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Supporting Information

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**Evidence for a Precursor Complex in C–H Hydrogen Atom Transfer
Reactions Mediated by a Manganese(IV) Oxo Complex****

*Isaac Garcia-Bosch, Anna Company, Clyde W. Cady, Stenbjörn Styring, Wesley R. Browne,
Xavi Ribas, and Miquel Costas**

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1. Physical Methods

UV-vis spectroscopy was performed on a Cary 50 Scan (Varian) UV-vis spectrophotometer with 1 cm quartz cells. The low temperature control was performed with a cryostat from Unisoku Scientific Instruments, Japan. Elemental analyses were performed using a CHNS-O EA-1108 elemental analyzer from Fisons. NMR spectra were taken on Bruker Bruker DPX400 spectrometer using standard conditions. All HPLC-MS were obtained on a HPLC Agilent 1200 (G1354A) connected to a Detector Diode Array Agilent Serie 1200 (G1315B) and a Mass Detector Agilent

Serie G6100AA. Raman spectra were recorded using a fiber optic equipped dispersive Raman spectrometer (785 nm, Perkin Elmer RamanFlex). Electrochemical measurements were carried out on a model 630B Electrochemical Workstation (CH Instruments). Complex concentrations were typically 1mM using different solvent mixtures which contained 0.1M tetrabutylammonium hexafluorophosphate. A Teflon-shrouded glassy carbon working electrode and a SCE reference electrode were employed. Cyclic voltammograms were obtained at sweep rates between 100mV s⁻¹ and 1 V s⁻¹.

2. Materials

Reagents and solvents used were of commercially available reagent quality unless otherwise stated. Solvents were purchased from SDS and Scharlab. Preparation and handling of air-sensitive materials were carried out in a N₂ drybox (MBraun) with O₂ and H₂O concentrations < 1 ppm. Xanthene-d₂ and DHA-d₄ were synthesized as described somewhere else.¹

3. Synthesis and generation of complexes 2 and 3

Complex [Mn(CF₃SO₃)₂](^{H,Me}Pytacn), **1** was synthesized as previously described.²

3.1 Synthesis of complex [Mn(OH)₂](^{H,Me}Pytacn)](CF₃SO₃)₂ (**2**):

40 mg of complex [Mn^{II}(CF₃SO₃)₂](^{H,Me}Pytacn)] (0.067 mmols) were solved in 1 mL of CH₃CN in an ice bath. Then, 67 μL of commercially available H₂O₂ 33% (0.67 mmols) were added directly to the mixture, observing a color change from colorless to deep purple. After 1 hour of stirring, the solution was frozen in a liquid N₂ bath, and 100 mL of cold diethyl ether (-80°C) were added. The two-fase mixture was left overnight, and then 37 mg of complex **2** were obtained by removing the solvents by decantation and drying by vacuum (0.058 mmols, 88%). Crystalline material suitable for X-Ray diffraction analysis was obtained by recrystallization of the purple material solving some of the purple material in acetonitrile and adding diethyl ether forming two phases, and leaving the solutions in the freezer (-40 °C) for several days. Anal. Calcd for C₁₆H₂₆F₆MnN₄O₈S₂: C, 30.24; H, 4.12; N, 8.82; S, 10.09 %. Found: C, 30.00; H, 4.23; N, 8.73; S, 9.90 %.

3.2 Generation of complex $[\text{Mn}(\text{O})(\text{OH})(^{\text{H,Me}}\text{Pytacn})](\text{CF}_3\text{SO}_3)_2$ (**3**):

1.33 mg of complex **2** (0.002 mmols) were solved in 2 mL of a CH_3CN :water 5:1 w:w ($[\text{2}] = 1 \text{ mM}$) and then cooled to 0°C . Afterwards, $67 \mu\text{L}$ of an aqueous solution containing 1.0 equiv. of $t\text{BuOK}$ was added, generating the deprotonated species **3**. UV-Vis of the reaction showed an isosbestic point meaning of a full and clean transformation from **2** to **3** (Figure 2). Furthermore, the addition of 1 equivalent of $\text{CF}_3\text{SO}_3\text{H}$ takes us to a 95% recover of complex **2**, showing the reversibility of the protonation/deprotonation process.

4. Characterization of complexes **2** and **3**.

4.1 Characterization of complexes **2** and **3** by ESI-MS and their exchange with H_2^{18}O .

1.33 mg of complex **2** (0.002 mmols) were solved in 2 mL of a CH_3CN :water 5:1 w:w ($[\text{2}] = 1 \text{ mM}$) and the resultant solution was analyzed the ESI-MS (Figure S1, top left), observing the mass $m/z = 168.5$ which corresponds to the complex **2** without the counteranions. When the same solution was prepared using H_2^{18}O , the peak of 168.5 slowly disappeared (30 minutes) and a new peak with a mass of $m/z = 170.5$ appeared (Figure S1, bottom left) which corresponds to the complex **2**- ^{18}O .

Complex **3** was generated adding 1 equiv. of $t\text{BuOK}$ to a complex **2** solution. A peak at $m/z = 336$ was recorded, which corresponds to complex **3** after losing the triflate counteranion (Figure S1, top right). When the same solution was generated using H_2^{18}O , this peak slowly disappeared (30 minutes) and a new peak at $m/z = 340$ appeared, which corresponds to the substitution of the two oxygen atoms by the labelled ones (Figure S1, bottom right).

Figure S1. ESI-MS spectra of complexes **2** and **3** and their exchange with H_2^{18}O .

4.2 Characterization of complexes **2** and **3** by raman spectroscopy

6.6 mg of complex **2** (0.01 mmols) were dissolved in 0.1 mL of a CH_3CN :water 5:1 w:w ($[\text{2}] = 100\text{mM}$). Raman spectra were recorded with $\lambda_{\text{exc}} 785\text{ nm}$. A band is observed at 662 cm^{-1} that is absent in the spectrum of the manganese(II) complex **1** at the same concentration.

Figure S2. Raman Spectra of complex **1** ($[\text{LMn}^{\text{II}}\text{OTf}]_2$, 0.1 M) in CH_3CN at $\lambda_{\text{exc}} 785\text{ nm}$ with (red) H_2^{16}O and (black) H_2^{18}O .

Addition of H_2^{18}O instead of H_2^{16}O results in a shift of the 672 cm^{-1} band to 642 cm^{-1} with no other significant changes to the Raman spectrum being observed. The expected isotope shift based on the two atom (Mn-O) approximation is 29 cm^{-1} and hence the band is assigned to the manganese-oxygen vibration of the $\text{Mn}^{\text{IV}}\text{-(OH)}_2$ moiety (Figure 2).

Figure S3. Raman Spectra of complex **2** (0.1 M) in CH_3CN at λ_{exc} 785 nm with (red) H_2^{16}O and (black) H_2^{18}O .

Addition of 0.5 equivalents of base (e.g., $^t\text{BuOK}$) to a solution of **2** results in the formation of **3** in situ and the concomitant disappearance of bands at 800 cm^{-1} (which is unaffected by addition of H_2^{18}O) and the Mn-O band of **2** at 662 cm^{-1} . Two new bands at 749 and 712 cm^{-1} are observed in the spectrum of **3**. Addition of H_2^{18}O results in the disappearance of the band at 749 cm^{-1} and the shift of the band at 712 cm^{-1} to 682 cm^{-1} . The shift expected for the manganese oxygen bond based on the two atom approximation is 31 cm^{-1} which is in agreement with the observed 30 cm^{-1} shift.

Figure S4. Raman Spectra of complex **3** (0.1 M) in CH₃CN at λ_{exc} 785 nm with (green) H₂¹⁶O and (black) H₂¹⁸O.

4.3 Characterization of complexes **2** and **3** by EPR

All EPR were run at 5K using a acetone:water 5:1 w:w solvent mixture. EPR of **1** (Figure S2 left, blue line) shows an interesting asymmetry which may be due to electron density localizing toward the solvent ligands rather than being spread evenly around the large multi dentate ligand. When oxidized to **2** the EPR (Figure S5 left, red line) shows a characteristic Mn(IV) signal with features at around $g = 4$ and 2. In addition to the characteristic Mn(IV) peak a small amount of multiline is located in the $g = 2$ region. The multiline signal can be assigned as a 16 line signal corresponding to a small amount of Mn(III,IV) dimer. EPR spectra of **2** after the addition of ^tBuOK show the transition between **2** and **3** (Figure S5, right). The broad feature at 1600 G can be seen to transition to the multiline feature at 1500 G. The multiline signal at 1500 G is most consistent with a slightly altered Mn(IV) monomer signal as stated and referenced in the text of the main article.

Figure S5. Left: EPR spectra (5K) of complexes **1** (blue line) and **2** (red line) a acetone:water 5:1 w:w solvent mixture. Right: EPR spectra of complexes **2** (green line), after addition of 0.5 equiv. of ^tBuOK (red line) and after addition of 1 equiv. of ^tBuOK (blue line) which corresponds to complex **3**.

4.4 Determination of μ_{eff} and unpaired electrons for complexes **2** and **3** by the Evans' method

To run the experiments, a special coaxial insert tube purchased from Wilmad Glass Co was used. An exact amount of complex **2** (2.66 mg) was solved in 0.4 mL of a mixture CD₃CN:D₂O 5:1 w:w which contained 8 μ L of CH₂Cl₂ and the resulting mixture was placed in the outer tube of the coaxial tube. The inner tube was filled with a reference solution which contained 4 μ L of CH₂Cl₂ in a 0.2 mL of a CD₃CN:D₂O 5:1 w:w. ¹H-NMR spectra of samples showed two different signals for CH₂Cl₂ corresponding to inner and outer tubes. The difference in the chemical shift between the two peaks was used to determine the μ_{eff} and the unpaired electrons of the metal center. For complex **3** the same procedure was followed, generating complex **3** by adding 1 equiv of ^tBuOK in the inner and the outer tubes of the sample used for complex **2**.

4.5 Determination of the redox potentials for complexes **2** and **3** by cyclic voltammetry

Cyclic voltammetry was employed to elucidate the electrochemical properties of complexes **2** and **3** (Figure S6). Complex **2** shows a reversible reduction (Mn(IV)/Mn(III)) at $E_{1/2} = 0.55$ V (vs SCE, 0.78 V vs SHE) in anhydrous acetonitrile (with 0.1 M NBu₄PF₆). Scanning from the open circuit potential initially to positive potentials shows that no oxidative redox processes (e.g. Mn(IV)/Mn(V)) occur within the potential window. When a mixture of acetonitrile:H₂O is used, the redox wave becomes irreversible, and a second reversible oxidation/reduction process is observed at $E_{1/2} = 0.86$ V (vs SCE) on the return scan indicating a change to the complexes ligand environment occurs upon reduction. When the pH is set to pH 6.1, the 1e⁻ reduction wave becomes reversible.

The cyclic voltammetry of complex **3**, obtained by in situ deprotonation of **2**, was performed at 0 °C in an acetonitrile:water mixture 5:1, at pH 9.1. In addition to the reduction wave at 0.55 V a second reduction was

observed at 0.05V (vs SCE) which is assigned tentatively to the reduction of the manganese(IV)(O)(OH) complex **3** to the related manganese(III)(O)(OH) complex which is rapidly protonated because of its higher basicity, and hence the redox processes of complex **2** are observed also.

Figure S6. Cyclic voltammetry of complexes **2** (pH = 2.3 in red and pH = 6.1 in blue, left) and **3** (pH = 9.1, right).

4.6 Determination of the pK_a value for the deprotonation of complex **2** to **3**:

The pK_a value for the deprotonation process was obtained by a potentiometric titration. In a typical experiment, 3.3 mg of complex were solved in 0.5 mL of an CH_3CN :water 5:1 w:w ($[2] = 10\text{mM}$) and cooled to 0°C . After fixing the pH = 2 using a solution of $\text{CF}_3\text{SO}_3\text{H}$, several additions of a solution of $^t\text{BuOK}$ were done measuring the pH after each one. From the measurements, a plot of the added equivalents of base vs the pH allowed us to calculate the pK_a value for the deprotonation of complex **2** (Figure S7, right). The same experiment was also followed by UV-Vis measuring both, pH and UV-vis spectra, and an isobestic point was observed for the transformation between **2** and **3**, indicating the cleanliness of the deprotonation (Figure S7, left). Despite the fact that a second deprotonation process was observed at pH around 10-12, when this second reaction was followed by UV-Vis, a loss of the isobestic point was observed, and an increase of a band around 400 nm was observed, typical of a manganese(III) species, what can be understood as a decomposition of the manganese(IV) species at high pH.

Figure S7. Potentiometric titration followed by UV-Vis (left) and plot of the equivalents of base added vs pH (right).

In order to corroborate the value obtained for the deprotonation, spectrophotometric titrations using soft bases such as 2,6-lutidine and 2-methylimidazole were performed. The reactions were followed by UV-vis monitoring the formation of complex **3** with the addition of several equivalents of the base. In order to calculate the pK_a of the deprotonation, the pK_a values for the two soft bases protonation in the reaction condition were also calculated using potentiometric titrations ($pK_a(2,6\text{-lutidine}) = 11.2$, $pK_a(2\text{-methylimidazole}) = 9.5$). A value of 7.4 using 2,6-lutidine and 7.0 using 2-methylimidazole were obtained, confirming the pK_a value of 7.1 ± 0.1 .

4.7 Calculation of the BDE_{C-H} as a driving force for the hydrogen atom abstraction ability.

The BDE of the complex **3-H** (Scheme S1) was calculated using the Bordwell equation $BDE = 1.37 pK_a + 23.06 E_{1/2} + C$ ($C = 55.7 \text{ kcal}$) applying the pK_a found for the deprotonation between complexes **2** and **3**, and the $E_{1/2}$ value of the reduction of complex **2** ($BDE_{O-H}(\mathbf{3-H}) = 83.5 \text{ kcal}\cdot\text{mol}^{-1}$). However, we were not able to calculate this value for complex **2-H**.

Scheme S1. Redox potentials, pK_a values and BDE_{O-H} for manganese complexes ($L = {}^{\text{H,Me}}\text{Pytacn}$).

5. Complexes reactivity towards C-H bonds.

5.1 Reactivity of complex **2** and **3** towards C-H bonds. Products analysis and final oxidation state of manganese.

2.66 mg of complex **2** were solved in 3.34 mL of a deoxygenated $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ w:w 4:1 mixture ($[\mathbf{2}] = 1 \text{ mM}$). Then, 0.66 mL of deoxygenated CH_3CN containing 10 equivalents of substrate (xanthene, 9,10-dihydroanthracene, fluorene) were added. The reaction was left for 2 days, and to the final solution, 80 μL of a solution containing 4×10^{-6} mols of biphenyl were added as internal standard to the crude. 2 mL of the solution were analyzed by HPLC-MS after passing the solution through basic alumina. After this analysis, the solution was evaporated and the obtained products and their respective yields were also confirmed by $^1\text{H-NMR}$. The results are summarized in

Table 1, from which we can observe the inability of complex **2** to oxidize fluorene. The same experiments were carried out in the presence of oxygen, from which we observed the increase of the products in most of the cases. The other 2 mL of the reaction crude were used to determine the final oxidation state of the manganese: the crude solution was acidified using 0.2 mL of aqueous H₂SO₄ 0.5 M and 0.1 mL of aqueous KI 0.5M was added and the formation of the I₂ was observed (color changes to intense yellow). The I₂ produced was quantified using a solution of 0.002 M of Na₂S₂O₃ from which we calculated the final oxidation state of the manganese, 3.3 ± 0.1 (average of 4 different experiments). Both product yields and final oxidation state of manganese point out that complex **2** acts as a 1e⁻ oxidant.

For complex **3**, the same procedure was followed for both, products analysis and final oxidation state analysis. The final oxidation state of the complex is 3.2 ± 0.2 (average of 6 different experiments) and together with the quantification analysis pointed out that complex **3** was also acting as a 1e⁻ oxidant.

Table S1. Products quantification analysis of the oxidation of xanthene, 9,10-dihydroanthracene fluorine, xanthene-d₂ and 9,10-dihydroanthracene-d₄ by complexes **2** and **3** by HPLC-MS and ¹H-NMR.

Substrate	Product	2 (N ₂)	2 (O ₂)	3 (N ₂)	3 (O ₂)
		Yield (yield e-)	Yield	Yield (yield e-)	Yield
Xanthene	9-xanthidrol	$38 \pm 5\%$ (76%)	29%	$25 \pm 4\%$ (50%)	30%
	Xanthone	$6 \pm 1\%$ (24%)	26%	$8 \pm 2\%$ (32%)	12%
	9,9'-bixanthyl	< 1%	< 1%	<1%	<1%
DHA	Anthracene	$28 \pm 5\%$ (56%)	28%	$26 \pm 3\%$ (52%)	29%
	Anthrone	< 1%	< 1%	<1%	< 1%
	Anthraquinone	$6 \pm 1\%$ (48%)	3%	$4 \pm 1\%$ (32%)	57%
Fluorene	9-hydroxyfluorene	< 1%	< 1%	$6 \pm 1\%$ (12%)	13%
	Fluorenone	< 1%	< 1%	$17 \pm 1\%$ (68%)	34%
	9,9'-bifluorenyl	< 1%	< 1%	< 1%	< 1%
Xanthene-d ₂	9-xanthidrol-d ₁	$13 \pm 5\%$ (26%)	-	$16 \pm 5\%$ (32%)	-
	Xanthone	$10 \pm 5\%$ (40%)	-	$10 \pm 5\%$ (40%)	-
	9,9'-bixanthyl-d ₂	< 1%	-	< 1%	-
DHA-d ₄	Anthracene-d ₂	$30 \pm 5\%$ (60%)	-	$25 \pm 5\%$ (50%)	-
	Anthrone-d ₂	< 1%	-	< 1%	-
	Anthraquinone	$4 \pm 5\%$ (32%)	.	$4 \pm 5\%$ (32%)	-

Furthermore, the quantification of the reaction products for the complex **3** was also carried out at different substrate concentrations, from we can observe that similar product ratios where obtained at non-saturated (2mM), intermediate (10mM) and saturated conditions (50mM) (Table S2).

Table S2. Products quantification analysis of the oxidation of xanthene, 9,10-dihydroanthracene fluorine, xanthene-d₂ and 9,10-dihydroanthracene-d₄ by complexes **3** by HPLC-MS and ¹H-NMR at different substrate concentrations (2mM, 10mM and 50mM).

		2mM	10mM	50mM
Substrate	Product	Yield (yield e-)	Yield (yield e-)	Yield (yield e-)
Xanthene	9-xanthidrol	10 ± 5% (20%)	25 ± 4% (50%)	24 ± 5% (48%)
	Xanthone	11 ± 5% (44%)	8 ± 2% (32%)	10 ± 5% (40%)
	9,9'-bixanthyl	< 1%	<1%	<1%
DHA	Anthracene	20 ± 5% (40%)	26 ± 3% (52%)	27 ± 5% (54%)
	Anthrone	< 1%	<1%	< 1%
	Anthraquinone	5 ± 5% (40%)	4 ± 1% (32%)	6 ± 5% (48%)
Fluorene	9-hydroxyfluorene	5 ± 5% (10%)	6 ± 1% (12%)	7 ± 5% (14%)
	Fluorenone	16 ± 5% (64%)	17 ± 1% (68%)	14 ± 5% (68%)
	9,9'-bifluorenyl	< 1%	< 1%	< 1%
Xanthene-d ₂	9-xanthidrol-d ₁	10 ± 5% (20%)	16 ± 5% (32%)	13 ± 5% (26%)
	Xanthone	13 ± 5% (52%)	10 ± 5% (40%)	12 ± 5% (48%)
	9,9'-bixanthyl-d ₂	< 1%	< 1%	< 1%
DHA-d ₄	Anthracene-d ₂	13 ± 5% (26%)	25 ± 5% (50%)	-
	Anthrone-d ₂	< 1%	< 1%	-
	Anthraquinone	6 ± 5% (48%)	4 ± 5% (32%)	-

In addition, we performed the reaction between complex **3** and toluene, and no presence of oxidized products were detected.

5.2 Reactivity of complex 2 towards C-H bonds. Kinetic analysis.

1.33 mg of complex **2** were solved in a 1.67 mL of a CH₃CN:H₂O w:w 4:1 mixture ([**2**] = 1 mM) in a UV-Vis cell at 25°C. 0.33 mL of CH₃CN containing the substrate was added, and the reaction was monitored by following the reaction at $\lambda = 545$ nm. The reaction rates were calculated applying the initial rates approximation (10% complex disappearance) in order to avoid the interference of secondary reactions. Complex **2** shows a pseudo-first order behavior for both substrate ([substrate] = 0.005-0.1 M) and complex ([**2**] = 0.0025-0.004 M) (Figure S8). We followed by UV-Vis the reactions between complex **2** and xanthene (BDE_{C-H} = 75.5 kcal·mol⁻¹), 1,4-cyclohexadiene (BDE_{C-H} = 77 kcal·mol⁻¹), 9,10-dihydroanthracene (BDE_{C-H} = 78 kcal·mol⁻¹) and fluorene (BDE_{C-H} = 80 kcal·mol⁻¹). For the complex with fluorene, or toluene we didn't observe decay of the complex band ($\lambda = 545$ nm) after several hours, precluding that complex **2** is unable to oxidize this substrate. For each substrate, a linear correlation between the substrate concentration and the rate observed was plotted (Figure 3) from where we calculate the second order reaction rate k_2' (which was corrected for the number of C-H reactive bonds).

Figure S8. Pseudo-first order behavior for both substrate concentration (left) and complex concentration (right) in the reaction between complex **2** and xanthene.

In order to get the kinetic isotopic effect (KIE) we carried out the reaction for both xanthene- d_2 and DHA- d_4 . Comparing the k_2' values obtained from the linear plots, we calculate a KIE of 8.0 for xanthene and 6.6 for DHA (Figure S9).

Figure S9. KIE experiments for the reactions between complex **2** and xanthenes/xanthenes- d_2 (left) and DHA/DHA- d_4 (right).

5.3 Reactivity of complex **3** towards C-H bonds. Kinetic analysis.

1.33 mg of complex **3** were solved in a 1.67 mL of a $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ w:w 4:1 mixture ($[2] = 1 \text{ mM}$) in a UV-Vis cell at 25°C . 66 μL of a solution containing 1 equiv. of $^t\text{BuOK}$ was added in order to generate complex **3**. After full the full formation of the complex, 0.33 mL of CH_3CN containing the substrate was added, and the reaction was monitored by following the reaction at $\lambda = 825 \text{ nm}$ (Figure S10). The reaction rates were calculated applying the initial rates approximation (10% complex disappearance) in order to avoid the interference of secondary reactions. In random cases we monitored the full decay of **3**, obtaining within error identical values to those obtained by the initial rate method. For the specific case of toluene, we didn't observe decay of the UV-vis spectroscopic features of **3** ($\lambda = 825 \text{ nm}$) after several hours. We conclude that complex **3** is unable to oxidize this substrate.

Figure S10. Reaction between complex **3** and 10 equiv. of xanthene.

Complex **3** shows a pseudo-first order for complex concentration ($[3] = 0.0025\text{-}0.004\text{ M}$). However, a saturation behavior was observed with an increase in the substrate concentration. Furthermore, these saturation curves were observed for all the substrates (xanthene, 1,4-CHD, DHA and fluorene) (Figure 3). These saturation plots are characteristic for reactions where an initial pre-equilibrium occurred previous to the rate determining step, and can be adjusted using the Equations 1 and 2, from where we can extract the equilibrium constant K_{eq} and the first order rate constant k_2 of the rate determining step (values summarized in Table 1) (Figure S11).

$$k_{obs} = \frac{k_2 K_{eq} [C - H]}{1 + K_{eq} [C - H]} \quad (\text{Equation 1})$$

$$\frac{1}{k_{obs}} = \frac{1}{k_2 K_{eq}} \frac{1}{[C - H]} + \frac{1}{k_2} \quad (\text{Equation 2})$$

Figure S11. Saturation curves obtained for the reaction between complex **3** and substrates (left) and the adjust of the data using equation 2 (right) from where K_{eq} and k_2 were calculated.

The formation of the intermediate **I** was observed when complex **3** reacted with DHA under saturation conditions (10 equiv.). The band at 535 nm shifted to 539 nm (Figure S12).

Figure S12. Reaction between complex **3** and 10 equiv. of DHA.

For the xanthene and the DHA, we also carried out kinetic isotopic effect experiments using their deuterated analogs (Figure S13). Curiously, while the pre-equilibrium constant K_{eq} was not effected for the deuteration (similar values for both xanthene/xanthene- d_2 and DHA/DHA- d_4 couples), k_2 presented a primary KIE for both xanthene (2.1) and DHA (3.1).

Figure S13. KIE experiments for the reactions between complex **3** and xanthenes/xanthenes- d_2 (left) and DHA/DHA- d_4 (right).

5.4 Reactivity of complex **2** and **3** towards C-H bonds. Kinetic analysis varying the temperature. Eyring and van't Hoof plots.

Table S3. Rate constants for the reaction of complexes **2** and **3** with 9,10-dihydroanthracene at different temperatures.

Substrate	T(K)	2	3	$k_2^{(O)}(10^{-4} \text{ s}^{-1})$	$K_{eq}k_2^{(O)} (\text{M}^{-1}\text{s}^{-1})$
		$k_2^{(OH)}(10^{-4} \text{ M}^{-1} \text{ s}^{-1})$	$K_{eq} (\text{M}^{-1})$		
9,10-DHA	298	16 ± 1	523 ± 33	65 ± 4	3.40
	293	13 ± 1	583 ± 10	45 ± 1	2.62
	288	10 ± 1	680 ± 36	29 ± 1	1.97
	283	8.4 ± 1	713 ± 40	23 ± 1	1.64
	278	6.4 ± 1	838 ± 10	18 ± 1	1.51
	273	5.2 ± 1	923 ± 4	11 ± 1	1.01

The impact of the temperature in the kinetic experiments was evaluated for both complexes using DHA as substrate. The test were carried out from 273-298K (6 different temperatures) and varying the concentration of the DHA was varied using at least 5 different concentrations (Figure S14). The values for complex **2** (k_2) and complex **3** (K_{eq} and k_2) were obtained for each temperature, from where we can construct the Eyring and van't Hoff plots.

Figure S14. Reaction rates obtained for the hydrogen atom abstraction of DHA performed by complexes **2** and **3** at different temperatures.

From the Eyring plot (Figure S15, left), we can calculate the activation parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ (298K) of the rate determining step for both complexes **2** and **3**. Furthermore, the construction of a van't Hoff plot (Figure S15, right) allows us to calculate the thermodynamic parameters for the first pre-equilibrium step occurred when complex **3** reacts with DHA (Table S4).

Table S4. Thermodynamic and activation parameters for the reaction of complexes **2** and **3** with DHA.

	ΔH	ΔS	ΔG^a	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^{\ddagger a}$
Complex	(kcal/mol)	(cal/mol·K)	(kcal/mol)	(cal/mol)	(cal/mol·K)	(kcal/mol)
2	-	-	-	6.6 ± 0.1	-51.9 ± 0.4	22.1 ± 0.1
3	-3.6 ± 0.2	0.2 ± 0.4	-3.7 ± 0.2	10.3 ± 0.7	-37 ± 2	21.3 ± 0.7

^a Calculated at 298K.

Figure S15. Eyring plots (left) and van't Hoff plot (right) for the hydrogen atom abstraction of DHA performed by complex 2 (—●—) and complex 3 (—●—).

5.5 Reactivity of complex 2 and 3 towards C-H bonds. Rate constants vs BDE_{C-H} .

The correlation between the observed rate constants ($\log k_2'$) vs the BDE_{C-H} of the different substrates was plotted. For both complexes, a linear correlation was observed, pointing out the fact that, the C-H bond cleavage occurred during the rate determining step. However, a major impact was observed for complex 2 (slope = -0.36) than for complex 3 (slope = -0.15).

Figure S16. Dependence of the $\log(k_2')$ vs BDE_{C-H} for complex 2 (—●—) and complex 3 (—●—).

6. References

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