

Electronic Supplementary Information for the paper Mono-, di- and polymetallic TI^I complexes stabilized by a 2,5- bis(2-pyridyl)-1-phenyl-phosphole ligand

Stefan Welsch,^a Christophe Lescop,^b Régis Réau*^b and Manfred Scheer*^a

^a Institut für Anorganische Chemie der Universität Regensburg, 93040 Regensburg, Germany. Fax: (+49) 941-943-4439; E-mail: manfred.scheer@chemie.uni-regensburg.de

^b Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France. Fax: (+33) 2-23-23-69-39; E-mail: regis.reau@univ-rennes1.fr

Experimental Details

All experiments were performed under an atmosphere of dry argon or nitrogen using standard Schlenk and drybox techniques. Commercially available reagents were used as received without further purification. 2,5-bis(pyridyl)phosphole **A**¹ and TI[Al{OC(CF₃)₃]₄ **B**² were synthesized as reported in the literature. Solvents were freshly distilled under argon from Na/K alloy (*n*-pentane) or from CaH₂ (CH₂Cl₂, CH₃CN). ¹H, ¹³C and ³¹P NMR spectra were recorded at room temperature on Bruker AV300 or AV600 spectrometers. ¹H, ¹³C, ³¹P and ¹⁹F NMR chemical shifts are reported in parts per million (ppm) relative to external standards Me₄Si, H₃PO₄ (85%) or CFC₁₃. Assignment of hydrogen and carbon atoms was based on COSY, HSQC and HMBC experiments. The labeling scheme for the ligand **A** is depicted below (Fig. S1). Elemental analyses were performed by the microanalytical laboratory of the Universität Regensburg. For the ESI-MS a Finnigan Thermoquest TSQ 7000 mass spectrometer was used.

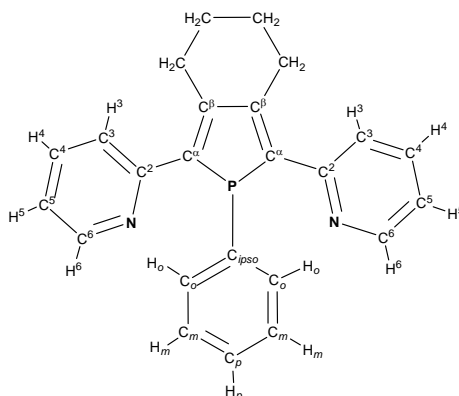


Fig. S1 NMR labelling scheme for ligand **A**.

Synthesis of **1**

A mixture of TI[Al{OC(CF₃)₃]₄ **B** (53 mg, 0.045 mmol), phosphole **A** (33 mg, 0.090 mmol) and CH₂Cl₂ (10 mL) was stirred overnight at room temperature. Afterwards, it was layered with toluene (15 mL) and, after complete diffusion, reduced in volume to 8 mL. Single crystals of **1** × C₇H₈ suitable for X-ray diffraction analysis could be obtained from this solution at -28°C. The crystals were isolated by filtration, washed with *n*-pentane (3 × 2 mL) and dried in the vacuum. According to the ¹H NMR spectrum and the elemental analysis 50% of the not coordinating toluene molecules get lost during this drying process; yield: 61 mg (66%). ¹H NMR (300 MHz, CD₂Cl₂): δ = 1.42–1.59 (broad m, 4H; C=CCH₂CH₂), 1.74–1.91 (broad m, 4H; C=CCH₂CH₂), 2.34 (s, 4.5H; CH₃ toluene), 2.49–2.65 (broad m, 4H; C=CCH₂), 3.00–3.19 (broad m, 4H; C=CCH₂), 7.03–7.13 (broad m; H⁵ Py, *m*-Ph), 7.13–7.28 (broad m; *p*-Ph, *o*-Ph, CH_{toluene}), 7.52 (broad d, ³J_{H,H} = 8.0 Hz, 4H; H³ Py), 7.71 (broad ddd, ³J_{H,H} = 7.8 Hz, ³J_{H,H} = 7.8 Hz, ⁴J_{H,H} = 1.5 Hz, 4H; H⁴ Py), 8.53 (broad d, ³J_{H,H} = 4.9 Hz, 4H; H⁶ Py); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ = 21.5 (s; CH₃ toluene), 22.8 (s; C=CCH₂CH₂), 28.9 (d, ³J_{P,C} = 2.2 Hz; C=CCH₂), 121.6 (q, ¹J_{F,C} = 292.6 Hz; CF₃), 122.0 (s; C⁵ Py), 124.3 (d, ³J_{P,C} = 5.6 Hz; C³ Py), 125.6 (s; *p*-C_{toluene}), 128.5 (s; *m*-C_{toluene}), 129.1 (s; *o*-C_{toluene}), 129.3 (d, ³J_{P,C} = 9.3 Hz; *m*-C_{Ph}), 130.0 (m; *ipso*-Ph), 130.4 (s; *p*-C_{Ph}), 133.6 (d, ²J_{P,C} = 15.9 Hz; *o*-C_{Ph}), 137.5 (s; C⁴ Py), 143.4 (d, ¹J_{P,C} = 13.9 Hz; C^α), 149.4 (d, ²J_{P,C} = 10.1 Hz; C^β), 149.8 (s; C⁶ Py), 154.5 (d, ²J_{P,C} = 15.0 Hz; *ipso*-C_{toluene} not observed; ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ = 44.8 (broad s, ω_{1/2} = 15 Hz; P_{phosphole}); ¹⁹F{¹H} NMR (282 MHz, CD₂Cl₂): δ = -75.61 (s; CF₃); ESI-MS (cations, CH₂Cl₂): *m/z* (%) = 941.3 (100.0) [(C₂₄H₂₁N₂P)₂TI]⁺; ESI-MS (anions, CH₂Cl₂): *m/z* (%) = 967.0 (100.0) [Al{OC(CF₃)₃]₄]⁻; elemental analysis calculated for **1** × 0.5 C₇H₈ (2046.53 g/mol): C 43.72, H 2.66, N 2.74; found C 44.01, H 2.62, N 2.65.

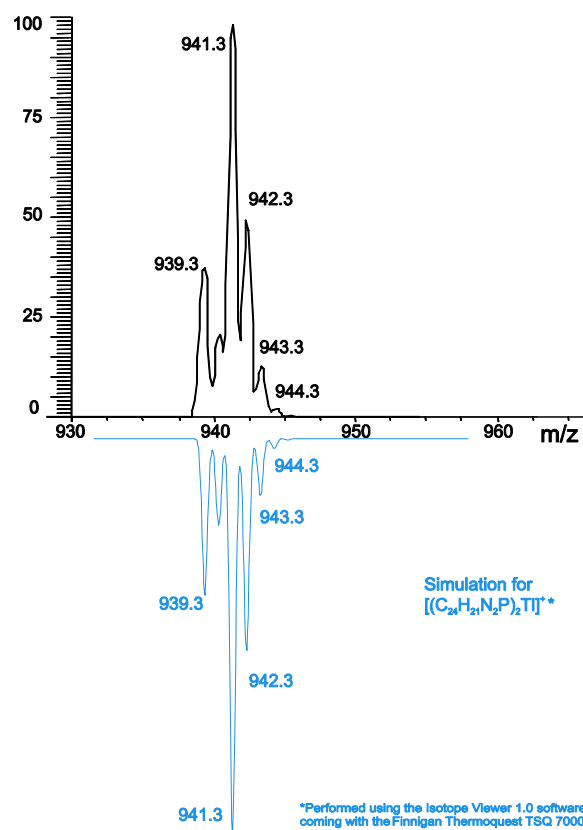


Fig. S2 High resolution ESI mass spectrum of **1** in CH₂Cl₂ (upwards) and simulation (downwards).

Synthesis of **2**

A mixture of Ti[Al{OC(CF₃)₃}₄] **B** (59 mg, 0.05 mmol), phosphole **A** (37 mg, 0.10 mmol) and CH₂Cl₂ (5 mL) was stirred for 3h at room temperature. Afterwards it was concentrated in the vacuum to a volume of 2.5 mL. Addition of *n*-pentane (10 mL) led to the formation of a bright yellow precipitate of **2**. The solid was filtrated, washed with *n*-pentane (3 × 2 mL) and dried in the vacuum; yield: 71 mg (74%). Single crystals of **2** suitable for X-ray diffraction analysis could be obtained by slow diffusion of vapors of *n*-pentane into a CH₂Cl₂ solution of **2**. Solution NMR spectroscopic data of **2** in CD₂Cl₂ are identical to those observed for **2** (except from the missing toluene signals in the case of **2**); elemental analysis calculated for **2** (1908.32 g/mol): C 40.28, H 2.22, N 2.94; found C 40.20, H 2.21, N 2.87.

Synthesis of **3**

A mixture of TiPF₆ (35 mg, 0.10 mmol), **A** (74 mg, 0.20 mmol), CH₂Cl₂ (5 mL) and CH₃CN (1 mL) was stirred overnight at room temperature. Single crystals of **3** suitable for X-ray diffraction analysis could be obtained by slow diffusion of vapors of *n*-pentane into this solution. The crystals were isolated by filtration, washed with *n*-pentane (3 × 2 mL) and dried in the vacuum; yield: 46 mg (64%). ¹H NMR (600 MHz, CD₂Cl₂): δ = 1.55–1.65 (broad m, 4H; C=CCH₂CH₂), 1.80–1.89 (broad m, 4H; C=CCH₂CH₂), 2.65–2.74 (broad m, 4H; C=CCH₂), 3.13–3.22 (broad m, 4H; C=CCH₂), 7.06–7.12 (broad m, 8H; H⁵ Py, *m*-Ph), 7.18 (broad m, 2H; *p*-Ph), 7.26 (broad m, 4H; *o*-Ph), 7.52 (broad d, ³J_{H,H} = 8.0 Hz, 4H; H³ Py), 7.68 (broad ddd, ³J_{H,H} = 7.7 Hz, ³J_{H,H} = 7.7 Hz, ⁴J_{H,H} = 1.7 Hz, 4H; H⁴ Py), 8.53 (broad d, ³J_{H,H} = 4.7 Hz, 4H; H⁶ Py); ¹³C{¹H} NMR (151 MHz, CD₂Cl₂): δ = 23.0 (s; C=CCH₂CH₂), 29.0 (d, ³J_{P,C} = 1.5 Hz; C=CCH₂), 121.8 (s; C⁵ Py), 124.3 (d, ³J_{P,C} = 6.3 Hz; C³ Py), 129.1 (d, ³J_{P,C} = 8.0 Hz; *m*-C_{Ph}), 130.1 (s; *p*-C_{Ph}), 130.8 (d, ¹J_{P,C} = 4.1 Hz; *ipso*-C_{Ph}), 133.8 (d, ²J_{P,C} = 16.3 Hz; *o*-C_{Ph}), 137.2 (s; C⁴ Py), 143.7 (d, ¹J_{P,C} = 11.5 Hz; C^α), 149.4 (d, ²J_{P,C} = 10.1 Hz; C^β Py), 149.7 (s; C⁶ Py), 155.0 (d, ²J_{P,C} = 16.2 Hz; C² Py); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ = -143.6 (sept, ¹J_{P,F} = 713.1 Hz; PF₆), 37.0 (broad s, ω_{1/2} = 95 Hz; P_{phosphole}); ¹⁹F NMR (282 MHz, CD₂Cl₂): δ = -71.82 (d, ¹J_{P,F} = 712.7 Hz, PF₆); elemental analysis calculated for **3** (1435.50 g/mol): C 40.16, H 2.95, N 3.90; found C 40.15, H 3.08, N 3.87.

Crystallographic data

Single crystals suitable for single crystal X-ray diffraction analysis were obtained for derivatives **1**, **2**, and **3** as stated above. Single crystal data collection for **2** were performed with an APEX II Bruker-AXS (Centre de Diffraction, Université de Rennes 1, France) with Mo- $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$), for **1** and **3** an OXFORD Diffraction Gemini R Ultra CCD-diffractometer (Universität Regensburg) with Cu- $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) was used. In Rennes, reflections were indexed, Lorentz-polarization corrected and integrated by the *DENZO* program of the KappaCCD software package.³ The data merging process was performed using the SCALEPACK program.⁴ The data processing in Regensburg was done with the CrysAlis software package from Oxford Diffraction.⁵ Structure determinations were performed by direct methods with the solving programs SHELXS⁶ or SIR-97⁷ which revealed all the non-hydrogen atoms. The SHELXL program⁶ was used to refine the structures by full-matrix least-squares based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.⁸ In **1**, the $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ anion was found to be highly disordered. For each of the four $\text{C}(\text{CF}_3)_3$ groups two positions were refined. Therefore a relatively large number of restraints had to be applied: For all C-C and C-F bonds DFIX restraints were used and the distances between the F atoms within the CF_3 groups and between the C atoms within the $\text{C}(\text{CF}_3)_3$ groups were refined with SADI restraints. The four O atoms were also refined with SADI restraints fitting them to a regular tetrahedron. Furthermore, several weak and strong restraints for the anisotropic displacement parameters of the atoms of the anion had to be used to prevent the corresponding ADPs from becoming unphysically big, prolate, oblate, or NPD. Nevertheless, refining the anion completely anisotropic led to a significant improvement of the R values. The site occupation factors of the disordered $\text{C}(\text{CF}_3)_3$ groups were refined to 51%, 46%, 63%, 54%, and 49%, 54%, 37% and

Table S1 Structure determination summary of complexes **1**, **2** and **3**.

	1	2	3
Formula	$\text{C}_{78}\text{H}_{58}\text{AlF}_{36}\text{N}_4\text{O}_4\text{P}_2\text{Ti}$	$\text{C}_{64}\text{H}_{42}\text{AlF}_{36}\text{N}_4\text{O}_4\text{P}_2\text{Ti}$	$\text{C}_{48}\text{H}_{42}\text{F}_{12}\text{N}_4\text{P}_4\text{Ti}_2$
CCDC number	713903	713904	713905
M_r	2092.58	1908.32	1435.50
T[K]	100(1)	120(2)	123(1)
crystal system	monoclinic	triclinic	triclinic
space group	$P 2_1/c$ (14)	PT (2)	PT (2)
a [\AA]	9.6229(1)	11.3378(3)	10.8581(2)
b [\AA]	23.3032(2)	17.5125(4)	12.5163(2)
c [\AA]	36.1442(2)	18.9823(5)	18.3704(3)
α [$^\circ$]	90	111.9840(11)	91.335(2)
β [$^\circ$]	91.045(1)	91.1627(12)	91.937(2)
γ [$^\circ$]	90	98.9673(10)	102.785(2)
V [\AA^3]	8103.79(12)	3439.48(15)	2432.10(7)
Z	4	2	2
colour	pale yellow	colorless	pale yellow
crystal size [mm]	0.29 x 0.24 x 0.19	0.20 x 0.20 x 0.20	0.41 x 0.15 x 0.06
ρ_{calcd} [Mg m^{-3}]	1.715	1.842	1.960
$F(000)$	4136	1868	1376
μ [mm^{-1}]	5.541	2.557	14.583
λ [\AA]	1.54178	0.71069	1.54178
diffractometer	Oxford Diffraction Gemini Ultra	Bruker APEX II	Oxford Diffraction Gemini Ultra
Index ranges hkl	$-10 \leq h \leq 11$ $-22 \leq k \leq 26$ $-41 \leq l \leq 41$	$-14 \leq h \leq 14$ $-22 \leq k \leq 22$ $-20 \leq l \leq 24$	$-12 \leq h \leq 12$ $-14 \leq k \leq 14$ $-20 \leq l \leq 21$
θ limit ($^\circ$)	$3.09 \leq \theta \leq 62.38$	$2.76 \leq \theta \leq 27.53$	$2.41 \leq \theta \leq 66.64$
Reflections collected	33548	48350	37915
Independant reflections	12511	15786	8341
Reflections [$I > 2\sigma(I)$]	11802	15103	7663
Data/restraints/ parameters	12511/885/1566	15786/12/1121	8341/0/631
Goodness-of-fit on F^2	1.048	1.027	1.033
$R(\text{int})$	0.0199	0.0239	0.0398
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0516$ $wR2 = 0.1253$	$R1 = 0.0200$ $wR2 = 0.0517$	$R1 = 0.0362$ $wR2 = 0.0940$
R indices (all data)	$R1 = 0.0541$ $wR2 = 0.1270$	$R1 = 0.0213$ $wR2 = 0.0524$	$R1 = 0.0394$ $wR2 = 0.0963$
Largest diff peak and hole ($e \text{ \AA}^{-3}$)	3.228 and -1.491	0.970 and -0.515	1.985 and -2.117

46% respectively. Two toluene solvent molecules were found in the asymmetric unit, one of which was found disordered over two positions. The corresponding sofs refined to 67% and 33%, respectively. For the refinement of one of the two toluene positions a SADI restraint for the C-C bonds within the six-membered ring had to be applied. In **2**, a crystallographic inversion centre is located within the supramolecular aggregate, which generates the second monomeric unit of each dimer. One $\text{C}(\text{CF}_3)_3$ group of the anion was refined disordered over two positions with corresponding site occupation factors of 59% and 41%. During the refinement of this disorder DFIX and SADI restraints for the C-C distances had to be applied to obtain reasonable geometries for the two positions of the $\text{C}(\text{CF}_3)_3$ group. An EADP restraint was used for C52A and C52B to prevent C52B from going NPD.

In the context of the large number of restraints and the moderate R values of compound **1**, the general difficulties in the refinement of the perfluorinated alkoxyaluminate anion must be considered. This anion shows a strong tendency to be disordered despite using low temperature X-ray studies to 'freeze' the disorder. Being almost spherical, it can pack in crystal structures in different orientations from one cell to another with no conflict with its nearest environment. Thus, in most structures these anions are known to be disordered.^[9] If the number of orientations is limited and the X-ray data are good enough, the type of the disorder can be revealed. Otherwise, it can be described by atomic thermal parameters. For **1**, the disorder of all four $-\text{OC}_4\text{F}_9$ groups is revealed. In addition, the quality of the X-ray data is always a challenge, because the crystals containing the $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ ion often show diffuse patterns with a limited number of strong reflections, which fade at high angles.⁹

CCDC reference numbers 713903, 713904, 713905 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

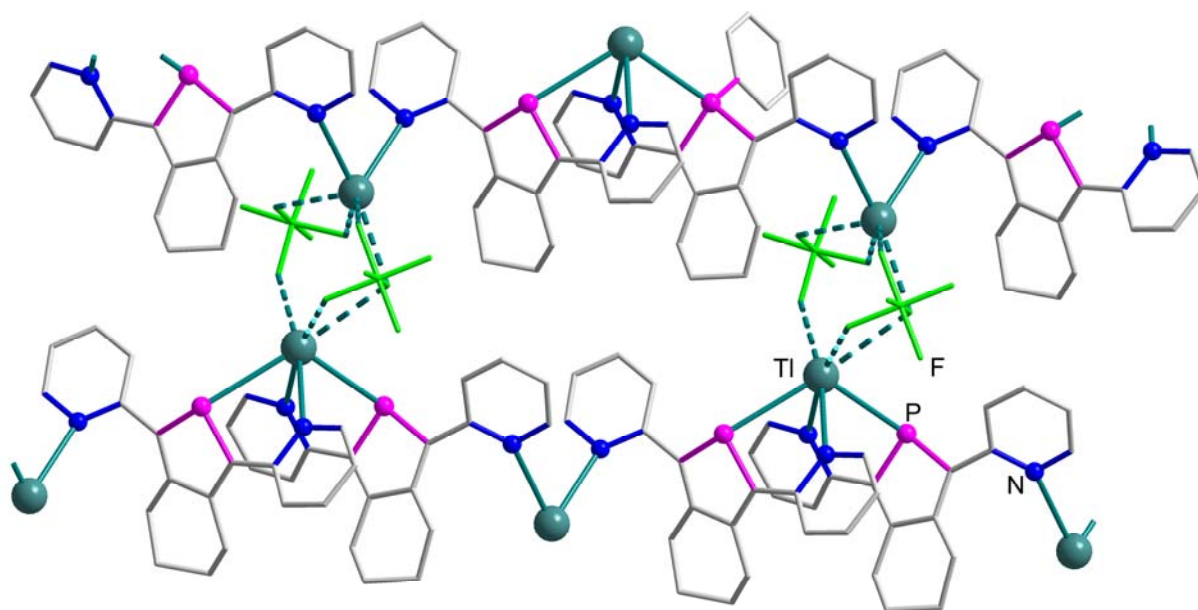


Fig. S3 View of the 2D polymeric network of **3** in the solid-state. The phenyl moieties of the ligands **A** are omitted for clarity.

References

- 1 (a) D. Le Vilain, C. Hay, V. Deborde, L. Toupet, R. Réau, *Chem. Commun.*, **1999**, 345; (b) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulaszi, R. Réau, *Chem. Eur. J.*, **2001**, 7, 4222.
- 2 M. Gonsior, I. Krossing, N. Mitzel, *Z. Anorg. Allg. Chem.*, **2002**, 628, 1821.
- 3 Area-Detector Integration Software; Siemens Industrial Automation, Inc.: Madison, WI, **1995**.
- 4 Z. Otwinowski, W. Minor, in *Methods in Enzymology*, (Ed.: C. W. Carter, Jr. & R. M. Sweet), New York: Academic Press, **1997**, 276, 307.
- 5 CrysAlis CCD, Oxford Diffraction Ltd., Version 1.171.32.15 (release 10-01-2008 CrysAlis171 .NET).
- 6 G. M. Sheldrick, SHELX97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.
- 7 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. of Applied Cryst.*, **1999**, 32, 115.
- 8 International Tables for X-ray Crystallography, vol C, Ed. Kluwer, Dordrech, **1992**.
- 9 See for example: (a) I. Krossing, A. Reisinger, *Eur. J. Inorg. Chem.*, **2005**, 1979; (b) A. Decken, G. B. Nikiforov, J. Passmore *Polyhedron*, **2005**, 24, 2994; (c) W. Petz, B. Neumüller, I. Krossing, *Z. Anorg. Allg. Chem.*, **2006**, 632, 859; (d) I. Krossing, A. Reisinger, *Coord. Chem. Rev.*, **2006**, 250, 2721.