

## Supporting Information

*For*

### **Pentafluoropyridine as a fluorinating reagent for preparing a hydrocarbon soluble $\beta$ -diketiminatolead(II) monofluoride**

*Anukul Jana, Sankaranarayana Pillai Sarish, Herbert W. Roesky,\* Dirk  
Leusser, Ina Objartel, and Dietmar Stalke\**

Institut für Anorganische Chemie

Universität Göttingen

Tammannstrasse 4, 37077 Göttingen (Germany)

Fax: (+49)551-39-3373

\*Authors to whom correspondence to be addressed: hroesky@gwdg.de and  
dstalke@chemie.uni-goettingen.de

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## 1. Experimental details and physical data

All manipulations were performed in a dry and oxygen free atmosphere ( $N_2$ ) using standard Schlenk techniques or inside a MBraun MB 150-GI glove box maintained at or below 1 ppm of  $O_2$  and  $H_2O$ . All solvents were dried by a MBraun solvent purifying system prior to use. The starting materials **1**<sup>1</sup> and **4**<sup>2</sup> were prepared using literature procedures. Other chemicals were purchased commercially and used as received.  $^1H$ ,  $^{19}F$ ,  $^{29}Si$ ,  $^{11}B$  and  $^{207}Pb$  NMR spectra were recorded on a Bruker Avance DRX instrument (300 or 500 MHz) and referenced to the  $SiMe_4$  in the case of the  $^1H$  and  $^{29}Si$  NMR,  $CF_2Cl_2$  for the  $^{19}F$  NMR,  $BF_3 \cdot OEt_2$  for  $^{11}B$  NMR and  $PbMe_4$  for  $^{207}Pb$  NMR spectra, respectively. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument.

**Synthesis of 2:** A solution of  $C_5F_5N$  (0.685 g, 4.05 mmol) in diethyl ether or THF (20 mL) was added to a diethyl ether or THF solution (50 mL) of **1** (2.676 g, 4.0 mmol) at room temperature. The reaction mixture was stirred for 12 h at this temperature. After that all volatiles were removed in vacuum. The residue was washed with *n*-hexane (35 mL). The solid thus obtained was dissolved in hot *n*-hexane and filtered through a celite pad. The resulting solution was kept overnight at room temperature for one day to afford pale yellow crystals of **2**. Yield: (2.06 g, 80 %), Mp: 227–229 °C;  $^1H$  NMR (500 MHz,  $C_6D_6$ ):  $\delta$  7.16–7.12 (m, 6H, Ar-*H*), 4.86 (s, 1H,  $\gamma$ -CH), 3.25 (br, 4H,  $CH(CH_3)_2$ ), 1.69 (s, 6H,  $CH_3$ ), 1.31 (br, 12H,  $CH(CH_3)_2$ ), 1.14 (d, 12H,  $CH(CH_3)_2$  ppm;  $^{13}C\{^1H\}$  NMR (125 MHz,  $C_6D_6$ ):  $\delta$  163.78,

142.68, 126.81, 124.47, 102.14, 27.92, 26.12, 24.46, 24.31 ppm;  $^{19}\text{F}\{\text{}^1\text{H}\}$  NMR (376.46 MHz, Tol-D<sub>8</sub>, -80 °C):  $\delta$  -102.7 ppm;  $^{207}\text{Pb}\{\text{}^1\text{H}\}$  NMR (104.72 MHz, Tol-D<sub>8</sub>, -80 °C):  $\delta$  787.4 (d,  $J(^{207}\text{Pb}-^{19}\text{F}) = 2792$  Hz) ppm; EI-MS (70 eV)  $m/z$  (%): 202(100) [ $\text{DippNCCH}_3$ ]<sup>+</sup> (Dipp=2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 644.3 (28) [M]<sup>+</sup>; elemental analysis (%) calcd for C<sub>29</sub>H<sub>41</sub>FN<sub>2</sub>Pb (643.85): C 54.10, H 6.42, N 4.35; found: C 53.47, H 6.35, N 4.28.

**Synthesis of 5:** LPbF (1.29 g, 2.0 mmol) was dissolved in toluene (15 mL) and then this solution was slowly added drop by drop to a stirred solution of **4** (0.61 g, 2.0 mmol) in toluene (30 mL) at -30 °C. The reaction mixture was warmed to room temperature and was stirred for additional 10 h. After removal of all the volatiles, the residue was washed several times with *n*-hexane –diethyl ether to remove the LPbCl. After that the insoluble residue was extracted with toluene (30 mL) to yield colorless compound **5** (0.35 g, 60 %). Mp: 224 °C;  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  1.00 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.2-1.6 (br, 3H, BH<sub>3</sub>), 6.70-6.89 (m, 5H, C<sub>6</sub>H<sub>5</sub>) ppm;  $^{13}\text{C}$  NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz):  $\delta$  30.74 (C(CH<sub>3</sub>)<sub>3</sub>), 54.48 (C(CH<sub>3</sub>)<sub>3</sub>), 127.19, 127.91, 128.29, 128.32, 129.64, 130.79 (C<sub>6</sub>H<sub>5</sub>), 176.20 (NCN) ppm;  $^{11}\text{B}$  NMR (C<sub>6</sub>D<sub>6</sub>, 160 MHz):  $\delta$  -46.47 (q,  $J(^{11}\text{B}-^1\text{H}) = 93.24$  Hz,) ppm;  $^{19}\text{F}$  NMR (C<sub>6</sub>D<sub>6</sub>, 188 MHz):  $\delta$  -121.59 ppm;  $^{29}\text{Si}$  NMR (C<sub>6</sub>D<sub>6</sub>, 99 MHz):  $\delta$  23.63 (d,  $J(^{29}\text{Si}-^{19}\text{F}) = 438.17$  Hz and q,  $J(^{29}\text{Si}-^{11}\text{B}) = 66.78$  Hz) ppm; EI-MS (70 eV):  $m/z$  (%): 260 (100) [M<sup>+</sup>-BH<sub>3</sub>]; elemental analysis (%) calcd for C<sub>15</sub>H<sub>26</sub>BFN<sub>2</sub>Si (292.19): C 61.64, H 8.97, N 9.58; found: C 60.15, H 8.78, N 9.25.

**Synthesis of 6:** A solution of PhCOCF<sub>3</sub> (0.174 g, 1.0 mmol) in toluene (10 mL) was added to a solution of **2** (0.644 g, 1.0 mmol) in toluene (10 mL) at -40 °C. The reaction mixture was warmed to room temperature and stirred for 10 h. All volatiles were removed *in vacuo*. The remaining residue was extracted with *n*-pentane –THF mixture (15 mL). The solution was concentrated and stored at -32 °C in a freezer. Colorless crystals of **6** were formed after one day. Yield: (0.50 g, 72.48 %); Mp: 157–159 °C;  $^1\text{H}$  NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.69–6.80 (several multiplets, 22 H, Ar-*H*), 5.19 (d, 2H,  $\gamma\text{CH}$ ), 3.47 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.43 (sept,

2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.96 (s, 6H,  $\text{CH}_3$ ), 2.85 (sept, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.86 (s, 6H,  $\text{CH}_3$ ), 1.34–1.29 (3d, 18H,  $\text{CH}(\text{CH}_3)_2$ ), 1.25 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.19 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.90 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.714 (sept, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 0.52 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.40 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  178.06, 168.94, 146.13, 144.35, 143.26, 139.92, 138.26, 137.69, 135.86, 130.02, 129.07, 128.85, 128.80, 128.51, 126.84, 126.34, 124.83, 124.35, 124.32, 123.99, 122.57, 84.0, 65.92, 28.85, 27.26, 26.96, 26.94, 26.29, 26.21, 25.46, 24.81, 24.41, 23.68, 22.91, 22.77, 21.60, 19.91 ppm;  $^{19}\text{F}\{^1\text{H}\}$  NMR (188 MHz):  $\delta$  -76.15 ppm;  $^{207}\text{Pb}\{^1\text{H}\}$  NMR (104.72 MHz):  $\delta$  854 ppm; EI-MS (70 eV):  $m/z$  (%): 202(100) [ $\text{DippNCCH}_3$ ] $^+$  (Dipp=2,6-*i*Pr $_2$ C $_6$ H $_3$ ); elemental analysis (%) calcd for  $\text{C}_{74}\text{H}_{92}\text{F}_6\text{N}_4\text{O}_2\text{Pb}$  (1390.74): C 63.91, H 6.67, N 4.03; found: C 59.27, H 6.57, N 3.45. (Attempts to acquire satisfactory elemental analysis data for **6** was not successful because of its sensitivity to air and moisture.)

## 2. Crystallographic details

A shock cooled crystal of **2** was selected and mounted under nitrogen atmosphere using the X-TEMP2.<sup>3</sup> The data set for **2** was collected on a Bruker TXS-Mo rotating anode equipped with INCOATEC Helios mirror optics (Mo  $\text{K}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ , 100K). Data for **6** was collected on an INCOATEC Microfocus with mirror optics instrument equipped with a Bruker Apex II detector (Mo  $\text{K}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ , 100 K).<sup>4</sup> The integration was performed with SAINT, which was followed by a numerical (**2**) or empirical (**6**) absorption correction with SADABS. The structures were solved by direct methods (SHELXS) and refined against  $F^2$  using the full-matrix least-squares methods with SHELXL.<sup>5</sup> For **2** the contributions of the extremely disordered non-coordinating THF molecules to the scattering factors were removed with SQUEEZE.<sup>6</sup>

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