Photodynamics of [FeFe]-Hydrogenase Model Compounds with Bidentate Heterocyclic Ligands

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Abstract

Two asymmetrically structured model compounds for the hydrogen-generating [Fe-Fe]hydrogenase active site were investigated to determine the ultrafast photodynamics, structural intermediates, and photoproducts compared to more common symmetric di-iron species. The bidentate-ligand containing compounds studied were $Fe_2(\mu-S_2C_3H_6)(CO)_4(bipy)$, **1**, and $Fe_2(\mu-S_2C_3H_6)(CO)_4(phen)$, **2**, in dilute room temperature acetonitrile solution and low-temperature 2Me-THF matrix isolation using static FTIR difference and time-resolved infrared spectroscopic methods (TRIR). Ultraviolet-visible spectra were also compared to time-dependent Density Functional theory (TD-DFT) to ascertain the orbital origins of long wavelength electronic absorption features. The spectroscopic evidence supports the conclusions that only a propyl-bridge flip occurs in low-temperature matrix, while early-time CO-ejection leads to formation of solvated isomeric species on the 25 ps timescale in room temperature solution.

Introduction

The [FeFe]-hydrogenases are extraordinarily efficient enzymatic catalysts for producing hydrogen gas.¹⁻⁹ These enzymes perform very rapidly under mild pH chemical conditions. The active site of the enzyme is made up of a di-iron core with a di-bridging azadithiolate ligand. The irons also have cyano and carbonyl pendant ligands. The di-iron core links to the rest of the protein through a sulfur on a cysteine residue which also attaches the di-iron active site to a [4Fe-4S] cubane structure.^{8, 10-12} The exact form of the active site varies depending on the oxidation state and the reduced form is shown in Figure 1.¹¹



Figure 1. Reduced form of the active site of the [FeFe]-hydrogenase enzyme. X can be water, OH⁻, or CO (in the CO-inhibited form).¹¹

A wide variety of small-molecule models of the [FeFe]-hydrogenase active site have been developed. Simple models are based on $Fe_2(\mu-S_2C_3H_6)(CO)_6$ which is shown in Figure 2a. Variants of this model compound alter the bridging and/or pendant ligands and different pendant ligands changes the electronic properties around the active site. While these models show structural similarities to the hydrogenase active site, they are generally poor catalysts in and of themselves.¹³⁻¹⁵

One potential use for hydrogenase model compounds is to combine them with a photosensitizer, using the absorption of light to drive the production of hydrogen. Photosensitizers can be bound through one of the pendant ligands¹⁶⁻¹⁷ or through the bridging ligand¹⁸⁻²⁷ (some model compounds may be photocatalytically active, even without a distinct photosensitizer, as well). The mechanisms for hydrogen production using photosensitization methods are complicated by the fact that the di-iron core absorbs both UV and visible light, and these absorptions can lead to

substantial dynamic changes to the di-iron core. Depending on the substitution of the particular model compounds, these dynamics can include excitation to a relatively long-lived (150 ps) excited state,²⁸⁻³⁰ CO loss mechanisms,²⁸⁻³² and isomerization of the active site.²⁹⁻³² Some of these changes persist out to even longer timescales (at least several microseconds), which could be long enough to affect catalytic mechanisms.

While initial work has been performed to extract the UV or visible light-driven dynamics of simple model compounds, no studies have been completed on the ultrafast dynamics of model compounds that contain a photosensitizer. In this work, two model compounds containing basic photosensitizer moieties are studied using ultrafast visible pump, infrared probe time resolved spectroscopy. The compounds studied are $Fe_2(\mu-S_2C_3H_6)(CO)_4(bipy)$, **1**, and $Fe_2(\mu-S_2C_3H_6)(CO)_4(phen)$, **2**, shown in Figure 2 where bipy = $2,2^2$ -bipyridine and phen = 1,10-phenanthroline. The bipyridine and phenanthroline ligands change the ground-state electronic structure of the model compound significantly, as is readily observed as new broad visible absorptions in the ultraviolet-visible (UV-Vis) spectra in Figure 3a. Figure 3b,c show calculated electronic absorption spectra using two different calculational models, as described later. Measuring the dynamics of these compounds gives direct insight into the potential changes in model compound dynamics that result from the presence of photosensitizers, as well as the asymmetric nature of these models.



Figure 2. Structures of (a) $Fe_2(\mu-S_2C_3H_6)(CO)_6$, 3, (b) $Fe_2(\mu-S_2C_3H_6)(CO)_4(bipy)$, 1, and (c) $Fe_2(\mu-S_2C_3H_6)(CO)_4(phen)$, 2.



Figure 3. (a) Experimental UV-Vis spectra of **1**, **2**, **3**, and 2,2'-bipyridine (bipy) ligand in dilute room temperature (293 K) acetonitrile solution. (b) Computed TD-DFT absorption spectra using statistical average of orbital potentials (SAOP) model for **1** and **2**. (c) Computed TD-DFT

absorption spectra using TZVP basis with the modified LANL2DZ effective core potential/basis set on the two Fe atoms and acetonitrile solvation via SMD (solvent model, density) for 1, 2, and 3 for comparison to experimental spectra.

Methods

Synthesis 3 1

Compounds **1**, **2**, and **3** were prepared using previously reported procedures. ^{13, 33-34} Purity of the compounds was checked using ¹H NMR, ¹³C NMR, and FT-IR.

Steady-State Spectra of 1 and 2

Steady-state IR spectra were obtained using Thermo Nicolet 6700 and Perkin-Elmer Spectrum 1000 infrared spectrometers³⁵ using 1 cm⁻¹ and 4 cm⁻¹ resolution, respectively. Concentrations were 1.5 mM, using a cell with CaF₂ windows and a pathlength of 1 mm. UV-Vis spectra were obtained with an HP 8453 UV-Vis spectrometer using quartz cuvettes with 1 cm pathlength. Concentrations for the UV-Vis spectra were 0.15 mM.

Matrix-Isolation FTIR

The 2-methyltetrahydrofuran (2-MeTHF) matrix solvent was distilled in the presence of sodium wire under argon atmosphere immediately prior to use. Samples for photochemical experiments were prepared by dissolving **1** or **2** in 2-MeTHF to 2 mM yielding a *ca*. 5000:1 matrix:sample dilution. The samples were then degassed by several freeze-pump-thaw cycles and finally injected into an argon-flushed infrared cell with NaCl windows and a pathlength of 1 mm. The sample was cooled using a liquid N₂ optical cryostat (Graesby Specac GS21525) outfitted with NaCl windows

and the cryostat evacuated to a pressure of 1.3×10^{-3} Pa (10^{-5} Torr). The sample was maintained at a temperature of 85 K during all experiments.

All photolyses were conducted using the filtered output of a 350 W high-pressure Hg lamp (Newport Corporation). The output of this lamp was first filtered through a 5 cm pathlength quartz water jacket to absorb the infrared component of its output, then the desired photolysis wavelengths were selected using combinations of optical bandpass and cutoff filters. Infrared spectra (Perkin Elmer Spectrum 1000, 4 cm⁻¹ resolution, 1024 scans averaged) were measured prior to photolysis as well as after each photolysis condition to characterize wavelength dependent photochemistry. A Ge window was placed in the infrared beampath prior to the sample to exclude any photolysis events initiated by residual visible radiation from the globar.

Ultrafast TRIR

Ultrafast TRIR experiments were performed using an 80 fs Ti:sapphire-based amplified laser system. The system is seeded using a 30 fs Kapteyn-Murnane 80 MHz oscillator centered at 800 nm. This seeds a home-built Ti:sapphire regenerative amplifier also centered with 800 nm output. The resulting pulses are 80 fs, 700 μ J at 1 kHz repetition rate used to pump a Spectra-Physics OPA-800F optical parametric amplifier (OPA). The resulting signal and idler pulses are difference frequency mixed in a 1 mm thick AgGaS crystal yielding 120 fs infrared pulses with an intensity of about 1 μ J. These output probe pulses are centered around 2000 cm⁻¹ with a 230 cm⁻¹ FWHM bandwidth. Residual 800 nm light from the OPA is frequency doubled in a 100- μ m thick BBO crystal to generate 400 nm, 70 fs, 10 μ J excitation pulses.

The timing of the IR probe pulses relative to the excitation pulses is controlled using a 500 mm, computer-controlled optical delay stage (maximum delay time, 300 ps). The 400 nm pump and IR probe pulses are overlapped and collinearly transmitted through a sample flow cell. The pump

beam is chopped at a 500 Hz rate, allowing for single-shot comparison of the spectra, and a separate reference beam is transmitted through an unexcited portion of the sample to account for shot-to-shot amplitude and spectral variations of the probe pulses.

The sample cell is a 2 mm pathlength flow cell with CaF_2 windows. The cell is translated in both the x and y directions during experiments to reduce photoproduct buildup on the windows. Solutions studied were room temperature, 1 mM concentrations in acetonitrile and continually purged with argon to reduce sample degradation. Resulting optical densities were less than one in both the UV and IR spectral regions.

The reference and probe IR beams were dispersed in a computer-controlled scanning monochromator with ca. 4 cm⁻¹ FWHM resolution. Signals were collected using a matched pair of Mercury-Cadmium-Telluride (MCT) detectors with biased high gain pre-amplifiers and processed on a shot-to-shot basis using two boxcar averagers (Stanford Research Systems 250). The two boxcar output signals were digitized, processed for each laser shot and spectral/time-dependent results recorded on a computer.

Two types of ultrafast TRIR scans were conducted. First, a small number of delay time points were selected and entire TRIR spectra were collected at those time points. From spectral data scans, important wavelengths were identified and time-delay pump-probe scans were conducted at a fixed probe wavelength with higher time resolution. The delay time was scanned from -35 ps to 285 ps with time resolution of 2 ps. To obtain higher resolution near the t=0 origin, a second time-delay scan was conducted from -6 ps to 25 ps with resolution of 0.2 ps. Transient spectra and time-dependent single wavelength scans displayed below were typically obtained by averaging 1000 laser shots per spectral point (at 2 cm⁻¹ and 0.2 ps or 2 ps delay steps) and two independent

runs further averaged to obtain highest signal-to-noise with ca. 0.001 OD noise (type b, k=2 averages).

For time-dependent scans at each wavenumber, scans with high and low density of time points were combined and fit together with a single-exponential decay plus an offset

$$\Delta OD = A_1 e^{-t/\tau_1} + C \tag{1}$$

For both **1** and **2**, one of the sets of time-dependent scans clearly showed a signal increase followed by a decay. These scans were fit using the equation:

$$\Delta OD = A_1 \left(1 - e^{-t/\tau_1} \right) e^{-t/\tau_2} + C \tag{2}$$

To avoid effects from the rising edge and coherence effects, only data at a time greater than 1 ps after the time origin was included in the fits.

DFT Calculations

DFT-predicted gas phase IR spectra were calculated using Gaussian 09W.³⁶ Calculations were performed using the BP86 functional³⁷⁻⁴² and TZVP basis set.⁴³⁻⁴⁴ Both **1** and **2** can exist as four different isomers. The isomers for **1** are shown in Figure 4 (isomers for **2** are the same, replacing the bipy ligand with phen, as shown in SI Figure S1). In addition, potential photofragments were run under the same conditions.



Figure 4. Four potential isomeric structures of **1**. Dipole moments (in Debye, D) and ΔG values (in kcal/mol) were calculated for gas-phase, isolated molecules using DFT.

Electronic spectra of observed species were simulated in two different ways. The first was using the Amsterdam Density Functional (ADF2014.02) program.⁴⁵⁻⁴⁷ Electronic configurations of atoms were described by an all-electron triple-ζ Slater-type orbital basis set modified by a polarization function (TZP STO).⁴⁸ Geometry optimizations and vibrational frequency calculations were performed using the GGA functional of Becke³⁷ and Perdew.⁴⁰⁻⁴¹ Electronic excitation energies were computed using the statistical average of orbital potentials (SAOP) model,⁴⁹⁻⁵⁰ with solvent interactions approximated by the COSMO model.⁵¹⁻⁵³

Additional Time-Dependent DFT (TD-DFT)⁵⁴ calculations were performed using the Gaussian16 software package.⁵⁵ Due to slight differences in numerical integration grids between Gaussian16 and Gaussian09W, geometries of the lowest energy isomers of **1** and **2** were reoptimized with the BP86 functional. The basis set for TD-DFT calculations utilized the Hay and Wadt basis set and effective core potential (ECP) combination (LANL2DZ)⁵⁶⁻⁵⁷ as modified by Couty and Hall,⁵⁸ where the two outermost p functions of Fe have been replaced by a split of the optimized 4p basis function, respectively. All other atoms utilized the TZVP basis set. Aqueous solvation energies were computed using the SMD model with standard cavity parameters for acetonitrile.⁵⁹ The simulated UV-vis spectra were produced with an in-house program using a Gaussian broadening of 40 nm. All energy-minimized x,y,z atomic coordinates for the vibrational and electronic TD-DFT methods employed above for selected ground state structures are listed at the end of the Supplemental Information.

Results and Discussion

Electronic Structures of 1 and 2

The substitution of two CO ligands by a 2,2'-bipyridine or 1,10-phenanthroline polypyridyl ligand results in pronounced changes to the electronic structure of **1** and **2** relative to that of the parent $(\mu$ -pdt)Fe₂(CO)₆ complex, as is readily apparent by their dark green color (in contrast to the orange-red color of the unsubstituted hexacarbonyl complex). The poorer π -acceptor ability of the polypyridyl ligands relative to that of CO results in a more electron-rich metal environment, and an increase of the remaining Fe-CO bond strengths through strengthening of the Fe-CO π backbond. In the present case, this is observed as a *ca*. 80 cm⁻¹ redshift of the v(CO) stretching vibrational modes relative to those of the hexacarbonyl complex v(CO) vibrational modes. Beyond the increase of electron density on the metal centers, the low-lying π^* orbitals of the polypyridyl ligands introduce metal-to-ligand charge-transfer (MLCT) bands of bipy $\pi^* \leftarrow$ Fe character as potential low-energy electronic excitations. Additionally, ligation of the polypyridyl ligand to a single Fe center yields an asymmetrically substituted complex that breaks the near-degeneracy of the two Fe centers, yielding unique {Fe(CO)₃} and {Fe(CO)L₂} moieties, each of which is anticipated to exhibit distinct chemistry.

Qualitatively, the above-mentioned changes to the bonding and electronic structures of 1 and 2 can be expected to result in distinctly different photochemical behavior compared to (μ pdt)Fe₂(CO)₆. Photodecarbonylation is anticipated to become less efficient due to the increased electron density and promotion of the Fe-CO π backbond, as well as the introduction of bipy $\pi^* \leftarrow$ Fe MLCT excited states that result in less pronounced changes to the Fe-CO bonding interactions in electronically excited states. The introduction of these vacant bipy π^* orbitals also introduces new, non-decarbonylative, electronic relaxation pathways taking place through the polypyridyl ligand rather than through photodecarbonylation mechanisms. Finally, it may also be expected that decarbonylation will be preferred on the { $Fe(CO)_3$ } moiety relative to the { $Fe(CO)L_2$ } moiety as the { $Fe(CO)_3$ } group is somewhat less electron-rich, resulting in slightly weaker Fe-CO bonds compared to the { $Fe(CO)L_2$ } group. Experimentally, this final expectation is realized, in part, by CO substitution occurring preferentially on the { $Fe(CO)_3$ } moiety by PPh₃ in the presence of Me₃NO rather than on the { $Fe(CO)L_2$ } moiety.⁶⁰

The experimental and TD-DFT calculated electronic spectra of **1** and **2** are presented in Figure 3. Experimentally, in the region from 500 nm extending into the near-IR, **1** exhibits three overlapping absorption maxima centered at 535 nm, 620 nm and 695 nm with a tail extending to *ca.* 840 nm. In slight contrast, **2** exhibits three maxima centered at 523 nm, 610 nm, and 705 nm also with a tail extending to *ca.* 840 nm in the NIR. In both cases, directly analogous absorption bands are absent in the unsubstituted (μ -pdt)Fe₂(CO)₆, allowing these transitions to be reasonably assigned as polypyridyl $\pi^* \leftarrow$ Fe MLCT excitations. Extending to higher energies, from 500 nm into the UV, **1** exhibits maxima at 407 nm, 344 nm, and 288 nm while **2** exhibits absorption maxima at 390 nm, 345 nm, and 270 nm. In this same region, (μ -pdt)Fe₂(CO)₆ exhibits several absorptions assigned as excitations into Fe₂ σ^* , Fe₂S₂ π^* , and Fe-CO π^* orbitals.⁶¹ However, directly analogous assignments of **1** and **2** cannot be made due to the introduction and contribution of polypyridine-based transitions that may occur in this region.

To better understand the precise nature of the electronic structure of **1** and **2**, TD-DFT computations were performed on **1** and **2** using the SAOP model. The results of these computations are summarized in the SI Tables S1 and S2 and Figure 5 showing some of the electron density

orbitals for several electronic states. Analogous electron density orbitals for **2** may be found in SI Figure S2. Qualitatively, the calculated and experimental spectra (Figures 3a and b) agree reasonably well, with stronger absorptions at shorter wavelengths and several weaker absorptions above 400 nm, although the quantitative agreement between the spectra is not great. Somewhat better agreement is seen with the TZVP, SMD calculations shown in Figure 3c.

As anticipated, the three low-energy excitations are dominated by transitions of MLCT character, corresponding to excitations from the HOMO, HOMO -1, and HOMO -2 into the LUMO. The HOMO is a bonding interaction of the {Fe(CO)₃} dz² and {Fe(bipy)(CO)} d_{xv} orbitals. The HOMO -1 orbital predominantly consists of an Fe t_{2g} set, and the HOMO -2 can be described by the {Fe(CO)₃}-S₂ π bond as well as a carbonyl backbonding interaction of the $\{Fe(CO)(bipy)\}\$ moiety. The LUMO corresponds to the first bipy π^* molecular orbital. At slightly higher energy, the first transition that is not completely MLCT in character is the LUMO +1 \leftarrow HOMO excitation, which can be described as the Fe₂ $\sigma^* \leftarrow$ Fe₂ σ transition and calculated to occur at 480 nm. As energy increases towards the UV, excitations continue to be dominated by MLCT transitions. Relevant to the pump-probe experiments conducted in these studies, transitions near 400 nm are calculated to result in excitation from the HOMO -1 and the HOMO -2 into the first four unoccupied molecular orbitals. The LUMO +2 is described as an Fe₂S₂ π^* molecular orbital, while the LUMO +3 is described as predominantly a bipy π^* molecular orbital. Excitations in the 266 nm region are calculated to include combinations of transitions similar to those near 400 nm, but also include excitations from lower energy orbitals consisting of the bipy π orbitals (HOMO -7 and HOMO -10) and into higher energy orbitals consisting of {Fe(CO)₂-CO} π^* interactions (LUMO +6 and LUMO +7).



Figure 5. Selected Kohn-Sham orbital electron densities for 1.

Steady-State IR Spectroscopy

The steady-state IR spectrum for **1** in acetonitrile is shown in Figure 6a. DFT-calculated vibrational spectra for each isomer are also shown in Figure 6b. Vibrational assignments for each band (as calculated using DFT BP86/TZVP) are given in Table S3. As seen in other work,^{29, 31} the position of the propyl bridge does not significantly affect the steady-state IR spectra (resulting in only minor band shifts), and so isomers **1-1** and **1-2** yield very similar spectra (as do **1-3** and **1-4**).



Figure 6. (a) Experimental IR of **1** in acetonitrile in the CO region. (b) DFT-calculated gas-phase IR spectra of the four isomers of **1**. (c) Simulated IR spectra of **1** assuming only isomer **1-1** (purple line) and a room-temperature Boltzmann population of isomers (brown line, almost indistinguishable from the purple line).

Both the crystal structure³⁴ and DFT-calculated energies predict that **1-1** will be the dominant ground state isomer, with the bipy ligand in the axial/axial position and the propyl bridge pointing away from the bipy ligand. Isomer **1-2** (axial/axial with the bridge pointing towards the bipy) is only slightly higher in energy (1.2 kcal/mol) and may contribute a small amount to the IR spectrum at room temperature (roughly 13% using the gas phase energies and the Boltzmann distribution). This contribution is difficult to detect in the steady-state IR spectrum in the CO-stretch region, given the similarities of the spectra. The energies of the rotated isomers with the bipy ligand in an axial/equatorial position (**1-3** and **1-4**) are sufficiently high that they do not significantly contribute to the steady-state IR spectrum.

The experimental IR spectra of **1** and **2** are essentially identical, as may be found in SI Figure S3. The DFT-predicted results for the isomers are also very similar. Therefore, the vibrational analysis for **2** is essentially the same as for **1**. The experimental and DFT-predicted spectra for **2** are also shown in SI Figure S4.

Matrix-isolation Photochemistry

The photochemistry of the unsubstituted (μ -pdt)Fe₂(CO)₆ parent complex has been previously studied at cryogenic temperatures in hydrocarbon matrices.⁶¹ This complex was found to exhibit wavelength dependent photochemistry resulting in apical and basal photodecarbonylation, geometric isomerization to yield a bridging-carbonyl species, and β -hydride activation of the alkyl dithiolate bridge to give a metal-hydride following photodecarbonylation. The polypyridyl substituted complexes have the potential to undergo any of these same processes, but two additional isomerizations may also occur. Due to the asymmetry of the two Fe centers introduced by the polypyridine ligand, two distinct propyl-bridge flipamers (1-1 and 1-2) exist that may potentially undergo selective interconversion, and an additional isomerization reaction is possible where the polypyridyl ligand reorients from a dibasal coordination mode (1-1 or 1-2) to an apical-basal coordination mode (1-3 and 1-4).

Due to their insolubility in hydrocarbon matrices, the photochemistry of **1** and **2** were studied in a 2-MeTHF matrix which has the potential to act as a ligand when vacant coordination sites are created following photodecarbonylation. In 2-MeTHF at 85K, **1** exhibits 3 well-defined v(CO) absorptions at 2007 cm⁻¹, 1939 cm⁻¹, and 1900 cm⁻¹, Figure 7a. Following long wavelength 800 nm> λ_{irr} >525 nm photolysis, **1** exhibits no measurable change in the v(CO) region with photolysis durations extending past 180 minutes. This indicates that the low-energy MLCT excitations of this molecule result in no photoproductive behavior under these conditions. Using wavelengths 525 nm> λ_{irr} >220 nm, a single photochemical process is observed, resulting in formation of new v(CO) absorption bands at 2000 cm⁻¹, 1925 cm⁻¹, and 1896 cm⁻¹, and bleaching of ground state v(CO) absorption bands at 2006 cm⁻¹, 1939 cm⁻¹, and 1883 cm⁻¹ (see Figure 7b). No absorption band assignable to matrix-trapped "free" CO near 2134 cm⁻¹ is observed, indicating that if photodecarbonylation occurs at these wavelengths, 2-MeTHF is a sufficiently poor ligand that liberated CO displaces it even at these cryogenic temperatures. Back photolysis of the 525 nm> λ_{irr} >220 nm irradiated sample at long (λ_{irr} >525 nm) wavelengths did not result in reversion to the parent complex, nor did annealing the sample to 130 K. Compound **2** exhibited the same photobehavior as **1** following 500 nm> λ_{irr} >220 nm photolysis (see SI Figure S5), however, the reaction of **2** does photo-revert following 350 nm> λ_{irr} >220 nm photolysis.



Figure 7. (a) FTIR of **1** in 2-MeTHF at 85 K. (b) FTIR difference spectrum following 10 min of $525>\lambda_{irr}>220$ nm photolysis. (c) Simulated difference spectrum based on DFT-calculated (gas-phase BP86/TZVP) absorptions representing loss of **1-1** isomer and increase of **1-2** isomer.

In the absence of any evidence of photodecarbonylation in 2-MeTHF matrices, two reactions remain likely for 1: (1) interconversion of flipamers 1-1 and 1-2, or (2) interconversion to rotamers 1-3 or 1-4. As the photoproduct absorption bands results in only slight (6-14 cm⁻¹) shift in v(CO) absorptions, signifying only a minor change in electronic structure and thus retaining C_s molecular symmetry (as evidenced by the retention of the number of v(CO) absorption bands), formation of rotamers 1-3 and 1-4 can be rejected. Either of these processes would result in breaking of the molecular symmetry leading to a greater number of v(CO) absorptions, see Figure 7 b. Consistent with this model of interconversion between two flipamers driven by the absorption of light, synthetic DFT calculated difference spectra of interconversion of 1-1 to 1-2 qualitatively reproduces the experimentally measured spectrum, see Figure 7c.

While evidence for involvement of the alkyldithiolate bridge in the vibrational relaxation process has been reported for the parent complex (μ -pdt)Fe₂(CO)₆, its two flipamers cannot be resolved spectroscopically due to the symmetry of the molecule. As **1** and **2** possess two non-equivalent Fe centers, interconversion of the two flipamers does result in spectroscopically distinct species, as observed in these matrix-isolation experiments. To better understand the energetics associated with the interconversion of **1-1** and **1-2**, a DFT investigation was performed studying the **1-1** \leftrightarrow **1-2** reaction coordinate, Scheme 1. At 85 K, isomer **1-1** is calculated to be the lowest energy isomer, with **1-2** lying just slightly higher in energy at $\Delta G_{85} = 0.65$ kcal mol⁻¹. Connecting these two stationary points is a transition state along the C_s plane of the molecule, with the alkyl dithiolate ligand oriented perpendicular to the Fe-Fe bond, at $\Delta G_{85} = 8.62$ kcal mol⁻¹, in good agreement with the value for the same process occurring in (μ -pdt)Fe₂(CO)₆.⁶²



Scheme 1. Reaction profile for interconversion of flipamers 1-1 and 1-2

Ultrafast TRIR

Ultrafast TRIR data was collected in two ways for each compound, with resulting difference spectra and time-dependent dynamics presented here. Full spectra at a few individual time points are shown in Figure 8 for 1. Significant spectral positions were selected, and time-delayed pump-probe scans were run at those individual wavenumbers with much higher density of time points investigated. Select results for the time-dependent data are shown in Figure 9 for 1. A complete set of time-dependent data for 1 with the associated fits can be found in Figure S6.



Figure 8. (a) UV-TRIR spectra of **1** in acetonitrile with pump wavelength of 400 nm. (b) FTIR absorption spectrum of ground state **1** in acetonitrile.



Figure 9. Time-dependent scans at selected wavenumbers for **1** in acetonitrile using 400 nm pump wavelength. (a) 2006 cm^{-1} (b) 1984 cm^{-1} (c) 1921 cm^{-1} .

In the time-resolved spectra for each compound, the bleaches at 1896 cm^{-1} , 1935 cm^{-1} , and 2006 cm^{-1} , all show relatively simple dynamics. Each bleach exhibits rapid single exponential decay with a time constant between 10 and 25 ps. The 1935 cm^{-1} and 2006 cm^{-1} bleaches leave a small residual signal, while the 1896 cm^{-1} decays essentially back to baseline. The 1896 cm^{-1} band is the weakest of the bleaches, but its behavior might also be due to overlap with new absorptions on the low wavenumber side of the ground state absorption band.

For the new absorption features, there are three regions of time-dependent behavior to consider. There is an initial spectrum, which rapidly decays (between 5 and 15 ps), there is a second signal that grows in with a similar time constant and then decays, and a long-lived signal that does not decay on the timescales measured. Specific fit results for each band discussed are shown in Table 1.

Table 1. Fit results from Equation (1) for ultrafast TRIR dynamics of 1 in acetonitrile. Positive and negative 95% confidence intervals are reported.

Band	Bleach/	$A_1 (\Delta OD)$	τ_1 (ps)	τ_2 (ps)	C (DOD)
(cm^{-1})	Absorbance				
1872	Abs	0.011 +0.0033	30+34		0.0005 ^a +0.0014
		-0.0029	-14		-0.0015
1896	Bleach	-0.007 +0.0024	10+14		$-0.0002^{a} + 0.0012$
		-0.0048	-6		-0.0011
1921	Abs	0.014 +0.0027	16+5.7	54 +22	-0.00034 ^a +0.0007
		-0.0026	-4.3	-17	-0.0028
1935	Bleach	-0.025 +0.0015	21 +3.5		-0.0067 +0.00084
		-0.0030	-4.4		-0.00090
1958	Abs	0.010 +0.0013	8 +1.9		0.0023 +0.00035

		-0.0012	-1.6	-0.00035
1984	Abs	0.0085 +0.00094	37 +12	0.0016 +0.00037
		-0.00075	-8	-0.00037
2006	Bleach	-0.033 +0.0018	14.2 +1.4	-0.0043 +0.00052
		-0.0012	-0.9	-0.00049
2023	Abs	0.0085 ± 0.0014	9+15	0.0002 ^a +0.00026
		0.0003 \ 0.0011	1.0	-0.00024
		-0.0007	-1.9	

^a Not significantly different from zero.

The initial, short-lived spectral signatures (dark green in Figure 8) have new absorption bands around 1872 cm⁻¹, 1960 cm⁻¹, 1984 cm⁻¹, and 2023 cm⁻¹. These short-lived bands do not match the bands seen in the low-temperature glass data, so they cannot be attributed to a bridge flipamer generating the **1-2** isomer. They also do not appear to be the result of the rotated **1-3** or **1-4** isomers (calculated spectra shown in Figure 10), as those isomers would show at least one new absorption band in the 1920 cm⁻¹ region (between the two lower energy vibrational modes, roughly 1935 cm⁻¹ in the calculated spectra) and no new absorption bands below 1900 cm⁻¹. The signals do match reasonably well with a mixture of CO-loss isomers from the parent **1-1** isomer shown in Figure 10b. Some component from the CO-loss isomers of the bridge-flipped **1-2** isomer could also be present, as the predicted spectra of the CO-loss isomers are quite similar to the ones from **1-1**, and the data is not sensitive enough to differentiate these isomers. Figure S7 shows the potential CO-loss isomers for **1**, along with the naming convention used (Figure S8 shows the same information for **2**). Table S3 shows the detailed vibrational assignments and results for the lowest ground state **1** and **2** isomers, based on the BP86/TZVP results. Table S4 gives calculated results for all 4CO isomers of **1**. Table S5 gives similar results for the single CO-loss isomers of **1**, while Tables S6 and S7 provide analogous results for the isomers of **2**.



Figure 10. Results of DFT calculations on (a) 4-CO isomers of 1, (b) CO-loss (3CO) isomers of 1 resulting from the parent 1-1 isomer, (c) CO-loss isomers from the 1-2 isomer (d) CO-loss isomers from the 1-3 isomer, and (e) CO-loss isomers from the 1-4 isomer.

The spectral feature that grows in with time exhibits a new absorption band at 1920 cm⁻¹. This band is not seen in the initial signal. Thus, the 1920 cm⁻¹ band clearly grows in intensity with a 16 ps time constant and then decays with a 54 ps time constant. The 1920 cm⁻¹ band is the only

place where this time behavior is seen clearly. Given the low signal-to-noise levels, detecting a new absorption growing in at the same time as an existing absorption is decaying away would be quite difficult, especially since the time constant of the rise and decay would be quite similar. There may be some evidence for a rise and longer decay component in the 1872 cm^{-1} and 1984 cm⁻¹ time-decay data (see Figure 9b for the 1984 cm⁻¹ data). There appears to be a weak rise in the signal above the fit in the few picosecond range, and the decay constant is longer and has larger error bars than most of the other decays, which could result from two overlapping decays. Unfortunately, repeated attempts to fit these data to a more complicated functional form including the decay, rise, and subsequent decay were not successful, as the signal-to-noise ratio is not good enough to pull out this effect. The location of the signal at 1920 cm^{-1} is not consistent with 1-1, 1-2, or any of the CO-loss isomers from the parent isomer, as none of those have a band in the 1920 cm⁻¹ region. The signal could be consistent with the 4CO **1-3** or **1-4** isomers, or the signal would also be consistent with CO-loss isomers of 1-3 or 1-4 (spectra shown in Figure 10d and e), as all of these species would have a band in the 1920 cm⁻¹ region. If the rise in the 1872 cm⁻¹ band is real, this would point toward the CO-loss species, as the 4CO 1-3 and 1-4 isomers do not have a band in this region, but the existence of that rise is highly uncertain.

The long-lived new absorption signals are extremely weak, but they seem to be present at 1872 cm⁻¹, 1960 cm⁻¹, and perhaps 1984 cm⁻¹ (the 1872 cm⁻¹ feature does not show an offset in the time-dependent data, but Figure 8 does seem to show a long-lived signal in this region). This is similar to the initial, short-lived species, with the exception of the missing 2023 cm⁻¹ band and would again be consistent with CO-loss isomers from the 1-1 parent isomer or 1-2, especially if isomers 1-1.1 and 1-2.1 are now missing.

The analysis for **2** is nearly identical to that for **1**. The spectra for **2** are shown in Figure 11 and select time-resolved scans are shown in Figure 12, with fit results shown in Table 2 (all of the time-resolved scans and their fits are included in Figure S9). Figure S10 shows the calculated IR absorptions for the isomers of **2** and all of the possible CO-loss products. There are two main differences from the data from **1**. First, there are somewhat lower signal levels, especially at long times, making identifying the long-lived signals more difficult. Second, the 2023 cm⁻¹ band in **2** is not as clearly present at short times, as it is in **1**, however, the 2023 cm⁻¹ absorption can be seen weakly in the time-dependent data.



Figure 11. (a) UV-TRIR spectra of **2** in acetonitrile with a pump wavelength of 400 nm. (b) IR spectrum of **2** in acetonitrile at 293 K.



Figure 12. Time-dependent scans at selected wavenumbers for 2 in acetonitrile using 400 nm pump wavelength. (a) 2004 cm^{-1} (b) 1984 cm^{-1} (c) 1919 cm^{-1} .

Band	Bleach/	$A_1 (\Delta OD)$	τ_1 (ps)	τ_2 (ps)	$C (\Delta OD)$
(cm^{-1})	Absorbance				
1872	Abs	0.007 +0.0016	23 +17		0.0025 +0.00066
		-0.0016	-9		-0.00068
1901	Bleach	-0.010 +0.0013	7 +1.8		$-0.00027^{a} + 0.00033$
		-0.0018	-1.8		-0.00034
1919	Abs	0.005 +0.0032	16 +7.8	48 + 32	-0.0005 ^a +0.0005
		-0.0029	-4.9	-19	-0.0095
1937	Bleach	-0.0100 +0.00074	33 +8.0		-0.0012 +0.00046
		-0.00098	-7.1		-0.00046
1964	Abs	0.0012 +0.00052	43 +162		0.0010 + 0.00021
		-0.00046	-35		-0.00021
1984	Abs	0.0039 +0.00056	37 +16		$-0.0002^{a}+0.00030$
		-0.00054	-10		-0.00036
2004	Bleach	-0.011 +0.0008	15 +2.7		$-0.0008^{a} + 0.0004$
		-0.0015	-3.3		-0.0040
2023	Abs	0.0037 +0.0012	9 +4.1		-0.00052 +0.00020
		-0.0004	-4.4		-0.00026
				1	

Table 2. Fit results from Equation (1) for ultrafast TRIR dynamics of 2 in acetonitrile

^a Not significantly different from zero.

One important trend to note are the relatively low signal levels compared to other [FeFe]hydrogenase model compounds studied.²⁸⁻³¹ One possible explanation for these low signal levels is the additional absorptions seen in the UV-Vis spectra for **1** and **2** compared to $Fe_2(\mu$ - $S_2C_3H_6)(CO)_6$, **3** (see Figure 3 (a)). These absorptions cannot arise directly from the bipy or phen ligands themselves, as these absorb only in the UV. The interactions between the bipy or phen ligands and the di-iron core result in additional transitions not seen in other model compounds, however (see above and Figure 3 (b) and (c)). These competing absorptions suggest that less light is absorbed by the transitions that result in CO-loss or electronic excitation, resulting in smaller TRIR signals.

Conclusions

The photochemical reaction dynamics of two asymmetric model compounds for the Fe-Fe hydrogenase active site were investigated. The species $Fe_2(\mu-S_2C_3H_6)(CO)_4(bipy)$, 1, and $Fe_2(\mu-S_2C_3H_6)(CO)_4(bipy)$, 1, and 1, a $S_2C_3H_6)(CO)_4$ (phen), 2, in dilute room temperature acetonitrile solution and low-temperature 2Me-THF matrix isolation were studied using static UV-Visible, FTIR difference and ultrafast time-resolved infrared spectroscopic methods (TRIR). Through substitution of two pendant CO ligands on one Fe with bipy and phen heterocycles, these asymmetric species exhibit much lower energy absorptions (predominantly from iron donation to the bipy and phen ligands) compared to symmetric model compounds and the native reaction site. For these compounds in lowtemperature matrix, we find that UV excitation (<525 nm) results in only propyl-bridge flipamer product with no CO ejection. In room temperature solution, however, clear evidence for COcleavage occurs on ultrafast timescales (with 400 nm excitation) and DFT-supported calculations suggest new 3-CO containing isomers are generated. Ultrafast infrared spectra and dynamics for these species supports the picture that the new photoproducts are formed within 50 ps but persist to times longer than available time delays (>300 ps). These findings are significantly different from earlier photochemical studies, where symmetric species with intermediate states persisted for ca. 150 ps for CN-substituted mimics,³¹ showed multi-exponential behavior for the parent (µpdt)Fe₂(CO)₆ complex²⁸ or extremely long lifetimes (>200 ps) for triphenylphosphene subsitutions.²⁹⁻³⁰ Results from all studies collected thus far strongly suggest that the

photochemistry of the active site is strongly controlled by the redox states of the central Fe-Fe core and further studies of asymmetric models are warranted to search for bridging CO production or other intermediates relevant to proton substitution and H₂ evolution.

Supporting Information. Isomeric structures for photolyzed **1** and **2** including DFT relative energy calculations and computed infrared spectra, TD-DFT electronic transitions with transition assignments, ground state FTIR absorption spectra, and Tables with relative structure energies and vibrational mode assignments and minimized starting atomic coordinates for all DFT calculations are included in the Supporting Information file.

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This manuscript and content were written through contributions from all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally. \$Deceased.

Acknowledgments:

This work was supported by internal NIST STRS (Scientific Technical and Research Services).

Additional funding was provided by the Hood College Summer Research Institute. We kindly

thank Dr. Timothy Magnanelli for performing temporal decay data fitting and extraction of parameter confidence limits reported in this work.

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Photodynamics of [FeFe]-Hydrogenase Model Compounds with Bidentate Heterocyclic Ligands

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Supplementary Information



Figure S1. Four potential isomers of **2**. Dipole moments and ΔG values (in kcal/mol) were calculated for gas-phase, isolated molecules using DFT.



Figure S2. Selected Kohn-Sham orbitals of 2.



Figure S3. Experimental FTIR extinction spectra of **1** and **2** in acetonitrile at room temperature (293 K).



Figure S4. (a) Experimental IR spectra of **2** in acetonitrile in the CO-stretching region. (b) DFT-calculated gas-phase IR spectra of the four isomers of **2**. (c) Simulated IR spectra of **2** assuming only isomer **2-1** (purple line) and a room-temperature Boltzmann population of isomers (brown line, almost indistinguishable from the purple line).



Figure S5. (a) FTIR of **2** in 2-MeTHF at 85 K. (b) FTIR difference spectrum following 10 min of $525>\lambda_{irr}>220$ nm photolysis. (c) Simulated difference spectrum based on DFT-calculated (gas-phase) absorptions representing loss of **2-1** isomer and increase of **2-2** isomer.



Figure S6. Time-dependent scans at selected wavenumbers for **1** in acetonitrile using 400 nm pump wavelength. (a) 1872 cm^{-1} (b) 1896 cm^{-1} (c) 1921 cm^{-1} (d) 1935 cm^{-1} (e) 1958 cm^{-1} (f) 1984 cm^{-1} (g) 2006 cm^{-1} (h) 2023 cm^{-1} .



Figure S7. The structures of all possible CO-loss isomers for 1.



Figure S8. The structures for all possible CO-loss isomers for 2.



Figure S9. Time-dependent scans at selected wavenumbers for **2** in acetonitrile using 400 nm pump wavelength. (a) 1872 cm^{-1} (b) 1901 cm^{-1} (c) 1919 cm^{-1} (d) 1935 cm^{-1} (e) 1964 cm^{-1} (f) 1984 cm^{-1} (g) 2004 cm^{-1} (h) 2023 cm^{-1} .



Figure S10. Results of DFT calculations on a) 4-CO isomers of **2**, b) CO-loss (3CO) isomers of **2** resulting from the parent **2-1** isomer, c) CO-loss isomers from the **2-2** isomer d) CO-loss isomers from the **2-3** isomer, and e) CO-loss isomers from the **2-4** isomer.

Transition	Wavelength (nm)	Oscillator Strength	Character
LUMO ← HOMO	623	0.1933	bpy $\pi^* \leftarrow Fe_2 \sigma$
LUMO ← HOMO -1	580	0.0023	bpy $\pi^* \leftarrow Fe_2 T_{2g}$
LUMO ← HOMO -2	533	0.0015	bpy $\pi^* \leftarrow {\text{Fe(bpy)-CO }\pi}$
LUMO +1 ← HOMO (62%) LUMO ← HOMO -3 (28%)	480	0.0657	$Fe_2 \sigma^* \leftarrow Fe_2 \sigma$ bpy $\pi^* \leftarrow \{Fe(bpy)\text{-}CO \pi\}$
LUMO ← HOMO -3 (53%) LUMO +3 ← HOMO (37%)	472	0.0067	bpy $\pi^* \leftarrow \{Fe(bpy)\text{-CO }\pi\}$ bpy $\pi^* \leftarrow Fe_2 \sigma$
LUMO +2 ← HOMO	468	0.0006	$\operatorname{Fe}_2 S_2 \pi * \leftarrow \operatorname{Fe}_2 \sigma$
LUMO ← HOMO -4	462	0.0001	bpy $\pi^* \leftarrow {Fe(CO)(bpy)} - S_2 \pi$
LUMO +4 ← HOMO	439	0.0656	bpy $\pi^* \leftarrow \operatorname{Fe}_2 \sigma$
$LUMO +1 \leftarrow HOMO -1 (53\%)$ $LUMO +3 \leftarrow HOMO -1 (41\%)$	437	0.009	$Fe_2 \sigma^* \leftarrow Fe_2 T_{2g}$ $bpy \pi^* \leftarrow Fe_2 T_{2g}$
LUMO +2 ← HOMO-1	429	0.0001	$\operatorname{Fe}_2 S_2 \pi * \leftarrow \operatorname{Fe}_2 \operatorname{T}_{2g}$
LUMO ← HOMO-5 (68%) LUMO +3 ← HOMO (16%)	425	0.0079	bpy $\pi^* \leftarrow \{Fe(CO)_2 - CO\} \pi$ bpy $\pi^* \leftarrow Fe_2 \sigma$
LUMO ← HOMO -5 (30%) LUMO +3 ← HOMO (25%) LUMO +1 ← HOMO (11%)	412	0.0384	bpy $\pi^* \leftarrow \{Fe(CO)_2 \pi $ bpy $\pi^* \leftarrow Fe_2 \sigma$ $Fe_2 \sigma^* \leftarrow Fe_2 \sigma$
LUMO +1 ← HOMO -2 (72%) LUMO +4 ← HOMO -1 (20%)	411	0.0019	$Fe_2 \sigma^* \leftarrow \{Fe(bpy)\text{-}CO \pi\}$ bpy $\pi^* \leftarrow Fe_2 T_{2g}$
LUMO +4 ← HOMO -1(79%) LUMO +1 ← HOMO -2 (16%)	408	0.0031	bpy $\pi^* \leftarrow Fe_2 T_{2g}$ Fe ₂ $\sigma^* \leftarrow \{Fe(bpy)\text{-CO }\pi\}$
LUMO +2 ← HOMO -2 (49%) LUMO +3 ← HOMO -1 (30%) LUMO +1 ← HOMO -1 (16%)	397	0.0001	$Fe_{2}S_{2} \pi^{*} \leftarrow \{Fe(bpy)\text{-}CO \pi\}$ $bpy \pi^{*} \leftarrow Fe_{2} T_{2g}$ $Fe_{2} \sigma^{*} \leftarrow Fe_{2} T_{2g}$
LUMO +3 ← HOMO -2	386	0.0056	bpy $\pi^* \leftarrow {\text{Fe(bpy)-CO }\pi}$
LUMO ← HOMO -6	384	0.0121	bpy $\pi^* \leftarrow {Fe(CO)_3}-S_2 \pi$

 Table S1. Selected SAOP Electronic Transition Descriptions and Excitation Energies of 1

Transition	Wavelength (nm)	Oscillator Strength	Character
LUMO ← HOMO	637	0.2238	phen $\pi^* \leftarrow Fe_2 \sigma$
LUMO +1 ← HOMO	621	0.0419	phen $\pi^* \leftarrow Fe_2 \sigma$
LUMO ← HOMO -1	583	0.0035	phen $\pi^* \leftarrow Fe_2 T_{2g}$
LUMO +1 ← HOMO -1	557	0.0002	phen $\pi^* \leftarrow Fe_2 T_{2g}$
LUMO ← HOMO -2	529	0.0014	phen $\pi^* \leftarrow {\text{Fe(phen)-CO }\pi}$
LUMO +1 ← HOMO -2	494	0.0043	phen $\pi^* \leftarrow {Fe(CO)(phen)} - S_2 \pi$
LUMO ← HOMO -3 (61%) LUMO +1 ← HOMO (31%)	486	0.0392	phen $\pi^* \leftarrow \{\text{Fe(phen)-CO }\pi\}$ phen $\pi^* \leftarrow \text{Fe}_2 \sigma$
LUMO +3 ← HOMO	479	0.0012	$Fe_2S_2 \pi^* \leftarrow Fe_2 \sigma$
LUMO ← HOMO -4	456	0.0013	phen $\pi^* \leftarrow Fe(CO)_2 - CO \pi$ }
LUMO +1 ← HOMO -4	453	0.0144	phen $\pi^* \leftarrow Fe(CO)_2$ -CO π }
LUMO +2 ← HOMO (41%) LUMO ← HOMO -4(20%)	438	0.0243	$Fe_2 \sigma^* \leftarrow Fe_2 \sigma$ phen $\pi^* \leftarrow \{Fe(phen)\text{-}CO \pi\}$
LUMO +3 ← HOMO -1	435	0.0008	$\operatorname{Fe}_2 S_2 \pi^* \leftarrow \operatorname{Fe}_2 \operatorname{T}_{2g}$
LUMO +1 ← HOMO -4	427	0.0262	phen $\pi^* \leftarrow {Fe(CO)_2-CO \pi}$
LUMO ← HOMO -5	417	0.0072	phen $\pi^* \leftarrow Fe_2 T_{2g}$
LUMO +2 ← HOMO -1 (57%) LUMO +3 ← HOMO -2 (31%)	408	0.0090	Fe ₂ $\sigma^* \leftarrow$ Fe ₂ T _{2g} Fe ₂ S ₂ $\pi^* \leftarrow$ {Fe(CO)(phen)} -S ₂ π
LUMO +2 ← HOMO -2	406	0.0001	$Fe_2 \sigma^* \leftarrow \{Fe(CO)(phen)\} - S_2 \pi$
LUMO +1← HOMO -5	397	0.0026	phen $\pi^* \leftarrow \operatorname{Fe}_2 \operatorname{T}_{2g}$

Table S2. Selected SAOP Electronic Transition Descriptions and Excitation Energies of 2

Table S3. Symmetry assignments for **1-1** and **2-1** ground state isomers. The vibrational frequencies are DFT-calculated frequencies. Symmetry assignments assume nominal C_s symmetry. The assignment of the CO-stretch frequency contributions is shown in the figure below the table.

1-1 UDFT (cm ⁻¹)	2-1 UDFT (cm ⁻¹)	Symmetry	Description
1921	1921	A'	CO 1 stretch
			CO 2 stretch w/ some CO 3 and 4 symmetric
1953	1953	A'	
			stretch (antisymmetric to CO 2) contribution
1955	1955	A"	CO 3 and 4 antisymmetric stretch
2008	2008	A'	CO 2, 3, and 4 all symmetric stretch



Table S4. The ΔG values, which are the energy difference compared to the lowest energy configuration (1-1), dipole moments, and the band frequencies and intensities of the isomers of 1, calculated using DFT BP86/TZVP.

isomer	ΔG (kcal/mol)	dipole moment	band frequency	band intensity
		(D)	(CIII -)	(ard. units)
			1921	853
11	0.00	4.0	1953	712
1-1	0.00	4.9	1955	499
			2008	968
			1925	878
1.2	1 15	5.0	1951	708
1-2	1.15	5.0	1952	504
			2006	942
			1935	282
1.2	10.27	0.0	1949	632
1-3	10.37	9.9	1962	1049
			2015	1270
			1932	252
1.4	10 61	0.0	1947	630
1-4	10.61	9.9	1963	959
			2017	1330

isomor	AC (lzeel/mol)	dipole moment	band frequency	band intensity
ISUIIICI		(D)	(cm ⁻¹)	(arb. units)
			1957	700
1-1.1	40.31	5.8	1965	498
			2017	977
			1917	566
1-1.2	34.68	3.3	1920	874
			1964	909
			1915	946
1-1.3	35.20	4.6	1921	900
			1962	1003
			1915	947
1-1.4	35.19	4.6	1921	900
			1962	1003
			1957	683
1-2.1	39.71	5.9	1964	507
			2017	981
			1914	573
1-2.2	36.71	3.2	1922	907
			1962	886
			1915	763
1-2.3	34.66	4.6	1921	1124
			1961	964
			1915	765
1-2.4	34.66	4.6	1921	1122
			1961	964
			1799	455
1-3.1	39.24	11.2	1939	663
			1982	1809
			1916	452
1-3.2	43.22	9.5	1938	675
			1977	1548
			1914	28
1-3.3	40.86	10.0	1931	1291
			1978	1598
			1903	484
1-3.4	42.39	8.9	1921	929
			1967	1591
			1941	670
1-4.1	42.93	8.8	1946	771
			1997	1368

Table S5. The Δ G values, which are the energy difference of (fragment + CO) compared to the lowest energy configuration (1-1), dipole moments, and the band frequencies and intensities of the CO-loss isomers of 1, calculated using DFT BP86/TZVP.

			1914	523
1-4.2	44.11	9.8	1937	534
			1977	1642
			1912	33
1-4.3	39.28	9.4	1933	1232
			1981	1599
			1895	472
1-4.4	40.45	8.5	1926	859
			1972	1578

Table S6. The Δ G values, which are the energy difference compared to the lowest energy configuration (2-1), dipole moments, and the band frequencies and intensities of the isomers of 2, calculated using DFT BP86/TZVP.

isomer	ΔG (kcal/mol)	dipole moment (D)	band frequency (cm ⁻¹)	band intensity (arb. units)
			1921	863
2.1	0.00	5 1	1953	726
2-1	0.00	5.1	1955	463
			2008	980
			1924	885
2.2	0.88	5.2	1951	717
2-2	0.00	5.2	1952	470
			2006	956
			1934	309
2.2	10.97	10.2	1947	605
2-3	10.07	10.2	1962	1015
			2016	1342
			1932	257
2.4	10.51	10.0	1947	620
2-4	10.51	10.0	1964	928
			2018	1395

isomer	ΔG (kcal/mol)	dipole moment	band frequency	band intensity
		(D)	(cm ⁻¹)	(arb. units)
			1957	702
2-1.1	39.84	5.8	1965	472
			2017	1016
			1917	531
2-1.2	34.44	3.4	1920	891
			1963	906
			1915	937
2-1.3	34.66	4.7	1920	917
			1962	1021
			1915	938
2-1.4	34.66	4.7	1920	916
			1962	1021
			1957	681
2-2.1	39.39	5.8	1964	481
			2017	1020
			1914	537
2-2.2	36.41	3.4	1922	921
			1961	881
			1915	751
2-2.3	34.36	4.9	1921	1141
			1961	981
			1915	751
2-2.4	34.36	4.9	1921	1141
			1961	981
			1797	444
2-3.1	39.57	11.4	1940	658
			1983	1916
			1915	464
2-3.2	43.35	9.8	1938	609
			1976	1634
			1905	469
2-3.3	42.39	9.2	1920	946
			1966	1637
			1914	37
2-3.4	40.98	10.2	1931	1275
			1978	1672
			1941	637
2-4.1	42.91	9.0	1946	792
			1997	1451

Table S7. The ΔG values, which are the energy difference of (fragment + CO) compared to the lowest energy configuration (2-1), dipole moments, and the band frequencies and intensities of the CO-loss isomers of 2, calculated using DFT BP86/TZVP.

			1913	546
2-4.2	44.15	9.8	1936	445
			1978	1723
			1914	17
2-4.3	39.54	10.0	1932	1259
			1978	1647
			1898	465
2-4.4	40.36	8.8	1925	875
			1971	1628

Cartesian coordinates (in Angstroms) for stationary points of reported computations at the BP86/TZVP level of theory.

Fe₂(µ-S₂C₃H₆)(CO)₄(bpy) **1-1**

H, 22.1106126971, 9.3250959651, 15.1785053314 0,21.7606085821,5.9373307819,18.3389108514 0,25.6357176546,6.4805337069,20.5111481832 C, 22.4187300935, 6.8218951898, 18.7108614256 C,24.7781356142,7.127902961,20.0654844691 H, 20.8680538225, 10.238199988, 17.1131403383 H, 22.1008803103, 8.1736690045, 16.5199050562 Fe, 24.6611310393, 10.3869324205, 19.2182911139 Fe,23.4538222447,8.1080992369,19.4039329008 S, 22.4524642694, 10.1209267796, 18.904461466 S,24.9036476516,8.7262350324,17.7236887231 0,25.0716672273,12.6437733811,17.4133711276 0,22.2482784222,8.3302327228,22.0745334407 N, 24.3975280772, 11.2536371494, 20.96379692 N, 26.4512481756, 10.0878768443, 19.9752166448 C,23.3122763677,11.9668706358,21.3644919796 H, 22.5173075635, 12.0618640526, 20.6247231917 C, 23.194029191, 12.5175457731, 22.6321941076 H, 22.289396954, 13.0685982194, 22.8919459367 C, 24.2368566539, 12.3482522445, 23.5555920998 H,24.1685811615,12.7624698631,24.5625362345 C, 25.3671035213, 11.6479395157, 23.1524972431 H,26.2031470921,11.5107037301,23.8388200556 C, 25.4381444143, 11.1177383429, 21.8539911696 C, 26.6049658581, 10.4558037162, 21.2923091247 C, 27.8175401562, 10.2584202611, 21.9726998015 H, 27.9027831866, 10.5479180691, 23.0204376559 C, 28.9033692872, 9.7011047356, 21.3088507918 H, 29.8496255062, 9.5399942373, 21.8273253039 C,28.7540581561,9.3626588564,19.9553356591 H,29.577275367,8.9330652251,19.3832845239 C, 27.532141404, 9.5719350196, 19.3329274355 H, 27.3712231382, 9.3067846985, 18.2879062581 C, 24.9367369971, 11.7606735505, 18.1719902558 C, 22.7228477883, 8.2501783607, 21.0156350867 C, 21.967996107, 10.244031857, 17.1099771633 H, 22.3053039619, 11.2387452801, 16.7804119337 C, 22.5005124299, 9.1473709354, 16.1984406664 C,24.0191915236,9.0765055965,16.1217984852 H, 24.4464115246, 10.0202253746, 15.7494638491 H, 24.3306053972, 8.2677836748, 15.4443768549 Electronic Energy= Sum of electronic and zero-point Energies= Sum of electronic and thermal Energies= Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies=

-4391.652559 -4391.376306 -4391.349101 -4391.348157 -4391.435202

$Fe_2(\mu-S_2C_3H_6)(CO)_4(bpy)$ **1-2**

Fe, -2.4910826108, -0.2974812869, 0.2544665981 Fe, -0.5451667219, 1.1450211788, 1.1504906849 C, 0.8983243879, 1.9209034456, -1.1687442773 C,-0.7338842486,3.5167523761,-0.6494896872 C, 1.2724618993, 2.6518124295, -2.3076072094 C, 1.5703584903, 0.7206705244, -0.69584095 C, -0.398865237, 4.2808504578, -1.7580793171 H, -1.5288135885, 3.8178731319, 0.0326847701 C, 0.618564959, 3.8384008891, -2.6164290367 H, 2.0787272575, 2.2859563349, -2.9439596687 C, 2.6835881028, 0.1299755688, -1.3147450455 H, -0.9359711621, 5.2112190882, -1.9462770457 H,0.8975443246,4.4135879017,-3.5004713925 C, 1.6958345817, -0.8224233046, 1.0601615967 C, 3.3061173933, -0.9637084881, -0.7254512571 H, 3.0575211122, 0.5353289042, -2.2553407045 C, 2.8028825311, -1.4386870853, 0.4947268873 H,1.2651930689,-1.1711450171,1.9987232315 H, 4.1696219266, -1.4338418541, -1.1982470676 H, 3.2607794595, -2.2859164337, 1.0066063705 N, 1.0566136419, 0.2276778437, 0.4812614124 N, -0.1259915639, 2.3387043959, -0.3509291518 S, -1.2923928316, -0.7244367903, 2.1647271909 S, -2.7034290114, 1.7954046635, 1.1730569122 C, -3.524991289, 1.6946398657, 2.843138006 C, -2.7139273129, 1.0313655583, 3.948533321 H, -4.481712473, 1.1774803622, 2.677349763 H,-3.7465277407,2.7392848257,3.1082681873 C, -2.3416424679, -0.4198879802, 3.6750255585 H, -3.3092139096, 1.0650078867, 4.8805575823 C, 0.1565776471, 2.0596050326, 2.4695231258 0,0.6153744019,2.6690071774,3.3584425786 C,-4.077455905,-1.0529345046,0.5894738282 C, -2.7863990983, 0.4446053536, -1.3341294965 C, -1.6183375513, -1.6437816271, -0.5117844953 0, -5.1096801864, -1.5579194318, 0.7729856152 0, -2.9828344502, 0.9177271327, -2.3788060235 0,-1.0573589594,-2.5256691738,-1.0230160456 H,-1.8031802014,1.6172712305,4.1423975384 H, -1.7518642242, -0.8255103924, 4.5106506927 H, -3.2346367907, -1.0507607295, 3.5534164403 Electronic Energy= Sum of electronic and zero-point Energies= Sum of electronic and thermal Energies= Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies=

-4391.6513212 -4391.374963 -4391.347770 -4391.346826 -4391.433369

$Fe_2(\mu-S_2C_3H_6)(CO)_4(bpy)$ **1-3**

H, 22.6623011283, 9.7712304654, 15.1303253721 0,21.6988409991,6.1417067793,17.7429062146 0,25.2585236475,5.9997789409,20.3025137104 C, 22.3572822878, 6.9129170623, 18.3135485207 C, 24.5170148887, 6.8037680479, 19.9032786842 H,21.1444929786,10.4484265828,16.964214277 H, 22.4775347895, 8.4617777067, 16.3035512967 Fe, 24.5918811911, 10.2336283105, 19.6731719649 Fe, 23.3662360401, 8.0119322695, 19.3039977878 S, 22.4414986273, 10.112719152, 18.9478334545 S, 25.0658279789, 8.8002197206, 17.9500920392 0,21.8497882238,7.8855264379,21.8196081656 N, 25.3413380953, 11.8825271034, 18.9757963181 N, 26.4355663983, 9.9783401259, 20.2781248659 C,24.6658796425,12.9360758342,18.4522641806 H, 23.5813417199, 12.8938705694, 18.5542121425 C, 25.3000840633, 14.0040631935, 17.8280839897 H, 24.7012386401, 14.8223280567, 17.4261501352 C, 26.6986811633, 14.0017726719, 17.720018883 H, 27.2228381867, 14.8154753681, 17.2166560899 C, 27.4077418256, 12.9458871137, 18.2859599481 H, 28.4970052236, 12.9233611494, 18.2343859789 C, 26.7172976167, 11.9081992303, 18.9304128262 C, 27.3413255946, 10.8248718316, 19.687415925 C, 28.720388665, 10.6790954483, 19.9004999797 H,29.4221106231,11.3521273636,19.4064851521 C, 29.1836924071, 9.6777508227, 20.7488008793 H, 30.2535655887, 9.5478191223, 20.9191992084 C, 28.2493291763, 8.8524772913, 21.3897040714 H,28.562147466,8.064323454,22.0751542882 C,26.8950677096,9.0321168142,21.1291900847 H, 26.1339260734, 8.402436596, 21.5875290119 C, 22.4494764061, 7.957457847, 20.8274415813 C, 22.2333530785, 10.4420213284, 17.1206208764 H, 22.6027349227, 11.4665942258, 16.9513898942 C,22.9047350348,9.4664245938,16.1659873893 C,24.4181227554,9.4018105636,16.3080988405 H, 24.8730584043, 10.3929548467, 16.1484719533 H, 24.8451925904, 8.7110413139, 15.5663742453 C, 23.9888145518, 10.7170807493, 21.2693621531 0,23.6084715763,11.0261979752,22.3286322201 Electronic Energy= Sum of electronic and zero-point Energies= Sum of electronic and thermal Energies= Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies=

-4391.6354955 -4391.359806 -4391.332389 -4391.331444 -4391.418675

$Fe_2(\mu-S_2C_3H_6)(CO)_4(bpy)$ **1-4**

0,21.5250078955,6.3432736252,18.1346204635 0,24.9115189087,6.1680588567,21.0373316695 C, 22.2233716162, 7.0768427871, 18.7067797246 C,24.2881398803,6.9694586525,20.4664782721 H, 21.8760027514, 11.1321851255, 16.7458249946 Fe, 24.8329191014, 10.2490178518, 19.4482199168 Fe,23.3080894053,8.1741957936,19.6052920041 S, 22.6320456814, 10.2537801477, 18.8442020151 S, 25.023978518, 8.4244232571, 18.0843514918 0,21.6293694297,8.589436479,21.9908803174 N, 25.5387110624, 11.888017164, 18.6947415924 N, 26.7260252886, 10.0051262368, 19.9336585196 C,24.8097348604,12.8954777223,18.1370275699 H, 23.7321173273, 12.738241977, 18.124100424 C, 25.3813739442, 14.0552658817, 17.6346766505 H, 24.7372143122, 14.8215079711, 17.2010847492 C, 26.7738867414, 14.2224271394, 17.6948569965 H, 27.2493836918, 15.1235778989, 17.3054952556 C, 27.5319077758, 13.2157357868, 18.2838960741 H, 28.6144463231, 13.3192258836, 18.3677670766 C, 26.9026767742, 12.0641706708, 18.778994393 C, 27.5808219227, 10.9719393386, 19.4678253031 C, 28.964388155, 10.8894553662, 19.685113527 H,29.622594653,11.667672288,19.2972868385 C, 29.4890698612, 9.8130494444, 20.3939591631 H, 30.5633426368, 9.7357017842, 20.5688680588 C,28.6093102657,8.8372329149,20.8795739761 H,28.9684901166,7.9771674146,21.4455185005 C, 27.2471847043, 8.9678189824, 20.6305522592 H, 26.5298142346, 8.2334345559, 20.991429069 C, 22.3039889659, 8.4521147566, 21.0565049061 C, 22.35173681, 10.1722911456, 16.999507282 C,24.2898606617,8.6208389243,16.3820645433 H, 25.1464765153, 8.5103458045, 15.7003123275 C, 24.3882811432, 10.7742756989, 21.0755140172 0,24.15709306,11.1067590957,22.1708531393 C,23.5857028606,9.9479830437,16.1342647281 H,24.3020990912,10.7719951671,16.2829804459 H,23.2753638017,9.9869464971,15.0727940458 H,23.6140820376,7.7682050279,16.2180630483 H,21.6050187139,9.3799185208,16.8381299407 Electronic Energy= Sum of electronic and zero-point Energies= Sum of electronic and thermal Energies= Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies=

-4391.6355431 -4391.359643 -4391.332302 -4391.331358 -4391.418301

Fe₂(µ-S₂C₃H₆)(CO)₄(bpy) **2-1**

H, 10.4600757096, 6.4498534377, 13.8529112204 H, 10.3531205312, 7.357486311, 11.5534442541 C, 12.800231471, 4.1659677212, 10.9838766264 C,14.18983982,5.7394405954,9.2283341541 C, 15.4836505219, 4.6842510428, 11.123734108 C, 11.2793210311, 7.4445541974, 12.1404539472 C, 11.3417414648, 6.3453672355, 13.1928112112 C, 12.5915484213, 6.3737408322, 14.0626918569 C, 18.6530285331, 7.2306942491, 13.270997682 C, 17.2543823828, 7.2692299114, 13.1965303208 0,12.1150692064,3.2271396932,10.9288211017 0,14.36225083,5.8536989955,8.0836449739 0,16.4945001582,4.1147822684,11.2073327289 S, 12.6485187597, 7.4528301019, 10.8777895826 S, 14.2164906322, 6.1737018849, 13.1747318495 Fe, 13.9393187028, 5.5476497644, 10.9755859046 H,16.6318544841,6.8738423176,14.0001833497 H, 19.1175225758, 6.7997643332, 14.1590237781 H, 12.6727517512, 7.3219886469, 14.6158214021 H,12.5652524471,5.5522254132,14.7937567687 H,11.2506289649,5.3619389319,12.7071663171 C, 14.1882111245, 9.2148820785, 12.8482149797 C,14.5444813811,9.4805271104,9.2272235625 C, 15.1354777595, 10.1012166583, 8.1187414551 C,16.5188210125,10.1054865462,7.9672997496 C, 17.308020878, 9.4853124923, 8.9586418717 C, 18.7450111491, 9.4456380868, 8.9524423731 C, 19.4469710019, 8.8727338883, 9.980567457 C,18.7762537924,8.2871005153,11.1091698481 C, 19.4287052137, 7.7307503685, 12.2294230131 C, 17.3555165142, 8.2783116276, 11.1076449121 C, 16.6301978782, 8.8702765464, 10.0453152047 N, 15.2598438172, 8.8495973183, 10.1812715498 N, 16.5908913958, 7.7634961022, 12.130918972 0,13.8098915282,10.0537694587,13.5740208346 Fe, 14.6447949786, 7.8921701335, 11.7995705018 H,20.5194500038,7.7066676779,12.274926191 H,20.5394332074,8.8653632525,9.9648325646 H, 19.2731486034, 9.8988404779, 8.1101417573 H, 16.991929514, 10.5855355955, 7.1081874582 H, 14.4891524377, 10.5767750855, 7.3797263875 H,13.4615966624,9.4606030191,9.3565138295 H, 11.2990424171, 8.4431832253, 12.603069129 Electronic Energy= -4467.9059594 Sum of electronic and zero-point Energies= -4467.617841 Sum of electronic and thermal Energies= -4467.589801 Sum of electronic and thermal Enthalpies= -4467.588856 Sum of electronic and thermal Free Energies= -4467.676860

Fe₂(µ-S₂C₃H₆)(CO)₄(bpy) **2-2**

H, 10.5005742243, 8.1674325942, 11.3821749695 C,12.8275942442,4.4784246137,10.0351024242 C,14.410924911,6.3053192167,8.7044261685 C, 15.522136983, 4.8794683952, 10.4737976659 C,11.1481124067,7.2889748196,11.5225249986 C, 12.2749989537, 5.8456933633, 13.3157963549 C, 18.3974524864, 6.8925678235, 13.3863535514 C, 17.0111634228, 6.977412479, 13.1984667102 0,12.0880450031,3.6110762028,9.8006549219 0,14.6838283704,6.6301712891,7.6209853098 0,16.5163352939,4.2784985046,10.5389769627 S, 12.6687158323, 7.6561701552, 10.507978829 S, 14.0137490704, 5.9333078045, 12.6481378203 Fe, 13.9996844521, 5.7907745835, 10.3561713434 H, 16.3156214096, 6.451115061, 13.8531970314 H,18.7766623021,6.2897133223,14.2126496443 H, 12.3993792439, 5.735775108, 14.4034921524 C,14.0741024732,9.0691779788,12.948699718 C, 14.6853251345, 9.9558739845, 9.4978985651 C, 15.3778405655, 10.7592776595, 8.5817870483 C, 16.7688310484, 10.7630215596, 8.5574992985 C, 17.4622414899, 9.9528129279, 9.4813809665 C,18.8935943025,9.8834876707,9.5951164684 C, 19.4962451348, 9.1117951012, 10.5540189516 C, 18.7227769033, 8.3387156308, 11.487085267 C, 19.2672862462, 7.5637655707, 12.5329175521 C, 17.3083130806, 8.3639617831, 11.3597581905 C, 16.6856618091, 9.1613948969, 10.3691557905 N, 15.3089651004, 9.1438169045, 10.375925114 N, 16.45118015, 7.6810244241, 12.1931602433 0,13.7470894027,9.8358835462,13.7716690273 Fe,14.5476029233,7.9128966269,11.7200506857 H,20.3492289896,7.5053852164,12.6684623605 H,20.5855829002,9.082670099,10.6331805743 H, 19.4984920231, 10.474631441, 8.9034336015 H, 17.3200134523, 11.3841571558, 7.8484371624 H,14.8033553977,11.3775836436,7.8906490712 H,13.5952420669,9.9348789343,9.5249472377 C, 11.3834953369, 7.0407458258, 13.0063647099 H, 11.8071720805, 7.9447181445, 13.4676517362 H,10.4019921433,6.8741398112,13.4890632441 H,10.6610944228,6.4291153498,11.038989158 H,11.8479701824,4.9089762268,12.9277761591 Electronic Energy= -4467.9047619 Sum of electronic and zero-point Energies= -4467.616606 Sum of electronic and thermal Energies= -4467.588565 Sum of electronic and thermal Enthalpies= -4467.587621 Sum of electronic and thermal Free Energies= -4467.675456

Fe₂(µ-S₂C₃H₆)(CO)₄(bpy) **2-3**

Fe, 3.2404746502, -0.0012252062, -0.4243437302 Fe, 2.0648061209, -0.9589170048, 1.6466918669 C, -0.5455416119, -1.8408735628, 2.1628050773 C, 0.136223977, -2.739258238, 0.1341296986 C,-0.1507470299,-1.1507178421,3.3398380626 C, -1.8504563294, -2.3862138047, 2.0464867731 C, -1.1319676213, -3.3126702124, -0.0614291674 H, 0.9320522593, -2.8654874463, -0.5986563113 C,-1.0524736021,-0.9955822033,4.4245434754 C, -2.7727434861, -2.1599212135, 3.1258021512 C, -2.1381340027, -3.1289161873, 0.8793059741 H,-1.3092784718,-3.8919392476,-0.9683877452 C, -0.5572733258, -0.379530088, 5.5962677217 C, -2.3912820039, -1.4945794942, 4.2625669949 C, 1.6057832237, -0.1885979722, 4.514232345 H,-3.7892451859,-2.5494487334,3.0318333707 H, -3.1308821143, -3.5603702536, 0.7342664057 C, 0.779845782, 0.002461587, 5.6328642257 H, -1.2107715682, -0.2311690438, 6.458317131 H, -3.1014207968, -1.3525897133, 5.0807992774 H, 2.6592959037, 0.0902814001, 4.5334208383 H,1.2083287432,0.4546660959,6.5286226333 N, 0.4351211633, -1.9953162353, 1.2129044985 N, 1.1619442575, -0.7318212585, 3.3622402805 C, 3.0577424761, -2.4040160221, 1.9104127478 0,3.6894685647,-3.373664532,2.062414246 S, 1.1966973508, 0.7243797155, 0.3711282639 C,1.3391879386,2.4193032577,1.1367120262 H, 0.7984731861, 3.0849128553, 0.4476889299 H, 0.76648547, 2.374508545, 2.0772629339 C, 2.7484198449, 2.9407145906, 1.3790803133 H, 3.2746327865, 3.0447339335, 0.4184716385 H, 2.6746804368, 3.9583219185, 1.8072814393 C, 4.5997373137, -1.1401673954, -0.5827034735 C, 2.3672175643, -0.7918378725, -1.7476227024 C, 3.9211704524, 1.3688968527, -1.3538367945 0,1.8102663399,-1.3137926163,-2.6275371748 0,5.4905056865,-1.8722773557,-0.7199363708 ,4.3806397993,2.1976836647,-2.0291914966 C, 3.5784732347, 2.0822769468, 2.3216086984 H, 3.0921738907, 2.0068801396, 3.3077283496 H, 4.5734734785, 2.5268120122, 2.4716496165 S, 3.9268514648, 0.3306176404, 1.7724845012 Electronic Energy= -4467.8881644 Sum of electronic and zero-point Energies= -4467.600283 Sum of electronic and thermal Energies= -4467.572150 Sum of electronic and thermal Enthalpies= -4467.571206 Sum of electronic and thermal Free Energies= -4467.659544

$Fe_2(\mu-S_2C_3H_6)(CO)_4(bpy)$ **2-4**

H, 10.6752847806, 8.2276462299, 11.0861282103 C,12.6540751227,4.2807732449,11.2861083395 C,14.4115648108,5.1974408605,9.4063831776 C, 15.3422317106, 4.3971823376, 11.6384232861 C,11.2897392988,7.4571338896,11.5755121932 C, 12.3602734315, 6.8022460738, 13.8037545551 C, 14.7863542364, 11.1852444988, 14.2485181455 C, 14.6727638406, 9.8841697662, 13.7412521672 0,11.7839297166,3.5134804489,11.3705019492 0,14.6893150286,5.0202964621,8.2891858343 0,16.1903569023,3.6773196059,11.9687165497 S, 12.8092968509, 7.3296765891, 10.5036966115 S, 14.0921917192, 6.4556687365, 13.1953879579 Fe, 13.9949681267, 5.446869935, 11.1147012871 H,14.4620473228,9.0384651453,14.3950397169 H, 14.641362449, 11.3414324081, 15.3186771046 H, 12.4909211069, 7.1255668172, 14.8480740439 C, 15.4358389068, 8.5898891539, 8.671940505 C, 15.7454971283, 9.5093927214, 7.6551386713 C, 15.8721384822, 10.8618119138, 7.9469710414 C, 15.677197728, 11.2917373572, 9.2783795132 C, 15.7859072791, 12.6526410978, 9.7277602969 C, 15.5944209144, 12.985588601, 11.0439533241 C, 15.2729759921, 11.9905820465, 12.0311661749 C, 15.0768378678, 12.2541372228, 13.4048236648 C, 15.1399440868, 10.6457211022, 11.5983410165 C, 15.3557084691, 10.2986912346, 10.2406884097 N, 15.2415601104, 8.9610520829, 9.9492212401 N, 14.8313055496, 9.5889726344, 12.4298030312 Fe, 14.7778188432, 7.8595489818, 11.5347932562 H, 15.1637316665, 13.2719592522, 13.7899913771 H, 15.6905604982, 14.0248262005, 11.3674564565 H,16.030880872,13.4249245754,8.9946945198 H, 16.1205893882, 11.5857626331, 7.1678319904 H,15.8888394236,9.1372686588,6.63995599 H, 15.346316193, 7.5258068868, 8.4586962189 C, 16.4468820207, 7.320849355, 11.7407698321 0,17.5667047409,6.9974703948,11.8142496763 C, 11.5611618674, 7.8390416096, 13.0241100056 H, 12.0829562316, 8.8093038217, 13.0500528195 H,10.5914306107,7.9856090043,13.5365602213 H,10.7534363193,6.4991679943,11.5028101234 H,11.8415990953,5.8315256337,13.8208401641 Electronic Energy= -4467.8884776 Sum of electronic and zero-point Energies= -4467.600900 Sum of electronic and thermal Energies= -4467.572641 Sum of electronic and thermal Enthalpies= -4467.571697 Sum of electronic and thermal Free Energies= -4467.660106

Cartesian coordinates (in Angstroms) for stationary points of reported computations at the TZVP + mod-LANLDZ + SMD level of theory.

$Fe_2(\mu-S_2C_3H_6)(CO)_4(bpy)$ 1-1

H,4.5535834942,0.0174811064,2.2564626897 0,4.1089517018,0.0219826264,-2.3858761643 0,0.2730972456,-2.1257973862,-2.7576873208 C, 3.0947220135, 0.003401658, -1.8072931509 C, 0.7393266769, -1.2891760021, -2.091143907 H, 3.5583402977, 2.1673488089, 1.5678329828 H, 4.1599791353, -0.0008836557, 0.5312561748 Fe,-0.1568288506,0.0044395694,0.8775762557 Fe,1.4624413152,-0.0184679557,-1.1274003241 S,1.4678929762,1.5359622785,0.5876823859 S, 1.4658494339, -1.5356483886, 0.6233260513 0,-0.352246887,0.0204687151,3.7663244262 0,0.1753150434,2.0168909248,-2.7750385844 N,-1.5719111119,1.2885118412,0.4028841069 N, -1.5753014153, -1.2811911752, 0.4045296609 C,-1.5437492776,2.6317346525,0.5839132052 H,-0.6457744213,3.0275034153,1.0579945665 C, -2.5782858751, 3.4682716855, 0.1818484382 H,-2.4930978287,4.5424685615,0.3519643118 C,-3.7067575384,2.9122171468,-0.4350987245 H, -4.5312410401, 3.5435155936, -0.7706864124 C,-3.7649871949,1.5310721756,-0.594827846 H,-4.6393527368,1.0645552214,-1.0491553088 C, -2.6966408497, 0.7348342293, -0.154505819 C, -2.6966826336, -0.7249960849, -0.157327973 C, -3.7613975959, -1.5193492929, -0.6095869494 H,-4.6323055435,-1.0506333783,-1.0679592838 C, -3.7024797638, -2.9015106076, -0.4590284278 H,-4.5234070476,-3.5314710869,-0.8056667486 C, -2.5773136426, -3.4605124499, 0.16119572 H, -2.4912588089, -4.5359958442, 0.3226297435 C, -1.5466616156, -2.62535096, 0.5762770852 H,-0.650533803,-3.0236092116,1.052016924 C,-0.3006558345,0.0147971769,2.5917106032 C, 0.680967248, 1.20987505, -2.1004265923 C, 2.9166834931, 1.2887889211, 1.7312316549 H, 2.5009122029, 1.3529288598, 2.7486424233 C, 3.713781528, 0.0094907585, 1.5374784945 C, 2.9182682499, -1.2664842787, 1.7576867732 H,2.5076955298,-1.3133026378,2.7781654173 H,3.5596577311,-2.1474545802,1.6067754424

el energy=	-2110.85039234
zpe=	-2110.573750
th energy=	-2110.546756
th enthalpy=	-2110.545812
free energy=	-2110.631681

$Fe_2(\mu-S_2C_3H_6)(CO)_4(phen)$ 2-2

H,28.5497548185,9.3292048152,18.0759885555 H,28.3847218768,7.0382651504,18.975927804 C, 25.4239600052, 7.0263524474, 16.1960415947 C,24.0310601002,5.4925788729,17.9311244439 C, 22.9421588328, 7.593347132, 17.1303661721 C, 27.6015444002, 7.7776320695, 19.2002077897 C, 27.5574716291, 8.8434329042, 18.1175048025 C, 26.513870798, 9.9257582801, 18.3397874193 C, 20.5787584057, 10.1959818663, 20.0915981265 C, 21.9371564763, 9.8776149099, 19.935220921 0,25.89787417,6.8670026986,15.1407856733 0,23.6914320593,4.3816716742,18.0414577167 0,21.8863398191,7.8627239365,16.7124970238 s,26.0501160067,6.7737130334,19.4294285331 S, 24.7401646508, 9.3606242332, 18.3988128914 Fe, 24.5328634913, 7.1563607825, 17.7181315386 H, 22.6356446405, 10.5919316477, 19.4981346408 H,20.2311337256,11.1786146422,19.7691704112 H, 26.683719199, 10.4586998305, 19.2880760147 H, 26.5480010959, 10.6621526413, 17.5230985845 H, 27.3974171042, 8.3692445637, 17.1371311367 C,25.0477013708,8.8794588786,21.4199780023 C,24.1565780996,5.3914454533,21.6655754567 C, 23.4576486217, 4.3725098751, 22.3323599042 C, 22.0805796956, 4.4589452527, 22.4973134044 C,21.40844314,5.598294776,22.0015880427 C, 19.9983327345, 5.837062612, 22.1484232281 C,19.4242099653,6.9995476412,21.7028143988 C, 20.2100011435, 8.0241526424, 21.0707420341 C, 19.7019311356, 9.2729228031, 20.6485677415 C, 21.5951658349, 7.7814996772, 20.8714885312 C,22.1901287117,6.5786499198,21.3343900037 N, 23.5465592352, 6.4728719648, 21.1473513932 N, 22.4504033945, 8.6859138403, 20.2915536774 0,25.5898326623,9.4844921885,22.2699749075 Fe, 24.3070465278, 8.0044007392, 20.1373410813 H,18.6423766637,9.5041335297,20.7771353434 H,18.3546068525,7.1770202498,21.8371794026 H,19.3931016481,5.073760082,22.6430732779 H, 21.5214516392, 3.6752393053, 23.0128957497 H, 24.0176679247, 3.5183463544, 22.7159763352 H, 25.2369165239, 5.3351872402, 21.5277762993 H, 27.8172269014, 8.2154746376, 20.1869678243 el energy= -2187.10479749

-2186.816242
-2186.788431
-2186.787487
-2186.875102

$Fe_2(\mu - S_2C_3H_6)(CO)_6$ 3

C, 0.1274245131, 2.6754245506, -1.2733191907 C, 0.1069852183, 2.6741621247, 1.2765251879 H,-0.9130090117,3.0293032852,-1.3320845421 C, 0.801899556, 3.131473597, 0.0073235439 H,1.8550683982,2.8115720302,0.0155172666 H, 0.8092054018, 4.2361901116, 0.0077256368 H,-0.9351143759,3.0255738558,1.3181323292 H, 0.6341809812, 3.0542384824, 2.1638314368 H, 0.6702790831, 3.0543407653, -2.1516454486 0, -3.6736210936, 1.479352086, 0.0223028155 Fe,-1.28384764,-0.2078761554,-0.0083967566 S, 0.02606036, 0.8390972061, 1.5663839915 0, -2.0716982977, -2.1267691584, 2.0579473664 C, -1.7473252728, -1.3664097406, 1.2446200263 C,-2.7176829676,0.8222098641,0.0093053109 C, -1.7787811213, -1.3237895813, -1.2876067361 Fe,1.2119871367,-0.3777527678,0.007856614 0,1.7195133262,-2.3376830387,2.1183125992 0,3.920879142,0.7286514124,-0.0446532145 C,1.5061249128,-1.5588799927,1.2862967455 C,2.8295381443,0.3351837274,-0.0217440341 C, 1.446815381, -1.6035658878, -1.2403510577 S, 0.0443661583, 0.8407866944, -1.5650789157 0,-2.1283872126,-2.0510097329,-2.1205363732 0,1.6179692804,-2.4165107376,-2.0492896013 el energy= -1842.05012693 zpe= -1841.911727 th energy= -1841.890079 th enthalpy= -1841.889135 free energy= -1841.963423

Cartesian coordinates (in Angstroms) for **1-1** to **1-2** flipamer transformation geometries at the B88P86/TZVP level of theory.

Fe ₂ (µ-S ₂ C ₃ H ₆)	(CO) ₄ (bpy) 1-	-1	
Fe	0.3146	1.8566	0.0000
Н	1.2733	-1.7620	-2.1564
Н	2.3661	-0.6108	-1.3514
S	0.1277	0.2289	-1.5161
0	3.2249	2.0647	0.0000
Fe	-1.5847	0.0666	0.0000
S	0.1277	0.2289	1.5161
0	-2.5150	-2.7315	0.0000
0	-3.4308	1.0726	-2.0546
0	-3.4308	1.0726	2.0546
С	-2.6775	0.6889	1.2550
С	-2.6775	0.6889	-1.2550
С	-2.0953	-1.6443	0.0000
С	2.0515	2.0375	0.0000
Н	-0.4113	4.1254	-4.5393
Н	0.3753	2.3165	-3.0238
С	1.3881	-1.1088	1.2803
С	1.2701	-1.9232	0.0000
С	1.3881	-1.1088	-1.2803
Н	1.2733	-1.7620	2.1564
Н	2.3661	-0.6108	1.3514
Н	0.3156	-2.4669	0.0000
Н	2.0676	-2.6873	0.0000
С	-0.8264	4.3571	0.7260
С	-1.3072	5.4072	1.5228
С	-1.1773	5.3450	2.9035
С	-0.5507	4.2216	3.4631
С	-0.1026	3.2104	2.6275
Ν	-0.2462	3.2424	1.2783
Н	-1.7731	6.2714	1.0530
Н	-1.5458	6.1544	3.5334
Н	-0.4113	4.1254	4.5393
Н	0.3753	2.3165	3.0238
С	-0.8264	4.3571	-0.7260
С	-1.3072	5.4072	-1.5228
С	-1.1773	5.3450	-2.9035
С	-0.5507	4.2216	-3.4631
С	-0.1026	3.2104	-2.6275
Ν	-0.2462	3.2424	-1.2783
Н	-1.7731	6.2714	-1.0530
Н	-1.5458	6.1544	-3.5334
Bond Energy	(hartree):		-9.964989297964669
Zero-Point Energy (hartree):			0.276399440582524
Enthalpy (T=OK) (hartree):			-9.688589857382146

Fe ₂	$(\mu - S_2 C_3 H_6)$ (CO) 4 (bpy)	1-2		
Fe	0.6358	-0.0079	-0.1946	
Н	1.5028	1.3143	-4.0220	
Н	2.4986	2.1964	-2.8449	
S	0.4489	1.5083	-1.8223	
0	3.4408	-0.0224	0.6383	
Fe	-1.2636	-0.0079	-1.9846	
S	0.4489	-1.5240	-1.8223	
0	-1.9675	-0.0050	-4.8604	
0	-3.0769	2.0877	-0.9804	
0	-3.0790	-2.1047	-0.9870	
С	-2.3578	-1.2772	-1.3796	
С	-2.3566	1.2607	-1.3757	
С	-1.6693	-0.0062	-3.7347	
С	2.3244	-0.0162	0.2695	
Н	-0.2408	4.5362	2.0297	
Н	0.7227	3.0193	0.3078	
С	1.9482	-1.2543	-2.9862	
С	2.8315	0.0236	-2.8483	
С	1.9238	1.2733	-3.0066	
H	1.5447	-1.3262	-4.0068	
H	2.5437	-2.1585	-2.7976	
H	3.3625	0.0380	-1.8924	
H	3.5/39	0.0203	-3.6621	
C	-0./342	-0.7282	2.1942	
C	-1.3304	-1.5221	3.1001	
C	-1.1921	-2.9034	3.1433 2.1050	
C	-0.4300	-2 63/3	2.1030	
N	-0 0363	-2.0343	1 1/82	
ц	-1 8949	-1 0505	3 9887	
и П	-1 6526	-3 5313	3 9062	
н	-0 2816	-4 5412	2 0329	
н	0.6979	-3.0341	0.3116	
C	-0.7276	0.7276	2.1937	
C	-1.3155	1.5274	3.1848	
C	-1.1647	2.9073	3.1420	
C	-0.4056	3.4612	2.1025	
C	0.1424	2.6252	1.1406	
N	-0.0256	1.2770	1.1467	
Н	-1.8832	1.0614	3.9893	
Н	-1.6186	3.5398	3.9052	
	Bond Energy (hartre	ee):	-9.	963945314045061
	Zero-Point Energy	(hartree):	0.	276370827445356
	Enthalpy (T=OK) (ha	artree):	-9.	687574486599704

Fe	0.6062	-0.1343	0.0000
Н	1.1699	-3.9105	-1.9536
Н	2.4579	-2.7046	-1.9357
S	0.3644	-1.7496	-1.4953
0	3.5222	0.0627	0.0000
Fe	-1.3424	-1.9396	0.0000
S	0.3644	-1.7496	1.4953
0	-1.9916	-4.8232	0.0000
0	-3.1642	-0.9499	-2.0964
0	-3.1642	-0.9499	2.0964
С	-2.4404	-1.3400	1.2706
С	-2.4404	-1.3400	-1.2706
С	-1.7154	-3.6905	0.0000
С	2.3484	0.0256	0.0000
Н	-0.1026	2.1504	-4.5426
Н	0.6634	0.3290	-3.0327
С	1.6091	-3.0984	1.3594
C	2.1130	-3.6497	0.0000
C	1.6091	-3.0984	-1.3594
H	1,1699	-3.9105	1.9536
H	2.4579	-2.7046	1.9357
H	3,2068	-3.5456	
Н	1,9165	-4.7303	0.0000
C	-0.4970	2,3917	0.7273
C	-0.9643	3.4482	1.5239
C	-0.8413	3,3830	2,9051
C	-0.2348	2 2498	3 4653
C	0 2015	1 2308	2 6325
N	0 0646	1 2645	1 2806
н	-1 4164	4 3208	1 0535
н	-1 2017	4 1972	3 5342
н	-0 1026	2 1504	4 5426
н	0 6634	0 3290	3 0327
C	-0.4970	2 3917	-0 7273
C	-0 9643	3 4482	-1 5239
C	-0 8413	3 3830	-2 9051
C	-0 2348	2 2498	-3 4653
C	0.2015	1 2308	-2 6325
N	0.2013	1 2645	-1 2806
н	-1 A16A	4 3208	-1 0535
н	_1 2017	1.0200 4 1972	-3 5342
11	1.201/	7.1012	3.3312
Bond	Energy (hartree) .		-9 950924255453579
Zero-Point Energy (hartree).			0 276147481755421
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Enthalpy (T=OK) (hartree): -9.674776773698158