SUPPORTING INFORMATION FOR

Iron-Catalyzed Silylation of Alcohols by Transfer Hydrosilylation with Silyl Formates

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1. Experimental details...................................................................................................................... 3
   a) General considerations .............................................................................................................. 3
2. Optimization of the Reaction conditions .............................................................................. 4
3. Procedures for the transfer hydrosilylation of alcohols .................................................. 4
   a) Silylation of alcohols: general procedure for the study of the influence of the silyl
      formates (GP1) .......................................................................................................................... 4
   b) Silylation of alcohols: general procedure for the scope of the reaction (GP2)........ 4
   c) Silylation of carboxylic acids: general procedure (GP3)..................................................... 5
   d) Characterization of silyl ethers ............................................................................................... 5
   e) NMR spectra of isolated silyl ethers ....................................................................................... 11
4. Synthesis of silyl formates 2 .................................................................................................... 30
   a) Procedure for the preparation of silyl formates ................................................................. 30
   b) Characterization of silyl formates ......................................................................................... 30
   c) Procedure for the preparation of 2g .................................................................................... 31
   d) NMR spectra of isolated silyl formates ............................................................................... 33
5. Experimental mechanistic investigations ............................................................................. 39
   a) Reaction with HCOOH .......................................................................................................... 39
   b) Formation of the iron complex 22 ....................................................................................... 39
   c) Catalytic activity of the iron complex (22) ......................................................................... 40
6. Crystallography ....................................................................................................................... 41
7. References .................................................................................................................................. 42
1. Experimental details

a) General considerations
All reactions and manipulations were prepared at 20 °C in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and/or using Schlenk lines. Glassware was dried overnight at 120 °C or flame-dried under vacuum before use. $^1$H, and $^{13}$C NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. HCO$_2$H (99 %, highest grade commercially available) was obtained from Acros and degassed prior to use. Sodium formate (HCO$_2$Na) was purchased from Aldrich, finely grinded and dried at 120°C under high-vacuum for 2 hours prior to use. Chemical shifts for $^1$H and $^{13}$C NMR spectra were referenced to solvent impurities. Tetrahydrofuran (THF), $d_8$-tetrahydrofuran ($d_8$-THF) and $d_6$-benzene were dried over a sodium(0)/benzophenone mixture and vacuum-distilled before use. CD$_3$CN ($d_3$-acetonitrile), CH$_2$Cl$_2$ (DCM) and CD$_2$Cl$_2$ ($d_2$-DCM) were dried over CaH$_2$ and vacuum-distilled before use. Chlorosilanes TESCl (TES = triethylsilyl), TMSCl (TMS = trimethylsilyl), DPMSCl (DPMS = diphenylmethylsilyl), PDMSCl (PDMS = phenyldimethylsilyl), TIPSCl (TIPS = triisopropylsilyl), TBDMSCl (TBDMS = tertbutyldimethylsilyl), DMSCl$_2$ (DPMS = dimethylsilyl) and CDCl$_3$ ($d_1$-chloroform) were obtained from Aldrich and used as received. Alcohols were purchased from Aldrich and used as received.
2. Optimization of the Reaction conditions

$$\text{O} \quad \text{SiEt}_3$$

2a

+ $\text{H} \quad \text{SiEt}_3$ 3

$$\begin{array}{c}
\text{Fe(OAc)}_2 \\
(x \text{ mol%})
\end{array}$$

$$\begin{array}{c}
P(C_2H_4PPh_2)_3 \ (4) \\
(x \text{ mol%})
\end{array}$$

$\text{Solvent}$ $\text{T} \ (°C)$ $\text{t} \ [\text{h}]$ $\text{Yield} \ [\%]$ 

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$x \ (\text{mol%})$</th>
<th>Equiv. 1a</th>
<th>T $\ (°C)$</th>
<th>$t \ [\text{h}]$</th>
<th>Yield $\ [%]$</th>
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<tr>
<td>CD$_3$CN</td>
<td>5</td>
<td>1.2</td>
<td>70°C</td>
<td>1h30</td>
<td>73</td>
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<tr>
<td>C$_6$D$_6$</td>
<td>5</td>
<td>1.2</td>
<td>70°C</td>
<td>1h30</td>
<td>68</td>
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<tr>
<td>THF-$d_6$</td>
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<td>1.2</td>
<td>70°C</td>
<td>1h30</td>
<td>64</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>5</td>
<td>1.2</td>
<td>70°C</td>
<td>1h30</td>
<td>&gt;95 (97)</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>2</td>
<td>1.2</td>
<td>70°C</td>
<td>5h</td>
<td>&gt; 95</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
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<td>1.2</td>
<td>70°C</td>
<td>24h</td>
<td>(98)</td>
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<tr>
<td>CD$_2$Cl$_2$</td>
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<td>1.2</td>
<td>70°C</td>
<td>1h30</td>
<td>5</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
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<td>1.2</td>
<td>25°C</td>
<td>21h</td>
<td>(96)</td>
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<tr>
<td>CD$_2$Cl$_2$</td>
<td>2</td>
<td>1.2</td>
<td>90°C</td>
<td>1h30</td>
<td>(99)</td>
</tr>
</tbody>
</table>

Table S1: Reaction conditions: benzyl alcohol (3) (0.1 mmol), solvent (0.4 mL, 0.25 M). [a] time required to reach full conversion of 3. [b] Yields were determined by $^1$H NMR analysis of the crude mixture using mesitylene as an internal standard. Yields between brackets are isolated yields from scaled up experiments.

3. Procedures for the transfer hydrosilylation of alcohols

Caution: Formation of gases and evaporation of solvent generates high pressure in a sealed tube!

a) Silylation of alcohols: general procedure for the study of the influence of the silyl formates (GP1)

In a glovebox, a flame-dried flask equipped with a J-Young valve was charged with Fe(OAc)$_2$ (1.7 mg, 0.01 mmol, 2 mol%) and P(C$_2$H$_4$PPh$_2$)$_3$ (4) (6.7 mg, 0.01 mmol, 2 mol%) followed by CH$_2$Cl$_2$ (2 mL, C = 0.25 M). To the resulting white suspension were sequentially added the alcohol (0.5 mmol, 1 equiv.) and the silyl formate (0.6 mmol, 1.2 equiv.) reagents. The flask was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 70 °C (oil temperature). A purple coloration appeared when heated. At this temperature, all the reactions were generally complete within 5h with silyl formates 2. The coloration observed turned from purple to bright orange. Yields of silyl ethers were determined by $^1$H NMR integration versus mesitylene as an internal standard or weighted after isolation and purification by column chromatography on silica gel.

b) Silylation of alcohols: general procedure for the scope of the reaction (GP2)

In a glovebox, a flame-dried flask equipped with a J-Young valve was charged with Fe(OAc)$_2$ (1.7 mg, 0.01 mmol, 2 mol%) and P(C$_2$H$_4$PPh$_2$)$_3$ (4) (6.7 mg, 0.01 mmol, 2 mol%) followed
by CH₂Cl₂ (2 mL, C = 0.25 M). To the resulting white suspension were sequentially added the alcohol (0.5 mmol, 1 equiv.) and the silyl formate (0.6 mmol, 1.2 equiv. per hydroxyl group) reagents. The flask was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 90 °C (oil temperature). A purple coloration appeared when heated. At this temperature, all the reactions were generally complete within 1h30 with silyl formates 2. The coloration observed turned from purple to bright orange. Yields of silyl ethers were determined after isolation and purification by column chromatography on silica gel.

c) Silylation of carboxylic acids: general procedure (GP3)

In a glovebox, a flame-dried flask equipped with a J-Young valve was charged with Fe(OAc)₂ (1.7 mg, 0.01 mmol, 2 mol%) and P(C₂H₄PPh₂)₃ (4) (6.7 mg, 0.01 mmol, 1 mol%) followed by CH₂Cl₂ (2 mL, C = 0.25 M). To the resulting white suspension were sequentially added the carboxylic acid (0.5 mmol, 1 equiv.) and triethylsilyl formate 2a (0.6 mmol, 1.2 equiv.). The flask was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 90 °C (oil temperature). A purple coloration appeared when heated. The coloration observed turned from purple to bright orange. At this temperature, the reactions were complete within 45 min. Yields of silyl ethers were determined after isolation and filtration through a celite pad. No other purification has been achieved due to the sensitivity of the formed silyl ester towards moisture.

The formation of the known silyl benzoate 21a was confirmed by ¹H and ¹³C NMR analysis.

d) Characterization of silyl ethers

Following the standard procedure GP1, 5a is obtained in yield 95 % ¹H NMR Yield (determined with ie mesitylene ). The analytical data are in agreement with those reported in the literature.[¹]

¹H NMR (200 MHz, d₈-THF) δ 7.27 (m, 5H), 4.68 (s, 2H), 0.12 (s, 9H).

Following the standard procedure GP2, 6a is obtained as a colorless liquid in 94 % yield (162 mg) (95:5 petroleum ether/AcOEt). The analytical data are in agreement with those reported in the literature.[²]

¹H NMR (200 MHz, d₈-THF) δ 7.64 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 4.68 (s, 2H), 0.97 (t, J = 7.8 Hz, 9H), 0.65 (q, J = 7.7 Hz, 6H).

¹³C NMR (50 MHz, d₈-THF) δ 142.39, 138.02, 128.88, 92.57, 64.64, 7.12, 5.15, 1.38.
Following the standard procedure GP2, 7a is obtained as colorless liquid in 91% yield (121 mg) (95:5 petroleum ether/AcOEt). The analytical data are in agreement with those reported in the literature.\(^3\)

\(\^3\)H NMR (200 MHz, \(d_8\)-THF) \(\delta\) 7.56 (d, \(J = 8.8\) Hz, 2H), 4.87 (s, 2H), 0.99 (t, \(J = 7.8\) Hz, 9H), 0.82 – 0.56 (m, 6H).

\(\^3\)C NMR (50 MHz, \(d_8\)-THF) \(\delta\) 150.16, 127.23, 124.06, 64.35, 7.07, 5.08.

Following the standard procedure GP2, 8a is obtained as colorless liquid in 99% yield (126 mg) (95:5 petroleum ether/AcOEt). The analytical data are in agreement with those reported in the literature.\(^4\)

\(\^1\)H NMR (200 MHz, \(d_8\)-THF) \(\delta\) 7.20 (m, 5H), 3.90 – 3.41 (m, 2H), 2.85 (dd, \(J = 13.3, 6.9\) Hz, 1H), 1.26 (d, \(J = 7.0\) Hz, 3H), 0.91 (t, \(J = 7.8\) Hz, 9H), 0.70 – 0.39 (m, 6H).

\(\^3\)C NMR (50 MHz, \(d_8\)-THF) \(\delta\) 143.55, 127.01, 126.38, 125.05, 67.79, 41.73, 16.13, 5.25, 3.22.

Following the standard procedure GP2, 9a is obtained as colorless liquid in 97% yield (115 mg) (95:5 petroleum ether/AcOEt). The analytical data are in agreement with those reported in the literature.\(^5\)

\(\^1\)H NMR (200 MHz, \(d_8\)-THF) \(\delta\) 7.19 (m, 5H), 3.79 (t, \(J = 7.0\) Hz, 2H), 2.78 (t, \(J = 7.0\) Hz, 2H), 0.92 (t, \(J = 7.9\) Hz, 9H), 0.55 (q, \(J = 8.0\) Hz, 6H).

\(\^3\)C NMR (50 MHz, \(d_8\)-THF) \(\delta\) 140.15, 129.84, 128.85, 126.76, 64.92, 40.50, 7.09, 5.11.

Following the standard procedure GP2, 10a is obtained as colorless liquid in 87% yield (101 mg) (95:5 petroleum ether/AcOEt).

\(\^1\)H NMR (200 MHz, \(d_8\)-THF) \(\delta\) 3.70 (t, \(J = 7.2\) Hz, 2H), 3.11 (s, 3H), 1.71 (t, \(J = 7.2\) Hz, 3H), 1.12 (s, 6H), 0.97 (t, \(J = 7.6\) Hz, 9H), 0.58 (dt, \(J = 8.5, 4.1\) Hz, 6H).

\(\^3\)C NMR (50 MHz, \(d_8\)-THF) \(\delta\) 73.91, 59.71, 49.06, 43.78, 25.57, 7.15, 5.15.

\(\text{HRMS (ESI)}\) \(m/z\) [M + H]\(^+\) calcd. for \(\text{C}_{12}\text{H}_{29}\text{O}_{2}\text{Si}^+\) 233.1931; found: 233.1931.

Following the standard procedure GP2, 11a is obtained as colorless liquid in 87% yield (101 mg) (95:5 petroleum ether/AcOEt).

\(\^1\)H NMR (200 MHz, \(d_8\)-THF) \(\delta\) 3.70 (t, \(J = 7.2\) Hz, 2H), 3.11 (s, 3H), 1.71 (t, \(J = 7.2\) Hz, 3H), 1.12 (s, 6H), 0.97 (t, \(J = 7.6\) Hz, 9H), 0.58 (dt, \(J = 8.5, 4.1\) Hz, 6H).

\(\^3\)C NMR (50 MHz, \(d_8\)-THF) \(\delta\) 73.91, 59.71, 49.06, 43.78, 25.57, 7.15, 5.15.

\(\text{HRMS (ESI)}\) \(m/z\) [M + H]\(^+\) calcd. for \(\text{C}_{12}\text{H}_{29}\text{O}_{2}\text{Si}^+\) 233.1931; found: 233.1931.

Following the standard procedure GP2, 11b is obtained as colorless liquid in 99% yield (125 mg) (95:5 petroleum ether/AcOEt).
$^1$H NMR (200 MHz, $d_8$-THF) $\delta$ 7.21 (t, $J = 8.0$ Hz, 2H), 6.88 (d, $J = 8.0$ Hz, 3H), 4.11 – 3.83 (m, 4H), 0.98 (t, $J = 7.8$ Hz, 9H), 0.64 (q, $J = 7.8$ Hz, 6H).

$^{13}$C NMR (50 MHz, $d_8$-THF) $\delta$ 158.26, 128.16, 119.31, 113.25, 68.13, 60.69, 5.23, 3.32.

HRMS (ESI) $m/z [M + Na]^+$ calcd. for C$_{14}$H$_{24}$O$_2$SiNa$^+$ 275.1438; found : 275.1439.

Following the standard procedure GP2, 12a is obtained as colorless liquid in 97% yield (180 mg) (95:5 petroleum ether/AcOEt). The analytical data are in agreement with those reported in the literature.$^6$

$^1$H NMR (200 MHz, $d_8$-THF) $\delta$ 5.04 – 4.63 (m, 2H), 4.03 (s, 2H), 1.67 (s, 3H), 0.97 (t, $J = 7.8$ Hz, 9H), 0.81 – 0.48 (m, 6H).

$^{13}$C NMR (50 MHz, $d_8$-THF) $\delta$ 145.56, 109.25, 19.06, 7.11, 5.16.

Following the standard procedure GP2, 13a is obtained as colorless liquid in 96% yield (110 mg) (95:5 petroleum ether/AcOEt).

$^1$H NMR (200 MHz, $d_8$-THF) $\delta$ 3.90 (dd, $J = 7.3$, 3.4 Hz, 1H), 2.01 – 1.24 (m, 12H), 0.96 (t, $J = 7.8$ Hz, 9H), 0.58 (q, $J = 7.8$ Hz, 6H).

$^{13}$C NMR (50 MHz, $d_8$-THF) $\delta$ 71.44, 36.95, 27.25, 21.43, 5.41, 3.79.

Following the standard procedure GP2, 14a is obtained as colorless liquid in 98% yield (116 mg) (95:5 petroleum ether/AcOEt). The analytical data are in agreement with those reported in the literature.$^7$

$^1$H NMR (200 MHz, $d_8$-THF) $\delta$ 7.52 – 7.04 (m, 5H), 4.89 (q, $J = 6.2$ Hz, 1H), 1.37 (d, $J = 6.3$ Hz, 2H), 0.91 (t, $J = 8.1$ Hz, 9H), 0.84 – 0.46 (m, 6H).

$^{13}$C NMR (50 MHz, $d_8$-THF) $\delta$ 146.03, 126.92, 125.62, 124.08, 69.66, 25.96, 5.29, 3.66.

Following the standard procedure GP2, 15a is obtained as colorless liquid in 73% yield (108 mg) (95:5 petroleum ether/AcOEt). The analytical data are in agreement with those reported in the literature.$^8$
$^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 7.48 – 7.09 (m, 10H), 5.76 (s, 1H), 0.88 (t, $J = 7.8$ Hz, 9H), 0.57 (q, $J = 7.7$ Hz, 6H).

$^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$ 146.23, 129.14, 127.94, 127.33, 7.79, 5.85.

Following the standard procedure GP2, 16b is obtained as white powder in 92 % yield (165 mg) (95:5 petroleum ether/AcOEt).

$^1$H NMR (200 MHz, d$_8$-THF) $\delta$ 5.59 (s, 1H), 3.58 (m, 2H), 1.89 (m, 14H), 1.20 (s, 3H), 1.12 – 0.78 (m, 4H), 0.75 (s, 3H), 0.06 (s, 9H).

$^{13}$C NMR (50 MHz, d$_8$-THF) $\delta$ 195.30, 167.91, 122.75, 80.52, 53.42, 49.26, 41.92, 37.52, 35.86, 35.00, 34.79, 32.75, 31.49, 30.85, 29.81, 22.38, 19.69, 15.74, 9.80, -1.61.

HRMS (ESI) m/z [M + H]$^+$ calcd. for C$_{14}$H$_{25}$O$_2$Si$^+$ 361.2557; found : 361.2557.

Following the standard procedure GP2, 17a is obtained as colorless liquid in 96 % yield (146 mg) (95:5 petroleum ether/AcOEt).

$^1$H NMR (200 MHz, d$_8$-THF) $\delta$ 6.74 (s, 4H), 3.68 (s, 3H), 0.99 (t, $J = 7.7$ Hz, 9H), 0.74 (q, $J = 7.7$ Hz, 6H).

$^{13}$C NMR (50 MHz, d$_8$-THF) $\delta$ 155.38, 150.07, 121.02, 115.11, 55.55, 6.98, 5.63.

HRMS (ESI) m/z [M + H]$^+$ calcd. for C$_{13}$H$_{23}$O$_2$Si$^+$ 239.1462; found : 239.1461.

Following the standard procedure GP2, 18a is obtained as colorless liquid in 90 % yield (140 mg) (95:5 petroleum ether/AcOEt).

$^1$H NMR (200 MHz, d$_8$-THF) $\delta$ 7.35 (m, 5H), 6.79 (q, $J = 9.2$ Hz, 4H), 4.96 (s, 2H), 0.99 (t, $J = 7.7$ Hz, 9H), 0.72 (q, $J = 7.7$ Hz, 6H).

$^{13}$C NMR (50 MHz, d$_8$-THF) $\delta$ 152.72, 148.47, 136.95, 127.20, 126.46, 126.29, 119.20, 114.34, 69.05, 5.14, 3.79.

HRMS (ESI) m/z [M + H]$^+$ calcd. for C$_{19}$H$_{27}$O$_2$Si$^+$ 315.1775; found : 315.1775.
Following the standard procedure GP2, **19b** is obtained as colorless liquid in 84 % yield (104 mg) (95:5 petroleum ether/AcOEt). The analytical data are in agreement with those reported in the literature.\[9\]

\[\begin{align*}
\text{H NMR (200 MHz, } \text{d}_8-\text{THF}) & \delta 7.33 \text{ (d, } J = 8.9 \text{ Hz, 2H), 6.76 \text{ (d, } J = 8.9 \text{ Hz, 2H), 0.24 \text{ (s, 9H).}} \\
\text{C NMR (50 MHz, } \text{d}_8-\text{THF}) & \delta 155.58, 133.15, 122.75, 114.39, 0.01.
\end{align*}\]

Following the standard procedure GP2, **20b** is obtained as colorless liquid in 91 % yield (121 mg) (95:5 petroleum ether/AcOEt). The analytical data are in agreement with those reported in the literature.\[3\]

Colorless oil

\[\begin{align*}
\text{H NMR (200 MHz, } \text{d}_8-\text{THF}) & \delta 7.27 \text{ (m, 5H), 4.72 \text{ (t, } J = 5.9 \text{ Hz, 1H), 3.56 \text{ (d, } J = 5.9 \text{ Hz, 2H), 0.06 \text{ (m, 18H).}} \\
\text{C NMR (50 MHz, } \text{d}_8-\text{THF}) & \delta 143.18, 128.48, 127.77, 126.94, 76.62, 69.81, 0.19, -0.57.
\end{align*}\]

Following the standard procedure GP3, **21a** is obtained as orange oil in 97 % yield (230 mg).

\[\begin{align*}
\text{H NMR (200 MHz, } \text{d}_8-\text{THF}) & \delta 8.04 \text{ (dd, } J = 8.3, 1.4 \text{ Hz, 2H), 7.72 – 7.37 \text{ (m, 3H), 1.26 – 0.68 \text{ (m, 15H).}} \\
\text{C NMR (50 MHz, } \text{d}_8-\text{THF}) & \delta 164.77, 131.81, 130.51, 128.96, 127.26, 5.08, 3.48.
\end{align*}\]
Following the standard procedure GP1, 5e is obtained in yield 95 %. \(^1\)H NMR Yield (determined with \(\text{mesitylene}\)). The analytical data are in agreement with those reported in the literature.\(^{[10]}\)

\(^1\)H NMR (200 MHz, \(\text{\(d_8\)-THF})\) \(\delta\) 7.81 – 7.47 (m, 4H), 7.50 – 7.17 (m, 10H), 4.78 (s, 2H), 0.63 (s, 3H).

Following the standard procedure GP2, 5f is obtained as colorless liquid in 99 % yield (240 mg) (95:5 petroleum ether/AcOEt). The analytical data are in agreement with those reported in the literature.\(^{[10]}\)

\(^1\)H NMR (200 MHz, \(\text{\(d_8\)-THF})\) \(\delta\) 7.73 – 7.44 (m, 2H), 7.44 – 7.13 (m, 8H), 4.71 (s, 2H), 0.39 (s, 6H).

\(^1\)C NMR (50 MHz, \(\text{\(d_8\)-THF})\) \(\delta\) 142.08, 138.60, 134.30, 133.79, 130.35, 128.84, 128.60, 128.48, 127.63, 127.07, 65.46, -1.55.

Following the standard procedure GP2, 5g is obtained as colorless liquid in 85 % yield (61 mg).

\(^1\)H NMR (200 MHz, \(\text{\(d_8\)-THF})\) \(\delta\) 7.30 – 7.10 (m, 10H), 4.76 (s, 4H), 0.16 (s, \(J = 0.7\) Hz, 6H).

\(^1\)C NMR (50 MHz, \(\text{\(d_8\)-THF})\) \(\delta\) 141.73, 128.67, 127.49, 126.96, 64.78, -3.24.
e) NMR spectra of isolated silyl ethers

\[ ^1H \quad ^{13}C \]

Figure S1: \(^1H\) and \(^{13}C\) NMR spectra of 6a in d8-THF
Figure S2: $^1$H and $^{13}$C NMR spectra of 7a in $d_8$-THF
Figure S3: $^1$H and $^{13}$C NMR spectra of 8a in d$_8$-THF
Figure S4: $^1$H and $^{13}$C NMR spectra of 9a in d$_8$-THF
Figure S5: $^1$H and $^{13}$C NMR spectra of 10a in $d_8$-THF
Figure S6: $^1$H and $^{13}$C NMR spectra of 11b in $d_8$-THF
Figure S7: $^1$H and $^{13}$C NMR spectra of 12a in d$_8$-THF
Figure S8: $^1$H and $^{13}$C NMR spectra of 13a in $d_8$-THF
Figure S9: $^1$H and $^{13}$C NMR spectra of 14a in d8-THF
Figure S10: $^1$H and $^{13}$C NMR spectra of 15a in CDCl$_3$
Figure S11: $^1$H and $^{13}$C NMR spectra of 16b in $d_8$-THF
Figure S12: $^1$H and $^{13}$C NMR spectra of 17a in $d_8$-THF
Figure S13: $^1$H and $^{13}$C NMR spectra of 18a in $d_8$-THF
Figure S14: $^1$H and $^{13}$C NMR spectra of 19b in $d_8$-THF
Figure S15: $^1$H and $^{13}$C NMR spectra of 20b in $d_8$-THF
Figure S16: $^1$H and $^{13}$C NMR spectra of 21a in $d_8$-THF
Figure S17: $^1$H NMR spectrum of 5b in d$_8$-THF

Figure S18: $^1$H NMR spectrum of 5e in d$_8$-THF
Figure S19: $^1$H NMR spectrum of 5f in d$_8$-THF
Figure S20: $^1$H and $^{13}$C NMR spectra of 5g in d$_8$-THF
4. Synthesis of silyl formates 2

a) Procedure for the preparation of silyl formates
In a glovebox, a flame-dried round bottom flask equipped with a Solv-seal connection and a J-Young valve was charged with sodium formate (42 mmol, 1.4 equiv.) and suspended in diethyl ether (30 mL, C = 1 M). To the resulting suspension was added the silyl chloride (30 mmol, 1 equiv.). The flask was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 90 °C (oil temperature). Unless otherwise stated, the reactions were generally complete within 15 h. The mixture was then filtered over a sintered glass funnel and the solvent removed by distillation under vacuum at 0 °C. No other purification was needed. The formation of silyl formate was confirmed by 1H, 13C NMR and elemental analysis.

b) Characterization of silyl formates

![silyl formate](image)

Colorless liquid
82 % isolated yield (4.1 g). It has been found that heating the reaction mixture at 50 °C (below the boiling point of the corresponding silyl chloride) was essential to obtain a significant conversion within 15 h. Moreover, removal of the solvent must be carried out at −20 °C to avoid the evaporation of the silyl formate under vacuum.

1H NMR (200 MHz, d8-THF) δ 8.01 (s, 1H), 0.28 (s, 9H).
13C NMR (50 MHz, d8-THF) δ 161.25, -0.50.

Elemental Analysis: calcd (%) for C4H10O2Si (118.2 g.mol⁻¹): C 40.64, H 8.53, found: C 40.79, H 8.50.

![silyl formate](image)

Colorless liquid
94 % isolated yield (9.4 g). The evaporation of the solvent must be carried out at 0 °C to avoid evaporation of the silyl formate under vacuum.

1H NMR (200 MHz, d8-THF) δ 8.06 (s, 1H), 0.99 (t, J = 7.6 Hz, 9H), 0.86 – 0.71 (m, 6H).
13C NMR (50 MHz, d8-THF) δ 161.30, 6.67, 5.16.

Elemental Analysis: calcd (%) for C7H16O2Si (160.3 g.mol⁻¹): C 52.45, H 10.06, found: C 52.54, H 9.61.

![silyl formate](image)

Colorless liquid
99 % isolated yield (4.95 g). Full conversion reached after 48 h at 90 °C.
\( ^1H \text{ NMR (200 MHz, } d_8\text{-THF}) \delta (s, 1H), 7.70 - 7.57 \text{ (m, 2H), 7.44 - 7.24 \text{ (m, 3H), 0.55 (s, 6H).} \)

\( ^{13}C \text{ NMR (50 MHz, } d_8\text{-THF}) \delta 159.44, 134.30, 132.50, 129.11, 126.79, -3.37. \)

**Elemental Analysis:** calcd (%) for \( C_9H_{12}O_2Si \) (180.3 g.mol\(^{-1}\)): C 59.96, H 6.71, found: C 59.40, H 6.68.

Colorless liquid
98% isolated yield (4.9 g). Full conversion reached after 48 h at 90 °C.

\( ^1H \text{ NMR (200 MHz, } d_8\text{-THF}) \delta 8.18 (s, 1H), 7.71 - 7.56 \text{ (m, 4H), 7.38 (m, 6H), 0.85 (s, 3H).} \)

\( ^{13}C \text{ NMR (50 MHz, } d_8\text{-THF}) \delta 160.88, 135.09, 134.47, 130.99, 128.53, -2.64. \)

**Elemental Analysis:** calcd (%) for \( C_{14}H_{14}O_2Si \) (243.3 g.mol\(^{-1}\)): C 69.39, H 5.82, found: C 69.03, H 5.67.

Colorless liquid
92% isolated yield (4.6 g). The evaporation of solvent must be done under 0 °C to avoid evaporation of the silyl formate under vacuum.

\( ^1H \text{ NMR (200 MHz, } d_8\text{-THF}) \delta 8.09 (s, 1H), 0.93 (s, 9H), 0.28 (s, 6H). \)

\( ^{13}C \text{ NMR (50 MHz, } d_8\text{-THF}) \delta 161.24, 25.54, 17.84, -4.63. \)

**Elemental Analysis:** calcd (%) for \( C_7H_{16}O_2Si \) (160.3 g.mol\(^{-1}\)): C 52.45, H 10.06, found: C 52.75, H 9.96.

c) **Procedure for the preparation of 2g**

In a glovebox, a flame-dried round bottom flask equipped with a Solv-seal connection and a J-Young valve was charged with sodium formate (5.8 g, 85 mmol, 3 equiv.) and dissolved in diethyl ether (30 mL, \( C = 1 \text{ M} \)). To the resulting heterogeneous solution was added the diethyldisilyl chloride (4.3 mL, 28.4 mmol, 1 equiv.). The flask was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 90 °C (oil temperature). At this temperature, the reactions were complete within 48 h. The mixture was then filtered and the solvent removed by distillation under vacuum at 0°C. No other purifications were needed.

The formation of silyl formate 2g was confirmed by \(^1H\), \(^{13}C\) NMR and elemental analysis.

Colorless liquid
94% isolated yield (4.7 g)

\( ^1H \text{ NMR (200 MHz, } d_8\text{-THF}) \delta 8.06 (s, 2H), 0.50 (s, 9H). \)
$^{13}$C NMR (50 MHz, $d_8$-THF) $\delta$ 160.23, -1.73.

**Elemental Analysis:** calcd (%) for C$_4$H$_8$O$_4$Si (148.2 g.mol$^{-1}$): C 32.42, H 5.44, found: C 32.63, H 5.56.
d) NMR spectra of isolated silyl formates

Figure S21: $^1$H and $^{13}$C NMR spectra of 2b in $d_8$-THF
$^1$H and $^{13}$C NMR spectra of 2a in $d_8$-THF

Figure S22: $^1$H and $^{13}$C NMR spectra of 2a in $d_8$-THF
Figure S23: $^1$H and $^{13}$C NMR spectra of 2f in $d_8$-THF
Figure S24: $^1$H and $^{13}$C NMR spectra of 2e in $d_8$-THF
Figure S25: $^1$H and $^{13}$C NMR spectra of 2c in d$_8$-THF
Figure S26: $^1$H and $^{13}$C NMR spectra of 2g in d$_8$-THF
5. Experimental mechanistic investigations

a) Reaction with HCOOH

\[
\begin{array}{c}
\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \\
\end{array}
\]

In a glovebox, a flame-dried 2.5-mL NMR tube equipped with a J-Young valve was charged with Fe(OAc)_2 (0.9 mg, 5 µmol, 5 mol%) and P(C_2H_4PPh_2)_3 (4) (3.4 mg, 5 µmol, 5 mol%) followed by d_2-DCM (0.4 mL, C = 0.25 M). To the resulting white suspension was added formic acid (3.8 µL, 0.1 mmol, 1 equiv.). Gas release was observed through the apparition of bubbles in the tube. The tube was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 90 °C (oil temperature). After 30 min at 90 °C, formic is completely consumed and the formation of H_2 and CO_2 is confirmed through \(^1\)H and \(^{13}\)C NMR and GC analyses.

Discussion: The catalytic dehydrogenation of formic acid under base-free conditions demonstrates the ability of the P(C_2H_4PPh_2)_3/Fe(OAc)_2 catalytic system to promote a decarboxylation path.

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b) Formation of the iron complex 22

In a glovebox, a flame-dried flask equipped with a J-Young valve was charged with Fe(OAc)_2 (42.5 mg, 0.025 mmol, 1 equiv.) and P(C_2H_4PPh_2)_3 (4) (168 mg, 0.025 mmol, 1 equiv.) followed by DCM (20 mL, C = 0.25 M). To the resulting white solution was added
triethylsilyl formate (109µL, 0.6 mmol, 2.4 equiv.). The flask was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 70 °C (oil temperature). After 4h, the volatiles were removed under reduced pressure to yield an orange powder. Single crystals suitable for X-Ray diffraction were obtained by diffusion of pentane in a solution of the crude powder in dichloromethane. The analytical data are in agreement with those reported in the literature. [11,12]

c) Catalytic activity of the iron complex (22)
In a glovebox, a flame-dried 2.5-mL NMR tube equipped with a J-Young valve was charged with 22 (0.8mg, 1 µmol, 1 mol%) and d_{2}-DCM (0.4 mL, C = 0.25 M). To the resulting white suspension was subsequently added triethylsilyl formate (22.5 µL, 0.12 mmol, 1.2 equiv.) and benzyl alcohol (10.3 µL, 0.1 mmol, 1 equiv.). The tube was then sealed, brought out of the glovebox, and immersed in a pre-heated oil bath at 90 °C (oil temperature). After 5 h at 90 °C, silyl ether 5a was formed quantitatively, thereby proving the catalytic activity of 22.

Figure S28: $^1$H NMR spectra of the crude reaction after 10 min at RT (upper spectrum) and after 5 h at 90 °C (lower spectrum)
6. Crystallography

The data for compound 22 were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer\textsuperscript{[13]} using graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). The crystal was introduced into a glass capillary with a protective coating of Paratone-N oil (Hampton Research). The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of $\varphi$- and $\omega$-scans with a minimum redundancy of 4 for 90\% of the reflections) were processed with HKL2000.\textsuperscript{[14]} Absorption effects were corrected empirically with the program SCALEPACK.\textsuperscript{[12]} The structure was solved by intrinsic phasing with SHELXT\textsuperscript{[15]} and refined by full-matrix least-squares on $F^2$ with SHELXL-2014.\textsuperscript{[16]} All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydride atom H1 was found on a difference Fourier map and it was fully refined. The hydrogen atoms bound to carbon atoms were introduced at calculated positions and they were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. The structure was refined as corresponding to a 2-component inversion twin with a Flack parameter of 0.49(2). The molecular plot was drawn with ORTEP-3.\textsuperscript{[17]} CCDC-1568433 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Crystal data for compound 22.** $C_{42}H_{43}ClFeP_4$, $M = 762.94$, orthorhombic, space group $Pca2_1$, $a = 23.1883(13)$, $b = 10.6820(6)$, $c = 14.7560(4)$ Å, $V = 3655.0(3)$ Å$^3$, $Z = 4$, $D_c = 1.386$ g cm$^{-3}$, $\mu = 0.691$ mm$^{-1}$, $F(000) = 1592$. Refinement of 438 parameters on 6637 independent reflections out of 90796 measured reflections ($R_{int} = 0.032$) led to $R_1 = 0.036$, $wR_2 = 0.100$, $S = 1.001$, $\Delta\rho_{\text{max}} = 0.35$, $\Delta\rho_{\text{min}} = -0.32$ e Å$^{-3}$. 
Figure S29 : View of complex 22. Displacement ellipsoids are drawn at the 50% probability level and carbon-bound hydrogen atoms are omitted.

7. References


