Supporting Information

Synthesis and Characterization of Organo-Scandium and Yttrium Complexes Stabilized by Phosphinoamide Ligands

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NMR Spectroscopy: Characterization of phosphinoamide supported yttrium-alkyl complexes.

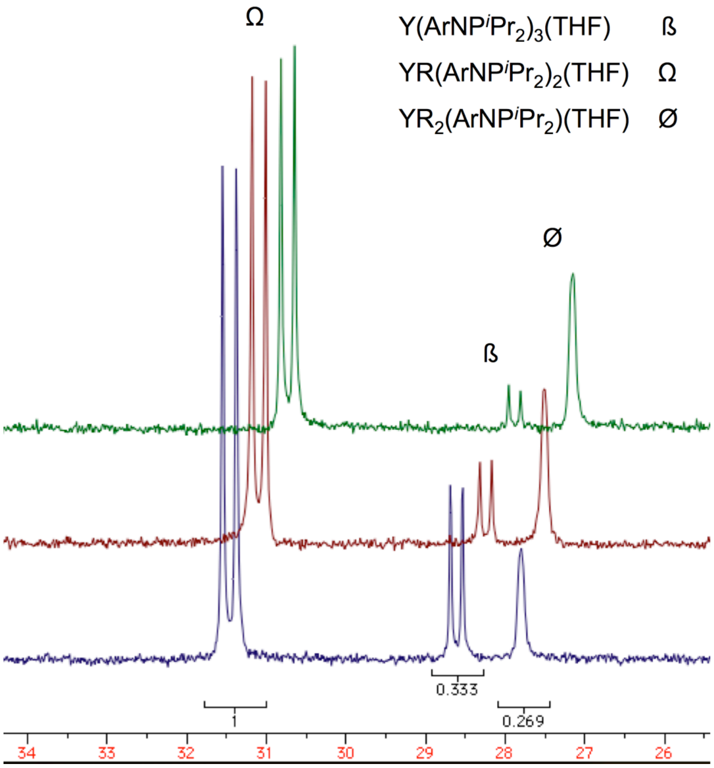

Figure S1: $^{31}P\{^1H\}$ NMR spectrum (160 MHz, 298K, C_6D_6): 1:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) [Blue], 2:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) [Red], 3:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) [Green]; where R = CH_2SiMe_3 and Ar = 3,5-dimethylphenyl.

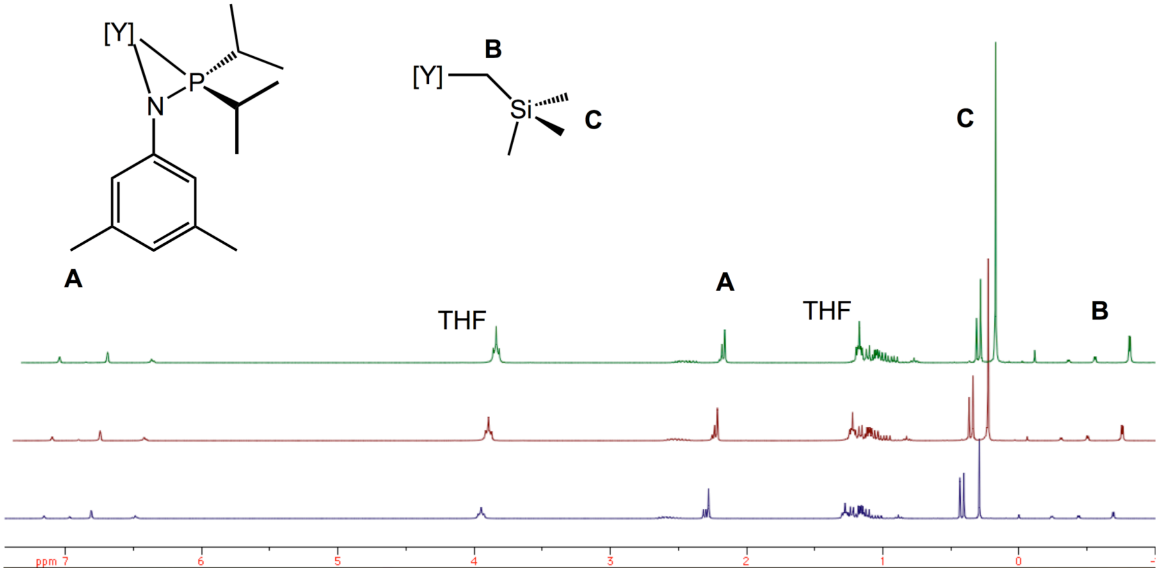

Figure S2: Full ^{1}H NMR spectra (400 MHz, 298K, C_6D_6): 1:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) [Blue], 2:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) [Red], 3:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) [Green]; where R = CH_2SiMe_3 and Ar = 3,5-dimethylphenyl.

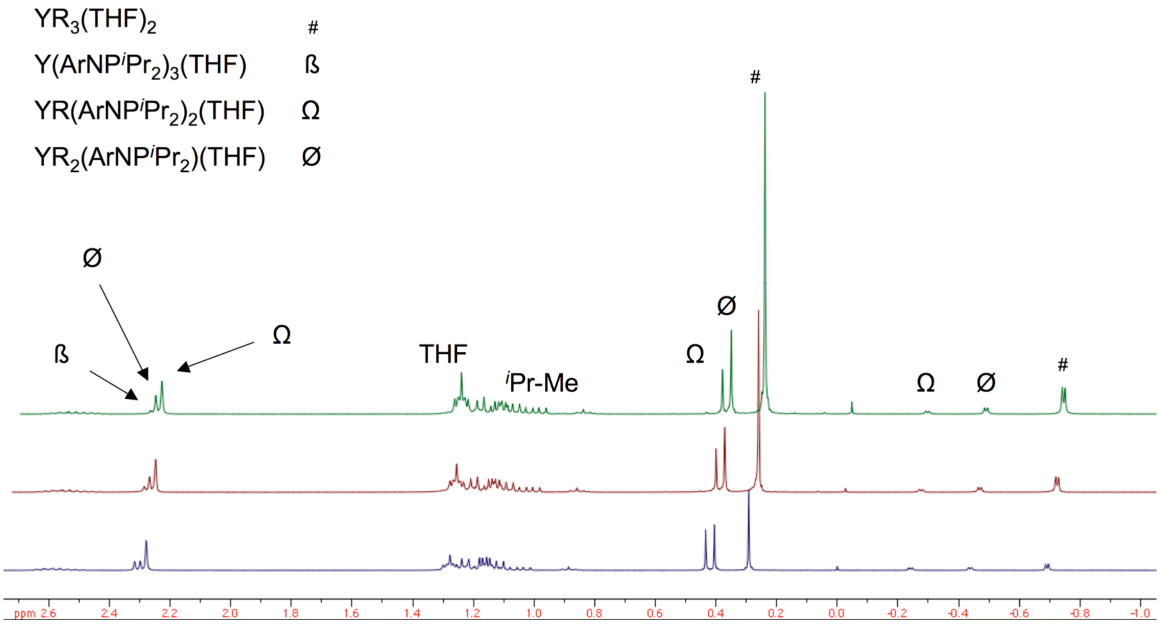

Figure S3: ^{1}H NMR spectra of the region from -1.0 ppm to 2.6 ppm (400 MHz, 298K, C_6D_6): 1:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) [Blue], 2:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) [Red], 3:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) [Green]; where R = CH_2SiMe_3 and Ar = 3,5-dimethylphenyl.

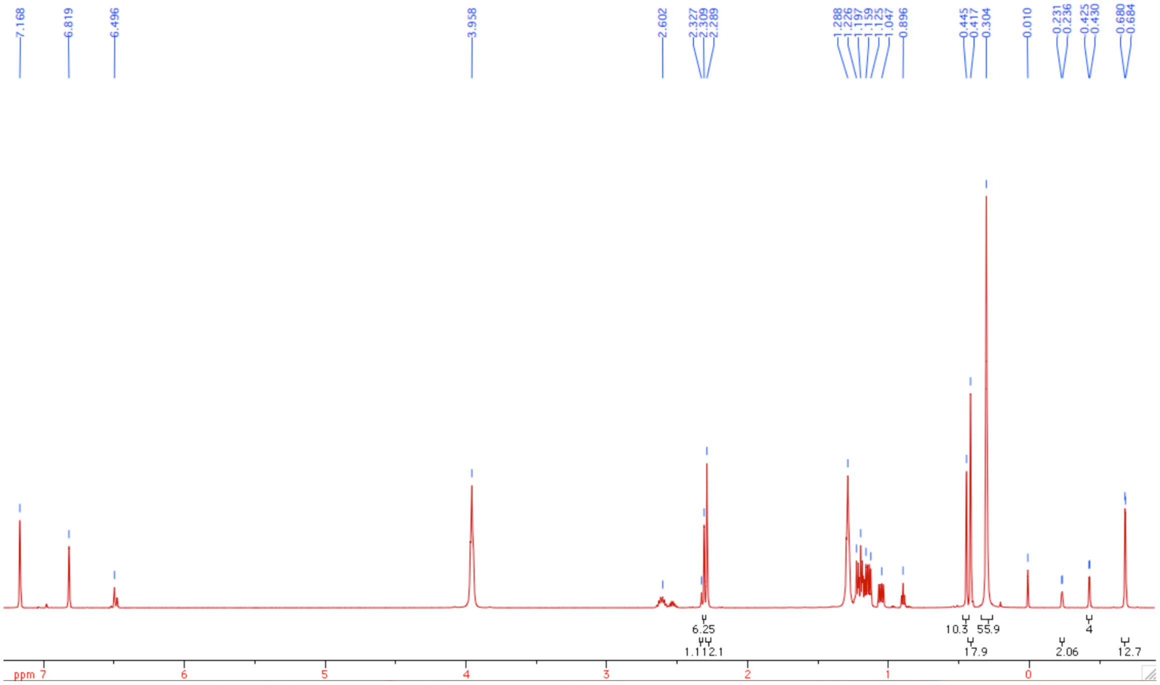

Figure S4: ^{1}H NMR spectrum (600 MHz, 298K, C_6D_6) of a solution of 3:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) which displays the integrations to support assignments of $YR(ArNP^iPr_2)_2(THF)$ and $YR_2(ArNP^iPr_2)(THF)$ where R = CH_2SiMe_3 and Ar = 3,5-dimethylphenyl.

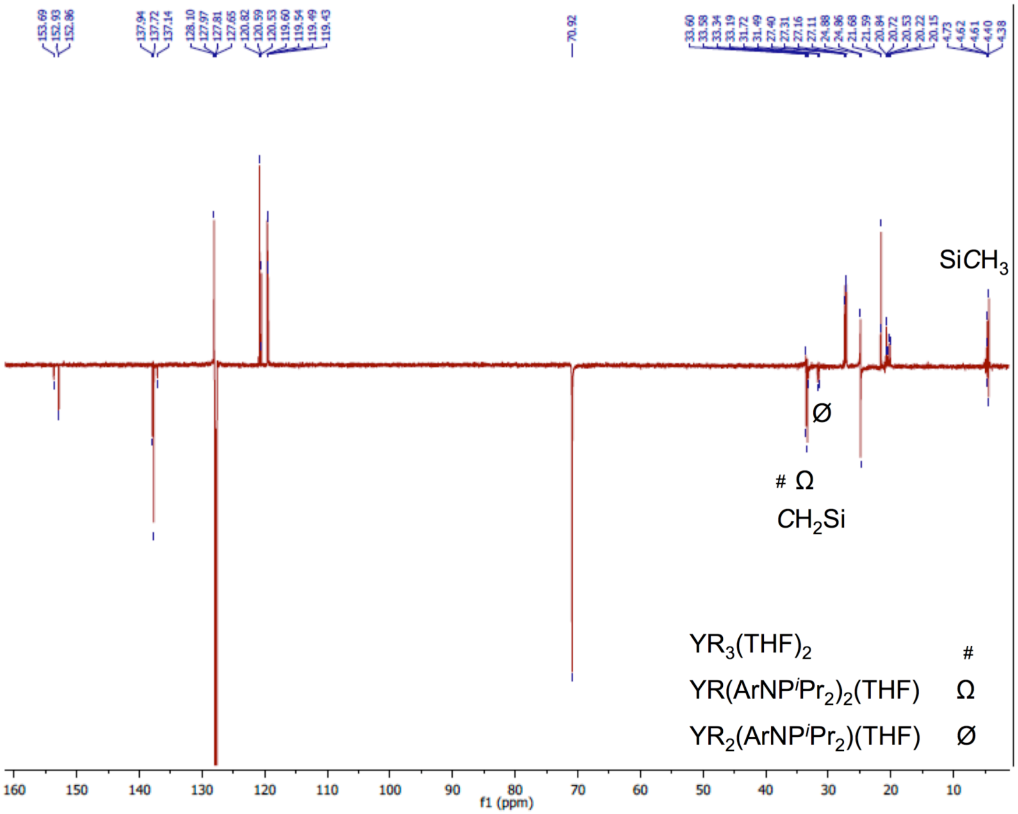

Figure S5: ^{13}C-APT (attached proton test) NMR spectrum (150 MHz, 298K, C_6D_6) of a solution of 3:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) which displays quarternary carbons and methylene carbons in a negative phase, and methine and methyl carbons in a positive phase.

NMR Spectroscopic Analysis:

Figures S1 and S2 display the consumption of $(ArNP^iPr_2)_3Y(THF)$ as $YR_3(THF)_2$ is added to a benzene solution. The generation of two new species is apparent, in particular by inspection of the $^{31}P\{^1H\}$ NMR (Figure S1) spectrum and by the resonances labeled **C** in the ^{1}H NMR spectrum (Figure S2). Integration of certain resonances in the ^{1}H NMR spectrum presented in Figure S4 allows for comparison of the tolyl-resonances (labeled **A** in Figure S2) of the ligand-backbone and the alkyl resonances (labeled **B** and **C** in Figure S2). These integrations support our assignments of the species as $YR(ArNP^iPr_2)_2(THF)$ and $YR_2(ArNP^iPr_2)(THF)$, which are present in a ratio of approximately 1:1. Figures S5 and S6 show that the ^{1}H resonances assigned as YCH_2SiMe_3 correlate to methylene-type carbons, while we have observed coupling constants of $^2J_{HY}$ = 3 Hz in the ^{1}H NMR spectrum for YCH_2SiMe_3 resonances (labeled **B** in Figure S2), we are not able to resolve any $^1J_{CY}$ coupling constants in Figure S5.

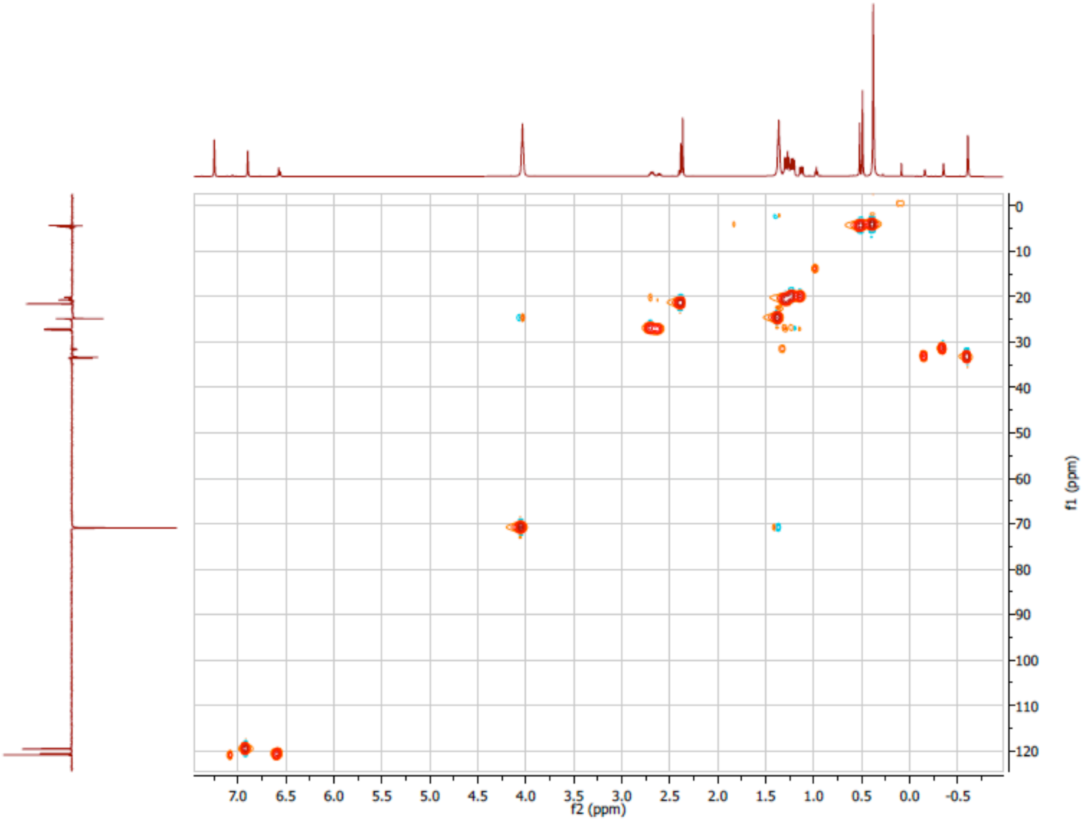

Figure S6: HSQC (Heteronuclear Single-Quantum Correlation) NMR spectrum (298K, C_6D_6) of a solution of 3:1 ($YR_3(THF)_2$: $Y(ArNP^iPr_2)_3(THF)$) which shows one-bond correlations between signals in the ^1H NMR spectrum (x-axis) and signals in the ^{13}C-APT spectrum (y-axis).

NMR Spectroscopy: Variable Temperature NMR studies of **3**, Sc(ArNP^{i}Pr$_2$)$_2$(CH$_2$SiMe$_3$)(THF), dissolved in THF-d_8.

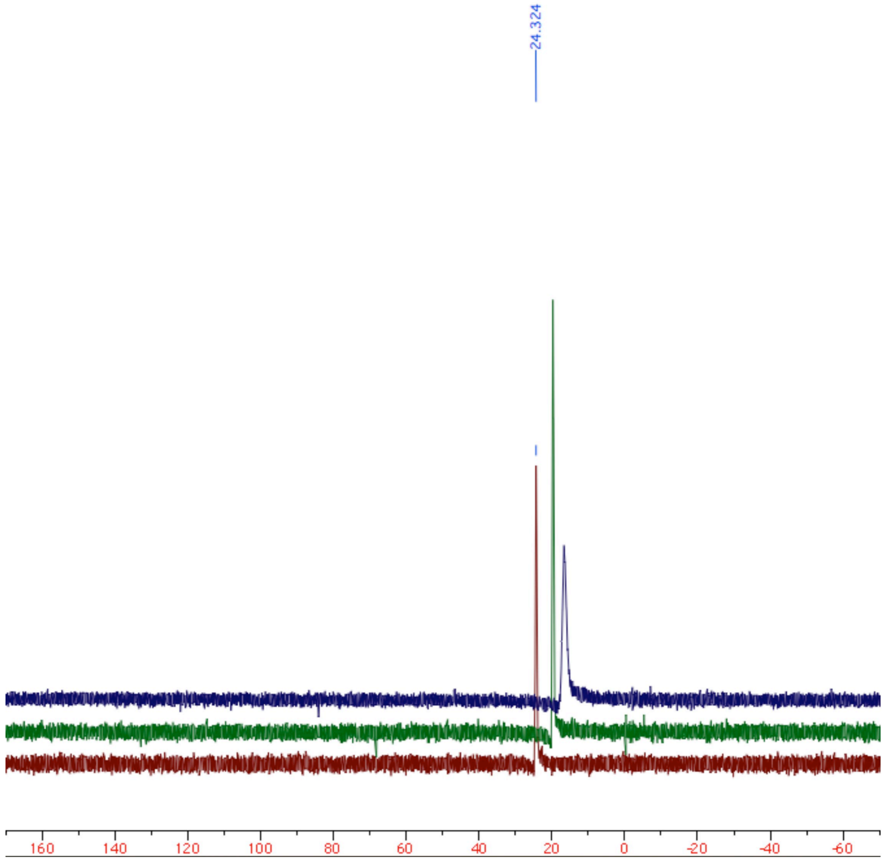

Figure S7: Stackplot of ^{31}P NMR spectra (x-axis in ppm) of complex **3** (THF-d_8, 298K, 243K, 203K).

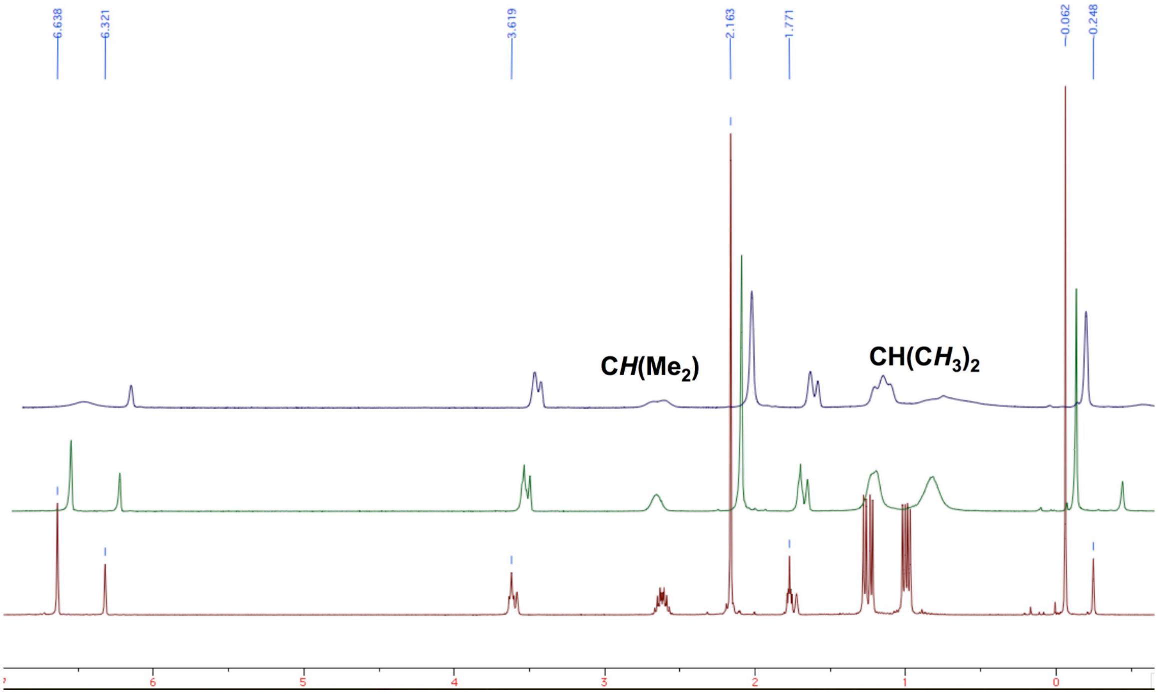

Figure S8: Stackplot of ^{1}H NMR spectra (x-axis in ppm) of complex **3** (THF-d_8, 298K, 243K, 203K).

Details of X-ray Crystallographic Studies

Suitable single crystals were selected, coated in Fomblin oil and mounted on a glass fiber. X-ray data were collected on a Bruker X8 Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) integrated using the Bruker SAINT software package.[1] Crystals of **3** were non-merohedrally twinned. Both twin domains are related by a 180° rotation about the c-axis (1 0 0 axis). Out of 41335 measured reflections, 14258 data (4642 unique) involved domain 1 only, 14249 data (4674 unique) involved domain 2 only and 12828 data (4403 unique) were part of both domains. The twinned structure was solved by direct methods using the non-overlapping reflections in an HKL4-formatted data set and refined using an HKL5-formatted data set that also included the overlapping reflections. The reflection data were prepared for refinement using the TWINABS program.[2] The absorption correction for **2b** was performed using the multi-scan technique (SADABS).[3] Structure **2b** was solved by direct methods and refined using all reflections with the SHELX-97 program package.[4] All non-hydrogen atoms were refined anisotropically. For a disordered Et_2O or pentane molecule in **2b** and no satisfactory model was obtained. For further refinement, the contribution of this solvent molecule was subtracted from the reflection data using the SQUEEZE[5] routine in the PLATON program package.[6] All hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter. Structures were solved and refined using the WinGX (version 1.80.05) software package.[7]

Table S1: Crystal structure and refinement data

	$\mathbf{(ArNP^{\mathit{i}}Pr_2)_3Y(THF)}$	$\mathbf{(ArNP^{\mathit{i}}Pr_2)_2Sc(CH_2SiMe_3)(THF)}$
Chemical formula	$C_{46}H_{77}N_3OP_3Y$	$C_{36}H_{65}N_2OP_2ScSi$
M_r	869.93	676.89
Crystal system	Monoclinic	Monoclinic
Space group	P 21/n	P 21/c
a / Å	17.0260(9)	11.5520(8)
b / Å	13.4302(6)	19.4650(15)
c / Å	23.0701(13)	18.3410(11)
a / °	90	90
b / °	104.7330(10)	98.253(3)
g / °	90	90
Volume / Å^3	5101.8(5)	4081.4(5)
T / K	100(2)	100(2)
Z	4	4
μ / mm^{-1}	1.27	0.315
ρ (calcd) / g/cm^3	1.133	1.102
F(000)	1864	1472
Absorption Correction	Multi-scan	Semi-empirical from equivalents
Crystal size / mm^3	0.28 x 0.20 x 0.14	0.26 x 0.24 x 0.20
Wavelength / Å	0.71073	0.71073
Reflections collected	35458	41335
Independent reflections	9023 [R(int) = 0.0368]	13719 [R(int) = 0.0502]
Data / restraints / parameters	9023 / 0 / 529	13719 / 0 / 404
Goodness-of-fit on F^2	1.075	1.09
R indices [I>2σ(I)] (R1, *w*R2)	0.0327, 0.0859	0.0441, 0.1230
R indices [all data] (R1, *w*R2)	0.0463, 0.0908	0.0519, 0.1266
Completeness to theta = 25.16^c	99.80%	98.70%
Max. and min. transmission	0.837 and 0.745	0.9396 and 0.9225
Theta range for data collection	1.34 to 25.06°	1.53 to 25.16°

$R1 = \Sigma \,||Fo|-|Fc|| / \Sigma|Fo|;\ wR2 = [\, \Sigma\, (w(Fo^2 - Fc^2)^2) / \Sigma\, w(Fo^2)^2]^{1/2}$

Supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif: CCDC 837086 & CCDC 837087.

References

(1) SAINT, Version 7.56, Bruker AXS Inc., Madison, Wisconsin, USA (**2008**).
(2) TWINABS, Version 2008/2, Bruker AXS Inc., Madison, Wisconsin, USA (**2008**).
(3) SADABS, Bruker area detector scaling and absorption correction - Version 2008/1, Bruker AXS Inc., Madison, Wisconsin, USA (**2008**).
(4) G. M. Sheldrick, *Acta Cryst. 2008*, **A64**, 112.
(5) P. v. d. Sluis, A. L. Spek, *Acta Cryst. 1990*, **A46**, 194.
(6) A. L. Spek, *J. Appl. Cryst. 2003*, **36**, 7.
(7) L. J. Farrugia, *J. Appl. Cryst. 1999*, **32**, 837.