Mechanistic Studies on the Hexadecafluorophthalocyanine–Iron-Catalyzed Wacker-Type Oxidation of Olefins to Ketones

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# Table of Content

1 Additional Spectroscopic Data of the Complexes FePcF<sub>16</sub> and O(FePcF<sub>16</sub>)<sub>2</sub> ................................................................. 2

1.1 ESI-MS of the Complex O(FePcF<sub>16</sub>)<sub>2</sub> ........................................................................................................ 2

1.2 UV/Vis Data of FePcF<sub>16</sub> and O(FePcF<sub>16</sub>)<sub>2</sub> ......................................................................................... 3

2 Experimental Procedures for the Synthesis of the Substrates ........................................................................... 4

2.1 Synthesis of 2-(1-Deuterovinyl)naphthalene ([α-D]-1) ..................................................................................... 4

2.2 Synthesis of 2-(Naphthen-2-yl)oxirane (9) ................................................................................................. 5

3 Variation of Hydrosilanes in the Wacker-type Oxidation of 2-Vinyl naphthalene (1) ........................................... 6

3.1 Spectroscopic Data of the Observed Ethoxysilanes and Silanoles .............................................................. 6

4 Experimental Procedure for the Iron-Catalyzed Oxidation of 2-Vinyl naphthalene (1) ........................................... 9

5 Mechanistic Investigations .............................................................................................................................. 10

5.1 Attempted Solvolysis of Ph<sub>3</sub>SiH and Ph<sub>3</sub>SiOH in Ethanol ............................................................................. 10

5.2 Reaction of Ph<sub>3</sub>SiH with Ethanol in the Presence of FePcF<sub>16</sub> or O(FePcF<sub>16</sub>)<sub>2</sub> ........................................ 11

5.3 Stoichiometric Reaction of O(FePcF<sub>16</sub>)<sub>2</sub> with Triphenylsilane (2k) the Absence of O<sub>2</sub> .................. 12

5.4 Reaction of Ph<sub>3</sub>SiOH with Ethanol in the Presence of FePcF<sub>16</sub> or O(FePcF<sub>16</sub>)<sub>2</sub> ............................... 13

5.5 Mechanistic Experiments Using C<sub>2</sub>D<sub>2</sub>OD as solvent ......................................................................... 14

5.6 Interception of the Intermediate Benzyl Radical using TEMPO as Radical Scavenger ................................. 14

5.7 Examination of a Presumed Radical Chain Mechanism ............................................................................. 15

5.8 Reaction Using Et<sub>3</sub>SiD as Reductive Additive .................................................................................. 15

5.9 Reaction under an <sup>18</sup>O<sub>2</sub>-Atmosphere ........................................................................................................ 16

5.10 Reaction Using Et<sub>3</sub>SiD as Reductive Additive under an <sup>18</sup>O<sub>2</sub>-Atmosphere .............................................. 17

5.11 Reaction with [α-D]-1 as Substrate ........................................................................................................ 19

5.12 Iron-Catalyzed Reduction of the Ketone 3 with Et<sub>3</sub>SiD to the Alcohol [α-D]-4 ........................................... 19

5.13 Examination of a Presumed Meinwald Rearrangement ........................................................................ 20

6 Mössbauer Spectroscopy ............................................................................................................................. 21

7 References ................................................................................................................................................. 25

8 NMR Spectra ............................................................................................................................................ 26
1 Additional Spectroscopic Data of the Complexes FePcF$_{16}$ and O(FePcF$_{16}$)$_2$

1.1 ESI-MS of the Complex O(FePcF$_{16}$)$_2$

Figure S1. MS (ESI, +10 V) of O(FePcF$_{16}$)$_2$. 
1.2 UV/Vis Data of FePcF$_{16}$ and O(FePcF$_{16}$)$_2$

![Normalized UV/Vis absorption spectrum of FePcF$_{16}$ in different solvents.](image1)

**Figure S2.** Normalized UV/Vis absorption spectra of FePcF$_{16}$ in different solvents.

![Normalized UV/Vis absorption spectrum of O(FePcF$_{16}$)$_2$ in different solvents.](image2)

**Figure S3.** Normalized UV/Vis absorption spectra of O(FePcF$_{16}$)$_2$ in different solvents. Compared to FePcF$_{16}$, the absorption maxima of the μ-oxo-bridged iron complex are slightly blue-shifted.
**Table S1.** UV/Vis absorption maxima of the iron complexes FePcF₁₆ and O(FePcF₁₆)₂.

| Solvent  | \(\lambda_{\text{max}}\) [nm] FePcF₁₆ | \(\lambda_{\text{max}}\) [nm] O(FePcF₁₆)₂ |
|---------|----------------------------------|---------------------------------|
| Acetone | 569 (sh), 628, 701 (sh)           | 570 (sh), 625                   |
| CH₂Cl₂  | 633                              | 622, 713 (sh)                   |
| DMF     | 597 (sh), 629 and 660 (twin maximum) | 572 (sh), 627                   |
| DMSO    | 596 (sh), 628 (sh), 656           | 579 (sh), 629                   |
| Ethanol | 632, 661 (sh)                     | 572 (sh), 625                   |
| Methanol| 629 and 655 (twin maximum), 685 (sh) | 622                             |
| Pyridine| 598 (sh), 634 and 659 (twin maximum)[a] | 573 (sh), 631                   |

[a] In agreement with Jones and Twigg.[1]

## 2 Experimental Procedures for the Synthesis of the Substrates

### 2.1 Synthesis of 2-(1-Deuterovinyl)naphthalene ([α-D]-1)

![Synthesis of 2-(1-Deuterovinyl)naphthalene ([α-D]-1)](image)

Sodium borodeuteride (412 mg, 9.84 mmol, 99% D content) was added in four portions at room temperature over a period of 40 min to a stirred solution of 1-(naphthalen-2-yl)ethanone (3) (1.00 g, 5.88 mmol) in dried and degassed ethanol (10 mL) under an atmosphere of argon. Then, the solution was additionally stirred for 5 h at room temperature. Hydrochloric acid (2 M, ca. 10 mL) was added dropwise at room temperature to the solution until gas evolution stopped. The reaction mixture was transferred to a separating funnel with diethyl ether (25 mL) and washed with a saturated aqueous solution of sodium hydrogencarbonate (25 mL), and with brine (25 mL). The organic layer was dried over MgSO₄, filtered, and the solvent was evaporated in vacuum to provide [α-D]-4 (1.02 g, 5.88 mmol, 100%) as colorless solid [CAS 1424361-48-7].

![Deuterated alcohol [α-D]-4](image)

IR (ATR) \(\nu = 3294\) (br), 3052, 3018, 2971, 2922, 2863, 2126, 1952, 1921, 1599, 1503, 1450, 1398, 1364, 1275, 1256, 1218, 1185, 1124, 1074, 1014, 945, 925, 898, 860, 817, 772, 740, 694, 648, 618 cm⁻¹; \(^1\)H NMR (600 MHz, CDCl₃): \(\delta = 1.58\) (s, 3 H), \(1.78\) (br s, 1 H), \(7.45–7.50\) (m, 2 H), \(7.51\) (dd, \(J = 8.5, 1.7\) Hz, 1 H), \(7.81–7.86\) (m, 4 H); \(^1\)C NMR and DEPT (151 MHz, CDCl₃): \(\delta = 25.16\) (CH₃), \(70.28\) (t [1:1:1], \(J = 22.0\) Hz, C), \(123.99\) (CH), \(125.95\) (CH), \(126.86\) (CH), \(126.31\) (CH), \(127.82\) (CH), \(128.08\) (CH), \(128.47\) (CH), \(133.08\) (C), \(133.47\) (C), \(143.26\) (C); MS (EI): m/z (%) = 173 (40, [M⁺]), 158 (46), 155 (10), 130 (100), 129 (36), 128 (23), 127 (17). HRMS (ESI): m/z calcd for C₃₀H₁₉D⁺ [M-OH]⁺: 156.0918; found: 156.0914. According to the \(^1\)H NMR spectrum, the deuterium content was 99%.

Spectroscopic data are in agreement with those reported in the literature.[2,3]

The deuterated alcohol [α-D]-4 (1.01 g, 5.82 mmol) was dissolved in dry CH₂Cl₂ (10 mL) under an atmosphere of argon. Then, freshly distilled triethylamine (5.00 mL, 35.9 mmol) was added dropwise. While vigorously stirring, methanesulfonyl chloride (1.75 mL, 22.6 mmol) was added dropwise over a period of 10 min to the reaction mixture at room temperature and the solution was additionally stirred for 3 h. The reaction mixture was transferred to a separating funnel with diethyl ether (25 mL) and washed with a saturated aqueous solution of sodium hydrogencarbonate (30 mL), and with brine (30 mL). The organic layer was dried over MgSO₄, filtered, and the solvent was removed in vacuum to provide a brownish solid, which was used without further purification.
The obtained solid was dissolved in THF (15 mL) under an argon atmosphere and the solution was vigorously stirred. At room temperature, potassium tert-butoxide was added in five portions over a period of 25 min (1.02 g, 9.06 mmol) and the solution was stirred for another 1.5 h at 50 °C. Then, the reaction mixture was cooled to room temperature, transferred to a separating funnel with diethyl ether (30 mL), and the organic layer was washed with water (25 mL), a saturated aqueous solution of sodium hydrogencarbonate (25 mL), and with brine (25 mL). The aqueous layers were combined and reextracted with diethyl ether (1 x 30 mL). The combined organic layers were dried over MgSO₄, filtered, and the solvent was evaporated in vacuo. Purification of the residue by automated chromatography on silica gel (3–20% EtOAc in isohexane, 90 min) provided [α-D]-1 (671 mg, 4.32 mmol, 74% over two steps) as colorless crystalline solid [CAS 114838-30-1].

IR (ATR) ν = 3081, 3054, 3012, 2965, 2926, 2866, 2230, 1954, 1920, 1806, 1732, 1699, 1612, 1591, 1570, 1542, 1502, 1433, 1403, 1349, 1275, 1184, 1127, 1015, 993, 966, 950, 894, 860, 818, 747, 690, 616 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 5.35 (s, 1 H), 5.88 (t [1:1:1], J = 2.4 Hz, 1 H), 7.43–7.49 (m, 2 H), 7.65 (dd, J = 8.5, 1.6 Hz, 1 H), 7.76 (s, 1 H), 7.79–7.83 (m, 3 H); ¹³C NMR and DEPT (151 MHz, CDCl₃): δ = 114.17 (CH), 123.30 (CH), 126.05 (CH), 126.38 (CH), 126.48 (CH), 127.81 (CH), 128.19 (CH), 128.29 (CH), 133.27 (C), 133.42 (C), 135.00 (C), 135.76 (l [1:1:1], J = 23.7 Hz, C), MS (EI): m/z (%) = 155 (100, [M⁺]), 154 (81), 153 (51), 152 (24), 128 (12), 76 (15); MS (ESI, +25 V): 156.1 [M+H⁺]. According to the ¹H NMR spectrum, the deuterium content was 88%.

The spectroscopic data are in agreement with those reported.[3,4]

2.2 Synthesis of 2-(Naphthalen-2-yl)oxirane (9)

Compound 9 was prepared according to a literature procedure.[3] Meta-chloroperbenzoic acid (948 mg, 5.49 mmol) was added to a mixture of 2-vinylnaphthalene (1) (502 mg, 3.25 mmol) and sodium hydrogen carbonate (273 mg, 3.25 mmol) in CH₂Cl₂ (20 mL). The reaction mixture was vigorously stirred at room temperature under ambient air for 17 h. Then, the reaction mixture was transferred to a separating funnel with ethyl acetate (30 mL) and washed with an aqueous solution of sodium metabisulfite (5%, 2 x 50 mL), with sodium hydrogencarbonate solution (5%, 4 x 50 mL), and with brine (50 mL). The organic layer was dried over MgSO₄, filtered, and the solvent was removed in vacuum to provide the epoxide 9 (504 mg, 2.96 mmol, 91%) as colorless solid [CAS 20861-99-8].

IR (ATR) ν = 3051, 2982, 2909, 1914, 1838, 1732, 1687, 1652, 1600, 1571, 1554, 1505, 1469, 1398, 1363, 1335, 1273, 1242, 1214, 1119, 1076, 1017, 979, 949, 892, 863, 842, 819, 784, 744, 695, 651, 615 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 2.91 (dd, J = 5.4, 2.5 Hz, 1 H), 3.23 (dd, J = 5.4, 4.1 Hz, 1 H), 4.04 (dd, J = 3.9, 2.7 Hz, 1 H), 7.33 (dd, J = 8.5, 1.6 Hz, 1 H), 7.45–7.52 (m, 2 H), 7.80–7.86 (m, 4 H); ¹³C NMR and DEPT (126 MHz, CDCl₃): δ = 51.44 (CH₂), 52.77 (CH), 122.79 (CH), 125.32 (CH), 126.22 (CH), 126.50 (CH), 127.91 (2 CH), 128.54 (CH), 133.35 (C), 133.48 (C), 135.20 (C); MS (EI): m/z (%) = 170 (25, [M⁺]), 142 (20), 141 (100), 139 (15), 115 (39); elemental analysis (%) calcd for C₁₂H₁₀O: C 84.68, H 5.92; found: C 84.45, H 6.13.

The spectroscopic data are in agreement with those reported.[3,5]
3 Variation of Hydrosilanes in the Wacker-type Oxidation of 2-Vinylnaphthalene (1)

3.1 Spectroscopic Data of the Observed Ethoxysilanes and Silanoles

Tetraethoxysilane (5d) [CAS 78-10-4]

\[
\text{\begin{tikzpicture}
  \node[shape=circle,fill=white,draw=black] (a) at (0,0) {\text{O}};
  \node[shape=circle,fill=white,draw=black] (b) at (0,-0.5) {\text{O}};
  \node[shape=circle,fill=white,draw=black] (c) at (0,-1) {\text{O}};
  \node[shape=circle,fill=white,draw=black] (d) at (0,-1.5) {\text{O}};
  \node[shape=circle,fill=white,draw=black] (e) at (0,-2) {\text{Si}};
\end{tikzpicture}}
\]

MS (ESI, +10 V): 209.3 [M+H]^+.

Diethoxy(methyl)(phenyl)silane (5f) [CAS 775-56-4]

\[
\text{\begin{tikzpicture}
  \node[shape=circle,fill=white,draw=black] (a) at (0,0) {\text{Me}};
  \node[shape=circle,fill=white,draw=black] (b) at (0,-0.5) {\text{O}};
  \node[shape=circle,fill=white,draw=black] (c) at (0,-1) {\text{Si}};
\end{tikzpicture}}
\]

Colorless liquid. IR (ATR) \(\nu = 3071, 3051, 2972, 2922, 2879, 1592, 1457, 1430, 1390, 1258, 1164, 1101, 1072, 948, 820, 793, 765, 735, 699, 649 \text{ cm}^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.36 \text{ (s, 3 H)}, 1.24 \text{ (t, } J = 6.9 \text{ Hz, 6 H)}, 3.82 \text{ (qd, } J = 7.0, 1.4 \text{ Hz, 1.4 Hz, 4 H)}, 7.35–7.43 \text{ (m, 3 H)}, 7.62–7.67 \text{ (m, 2 H)}\); \(^13\)C NMR and DEPT (75 MHz, CDCl\(_3\)): \(\delta = -4.02 \text{ (CH}_3\text{)}, 18.49 \text{ (2 CH}_3\text{)}, 58.68 \text{ (2 CH}_2\text{)}, 127.97 \text{ (2 CH)}, 134.16 \text{ (2 CH)}, 134.97 \text{ (C)}\); MS (EI): \(m/z (\%) = 210 \text{ (6, } [M]^+\text{)}, 195 \text{ (100)}, 151 \text{ (37)}, 139 \text{ (25)}, 137 \text{ (15)}, 132 \text{ (10)}, 123 \text{ (17)}, 121 \text{ (19)}, 105 \text{ (20)}, 91 \text{ (21)}, 77 \text{ (19)}\); MS (ESI, +10 V): 211.0 [M+H]^+; elemental analysis (% calcd for C\(_{11}\)H\(_{10}\)O\(_2\)Si: C 62.81, H 8.63; found: C 62.49, H 8.84.

Ethoxy(methyl)(phenyl)silanol (6f) [CAS 65007-38-7]

\[
\text{\begin{tikzpicture}
  \node[shape=circle,fill=white,draw=black] (a) at (0,0) {\text{Me}};
  \node[shape=circle,fill=white,draw=black] (b) at (0,-0.5) {\text{O}};
  \node[shape=circle,fill=white,draw=black] (c) at (0,-1) {\text{Si}};
  \node[shape=circle,fill=white,draw=black] (d) at (0,-1.5) {\text{O}};
\end{tikzpicture}}
\]

MS (ESI, +10 V): 182.0 [M+H]^+.

Diethoxydiphenylsilane (5g) [CAS 2553-19-7]

\[
\text{\begin{tikzpicture}
  \node[shape=circle,fill=white,draw=black] (a) at (0,0) {\text{Me}};
  \node[shape=circle,fill=white,draw=black] (b) at (0,-0.5) {\text{O}};
  \node[shape=circle,fill=white,draw=black] (c) at (0,-1) {\text{Si}};
  \node[shape=circle,fill=white,draw=black] (d) at (0,-1.5) {\text{O}};
\end{tikzpicture}}
\]

Colorless solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 1.26 \text{ (t, } J = 6.9 \text{ Hz, 6 H)}, 3.88 \text{ (q, } J = 6.9 \text{ Hz, 4 H)}, 7.33–7.44 \text{ (m, 6 H)}, 7.64–7.70 \text{ (m, 4 H)}\); MS (EI): \(m/z (\%) = 272 \text{ (6, } [M]^+\text{)}, 227 \text{ (18)}, 199 \text{ (12)}, 197 \text{ (22)}, 196 \text{ (13)}, 195 \text{ (68)}, 194 \text{ (100)}, 183 \text{ (26)}, 181 \text{ (13)}, 167 \text{ (19)}, 154 \text{ (11)}, 152 \text{ (14)}, 151 \text{ (35)}, 150 \text{ (16)}, 139 \text{ (42)}, 123 \text{ (27)}, 105 \text{ (22)}, 104 \text{ (29)}, 91 \text{ (12)}, 78 \text{ (11)}, 77 \text{ (23)}\); MS (ESI, +10 V): 273.1 [M+H]^+; 290.1 [M+NH\(_4\)]^+.
Ethoxydiphenylsilanol (6g) [CAS 262360-58-7]

![Ethoxydiphenylsilanol structure]

Colorless solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 1.27$ (t, $J = 6.9$ Hz, 3 H), 2.93 (br s, 1 H), 3.90 (q, $J = 6.9$ Hz, 2 H), 7.37–7.46 (m, 6 H), 7.67–7.73 (m, 4 H); MS (EI): $m/z$ (%) = 244 (18, [M$^+$]), 200 (10), 199 (49), 197 (16), 167 (46), 166 (67), 154 (17), 152 (12), 139 (100), 123 (25), 122 (16), 121 (14), 105 (18), 104 (54), 78 (16), 77 (29), 51 (15), 45 (19).

Ethoxydimethyl(phenyl)silane (5h) [CAS 1825-58-7]

![Ethoxydimethyl(phenyl)silane structure]

Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.39$ (s, 6 H), 1.19 (t, $J = 7.0$ Hz, 3 H), 3.68 (q, $J = 7.0$ Hz, 2 H), 7.35–7.42 (m, 3 H), 7.55–7.62 (m, 2 H); MS (EI): $m/z$ (%) = 180 (8, [M$^+$]), 166 (14), 165 (100), 137 (47), 135 (24), 121 (60), 105 (16), 91 (13), 77 (11), 61 (14), 45 (14), 43 (10).

Dimethyl(phenyl)silanol (6h) [CAS 5272-18-4]

![Dimethyl(phenyl)silanol structure]

Colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.41$ (s, 6 H), 1.93 (br s, 1 H), 7.36–7.42 (m, 3 H), 7.59–7.62 (m, 2 H); MS (EI): 152 (11, [M$^+$]), 138 (12), 137 (100), 45 (14).

[3,5-Bis(trifluoromethyl)phenyl]ethoxydimethylsilane (5i) [CAS 2247633-95-8]

![3,5-Bis(trifluoromethyl)phenyl]ethoxydimethylsilane structure]

Colorless crystalline solid. $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 0.44$ (s, 6 H), 1.22 (t, $J = 6.9$ Hz, 3 H), 3.72 (q, $J = 6.9$ Hz, 2 H), 7.88 (s, 1 H), 7.98 (s, 2 H); $^{13}$C NMR and DEPT (151 MHz, CDCl$_3$): $\delta = -1.59$ (2 CH$_3$), 18.51 (CH$_3$), 59.19 (CH$_2$), 123.43 (sept, $J = 3.5$ Hz, CH), 123.73 (q, $J = 272.8$ Hz, 2 C), 130.99 (q, $J = 32.4$ Hz, 2 C), 133.32 (q, $J = 2.3$ Hz, 2 CH), 141.94 (C); $^{19}$F NMR ($^1$H) (282 MHz, CDCl$_3$): $\delta = -63.48$ (6 F).

[3,5-Bis(trifluoromethyl)phenyl]dimethylsilanol (6i) [CAS 2407615-38-5]

![3,5-Bis(trifluoromethyl)phenyl]dimethylsilanol structure]

MS (EI): $m/z$ (%) = 288 (2, [M$^+$]), 274 (17), 273 (100), 269 (11), 194 (10), 75 (10).
Ethoxy(methyl)diphenylsilane (5j) [CAS 1825-59-8]

![Chemical Structure]

Colorless solid. $^{1}H$ NMR (300 MHz, CDCl$_3$): $\delta = 0.65$ (s, 3 H), 1.23 (t, $J = 6.9$ Hz, 3 H), 3.79 (q, $J = 6.9$ Hz, 2 H), 7.34–7.43 (m, 6 H), 7.58–7.63 (m, 4 H); MS (ESI, +10 V): 243.0 [M+H]$^+$. 

Methyl(diphenyl)silanol (6j) [CAS 778-25-6]

![Chemical Structure]

Colorless solid. $^{1}H$ NMR (300 MHz, CDCl$_3$): $\delta = 0.68$ (s, 3 H), 2.40 (br s, 1 H), 7.36–7.45 (m, 6 H), 7.60–7.65 (m, 4 H); MS (ESI, +10 V): 215.2 [M+H]$^+$. 

4 Experimental Procedure for the Iron-Catalyzed Oxidation of 2-Vinynaphthalene (1)

Photographic Guide for the Oxidation of 2-Vinynaphthalene (1) with FePcF$_{16}$ as Catalyst and PhSiH$_3$ (2k) as Additive:

Figure S4. Left: Chemicals used for a catalytic run (2-vinynaphthalene [1], ethanol, triphenylsilane [2k], and FePcF$_{16}$). Middle and right: FePcF$_{16}$-catalyzed Wacker-type oxidation of 1 at room temperature with an oxygen filled balloon.

Figure S5. TLC (isohexane/EtOAc 4:1) after 30 min and after 2.5 h. Visualization was performed with anisaldehyde solution and heat.

Figure S6. Sepacore column chromatogram (5–22% EtOAc in isohexane, 90 min). Numbering: (1) Ph$_3$SiOEt (5k), (2) 1-(naphthalen-2-yl)ethanone (3), (3) Ph$_3$SiOH (6k), (4) 1-(naphthalen-2-yl)ethanol (4). Detector intensity: 5 e$^{-1}$.
5 Mechanistic Investigations

5.1 Attempted Solvolysis of Ph$_3$SiH and Ph$_3$SiOH in Ethanol

Figure S7. Kinetics of the presumed solvolysis of Ph$_3$SiH (2k) (342 mg, 1.31 mmol) in dry ethanol (10 mL) at room temperature under an atmosphere of molecular oxygen followed by $^1$H NMR spectroscopy (300 MHz). No Ph$_3$SiOH (6k) was formed, Ph$_3$SiOEt (5k) was detected only in traces after 96 h by GC-MS.

Figure S8. Kinetics of the presumed solvolysis of Ph$_3$SiOH (6k) (364 mg, 1.32 mmol) in dry ethanol (10 mL) at room temperature under an atmosphere of molecular oxygen followed by $^1$H NMR spectroscopy (300 MHz). No Ph$_3$SiOEt (5k) was formed during observation time.
5.2 Reaction of Ph₃SiH with Ethanol in the Presence of FePcF₁₆ or O(FePcF₁₆)₂

**Figure S9.** Kinetics of the reaction of Ph₃SiH (2k) (338 mg, 1.29 mmol) in dry ethanol (10 mL) at room temperature under an atmosphere of molecular oxygen followed by ¹H NMR spectroscopy (300 MHz). FePcF₁₆ (27.2 mg, 31.8 µmol) was added after 2 h and Ph₃SiOEt (5k) (red boxes) was formed immediately. Two hours after the addition of the iron complex FePcF₁₆, the blue color turned green and further to brown, indicating catalyst degradation. After 48 h, Ph₃SiOH (6k) was detected by GC-MS only in traces.

**Figure S10.** Kinetics of the reaction of Ph₃SiH (2k) (339 mg, 1.30 mmol) in dry ethanol (10 mL) at room temperature under an atmosphere of molecular oxygen followed by ¹H NMR spectroscopy (300 MHz). O(FePcF₁₆)₂ (13.5 mg, 7.81 µmol) was added after 2 h and Ph₃SiOEt (5k) was formed immediately. Two hours 2 h after the addition of O(FePcF₁₆)₂, the blue color turned green and further to brown, indicating catalyst degradation. After 48 h, Ph₃SiOH (6k) was detected by GC-MS only in traces.
5.3 Stoichiometric Reaction of O(FePcF_{16})_2 with Triphenylsilane (2k) the Absence of O_2

\[
\text{Ph}_3\text{SiH} + \text{O(FePcF}_{16}\text{)}_2 \xrightarrow{\text{EtOH, argon, rt, 2.5 h}} \text{Ph}_3\text{SiOEt} + \text{Ph}_3\text{SiOH}
\]

A solution of triphenylsilane (2k) (37.5 mg, 0.144 mmol) and O(FePcF_{16})_2 (253 mg, 0.145 mmol) in degassed absolute ethanol (5 mL) was vigorously stirred at room temperature for 2.5 hours under an atmosphere of argon. The crude mixture was directly adsorbed at silica gel and purified by automated column chromatography (3–20% EtOAc in isohexane, 90 min) to provide triphenylethoxysilane (5k) (40.3 mg, 0.132 mmol, 92%) as colorless crystals and triphenylsilanol (6k) (1.2 mg, 4.3 µmol, 3%) as colorless solid.
5.4 Reaction of Ph$_3$SiOH with Ethanol in the Presence of FePcF$_{16}$ or O(FePcF$_{16}$)$_2$

**Figure S11.** Kinetics of the reaction of Ph$_3$SiOH (6k) (360 mg, 1.30 mmol) in dry ethanol (10 mL) at room temperature under an atmosphere of molecular oxygen followed by $^1$H NMR spectroscopy (300 MHz). FePcF$_{16}$ (27.1 mg, 31.7 µmol) was added after 2 h. Ph$_3$SiOEt (5k) was not detected. Also, no catalyst degradation was observed.

**Figure S12.** Kinetics of the reaction of Ph$_3$SiOH (6k) (360 mg, 1.30 mmol) in dry ethanol (10 mL) at room temperature under an atmosphere of molecular oxygen followed by $^1$H NMR spectroscopy (300 MHz). O(FePcF$_{16}$)$_2$ (13.4 mg, 7.75 µmol) was added after 2 h. Ph$_3$SiOEt (5k) was not detected. Also, no catalyst degradation was observed.
5.5  Mechanistic Experiments Using C\textsubscript{2}D\textsubscript{5}OD as solvent

2-Vinylnaphthalene (1) (50.9 mg, 0.330 mmol), FePcF\textsubscript{16} (14.0 mg, 16.4 μmol), and Ph\textsubscript{3}SiH (170 mg, 0.653 mmol) were added to a 25 mL round-bottom flask, which was flame-dried in high vacuum. The flask was degassed and filled five times with argon and finally set under vacuum. A balloon filled with oxygen was placed on the flask followed by the addition of C\textsubscript{2}D\textsubscript{5}OD (5 mL, 99% D content). The solution was vigorously stirred at room temperature for 2.5 h. The crude mixture was purified by column chromatography on silica gel (5–22% EtOAc in isohexane, 90 min) to provide 3 (31.4 mg, 0.185 mmol, 56%) as colorless solid, 4 (3.6 mg, 20.9 μmol, 6%) as colorless solid, \([\text{D}_5\text{-ethoxytriphenylsilane}]\) (184 mg, 0.595 mmol, 91%) as a colorless crystalline solid, and 6k (13.4 mg, 48.5 μmol, 7%) as colorless solid.

D\textsubscript{5}-Ethoxytriphenylsilane ([D\textsubscript{5}]\textsuperscript{-5k}) [CAS none]

![](image)

\(^1\text{H}\) NMR (600 MHz, CDCl\textsubscript{3}): δ = 7.37–7.41 (m, 6 H), 7.43–7.46 (m, 3 H), 7.62–7.66 (m, 6 H); \(^{13}\text{C}\) NMR and DEPT (151 MHz, CDCl\textsubscript{3}): δ = 127.98 (6 CH), 130.10 (3 CH), 134.59 (3 CH), 135.52 (6 C) (the carbon atoms of the ethoxy side chain were not observed); MS (EI): \(m/z\)% = 309 (63, [M]+), 259 (12), 233 (21), 232 (100), 231 (30), 230 (43), 200 (46), 198 (16), 197 (13), 185 (26), 184 (100), 183 (13), 182 (37), 181 (43), 180 (14), 156 (13), 155 (71), 154 (22), 153 (15), 152 (15), 125 (17), 105 (18), 79 (11), 78 (15), 77 (31), 51 (17), 46 (11); MS (ESI, +10 V): 310.1 [M+H]+.

5.6  Interception of the Intermediate Benzylic Radical using TEMPO as Radical Scavenger

A mixture of 2-vinylnaphthalene (1) (102 mg, 0.66 mmol), FePcF\textsubscript{16} (27.6 mg, 32.2 μmol), \((2,2,6,6\text{-tetramethylpiperidin-1-yl})oxyl\) (7) (1.01 g, 6.48 mmol), and Et\textsubscript{3}SiH (156 mg, 1.34 mmol) was stirred in EtOH (10 mL) at room temperature and under air for 6 h. Removal of the solvent under reduced pressure and purification of the residue by automated column chromatography on silica gel (1–3%, 45 min; 3–15%, 45 min; EtOAc in isohexane) afforded interception product 8 (123.5 mg, 0.397 mmol, 60%) as a colorless solid, and recovered starting material 1 (40.2 mg, 0.495 mmol, 39%).
2,2,6,6-Tetramethyl-1-[1-(2-naphthyl)]ethoxy|piperidine (8) [CAS 178625-98-4]

IR (ATR) v = 3051, 3004, 2974, 2933, 2912, 2866, 2155, 1954, 1924, 1726, 1600, 1507, 1455, 1444, 1397, 1374, 1361, 1308, 1281, 1254, 1209, 1172, 1128, 1053, 1018, 982, 951, 928, 892, 790, 773, 746, 698, 665, 619 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 0.62 (br s, 3 H), 1.04 (br s, 3 H), 1.21 (br s, 3 H), 1.30 (br s, 1 H), 1.34 (br s, 3 H), 1.37 (br s, 2 H), 1.51 (br s, 2 H), 1.56 (d, J = 6.8 Hz, 3 H), 1.57 (br s, 1 H), 4.94 (q, J = 6.7 Hz, 1 H), 7.42–7.48 (m, 2 H), 7.51 (dd, J = 8.5, 1.7 Hz, 1 H), 7.71 (d, J = 0.8 Hz, 1 H), 7.80–7.84 (m, 3 H); ¹³C NMR and DEPT (151 MHz, CDCl₃): δ = 17.36 (CH₂), 20.49 (2 CH₃), 23.79 (CH₃), 34.47 (2 CH₃), 40.50 (2 CH₂), 59.78 (2 C), 83.54 (CH), 125.09 (CH), 125.30 (CH), 125.51 (CH), 125.92 (CH), 127.78 (CH), 127.89 (CH), 128.05 (CH), 132.79 (C), 133.38 (C), 143.43 (C); MS (EI) m/z (%): 311 (2, [M⁺]), 310 (5), 197 (2), 155 (100), 154 (18), 153 (17), 152 (8), 128 (10), 115 (8); elemental analysis (%) calcd for C₂₁H₂₉NO: C 80.98, H 9.38, N 4.50; found: C 80.70, H 9.16, N 4.18.

5.7 Examination of a Presumed Radical Chain Mechanism

Using AIBN (azobisisobutyronitrile): A solution of 1 (100 mg, 0.648 mmol), AIBN (11.6 mg, 70.6 μmol), and Et₃SiH (153 mg, 1.32 mmol) in dried and degassed ethanol (10 mL) was heated at 60 °C under an atmosphere of oxygen for 6 h. Purification of the crude mixture (silica gel; 5–22% EtOAc in isohexane, 90 min) provided only 1 (84.0 mg, 0.545 mmol, 84%).

Using DBPO (dibenzoyl peroxide): A solution of 1 (101 mg, 0.655 mmol), dibenzoyl peroxide (15.6 mg, 64.4 μmol), and Et₃SiH (156 mg, 1.34 mmol) in dried and degassed ethanol (10 mL) was heated at 60 °C under an atmosphere of oxygen for 6 h. Purification of the crude mixture (silica gel; 5–22% EtOAc in isohexane, 90 min) provided only 1 (44.1 mg, 0.286 mmol, 44%).

5.8 Reaction Using Et₃SiD as Reductive Additive

Removal of the solvent under reduced pressure and purification of the crude residue by automated chromatography on silica gel (5–22% EtOAc in isohexane, 90 min) provided [D⁻]⁻-3 (84.1 mg, 0.491 mmol, 75%), and [D⁻]-4 (14.0 mg, 80.8 μmol, 12%) as colorless solids. The ¹H and ¹³C NMR data for both compounds are in agreement with those reported by us previously.[3, 6]
The \(^1\)H NMR analysis confirmed for the twofold deuterated alcohol a deuterium-content with a ratio of H/D 19:1 at the benzylic position.

2-Deutero-1-(naphthalen-2-yl)ethanone ([D\(_1\)]-3) [CAS 156053-95-1]

![Chemical Structure]

IR (ATR) \(\nu = 3319, 3308, 2990, 1844, 1735, 1698, 1667, 1627, 1594, 1463, 1395, 1363, 1348, 1295, 1214, 1186, 1140, 1122, 1057, 1013, 964, 944, 900, 868, 829, 752, 663, 615 \text{ cm}^{-1}\); \(^1\)H NMR (CDCl\(_3\), 500 MHz); \(\delta = 2.71 (t \ [1:1:1], J = 2.1, 2 \text{ Hz}, 2 \text{ H}), 7.54–7.58 (m, 1 \text{ H}), 7.58–7.63 (m, 1 \text{ H}), 7.86–7.91 (m, 2 \text{ H}), 7.97 (d, \ J = 8.2 \text{ Hz}, 1 \text{ H}), 8.04 (dd, \ J = 8.5, 1.6 \text{ Hz}, 1 \text{ H}), 8.47 (s, 1 \text{ H}); \(^1\)C NMR (CDCl\(_3\), 126 MHz); \(\delta = 26.58 (t \ [1:1:1], \ J = 19.4 \text{ Hz}, \text{ CH}), 124.02 (\text{ CH}), 126.91 (\text{ CH}), 127.92 (\text{ CH}), 128.55 (\text{ CH}), 128.60 (\text{ CH}), 129.68 (\text{ CH}), 130.33 (\text{ CH}), 132.65 (\text{ C}), 133.45 (\text{ C}), 143.29 (\text{ C}); \text{ MS (EI)}: m/z (%) = 171 (47, [M] +), 155 (99), 127 (100), 126 (23), 77 (12); \text{ MS (ESI, +10 V)}: 172.2 [M+H].

The \(^1\)H NMR spectrum confirmed a deuterium incorporation of 98%.

2-Deutero-1-(naphthalen-2-yl)ethanol ([D\(_1\)]-4) [CAS 2170825-97-3]

![Chemical Structure]

IR (ATR) \(\nu = 3454, 3308 (\text{ br}), 3052, 3020, 2967, 2924, 2848, 2733, 2178, 2056, 2030, 2009, 1953, 1918, 1844, 1773, 1724, 1652, 1599, 1494, 1467, 1402, 1363, 1292, 1273, 1161, 1139, 1120, 1051, 949, 896, 860, 821, 772, 740, 680, 639 \text{ cm}^{-1}\); \(^1\)H NMR (CDCl\(_3\), 500 MHz); \(\delta = 1.57 (d_7, \ J = 6.5, 1.8 \text{ Hz}, 2 \text{ H}), 1.98 (\text{ br s}, 1 \text{ H}, \text{ OH}), 5.07 (t, \ J = 6.5 \text{ Hz}, 1 \text{ H}), 7.45–7.52 (m, 3 \text{ H}), 7.80–7.85 (m, 4 \text{ H}); \(^1\)C NMR (CDCl\(_3\), 126 MHz); \(\delta = 24.97 (t \ [1:1:1], \ J = 19.1 \text{ Hz}, \text{ CH}), 70.66 (\text{ CH}), 123.94 (\text{ CH}), 125.94 (\text{ CH}), 126.30 (\text{ CH}), 127.80 (\text{ CH}), 128.06 (\text{ CH}), 128.46 (\text{ CH}), 133.04 (\text{ C}), 133.45 (\text{ C}), 143.29 (\text{ C}); \text{ MS (EI)}: m/z (%) = 173 (37, [M] +), 157 (42), 155 (13), 129 (100), 128 (59), 127 (33), 126 (11), 44 (11).

The \(^1\)H NMR spectrum confirmed a deuterium incorporation of 98%.

### 5.9 Reaction under an \(^{18}\)O\(_2\)-Atmosphere

![Chemical Structure]

2-Vinyl-naphthalene (1) (100 mg, 0.649 mmol), FePcF\(_{15}\) (27.6 mg, 32.2 \text{ µmol}), and Ph\(_3\)SiH (339 mg, 1.30 mmol) were added to a 25 mL round-bottom flask, which was flame-dried in high vacuum. The flask was filled five times with argon and finally set under vacuum. A balloon filled with \(^{18}\)O\(_2\) (content 97.17%) was placed on the flask followed by the addition of dry ethanol (5.18 mL) and round-bottom flask. The solution was vigorously stirred at room temperature for 3 h. The crude product was purified by column chromatography on silica gel (5–22% EtOAc in isohexane, 90 min) to provide \([^{18}\text{O}]-3\) (93.0 mg, 0.540 mmol, 83%, 95% \(^{18}\)O incorporation) as a colorless solid, \([^{18}\text{O}]-4\) (12.4 mg, 71.2 \text{ µmol, 11%}, 95% \(^{18}\)O incorporation) as a colorless solid, 5k (375 mg, 1.23 mmol, 95%) as colorless crystals, and \([^{18}\text{O}]-6k\) (5.8 mg, 21 \text{ µmol, 2%}, 95% \(^{18}\)O incorporation) as a colorless solid. The \(^{18}\)O-incorporation was determined by MS (EI). The \(^1\)H and \(^13\)C NMR data for \([^{18}\text{O}]-3\) and \([^{18}\text{O}]-4\) are in agreement with those reported by us previously.\(^{[8]}\)
$^{18}$O-1-(Naphthalen-2-yl)ethanone ([$^{18}$O]-3) [CAS 3046-63-7]

\[
\text{IR (ATR)} \nu = 3269, 3058, 2993, 2962, 2919, 2846, 2138, 2056, 2030, 2009, 1917, 1844, 1793, 1771, 1734, 1717, 1699, 1673, 1642, 1595, 1459, 1425, 1392, 1360, 1290, 1190, 1125, 1066, 1015, 962, 933, 900, 868, 832, 773, 752, 653, 615 \text{ cm}^{-1}; \text{H NMR (600 MHz, CDCl}_3); \delta = 2.74 (s, 3 H), 7.56 (dd, J = 8.2, 6.8, 1.2 Hz, 1 H), 7.61 (ddd, J = 8.2, 6.8, 1.2 Hz, 1 H), 7.89 (t, J = 9.0 Hz, 1 H), 8.04 (dd, J = 8.7, 1.9 Hz, 1 H), 8.47 (s, 1 H);
\]

$^{13}$C NMR and DEPT (151 MHz, CDCl$_3$): $\delta =$ 26.85 (CH$_3$), 124.04 (CH), 125.23 (CH), 127.51 (CH), 128.57 (CH), 128.62 (CH), 129.70 (CH), 130.35 (CH), 134.63 (C), 135.74 (C), 198.23 (C=O);

$^{18}$O-Triphenylsilanol ([$^{18}$O]-6k) [CAS 2244602-13-7]

\[
\text{IR (ATR)} = 3220 (br), 3067, 3008, 2952, 2924, 2850, 1964, 1888, 1825, 1772, 1726, 1589, 1470, 1457, 1426, 1267, 1187, 1117, 1070, 1026, 997, 818, 738, 709, 694 \text{ cm}^{-1}; \text{H NMR (600 MHz, CDCl}_3); \delta = 2.52 (br s, 1 H), 7.37–7.41 (m, 6 H), 7.43–7.47 (m, 3 H), 7.62–7.65 (m, 6 H); \text{C NMR and DEPT (151 MHz, CDCl}_3); \delta = 128.08 \text{ (CH), 130.29 (3 CH), 135.13 (6 CH), 135.26 (3 C); MS (EI): } m/z (\%) = 278 \text{ (28, [M]+), 277 (15), 276 (50), 202 (10), 201 (56), 199 (100), 198 (10), 197 (16), 181 (17), 152 (16), 122 (17), 78 (16), 77 (36), 51 (21).}
\]

5.10 Reaction Using Et$_3$SiD as Reductive Additive under an $^{18}$O$_2$-Atmosphere

2-Vinylnaphthalene (1) (50.2 mg, 0.326 mmol), and FePcF$_{16}$ (14.1 mg, 16.5 μmol) were added to a 25 mL round-bottom flask, which was flame-dried in high vacuum. The flask was degassed and filled five times with argon and finally set under
vacuum. A balloon filled with $^{18}$O$_2$ (content 97.17%) was placed on the flask followed by the addition of dried (water content 6.5 ppm determined by Karl-Fischer titration) and degassed ethanol (5 mL), and Et$_3$SiD (88.4 mg, 0.754 mmol, 98% D content) via syringe. The solution was vigorously stirred at room temperature for 6 h. The crude product was purified by column chromatography on silica gel (5–22% EtOAc in isohexane, 90 min) to afford [D$_4$]$_3$[16]O-3 (43.9 mg, 0.253 mmol, 78%, 90% $^{16}$O incorporation) as a colorless solid and [D$_3$]$^{18}$O-4 (6.3 mg, 36 µmol, 11%, 88% $^{16}$O incorporation) as a colorless solid. Unlabelled ethoxytriethysilane was detected by MS (EI). The $^{16}$O-incorporation was determined by MS (EI).

The $^1$H NMR analysis confirmed for the twofold deuterated alcohol a deuterium-content with a ratio of H/D to be 10:1 at the benzylic position.

D$_1$-$^{16}$O-1-(Naphthalen-2-yl)ethanone ([D$_1$]$^{16}$O-3) [CAS none]

IR (ATR) $\nu = 3263, 3058, 2989, 2919, 2846, 2132, 2056, 2030, 2009, 1843, 1771, 1734, 1717, 1699, 1671, 1639, 1594, 1576, 1462, 1421, 1395, 1363, 1347, 1331, 1294, 1215, 1186, 1140, 1122, 1058, 1012, 963, 944, 899, 868, 829, 796, 753, 646, 613 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 2.71$ (t [1:1:1], $J = 2.1, 2$ Hz), 7.56 (ddd, $J = 8.2, 6.9, 1.2$ Hz, 1 H), 7.61 (ddd, $J = 8.2, 6.9, 1.2$ Hz, 1 H), 7.89 (t, $J = 9.2$ Hz, 2 H), 7.97 (d, $J = 7.9$ Hz, 1 H), 8.04 (dd, $J = 8.4, 1.4$ Hz, 1 H), 8.47 (s, 1 H); $^{13}$C NMR and DEPT (151 MHz, CDCl$_3$): $\delta = 26.60$ (t [1:1:1], $J = 19.7$ Hz, CH$_3$), 124.04 (CH), 126.92 (CH), 127.93 CH), 128.57 (CH), 128.62 (CH), 129.70 (CH), 130.35 (CH), 132.66 (C), 134.63 (C), 135.74 (C), 198.27 (C=O). MS (EI): $m/z$ (%) = 173 (38, [M$^+$]), 171 (4), 158 (28), 157 (74), 155 (10), 128 (35), 127 (100), 126 (28), 77 (12), 75 (13), 74 (11), 46 (15). MS (ESI, +10 V): 174.0 [M+H$^+$].

The $^1$H NMR spectrum confirmed a deuterium incorporation of 98%.

D$_1$-$^{16}$O-1-(Naphthalen-2-yl)ethanol ([D$_1$]$^{16}$O-4) [CAS none]

IR (ATR) $\nu = 3293$ (br), 3052, 3021, 2965, 2928, 2869, 2185, 2056, 2030, 2003, 1947, 1917, 1725, 1599, 1498, 1455, 1403, 1363, 1274, 1169, 1120, 1047, 949, 898, 860, 821, 772, 740, 619 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 1.57$ (dt, $J = 6.4, 1.9$ Hz, 2 H), 5.08 (t, $J = 6.4$ Hz, 1 H), 7.45–7.50 (m, 2 H), 7.51 (dd, $J = 8.5, 1.7$ Hz, 1 H), 7.81–7.86 (m, 4 H) (the chemical shift of the OH group was not determined due to overlapping with the CH$_2$D group); $^{13}$C NMR and DEPT (151 MHz, CDCl$_3$): $\delta = 25.01$ (t [1:1:1], $J = 19.7$ Hz, CH$_3$), 70.65 (CH), 123.95 (CH), 123.96 (CH), 125.95 (CH), 126.31 (CH), 127.82 (CH), 128.08 (CH), 128.48 (CH), 133.06 (C), 134.46 (C), 143.30 (C); MS (EI): $m/z$ (%) = 175 (31, [M$^+$]), 173 (4), 159 (26), 129 (100), 128 (44), 127 (27), 126 (11).

Triethylthoxysilane (5a) [CAS 18023-47-7]

MS (EI): 160 (4, [M$^+$]), 131 (100), 103 (70), 87 (16), 75 (21), 59 (10), 45 (11).
5.11 Reaction with [α-D]-1 as Substrate

Using Et$_3$SiH: Deuterated 2-vinylnaphthalene ([α-D]-1) (104 mg, 0.670 mmol), and FePcF$_{16}$ (28.6 mg, 33.4 μmol) were added to a 25 mL round-bottom flask. The flask was sealed with a septum, filled with oxygen using a balloon, and dried and degassed ethanol (10 mL) was added. Then, Et$_3$SiH (156 mg, 1.34 mmol) was added via syringe and the solution was vigorously stirred at room temperature under an atmosphere of oxygen for 6 h. The crude product was purified by automated column chromatography on silica gel (5–22% EtOAc in isohexane, 90 min) to provide 3 (78.8 mg, 0.463 mmol, 69%), and 4 (16.4 mg, 95.2 mmol, 14%). The $^1$H NMR (300 MHz) spectrum of the alcohol [α-D]-4 confirmed at the benzylic position a ratio of hydrogen to deuterium of 19/81.

Using Ph$_3$SiH: Deuterated 2-vinylnaphthalene ([α-D]-1) (102 mg, 0.657 mmol), FePcF$_{16}$ (28.6 mg, 33.4 μmol), and Ph$_3$SiH (345 mg, 1.33 mmol) were added to a 25 mL round-bottom flask. The flask was sealed with a septum, filled with oxygen using a balloon, and dried and degassed ethanol (10 mL) was added. The solution was vigorously stirred under an atmosphere of oxygen at room temperature for 2.5 h. The crude product was purified by column chromatography on silica gel (5–22% EtOAc in isohexane, 90 min) to provide 3 (80.9 mg, 0.475 mmol, 72%), [α-D]-4 (15.5 mg, 89.5 μmol, 14%), 5k (367 mg, 1.21 mmol, 91%), and 6k (7.3 mg, 26 μmol, 2%). The $^1$H NMR (300 MHz) spectrum of the alcohol [α-D]-4 confirmed at the benzylic position a ratio of hydrogen to deuterium of 15/85.

5.12 Iron-Catalyzed Reduction of the Ketone 3 with Et$_3$SiD to the Alcohol [α-D]-4

A reaction of 3 (111 mg, 0.652 mmol), FePcF$_{16}$ (28.3 mg, 33.1 μmol), and Et$_3$SiD (162 mg, 1.38 mmol, 98% D content) was performed in dried and degassed ethanol (10 mL). The solution was vigorously stirred at room temperature under an atmosphere of oxygen using a balloon. After 6 h reaction time, the crude mixture was directly adsorbed on silica gel and purified by automated column chromatography (5–22% EtOAc in isohexane, 90 min) to provide [α-D]-4 (5.0 mg, 29 μmol). Ketone 3 was reisolated in 89% (98.4 mg, 0.578 mmol).

The $^1$H NMR and the $^{13}$C NMR data and the mass shift of +1 in the MS (EI) for [α-D]-4 are in agreement with those described above (see 2.1). The $^1$H NMR (300 MHz) spectrum of the alcohol [α-D]-4 confirmed at the benzylic position a ratio of hydrogen to deuterium of 2/98.
5.13  Examination of a Presumed Meinwald Rearrangement

A solution of 9 (111 mg, 0.652 mmol), FePcF16 (27.9 mg, 32.6 μmol), and Et3SiH (153 mg, 1.32 mmol) in ethanol (10 mL) was stirred at room temperature under an atmosphere of oxygen for 6 h. After evaporation of the solvent in vacuum, the crude reaction mixture was purified by automated column chromatography (silica gel; 5–22 % EtOAc in isohexane) to afford only starting material in 39 % (43.3 mg, 0.254 mmol). Neither compound 3 nor compound 4 were formed.
# Mössbauer Spectroscopy

Table S2. Mössbauer measurements of FePcF$_{16}$ and O(FePcF$_{16}$)$_{2}$ for different samples. The collected data show consistency for different samples of FePcF$_{16}$ and of O(FePcF$_{16}$)$_{2}$.

| Sample                              | T [K] | $\Delta E_{Q1}$ [mm s$^{-1}$] | $\Delta E_{Q2}$ [mm s$^{-1}$] | $\Delta E_{Q3}$ [mm s$^{-1}$] | $\delta_1$ [mm s$^{-1}$] | $\delta_2$ [mm s$^{-1}$] | $\delta_3$ [mm s$^{-1}$] | $A_1$ [%] | $A_2$ [%] | $A_3$ [%] |
|-------------------------------------|-------|-------------------------------|-------------------------------|-------------------------------|-------------------------|-------------------------|-------------------------|----------|----------|----------|
| FePcF$_{16}$ Sample 1               | 300   | 1.754(12)                     | 0.769(8)                      | 2.599(37)                     | 0.203 (15)             | 0.382(12)               | 0.402(18)               | 11.8(3)  | 83.8(3)  | 2.4(3)   |
| FePcF$_{16}$ Sample 2               | 299   | 1.686(25)                     | 0.824(7)                      | 2.559(8)                      | 0.209(14)              | 0.364(13)               | 0.401(14)               | 18.1(9)  | 71.1(9)  | 10.8(9)  |
| O(FePcF$_{16}$)$_{2}$ Sample 3      | 299   | 1.650(5)                      | 0.715(4)                      | –                             | 0.097(13)              | 0.352(12)               | –                       | 40.44(36) | 59.56(36) | –        |
| FePcF$_{16}$ in ethanol Sample 4     | 90.5  | 1.519(5)                      | 0.665(4)                      | 2.530(33)                     | 0.248(13)              | 0.448(12)               | 0.449(25)               | 41.9(4)  | 53.2(3)  | 4.9(10)  |
| O(FePcF$_{16}$)$_{2}$ Sample 5      | 295   | 1.493(8)                      | 0.665(2)                      | –                             | 0.092(14)              | 0.330(14)               | –                       | 33.3(4)  | 66.7(4)  | –        |
|                                     | 90.5  | 1.427(4)                      | 0.551(4)                      | –                             | 0.175(15)              | 0.383(10)               | –                       | 64.33(12) | 35.67(12) | –        |
| FePcF$_{16}$ Sample 6               | 295   | 1.691(20)                     | 0.817(7)                      | 2.546(12)                     | 0.192(20)              | 0.367(13)               | 0.409(16)               | 19.7(7)  | 71.4(7)  | 8.9(15)  |
|                                     | 90.5  | 1.672(8)                      | 0.762(4)                      | 2.606(5)                      | 0.274(13)              | 0.448(12)               | 0.492(13)               | 28.1(4)  | 59.1(4)  | 12.8(4)  |
| O(FePcF$_{16}$)$_{2}$ in ethanol Sample 7 | 77    | 1.580(10)                     | 0.469(25)                     | –                             | 0.192(15)              | 0.353(25)               | –                       | 64.7(10) | 35.3(10) | –        |
| O(FePcF$_{16}$)$_{2}$ Sample 5      | 295   | 1.479(4)                      | 0.666(5)                      | –                             | 0.095(12)              | 0.332(11)               | –                       | 33.9(3)  | 66.1(3)  | –        |
|                                      |       |                               |                               |                               |                        |                        |                         |          |          |          |
| FePcF$_{16}$ Sample 6 (after 14 days) | 295   | 1.671(10)                     | 0.807(4)                      | 2.53(5)                       | 0.192(15)              | 0.364(12)               | 0.401(13)               | 19.8(5)  | 70.9(4)  | 9.3(6)   |
| Reaction 10 min Sample 10           | 90    | 1.66(8)                       | 0.78(4)                       | 2.61(4)                       | 0.20(4)                | 0.452(23)               | 0.452(28)               | 32.1(29) | 36.5(3)  | 10.9(25) |
| Reaction 1 day Sample 11             | 90    | 1.692(12)                     | 0.79(8)                       | 2.39(12)                      | 0.162(15)              | 0.473(14)               | 0.427(15)               | 32.3(10) | 41.1(8)  | 23.0(9)  |
Figure S16. Temperature-dependent Mössbauer spectroscopy of the complex O(FePcF$_{16}$)$_2$ from 299 K to 15 K.
The O(FePcF₁₆)₂ powder spectra shown in Figure S16 for the temperature range 299 K to 15 K show two signals, both exhibit quadrupole splitting. At room temperature signal 1 has a quadrupole splitting of $\Delta E_Q = 1.650(5)$ mm s⁻¹, an isomer shift of $\delta = 0.097(13)$ mm s⁻¹, and a proportion of $A = 40.44(36)\%$. Signal 2 has a quadrupole splitting of $\Delta E_Q = 0.715(4)$ mm s⁻¹, an isomer shift of $\delta = 0.352(13)$ mm s⁻¹, and a proportion of $A = 59.56(36)\%$.

With decreasing temperature, signal 1 increases whereas signal 2 decreases. At 15 K, signal 1 dominates the spectrum with a proportion of $A = 88.8(11)\%$. On reheating to 299 K the first spectrum is reproduced.

For O(FePcF₁₆)₂ both iron atoms have the same chemical surrounding and thus, only one signal for iron is expected. However, two signals are observed. The large temperature dependence of the proportions of the signals 1 and 2 obtained from the O(FePcF₁₆)₂ powder spectra depicted in Figure S16 indicates a reversible temperature-dependent transition from one signal to the other. Alternatively, the Debye–Waller factor and hence the intensity of signal 1 could have a considerably stronger temperature dependence than signal 2. To estimate the effect of the strong temperature dependence of signal 1, the Debye–Waller factor for signal 2 can be assumed as temperature-independent. As the proportion of signal 1 is given by the quotient of the area of signal 1 ($a_1$) by the total area, one can calculate the increase in $a_1$ from $A = 40.44(36)\%$ at 299 K to $A = 88.8(11)\%$ at 15 K.

\[ A_1 = \frac{a_1}{a_1 + a_2} \]
\[ a_2(T) = (A_1(T)^{-1} - 1) \cdot a_1(T) \]
\[ a_1(15 \text{ K}) = \frac{(A_1(299 \text{ K})^{-1} - 1)}{(A_1(299 \text{ K})^{-1} - 1)} \]

From the value $\frac{a_1(15 \text{ K})}{a_1(299 \text{ K})} \approx 3$, an increase in overall resonant proportion of at least $11 \times 0.4044 + 0.5956 \approx 5$ is calculated, considerably larger than the actual increase of $\approx 3$. Additionally, the second signal would have some increase in resonant proportion, further increasing the overall signal. Hence, different Debye–Waller factor temperature dependencies can be ruled out as source of the development of signal proportions. Both signals are consistent with iron in the oxidation state of $+III$. A reversible temperature-dependent transition may be caused by spin crossover or structural change of the investigated molecules. The magnetic susceptibility shows a linear behaviour for the temperature range investigated by Mössbauer spectroscopy (Figure 4), thus ruling out a spin crossover as source of the reversible temperature-dependent transition. Therefore, structural changes are considered as the origin for the two signals of O(FePcF₁₆)₂. Most likely, this structural change corresponds to a transition between a linear form with a parallel alignment of the two FePcF₁₆ planes connected by the oxygen atom and a bent form (Figure S17).

![Figure S17. Structures of linear O(FePcF₁₆)₂ and bent O(FePcF₁₆)₂.](image-url)
Figure S18. Mössbauer spectra of frozen solutions ($T = 90$ K and $90.5$ K) for the reaction of 2-vinylphenalene (1), FePcF$_{16}$, and 2 equivalents of triethylsilane (2a) in ethanol under an atmosphere of oxygen after a reaction time of a) 10 min and b) 1 day. Experimental data are shown as black dots along with the overall fit (dark blue line). Contributions are shown in color as upper traces. See text for parameters.
Figure S18 shows the Mössbauer spectra of two frozen reaction solutions, one shortly after the start of the reaction (10 min) and the second one after a reaction time of 1 day, when the reaction was already finished. Four signals are observed. The first three signals are similar to the three signals observed in the ethanolic solution of FePcF₁₆. The third signal increases from A = 11.0(25) % for the 10 min-sample to A = 23.0(9) % for the 1 day-sample. The fourth signal in the 10 min-solution shows a quadrupole splitting of $\Delta E_Q = 2.83(4) \text{ mm s}^{-1}$, an isomer shift of $\delta = 1.49(4) \text{ mm s}^{-1}$, and a proportion of A = 20.5(25) %. The fourth signal in the 1 day-solution shows a quadrupole splitting of $\Delta E_Q = 2.73(5) \text{ mm s}^{-1}$, an isomer shift of $\delta = 1.67(4) \text{ mm s}^{-1}$, and a proportion of A = 3.6(12) %. The first three signals are identified as FePcF₁₆ and $[\text{FePcF₁₆}]^2$, respectively. The isomer shift of the additional observed signal 4 indicates an iron specie in the oxidation state of +II (high-spin, $S = 2$), which cannot be clearly assigned. The most significant differences between the 10 min- and 1 day-solutions are the decrease of the intensity of the fourth and the increase of the intensity of the third signal. This observation indicates that the Fe$^{+2}$-signal ($S = 2$) is produced only in presence of the substrate when the reaction is still proceeding, whereas FePcF₁₆ still remains even after the reaction is finished.

### References

1. J. G. Jones, M. V. Twigg. *Inorg. Chem.* 1969, 8, 2018–2019.
2. M. Xiao, X. Yue, R. Xu, W. Tang, D. Xue, C. Li, M. Lei, J. Xiao, C. Wang, *Angew. Chem. Int. Ed.* 2019, 58, 10528–10536; *Angew. Chem. 2019*, 131, 10638–10646.
3. F. Puls, P. Linke, O. Kataeva, H.-J. Knölker, *Angew. Chem. Int. Ed.* 2021, 60, 14083–14090; *Angew. Chem. 2021*, 133, 14202–14209.
4. T. R. Puleo, A. J. Strong, J. S. Bandar, *J. Am. Chem. Soc.* 2019, 141, 1467–1472.
5. M. W. C. Robinson, A. M. Davies, R. Buckle, I. Mabbett, S. H. Taylor, A. E. Graham, *Org. Biomol. Chem.* 2009, 7, 2559–2564.
6. F. Puls, H.-J. Knölker, *Angew. Chem. Int. Ed.* 2018, 57, 1222–1226; *Angew. Chem. 2018*, 130, 1236–1240.
7. P. Gütlich, C. Schröder, V. Schünemann, *Spectrosc. Eur.* 2012, 24, 21–32.
NMR Spectra

[α-D]-4, ¹H NMR, 600 MHz, CDCl₃
$^{13}$C NMR + DEPT, 151 MHz, CDCl$_3$
[α-D]-1, 1H NMR, 600 MHz, CDCl₃
[α-D]-1, $^{13}$C NMR + DEPT, 151 MHz, CDCl$_3$
$^1$H NMR, 500 MHz, CDCl$_3$
3. $^1$H NMR, 500 MHz, CDCl$_3$
3. $^{13}$C NMR + DEPT, 126 MHz, CDCl$_3$
4. $^1$H NMR, 500 MHz, CDCl$_3$
4, $^{13}$C NMR + DEPT, 126 MHz, CDCl$_3$
$5f$, $^1$H NMR, 300 MHz, CDCl$_3$
$^{13}$C NMR + DEPT, 75 MHz, CDCl$_3$
5g. $^1$H NMR, 300 MHz, CDCl$_3$
6g, $^1$H NMR, 300 MHz, CDCl$_3$
$5h$, $^1$H NMR, 300 MHz, CDCl$_3$
Me-Si-OH
Me
6h, $^1$H NMR, 300 MHz, CDCl$_3$
F₃C

Me-Si-O

Me

5i, ¹H NMR, 600 MHz, CDCl₃
$^{13}$C NMR + DEPT, 151 MHz, CDCl$_3$
$^{19}$F NMR ($^1$H), 282 MHz, CDCl$_3$
$\text{Si-O}$

5j. $^1\text{H NMR, 300 MHz, CDCl}_3$
6j. $^1$H NMR, 300 MHz, CDCl$_3$
5k, $^1$H NMR, 600 MHz, CDCl$_3$
$^{13}$C NMR + DEPT, 151 MHz, CDCl$_3$
$6k$. $^1$H NMR, 600 MHz, CDCl$_3$
$^{13}$C NMR + DEPT, 151 MHz, CDCl$_3$
[D$_2$]-5k, $^1$H NMR, 600 MHz, CDCl$_3$
[D₃]$_{5k}$, $^{13}$C NMR + DEPT, 151 MHz, CDCl₃
8, $^1$H NMR, 600 MHz, CDCl$_3$
8. $^{13}$C NMR + DEPT, 151 MHz, CDCl$_3$
[D₃]-3, ¹H NMR, 500 MHz, CDCl₃
[D₄]-4, 'H NMR, 500 MHz, CDCl₃
[D$_4$]-5, $^{13}$C NMR + DEPT, 151 MHz, CDCl$_3$
[\textsuperscript{18}O]-3, \textsuperscript{1}H NMR, 600 MHz, CDCl\textsubscript{3}
$[^{18}\text{O}]$-3, $^{13}\text{C}$ NMR + DEPT, 151 MHz, CDCl$_3$
[\textsuperscript{18}O]-4, \textsuperscript{1}H NMR, 600 MHz, CDCl\textsubscript{3}
[18O]-4, 13C NMR + DEPT, 151 MHz, CDCl₃
[1^18O]-6k, ^1H NMR, 600 MHz, CDCl₃
[\text{\textsuperscript{18}}\text{O}]6k, \text{\textsuperscript{13}}\text{C NMR + DEPT, 151 MHz, CDCl}_3
[D$_1$]'H$_3$]-3, $^1$H NMR, 600 MHz, CDCl$_3$
[D$_2$][^{18}O]-3, $^{13}$C NMR + DEPT, 151 MHz, CDCl$_3$
[D$_2$][$^{18}$O]-4, $^1$H NMR, 600 MHz, CDCl$_3$
[D$_2$]$_{1^{18}O}$-4, $^{13}$C NMR + DEPT, 151 MHz, CDCl$_3$