Supplementary Information

Sterically Induced Reductive Linkage of Iron Polypnictides with Bulky Lanthanide Complexes by Ring-Opening of THF

Christoph Schoo,^a Sebastian Bestgen,^a Monika Schmidt,^d Sergey N. Konchenko,^{a,b,c} Manfred Scheer^d and Peter W. Roesky^a*

^{a.} Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstrasse 15, 76131 Karlsruhe, Germany. E-mail: roesky@kit.edu.

^{b.} Nikolaev Institute of Inorganic Chemistry SB RAS, Prosp. Lavrentieva 3, 630090 Novosibirsk, Russia. E-mail: konch@niic.nsc.ru

^{c.} Novosibirsk State University, Pirogovastr. 2, 630090 Novosibirsk, Russia.

^{d.} Institute of Inorganic Chemistry, University of Regensburg, 93040 Regensburg, Germany. E-mail: Manfred.Scheer@chemie.uni-regensburg.de

Experimental Section

General Considerations

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10⁻³ torr) line, or in an argon-filled MBraun glove box. Elemental analyses were carried out with an Elementar vario Micro Cube. Hydrocarbon solvents were predried by using an MBraun solvent purification system (SPS-800) and degassed, dried and stored in vacuo over LiAlH₄. Tetrahydrofuran was distilled under nitrogen from potassium benzophenoneketyl before storage over LiAlH₄. IR spectra were obtained on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector and a diamond ATR (attenuated total reflection) unit; for the mid infrared region a KBr beamsplitter was used. DippFormH,¹ [Sml₂(thf)₂],² [Cp*FeE₅] (E=P, As)³ were prepared according to literature procedures.

Synthesis

NOTE: All yields are based on single crystalline material.

Modified synthesis of [(DippForm)₂Sm(thf)₂]:⁴

DippFormH (2.92 g, 8.00 mmol) and [Sml₂(thf)₂] (2.19 g, 4.00 mmol) were dissolved in ca. 50 mL of thf. A chunk of potassium (328 mg, 8.40 mmol) was added and the reaction mixture was refluxed for 6 h. The mixture was cooled to ambient temperature and stirred overnight. The volatiles were removed in vacuum and extracted with toluene. The toluene solution was concentrated and stored at -30 °C for a few days to yield green crystals of [(DippForm)₂Sm(thf)₂]. Yield: 86 % (3.47 g). Analytical data matched with those reported in literature.

Synthesis of complex 1

 $[(DippForm)_2Sm(thf)_2]$ (200 mg, 0.196 mmol) and $[Cp*FeP_5]$ (34 mg, 0.098 mmol) were dissolved in ca. 20 mL of *n*-heptane and refluxed for one week yielding a brownish solution. After a week the reaction solution was filtered in a two section ampule and flame sealed to grow crystals by slow evaporation. The single crystals were washed carefully with *n*-heptane. Yield: 59 % (138 mg). mp: 174 °C (dec). IR (cm⁻¹): v = 3058 (w), 2959 (vs), 2926 (s), 2867 (s), 1664 (vs), 1587 (m), 1441 (m), 1382 (m), 1361 (m), 1331 (m), 1288 (s), 1256 (m), 1235 (m), 1183 (m), 1097 (m), 1043 (m), 1002 (m), 934 (w), 821 (w), 799 (m), 766 (w), 753 (m). NIR (cm⁻¹): v = 9931 (m), 9739 (s), 9463 (s), 9273 (s), 8916 (s), 7805 (s), 7709 (s), 7329 (vs), 7223 (vs), 7160 (vs), 6383 (m), 5865 (m). Anal. calcd. (%) for $[C_{118}H_{171}P_5FeN_8O_2Sm_2]$ (2245.15): C 63.13; H 7.68; Fe 2.49; N 4.99; found C 60.85, H 7.78, N 4.42. Constantly low carbon values were obtained for **1**. Synthesis of complex 2

 $[(DippForm)_2Sm(thf)_2]$ (200 mg, 0.196 mmol) and $[Cp*FeAs_5]$ (55 mg, 0.098 mmol) were dissolved in ca. 20 mL of *n*-heptane and stirred for three days yielding an orange solution. After three days the reaction solution was filtered in a two section ampule and flame sealed to grow crystals by slow evaporation. The single crystals were washed carefully with *n*-heptane. Yield: 74 % (188 mg). mp: 162 °C (dec). IR (cm⁻¹): v = 3063 (w), 2959 (vs), 2927 (s), 2867 (s), 1663 (vs), 1588 (m), 1521 (m), 1456 (m), 1439 (m), 1382 (m), 1361 (m), 1331 (m), 1318 (m), 1286 (s), 1256 (m), 1234 (m), 1180 (m), 1098 (w), 1056 (w), 1044 (w), 1001 (w), 934 (w), 821 (w), 799 (m), 767 (m), 753 (m). NIR (cm⁻¹): v = 9822 (w), 9700 (w), 9644 (m), 9528 (m), 8910 (m), 8753 (s), 7803 (m), 7709 (m), 7330 (s), 7264 (vs), 7215 (vs), 7129 (s), 6225 (m), 5472 (s), 5408 (s), 5367 (vs), 5315 (vs), 5219 (s).. Anal. calcd. (%) for $[C_{118}H_{171}As_5FeN_8O_2Sm_2]$ (2464.89): C 57.50, H 6.99, N 4.55; found. C 57.79, H 7.18, N 4.77.

IR-Spectra and NIR Spectra

IR spectra were obtained on a Bruker Tensor 37. NIR measurements of **1** and **2** were performed with the help of an ATR diamond at room temperature using the FTIR spectrometer Bruker Tensor 37 by means of an NIR lamp, a CaF2 beamsplitter and a room temperature InGaAs detector.



Figure S1: IR spectrum of 1 in the solid state.



Figure S2: NIR-spectrum of 1.



Figure S3: IR spectrum of 2 in the solid state.



Figure S4: NIR-spectrum of 2.

X-ray Crystallographic Studies of 1-3. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 or STOE StadiVari diffractometer.

Using Olex2,⁵ the structures were solved using SHELXS⁶ and refined with the ShelXL⁷ refinement package using Least Squares minimization. The remaining non-hydrogen atoms were located from difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $(F_o-F_c)^2$, where the weight is defined as $4F_0^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. Carbon-bound hydrogen atom positions were calculated. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond lengths and angles have been deposited as supporting information. For structure **3**, one molecule of disordered *n*-heptane was removed by using OLEX2 solvent mask.⁵

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-1503451-1503453. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: <u>deposit@ccdc.cam.ac.uk</u>).

Compound	1 • <i>n</i> -heptane	2 • <i>n</i> -heptane	3
Chemical formula	C ₁₂₅ H ₁₈₇ FeN ₈ O ₂ P ₅ Sm ₂	$C_{125}H_{187}As_5FeN_8O_2Sm_2$	$C_{59}H_{88}N_5OSm$
Formula Mass	2345.21	2563.96	1033.69
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	13.120(3)	13.1985(10)	12.769(2)
b/Å	20.386(4)	20.5277(9)	13.1625(14)
c/Å	24.637(5)	24.6698(12)	20.932(3)
α/°	109.26(3)	108.733(4)	76.406(10)
<i>θ</i> /°	93.54(3)	93.697(5)	80.735(12)
γ/°	93.97(3)	93.654(5)	63.678(9)
Unit cell volume/Å ³	6180(2)	6291.4(6)	3058.4(8)
Temperature/K	110	150	150
No. of formula units per unit cell, Z	2	2	2
Radiation type	Μο Κα	Μο Κα	Μο Κα
Absorption coefficient, μ /mm ⁻¹	1.169	2.389	0.998
No. of reflections measured	56801	43132	22601
No. of independent reflections	23995	22528	11699
R _{int}	0.0566	0.0471	0.0544
Final R_1 values ($l > 2\sigma(l)$)	0.0344	0.0381	0.0397
Final $wR(F^2)$ values ($l > 2\sigma(l)$)	0.0662	0.0623	0.0689
Final R_1 values (all data)	0.0555	0.0835	0.0652
Final wR(F ²) values (all data)	0.0702	0.0712	0.0734
Goodness of fit on F ²	0.850	0.856	0.832

Table S1: Crystal data and structure refinement



Figure S5: Molecular structure of **3** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Sm1-O1 2.179(2), Sm1-N1 2.425(43), Sm1-N2 2.533(3) , Sm1-N3 2.475(3), Sm1-N4 2.462(3), Sm1-N5 2.455(3), O1-N1 1.436(4).

References

- 1. K. Hirano, S. Urban, C. Wang and F. Glorius, *Org. Lett.*, 2009, **11**, 1019.
- 2. P. L. Watson, T. H. Tulip and I. Williams, Organometallics, 1990, 9, 1999.
- 3. (a) O. Scherer, C. Blath and G. Wolmershäuser, *J. Organomet. Chem.*, 1990, **387**, C21; (b) M. Detzel, T. Mohr, O. J. Scherer and G. Wolmershäuser, *Angew. Chem. Int. Ed.*, 1994, **33**, 1110.
- 4. G. B. Deacon, P. C. Junk, J. Wang and D. Werner, *Inorg. Chem.*, 2014, 53, 12553.
- 5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
- 6. G. Sheldrick, Acta Crystallogr. Sect. A, 2008, 64, 112.
- 7. G. Sheldrick, Acta Crystallogr. Sect. C, 2015, 71, 3.