Electronic Supplementary Information

Binding of molecular oxygen by an artificial heme analogue: Investigation on the formation of an Fe-tetracarbene superoxo complex

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Summary

1. General Information

Experimental remarks: Unless otherwise stated, all manipulations were carried out under an argon atmosphere using standard Schlenk and glovebox techniques. Dry, degassed acetonitrile was obtained from an Mbraun solvent purification system. All other nitriles and acetonitrile-d_3 were dried over phosphorous pentoxide, distilled, and stored over molecular sieves prior to use. Acetone and acetone-d_3 were distilled from anhydrous $CaCl_2$ under argon and stored under inert gas prior to use. All solvents were degassed by using at least three freeze/pump/thaw cycles. Iron complex **1** and deuterated hydroquinone (D2Q) were synthesized according to the literature.[7,23] All other reagents were purchased from commercial suppliers and were used without further purification. NMR spectra were recorded on a Bruker Avance DPX 400 (^{1}H NMR, 400.13 MHz; ^{13}C NMR, 100.53 MHz) and chemical shifts are reported relative to the residual signal of the deuterated solvent. UV/Vis –spectra were obtained from liquid samples using a JASCO V-500 spectrometer. Elemental analyses were obtained by the microanalytical laboratory at the Technische Universität München.

DFT calculations: All calculations were performed with Gaussian 09[S1] using the density functional/Hartree-Fock hybrid model Becke3LYP.[S2,S3] For geometry optimizations the split valence double-ζ (DZ) basis set 6-31G(d)[S4-S6] was used for all atoms except Fe, which was described with the SDD basis set as implemented in Gaussian 09, applying an ECP with a DZ description of the valence electrons.[S7] Solvation effects were taken into account by using the CPCM solvation model with acetone as solvent.[S8,S9] No symmetry or internal coordinate constraints were applied during optimizations. All reported ground states were verified as being true minima by the absence of negative eigenvalues in the vibrational frequency analysis. XYZ coordinates for the calculated structure can be found in the supporting information. Single point calculations on the optimized structure were performed to ensure energy convergence by using the triple-ζ (TZ) basis set 6-311++G(d,p) on all atoms.[S10-S14]

Single crystal X-ray diffraction: Single crystals of **4** suitable for X-ray diffraction were obtained by slow diffusion of oxygenated diethyl ether into an acetone solution of the respective compound. **4**: black purple, tetragonal crystal system, space group *P* 41 21 2(No. 92), a = 13.6871(3) Å, b = 13.6871(3) Å, c = 25.6258(6) Å, a = β = g = 90°, V = 4800.65(19) Å^3. Crystallographic data for structure **4** has been deposited with the Cambridge Crystallographic Data Centre (CCDC 1428063).

Catalytic Oxygen Activation: In a typical reaction setup, **1** (1.00 mg, $1.33\cdot10^{-3}$ mmol) was filled into a dry Schlenk tube under an argon atmosphere and H_2Q (14.6 mg, 0.13 mmol) was added as colorless needles. The reactants were dissolved in 1 mL of dried and degassed CD_3CN and stirred for some seconds. The clear yellow solution was frozen in liquid nitrogen and the reaction tube was evacuated up to ~$2\cdot10^{-2}$ mbar. Oxygen (2 bar, Purity: 5.0, Westfalengas) was added and the reaction mixture was stirred a 25 °C (water bath) for 2 hours. The pressure was released and a sample (0.5 mL) of the solution was withdrawn, transferred into an NMR-tube and immediately measured. The residual solution was frozen and evacuated. Oxygen (2 bar) was added and the solution was stirred again at 25 °C till the successive sampling step. The conversion was determined by integration of the relative signals for H_2Q [6.63 (s, 4H, C*H*); 6.37 (s, 2 H, O*H*) ppm] and for BQ [6.77 (s, 4*H*, CH)] ppm) in the ^{1}H NMR spectrum of the reaction mixture. No additional products could be detected by NMR or GC analysis.

2. Experimental Data

η^2-superoxo[calix[4]imidazoyl]iron(III) hexafluorophosphate (3): Trans-diacetonitrile[calix[4]imidazoyl]iron(II) hexafluorophosphate (0.1 g, 0.13 mmol) was dissolved in 3 mL acetone at -40 °C. Oxygen (4 mL) was added and the dark orange solution was stored in a freezer (-35 °C) overnight. The solution was filtered at -40 °C and the clear reddish filtrate was precipitated with 15 mL of cold (-40°C) diethyl ether. The reddish solid obtained was washed with cold diethyl ether (2 x 5 mL) and carefully dried at -21°C in an ice bath. (60 mg, 64 % Yield)

^{1}H NMR (400 MHz, acetone-d_6, 273 K): δ 7.85 (s, 8H, *CH*), 6.48 (d, 4H, $^2J_{HH}$ = 13.3Hz, CH_2), 6.31(d, $^2J_{HH}$ = 13.3 Hz, 4H, CH_2)

Bis-m^2-oxo[calix[4]imidazoyl]iron(III) hexafluorophosphate (4): Trans-diacetonitrile[calix[4]imidazoyl]iron(II) hexafluorophosphate (0.2 g, 0.27 mmol) was dissolved in 5 mL of acetone at -40 °C. Oxygen (1 bar) was added and the dark solution was stirred overnight while slowly warming to r.t.. The supernatant, clear brownish solution was filtered off and the dark precipitate was washed with a small amount of acetone and with diethyl ether (2 x 5 mL). After drying under vacuum a dark blue powder was obtained (120 mg, 67 % yield).

^{1}H NMR (400 MHz, CD_3CN, 296 K): δ 7.57 (s, 16H, *CH*), 6.08 (d, 8H, $^2J_{HH}$ = 13.1Hz, CH_2), 5.94 (d, $^2J_{HH}$ = 13.1 Hz, 8H, CH_2). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN, 296 K): δ 175. (bp, $C_{carbene}$), 122.72 (*CH*), 64.05(CH_2). Anal. Calcd for $C_{32}H_{32}F_{24}Fe_2N_{16}OP_4$: C 28.51; H 2.39; N 16.62. Found: C 28.31; H 2.38; N 16.35.

3. UV/Vis-Spectra

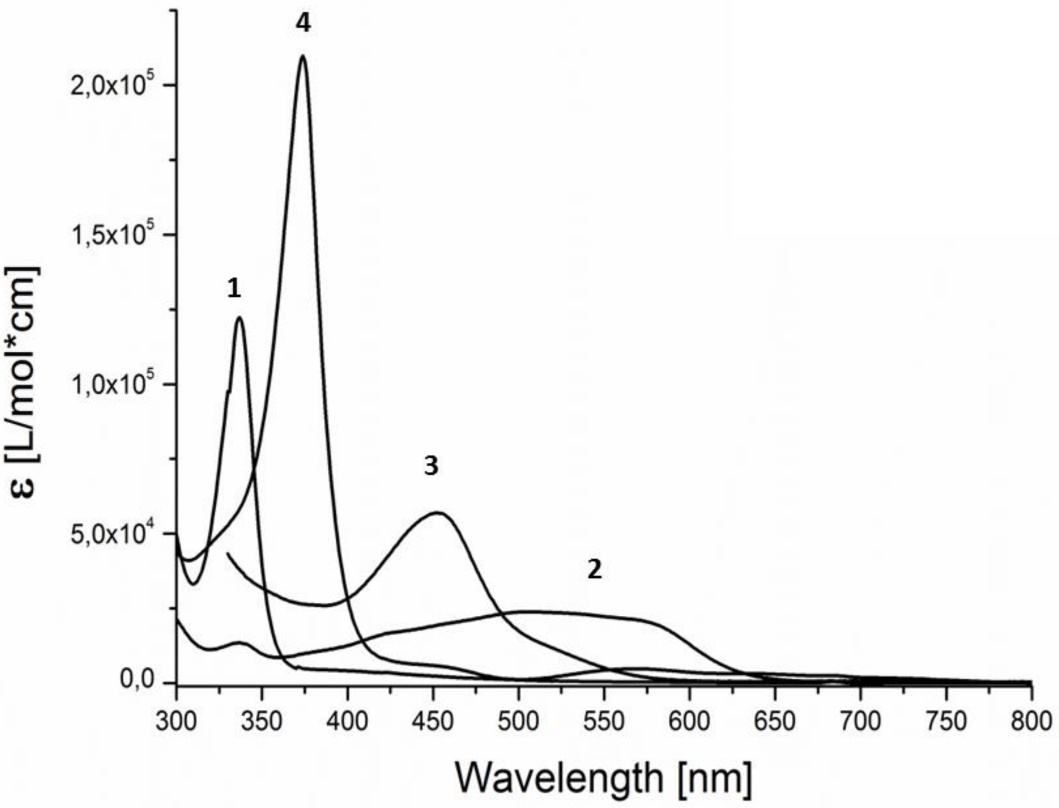

Fig. S1: Normalized UV/Vis-spectra of all Fe-NHC complexes reported in the manuscript. All spectra were recorded in dry and degassed acetonitrile at 25 °C with exception of **3** which was measured in dry and degassed acetone at -40°C.

4. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR Spectra

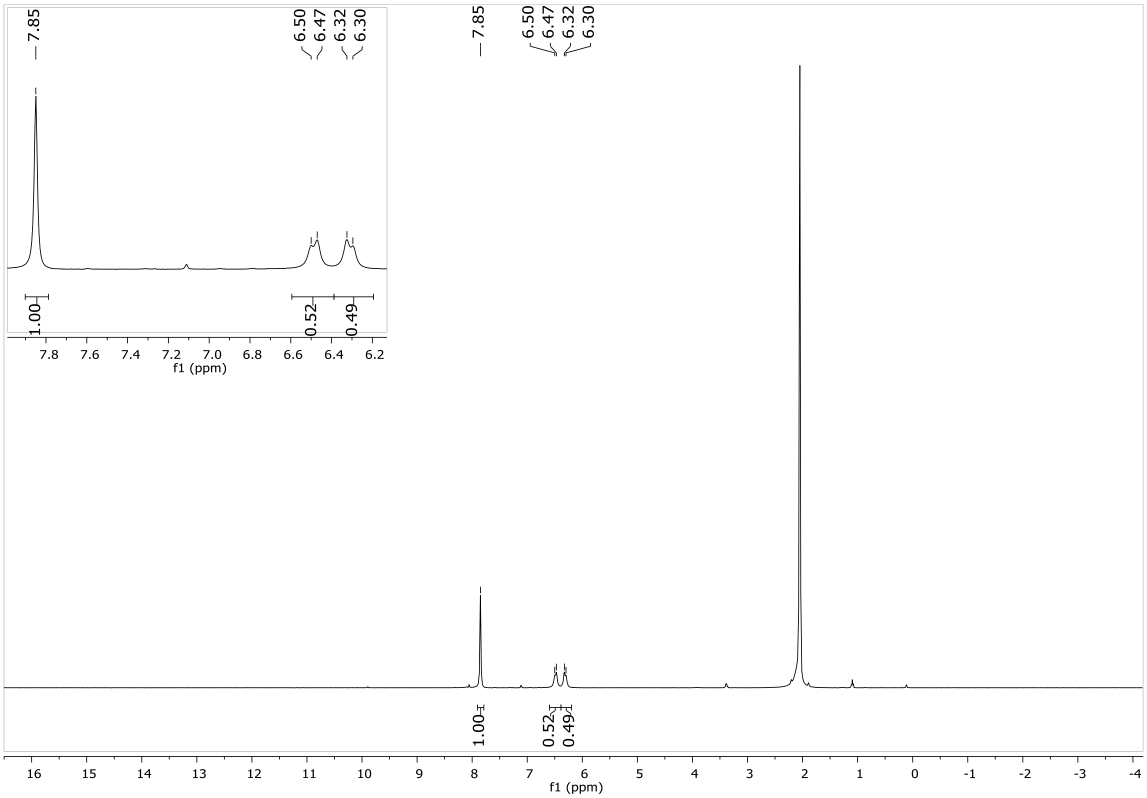

Figure S2. ^{1}H-NMR spectrum of **3** at -40 °C in acetone-d_6.

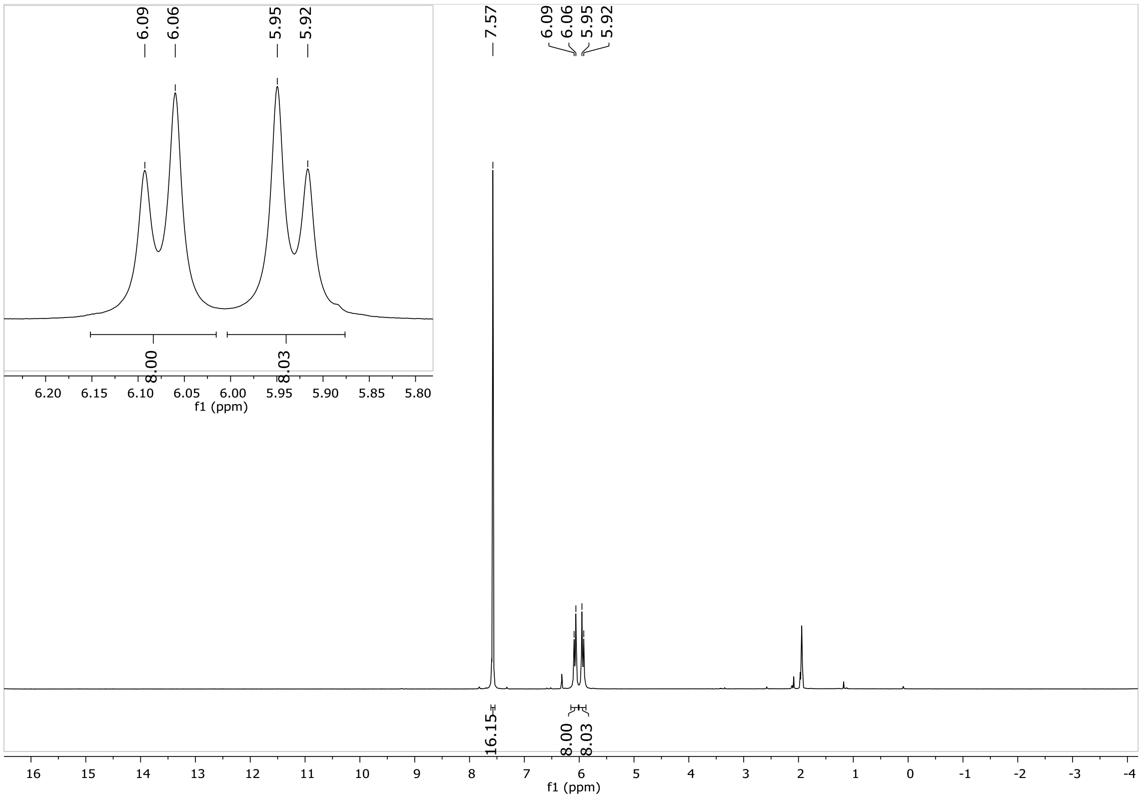

Figure S3. ^{1}H-NMR spectrum of **4** at 296 K in CD_3CN.

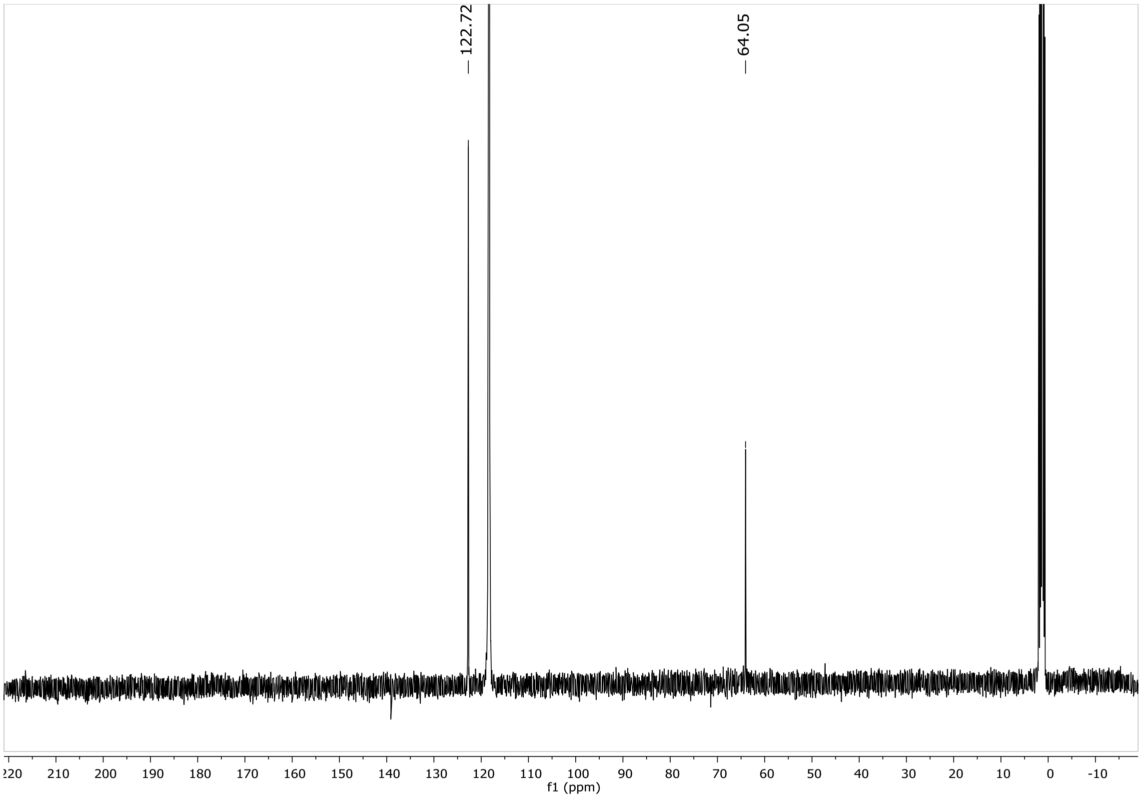

Figure S4. $^{13}C\{1H\}$-NMR spectrum of **4** in CD_3CN.

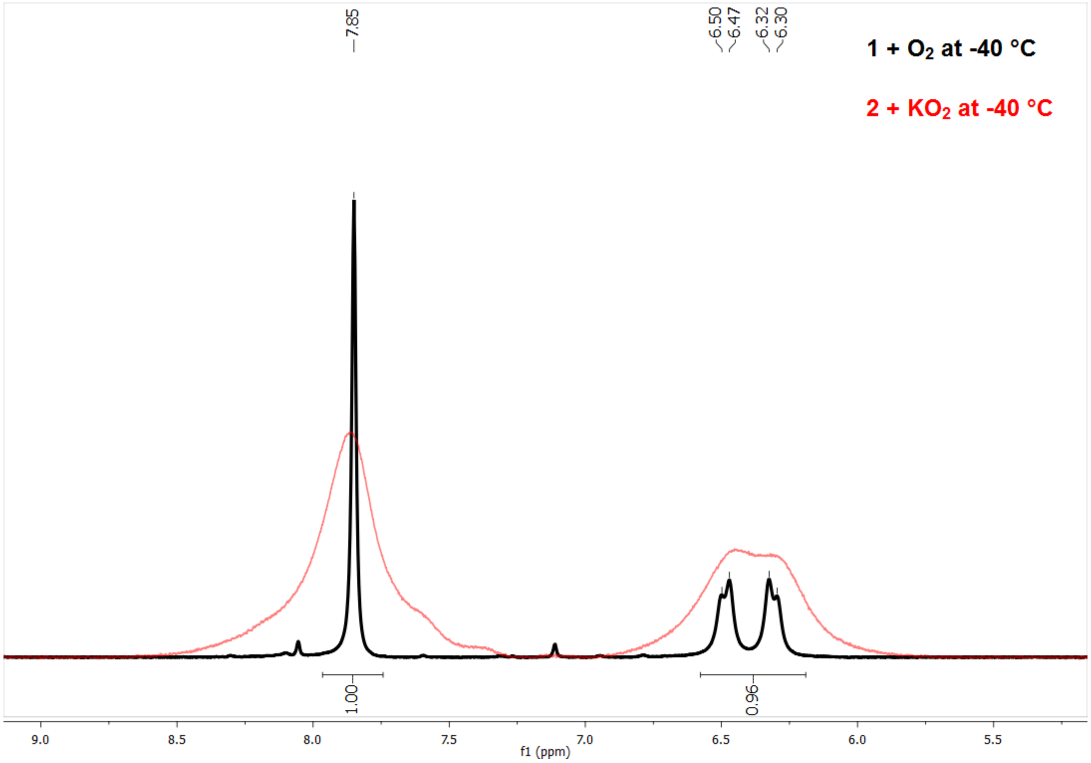

Figure S5. Overlay of the ^1H-NMR spectra recorded for the formation of **3** from **1** and O_2 (**black**) and from **2** and KO_2 (**red**) at -40 °C. The peak broadening observed in the latter case can be attributed to the addition of an excess of paramagnetic KO_2, chemical shifts remained unchanged.

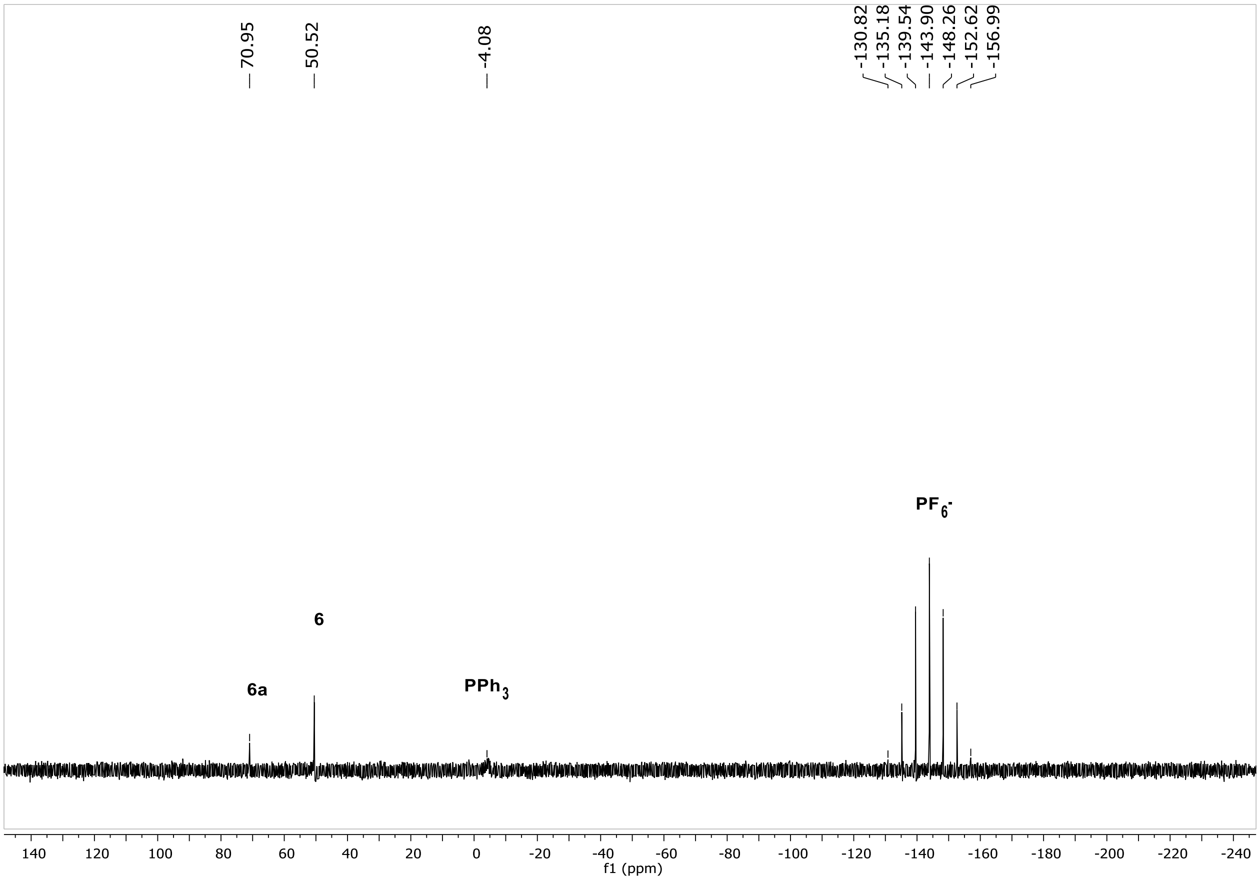

Figure S6. ^{31}P-NMR spectrum of **1** in the presence of **2** equiv. PPh_3 at 296 K in CD_3CN. Complexes **6** and **6a** (monophosphine derivative) are formed under these conditions.

5. ^{1}H-NMR-Kinetics

5.1 Formation and decay of 3 from 2

2 (30mg, 0.036 mmol) was dissolved in 0.4 mL dry and degassed acetone in a dried *J-Young* NMR tube. A blank spectrum of the dark red solution was collected at -80°C. KO_2 (yellow solid) (10 mg, 0.141 mmol) was added to the cold solution at -60 °C and vigorously shaken. The sample was allowed to slowly warm up to -40 °C while **3** was formed from **2** and KO_2. Measurements were collected every 10 min. After 3 h the solution was allowed to warm up in 25°C, which was followed by the vanishing of the respective 1H-signals of **3** and the formation of a dark blue precipitate **4**.

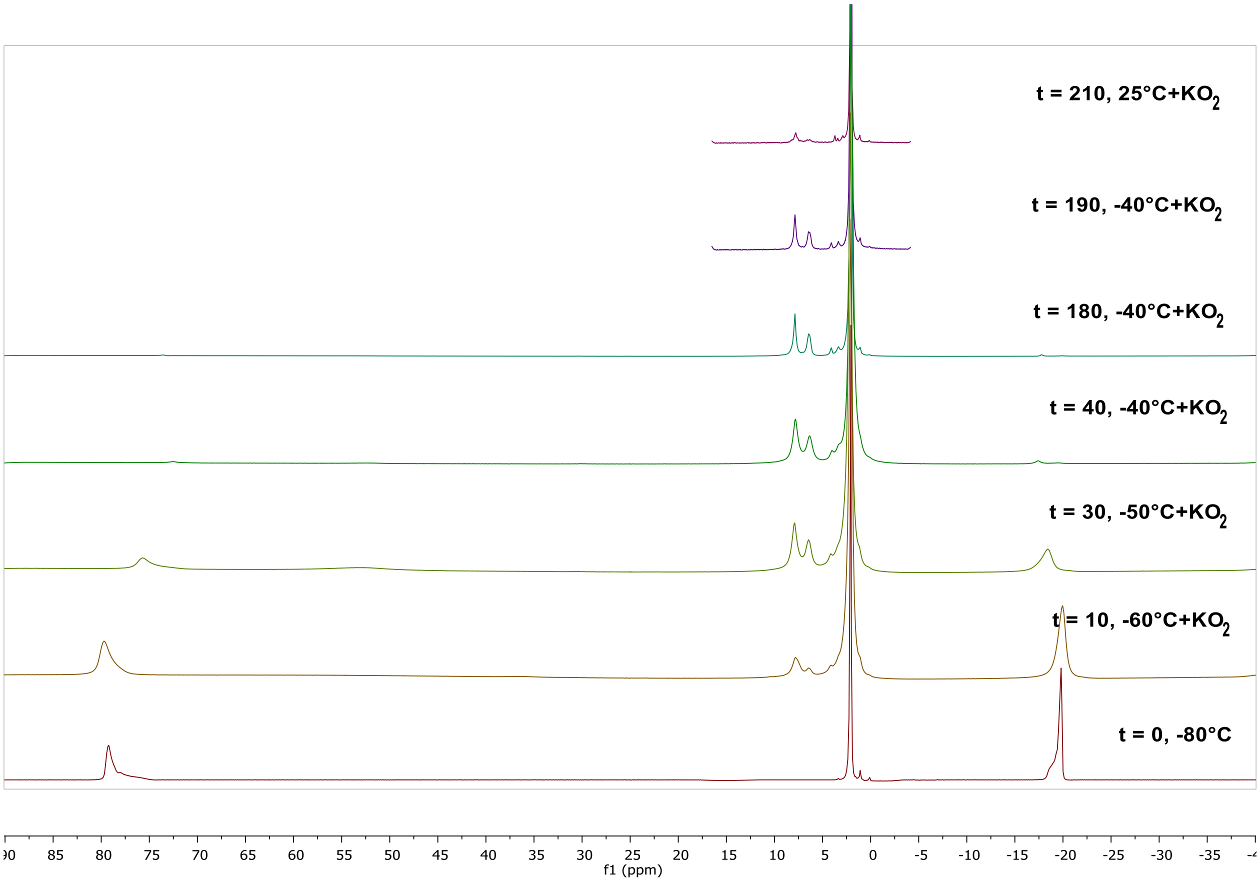

Figure S7. Formation and decay of **3** (red) from **2** (green) and KO_2 in acetone, monitored by ^{1}H-NMR.

5.2 Formation of 3 from 1+O_2 and decay to 4

1, (10 mg, 0.013 mmol) was dissolved in 0.4 mL of dry, degassed acetone-d_6 in a dry *J-Young* NMR tube. A blank spectra was collected and the bright yellow solution was frozen at -110 °C (THF/N_2(l)). The argon atmosphere was removed and 1 bar of O_2 was added. The frozen sample was put into the precooled NMR at -40 °C. Because diffusion is slow and spinning is not possible it was shortly shaken and measurements were collected every 5 min. After 3 h, the solution was allowed to warm up to r.t. in steps of 10 °C. After the reaction was completed a blue precipitate (**4**) was found in the NMR tube. The relative amounts of **1** and **3** were determined by integrating the respective signals at 7.89 (s, 8H-**1**+8H-**3**) and 6.30 (d, 4H-**3**) using diethyether (3.38 ppm, q) as an internal standard.

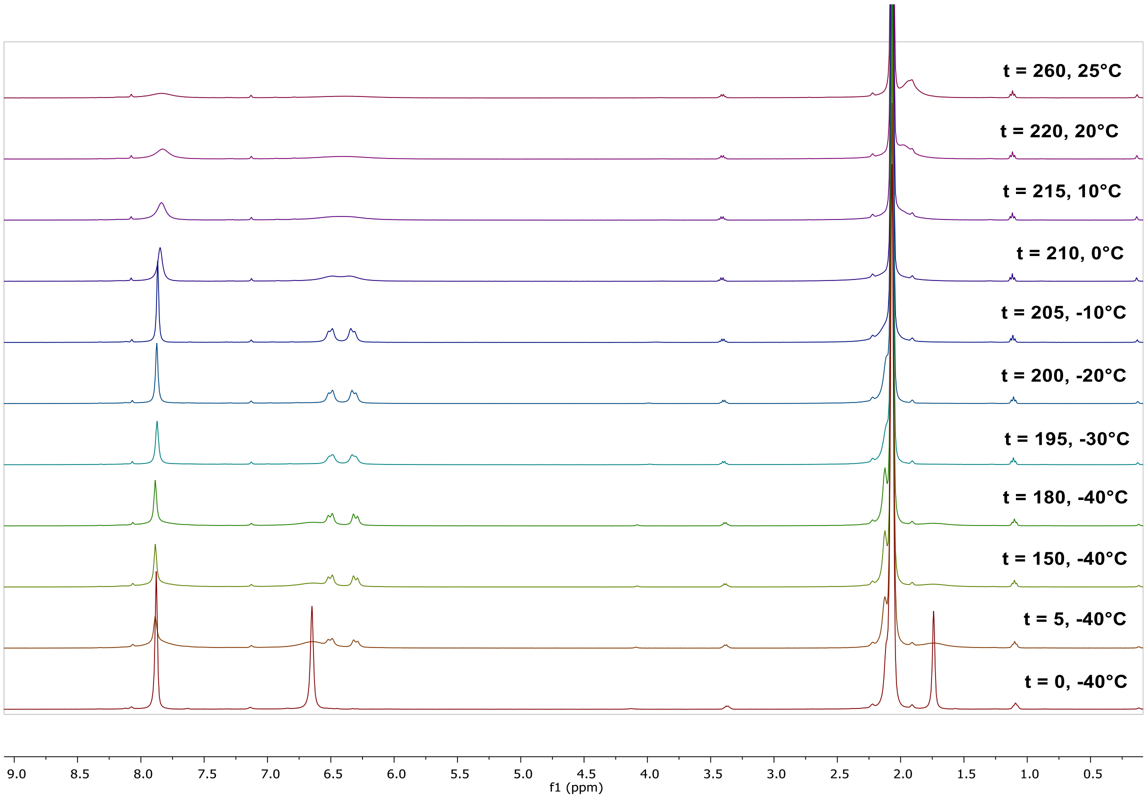

Figure S8. Formation of **3** from **1** and O_2 and subsequent decay of **3** to **4**, monitored by ^{1}H-NMR in acetone-d_6.

5.3 Formation of 1 from the decay to 4 in MeCN

4 was stored at r.t. under Ar in CD_3CN for 4 days. The evolution of the sample was monitored periodically by ^{1}H-NMR. The corresponding signals at 6.29 ppm (**1**) and 6.12-5.90 ppm (**4**) were compared.

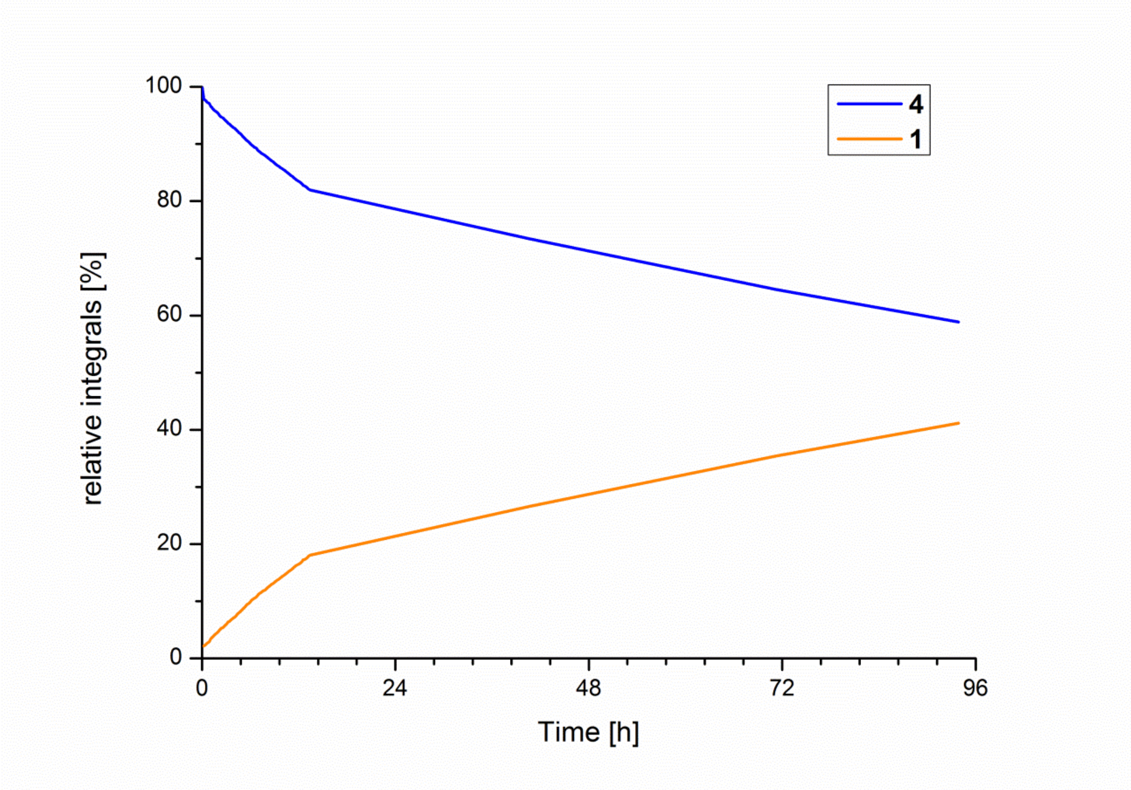

Figure S9. Decay of **4** (blue) and formation of **1** (orange) by storing **4** under argon in CD_3CN for 4 d.

6. Measurement of the amount of O_2 consumed upon formation of 2 from 1 in MeCN.

The measurement was carried out in a Buchi “Tinyclave” autoclave geared with a 10 mL borosilicate reaction vessel, a manometer and a Swagelok shut-off valve. The autoclave was connected through a “T” junction to both a vacuum pump and an O_2 cylinder. The autoclave was charged in a glovebox with 5 mL of a MeCN solution of **1** (150 mg, 0.2 mmol). The autoclave and the connecting pipe to the O_2 cylinder were evacuated and then filled with 51 psi (3.5 bar) of O_2; after 1 min the autoclave was isolated from the rest of the system by a closing the shut-off valve and allowed to stir for 1 h at r.t. (23 °C). Under these conditions (available volume in the reactor, V = 5 mL; T = 296.15 K), the initial amount of O_2 available upon the MeCN solution could be quantified as 0.72 mmol (PV = nRT). The reaction mixture turned from yellow to a dark red-violet color during the reaction within a few minutes. After 1 h the pressure inside the reactor had dropped to 39 psi (2.7 bar) and remained constant at this level for further 4 h. The complete conversion of **1** to complex **2** was confirmed by UV-Vis spectroscopy. Accordingly, it was possible to calculate that, after reaction of **1** and O_2, the O_2 atmosphere upon the MeCN solution would contain 0.55 mmol O_2. Therefore, 0.17 mmol of O_2 were consumed during the process. The ratio between the moles of O_2 and of complex **1** consumed during the process (0.17/0.2 = 0.85) is in rough agreement with a stoichiometric reaction in a 1:1 proportion between **1** and O_2. In a blank experiment it was confirmed that under identical reaction conditions, but in the absence of **1** in the MeCN solution, no pressure drop could be observed. This proves that the O_2 pressure drop during our measurement was due to the consumption of O_2 by its reaction with **1** and not by a leak in the system.

7. Reaction of 1 and O_2 at variable O_2 pressure

The degree of conversion of **1** and O_2 to afford **2** at different O_2 pressure was monitored by UV-Vis spectroscopy highlighting a P-dependent behavior (Figure S12). For this study, 3 mL of a solution of **1** ([**1**]$_0$ = 1 mg/mL) in acetonitrile was prepared in a glovebox and added to a 10 mL autoclave. The desired amount of O_2 was added to the autoclave and the system was stirred at room temperature for 1 h. Following this period, the autoclave was reintroduced in the glovebox and a sample of the reaction was added to an air-tight UV cuvette for measurement of the UV-Vis spectrum. The three different measurements, carried out at 1, 2 and 3.5 bar O_2 show a different composition profile of the solutions of **1**. At 1 bar O_2, in spite of the change of color of the solution from yellow to red, no clear evidence of the broad band relative to complex **2** and centered at 505 nm could be observed, with **1** (λ_{max}= 337 nm) appearing as the main reaction component. When the same reaction was carried out at **2** bar, a higher degree of conversion of **1** to **2** could be observed with both species being identified in solution. Finally, when the O_2 pressure was set at 3.5 bar complete conversion of **1** to **2** observed.

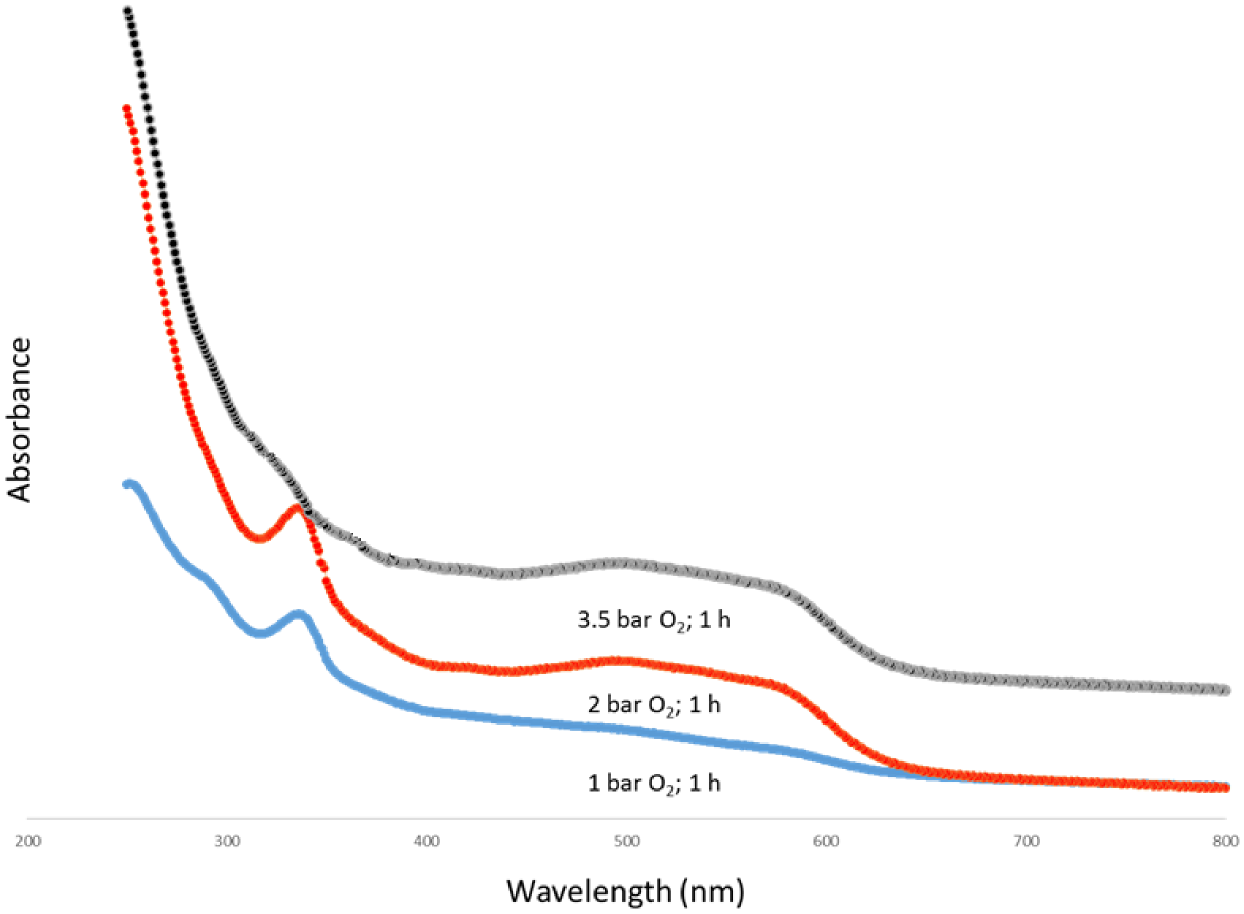

Figure S10. UV-Vis spectra for solutions of **1** ([**1**]$_0$ = 1 mg/mL) exposed to O_2 at different pressure.

8. EPR Studies

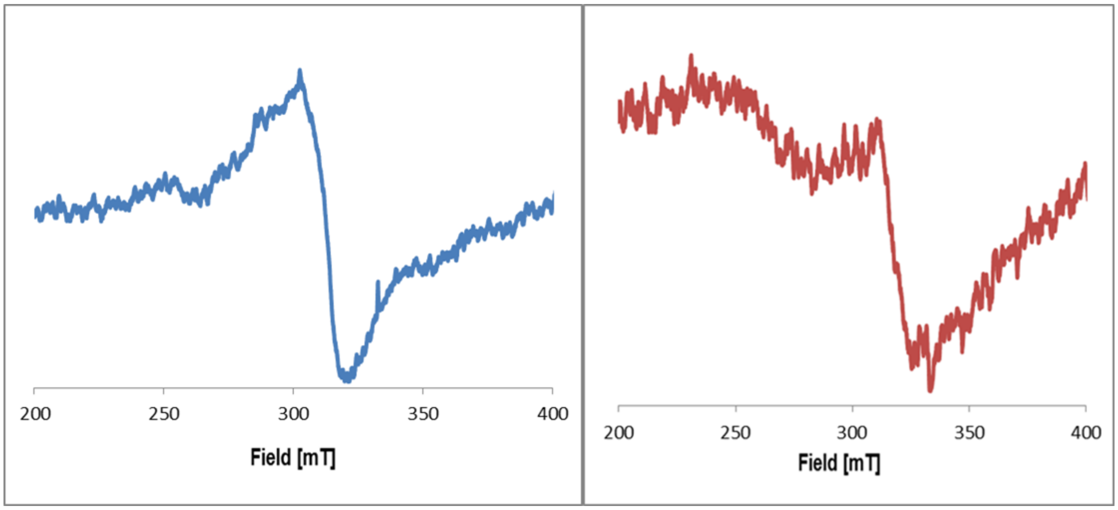

Figure S16. EPR spectra of pure compound **2** (g = 2.1) in acetonitrile at 140 K (left); EPR spectra of a sample of the catalysis reaction after 2 h stirring at room temperature under 2 bar of O_2 (right).

Supplementary References:

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