Nitrosyl and carbene iron complexes bearing κ^3-SNS thioamide pincer type ligand

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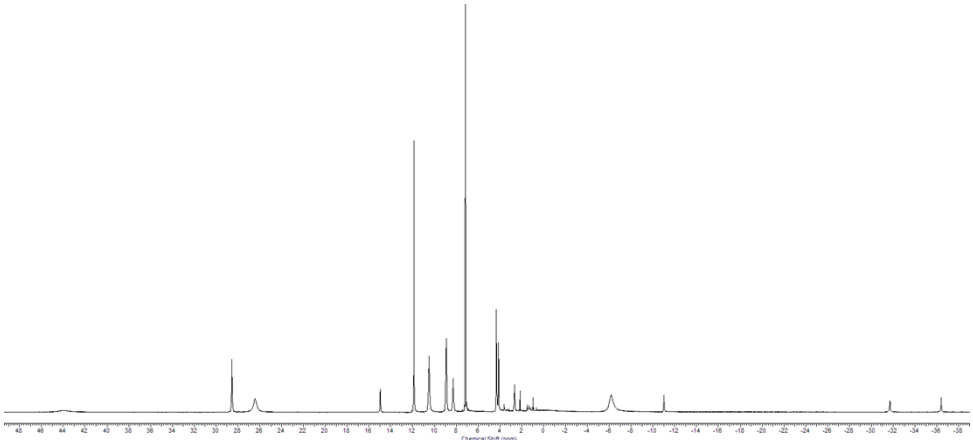

Fig. S1 ^{1}H-NMR spectrum of [Fe(NHC)(κ^3-$\mathbf{L^{DPM}}$)] in C_6D_6.

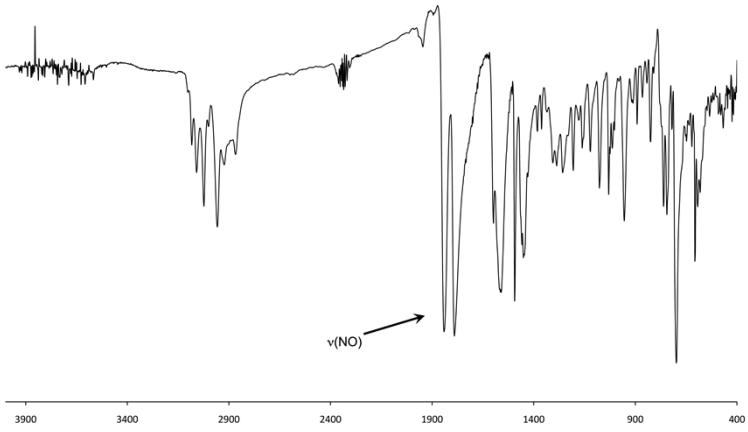

Fig. S2 IR spectrum of [Fe(NO)$_2$(κ^3-$\mathbf{L^{DPM}}$)].

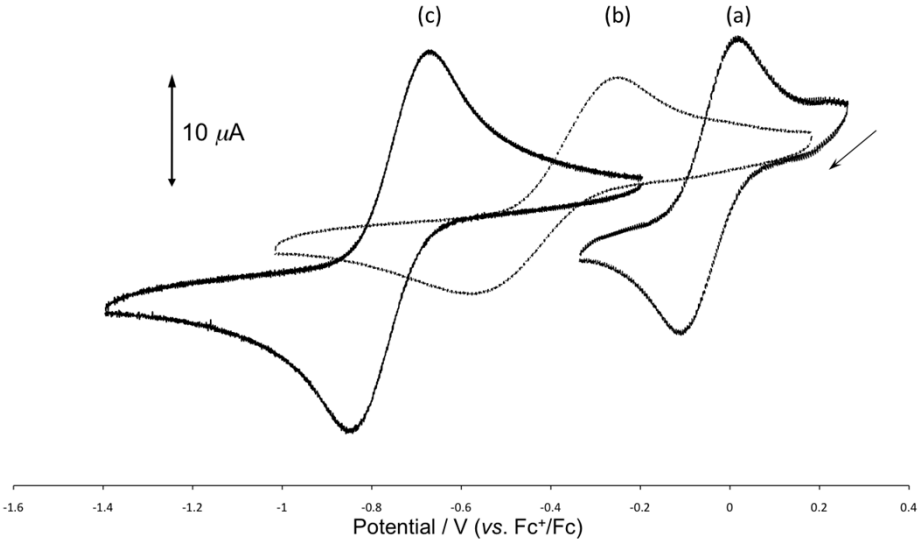

Fig. S3 Cyclic voltammogram of [Fe(THF)$_2$(κ^3-**L^{DPM}**)] (1 mM); (a), [Fe(NHC)(κ^3-**L^{DPM}**)] (1 mM); (b) and [Fe(NO)$_2$(κ^3-**L^{DPM}**)] (1 mM); (c) in THF under Ar at sweep rate of 100 mV s^{-1}.

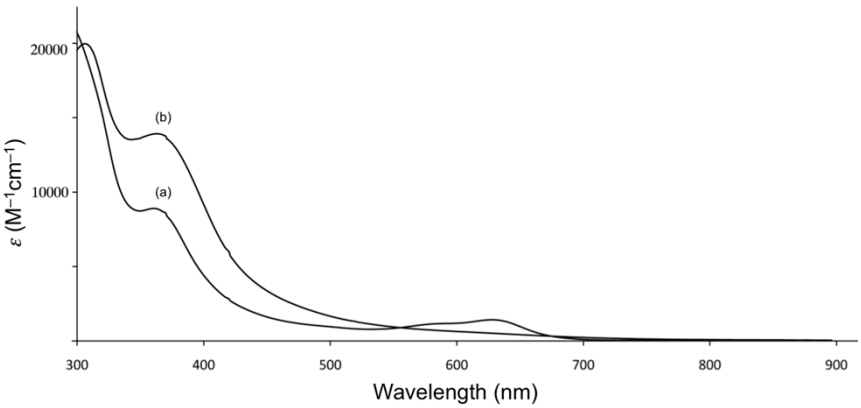

Fig. S4 UV/vis spectra of [Fe(NHC)(κ^3-**L^{DPM}**)] (a) and [Fe(NO)$_2$(κ^3-**L^{DPM}**)] (b) as 0.1 mM in THF.

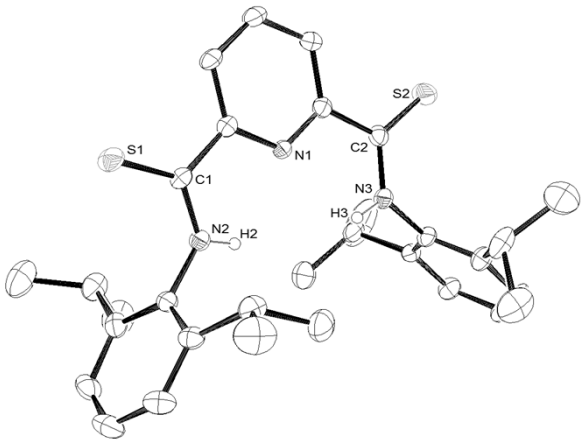

Fig. S5 ORTEP drawing of $\mathbf{H_2L^{DIP}}$ ligand with ellipsoids at 30% probability level. The hydrogen atoms and aromatic substituents on N–thioamide group are omitted for clarity except for H(2) and H(3) atoms. Selected bond lengths (Å): C(1)–N(2) 1.337(5), C(2)–N(3) 1.340(5), C(1)–S(1) 1.649(4), C(2)–S(2) 1.642(4).

Table S1. Crystallographic and structure refinement data for compounds $\mathbf{H_2L^{DIP}}$, [Fe($\boldsymbol{\kappa^3}$-$\mathbf{H_2L^{DIP}}$)$_2$](2·Br), [Fe(NHC)($\boldsymbol{\kappa^3}$-$\mathbf{L^{DPM}}$)], and [Fe(NO)$_2$($\boldsymbol{\kappa^3}$-$\mathbf{L^{DPM}}$)].

Compound	$\mathbf{H_2L^{DIP}}$	[Fe($\boldsymbol{\kappa^3}$-$\mathbf{H_2L^{DPM}}$)$_2$](2·Br)	[Fe(NHC)($\boldsymbol{\kappa^3}$-$\mathbf{L^{DPM}}$)]	[Fe(NO)$_2$($\boldsymbol{\kappa^3}$-$\mathbf{L^{DPM}}$)]
Chemical formula	$C_{31}H_{39}N_3S_2 \cdot CHCl_3$	$C_{62}H_{78}FeN_6S_4 \cdot 2Br \cdot 3(C_2H_6O)$	$C_{104}H_{101}FeN_5S_2 \cdot 2(C_6H_6) \cdot C_5H_{12}$	$C_{77}H_{65}FeN_5O_2S_2 \cdot CH_2Cl_2$
Formula weight	637.17	1389.44	1771.33	1297.29
Temp (°C)	–100	–100	–120	–100
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	P21/n (#14)	*P*-1 (#2)	*P*2/*n* (#13)	*P*-1 (#2)
a / Å	12.089(3)	12.572(2)	19.615(3)	8.53160(10)
b / Å	15.277(3)	15.106(3)	22.908(3)	17.3689
c / Å	18.575(4)	18.852(3)	20.265(3)	23.9404(2)
α / °		87.160(4)		73.322(4)
β / °	97.530(3)	84.309(4)	108.4184(12)	84.257(4)
γ / °		87.522(4)		79.592(4)
V / Å^3	3400.9(11)	3805(2)	8639(2)	3338.07(8)
Z	4	2	2	2
D_{calc}/g cm^{-3}	1.244	1.298	1.142	1.291
μ(Mo-Kα) / cm^{-1}	4.171	15.036	2.375	4.197
F(000)	1344	1460	1892	1356
Reflections collected	26859	28056	40001	26248
Independent reflections	7774	15634	11790	14602
R(int)	0.0721	0.0500	0.0359	0.0228
R1 ($I > 2\sigma(I)$)[a]	0.0846	0.0568	0.0552	0.0520
R1 (all)	0.1507	0.0768	0.0667	0.0704
w*R*2 (all)	0.1941	0.1459	0.1556	0.1453
GOF	1.074	1.035	1.079	1.052
CCDC number	1028474	1028475	1028476	1028477

[a] $R = \sum \| F_o | - | F_c \| / \sum | F_o |$, $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$