state 3 at 2020, 1951, 1931, 1904, and 1875 cm⁻¹ with a Δν_{avg}(CO) of 57 cm⁻¹ with respect to 1. This shift (42 cm⁻¹ with respect to 2) is much smaller than that expected for a two-electron reduction on iron, indicating that both electrons are equally distributed over iron and ligand, leading to a resting state in which two electrons (and two protons) are stored on the phosphole ligand. Comparison of the IR region between 1570 and 1670 cm⁻¹ to the IR spectra of the reduced and protonated states of 4,4'-bipyridine (33) confirms the reduction and protonation states of the ligand (figs. S31 and S32 and table S6). Modeling of the redox and chemical processes in the catalytic wave shows that the only plausible catalytic mechanism is of the ECE type (Fig. 7B, fig. S33, and table S7). Advancing through the catalytic cycle, the resting state 3 is protonated (k = 10^5 M⁻¹ s⁻¹) to release H₂ in a rate-determining step. The newly formed species 4 has the same overall reduction/protonation state as 2. Spectroelectrochemistry could not successfully identify species 4, which is caused by the very short lifetime of this species under catalytic conditions. It seems reasonable that 4 is converted into 2 by an (overall) intramolecular proton and electron transfer from the phosphole ligand to iron.

One of the interesting features of the catalytic mechanism is that, in the catalytic cycle, an electron is transferred from the ligand to an iron center. The ligand thus acts as an electron reservoir during catalysis,
similar to the enzyme’s catalytic cycle where the H$_{\text{red}}$ state is protonated with concomitant electron transfer from the ferredoxin cluster to [2Fe-2S] (16). A major implication of this peculiar behavior is the leveling of redox potentials within the catalytic cycle (a difference of only 0.1 V). In contrast, weak acid catalysis using the parent compound (μ-bdt)Fe$_2$(CO)$_6$ shows that this complex operates with a similar ECEC mechanism but with the reduction potentials spaced almost 0.8 V apart (~1.31 and ~2.08 V) (28). Redox potential leveling is essential for both electron transfers to occur with similar driving force (10). In catalyst 1, this leveling is induced by a balancing of charges through protonation of the ligand concomitant with electron transfer, which is clearly seen in the anodic shift in the reduction potential by ca. 0.3 V upon addition of a proton source. In control experiments carried out with the analogous complex 1$^{\text{Ph}}$ with phenyl groups instead of pyridyl moieties, such shift was not seen, and the resulting redox reaction follows an ECE mechanism instead of the ECCE mechanism observed for 1 (figs. S34 to S36). This signifies the role of the pyridyl moiety in the reduction process and illustrates the applicability of the dipyridylphosphole as a redox and proton-reactive ligand.

**Catalysis in aqueous media**

Complex 1 at 2.0 μM concentration is soluble in 1 M sulfuric acid as a result of the protonation of the pyridyl moieties attached to the ligand building block, enabling proton reduction catalysis in water. Cyclic voltammetry using a gold-amalgam working electrode shows catalytic current densities up to 50 mA cm$^{-2}$ with a half-wave potential of ~0.7 V normal hydrogen electrode [versus normal hydrogen electrode (NHE)] and hydrogen evolution clearly visible on the electrode (Fig. 8A). Oxygen sensitivity is generally one of the critical properties of hydrogenase enzymes and many of the synthetic mimics, complicating their application in devices. We were pleased to find that catalysis in air-saturated solution retained 60% of catalytic performance (in terms of current densities) compared to experiments performed in properly degassed solvent (Fig. 8B), indicating that these mimics are not only water-soluble but also air-tolerant, both highly desired properties for H$_2$ase mimics (7, 8).

In 1 M H$_2$SO$_4$, plateau currents (required to establish catalytic rate constants) were not obtained, most likely as a result of rapid depletion of the acid. To determine a rate constant for the catalytic process in 1 M H$_2$SO$_4$, we performed foot-of-the-wave analysis to obtain a hypothetical value of 50 mA cm$^{-2}$ for the plateau current density $j_{\text{pl}}$ (fig. S37) (34). For foot-of-the-wave analysis, the dominant redox couple $E_{\text{cat}}$ for the catalyst under catalytic conditions must be known. Plateau currents were obtained in 1 M Na$_2$SO$_4$ (acidified with concentrated sulfuric acid to the desired pH) (Fig. 9A). Under these conditions, the catalytic half-wave potential converged to ~0.66 V (versus NHE) for pH < 1.5 (Fig. 9B), and this potential was used as the dominant redox couple $E_{\text{cat}}$ for the catalyst in 1 M H$_2$SO$_4$. Moreover, whether the catalyst is in a homogeneous solution or adsorbed on the electrode must be determined. In acidified 1 M Na$_2$SO$_4$, the linear dependence of catalytic current on proton concentration indicates that the catalyst is adsorbed on the gold-amalgam electrode (Fig. 9C). Because redox waves belonging to 1 are masked by catalytic current, we synthesized a water-soluble mimic of protonated 1 by alkylation at the pyridyl nitrogen atoms. This mimic was prepared by reacting 1 with 2 eq of (Et)$_3$O·BF$_4$ in dichloromethane at room temperature and characterized by NMR ($^1$H, $^{31}$P) and IR spectroscopy (figs. S38 to S40). Cyclic voltammetry
of this pyridine-ethylated analog Et21-(BF4)2 in neutral water shows an adsorption wave leading to a surface concentration \( I^0 \) of 0.73 × 10\(^{-11}\) mol cm\(^{-2}\) (figs. S41 and S42) (35). Assuming a similar behavior for I in acidic water, this surface concentration was used to determine catalytic efficiency. In line with catalysis from surface-adsorbed catalyst molecules, the addition of acetonitrile to the solution led to a decrease in catalytic current (noticeable from approximately 1% v/v) as a result of the desorption of the catalyst from the surface. In a separate control experiment, the free ligand was also used as a proton reduction catalyst but showed no activity (figs. S43 and S44).

The obtained catalytic rate constant in 1 M \( \text{H}_2\text{SO}_4 \) (calculated using \( k_{cat} = 2k_{cat}F0([\text{H}^+]0) \) (36, 37) is 3.5 × 10\(^4\) M\(^{-1}\) s\(^{-1}\), close to that found in dichloromethane (10\(^5\) M\(^{-1}\) s\(^{-1}\)), suggesting that the catalytic mechanism does not change significantly by changing the solvent. Moreover, turnover numbers (TONs) during one cyclic voltammetric scan are on the order of 10\(^3\) to 10\(^4\) (table S8), confirming the stability of the catalyst. With the rational benchmarking approach outlined by Artero and Savéant (38), a catalytic Tafel plot can be constructed from TOF\(_{\text{max}} = 2k_{cat}[\text{H}^+]0 = 7.0 \times 10^{4}\) s\(^{-1}\) and an overpotential of 0.66 V. Clearly, catalyst I displays high rates in aqueous phase but at an overpotential that is still higher than the natural enzyme.

CONCLUSION

We report here the first di-iron \( \text{H}_2\text{ase} \) mimic that is equipped with a redox-noninnocent phosphorus ligand. The redox-active ligand functions as an electron reservoir, donating an electron to the active site during the catalytic cycle when needed, in resemblance to the natural \( \text{H}_2\text{ase} \) system where an iron-sulfur cluster near the active site is responsible for this function. The catalyst operates in an aqueous environment, is oxygen-tolerant, and displays high TON and turnover frequency (TOF), which is a major step toward the development of catalysts for hydrogen-producing devices. Now that we have demonstrated that \( \text{H}_2\text{ase} \) mimics with electron reservoirs are easily accessible via a redox-active phosphorus ligand, further development should be directed toward analogs that operate at lower overpotentials and can be efficiently implemented in devices (for example, by anchoring to electrodes or metal-organic frameworks).

MATERIALS AND METHODS

General procedures

All syntheses were carried out under a nitrogen atmosphere using standard Schlenk techniques. All purifications involving column chromatography were performed in air with non-degassed solvents. Dichloromethane used for synthesis, UV-vis, fluorescence, electrochemistry, and spectroelectrochemistry was distilled over calcium hydride before use. Tetrahydrofuran and acetonitrile were used for synthesis (pro analysis grade) as received. The supporting electrolyte nBu4NPF6 (prepared from saturated solutions of KPF6 and nBuN4Br in water) was recrystallized from hot methanol and dried under vacuum at 80°C overnight. The phosphine ligand was synthesized according to a procedure in the literature (21). The acid Et4NHBF4 was synthesized according to a modified procedure in the literature (39), where the crude product was extracted with dichloromethane to remove residual \( \text{NH}_4\text{BF}_4 \). All commercially available chemicals were used as received.

Synthesis of 1

\( \text{Fe}_2(\mu-\text{bdtd})(\text{CO})_6 \) (1.0 g, 2.4 mmol), ligand (0.63 g, 1.7 mmol), and tetrahydrofuran (250 ml) were added to a 500-ml round-bottom flask. The solution was refluxed for 4 hours, and the crude product was purified on silica by eluting with pentane [elutes 0.40 g of \( \text{Fe}_2(\mu-\text{bdtd})(\text{CO})_6 \)] and then 5% methanol in dichloromethane containing 1 drop of \( \text{NH}_4\text{OH} \) per 100 ml (elutes the product). Removal of solvent yielded 0.60 g (46%) of the product as a red powder. \(^1\)H NMR (400 MHz, CD2Cl2) \( \delta \) 8.50 (br s, 4H), 7.92 (ddd, \( \delta \) 11.3, 8.0, 1.6 Hz, 2H), 7.66 (ddd, \( \delta \) 8.7, 4.7, 2.2 Hz, 3H), 7.06 (br s, 4H), 7.01 (dd, \( \delta \) 5.5, 3.2 Hz, 2H), 6.70 (dd, \( \delta \) 5.4, 3.2 Hz, 2H), 2.66 (d, \( \delta \) 17.6 Hz, 2H, 2.38 (d, \( \delta \) 17.9 Hz, 2H), 1.61 (m, 4H). \(^{31}\)P NMR (162 MHz, CD2Cl2) \( \delta \) 75.1 (s). IR (CH2Cl2 cm\(^{-1}\)): ν(CO) 2053 (s), 1995 (s), 1983 (m), 1941 (w). Mass spectrometry [field desorption (FD')] for \( \text{C}_{32}\text{H}_{35}\text{Fe}_2\text{N}_2\text{O}_5\text{PS}_2: m/z \) 759.6224 (calculated), 759.9753 (observed) [Δ(m/z) = 4.5 ppm].

Synthesis of 1Ph

A solution of \( \text{Fe}_2(\mu-\text{bdtd})(\text{CO})_6 \) (84.0 mg, 0.2 mmol) and ligand (73.3 mg, 0.2 mmol) in dichloromethane (20 ml) was treated with 4.0 ml of a 0.05 M solution of trimethylamine \( \text{N-oxide} \) dihydrate in acetonitrile. The solution was stirred at room temperature for 2 hours, and the crude product was purified on silica by eluting with pentane [elutes \( \text{Fe}_2(\mu-\text{bdtd})(\text{CO})_6 \)] and then dichloromethane/pentane (2:5) (elutes the product). Removal of solvent yielded 71 mg (45%) of the product as a red powder. \(^1\)H NMR (400 MHz, CD2Cl2) \( \delta \) 7.95 (ddd, \( \delta \) 11.0, 7.5, 2.1 Hz, 2H), 7.69 to 7.56 (m, 3H), 7.33 to 7.11 (m, 10H), 7.01 (dd, \( \delta \) 5.5, 3.2 Hz, 2H), 6.68 (dd, \( \delta \) 5.5, 3.2 Hz, 2H), 2.63 (d, \( \delta \) 17.6 Hz, 2H), 2.35 (d, \( \delta \) 18.3 Hz, 2H), 1.57 (4H, overlaps with water peak). \(^{31}\)P NMR (162 MHz, CD2Cl2) \( \delta \) 74.9 (s). IR (CH2Cl2 cm\(^{-1}\)): ν(CO) 2048 (s), 1992 (s), 1977 (m), 1939 (w). Mass spectrometry (FD') for \( \text{C}_{32}\text{H}_{35}\text{Fe}_2\text{N}_2\text{O}_5\text{PS}_2: m/z \) 757.97363 (calculated), 757.98919 (observed) [Δ(m/z) = 20.5 ppm].

Synthesis of Et21-(BF4)2

A solution of I (7.6 mg, 10 μmol) in dichloromethane (5.0 ml) was treated with a solution of Et4O-BF4 (0.50 ml of 0.04 M in dichloromethane, 20 μmol) and stirred at room temperature for 10 min. All of the solvent was evaporated, and the residue was dissolved in dichloromethane and filtered through a polytetrafluoroethylene filter (pore size, 0.45 μm). Removal of solvent yielded the product as a red solid in quantitative yield. \(^1\)H NMR (400 MHz, CD2Cl2) \( \delta \) 8.69 to 8.52 (m, 4H), 7.93 to 7.63 (m, 7H), 7.49 to 7.40 (m, 2H), 7.12 to 6.92 (m, 2H), 6.86 to 6.68 (m, 2H), 4.85 to 4.75 (m, 2H), 4.63 to 4.51 (m, 2H), 1.77 to 1.56 (m, 4H), 1.37 to 1.21 (m, 7H), 0.93 to 0.84 (m, 3H). \(^{31}\)P NMR (162 MHz, CD2Cl2) \( \delta \) 77.5 (s). IR (CH2Cl2 cm\(^{-1}\)): ν(CO) 2060 (s), 2002 (s), 1991 (m), 1945 (w), 1632 (w).

Electrochemistry in dichloromethane

Cyclic voltammetry was performed on 0.5 or 1 mM solutions of I in dichloromethylene containing 0.1 M nBu4NPF6, as the supporting electrolyte. The voltammograms were recorded using a 663-VA stand with a PGSTAT302N potentiostat (Metrohm/Autolab), a static mercury drop electrode (drop size 2) as a working electrode, a glassy carbon rod as an auxiliary electrode, and a leakless Ag+/Ag reference electrode (eDAQ ETO69). Single equivalents of Et4NHBF4 were added as a 25% m/v solution in dichloromethane. To convert the potential values of the Ag+/Ag reference into Fe3+/Fe2+, a correction factor was used, as determined by cyclic voltammetry of 1 mM ferrocene in dichloromethane using the same reference electrode. At the end of each experiment, ferrocene
was added to the solution to check for reference electrode drift. All cyclic voltammetric experiments in dichloromethane (except when measuring catalytic waves) were compensated to about 95% of solution resistance.

**Electrochemistry in 1 M H₂SO₄ and in acidified 1 M Na₂SO₄**

Cyclic voltammetry was performed on deoxygenated solutions, unless stated otherwise. Compound 1 was added as a 2 mM solution in methanol. The voltammograms were recorded using a 663-VA stand with a PGSTAT302N potentiospectrometer (Metrohm/Autolab), a AuHg wire as a working electrode (vide infra), a platinum wire as an auxiliary electrode, and a Ag/AgCl (3 M KCl) reference electrode (Metrohm 6.0750.100). To convert the potential values of the Ag⁰/⁺ reference into NHE, a correction factor of +0.21 V was used. The working electrode was a gold wire (0.5 mm in diameter, 99.99%; Sigma-Aldrich 310980) soldered to a copper wire (using a Sn/Pb eutectic solder), with the copper wire, solder joint, and part of the gold wire molten into a polyethylene housing. The gold wire was cut to leave 3 to 5 mm exposed. Before the experiments, the wire was thoroughly rinsed with ethanol, dried, submerged in (triply distilled) mercury for 5 min, wiped well with a dry tissue (repeated three times; a flat and shiny surface should be obtained), and placed diagonally in a glass cell approximately 5 mm from the reference electrode. All measurements were performed as automated sequences to maximize reproducibility. Six voltammograms were recorded in each sequence, with only scan rate varying (0.1, 0.3, 1.0, 3.0, 10, and 0.1 V s⁻¹). Before each scan, the solution was purged with N₂ for 10 s (while stirring) and then left undisturbed for 5 s.

**DFT calculations**

The gas-phase geometries of molecules 1, 1⁻, and 1²⁻ were optimized with the Turbomole program package (40) at the r-i-DFT (41)/BP86 (42, 43) level. We used the def2-TZVP basis set (44, 45) for all atoms. These calculations also yielded the frontier orbitals and spin density plots.

**Time-resolved IR spectroscopy**

Using a previously described experimental setup (26), we generated a visible pump and a mid-IR probe. Two commercial beta barium borate (BBO)-based optical parametric amplifiers (OPAs; Spectra-Physics OPA-800C) were pumped by a Tsapphire laser (Spectra-Physics Hurricane, 600 µJ) at a repetition rate of 1 kHz. IR probe pulses were generated by difference-frequency mixing signal and idler from one of the OPAs in a AgGaS₂ crystal. The visible pump pulses (630 nm; pulse energy, 3 µJ) were generated by doubling the signal of the other OPA. The delay positions were scanned by mechanically adjusting the beam path of the UV pump using a Newport ESP300 translation stage. The sample cell with CaF₂ windows spaced 500 µm apart was placed in the IR focus. From the full width at half-maximum of the pump probe cross-correlation function, a temporal resolution of 200 fs was obtained. A custom-built 30-pixel mercury cadmium telluride (MCT) detector coupled to an Oriel MS260i spectrograph was used to record the transient spectra by subtracting nonpumped absorption spectra from the pumped absorption spectra.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/1/e1501014/DC1

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