Electronic Supplementary Information

for

Tying the alkoxides together: an iron complex of a new chelating bulky bis(alkoxide) demonstrates selectivity for coupling of non-bulky aryl nitrenes

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1. General experimental details

Air-sensitive reactions were carried out in a nitrogen-filled glovebox. 1,4-bis(2bromophenyl)benzene was synthesized using previously reported procedures.¹ FeCl₂ and KN(Si(CH₃)₃)₂ were purchased from Strem chemicals and Sigma-Aldrich and used as received. 2-bromophenylboronic acid, 1,4-diiodobenzene and K₂CO₃ were purchased from Sigma-Aldrich and used as received. Benzene-d₆ was purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves. HPLC grade non-deuterated solvents were purchased from Sigma-Aldrich and purified using an MBraun solvent purification system. Compounds were generally characterized by ¹H and ¹³C NMR, high-resolution mass spectrometry and/or elemental analysis. Selected compounds were characterized by X-ray crystallography. NMR spectra of the ligands and metal complexes were recorded at the Lumigen Instrument Centre on an Agilent 400 MHz Spectrometer and Agilent DD2-600 MHz Spectrometer in C₆D₆ or CDCl₃ at room temperature. Chemical Shifts and coupling constants (J) were reported in parts per million and Hertz respectively. Elemental analysis was carried out by Midwest Microlab LLC under air-free conditions. Thermo Fisher Scientific LTQ Orbittrap XL mass spectrometer at the Lumigen Instrument Centre was used for high resolution mass spectra. IR spectra of powdered samples were recorded on a Shimadzu IR Affinity-1 FT-IR Spectrometer outfitted with a MIRacle10 attenuated total reflectance accessory with a monolithic diamond crystal stage and pressure clamp. UV-Visible spectra were obtained on a Shimadzu UV-1800 spectrometer. GC-MS analysis were done using Agilent 6890N spectrometer, Thermo TG5MS $30m \times 0.32mm \times$ 0.25µm colomn, 7683 series injector and Agilent 5973 detector.

2. Synthesis and characterization of H₂[OO]^{Ph} ligand (1)

In a round bottom flask 1,4-bis(2-bromophenyl)benzene (2.00 g, 5.1 mmol) was dissolved in THF and cooled to -35 °C. To this cold solution, t-BuLi (1.5 M in pentane, 14.5 ml, 21.8 mmol) was added dropwise while maintaining the temperature. Following the addition, the reaction was allowed to warm to room temperature, stirred for 4 h and then transferred into a round bottom flask containing a solution of benzophenone (1.88 g, 10.3 mmol) in hexane. The reaction was stirred for 48 h followed by aqueous workup to form the protonated ligand. The organic layer was separated, dried with MgSO₄ and filtered followed by solvents evaporation. The crude product was purified through column chromatography (3% ethyl acetate in hexane) to obtain the desired product as a white solid in 72% yield (2.18 g, 3.7 mmol). ¹H NMR (C₆D₆, 600 MHz) δ 7.36 (d, *J* = 7.0 Hz, 8H, *ortho-H*), 7.09 (t, *J* = 7.6 Hz 8H, *meta-H*), 7.05 (t, *J* = 7.0 Hz, 4H, *para-H*), 6.98 (m, 6H), 6.90-6.93 (m, 2H), 3.00 (s, 2H, OH). ¹³C NMR (C₆D₆, 100 MHz) δ 147.80, 145.71, 141.29, 140.95, 132.33, 130.03, 128.99, 128.19, 126.97, 126.77, 126.41. HRMS (m/z): Calcd [M + Na]⁺ 617.2457, found 617.2446. Anal. Calcd for C₄₄H₃₄O₂: C, 88.86; H, 5.76. Found: C, 88.12; H, 5.65. Mp: 229 °C.



Scheme S1. Synthesis of $H_2[OO]^{Ph}(1)$

3. Synthesis and characterization of Fe[OO]^{Ph}(THF)₂ complex (2)

To a 5 ml solution of Fe[N(SiMe₃)₂]₂(THF)₂² (0.030 g, 0.057 mmol) in THF, the solution of ligand (0.034 g, 0.057 mmol) in THF was added dropwise. The color of the reaction changed from green to brown in course of 4 h. The volatiles were removed under vacuum and the crude product was recrystallized using DCM at -35 °C to give **2** in 82% yield (36 mg, 46 mmol). ¹H NMR (C₆D₆, 600 MHz) δ 46.4 (1H, $\Delta v_{1/2} = 124$ Hz), 40.8 (1H, $\Delta v_{1/2} = 214$ Hz), 39.7 (1H, $\Delta v_{1/2} = 153$ Hz), 32.2 (1H, $\Delta v_{1/2} = 38$ Hz), 26.3 (1H, $\Delta v_{1/2} = 110$ Hz), 24.1 (1H, $\Delta v_{1/2} = 40$ Hz), 16.3 (1H, $\Delta v_{1/2} = 36$ Hz), 8.1 (1H, $\Delta v_{1/2} = 34$ Hz), 6.7 (1H, $\Delta v_{1/2} = 61$ Hz), 2.9 (13H, $\Delta v_{1/2} = 94$ Hz), 1.1 (14H, $\Delta v_{1/2} = 32$ Hz), -1.1 (1H, $\Delta v_{1/2} = 131$ Hz), -5.3 (1H, $\Delta v_{1/2} = 74$ Hz), -7.9 (1H, $\Delta v_{1/2} = 35$ Hz), -10.1 (1H, $\Delta v_{1/2} = 71$ Hz), -45.9 (1H, $\Delta v_{1/2} = 280$ Hz). IR (cm⁻¹, selected peaks): 2376 (m), 1681 (s), 1520 (m), 1389 (m), 1289 (s), 1157 (s), 1065 (s), 988 (s), 926 (m), 840 (m). λ_{max} (ε_{M} (L⁻¹ cm⁻¹ mol⁻¹)) ~500 (sh, 43300) nm. Anal. Calcd for C₅₂H₄₆FeO₄: C, 81.48; H, 4.97. Found: C, 80.98; H, 5.32. $\mu_{eff} = 4.8 \,\mu$ B.

4. Synthesis and characterization of azoarenes

General procedure for catalytic formation of azoarenes. All azides were synthesized using previously reported procedures. Catalytic reactions were performed by adding 10 equiv of organic azide and 1,2,3-trimethoxy benzene (TMB), hexafluorobenzene (HFB) or hexamethyl benzene (HMB) internal standard solution in C_6D_6 to a C_6D_6 solution of 10.0-12.0 mg (0.0126-0.0151 mmol) catalyst in N₂ filled glovebox. The reaction mixture was stirred in 60 °C for 24 h. Crude products were identified by the combination of ¹H NMR spectroscopy and GC-MS; the yields of azoarenes were calculated using ¹H NMR by comparing with internal standard. Representative azoarenes were isolated in a pure state using silica gel column chromatography (hexane). The spectra of the isolated products were compared to the previously published NMR spectra of the corresponding azoarenes.¹⁸

Isolation of (4-MePh)N=N(4-MePh). Reactions were done according to the general procedure by reacting 28.0 mg (0.0354 mmol) of catalyst with 47.1 mg (0.354 mmol, 10 equiv) of 4-methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 76% yield (28.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.6 Hz, 4H), 7.31 (d, *J* = 7.8 Hz, 4H), 2.43 (s, *J* = Hz, 6H); ¹³C NMR (400 MHz, CDCl₃) δ 150.61, 140.97, 129.48, 122.49, 21.26, HR-MS m/z calcd for C₁₄H₁₅N₂ [M+H]⁺: 211.1230, found: 211.1224.

Isolation of $(4-^{i}PrPh)N=N(4-^{i}PrPh)$. Reactions were done according to the general procedure by reacting 34.9 mg (0.0441 mmol) of catalyst with 71.0 mg (0.441 mmol, 10 equiv) of 4methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 42% yield (20.0 mg). ¹H NMR (400 MHz, C_6D_6) δ 8.10 (d, *J*=8.0 Hz, 4H), 7.12 (d, *J*=8.0 Hz, 4H), 2.66 (sept, *J* = 8.0 Hz, 2H), 1.08 (d, *J* = 8.0 Hz, 12H). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J*=8.6 Hz, 4H), 7.34 (d, *J*=8.2 Hz, 4H), 3.03-2.96 (m, 2H) 1.3 (d, *J*=7.0 Hz, 12H); ¹³C NMR (400MHz, CDCl₃) δ 151.68, 150.84, 126.74, 122.45, 33.80, 23.55, HRMS m/z calcd for $C_{18}H_{23}N_2$ [M+H]⁺: 267.1855, found: 267.1856.

Isolation of (3,5-Me₂Ph)N=N(3,5-Me₂Ph). Reactions were done according to the general procedure by reacting 33.8mg (0.0427 mmol) of catalyst with 63.0 mg (0.428 mmol, 10 equiv) of 4-methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 61% yield (31.1 mg). ¹H NMR (400 MHz, C₆D₆) δ 7.82 (s, 4Hz 4H), 6.82 (s, 2H), 2.14 (s, 12H) (*trans* form). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (s, 4Hz 4H), 7.11 (s, 2H), 2.41 (s, 12H); ¹³C NMR (400 MHz, CDCl₃) δ 138.71, 132.48, 120.51, 118.02, 21.24, HRMS m/z calcd for C₁₆H₁₉N₂ [M+H]⁺: 239.1543, found: 239.1535.

Isolation of (4-FPh)N=N(4-FPh). Reactions were done according to the general procedure by reacting 30.2mg (0.0381mmol) of catalyst with 52.3 mg (0.381 mmol, 10 equiv) of 4-methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 74% yield (30.8 mg). ¹H NMR (400MHz, CDCl₃) δ 7.94-7.91 (m, 4H), 7.21-7.18 (m, 4H); ¹³C NMR (400MHz, CDCl₃) δ 164.99, 148.88, 124.63, 115.77, HRMS m/z calcd for C₁₂H₉N₂F₂ [M+H]⁺: 219.0728, found: 219.0731.

5. X-ray crystallographic details

The structures of ligand $H_2[OO]^{Ph}$ (1) and complex Fe[OO]Ph(THF)₂ (2) were confirmed by Xray analysis. The crystals of 1 (colorless prisms) and 2 (light-brown blocks) were obtained by recrystallization from CH₂Cl₂ (room temperature) and CH₂Cl₂/THF (-35 °C), respectively. The crystals were mounted on a Bruker APEXII/Kappa three circle goniometer platform diffractometer equipped with an APEX-2 detector. A graphic monochromator was employed for wavelength selection of the Mo K α radiation ($\lambda = 0.71073$ Å). The data were processed and the structure was solved using the APEX-2 software supplied by Bruker-AXS. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically. The structure of 2 contained co-crystallized molecule of CH₂Cl₂ (one molecule per two molecules of 2). In addition, one of the phenyl rings exhibited conformation disorder, which was successfully modeled. In the structure of 1, half the ligand occupied an asymmetric unit. The structure of 1 was collected at room temperature, as its cooling was found to lead to crystal decomposition.

	1	2
formula	$C_{22}H_{17}O_1$	$C_{52}H_{48}FeO_4{\times}0.5CH_2Cl_2$
fw	594.72	835.22
crystal	Triclinic	Orthorhombic
system		
space group	<i>P</i> -1	$P2_{1}2_{1}2_{1}$
<i>a</i> (Å)	8.5806(7)	14.4570(15)
<i>b</i> (Å)	10.2480(8)	16.9138(18)
<i>c</i> (Å)	10.6149(8)	17.4369(18)
α (deg)	95.974(4)	90.00
β (deg)	112.253(4)	90.00
γ (deg)	102.680(4)	90.00
$V(\text{\AA}^3)$	824.5(1)	4263.7(8)
$D_c (\text{g cm}^{-3})$	1.198	1.301
Ζ	2	4
$\mu (\text{mm}^{-1})$	0.072	0.463
$T(\mathbf{K})$	296(2)	100(2)
R_1	0.0500	0.0789
GOF	0.999	1.135

 Table S1. Crystal data and structure refinement for 1 and 2.

Table S2. Selected bond distances (Å) and angles (degrees) for $Fe[OO]^{Ph}(THF)_2$ (2)



Fe-O1	1.837(4)
Fe-O2	1.852(4)
Fe-O3	2.173(4)
Fe-O4	2.212(4)
O1-Fe-O2	155.5(2)
O3-Fe-O4	88.8(2)
C1-C2-C3-C4 (dihedral)	120.7(2)
C1-C2-C3-C4 (dihedral)	124.0(2)

6. Evans method formula and procedure

Evans method was carried out using a standard NMR tube and a Wilmad coaxial insert (purchased from Aldrich). Carefully weighted (10-15 mg) sample of the Fe complex was dissolved in 1 ml of C_6D_6 to prepare known concentrations of solutions which was further used for calculations. The insert with the solution was then placed inside an NMR tube containing C_6D_6 . The resulting NMR spectra was used to measure molar susceptibility χ_m . It was calculated using the equation (1).

$$\chi_m = \left[\frac{3\Delta\nu}{4\pi m \nu_0} + \chi_0\right] M \qquad (\text{Eq. 1})$$

Where Δv is the peak separation (Hz), *m* is the concentration of the solution (g/mL), v_0 is the spectrometer operating frequency in Hz, $\chi 0$ is the molar susceptibility of the solvent (in cm³/g), and *M* is the molar mass of the compound (g/mol). Diamagnetic corrections were calculated using Pascals constants. The solution state effective magnetic moment (μ_{eff}) was calculated using Equation 2:

$$\mu_{eff} = \sqrt{(2.383 \times 10^3)(\chi_m)}$$
 (Eq. 2)

1	4.98
2	4.85
3	4.71
average	4.84
standard deviation	0.01
μcalc (μB)	4.9

7. NMR Spectra



Figure S1. ¹H NMR of $H_2[OO]^{Ph}$.



Figure S2. ¹³C NMR of $H_2[OO]^{Ph}$.



Figure S3. ¹H NMR of Fe[OO]^{Ph}(THF)₂.



Figure S4. ¹H NMR spectrum demonstrating catalytic formation of (PhN=NPh) in C_6D_6 after 24 h at 60 °C.



Figure S5. ¹H NMR spectrum demonstrating catalytic formation of $(4-CH_3Ph)N=N(4-CH_3Ph)$ in C₆D₆ after 24 h at 60 °C.



Figure S6. ¹H NMR spectrum demonstrating catalytic formation of (4-EtPh)N=N(4-EtPh) in C_6D_6 after 24 h at 60 °C.



Figure S7. ¹H NMR spectrum demonstrating catalytic formation of $(4 - {}^{i} PrPh)N = N(4 - {}^{i} PrPh)$ in C₆D₆ after 24 h at 60 °C.



Figure S8. ¹H NMR spectrum demonstrating formation of $(4-CF_3Ph)N=N(4-CF_3Ph)$ in C₆D₆ after 24 h at 60 °C .



Figure S9. ¹H NMR spectrum demonstrating formation of $(4-CH_3COPh)N=N(4-CH_3COPh)$ in C₆D₆ after 24 h at 60 °C.



Figure S10. ¹H NMR spectrum demonstrating formation of $(4-NO_2Ph)N=N(4-NO_2Ph)$ in C₆D₆ after 24 h at 60 °C.



Figure S11. ¹H NMR spectrum demonstrating formation of (4-CH₃OPh)N=N(4-CH₃OPh) in C_6D_6 after 24 h at 60 °C.



Figure S12. ¹⁹F NMR spectrum demonstrating formation of (4-FPh)N=N(4-FPh) in C₆D₆ after 24 hours at 60° C.



Figure S13. ¹H NMR spectrum demonstrating formation of (4-ClPh)N=N(4-ClPh) after 24 hours at 60 ⁰C. The reaction was performed in C_6D_6 , however, since the peak of the solvent interfered with the spectrum, it was recollected in CD_2Cl_2 (above).



Figure S14. ¹H NMR spectrum demonstrating formation of (4-BrPh)N=N(4-BrPh) in C₆D₆ after 24 h at 60 °C



Figure S15. ¹H NMR spectrum demonstrating formation of $(3,5-Me_2Ph)N=N(3,5-Me_2Ph)$ in C_6D_6 (24 hours, 60 °C).



Figure S16. ¹⁹F NMR spectrum demonstrating formation of $(3-CF_3C_6H_4)N=N(3-CF_3C_6H_4)$ in C_6D_6 (24 h, 60 °C).



Figure S17. ¹H NMR (CDCl₃) spectrum of isolated (4-CH₃Ph)N=N(4-CH₃Ph).



Figure S18. ¹³ C NMR (CDCl₃) spectrum of isolated (4-CH₃Ph)N=N(4-CH₃Ph).



Figure S19.¹H NMR (CDCl₃) spectrum of isolated (4-FPh)N=N(4-FPh).



Figure S20. ¹³C NMR (CDCl₃) spectrum of isolated (4-FPh)N=N(4-FPh).



Figure S21. ¹H NMR (CDCl₃) spectrum of isolated $(4-^{i} PrPh)N=N(4-^{i} PrPh)$.



Figure S22. ¹³C NMR (CDCl₃) spectrum of $(4-^{i} PrPh)N=N(4-^{i} PrPh)$.



Figure S23. ¹ H NMR (CDCl₃) spectrum of isolated (3,5-Me₂Ph)N=N(3,5-Me₂Ph).





Figure S25. VT NMR (CD₂Cl₂) of $H_2[OO]^{Ph}$.

8. GC-MS Spectra



Figure S26. GC-MS spectrum demonstrating formation of (PhN=NPh) in C₆D₆ after 24 h at 60 $^{\circ}$ C



Figure S27. GC-MS spectrum demonstrating formation of $(4-CH_3Ph)N=N(4-CH_3Ph)$ in C₆D₆ after 24 h at 60 °C.



Figure S28. GC-MS spectrum demonstrating formation of (4-EtPh)N=N(4-EtPh) in C_6D_6 after 24 h at 60 $^{\circ}$ C.



Figure S29. GC-MS spectrum demonstrating formation of $(4 - {}^{i} PrPh)N=N(4 - {}^{i} PrPh)$ in C₆D₆ after 24 h at 60 °C.



Figure S30. GC-MS spectrum demonstrating formation of $(4-CF_3Ph)N=N(4-CF_3Ph)$ in C₆D₆ after 24 h at 60 ⁰C.



Figure S31. GC-MS spectrum demonstrating formation of $(4-CH_3COPh)N=N(4-CH_3COPh)$ in C_6D_6 after 24 h at 60 $^{\circ}C$.



Figure S32. ¹H NMR spectrum demonstrating formation of $(4-NO_2Ph)N=N(4-NO_2Ph)$ in C₆D₆ after 24 h at 60 ⁰C.



Figure S33. GC-MS spectrum demonstrating formation of $(4-CH_3COPh)N=N(4-CH_3COPh)$ in C₆D₆ after 24 h at 60 ^oC.



Figure S34. GC-MS spectrum demonstrating formation of (4-FPh)N=N(4-FPh) in C_6D_6 after 24 h at 60 0 C.



Figure S35. GC-MS spectrum demonstrating formation of (4-ClPh)N=N(4-ClPh) in C_6D_6 after 24 h at 60 $^{\circ}C$.



Figure S36. GC-MS spectrum demonstrating formation of (4-BrPh)N=N(4-BrPh) in C₆D₆ after 24 h at 60 $^{\circ}$ C.



Figure S37. GC-MS spectrum demonstrating formation of $(3,5-Me_2Ph)N=N(3,5-Me_2Ph)$ in C₆D₆ after 24 h at 60 ⁰C.



Figure S38. GC-MS spectrum demonstrating formation of $(3-CF_3Ph)N=N(3-CF_3Ph)$ in C₆D₆ after 24 h at 60 ⁰C.

9. HRMS



Figure S39. HRMS of $H_2[OO]^{Ph}$.



Figure 40. HRMS of isolated (4-MePh)N=N(4-MePh).



Figure 41. HRMS of isolated $(4-{}^{i}PrPh)N=N(4-{}^{i}PrPh)$.



Figure 42. HRMS of (3,5-MePh)N=N(3,5-MePh).



Figure 43. HRMS of (4-FPh)N=N(F-Ph).



Figure S44. UV-vis spectrum of $Fe[OO]^{Ph}(THF)_2$ (2).

11. IR Spectrum of 2



Figure S45. IR Spectrum of $Fe[OO]^{Ph}(THF)_2$ (2).

12. Computational Details

DFT calculations were performed using ORCA version 4.0.1.2.³ Geometry optimizations were performed at the BP86-D3/def2-SVP level of theory using default numerical settings (ensuring proper numerical convergence), Becke-Johnson damping, and the RI-J algorithm.^{4–10} Stationary points were verified as minima by analyzing the harmonic frequencies at the same level of theory. Standard approximations were used to derive the Gibbs free energies at 298.15 K, with the vibrational entropy calculated using the quasi-RRHO algorithm.¹¹ Subsequent single point energy refinements at the BP86-D3/def2-TZVP and B3LYP-D3/def2-TZVP levels of theory.^{9,12-} ¹⁵ The B3LYP single points employed the RIJCOSX algorithm. Triple-zeta free energies were estimated as $G_{TZ} = G_{DZ} - E_{DZ} + E_{TZ}$. Orbital and spin density isosurfaces were created by generating cube files with the ORCA utilities, then visualized using GaussView version 6.0.16.¹⁶

Figure S46. Relaxed surface scan about the dihedral angle aryl arms on either side of the bridging phenyl in $H_2[OO]^{Ph}$. Optimization performed at the BP86-D3/def2-SVP level of theory with BP86-D3/def2-TZVP and B3LYP-D3/def2-TZVP single point energy refinements. +90 degrees corresponds to the *anti* isomer, whereas the minimum near –60 degrees is similar to the *syn* isomer.



Table S3. Relative energies (in kcal/mol) corresponding to the relaxed surface scan in Figure S46.

Angle	BP86-D3/def2-SVP	BP86-D3/def2-TZVP	B3LYP-D3/def2-TZVP
90.00	0.00	0.00	0.00
80.53	0.20	0.14	-0.10
71.05	0.16	0.06	-0.02
61.58	0.15	0.33	0.61
52.11	0.65	0.96	1.42
42.63	1.42	1.72	2.38
33.16	2.71	2.97	3.89
23.68	4.57	4.88	6.22
14.21	6.70	7.06	8.81
4.74	7.84	9.45	11.92
-4.74	6.19	7.74	8.89
-14.21	3.73	5.30	6.02
-23.68	1.73	3.28	3.73
-33.16	0.27	1.77	1.97
-42.63	-0.57	0.87	0.87
-52.11	-0.78	0.58	0.43
-61.58	-0.48	0.77	0.42
-71.05	0.15	1.26	0.83
-80.53	1.02	2.02	1.60
-90.00	1.77	2.58	1.88

 $Fe[OO]^{Ph}(THF)_2$ was optimized as a singlet, triplet, and quintet as shown in **Figure S47**. The quintet was calculated to be lowest in Gibbs free energy followed by the singlet (+14.89 kcal/mol) and the triplet (+26.31 kcal/mol), consistent with the experimental magnetic moment. These energies are likely smaller than the true values due to the well-documented preference of pure functionals like BP86 to favor low-spin states.¹⁷ B3LYP-D3/def2-TZVP places these energies at 36.80 and 49.26 kcal/mol, respectively, though that function overstabilizes high-spin states. Both functionals predict the quintet to be lowest in energy. As **Table S3** demonstrates, only the quintet state has bond lengths that are consistent with the crystal structure, with significant deviations in the axial Fe–O_{THF} distance and evidence of Fe–phenyl interactions in both the singlet and triplet states.

Figure S47. Optimized structures of Fe[OO]^{Ph}(THF)₂ as a singlet (left), triplet (middle), and quintet (right).



Table S4. Important bond lengths (Å) in the optimized structures of $Fe[OO]^{Ph}(THF)_2$ compared to the crystallographically measured values.

Bond	<i>S</i> = 0	<i>S</i> = 1	<i>S</i> = 2	xtal
Fe-Oligand,left	1.859	1.860	1.846	1.837
Fe-O _{ligand,right}	1.859	1.862	1.858	1.853
Fe-O _{THF,ax}	2.385	2.392	2.282	2.213

Fe-O _{THF,eq}	2.180	2.188	2.186	2.173
Fe-C _{phenyl}	2.101	2.104	2.778	3.230
Fe-C _{phenyl}	2.094	2.098	2.852	3.206

The interalkoxide angle in the optimized structure of **2** is more linear at 178.7° than the crystallographically determined angle of 155.5°. Therefore, we ran a relaxed surface scan for **2** along the interalkoxide O–Fe–O angle (**Table S5**). Between the optimized value of 178.7° and 150.6°, which is slightly more acute than the experimentally observed angle, the energy is predicted to rise by only 2.6 kcal/mol at the BP86-D3/def2-SVP level of theory. Single point refinements with different functionals (BP86-D3 and B3LYP-D3) and the larger basis set def2-TZVP suggest the minimum at those levels of theory may be closer the experimental value, but in all cases the surface is *extremely shallow* between 150–180°. Given that our computational model does not account for the intermolecular forces present in the crystal structure, we are not overly concerned by this deviation because we cannot say whether it is due to the simplification of modeling the structure as an isolated molecule or the particular functional/basis set combination.

Angle	BP86-D3/def2-SVP	BP86-D3/def2-TZVP	B3LYP-D3/def2-TZVP
178.7	0.00	0.00	0.00
170.6	0.17	-0.24	-1.01
160.6	0.97	0.02	-1.21
150.6	2.57	1.19	-0.17
140.6	4.69	3.02	1.62
130.6	6.94	5.13	4.25
120.6	8.42	6.62	6.42
110.6	10.57	8.67	8.83

Table S5. Relative energies (in kcal/mol) for a relaxed surface scan of the interalkoxide angle (O–Fe–O) in the quintet state of **2**.

13. References

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