Supporting Information

For

A Rational Design for an Efficient Synthesis of a Monomeric Tin(II) Hydroxide

Anukul Jana, Sankaranarayana Pillai Sarish, Herbert W. Roesky, * Carola Schulzke and Prinson P. Samuel

(1) Experimental details and physical data

All manipulations were performed in a dry and oxygen-free atmosphere (N₂ or Ar) by using Schlenk-line and glove-box techniques. Solvents were purified with the M-Braun solvent drying system.

2: Preparation of LSn(NMe₂)Fe(CO)₄ (2). A flask was charged with 1 (5.80 g, 10.00 mmol) and Fe₂(CO)₉ (3.70 g, 10.20 mmol) in THF (140 mL). The solution was stirred for 24 h at ambient temperature. The byproduct was removed by filtration of the solution over celite, resulting in a clear pale brown filtrate. From the resulting solution the volatiles were removed, giving a pale brown solid. Crystallization of the crude product was attained by saturated THF solution of 2 and keeping it at -30 °C temperature in a freezer. 2 deposited as pale orange crystals with a composition of 2·0.5THF. Yield: 6.35 g (85%). Mp: 218 °C dec.

IR (KBr pellet): ν ~2034 s, 1957 s, 1935 s (CO) cm⁻¹. ¹H NMR (300.13 MHz, C₆D₆, 25 °C): δ 7.07-7.16 (m, 6H, ArH), 4.75 (s, 1H; γ-CH), 3.27 (sept, 2H, CH(CH₃)₂), 3.15 (sept, 2H, CH(CH₃)₂), 2.8-3.1 (br, 6H, N(CH₃)₂), 1.49 (s, 6H, CH₃), 1.42 (d, 6H, CH (CH₃)₂), 1.32 (d, 6H, CH(CH₃)₂), 1.21 (d, 6H, CH(CH₃)₂), 1.01 (d, 6H, CH(CH₃)₂) ppm. ¹³C NMR (75.46 MHz, C₆D₆, 25 °C): δ 216.40 (C=O), 169.47 (C=N), 144.86, 143.33, 141.09, 125.49, 124.74 (ArC), 99.26 (γ-C), 45.5-42.8 (br, N(CH₃)₂), 29.75 (CH₃), 28.21 (CH(CH₃)₂), 25.26 (CH(CH₃)₂), 24.94 (CH(CH₃)₂), 24.65 (CH(CH₃)₂), 24.44 (CH(CH₃)₂), 24.25 (CH(CH₃)₂) ppm. ¹¹⁹Sn NMR (111.92 MHz, C₆D₆, 25 °C): δ 94.00 ppm. EI-MS (70 eV; m/z (%)): 749 (45) [M]⁺, 705 (100) [M – NMe₂]⁻. Anal. Calcd for C₃₅H₄₇FeN₅O₄Sn (749.19): C, 56.18; H, 6.33; N, 5.62. Found: C, 56.24; H, 6.78; N, 5.51 (under vacuum THF is completely removed).
3: Preparation of L\text{Sn(OH)Fe(CO)₄} (3). Degassed water (72 μL, 4.00 mmol) was added to a solution of 2 (3.00 g, 4.00 mmol) in THF (50 mL) at -60 °C. Then, it was taken to room temperature and stirred for 1 h. Followed by removal of the solvent in a vacuum to give compound 3. 3 was washed with a small amount of \text{n-hexane} and crystallized from toluene at -32 °C to exhibit compound 3 as brown crystals. Yield: 2.10 g (73%). Mp: 233 °C dec. IR (KBr pellet): \(\tilde{v} = 3615\) s (OH), 2038 s, 1959 s, 1944 s (CO) cm\(^{-1}\). \(^1\)H NMR (300.13 MHz, \text{C}_6\text{D}_6, 25 °C): \(\delta\) 7.04-7.15 (m, 6H, ArH), 4.86 (s, 1H; \(\gamma\)-CH), 3.75 (sept, 2H, C\(\text{H}(\text{CH}_3)\)_2), 3.07 (sept, 2H, C\(\text{H}(\text{CH}_3)\)_2), 1.66 (s, 1H; OH), 1.51 (s, 6H; CH\(_3\)), 1.39 (d, 6H, CH (CH\(_3\)_2)), 1.34 (d, 6H, CH(CH\(_3\)_2)), 1.18 (d, 6H, CH(CH\(_3\)_2)), 1.04 (d, 6H, CH(CH\(_3\)_2)) ppm. \(^{13}\)C NMR (75.46 MHz, \text{C}_6\text{D}_6, 25 °C): \(\delta\) 213.15 (C\(_O\)), 169.68 (C\(_N\)), 145.01, 143.15, 139.96, 125.32, 124.85, 123.54 (ArC), 100.23 (\(\gamma\)-C), 29.39 (CH\(_3\)), 27.93 (CH(CH\(_3\)_2)), 25.59 (CH(CH\(_3\)_2)), 24.51 (CH(CH\(_3\)_2)), 24.44 (CH(CH\(_3\)_2)), 24.08 (CH(CH\(_3\)_2)), 23.39 (CH(CH\(_3\)_2)) ppm. \(^{119}\)Sn NMR (111.92 MHz, \text{C}_6\text{D}_6, 25 °C): \(\delta\) 45.03 ppm. EI-MS (70 eV; \(m/z\) (%)): 722 (10) [\text{M}^+], 705 (100) [\text{M} - \text{OH}]^+, 666 (85) [\text{M} - 2\text{CO}]^+. Anal. Calcd for C\(_{33}\)H\(_{42}\)FeN\(_2\)O\(_5\)Sn (722.15): C, 54.95; H, 5.87; N, 3.88. Found: C, 55.61; H, 6.43; N, 4.17.

(2) X-ray crystallography

Suitable crystals of 2·0.5THF and 3 were mounted on a glass fiber and data was collected on an IPDS II Stoe image-plate diffractometer (graphite monochromated Mo K\(\alpha\) radiation, \(\lambda = 0.71073\) Å) at 133(2) K. The data was integrated with X-Area. The structures were solved by Direct Methods (SHELXS-97)\(^{31}\) and refined by full-matrix least square methods against \(F^2\) (SHELXL-97).\(^{31}\) All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model. Complete crystallographic data are deposited at the Cambridge Crystallographic Data Centre, where it can be downloaded free of charge from www.ccdc.cam.ac.uk/ data_request/cif: at CCDC-740971 for (2·0.5THF) and 740972 for (3).
Crystallographic data for \([\text{LSn(NMe}_2\text{)Fe(CO)}_4]_2\cdot\text{THF}\)

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>(\text{C}<em>{74}\text{H}</em>{102}\text{Fe}_2\text{N}_6\text{O}_9\text{Sn}_2)</th>
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<tr>
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<td>Temperature</td>
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<tr>
<td>Wavelength</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>(P2_1/c)</td>
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<td>Unit cell dimensions</td>
<td>(a = 17.298(4) \text{ Å} ) (b = 20.371(4) \text{ Å} ) (\beta = 94.33(3)^\circ) (c = 21.502(4) \text{ Å} )</td>
</tr>
<tr>
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<tr>
<td>(Z)</td>
<td>4</td>
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<tr>
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<tr>
<td>Absorption coefficient</td>
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<tr>
<td>(F(000))</td>
<td>3248</td>
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<tr>
<td>Crystal size</td>
<td>0.50 \times 0.21 \times 0.16 \text{ mm}^3</td>
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<td>(\theta) range for data collection</td>
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<tr>
<td>Index ranges</td>
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<td>Reflections collected</td>
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<tr>
<td>Independent Reflections</td>
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<tr>
<td>Completeness to (\theta = 25.93^\circ)</td>
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<td>Refinement method</td>
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<td>Data / restraints / parameters</td>
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<td>Final (R) indices ([I&gt;2\sigma(I)])</td>
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<td>(R) indices (all data)</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.988 and -0.705 e.Å(^{-1})</td>
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Crystallographic data for LSn(OH)Fe(CO)₄

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<th>Property</th>
<th>Value</th>
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<td>Temperature</td>
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<tr>
<td>Wavelength</td>
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<tr>
<td>Crystal system</td>
<td>monoclinic</td>
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<tr>
<td>Space group</td>
<td>P2₁/n</td>
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<tr>
<td>Unit cell dimensions</td>
<td>a = 16.132(3) Å</td>
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<tr>
<td></td>
<td>b = 10.002(2) Å, β = 96.62(3)°</td>
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<td></td>
<td>c = 20.437(4) Å</td>
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<tr>
<td>Volume</td>
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<td>Z</td>
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<tr>
<td>Density (calculated)</td>
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<td>F(000)</td>
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<td>Crystal size</td>
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<td>θ range for data collection</td>
<td>1.53 to 26.00°</td>
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<tr>
<td>Index ranges</td>
<td>-19 ≤ h ≤ 18, -12 ≤ k ≤ 12, -24 ≤ l ≤ 25</td>
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<td>Reflections collected</td>
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<tr>
<td>Independent Reflections</td>
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<td>Completeness to θ = 26.00°</td>
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<td>Refinement method</td>
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<td>Data / restraints / parameters</td>
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<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.840 and -0.560 e.Å⁻³</td>
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