Supplementary Material (ESI) for Chemical Communications

Supporting Information

For

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

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(1) Experimental details and physical data

All manipulations were performed in a dry and oxygen-free atmosphere (N_2 or Ar) by using Schlenk-line and glove-box techniques. Solvents were purified with the M-Braun solvent drying system.

2: **Preparation of LSn(NMe$_2$)Fe(CO)$_4$ (2)**. A flask was charged with **1** (5.80 g, 10.00 mmol) and $Fe_2(CO)_9$ (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 ^oC 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): $\tilde{\nu}$ = 2034 s, 1957 s, 1935 s (CO) cm^{-1}. ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C): δ 7.07-7.16 (m, 6H, Ar*H*), 4.75 (s, 1H; γ-C*H*), 3.27 (sept, 2H, C*H*(CH$_3$)$_2$), 3.15 (sept, 2H, C*H*(CH$_3$)$_2$), 2.8-3.1 (br, 6H, N(C*H*$_3$)$_2$), 1.49 (s, 6H, C*H*$_3$), 1.42 (d, 6H, CH (C*H*$_3$)$_2$), 1.32 (d, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, 6H, CH(C*H*$_3$)$_2$), 1.01 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (75.46 MHz, C_6D_6, 25 °C): δ 216.40 (*C*O), 169.47 (*C*N), 144.86, 143.33, 141.09, 125.49, 124.74 (Ar*C*), 99.26 (γ-*C*), 45.5-42.8 (br, N(*C*H$_3$)$_2$), 29.75 (*C*H$_3$), 28.21 (*C*H(CH$_3$)$_2$), 25.26 (*C*H(CH$_3$)$_2$), 24.94 (CH(*C*H$_3$)$_2$), 24.65 (CH(*C*H$_3$)$_2$), 24.44 (CH(*C*H$_3$)$_2$), 24.25 (CH(*C*H$_3$)$_2$) ppm. ^{119}Sn NMR (111.92 MHz, C_6D_6, 25 °C): δ 94.00 ppm. EI-MS (70 eV; *m*/*z* (%)): 749 (45) [*M*]$^+$, 705 (100) [*M* – NMe$_2$]$^+$. Anal. Calcd for $C_{35}H_{47}FeN_3O_4Sn$ (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 LSn(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 *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): $\tilde{\nu}$ = 3615 s (OH), 2038 s, 1959 s, 1944 s (CO) cm^{-1}. ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C): δ 7.04-7.15 (m, 6H, Ar*H*), 4.86 (s, 1H; γ-C*H*), 3.75 (sept, 2H, C*H*(CH$_3$)$_2$), 3.07 (sept, 2H, C*H*(CH$_3$)$_2$), 1.66 (s, 1H; O*H*), 1.51 (s, 6H; C*H*$_3$), 1.39 (d, 6H, CH (C*H*$_3$)$_2$), 1.34 (d, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, 6H, CH(C*H*$_3$)$_2$), 1.04 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (75.46 MHz, C_6D_6, 25 °C): δ 213.15 (*C*O), 169.68 (*C*N), 145.01, 143.15, 139.96, 125.32, 124.85, 123.54 (Ar*C*), 100.23 (γ-*C*), 29.39 (*C*H$_3$), 27.93 (*C*H(CH$_3$)$_2$), 25.59 (*C*H(CH$_3$)$_2$), 24.51 (CH(*C*H$_3$)$_2$), 24.44 (CH(*C*H$_3$)$_2$), 24.08 (CH(*C*H$_3$)$_2$), 23.39 (CH(*C*H$_3$)$_2$) ppm. ^{119}Sn NMR (111.92 MHz, C_6D_6, 25 °C): δ 45.03 ppm. EI-MS (70 eV; *m*/*z* (%)): 722 (10) [*M*]$^+$, 705 (100) [*M* - OH]$^+$, 666 (85) [*M* - 2CO]$^+$. Anal. Calcd for $C_{33}H_{42}FeN_2O_5Sn$ (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 Kα radiation, λ = 0.71073 Å) at 133(2) K. The data was integrated with X-Area. The structures were solved by Direct Methods (SHELXS-97)[S1] and refined by full-matrix least square methods against F^2 (SHELXL-97).[S1] 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 $[LSn(NMe_2)Fe(CO)_4]_2 \cdot THF$

Empirical formula	$C_{74}H_{102}Fe_2N_6O_9Sn_2$
Formula weight	1568.70
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 17.298(4) Å
	b = 20.371(4) Å β = 94.33(3)°
	c = 21.502(4) Å
Volume	7555(3) Å^3
Z	4
Density (calculated)	1.379 Mg/m^3
Absorption coefficient	1.087 mm^{-1}
F(000)	3248
Crystal size	0.50 x 0.21 x 0.16 mm^3
θ range for data collection	1.18 to 25.93^0
Index ranges	$-21 \le h \le 21$, $-24 \le k \le 24$, $-26 \le l \le 26$
Reflections collected	60413
Independent Reflections	14600 (R_{int} = 0.0693)
Completeness to θ = 25.93º	98.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14600/0/862
Goodness-of-fit on F^2	1.130
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0316, $wR2$ = 0.0835
R indices (all data)	$R1$ = 0.0441, $wR2$ = 0.0863
Largest diff. peak and hole	0.988 and -0.705 e.Å^{-3}

Crystallographic data for $LSn(OH)Fe(CO)_4$

Empirical formula	$C_{33}H_{42}FeN_2O_5Sn$
Formula weight	721.23
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 16.132(3) Å
	b = 10.002(2) Å β = 96.62(3)°
	c = 20.437(4) Å
Volume	3275.7(11) $Å^3$
Z	4
Density (calculated)	1.462 Mg/m^3
Absorption coefficient	1.246 mm^{-1}
$F(000)$	1480
Crystal size	0.11 x 0.09 x 0.08 mm^3
θ range for data collection	1.53 to 26.00^0
Index ranges	$-19 \le h \le 18$, $-12 \le k \le 12$, $-24 \le l \le 25$
Reflections collected	27077
Independent Reflections	6328 (R_{int} = 0.0517)
Completeness to θ = 26.00º	98.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6328/0/390
Goodness-of-fit on F^2	1.079
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0388, $wR2$ = 0.0728
R indices (all data)	$R1$ = 0.0556, $wR2$ = 0.0775
Largest diff. peak and hole	0.840 and -0.560 e.$Å^{-3}$

S1 G. M. Sheldrick, *Acta Crystallogr. Sect. A,* 2008, **64**, 112-122.