Supporting Information

Exploring the Limits of Dative Boratrane Bonding: Iron as a Strong Lewis Base in Low-Valent Non-Heme Iron-Nitrosyl Complexes

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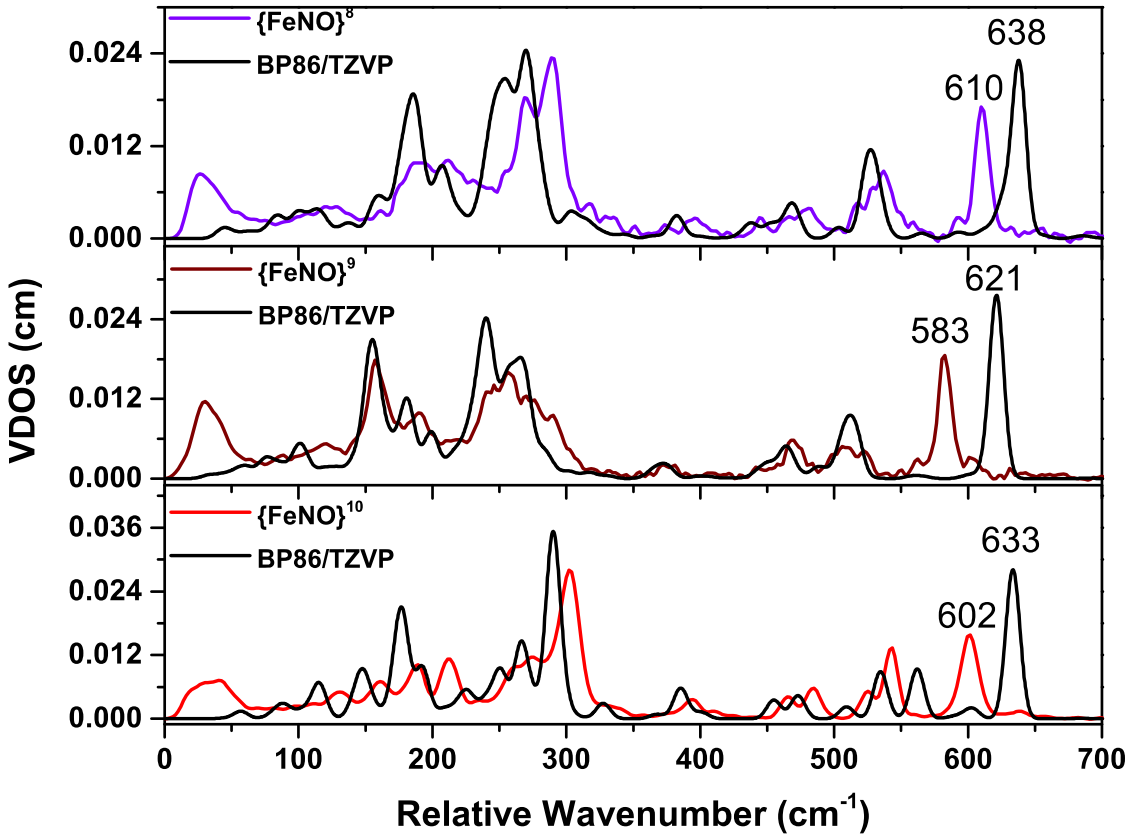

Figure S1. Experimental NRVS VDOS data of the ls-{FeNO}^{8} complex [Fe(TPB)(NO)](BAr$^{F}_{4}$) (purple), the ls-{FeNO}^{9} complex [Fe(TPB)(NO)] (brown) and the ls-{FeNO}^{10} complex [Na(12-crown-4)$_2$][Fe(TPB)(NO)] (red) vs BP86/TZVP DFT calculated spectra (black). The BP86 calculations reproduce the vibrational properties of the ls-{FeNO}$^{8-10}$ complexes, especially the Fe-NO and N-O stretching frequencies, quite well compared to experiment. The observed deviations of 10-30 cm^{-1} for the Fe-NO stretches are very reasonable for DFT frequency calculations.[1] Importantly, the calculations capture the unusual lack of correlation between the change in Fe-NO and N-O stretching frequencies along the ls-{FeNO}$^{8-10}$ series (Fe-NO stretch: 610/583/602 cm^{-1} (exp.) vs. 638/621/633cm^{-1} (BP86); N-O stretch: 1745/1667/1568 cm^{-1} (exp.) vs. 1751/1692/1607 cm^{-1} (BP86)). Thus, we use these calculations as the basis to further analyze the NRVS data and refine the force constants of the Fe-N-O units in the three complexes.

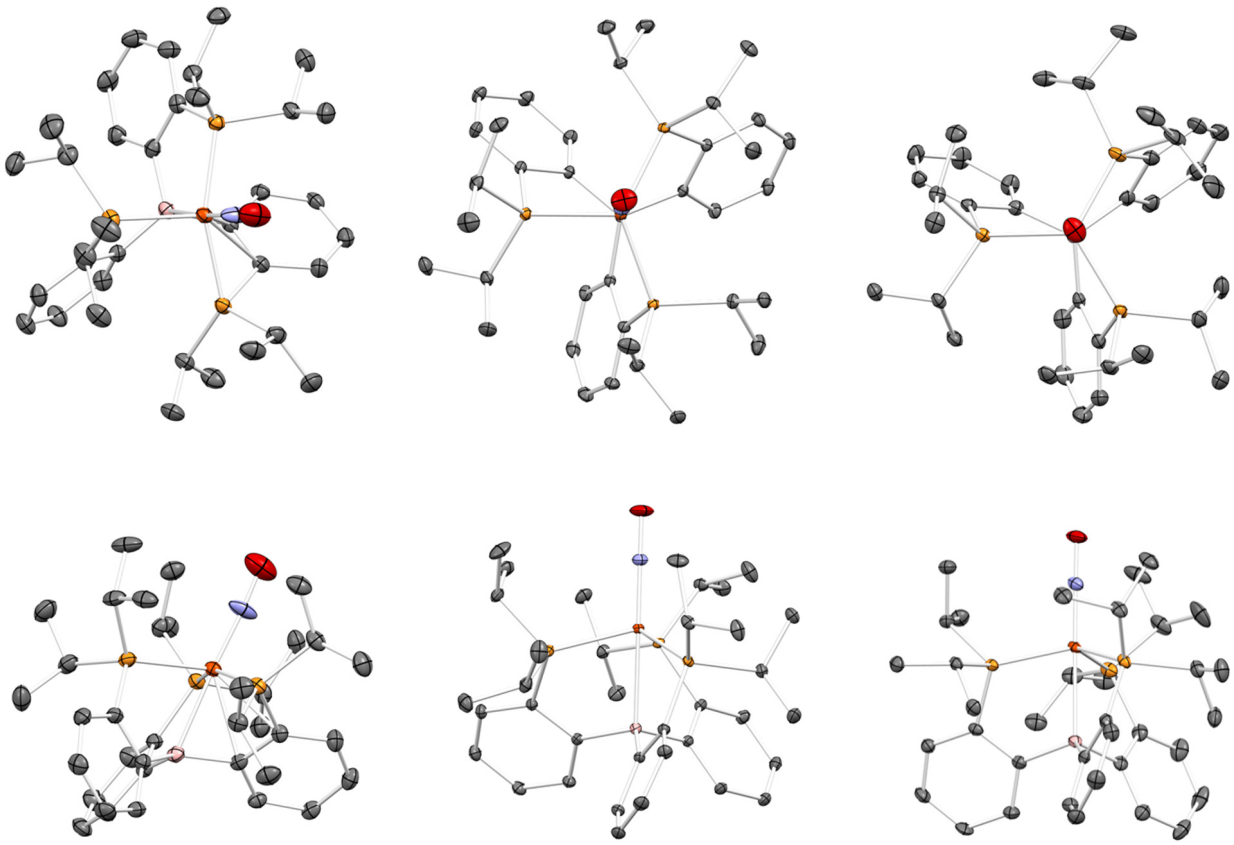

Figure S2. Top down view and side view of the crystral structures of the ls-{FeNO}$^{8\text{-}10}$ series.[2]

Pulse EPR data interpretation and simulation details:
In general, the ENDOR spectrum for a given nucleus with spin I= ½ (^{1}H, ^{31}P) coupled to the S = ½ electron spin exhibits a doublet at frequencies

$$\nu_{\pm} = \left|\frac{A}{2} \pm \nu_N\right| \quad (1)$$

Where ν_N is the nuclear Larmor frequency and A is the hyperfine coupling constant. For nuclei with $I \geq 1$ (^{2}H), an additonal splitting of the $\nu_{\pm}$ manifolds is produced by the nuclear quadrupole interaction (P)

$$\nu_{\pm,m_I} = \left|\nu_N \pm \frac{3P(2m_I - 1)}{2}\right| \quad (2)$$

In HYSCORE spectra, these signals manifest as cross-peaks or ridges in the 2-D frequency spectrum which are generally symmetric about the diagonal of a given quadrant. This technique allows hyperfine levels corresponding to the same electron-nuclear submanifold to be differentiated, as well as separating features from hyperfine couplings in the weak-coupling regime ($|A| < 2|\nu_I|$) in the (+,+) quadrant from those in the strong coupling regime ($|A| > 2|\nu_I|$) in the (−,+) quadrant. The (−,−) and (+,−) quadrants of these frequency spectra are symmetric to the (+,+) and (−,+) quadrants, thus typically only two of the quadrants are displayed in the literature. For systems with appreciable hyperfine anisotropy in frozen solutions or solids, HYSCORE spectra typically do not exhibit sharp cross peaks, but show ridges that represent the sum of cross peaks from selected orientations within the excitation bandwidth of the MW pulses at the magnetic field position at which the spectrum is collected. The length and curvature of these correlation ridges can allow for the separation and estimation of the magnitude of the isotropic and dipolar components of the hyperfine tensor, as shown in Figure S3.

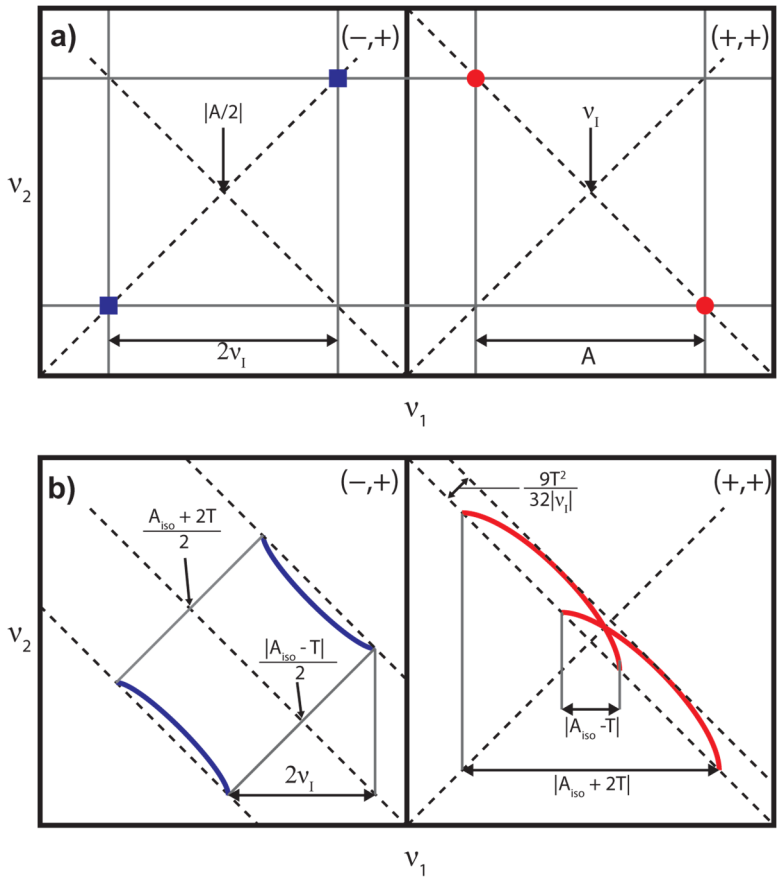

Figure S3. a) HYSCORE powder patterns for an S = 1/2, I = 1/2 spin system with an isotropic hyperfine tensor A. b) HYSCORE powder patterns for an S = 1/2, I = 1/2 spin system with an isotropic hyperfine tensor which contains isotropic (a_{iso}) and dipolar (T) contributions. Blue correlation ridges represent the strong coupling case; red correlation ridges represent the weak coupling case.

EPR Simulations. Simulations of all CW and pulse EPR data were achieved using the EasySpin[3] simulation toolbox (release 5.2.21) with Matlab 2018b using the following Hamiltonian:

$$\hat{H} = \mu_B \vec{B}_0 g \hat{S} + \mu_N g_N \vec{B}_0 \hat{I} + h\hat{S} \cdot \boldsymbol{A} \cdot \hat{I} + h\hat{I} \cdot \boldsymbol{P} \cdot \hat{I} \quad (3)$$

In this expression, the first term corresponds to the electron Zeeman interaction term where μ_B is the Bohr magneton, g is the electron spin g-value matrix with principle components g = [g_{xx}, g_{yy}, g_{zz}], and $\hat{S}$ is the electron spin operator; the second term corresponds to the nuclear Zeeman interaction term where μ_N is the nuclear magneton, g_N is the characteristic nuclear g-value for each nucleus (e.g. ^{1}H,^{2}H,^{31}P) and $\hat{I}$ is the nuclear spin operator; the third term corresponds to the electron-nuclear hyperfine term, where $\boldsymbol{A}$ is the hyperfine coupling tensor with principle components $\boldsymbol{A}$ = [A_{xx}, A_{yy}, A_{zz}]; and for nuclei with $I \geq 1$, the final term corresponds to the nuclear quadrupole (NQI) term which arises from the interaction of the nuclear quadrupole moment with the local electric field gradient (efg) at the nucleus, where $\boldsymbol{P}$ is the quadrupole coupling tensor. In the principle axis system (PAS), $\boldsymbol{P}$ is traceless and parametrized by the quadrupole coupling constant e^2Qq/h and the asymmetry parameter η such that:

$$\boldsymbol{P} = \begin{pmatrix} P_{xx} & 0 & 0 \\ 0 & P_{yy} & 0 \\ 0 & 0 & P_{zz} \end{pmatrix} = \frac{e^2Qq/h}{4I(2I-1)} \begin{pmatrix} -(1-\eta) & 0 & 0 \\ 0 & -(1+\eta) & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad (4)$$

where $\frac{e^2Qq}{h} = 2I(2I-1)P_{zz}$ and $\eta = \frac{P_{xx}-P_{yy}}{P_{zz}}$. The asymmetry parameter may have values between 0 and 1, with 0 corresponding to an electric field gradient with axial symmetry and 1 corresponding to a fully rhombic efg.

The orientations between the hyperfine and NQI tensor principle axis systems and the g-matrix reference frame are defined by the Euler angles (α, β, γ).

CW EPR data:

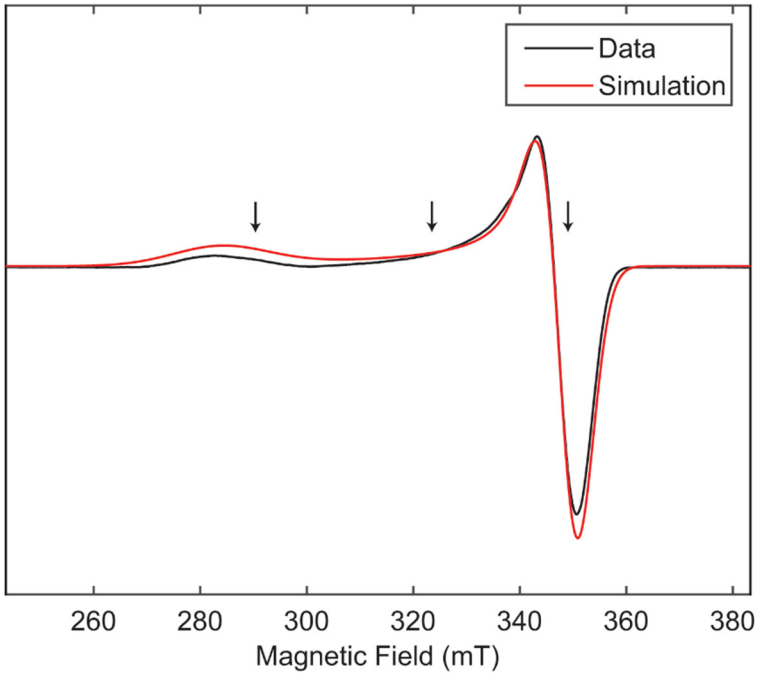

Figure S4. Pseudomodulated X-band ESE-EPR spectrum of the ls-{FeNO}^{9} complex [Fe(TPB)(^{15}NO)] (black) with simulation overlaid (red). Arrows denote field positions at which pulse EPR data were acquired.
Acquisition parameters: Temperature = 7 K; microwave frequency = 9.711 GHz; MW pulse length ($\pi/2$, π) = 160 ns, 80 ns; τ = 300 ns; shot repetition time (srt) = 1 ms.

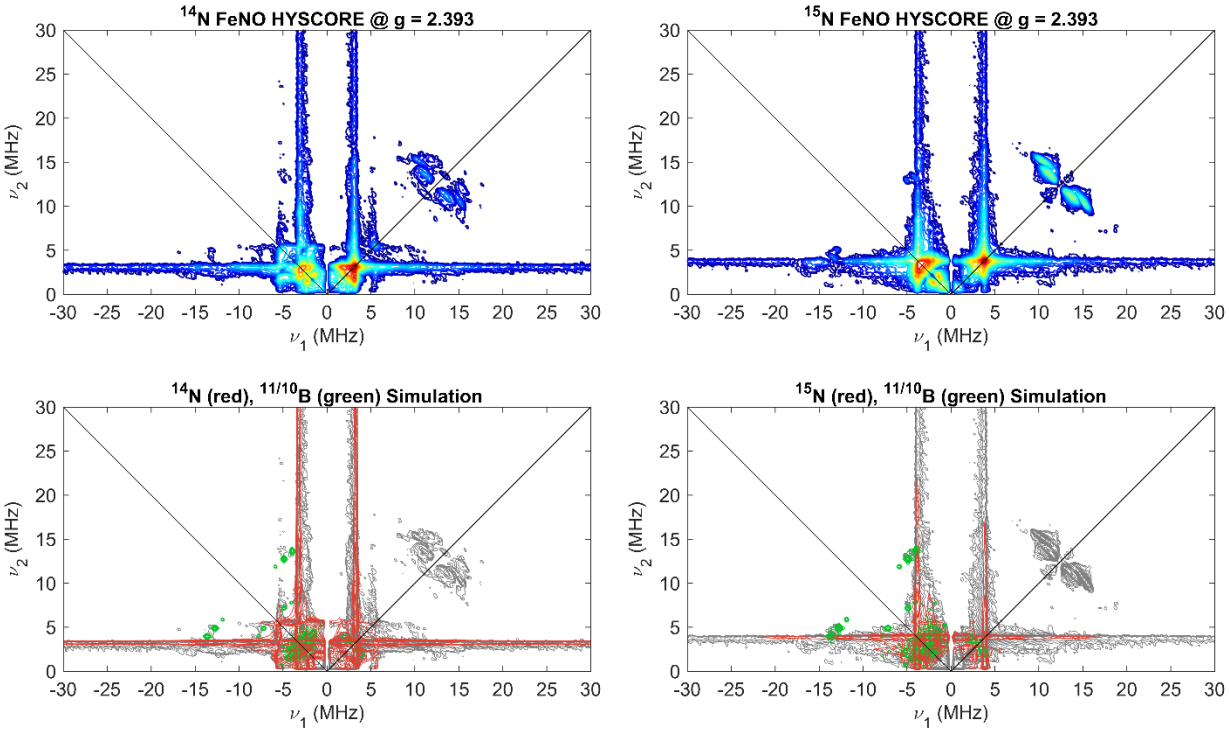

Figure S5. X-band HYSCORE spectra of the ls-{FeNO}^{9} complex [Fe(TPB)($^{14/15}$NO)]. The experimental data are plotted in color in the top panels, ranging from dark blue to red in increasing intensity. These same data are plotted in grey in the bottom panels, with $^{14/15}$N and ^{11}B simulations overlaid in red and green, respectively. Unsimulated features centered around 15 MHz in the (+,+) quadrant arise from weakly coupled ^{1}H nuclei of the ligand or from solvent.
Acquisition parameters: Temperature = 7 K; microwave frequency = 9.711 GHz; B_0 = 290 mT (g = 2.393); MW pulse length ($\pi/2$, π) = 8 ns, 16 ns; τ = 142 ns; $t_1 = t_2$ = 100 ns; $\Delta t_1 = \Delta t_2$ = 16 ns; shot repetition time (srt) = 1 ms.

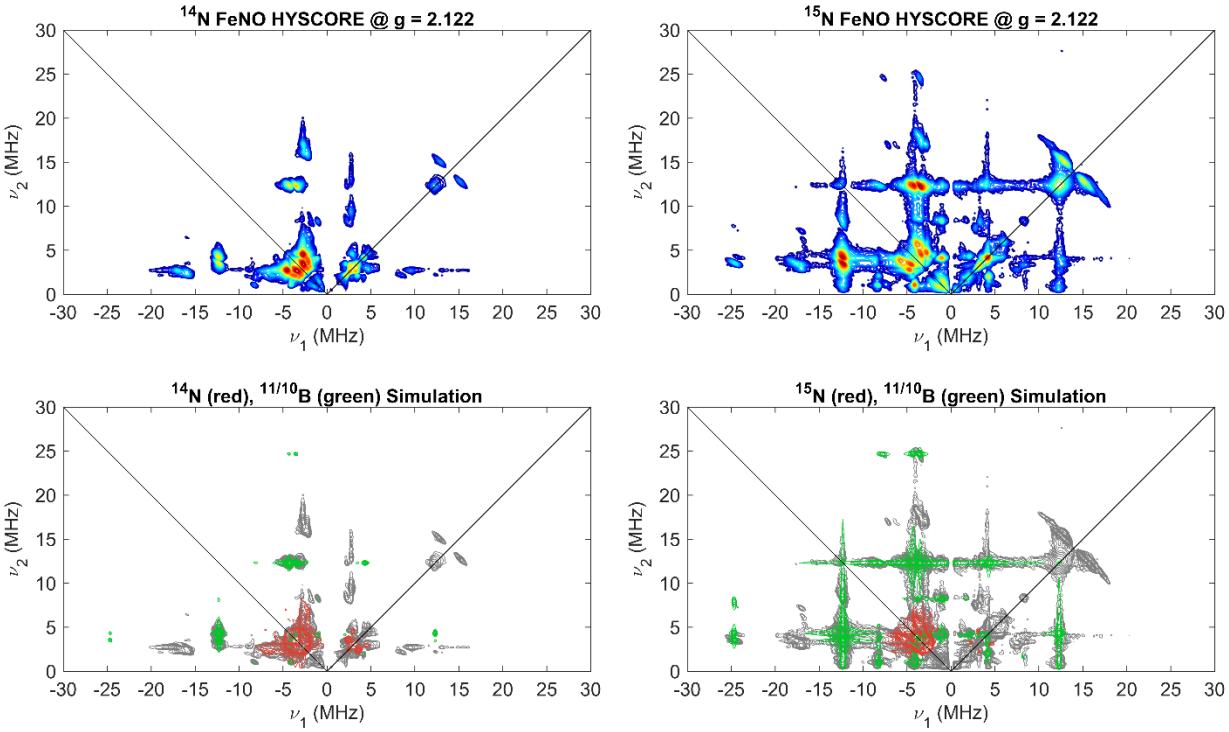

Figure S6. X-band HYSCORE spectra of the ls-{FeNO}^{9} complex [Fe(TPB)($^{14/15}$NO)]. The experimental data are plotted in color in the top panels, ranging from dark blue to red in increasing intensity. These same data are plotted in grey in the bottom panels, with $^{14/15}$N and ^{11}B simulations overlaid in red and green, respectively. Unsimulated features centered around 15 MHz in the (+,+) quadrant arise from weakly coupled ^{1}H nuclei of the ligand or from solvent.
Acquisition parameters: Temperature = 7 K; microwave frequency = 9.711 GHz; B_0 = 327 mT (g = 2.122); MW pulse length ($\pi/2$, π) = 8 ns, 16 ns; τ = 142 ns; $t_1 = t_2$ = 100 ns; $\Delta t_1 = \Delta t_2$ = 16 ns; shot repetition time (srt) = 1 ms.

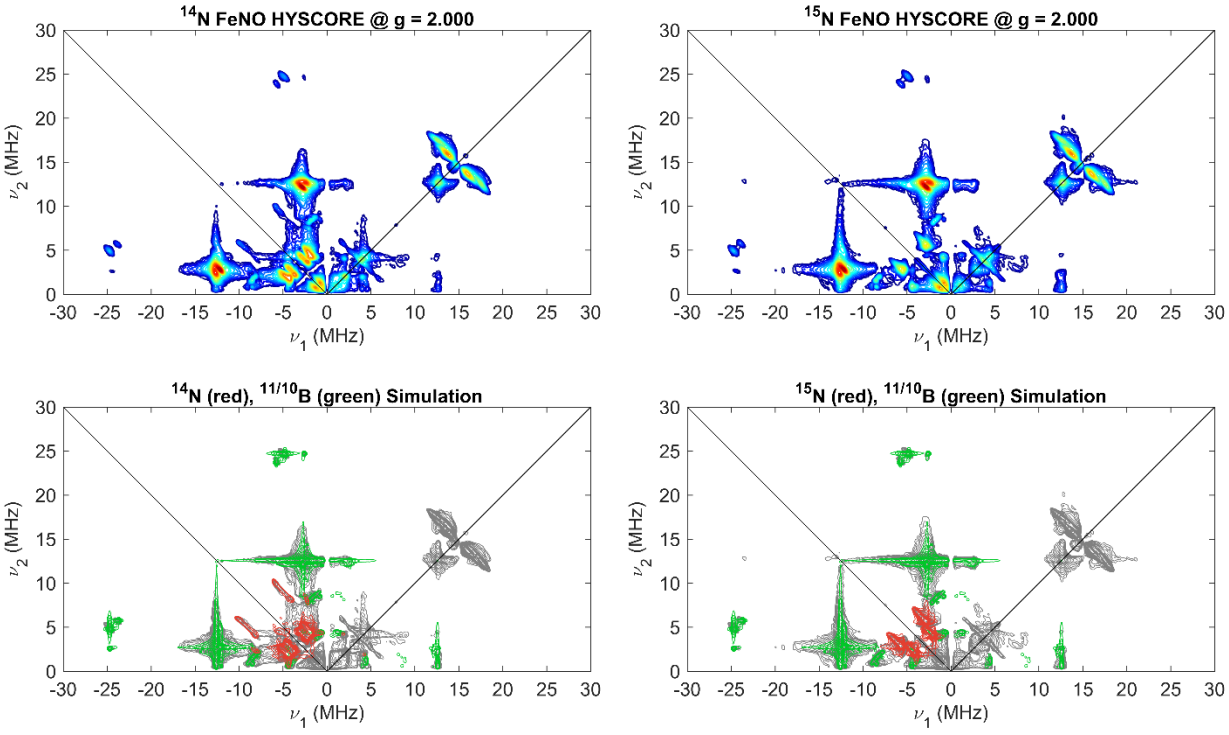

Figure S7. X-band HYSCORE spectra of the ls-{FeNO}^{9} complex [Fe(TPB)($^{14/15}$NO)]. The experimental data are plotted in color in the top panels, ranging from dark blue to red in increasing intensity. These same data are plotted in grey in the bottom panels, with $^{14/15}$N and ^{11}B simulations overlaid in red and green, respectively. Unsimulated features centered around 15 MHz in the (+,+) quadrant arise from weakly coupled ^{1}H nuclei of the ligand or from solvent.
Acquisition parameters: Temperature = 7 K; microwave frequency = 9.711 GHz; B_0 = 347 mT (g = 2.000); MW pulse length ($\pi/2$, π) = 8 ns, 16 ns; τ = 136 ns; $t_1 = t_2$ = 100 ns; $\Delta t_1 = \Delta t_2$ = 16 ns; shot repetition time (srt) = 1 ms.

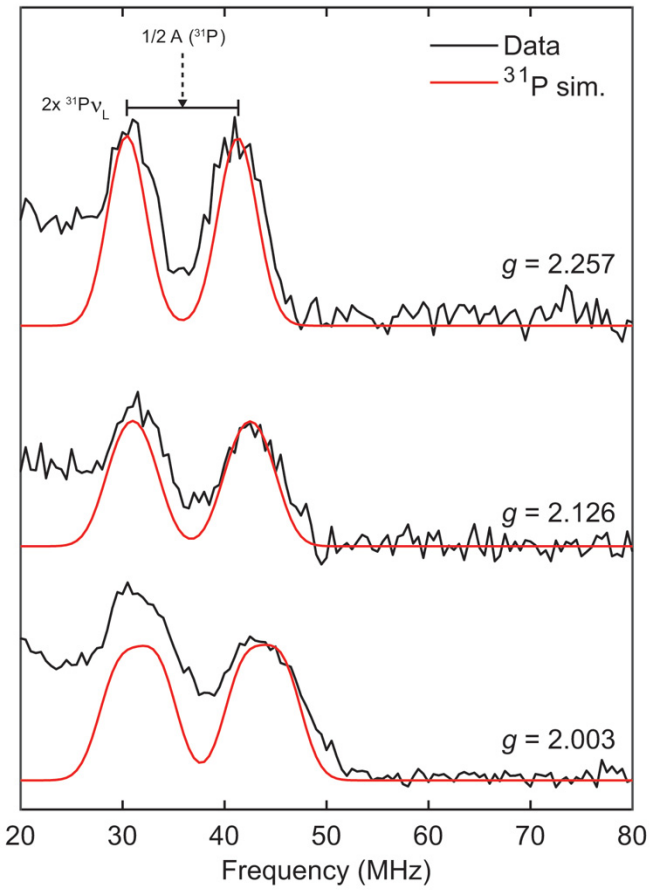

Figure S8. Field-Dependent Davies ENDOR spectra and ^{31}P simulations of [Fe(TPB)(NO)]. Acquisition parameters: Temperature = 5 K; microwave frequency = 9.730 GHz; B_0 = 308 mT (g = 2.257), 327 mT (g = 2.126), 347 mT (g = 2.003); MW pulse length ($\pi/2$, π) = 40 ns, 80 ns; RF pulse length = 40 μs; RF delay t_{RF} = 2 μs; τ = 340 ns; shot repetition time (srt) = 20 ms.

Table S1. Experimental structural and NRVS data of the ls-{FeNO}^{8} complex vs. B3LYP/TZVP closed shell (CS) and broken symmetry (BS) results.

	ls-{FeNO}^{8}		
	Exp.	**B3LYP (CS)**	**B3LYP (BS)**
d(N–O)	1.16	1.17	1.17
d(Fe–NO)	1.66	1.65	1.68
d(Fe–B)	2.31	2.37	2.37
<Fe–N–O	176	172	175
d(Fe–P)	2.28	2.35	2.37
d(Fe–P)	2.28	2.35	2.37
d(Fe–P)	2.29	2.36	2.36
P-Fe-P	100	100	100
P-Fe-P	101	101	101
P-Fe-P	154	152	152
ν(Fe–NO)	610	654	490
ν(N-O)	1745	1810	1793
δ(Fe-N-O)	537	529	442
δ(Fe-N-O)	540	537	461

Table S2. Optimized coordinates of the ls-{FeNO}^{8} complex in the closed-shell state with BP86/TZVP

Fe	-0.05211700	-0.58037100	0.57287600
N	-0.08444900	-1.48549100	1.96141600
O	-0.12932800	-2.02647000	3.00833400
H	-4.65434100	0.58675100	0.79021700
H	-5.44858500	-0.83677100	0.07135800
H	-5.52866100	0.73188400	-0.74148500
H	-3.06015700	-1.07727400	-2.93316100
H	-4.66401300	-0.31573400	-2.86425400
H	-4.41693400	-1.91572100	-2.13893100
H	-3.13767800	0.73954900	-1.22705600
H	-4.39533500	-1.43744200	2.27762000
P	-0.33472600	1.66933200	1.03634600
P	2.26683600	-0.70342400	0.34099600
P	-2.24081300	-1.11786100	-0.00778400
B	0.12683800	0.53761000	-1.44888900
C	-0.97462200	1.68433700	-1.57559800
C	-1.27723600	2.38752400	-0.39125700
C	-2.14191900	3.49211500	-0.39632600
C	-2.73421000	3.89666600	-1.59871700
C	-2.44666600	3.21158100	-2.78604000
C	-1.56576300	2.12262400	-2.77699400
C	1.62951100	1.01846000	-1.73807000
C	2.72546200	0.42767200	-1.05780900
C	4.04732400	0.76696200	-1.39419600
C	4.30263800	1.71074400	-2.39472600
C	3.23535400	2.32533100	-3.05564300
C	1.92056700	1.98259400	-2.72455400
C	-0.09234400	-1.00238200	-1.78868200
C	-1.06348600	-1.87951800	-1.18583600
C	-1.07150900	-3.26725600	-1.49533900
C	-0.24462100	-3.77782200	-2.48189600
C	0.65929500	-2.92581300	-3.14923000
C	0.77474300	-1.60216000	-2.75967500
C	-2.84780400	1.81475400	2.44487800
C	-1.34907400	2.09036500	2.60073400
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C	1.76851100	3.00628200	2.58037000
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C	0.88392400	4.26358500	0.59839400
C	2.76619700	-0.53388900	3.17335900
C	3.36757100	-0.16412700	1.80887700
C	4.84002000	-0.61345400	1.75934900
C	2.70155100	-3.45471800	1.06303400
C	2.73343100	-2.48963400	-0.13312400

C	4.02461700	-2.63206500	-0.95285000
C	-4.06559500	-3.38291700	0.28207200
C	-2.99115700	-2.54202400	0.99714200
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H	3.38684200	-0.09419000	3.97026200
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H	-4.26051200	-4.28669600	0.88124700
H	-2.10400300	-3.17553200	1.16746200
H	-2.74460900	-1.52912200	2.94398900
H	-3.79458400	-2.95598800	2.96455100

Table S3. Optimized coordinates of the ls-{FeNO}^{9} complex in the closed-shell state with BP86/TZVP

Fe	0.05214600	-0.03547700	-1.07312100
N	-0.03304400	-0.02020200	-2.73541600
O	-0.18593200	-0.02126000	-3.91846000
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H	4.20686000	-0.35698200	-3.60211200
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H	4.00625900	0.17743500	-1.16273600
H	2.82936100	-3.87213400	-1.95152500
P	0.21143900	2.18831300	-0.51278600
P	-2.11281100	-0.85066600	-0.57414600
P	2.06454800	-1.02738400	-0.47410100
B	-0.04218200	-0.05308800	1.34837500
C	-0.93231900	1.24310900	1.76020400
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H	1.50867000	3.82954600	-2.83258100
H	0.05078800	4.26392800	-3.74495000
H	0.49203200	2.55632200	-3.54435100
H	-0.31619200	4.45438400	-1.24960800
H	-1.95978700	2.31451300	-2.72526400
H	-2.52283100	3.19323500	-1.28091400
H	-2.21524700	4.07106500	-2.79891200
H	-3.62694100	1.03747200	-2.32033000
H	-4.96024300	1.61550500	-1.30651500
H	-4.97223500	-0.04929200	-1.91257800
H	-3.08288900	1.20618900	0.17415200
H	-5.11870200	-1.08081500	0.52506500
H	-4.06870300	-0.39581300	1.78601500
H	-5.32531500	0.60952900	1.03134500
H	-0.71573400	-2.52070900	-2.60432900
H	-1.99110100	-3.58009200	-3.24988000
H	-1.49165100	-3.72606000	-1.54713400
H	-2.82975100	-1.25997200	-2.80516300
H	-4.00907600	-3.58637000	-1.18073000
H	-4.88059000	-2.04995000	-1.38352100

H	-4.45197400	-3.02966700	-2.79793100
H	2.62739400	-3.09517800	1.74547600
H	3.71056100	-3.68215600	0.46041100
H	2.29159400	-4.63988700	0.93207300
H	0.74892400	-2.92035900	0.10541600
H	1.28598900	-3.12383500	-2.41547600
H	1.30181700	-4.64317800	-1.50013200

Table S4. Optimized coordinates of the ls-{FeNO}^{10} complex in the closed-shell state with BP86/TZVP

Fe	-0.00059000	0.00012300	-1.08463800
N	-0.00048800	-0.00167200	-2.73690100
O	-0.00005200	-0.00342200	-3.94914100
P	1.23211900	-1.81007700	-0.61305800
P	0.95078700	1.97244600	-0.61384400
P	-2.18438700	-0.16067300	-0.61300100
B	-0.00035900	-0.00036800	1.37269600
C	1.36291400	-0.74551700	1.88840200
C	2.04863300	-1.65318000	1.04576600
C	3.22484400	-2.30003400	1.46017400
C	3.75645100	-2.05485800	2.73290400
C	3.09184700	-1.17150700	3.59071100
C	1.91684400	-0.53470700	3.17083800
C	-0.03508400	1.55255900	1.88842400
C	0.40871600	2.60025000	1.04601400
C	0.38266800	3.94202000	1.46150100
C	-0.09401300	4.27944000	2.73487000
C	-0.52740900	3.26215800	3.59231100
C	-0.49322300	1.92646300	3.17149000
C	-1.32733200	-0.80861400	1.88778800
C	-2.45604600	-0.94888700	1.04486200
C	-3.60405800	-1.64471600	1.45900800
C	-3.65716700	-2.22847100	2.73142600
C	-2.56012000	-2.09420100	3.58949300
C	-1.42165400	-1.39385600	3.17018000
C	1.63412200	-4.75998100	-0.49086300
C	0.57363500	-3.64587200	-0.51670300
C	-0.36669800	-3.83971200	0.67666300
C	2.16508500	-2.65940500	-3.18384400
C	2.68258400	-2.15103500	-1.82794300
C	3.57038800	-0.92163300	-2.03075700
C	3.30545600	3.79474700	-0.49336000
C	2.87045800	2.31933500	-0.51829000
C	3.50815000	1.60229300	0.67544500
C	1.21755200	3.20383100	-3.18436100
C	0.52025100	3.39863400	-1.82769400
C	-0.98859300	3.55454700	-2.02911800
C	-4.93913700	0.96702500	-0.48699600
C	-3.44401700	1.32826900	-0.51102500
C	-3.14107500	2.23331300	0.68686600
C	-3.38567600	-0.53915800	-3.18450700
C	-3.20535100	-1.24326700	-1.82937300
C	-2.58598200	-2.62738900	-2.03393600
H	3.75552500	-2.97386400	0.78176900

H	4.68692400	-2.53841700	3.04431100
H	3.50145100	-0.96264000	4.58426300
H	1.43810700	0.18167700	3.84570200
H	0.70126900	4.73870100	0.78353300
H	-0.13902200	5.32688400	3.04699100
H	-0.91201000	3.51228400	4.58632900
H	-0.87496500	1.15355600	3.84582100
H	-4.45308000	-1.76709000	0.78071600
H	-4.54087400	-2.79318300	3.04247400
H	-2.58395900	-2.55373000	4.58288000
H	-0.56214700	-1.33679900	3.84535800
H	2.28555400	-4.77283900	-1.37567000
H	1.12855200	-5.74170900	-0.44258000
H	2.26851100	-4.68238600	0.40603900
H	-0.01605200	-3.74465200	-1.44330100
H	-1.16923000	-3.09478700	0.70476400
H	0.18444100	-3.76162400	1.62660900
H	-0.82623600	-4.84344400	0.63635300
H	1.55699100	-3.57156300	-3.09406200
H	3.01715800	-2.89329300	-3.84704200
H	1.55375000	-1.89576300	-3.68484400
H	3.29544400	-2.94174500	-1.36277300
H	4.01243900	-0.57444800	-1.08650700
H	2.98555100	-0.09479600	-2.45982700
H	4.39489300	-1.15878800	-2.72708400
H	2.99029300	4.36519900	-1.37812200
H	4.40849700	3.84753700	-0.44588200
H	2.92183300	4.30579200	0.40360900
H	3.25044600	1.85766800	-1.44496500
H	3.26170300	0.53545400	0.70568200
H	3.16704800	2.04284500	1.62508100
H	4.60738200	1.70349300	0.63381100
H	2.31176800	3.13532400	-3.09584900
H	0.99171200	4.05722600	-3.84863700
H	0.86293100	2.29107100	-3.68339400
H	0.89994000	4.32450800	-1.36318600
H	-1.51021300	3.75912300	-1.08369900
H	-1.41342200	2.63759300	-2.46354400
H	-1.19491400	4.39112500	-2.72086200
H	-5.27584300	0.41340100	-1.37447600
H	-5.53654400	1.89549400	-0.43427000
H	-5.18905600	0.37451200	0.40711100
H	-3.23430700	1.89236800	-1.43513900
H	-2.09414000	2.55406200	0.71732200
H	-3.35012600	1.71224400	1.63403400
H	-3.77932500	3.13420000	0.65083400

H	-3.87162400	0.44342300	-3.09386700
H	-4.01372600	-1.15921900	-3.84906700
H	-2.41818500	-0.39107400	-3.68437700
H	-4.19686000	-1.37815800	-1.36484500
H	-2.50361700	-3.18386900	-1.08994700
H	-1.57885900	-2.53541900	-2.46652800
H	-3.20638700	-3.22245700	-2.72814400

Table S5. Optimized coordinates of the ls-{FeNO}^{8} complex in the broken-symmetry state with B3LYP/TZVP

Fe	-0.04384400	-0.54803900	0.65283800
N	-0.06973100	-1.43476700	2.07697700
O	-0.09400400	-1.95637300	3.12180600
P	-0.27017900	1.78857800	0.96886700
P	2.29358400	-0.74513900	0.36711500
P	-2.27488100	-1.09306800	0.07541600
B	0.12562700	0.43941600	-1.49002800
C	-0.94289400	1.61173200	-1.63323500
C	-1.20219000	2.40302500	-0.50453800
C	-2.03862100	3.51714600	-0.58043000
C	-2.64453000	3.84493100	-1.78930600
C	-2.40160800	3.06876800	-2.91941200
C	-1.55237800	1.96828800	-2.84328200
C	1.63871400	0.86476800	-1.79592300
C	2.72885400	0.32160100	-1.08321800
C	4.04067600	0.65428600	-1.43252400
C	4.29516700	1.52926200	-2.48287000
C	3.23347600	2.08523600	-3.18532000
C	1.92756300	1.75909000	-2.83689700
C	-0.18576700	-1.09699800	-1.77719400
C	-1.19998100	-1.90177100	-1.17558600
C	-1.30627500	-3.26885500	-1.49634700
C	-0.51341600	-3.83471400	-2.47365600
C	0.44489400	-3.05361200	-3.12630500
C	0.63308500	-1.74196000	-2.74552600
C	-2.75049700	2.13040900	2.43571300
C	-1.23486000	2.32180700	2.52247700
C	-0.72535600	1.64781700	3.80441400
C	0.98357900	4.33886200	0.42722400
C	1.26162400	2.94844600	1.01073900
C	1.92137600	3.09676700	2.38628700
C	2.86125000	-0.48300900	3.16442700
C	3.45116800	-0.20076300	1.77676600
C	4.89853300	-0.71616600	1.72886000
C	3.94638600	-2.75974500	-0.92694100
C	2.68174200	-2.54827500	-0.08682800
C	2.64103500	-3.49248800	1.12242100
C	-3.44864700	-1.92654500	2.52143500
C	-3.01846800	-2.46491000	1.14689900
C	-4.15608400	-3.30000000	0.53852800
C	-4.12001900	-0.96480100	-2.12006200
C	-3.66832000	-0.20262800	-0.86805000
C	-4.86312800	0.18661300	0.01123100
H	-2.22102800	4.13876700	0.28682800

H	-3.30091900	4.70398300	-1.84913500
H	-2.87450300	3.32324200	-3.86032700
H	-1.37594700	1.37461200	-3.73352800
H	4.88030300	0.24343600	-0.89291700
H	5.31665600	1.77874000	-2.74110400
H	3.42116600	2.77476600	-3.99939900
H	1.11220800	2.20972200	-3.38910900
H	-2.03626500	-3.88865300	-0.99875800
H	-0.64320500	-4.87683400	-2.73871700
H	1.04923600	-3.48157800	-3.91668400
H	1.40774000	-1.16494000	-3.23117800
H	-3.19131300	2.55259800	1.53644100
H	-3.21869500	2.61649100	3.29532300
H	-3.01306700	1.07423900	2.48717500
H	-1.02917100	3.39504500	2.58865800
H	0.34029700	1.77359900	3.97161800
H	-0.94311800	0.57967800	3.80139000
H	-1.24239500	2.08213200	4.66378900
H	0.66403600	4.29974800	-0.61126800
H	1.90273200	4.92829000	0.47187600
H	0.22647700	4.88096600	0.99824900
H	1.96320100	2.44743300	0.34385600
H	2.14599500	2.14673000	2.86532700
H	1.30685500	3.68490400	3.06945600
H	2.86527800	3.63366500	2.26571500
H	1.86894300	-0.05803800	3.29290200
H	3.51216000	-0.04465500	3.92454500
H	2.79668400	-1.55111800	3.37131400
H	3.47957900	0.88111200	1.63138700
H	5.40783800	-0.52372200	0.78847400
H	4.95767500	-1.78432000	1.93327500
H	5.46849300	-0.20880200	2.51109600
H	3.95565500	-2.13996200	-1.82271300
H	3.98284300	-3.80379800	-1.24829200
H	4.85852700	-2.56273100	-0.36447400
H	1.82978000	-2.79789700	-0.71955300
H	1.72081900	-3.40121800	1.69743900
H	3.48213000	-3.33948700	1.79769800
H	2.69996200	-4.52319800	0.76498000
H	-2.66142400	-1.36484400	3.02022900
H	-3.71062000	-2.76659200	3.16853100
H	-4.32973800	-1.28927700	2.44518900
H	-2.15453400	-3.11712700	1.30134200
H	-3.94221900	-3.68362900	-0.45690100
H	-5.08508100	-2.73495100	0.48129800
H	-4.34298400	-4.15864900	1.18810200

H	-3.29367800	-1.17094900	-2.79917600
H	-4.84507500	-0.34978800	-2.65908400
H	-4.60913800	-1.90856700	-1.87851300
H	-3.18485000	0.71468900	-1.19394100
H	-4.57173400	0.72951700	0.90756800
H	-5.45877200	-0.67511500	0.30981600
H	-5.51618200	0.84337500	-0.56783400

Table S6. Optimized coordinates of the ls-{FeNO}^{8} complex in the closed-shell state with B3LYP/TZVP

Fe	-0.04990000	-0.55430600	0.63555400
N	-0.07894000	-1.38717800	2.05547500
O	-0.12410800	-1.83369500	3.13073700
P	-0.28719500	1.75694200	0.97033200
P	2.28524500	-0.74143400	0.37023100
P	-2.26428200	-1.10633300	0.06505800
B	0.13152100	0.46343900	-1.49212900
C	-0.94289400	1.62841300	-1.63481300
C	-1.21627000	2.39729200	-0.49445000
C	-2.06112600	3.50575600	-0.55695400
C	-2.66110600	3.84874100	-1.76459000
C	-2.40372500	3.09435300	-2.90628000
C	-1.54536100	2.00008900	-2.84345000
C	1.64541200	0.89076500	-1.78430000
C	2.73001900	0.33047800	-1.07533900
C	4.04453500	0.65502400	-1.42143100
C	4.30708700	1.53985100	-2.46176600
C	3.25106500	2.11527900	-3.15682600
C	1.94213800	1.79606200	-2.81317800
C	-0.16330800	-1.07597100	-1.77228100
C	-1.17042000	-1.89593900	-1.17813700
C	-1.25542800	-3.26493700	-1.50210500
C	-0.45463800	-3.81616600	-2.48024500
C	0.49490700	-3.02007900	-3.12882900
C	0.66820400	-1.70980300	-2.73968000
C	-2.77471700	2.07711300	2.43119700
C	-1.26089000	2.28141700	2.52148900
C	-0.75257500	1.62094200	3.81081400
C	0.97037700	4.30698900	0.43325900
C	1.24332200	2.92125900	1.03036200
C	1.88551900	3.08304700	2.41272400
C	2.84760700	-0.47827200	3.17093000
C	3.43838700	-0.19484100	1.78401900
C	4.88679600	-0.70796800	1.74009600
C	3.95099000	-2.76158200	-0.90370500
C	2.67861900	-2.54440300	-0.07691600
C	2.62168300	-3.48351900	1.13560200
C	-3.46385600	-1.96990900	2.49056900
C	-3.00876700	-2.49175900	1.11771700
C	-4.13001900	-3.33155800	0.48554700
C	-4.08524700	-0.96877500	-2.14889400
C	-3.65306200	-0.21579200	-0.88430800
C	-4.86167900	0.15564700	-0.01592900
H	-2.25522100	4.11102900	0.31922900

H	-3.32459400	4.70306000	-1.81459100
H	-2.87243500	3.36098300	-3.84588600
H	-1.35720400	1.42347000	-3.74246400
H	4.88066100	0.22999900	-0.88759500
H	5.33102500	1.78206100	-2.71758400
H	3.44542900	2.81360100	-3.96179300
H	1.13063700	2.25910600	-3.36085300
H	-1.97737900	-3.89596400	-1.00724300
H	-0.57126100	-4.85860600	-2.75013500
H	1.10402800	-3.43627700	-3.92175700
H	1.43667200	-1.12204400	-3.22169300
H	-3.21649500	2.49077800	1.52852600
H	-3.24936400	2.56431700	3.28666100
H	-3.02934800	1.01915000	2.48831500
H	-1.06587000	3.35698800	2.58169900
H	0.31302300	1.74616800	3.97806700
H	-0.97308000	0.55397600	3.82154800
H	-1.26866400	2.06671100	4.66462900
H	0.66747400	4.26042100	-0.60983200
H	1.88702700	4.89922400	0.48891000
H	0.20218900	4.85034100	0.98837700
H	1.95548100	2.41852300	0.37657400
H	2.11575800	2.13851500	2.89903900
H	1.25769500	3.66829500	3.08604800
H	2.82492800	3.62934600	2.29905700
H	1.85680600	-0.05092300	3.30093500
H	3.49962900	-0.04268500	3.93180300
H	2.78048400	-1.54655500	3.37650600
H	3.46579100	0.88723100	1.63971200
H	5.39894000	-0.51418000	0.80162700
H	4.94711400	-1.77608600	1.94451500
H	5.45340000	-0.19981200	2.52424700
H	3.97031700	-2.14433800	-1.80112800
H	3.98752400	-3.80658000	-1.22225500
H	4.85833300	-2.56582700	-0.33336200
H	1.83276600	-2.79519000	-0.71702500
H	1.69457800	-3.38548800	1.69886700
H	3.45531000	-3.33070400	1.82018100
H	2.68066400	-4.51602500	0.78357700
H	-2.68713900	-1.41282500	3.01047000
H	-3.73485600	-2.81841200	3.12263700
H	-4.34537700	-1.33425800	2.40678000
H	-2.14046600	-3.13673100	1.27888900
H	-3.90010400	-3.70088100	-0.51181000
H	-5.06390000	-2.77482000	0.42376600
H	-4.31670900	-4.19969800	1.12244300

H	-3.24980600	-1.16320100	-2.82012900
H	-4.80835200	-0.35322600	-2.68998500
H	-4.57094000	-1.91782700	-1.92186400
H	-3.17274000	0.70810900	-1.19538300
H	-4.58624200	0.69243400	0.88913400
H	-5.45405000	-0.71358200	0.26699200
H	-5.51282600	0.81237800	-0.59721200

Table S7. Optimized coordinates of the $\{FeN_2\}^9$ complex with BP86/TZVP

Fe	0.02872200	-0.02305000	-1.01287800
N	0.05219500	0.10160900	-2.80244100
N	0.07700400	0.16321300	-3.95070900
P	-2.11031400	-0.83385900	-0.68283300
P	2.00460500	-1.07964500	-0.70610700
P	0.16068500	2.18324900	-0.50526500
B	0.01800400	-0.18612900	1.30232400
C	-0.92738500	-1.46243300	1.71168300
C	-2.00673100	-1.84831200	0.87348900
C	-2.84511800	-2.92939900	1.19593300
C	-2.63254400	-3.66879500	2.36608200
C	-1.57866700	-3.30857200	3.21466100
C	-0.75062400	-2.22834200	2.88861600
C	1.54600900	-0.37444000	1.88380000
C	2.59207300	-0.81284400	1.03282500
C	3.91063400	-0.96899800	1.49318900
C	4.23248700	-0.68310800	2.82552500
C	3.22091100	-0.25224000	3.69195800
C	1.90887800	-0.10681300	3.22413900
C	-0.64256000	1.18923200	1.91211800
C	-0.63977400	2.39176600	1.16010000
C	-1.21333100	3.57431900	1.65750400
C	-1.81112000	3.59524700	2.92423500
C	-1.81906200	2.42554800	3.69310800
C	-1.24481900	1.25150200	3.19002100
C	-5.06860900	-0.81905900	-0.53820600
C	-3.81779400	0.07345500	-0.48656600
C	-3.86363300	0.91215600	0.79473900
C	-3.06187300	-1.41615400	-3.31489400
C	-2.63472200	-2.11470300	-2.01348200
C	-1.51973800	-3.12989500	-2.28623100
C	3.44062000	-3.66020400	-0.78882500
C	2.04564600	-3.01621900	-0.84586700
C	1.15638100	-3.66597000	0.21766300
C	3.32110700	-1.20926400	-3.24006200
C	3.53311100	-0.70481700	-1.80280700
C	3.86174700	0.78928200	-1.81536300
C	1.57010800	4.78592000	-0.13424000
C	1.76821100	3.26414500	-0.24304500
C	2.56231500	2.79423300	0.98063900
C	-0.01615700	3.61660000	-2.96994400
C	-0.77103300	3.42284700	-1.64372400
C	-2.21288800	2.98688100	-1.91303600
H	-3.65045700	-3.22670800	0.51813300
H	-3.27160100	-4.52448400	2.60252300

H	-1.39369300	-3.88294600	4.12849300
H	0.08338000	-1.98541000	3.55445400
H	4.70386100	-1.28245300	0.80807200
H	5.26333600	-0.78151800	3.17801200
H	3.45961100	-0.01324000	4.73352300
H	1.14570900	0.26625400	3.91413700
H	-1.22777700	4.48153100	1.04709700
H	-2.27701100	4.51119900	3.29940900
H	-2.29121700	2.42470900	4.68109500
H	-1.30048900	0.33934900	3.79316900
H	-5.16866400	-1.38814300	-1.47272400
H	-5.96819400	-0.18479000	-0.44197400
H	-5.08315200	-1.52722000	0.30450800
H	-3.83578400	0.75352400	-1.35388700
H	-3.02644600	1.61440100	0.87578800
H	-3.83342200	0.26568800	1.68498600
H	-4.80466400	1.48922200	0.82895400
H	-3.88417300	-0.70080000	-3.16365200
H	-3.40717800	-2.16712000	-4.04773800
H	-2.21999600	-0.87420500	-3.76808000
H	-3.49939900	-2.66381700	-1.60308500
H	-1.28131500	-3.71924000	-1.39004300
H	-0.60066100	-2.62309000	-2.61763200
H	-1.82970900	-3.83016300	-3.08222400
H	4.11391100	-3.32955100	-1.59188300
H	3.33992100	-4.75705300	-0.87482200
H	3.92790800	-3.45548000	0.17756500
H	1.60320400	-3.20945800	-1.83857000
H	0.14025100	-3.25683900	0.22122100
H	1.57142300	-3.50900300	1.22502600
H	1.09363000	-4.75479000	0.04402600
H	3.11801600	-2.28879900	-3.28848200
H	4.22600100	-1.01498200	-3.84301100
H	2.47985200	-0.69037900	-3.72129600
H	4.38507100	-1.24509400	-1.35522400
H	4.06153000	1.17587400	-0.80625000
H	3.01964100	1.35592700	-2.24005400
H	4.75295400	0.98061600	-2.43915300
H	1.10523400	5.23908000	-1.02060200
H	2.55428600	5.27055600	0.00180600
H	0.96268100	5.04457400	0.74721500
H	2.36271300	3.05588200	-1.14777200
H	2.76177600	1.71725900	0.97283400
H	2.01316700	3.01549800	1.90893700
H	3.53026900	3.32442600	1.02821200
H	1.01618100	3.96819700	-2.82503000

H	-0.53545200	4.36483100	-3.59545400
H	0.02738300	2.67797000	-3.54029500
H	-0.80351400	4.38708200	-1.10907200
H	-2.79200200	2.90422300	-0.98279700
H	-2.23661700	2.01100300	-2.42019800
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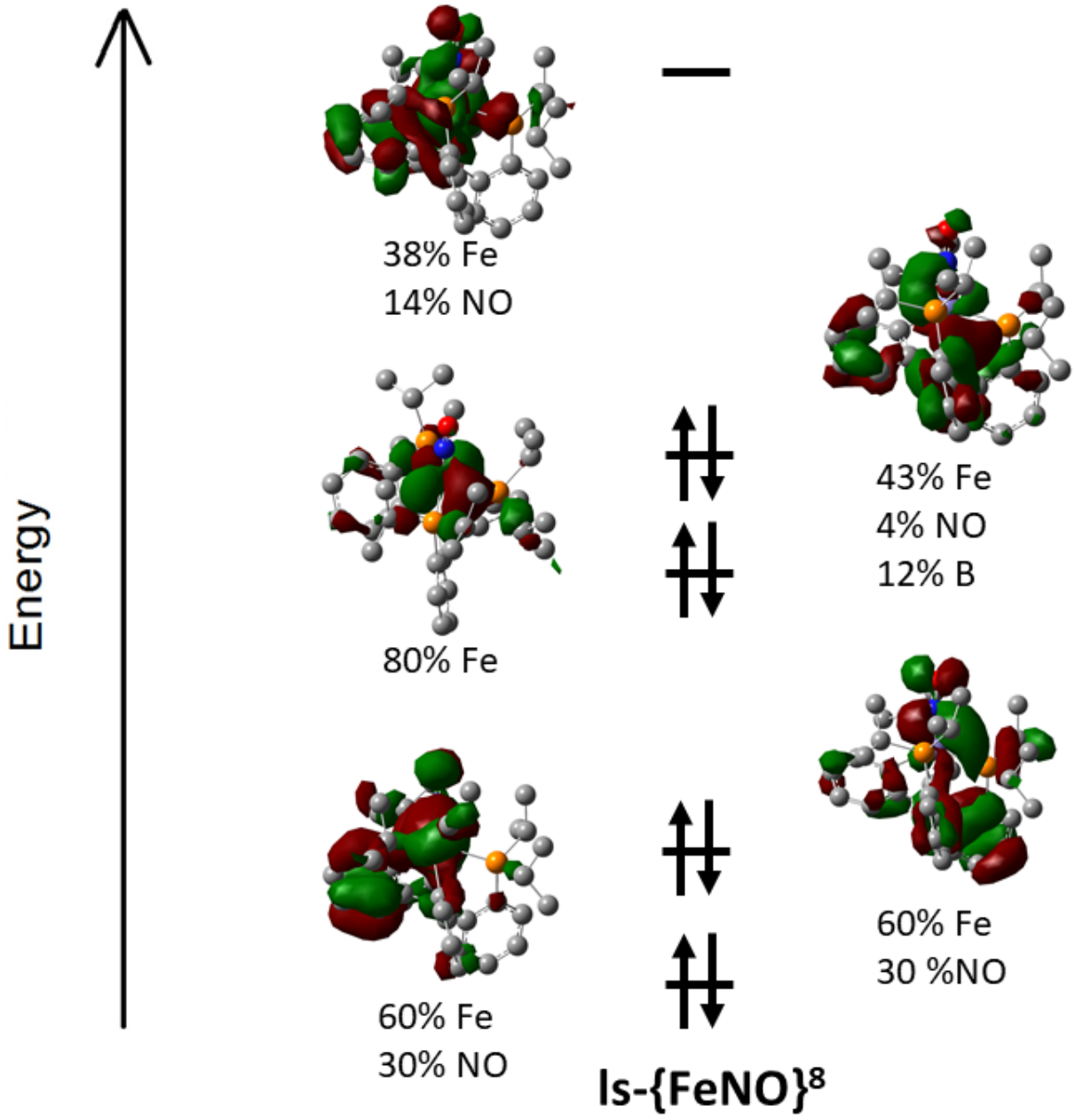

Figure S9. MO diagram of the ls-{FeNO}^{8} complex using quasi-restricted orbitals.[4] The charge distributions listed in the figure are those for the quasi-restricted MOs, not the canonical DFT orbitals discussed in the paper.

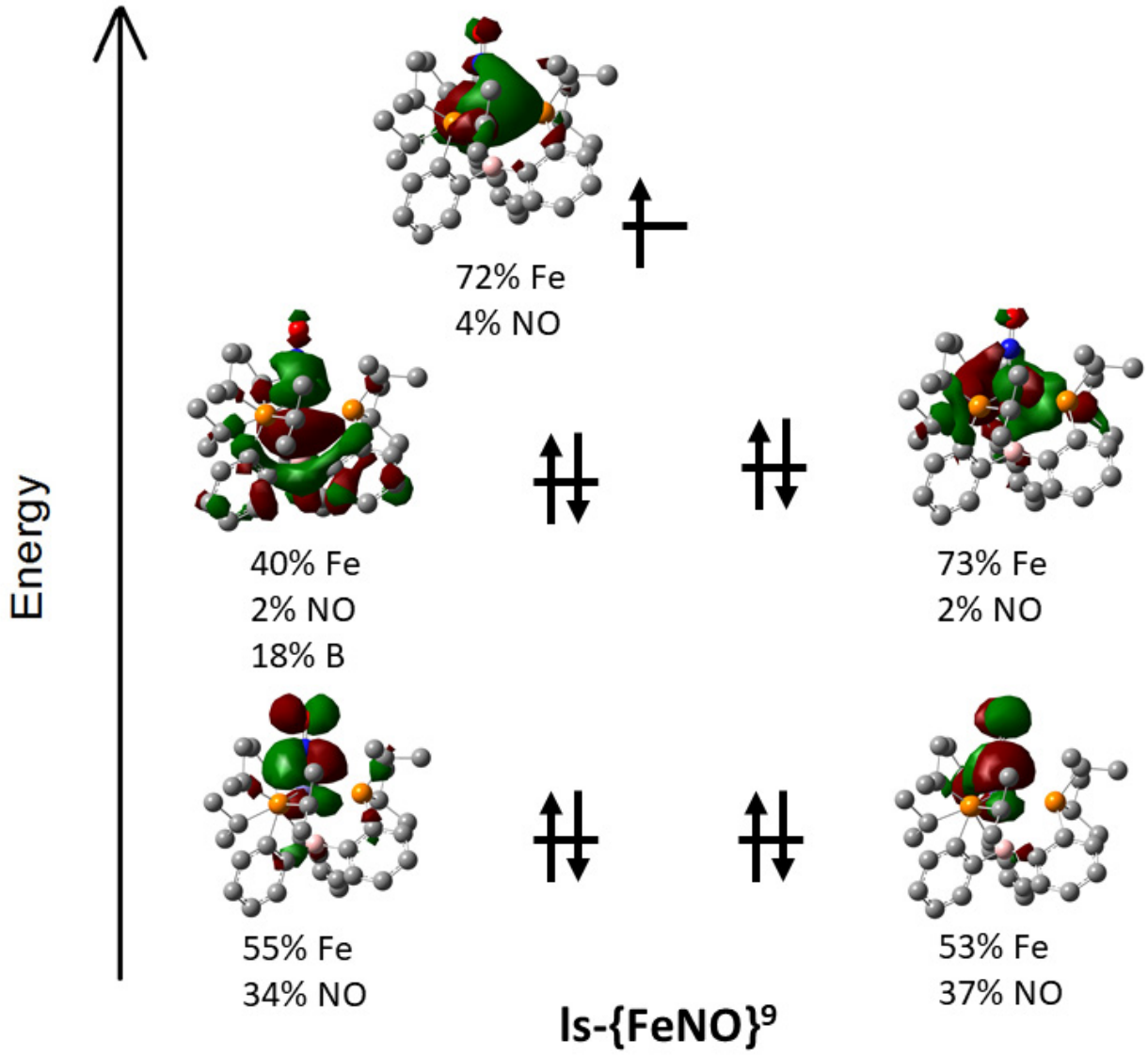

Figure S10. MO diagram of the ls-{FeNO}^{9} complex using quasi-restricted orbitals.[4] The charge distributions listed in the figure are those for the quasi-restricted MOs, not the canonical DFT orbitals discussed in the paper.

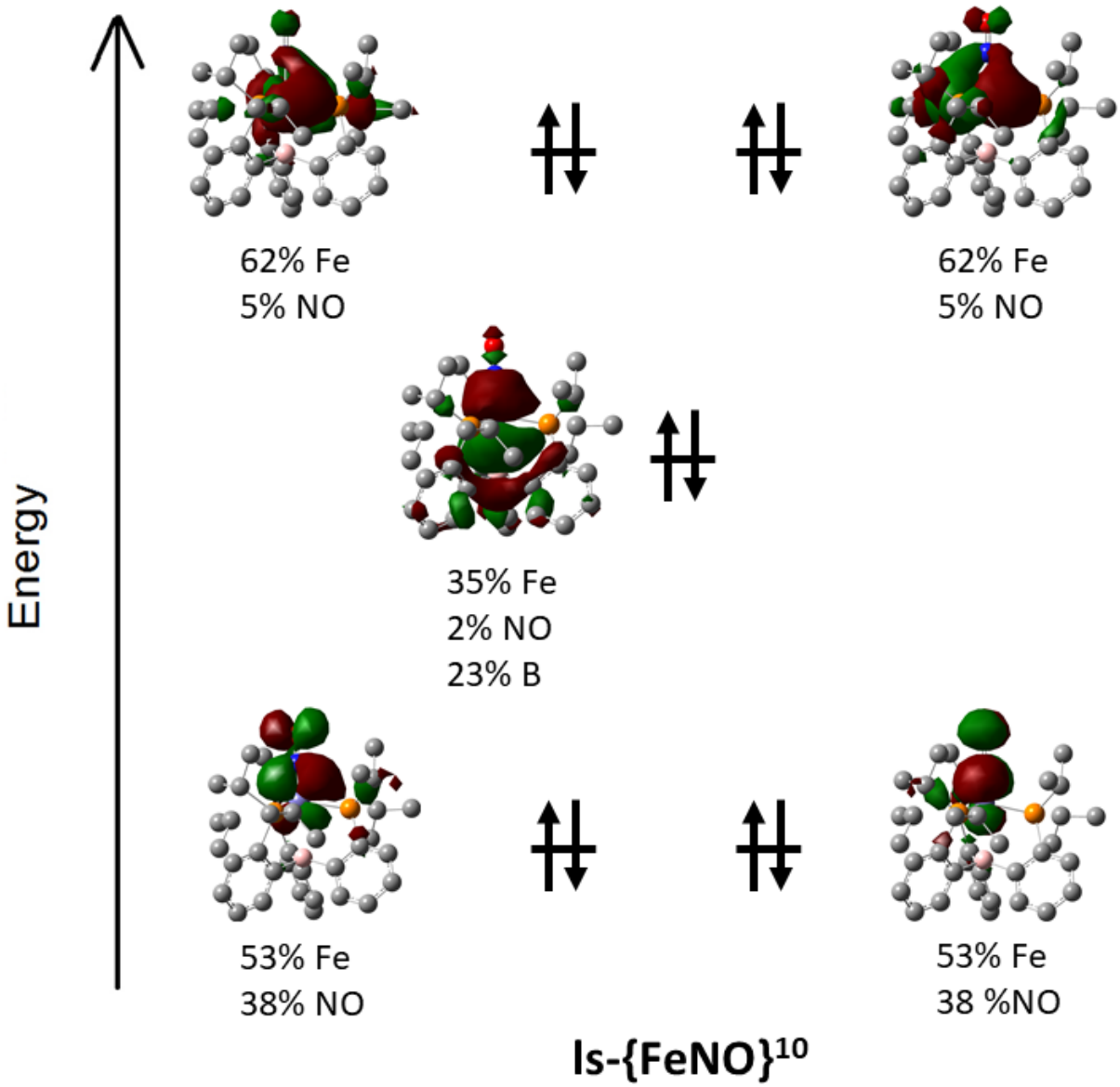

Figure S11. MO diagram of the ls-{FeNO}^{10} complex using quasi-restricted orbitals.[4] The charge distributions listed in the figure are those for the quasi-restricted MOs, not the canonical DFT orbitals discussed in the paper.

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