Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Kinetic studies on the reaction of NO with iron(II) complexes using low temperature stopped-flow techniques

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1 Calculation of activation parameters

Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from the slope and the y-intercept of the Eyring plot. The slope and the y-intercept including error values of the Eyring plot were determined by using the RGP-function of Microsoft Office 2016 and resolved using the Eyring-Polanyi equation according to $\Delta H^{\ddagger}$ (eq. 2.2) and $\Delta S^{\ddagger}$ (eq. 2.4). The exact calculations are listed below.

Eyring equation:

$$\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R}\cdot\frac{1}{T} + \ln\frac{k_{\mathrm{B}}}{h} + \frac{\Delta S^{\ddagger}}{R} \tag{1}$$

General equation:

$$y = m\cdot x + b \tag{2}$$

Calculation of activation enthalpy:

$$m = -\frac{\Delta H^{\ddagger}}{R} \tag{2.1}$$

$$\Delta H^{\ddagger} = -m\cdot R \tag{2.2}$$

Calculation of activation entropy:

$$b = \ln\frac{k_{\mathrm{B}}}{h} + \frac{\Delta S^{\ddagger}}{R} \tag{2.3}$$

$$\Delta S^{\ddagger} = R\cdot\left(b - \ln\frac{k_{\mathrm{B}}}{h}\right) \tag{2.4}$$

where:

k = reaction rate constant

T = absolute temperature

$\Delta H^{\ddagger}$ = activation enthalpy

$\Delta S^{\ddagger}$ = activation entropy

k_{B} = 1.38065 · 10^{-23} J / K = Boltzmann constant

h = 6.62607 · 10^{-34} J · s = Planck constant

R = 8.31446 J / K · mol = gas constant

m = slope

b = y-intercept

Table S1: Values and errors for slope (m, Δm) and activation enthalpy ($\Delta H^{\ddagger}$, $\Delta(\Delta H^{\ddagger})$) of the (2.1) MNIC formation, (2.2) DNIC formation, (2.3) the iron bztpen system and (2.4) the iron H-HPTB system.

Nr.	***m***	**Δ *m***	$\boldsymbol{\Delta H^{\ddagger}}$ **/ kJ / mol**	$\boldsymbol{\Delta(\Delta H^{\ddagger})}$ **/ kJ / mol**
2.1	-6667.5	±48.8	55.4	±0.4
2.2	-3869.3	±734	32	±6
2.3	-2136.6	±93.2	17.8	±0.8
2.4	-4529.1	±80.0	37.7	±0.7

Table S2: Values and errors for y-intercept (b, Δb) and activation entropy ($\Delta S^{\ddagger}$, $\Delta(\Delta S^{\ddagger})$) of the (2.1) MNIC formation, (2.2) DNIC formation, (2.3) the iron bztpen system and (2.4) the iron H-HPTB system.

Nr.	***b***	**Δ *b***	$\boldsymbol{\Delta S^{\ddagger}}$ **/ kJ / mol**	$\boldsymbol{\Delta(\Delta S^{\ddagger})}$ **/ J / mol**
2.1	25.3	±0.2	13	±2
2.2	0.48	±2.5	-193	±21
2.3	2.0	±0.4	-181	±3
2.4	15.8	±0.4	-66	±3

2 The reaction systems

2.1 MNIC

2.1.1 Rate constant k_{obs} versus nitrogen monoxide concentration

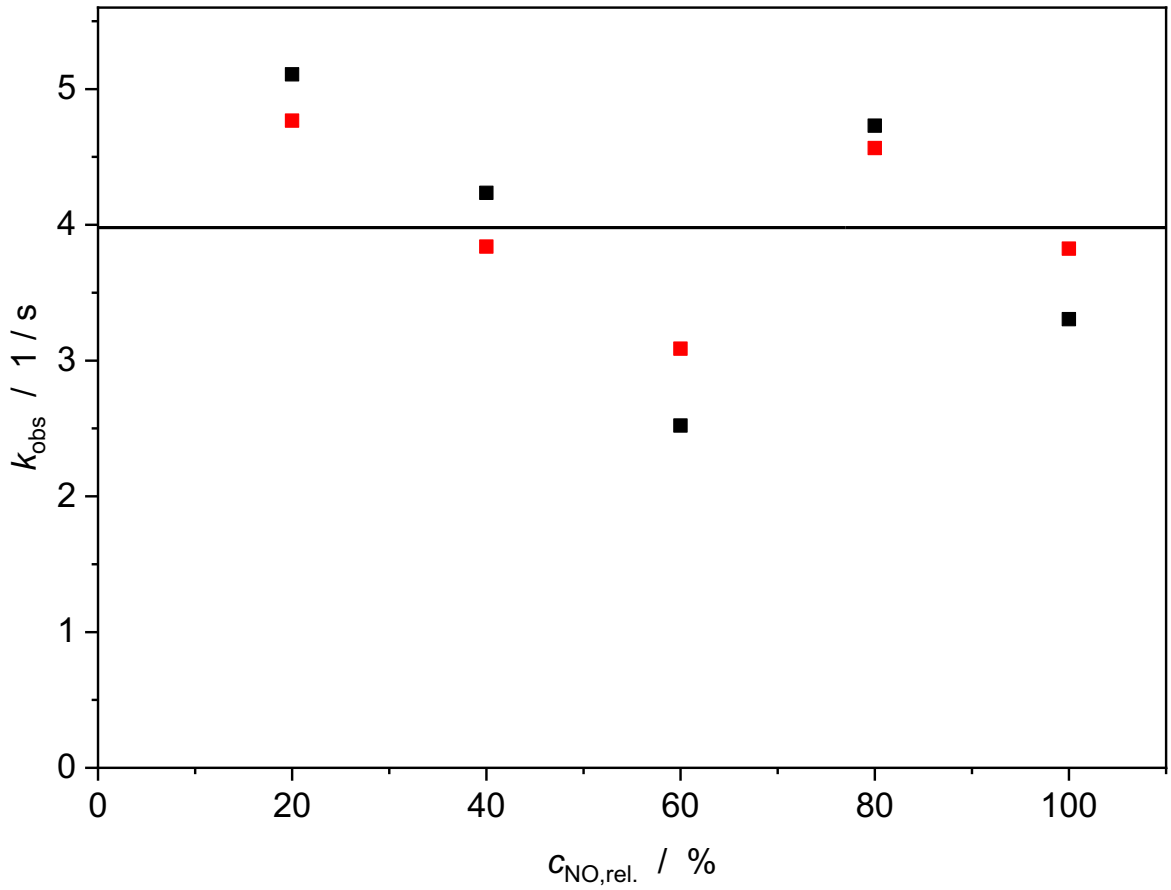

Figure S1: MNIC formation ($c_{complex} = 2 \cdot 10^{-3} \mathrm{mol\ L^{-1}}$): Plot of k_{obs} (black) and k_{cal} (red, from Eyring equation calculated values at -46.0 °C) versus nitrogen monoxide concentration at -46.0 °C in methanol (values in Table S3) ($c_{NO,rel.} = 100\% = 7.25 \cdot 10^{-3} \mathrm{mol\ L^{-1}}$).

Table S3: MNIC formation ($c_{complex} = 2 \cdot 10^{-3} \mathrm{mol\ L^{-1}}$): Values for k_{obs} and k_{cal} (at -46.0 °C) versus nitrogen monoxide concentration. k_{obs} at 464 nm (Figure S1). k_{cal} were calculated with the linear fit of the Eyring plots to get better comparison of the different values for a single temperature.

Nr.	$c_{NO.rel}$ / %	c_{NO} / mmol L^{-1}	T / °C	k_{obs} / s^{-1}	T_{cal} / °C	k_{cal} / s^{-1}
1	100	0.00725	-46.6	3.30430	-46.0	3.82449
2	80	0.00580	-45.6	4.72956	-46.0	4.56449
3	60	0.00435	-47.2	2.52040	-46.0	3.08793
4	40	0.00290	-45.2	4.23546	-46.0	3.83895
5	20	0.00145	-45.7	5.10802	-46.0	4.76683

2.1.2 Eyring plot

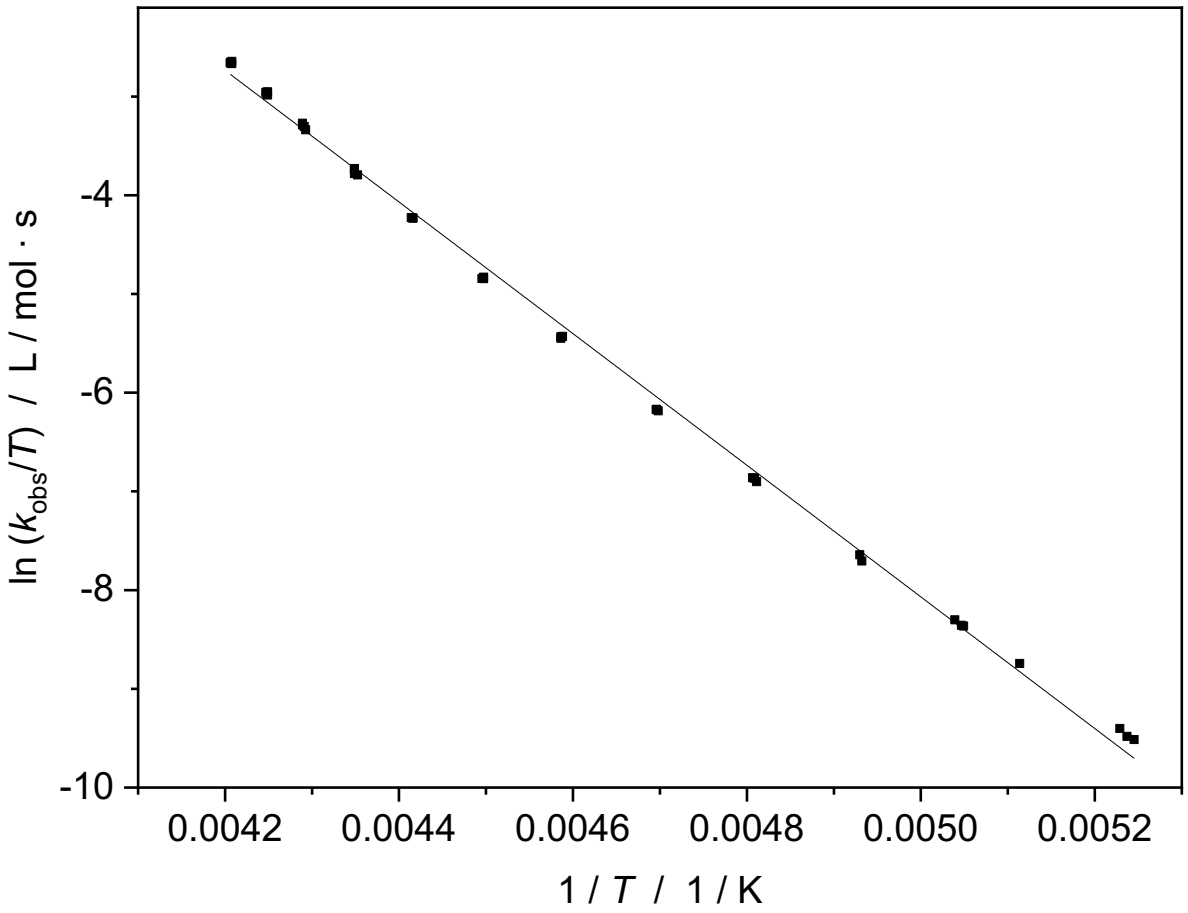

Figure S2: Eyring plot for formation of MNIC ($c_{\mathrm{complex}} = 2 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$) in methanol (Values in Table S4) ($c_{\mathrm{NO,rel.}} = 100\% = 7.25 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$).

Table S4: MNIC formation ($c_{\mathrm{complex}} = 2 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$): Determined rate constants k_{obs} (at 464 nm) and calculated values ln (k_{obs}/T) for Eyring plot ($c_{\mathrm{NO,rel.}} = 100\%$) at different temperatures (Figure S2).

Nr.	***T* / °C**	***T* / K**	T^{-1} / K^{-1}	k_{obs} / s^{-1}	ln (k_{obs}/T)
1	-82.5	190.65	0.005245	0.01406	-9.5149
2	-82.2	190.95	0.005237	0.01454	-9.4829
3	-81.9	191.25	0.005229	0.01578	-9.4026
4	-77.6	195.55	0.005114	0.03120	-8.7432
5	-75.1	198.05	0.005049	0.04617	-8.3639
6	-75.0	198.15	0.005047	0.04653	-8.3567
7	-74.7	198.45	0.005039	0.04922	-8.3020
8	-70.4	202.75	0.004932	0.09125	-7.7061
9	-70.3	202.85	0.004930	0.09724	-7.6430
10	-65.3	207.85	0.004811	0.20888	-6.9028
11	-65.2	207.95	0.004809	0.21658	-6.8671
12	-65.1	208.05	0.004807	0.21788	-6.8616
13	-60.3	212.85	0.004698	0.43884	-6.1842

Nr.	*T* / °C	*T* / K	T^{-1} / K^{-1}	k_{obs} / s^{-1}	ln (k_{obs}/T)
14	-60.2	212.95	0.004696	0.44393	-6.1731
15	-60.2	212.95	0.004696	0.44581	-6.1689
16	-55.1	218.05	0.004586	0.93697	-5.4498
17	-55.1	218.05	0.004586	0.95254	-5.4333
18	-55.2	217.95	0.004588	0.95465	-5.4307
19	-50.8	222.35	0.004497	1.74925	-4.8451
20	-50.8	222.35	0.004497	1.77479	-4.8306
21	-50.7	222.45	0.004495	1.75157	-4.8442
22	-46.7	226.45	0.004416	3.29022	-4.2316
23	-46.7	226.45	0.004416	3.28441	-4.2333
24	-46.6	226.55	0.004414	3.30430	-4.2277
25	-43.4	229.75	0.004353	5.16261	-3.7955
26	-43.2	229.95	0.004349	5.23905	-3.7817
27	-43.2	229.95	0.004349	5.51398	-3.7306
28	-43.2	229.95	0.004349	5.47037	-3.7385
29	-40.2	232.95	0.004293	8.27561	-3.3375
30	-40.1	233.05	0.004291	8.57222	-3.3027
31	-40.0	233.15	0.004289	8.70927	-3.2873
32	-40.0	233.15	0.004289	8.84656	-3.2717
33	-37.8	235.35	0.004249	11.89716	-2.9848
34	-37.8	235.35	0.004249	12.27515	-2.9535
35	-37.7	235.45	0.004247	12.11197	-2.9673
36	-37.7	235.45	0.004247	12.20397	-2.9597
37	-37.7	235.45	0.004247	12.22996	-2.9576
38	-35.5	237.65	0.004208	16.88807	-2.6442
39	-35.5	237.65	0.004208	16.48768	-2.6682
40	-35.4	237.75	0.004206	16.74455	-2.6531
41	-35.4	237.75	0.004206	16.61599	-2.6609

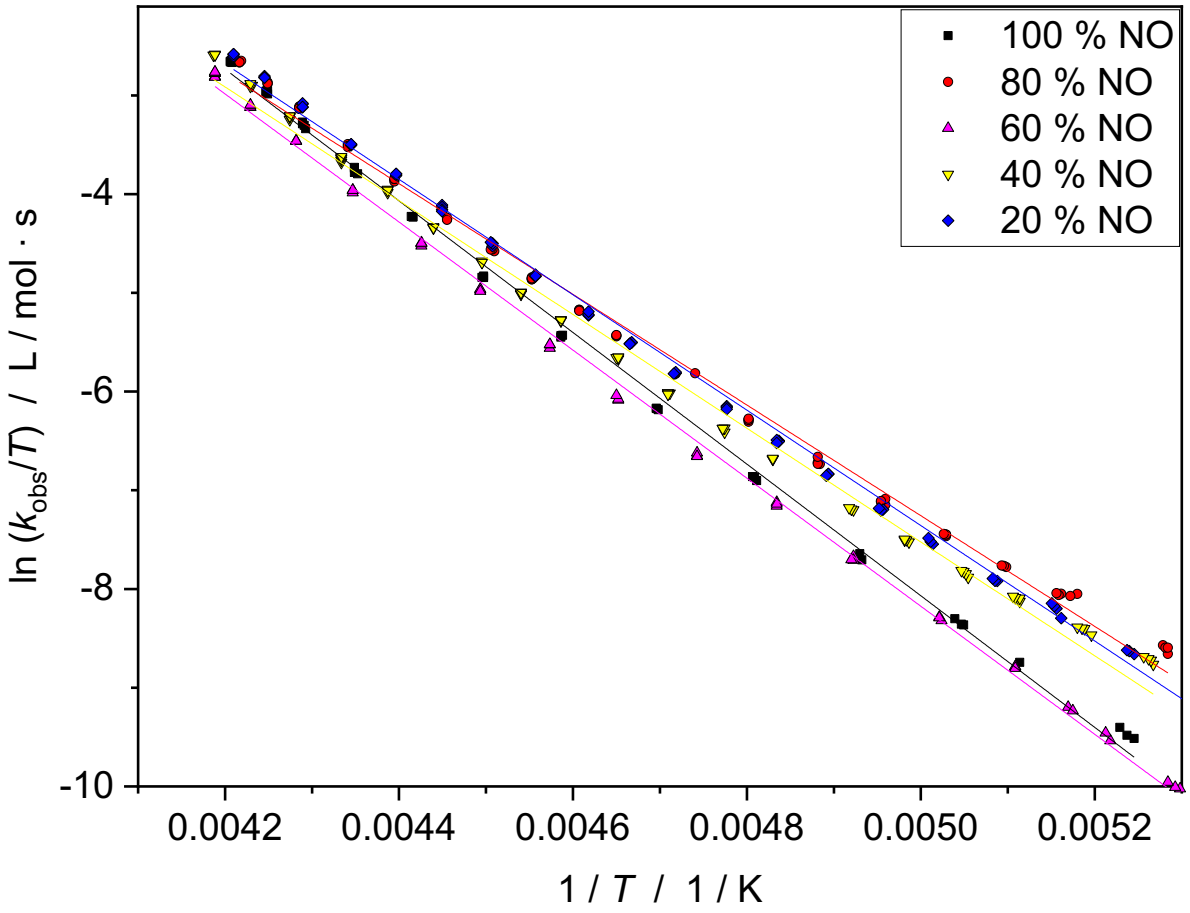

Figure S3: Eyring plot for formation of MNIC ($c_{\mathrm{complex}} = 2 \cdot 10^{-3}\mathrm{mol\,L^{-1}}$) in methanol at different nitrogen monoxide concentrations ($c_{\mathrm{NO,rel.}} =$ 100, 80, 60, 40 and 20%) (Values in Table S4, Table S5, Table S6, Table S7 and Table S8).

Table S5: MNIC formation ($c_{\mathrm{complex}} = 2 \cdot 10^{-3}\mathrm{mol\,L^{-1}}$): Determined rate constants k_{obs} (at 464 nm) and calculated values ln (k_{obs}/T) for Eyring plot ($c_{\mathrm{NO,rel.}} = 80\%$) at different temperatures (Figure S3).

Nr.	***T* / °C**	***T* / K**	***T*$^{-1}$ / K^{-1}**	***k*$_{obs}$ / s^{-1}**	**ln (*k*$_{obs}$/*T*)**
1	-83.9	189.25	0.005284	0.03290	-8.657
2	-83.7	189.45	0.005278	0.03591	-8.571
3	-83.8	189.35	0.005281	0.03503	-8.595
4	-83.9	189.25	0.005284	0.03501	-8.595
5	-80.1	193.05	0.005180	0.06162	-8.050
6	-79.8	193.35	0.005172	0.06037	-8.072
7	-79.4	193.75	0.005161	0.06192	-8.048
8	-79.3	193.85	0.005159	0.06110	-8.062
9	-79.2	193.95	0.005156	0.06232	-8.043
10	-77.0	196.15	0.005098	0.08221	-7.777
11	-76.9	196.25	0.005096	0.08315	-7.766
12	-76.8	196.35	0.005093	0.08350	-7.763
13	-74.3	198.85	0.005029	0.11378	-7.466
14	-74.3	198.85	0.005029	0.11557	-7.450

15	-74.3	198.85	0.005029	0.11568	-7.449
16	-74.2	198.95	0.005026	0.11649	-7.443
17	-71.5	201.65	0.004959	0.15827	-7.150
18	-71.5	201.65	0.004959	0.16822	-7.089
19	-71.3	201.85	0.004954	0.16375	-7.117
20	-71.3	201.85	0.004954	0.16494	-7.110
21	-68.4	204.75	0.004884	0.24351	-6.734
22	-68.3	204.85	0.004882	0.24750	-6.719
23	-68.3	204.85	0.004882	0.24402	-6.733
24	-68.3	204.85	0.004882	0.26206	-6.661
25	-64.9	208.25	0.004802	0.38030	-6.306
26	-64.9	208.25	0.004802	0.38782	-6.286
27	-64.9	208.25	0.004802	0.38641	-6.290
28	-64.9	208.25	0.004802	0.39163	-6.276
29	-61.2	211.95	0.004718	0.62832	-5.821
30	-62.2	210.95	0.004740	0.62954	-5.814
31	-62.2	210.95	0.004740	0.62974	-5.814
32	-58.1	215.05	0.004650	0.93244	-5.441
33	-58.1	215.05	0.004650	0.94049	-5.432
34	-58.1	215.05	0.004650	0.94328	-5.429
35	-56.1	217.05	0.004607	1.23162	-5.172
36	-56.1	217.05	0.004607	1.22827	-5.175
37	-56.1	217.05	0.004607	1.21937	-5.182
38	-53.5	219.65	0.004553	1.73099	-4.843
39	-53.5	219.65	0.004553	1.69376	-4.865
40	-53.5	219.65	0.004553	1.70984	-4.856
41	-53.5	219.65	0.004553	1.69715	-4.863
42	-53.5	219.65	0.004553	1.71339	-4.854
43	-51.4	221.75	0.004510	2.27495	-4.580
44	-51.3	221.85	0.004508	2.31996	-4.560
45	-51.3	221.85	0.004508	2.32190	-4.560
46	-51.2	221.95	0.004506	2.31663	-4.562
47	-48.7	224.45	0.004455	3.18928	-4.254
48	-48.7	224.45	0.004455	3.19618	-4.252
49	-48.7	224.45	0.004455	3.23518	-4.240
50	-48.7	224.45	0.004455	3.16769	-4.261
51	-45.6	227.55	0.004395	4.72956	-3.874
52	-45.6	227.55	0.004395	4.86005	-3.846
53	-45.6	227.55	0.004395	4.85377	-3.848
54	-45.6	227.55	0.004395	4.86305	-3.846
55	-42.8	230.35	0.004341	6.99381	-3.495
56	-42.8	230.35	0.004341	6.78765	-3.524
57	-42.8	230.35	0.004341	6.86821	-3.513
58	-39.8	233.35	0.004285	10.27770	-3.123
59	-39.8	233.35	0.004285	10.36741	-3.114

60	-39.8	233.35	0.004285	10.12575	-3.137
61	-39.8	233.35	0.004285	10.23808	-3.126
62	-37.8	235.35	0.004249	13.38919	-2.867
63	-37.8	235.35	0.004249	13.15643	-2.884
64	-37.8	235.35	0.004249	13.22064	-2.879
65	-36.0	237.15	0.004217	16.45601	-2.668
66	-36.1	237.05	0.004219	16.73378	-2.651
67	-36.0	237.15	0.004217	16.53915	-2.663

Table S6: MNIC formation ($c_{\mathrm{complex}} = 2 \cdot 10^{-3} \mathrm{mol\,L^{-1}}$): Determined rate constants k_{obs} (at 464 nm) and calculated values ln (k_{obs}/T) for Eyring plot ($c_{\mathrm{NO,rel.}} = 60\%$) at different temperatures (Figure S3).

Nr.	***T* / °C**	***T* / K**	T^{-1} / K^{-1}	k_{obs} / s^{-1}	ln (k_{obs}/T)
1	-84.4	188.75	0.005298	0.00837	-10.024
2	-84.2	188.95	0.005292	0.00852	-10.007
3	-83.9	189.25	0.005284	0.00897	-9.957
4	-81.5	191.65	0.005218	0.01384	-9.536
5	-81.3	191.85	0.005212	0.01499	-9.457
6	-79.7	193.45	0.005169	0.01960	-9.197
7	-79.9	193.25	0.005175	0.01889	-9.233
8	-77.4	195.75	0.005109	0.02991	-8.786
9	-77.4	195.75	0.005109	0.02995	-8.785
10	-77.4	195.75	0.005109	0.02943	-8.803
11	-74.1	199.05	0.005024	0.04855	-8.319
12	-74.0	199.15	0.005021	0.05027	-8.284
13	-74.0	199.15	0.005021	0.04999	-8.290
14	-70.0	203.15	0.004922	0.09487	-7.669
15	-70.0	203.15	0.004922	0.09134	-7.707
16	-69.9	203.25	0.004920	0.09185	-7.702
17	-66.3	206.85	0.004834	0.16717	-7.121
18	-66.3	206.85	0.004834	0.16078	-7.160
19	-66.3	206.85	0.004834	0.16427	-7.138
20	-62.3	210.85	0.004743	0.27311	-6.649
21	-62.3	210.85	0.004743	0.28111	-6.620
22	-62.3	210.85	0.004743	0.27121	-6.656
23	-58.2	214.95	0.004652	0.48917	-6.085
24	-58.2	214.95	0.004652	0.49411	-6.075
25	-58.1	215.05	0.004650	0.51343	-6.038
26	-54.5	218.65	0.004574	0.84199	-5.559
27	-54.5	218.65	0.004574	0.87067	-5.526
28	-54.5	218.65	0.004574	0.87524	-5.521
29	-50.6	222.55	0.004493	1.54800	-4.968
30	-50.6	222.55	0.004493	1.55753	-4.962
31	-50.6	222.55	0.004493	1.52577	-4.983

Nr.	*T* / °C	*T* / K	T^{-1} / K^{-1}	k_{obs} / s^{-1}	ln (k_{obs}/*T*)
32	-47.2	225.95	0.004426	2.45022	-4.524
33	-47.2	225.95	0.004426	2.52994	-4.492
34	-47.2	225.95	0.004426	2.50622	-4.502
35	-47.2	225.95	0.004426	2.52048	-4.496
36	-43.1	230.05	0.004347	4.27858	-3.985
37	-43.1	230.05	0.004347	4.39243	-3.958
38	-43.1	230.05	0.004347	4.38641	-3.960
39	-39.6	233.55	0.004282	7.31575	-3.463
40	-39.6	233.55	0.004282	7.34395	-3.460
41	-39.6	233.55	0.004282	7.32371	-3.462
42	-36.7	236.45	0.004229	10.43464	-3.121
43	-36.7	236.45	0.004229	10.44755	-3.119
44	-36.7	236.45	0.004229	10.60526	-3.104
45	-36.7	236.45	0.004229	10.69177	-3.096
46	-34.4	238.75	0.004188	14.36826	-2.810
47	-34.4	238.75	0.004188	14.40938	-2.808
48	-34.4	238.75	0.004188	14.32789	-2.813
49	-34.4	238.75	0.004188	14.87922	-2.775
50	-34.4	238.75	0.004188	15.04419	-2.764
51	-34.4	238.75	0.004188	15.07435	-2.762

Table S7: MNIC formation ($c_{\mathrm{complex}} = 2 \cdot 10^{-3} \mathrm{mol\,L^{-1}}$): Determined rate constants k_{obs} (at 464 nm) and calculated values ln (k_{obs}/*T*) for Eyring plot ($c_{\mathrm{NO,rel.}} = 40\%$) at different temperatures (Figure S3).

Nr.	*T* / °C	*T* / K	T^{-1} / K^{-1}	k_{obs} / s^{-1}	ln (k_{obs}/*T*)
1	-83.3	189.85	0.005267	0.02967	-8.764
2	-83.2	189.95	0.005265	0.03092	-8.723
3	-83.1	190.05	0.005262	0.03144	-8.707
4	-82.9	190.25	0.005256	0.03213	-8.686
5	-80.7	192.45	0.005196	0.04049	-8.467
6	-80.4	192.75	0.005188	0.04320	-8.403
7	-80.3	192.85	0.005185	0.04347	-8.398
8	-80.1	193.05	0.005180	0.04398	-8.387
9	-77.6	195.55	0.005114	0.05785	-8.126
10	-77.6	195.55	0.005114	0.05968	-8.095
11	-77.4	195.75	0.005109	0.06013	-8.088
12	-77.3	195.85	0.005106	0.06095	-8.075
13	-75.3	197.85	0.005054	0.07470	-7.882
14	-75.2	197.95	0.005052	0.07735	-7.847
15	-75.1	198.05	0.005049	0.07920	-7.824
16	-75.0	198.15	0.005047	0.08012	-7.813
17	-72.6	200.55	0.004986	0.10824	-7.524
18	-72.5	200.65	0.004984	0.11081	-7.502

Nr.	*T* / °C	*T* / K	T^{-1} / K^{-1}	k_{obs} / s^{-1}	ln (k_{obs}/*T*)
19	-72.4	200.75	0.004981	0.11034	-7.506
20	-72.4	200.75	0.004981	0.11148	-7.496
21	-70.0	203.15	0.004922	0.15178	-7.199
22	-69.9	203.25	0.004920	0.15310	-7.191
23	-69.8	203.35	0.004918	0.15520	-7.178
24	-66.1	207.05	0.004830	0.25855	-6.686
25	-66.1	207.05	0.004830	0.25876	-6.685
26	-66.1	207.05	0.004830	0.25813	-6.687
27	-66.1	207.05	0.004830	0.26079	-6.677
28	-63.7	209.45	0.004774	0.34373	-6.412
29	-63.6	209.55	0.004772	0.35764	-6.373
30	-63.7	209.45	0.004774	0.35801	-6.372
31	-63.6	209.55	0.004772	0.35699	-6.375
32	-60.9	212.25	0.004711	0.51733	-6.017
33	-60.8	212.35	0.004709	0.51927	-6.014
34	-60.8	212.35	0.004709	0.51663	-6.019
35	-60.8	212.35	0.004709	0.51143	-6.029
36	-58.2	214.95	0.004652	0.74055	-5.671
37	-58.1	215.05	0.004650	0.75186	-5.656
38	-58.2	214.95	0.004652	0.75553	-5.651
39	-58.2	214.95	0.004652	0.75316	-5.654
40	-55.1	218.05	0.004586	1.10333	-5.286
41	-55.1	218.05	0.004586	1.11791	-5.273
42	-55.1	218.05	0.004586	1.11526	-5.276
43	-55.1	218.05	0.004586	1.11362	-5.277
44	-52.9	220.25	0.004540	1.49334	-4.994
45	-52.9	220.25	0.004540	1.46305	-5.014
46	-52.9	220.25	0.004540	1.47725	-5.005
47	-52.9	220.25	0.004540	1.48668	-4.998
48	-50.7	222.45	0.004495	2.04277	-4.690
49	-50.7	222.45	0.004495	2.06370	-4.680
50	-50.7	222.45	0.004495	2.03828	-4.693
51	-47.9	225.25	0.004440	2.92181	-4.345
52	-47.9	225.25	0.004440	2.96012	-4.332
53	-47.9	225.25	0.004440	2.94043	-4.339
54	-45.2	227.95	0.004387	4.23546	-3.986
55	-45.2	227.95	0.004387	4.36700	-3.955
56	-45.2	227.95	0.004387	4.38019	-3.952
57	-45.2	227.95	0.004387	4.33517	-3.962
58	-42.4	230.75	0.004334	5.81738	-3.680
59	-42.4	230.75	0.004334	5.95028	-3.658
60	-42.4	230.75	0.004334	6.06008	-3.640
61	-42.4	230.75	0.004334	6.10549	-3.632
62	-42.4	230.75	0.004334	6.17163	-3.621

Nr.	*T* / °C	*T* / K	T^{-1} / K^{-1}	k_{obs} / s^{-1}	ln (k_{obs}/T)
63	-39.2	233.95	0.004274	9.09694	-3.247
64	-39.2	233.95	0.004274	9.35769	-3.219
65	-39.2	233.95	0.004274	9.45766	-3.208
66	-39.2	233.95	0.004274	9.43577	-3.211
67	-36.8	236.35	0.004231	12.99963	-2.900
68	-36.7	236.45	0.004229	12.88311	-2.910
69	-36.7	236.45	0.004229	13.23819	-2.883
70	-34.4	238.75	0.004188	17.91810	-2.590
71	-34.3	238.85	0.004187	17.85333	-2.594
72	-34.4	238.75	0.004188	18.04191	-2.583
73	-34.4	238.75	0.004188	17.93287	-2.589

Table S8: MNIC formation ($c_{\mathrm{complex}} = 2 \cdot 10^{-3} \mathrm{mol\,L^{-1}}$): Determined rate constants k_{obs} (at 464 nm) and calculated values ln (k_{obs}/T) for Eyring plot ($c_{\mathrm{NO,rel.}} = 20\%$) at different temperatures (Figure S3).

Nr.	*T* / °C	*T* / K	T^{-1} / K^{-1}	k_{obs} / s^{-1}	ln (k_{obs}/T)
1	-87.0	186.15	0.005372	0.01841	-9.221
2	-86.3	186.85	0.005352	0.01908	-9.189
3	-86.1	187.05	0.005346	0.02009	-9.139
4	-85.9	187.25	0.005340	0.02053	-9.118
5	-82.5	190.65	0.005245	0.03304	-8.660
6	-82.3	190.85	0.005240	0.03414	-8.629
7	-82.2	190.95	0.005237	0.03448	-8.619
8	-79.4	193.75	0.005161	0.04835	-8.296
9	-79.2	193.95	0.005156	0.05331	-8.199
10	-79.1	194.05	0.005153	0.05467	-8.175
11	-79.0	194.15	0.005151	0.05629	-8.146
12	-76.6	196.55	0.005088	0.07149	-7.919
13	-76.5	196.65	0.005085	0.07168	-7.917
14	-76.4	196.75	0.005083	0.07338	-7.894
15	-73.7	199.45	0.005014	0.10549	-7.545
16	-73.6	199.55	0.005011	0.10803	-7.521
17	-73.5	199.65	0.005009	0.11210	-7.485
18	-71.4	201.75	0.004957	0.15137	-7.195
19	-71.3	201.85	0.004954	0.14958	-7.207
20	-71.2	201.95	0.004952	0.15311	-7.185
21	-68.8	204.35	0.004894	0.21909	-6.838
22	-68.8	204.35	0.004894	0.22009	-6.834
23	-68.7	204.45	0.004891	0.21604	-6.853
24	-66.4	206.75	0.004837	0.31106	-6.499
25	-66.4	206.75	0.004837	0.30896	-6.506
26	-66.3	206.85	0.004834	0.31405	-6.490
27	-66.3	206.85	0.004834	0.30473	-6.520

Nr.	*T* / °C	*T* / K	T^{-1} / K^{-1}	k_{obs} / s^{-1}	ln (k_{obs}/T)
28	-63.8	209.35	0.004777	0.44778	-6.147
29	-63.8	209.35	0.004777	0.44262	-6.159
30	-63.8	209.35	0.004777	0.43443	-6.178
31	-61.2	211.95	0.004718	0.63172	-5.816
32	-61.2	211.95	0.004718	0.63891	-5.804
33	-61.1	212.05	0.004716	0.62994	-5.819
34	-58.9	214.25	0.004667	0.87174	-5.504
35	-58.9	214.25	0.004667	0.87470	-5.501
36	-58.8	214.35	0.004665	0.86418	-5.514
37	-58.8	214.35	0.004665	0.86026	-5.518
38	-56.6	216.55	0.004618	1.16177	-5.228
39	-56.6	216.55	0.004618	1.17069	-5.220
40	-56.6	216.55	0.004618	1.20735	-5.189
41	-53.7	219.45	0.004557	1.74882	-4.832
42	-53.7	219.45	0.004557	1.74687	-4.833
43	-53.7	219.45	0.004557	1.77748	-4.816
44	-53.7	219.45	0.004557	1.75670	-4.828
45	-51.3	221.85	0.004508	2.39636	-4.528
46	-51.3	221.85	0.004508	2.46620	-4.499
47	-51.3	221.85	0.004508	2.46228	-4.501
48	-51.2	221.95	0.004506	2.49828	-4.487
49	-48.4	224.75	0.004449	3.68689	-4.110
50	-48.4	224.75	0.004449	3.60823	-4.132
51	-48.4	224.75	0.004449	3.51978	-4.157
52	-48.4	224.75	0.004449	3.46284	-4.173
53	-45.7	227.45	0.004397	5.10802	-3.796
54	-45.7	227.45	0.004397	5.02840	-3.812
55	-45.7	227.45	0.004397	5.11416	-3.795
56	-43.0	230.15	0.004345	6.91074	-3.506
57	-43.0	230.15	0.004345	6.96530	-3.498
58	-43.0	230.15	0.004345	6.99451	-3.494
59	-43.0	230.15	0.004345	6.98696	-3.495
60	-40.0	233.15	0.004289	10.28302	-3.121
61	-40.0	233.15	0.004289	10.62827	-3.088
62	-40.0	233.15	0.004289	10.70680	-3.081
63	-40.0	233.15	0.004289	10.33433	-3.116
64	-37.6	235.55	0.004245	14.25241	-2.805
65	-37.6	235.55	0.004245	14.07845	-2.817
66	-37.6	235.55	0.004245	14.05327	-2.819
67	-35.6	237.55	0.004210	17.92641	-2.584
68	-35.6	237.55	0.004210	17.43033	-2.612
69	-35.6	237.55	0.004210	17.60981	-2.602
70	-35.6	237.55	0.004210	17.95502	-2.583

2.2 DNIC

2.2.1 Eyring plot

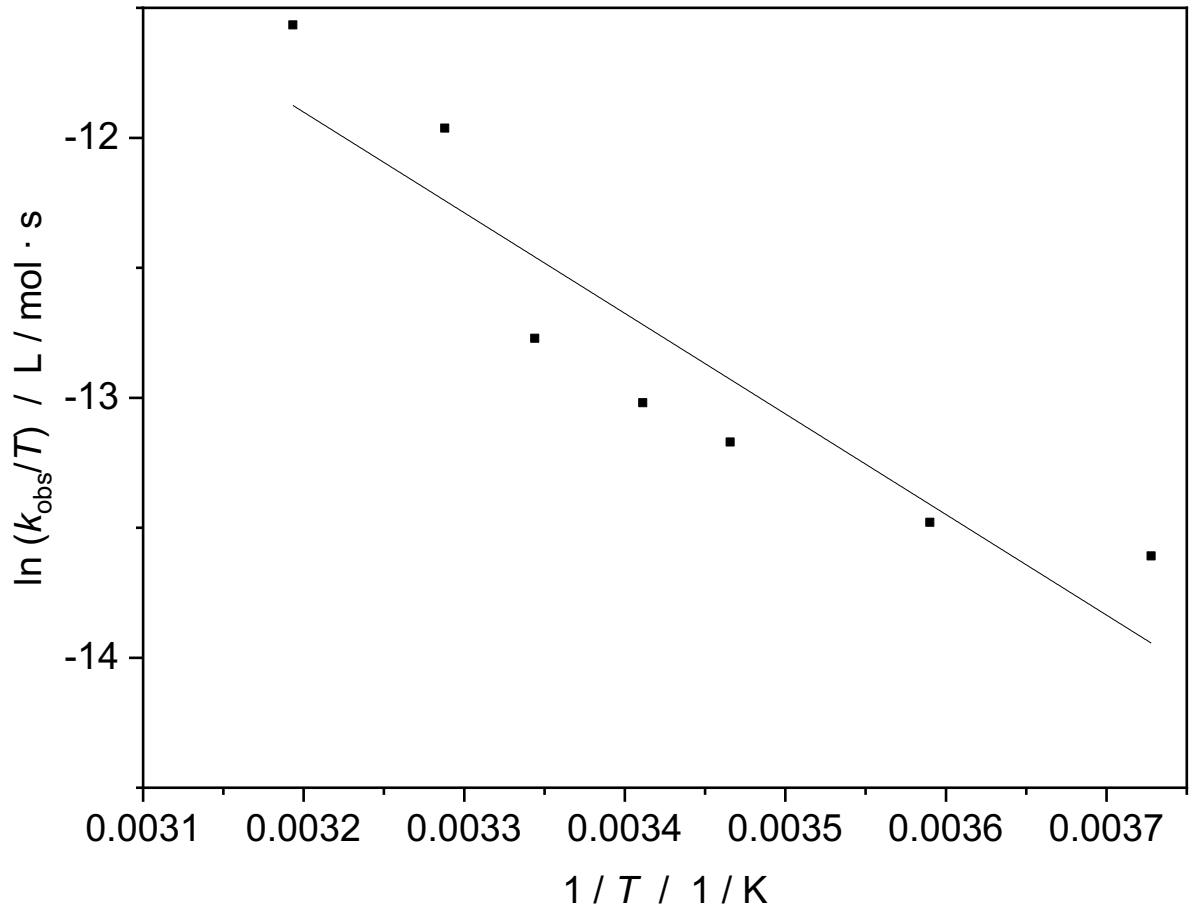

Figure S4: Eyring plot for formation of DNIC ($c_{\mathrm{complex}} = 1 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$) in methanol ($c_{\mathrm{NO,rel.}} = 100\% = 7.25 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$) (Values in Table S9).

Table S9: DNIC formation ($c_{\mathrm{complex}} = 1 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$): Determined rate constants k_{obs} (at 700 nm) and calculated values ln (k_{obs}/T) for Eyring plot at different temperatures (Figure S4).

Nr.	***T* / °C**	***T* / K**	***T*$^{-1}$ / K^{-1}**	***k*$_{obs}$ / s^{-1}**	**ln (*k*$_{obs}$/*T*)**
1	-4.9	268.25	0.003728	0.00033	-13.608
2	5.4	278.55	0.003590	0.00039	-13.479
3	15.4	288.55	0.003466	0.00055	-13.170
5	20.0	293.15	0.003411	0.00065	-13.019
4	25.9	299.05	0.003344	0.00085	-12.771
6	31.0	304.15	0.003288	0.00194	-11.963
7	40.0	313.15	0.003193	0.00297	-11.566

2.3 The iron bztpen system

2.3.1 Rate constant k_{obs} versus nitrogen monoxide concentration

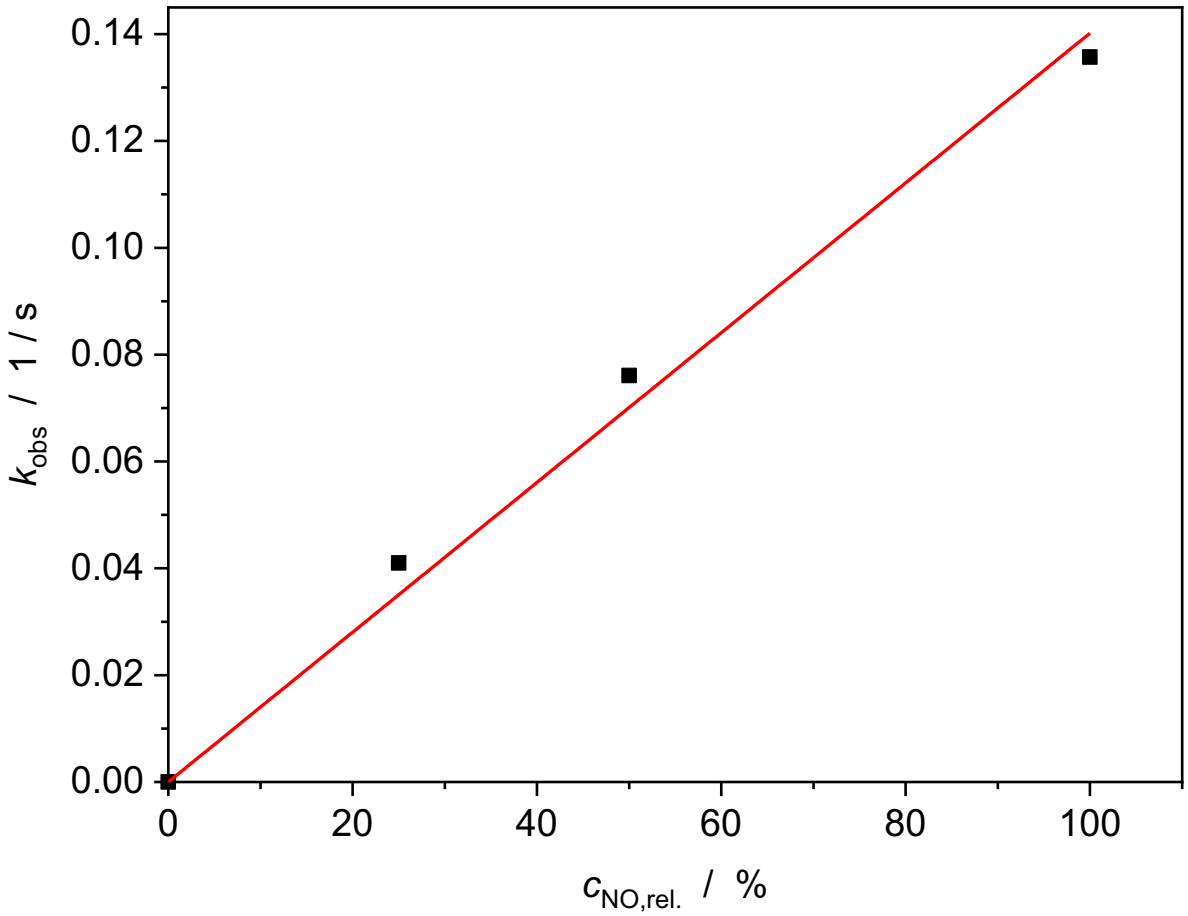

Figure S5: Formation of iron bztpen nitrosyl complex ($c_{complex} = 0.5 \cdot 10^{-3} \text{mol L}^{-1}$): Plot of k_{obs} versus nitrogen monoxide concentration at -47.8 °C in methanol (Values in Table S10) ($c_{NO,rel.} = 100\% = 7.25 \cdot 10^{-3} \text{mol L}^{-1}$).

Table S10: Formation of iron bztpen nitrosyl complex ($c_{complex} = 0.5 \cdot 10^{-3} \text{mol L}^{-1}$): Values for k_{obs} versus nitrogen monoxide concentration. k_{obs} at 550 nm (Figure S5).

Nr.	$c_{NO, rel.}$ **/ %**	***T* / °C**	***T* / K**	k_{obs} **/ s^{-1}**
1	100	-47.8	225.35	0.1357
2	50	-47.8	225.35	0.0761
3	25	-47.8	225.35	0.0410
4	0	-	-	0

2.3.2 Eyring plot

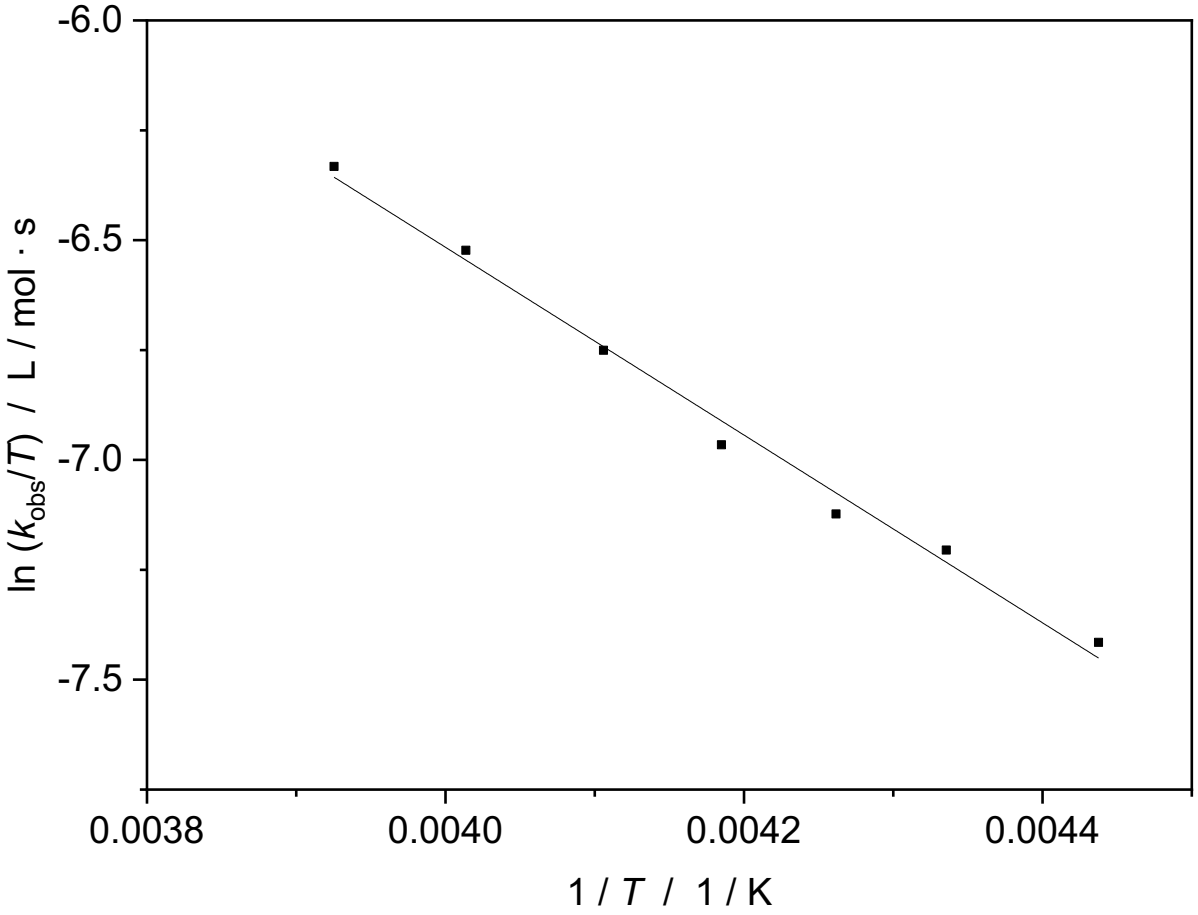

Figure S6: Eyring plot for formation of the iron bztpen nitrosyl complex ($c_{\mathrm{complex}} = 0.5 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$) in methanol ($c_{\mathrm{NO,rel.}} = 100\% = 7.25 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$) (Values in Table S11).

Table S11: Formation of iron bztpen nitrosyl complex ($c_{\mathrm{complex}} = 0.5 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$): Determined rate constants k_{obs} (at 550 nm) and calculated values ln (k_{obs}/T) for Eyring plot at different temperatures (Figure S6).

Nr.	***T* / °C**	***T* / K**	***T*$^{-1}$ / K^{-1}**	***k*$_{obs}$ / s^{-1}**	**ln (*k*$_{obs}$/*T*)**
1	-47.8	225.35	0.004438	0.1357	-7.415
2	-42.5	230.65	0.004336	0.1713	-7.205
3	-38.5	234.65	0.004262	0.1892	-7.123
4	-34.2	238.95	0.004185	0.2255	-6.966
5	-29.6	243.55	0.004106	0.2850	-6.751
6	-24.0	249.15	0.004014	0.3660	-6.523
7	-18.4	254.75	0.003925	0.4530	-6.332

2.3.3 Preparation and characterization of bztpen

Bztpen (*N*-Benzyl-*N*‘,*N*‘-tris-(2-pyridylmethyl)ethylenediamine) was prepared by procedure published previously by Duelund *et al.*[1]

^{1}H-NMR (400 MHz, $CDCl_3$-d_1, TMS): δ/ppm = 8.41 (m, 3H), 7.49 (m, 3H), 7.37 (s, 3H), 7.21 (m, 5H), 7.04 (m, 3H), 3.69 (s, 4H), 3.64 (s, 2H), 3.51 (s, 2H), 2.66 (m, 4H); ^{13}C-NMR (400 MHz, $CDCl_3$-d_1, TMS): δ/ppm = 159.2, 158.8, 148.0, 147.8, 138.2, 135.3, 127.7, 127.2, 125.9, 121.7, 121.6, 120.8, 120.8, 59.8, 59.6, 58.0, 51.3, 51.0.

Anal. calc. for $C_{27}H_{29}N_5$: C, 76.56; H, 6.90; N, 16.53. Found: C, 76.55; H 7.15; N, 16.41%.

Mass analysis (m/z): Calculated $[M+H]^+$ = 424.2496. Found: $[M+H]^+$ = 424.2498.

2.4 The iron H-HPTB system

2.4.1 Eyring plot

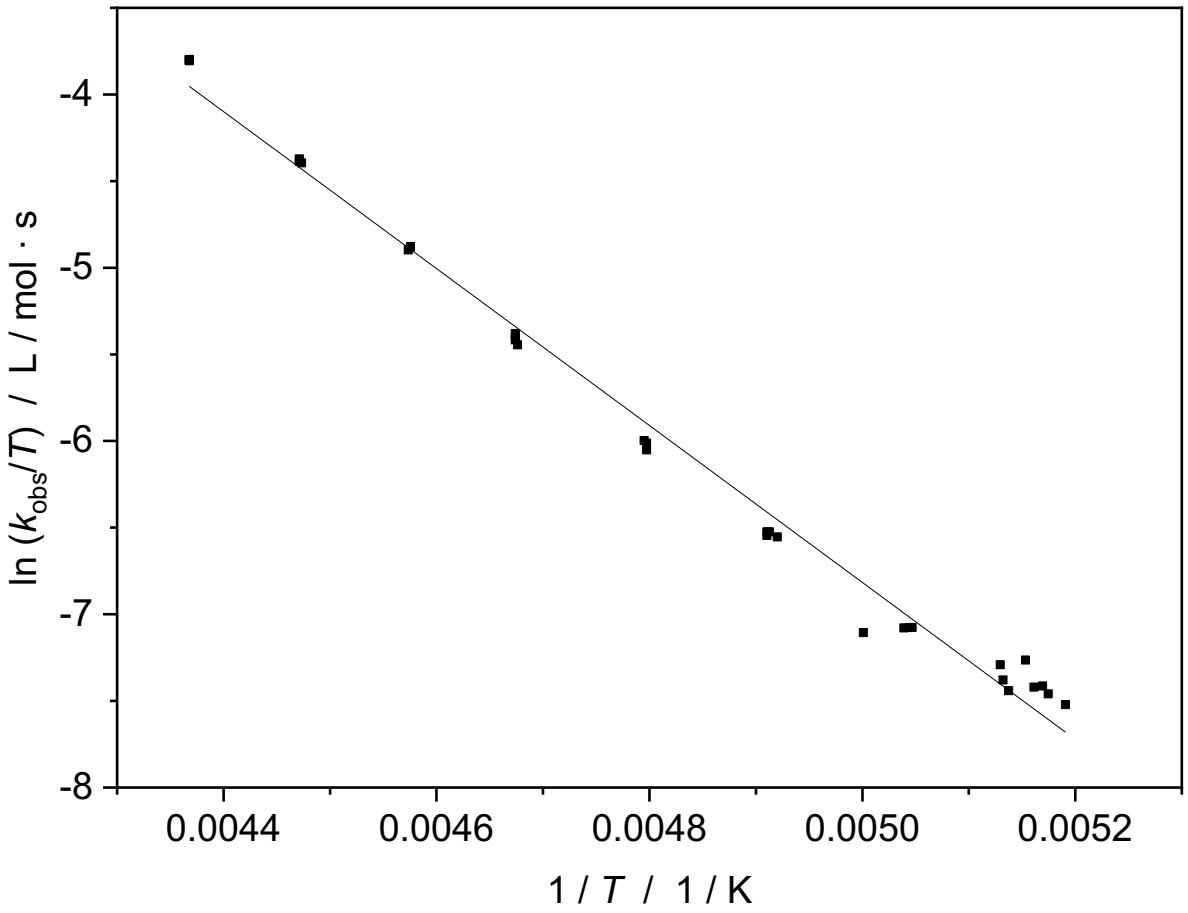

Figure S7: Eyring plot for formation of the dinuclear iron H-HPTB nitrosyl complex ($c_{\mathrm{complex}} = 1 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$) in methanol ($c_{\mathrm{NO,rel.}} = 100\% = 7.25 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$) (Values in Table S12).

Table S12: Formation of the dinuclear iron H-HPTB nitrosyl complex ($c_{\mathrm{complex}} = 1 \cdot 10^{-3}\mathrm{mol\ L^{-1}}$): Determined rate constants k_{obs} (at 452 nm) and calculated values ln (k_{obs}/T) for Eyring plot at different temperatures (Figure S7).

Nr.	***T* / °C**	***T* / K**	**T^{-1} / K^{-1}**	**k_{obs} / s^{-1}**	**ln (k_{obs}/T)**
1	-73.2	199.95	0.005001	0.16403	-7.106
2	-79.4	193.75	0.005161	0.11605	-7.420
3	-79.7	193.45	0.005169	0.11657	-7.414
4	-79.9	193.25	0.005175	0.11128	-7.460
6	-80.5	192.65	0.005191	0.10431	-7.521
7	-79.1	194.05	0.005153	0.13578	-7.265
8	-78.2	194.95	0.005130	0.13281	-7.292
9	-78.3	194.85	0.005132	0.12155	-7.380

Nr.	*T* / °C	*T* / K	T^{-1} / K^{-1}	k_{obs} / s^{-1}	ln (k_{obs}/*T*)
10	-78.5	194.65	0.005137	0.11412	-7.442
11	-75.0	198.15	0.005047	0.16738	-7.077
12	-74.9	198.25	0.005044	0.16733	-7.077
13	-74.7	198.45	0.005039	0.16725	-7.079
14	-69.9	203.25	0.004920	0.28967	-6.553
15	-69.5	203.65	0.004910	0.29270	-6.545
16	-69.5	203.65	0.004910	0.29872	-6.525
17	-69.6	203.55	0.004913	0.29846	-6.525
18	-64.7	208.45	0.004797	0.49067	-6.052
19	-64.7	208.45	0.004797	0.51044	-6.012
20	-64.6	208.55	0.004795	0.51821	-5.998
21	-59.3	213.85	0.004676	0.92336	-5.445
22	-59.2	213.95	0.004674	0.96457	-5.402
23	-59.2	213.95	0.004674	0.95009	-5.417
24	-59.2	213.95	0.004674	0.98541	-5.380
25	-54.6	218.55	0.004576	1.66322	-4.878
26	-54.6	218.55	0.004576	1.65928	-4.881
27	-54.5	218.65	0.004574	1.63192	-4.898
28	-49.5	223.65	0.004471	2.78377	-4.386
29	-49.5	223.65	0.004471	2.82416	-4.372
30	-49.6	223.55	0.004473	2.75795	-4.395
31	-44.2	228.95	0.004368	5.12898	-3.799
32	-44.2	228.95	0.004368	5.12205	-3.800
33	-44.2	228.95	0.004368	5.09419	-3.805

2.4.2 Preparation and characterization of H-HPTB

H-HPTB (N,N,N',N'-Tetrakis(2-benzimidazolylmethyl)-2-hydroxy-1,3-diaminopropane) was synthesized by procedure published previously by McKee *et al*.[2]

^{1}H-NMR (400 MHz, methanol-d_4, TMS): δ/ppm = 7.52 (m, 8H), 7.25 (m, 8H), 4.11 (m, 8H), 4.00 (s, 1H), 3.37 (s, 5H), 2.77 (t, 2H), 2.61 (t, 2H); ^{13}C-NMR (400 MHz, methanol-d_4, TMS): δ/ppm = 152.2, 136.5, 123.0, 114.1, 67.0, 58.7, 52.2.

Anal. calc. for $C_{35}H_{34}N_{10}O \cdot 2\,HCl$: C, 61.49; H, 5.31; N, 20.49. Found: C, 62.86; H 5.59; N, 20.61%.

Mass analysis (m/z): Calculated $[M+H]^+$ = 611.2990. Found: $[M+H]^+$ = 611.2993.

References

1 L. Duelund, R. Hazell, C. J. McKenzie, L. P. Nielsen and H. Toftlund, *J. Chem. Soc. Dalt. Trans.*, 2001, 152–156.

2 V. McKee, M. Zvagulis, J. V. Dagdigian, M. G. Patch and C. A. Reed, *J. Am. Chem. Soc.*, 1984, **106**, 4765–4772.