Electronic Supplementary Information for Dalton Transactions

Supplementary Material

Stable heteroleptic complexes of divalent lanthanides with bulky pyrazolylborate ligands – iodides, hydrocarbyls and triethylborohydrides

X. W. Zhang,[a] Graham H. Maunder,[b] Stefan Gießmann,[a] Robert MacDonald,[a] Michael J. Ferguson,[a] Andrew H. Bond,[c] Robin D. Rogers,[d] Andrea Sella[b]* and Josef Takats[a]*

[a]Department of Chemistry, University of Alberta, Edmonton AB. T6G 2G2, Canada.
[b]Department of Chemistry, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London. WC1H 0AJ, United Kingdom.
[c] Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, USA Current address: AndBeyond Enterprises, LLC651 S. Sutton Rd., Ste. 300, Streamwood, IL 60107, USA.
[d]Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA

Details of X-ray Data Collection, Structure Determination and Refinement on complexes:

$[(Tp^{Me2})YbI(THF)_2]$ 1-Yb; $[(Tp^{tBu,Me})YbI(CN^tBu)]$ 2-Yb- CN^tBu;

$[(Tp^{tBu,Me})SmI(THF)_2]$ 2-Sm; $[(Tp^{tBu,Me})YbCH(SiMe_3)_2]$ 5-Yb;

$[(Tp^{tBu,Me})SmCH(SiMe_3)_2]$ 5-Sm; $[(Tp^{tBu,Me})SmCH(SiMe_3)_2(THF)]$ 5a-Sm;

$[(Tp^{tBu,Me})SmCH_2SiMe_3(THF)]$ 6a-Yb

[(Tp^{Me2})YbI(THF)$_2$] 1-Yb

(structure determined by A.H. Bond and R.D. Rogers)

An orange single crystal of the title compound was mounted in a thin-walled glass capilary under inert atmosphere and transferred to the goniometer. The space group was determined to be either the centric Pnma or the acentric Pn2_1a from systematic absences. The subsequent solution and successful refinement of the structure was carried out in the centric space group Pnma. A summary of the data collection parameters is given in Table S1.

Least-squares refinement with isotopic thermal parameters led to R = 0.146. The hydrogen atoms were not included in the final refinement. No decay correction was applied. High thermal motion was observed in the coordinated THF molecule and a disorder model was investigated. Each disorder model gave poor bonding contacts and geometries, and high thermal parameters for the disordered positions. Consequently, the atoms were allowed to refine anisotropically at full occupancy. Due to the unresolvable disorder no H atom positions were calculated. Several undefined peaks with very low electron density were located in the holes of the ac plane and attempts were made to refine these positions; one position was on the mirror plane and two lay off. Attempts at refining these peaks as one half a THF molecule, with the other half symmetry generated, gave poor bonding contacts and high thermal parameters (which were nearly equal for the three positions). The site occupancy factor was then reduced to 10%, this resulted in reasonable thermal parameters but chemically impossible bonding parameters. Accounting for this electron density did have a favorable effect on the refinement parameters R, R$_w$, and GOF, but because no chemically sensible solution could be obtained the electron density remains unaccounted for. An additional complicating factor was the crystal decay that could be attributed to the loss of solvent (THF) molecules from the lattice. The unresolved disorder, unaccounted for H atom and lattice solvent electron density, decay, and low number of observed data contributed to the high parameters, although the important structure features remain clear. Refinemement of atoms with anisotropic temperature factors led to the final values of R = 0.073 and R$_w$ = 0.098.

The final values of the positional and thermal parameters, and bond distances and angles can be found in the deposited cif; CCDC

Table S1. Crystallographic Experimental Details on [{κ^3–HB(3,5-Me-pyrazolyl)$_3$}YbI(OC$_4$H$_8$)$_2$](**1-Yb**)

A. Crystal Data

formula	$C_{23}H_{38}BIN_6O_2Yb$
formula weight	741.35
crystal dimensions (mm)	0.75 × 0.20 × 0.15
crystal system	orthorhombic
space group	*Pnma* (No. 62)
unit cell parameters^a	
a (Å)	14.229 (7)
b (Å)	14.689 (9)
c (Å)	16.264 (4)
V (Å^3)	3399 (3)

Z	4
ρ_{calcd} (g cm^{-3})	1.45
μ (mm^{-1})	3.84

B. Data Collection and Refinement Conditions

diffractometer	Enraf-Nonius CAD4[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	20
scan type	θ–2θ scans ([0.80 + 0.35tanθ]°, 6.67–1.54°/min)
data collection 2θ limit (deg)	50.00
total data collected	3373 ($0 \leq h \leq 17$, $0 \leq k \leq 17$, $0 \leq l \leq 19$)
independent reflections	3373
number of observed reflections (*NO*)	1578 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F (*SHELX–76*[c])
absorption correction method	semi-empirical (ψ scans)
range of transmission factors	1.00–0.62
data/restraints/parameters	1578 / 0 / 169
goodness-of-fit (S)[d] [$F_o \geq 5\sigma(F_o)$]	1.93
final R indices[e]	
R_1 [$F_o \geq 5\sigma(F_o)$]	0.073
R_2 [$F_o \geq 5\sigma(F_o)$]	0.098
largest difference peak	3.6 e Å^{-3} (0.93 Å from Yb atom)

[a] Obtained from least-squares refinement of 24 reflections with $20.0° < 2\theta < 30.0°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Enraf-Nonius.

[c] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

[d] $S = [\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma(F_o^2) + 0.0033F_o^2]^{-1}$).

[e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{1/2}$.

[(Tp^{tBu,Me})YbI(CN^{t}Bu)] 2-Yb- CN^{t}Bu CCDC 776643

(structure determined with help from Prof. D.A. Tocher)

An orange single crystal of the title compound was mounted in a thin-walled glass capilary under inert atmosphere and transferred to the goniometer of Nicolet R3mv four-circle diffractometer. The unit cell was determined, using axial photographs and the space group was determined to be P21/n from systematic absences and confirmed by successful refinement. A summary of the data collection parameters is given in Table S2.

Structure solution was by direct methods. Alternating cycles of difference Fourier synthesis and full-matrix least-squares refinement led to the location of all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions with C–H and B–H bond lengths fixed at 0.96 Å and with the isotropic thermal parameter *U* set to 0.08 Å^2. Disorder in the t-butyl group was modelled over two sites with occupancies of 0.7/0.3. Refinemement of atoms with anistropic temperature factors led to the final values of R = 0.0385 and R$_w$ = 0.0878.

The final values of the positional and thermal parameters, and bond distances and angles can be found in the deposited cif; CCDC

Table S2. Crystallographic Experimental Details on [{κ^3–HB(3-^{t}Bu-5-Me-pyrazolyl)$_3$}YbI(CN^{t}Bu)] (**2-Yb-CN^{t}Bu**)

A. Crystal Data	
formula	$C_{29}H_{49}BN_7YbI$
formula weight	806.50
crystal dimensions (mm)	0.40 × 0.85 × 0.65
crystal system	monoclinic
space group	*C2/c*
unit cell parameters^a	
a (Å)	10.581(2)
b (Å)	21.078(6)
c (Å)	16.443(4)
β (deg)	90.70(2)
V (Å^3)	3667 (2)
Z	4
ρ_{calcd} (g cm^{-3})	1.461
μ (mm^{-1})	3.418
B. Data Collection and Refinement Conditions	
diffractometer	Nicolet R3mV Four circle diffractometer^b
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	293
scan type	ω - 2θ
data collection 2θ limit (deg)	50.02
total data collected	7676
independent reflections	7560

number of observed reflections (*NO*)	5774 [$I \geq 2\sigma(I)$]
structure solution method	Direct (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d,e])
absorption correction method	psi scans
range of transmission factors	1.000–0.551
data/restraints/parameters	6416 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 368
goodness-of-fit (S)[f]	1.088 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0385
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0878
largest difference peak and hole	0.500 and –0.800 e Å^{-3}

[a] Obtained from least-squares refinement of 26 reflections with 12.12° < 2θ < 30.19°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Nicolet.

[c] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[d] Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.

[e] Hydrogens were placed in calculated positions and refined isotropically with a riding model. One t-butyl group was modelled with a two component (70:30) disorder.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0288P)^2 + 10.5967P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

$[(Tp^{tBu,Me})SmI(THF)_2]\bullet(Et_2O)$ 2-Sm CCDC 776641

(structure determined with help from Prof. D.A. Tocher)

A blue/black single crystal of the title compound was mounted in a thin-walled glass capillary under inert atmosphere and transferred to the goniometer of Nicolet R3mv four-circle diffractometer. The unit cell was determined, using axial photographs and the space group was determined to be C2/m from systematic absences and confirmed by successful refinement. A summary of the data collection parameters is given in Table S3.

Structure solution was by direct methods. Alternating cycles of difference Fourier synthesis and full-matrix least-squares refinement led to the location of all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions with C–H and B–H bond lengths fixed at 0.96 Å and with the isotropic thermal parameter *U* set to 0.08 Å^2. Disorder in the ether of solvation was modelled by fixing the oxygen on the inversion centre. The two carbons were refined isotropically without riding hydrogen atoms. Refinement of all other non-hydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.0447$ and $R_w = 0.1069$.

The final values of the positional and thermal parameters, and bond distances and angles can be found in the deposited cif; CCDC

Table S3. Crystallographic Experimental Details on $[\{\kappa^3\text{–HB(3-}^t\text{Bu-5-Me-pyrazolyl)}_3\}SmI(OC_4H_8)_2]\bullet(Et_2O)_{0.5}$ (**2-Sm**)

A. Crystal Data	
formula	$C_{72}H_{120}B_2I_2N_{12}O_6Sm_2$
formula weight	1777.88
crystal dimensions (mm)	0.40 × 0.85 × 0.65
crystal system	monoclinic
space group	*C2/m*
unit cell parameters[a]	
a (Å)	21.609(3)
b (Å)	12.869(2)
c (Å)	15.323(3)
β (deg)	98.35(1)
V (Å^3)	4216 (1)
Z	2
ρ_{calcd} (g cm^{-3})	1.401
μ (mm^{-1})	2.161
B. Data Collection and Refinement Conditions	
diffractometer	Nicolet R3mV Four circle diffractometer[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	293
scan type	ω - 2θ

data collection 2θ limit (deg)	50.12
total data collected	4739
independent reflections	3981
number of observed reflections (*NO*)	3091 [$I \geq 2\sigma(I)$]
structure solution method	Direct (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d,e])
absorption correction method	psi scans
range of transmission factors	0.917–0.733
data/restraints/parameters	3868 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 219
goodness-of-fit (S)[f]	1.031 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0447
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1069
largest difference peak and hole	0.547 and –1.047 e Å^{-3}

[a] Obtained from least-squares refinement of 28 reflections with 21.07° < 2θ < 26.28°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Nicolet.

[c] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[d] Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.

[e] Hydrogens were placed in calculated positions and refined isotropically with a fixed model. The ether molecule was modelled as a two site disorder (50:50). Attempts to introduce hydrogens into the model did not result in any improvement and they were therefore omitted.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0288P)^2 + 10.5967P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$

==

[(Tp^{tBu,Me})YbCH(SiMe$_3$)$_2$]•(Et$_2$O)$_{0.5}$ 5-Yb CCDC 776647

(structure determined by A.H. Bond and R.D. Rogers)

A yellow single crystal of the title compound was mounted in a thin-walled glass capilary under argon and transferred to the goniometer. The crystal was cooled to –100 ˚C during data collection by using a stream of cold nitrogen gas. The space group was determined to be the centric C2/c (No. 15) or acentric Cc (No. 9) from systematic absences; with the former (*C*2/*c*) being confirmed as the correct choice through the subsequent solution and successful refinement of the structure. A summary of the data collection parameters is given in Table S4.

Hydrogen atoms were generated from the idealized *sp*^{2} or *sp*^{3} geometries of their parent carbon or boron atoms, and were given isotropic displacement parameters 120% of the U_{eq}'s of their attached atoms. One *t*-butyl group was found to be disordered. Its methyl carbons were split into two sets of positions ([C38A, C39A, C40A] and [C38B, C39B, C40B]) that were refined with occupancy factors of 0.60 and 0.40, respectively. In addition, the solvent diethyl ether molecule was found to be disordered across the crystallographic inversion center ($^1/4$, $^1/4$, $^1/2$); its non-hydrogen atoms were refined with an occupancy factor of 0.5 and with anisotropic displacement parameters.

The final values of the positional and thermal parameters, and bond distances and angles can be found in the deposited cif; CCDC

Table S4. Crystallographic Experimental Details on [{κ^3–HB(3-^{t}Bu-5-Me-pyrazolyl)$_3$}Yb{CH(SiMe$_3$)$_2$}]•(Et$_2$O)$_{0.5}$ (**5-Yb**)

A. Crystal Data	
formula	$C_{33}H_{64}BN_6O_{0.5}Si_2Yb$
formula weight	792.93
crystal dimensions (mm)	0.30 × 0.20 × 0.20
crystal system	monoclinic
space group	*C*2/*c* (No. 15)
unit cell parameters[a]	
a (Å)	16.487 (5)
b (Å)	18.263 (5)
c (Å)	27.122 (8)
β (deg)	92.320 (6)
V (Å^3)	8160 (4)
Z	8
ρ_{calcd} (g cm^{-3})	1.291
μ (mm^{-1})	2.380
B. Data Collection and Refinement Conditions	
diffractometer	Siemens PLATFORM/SMART 1K CCD [b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ϕ and ω scans (0.3°) (10 s exposures)

data collection 2θ limit (deg)	46.56
total data collected	15486 ($0 \leq h \leq 18$, $-20 \leq k \leq 20$, $-29 \leq l \leq 29$)
independent reflections	5782 ($R_{\mathrm{int}} = 0.063$)
number of observed reflections (*NO*)	4932 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[c])
absorption correction method	multi-scan (*SADABS*)
range of transmission factors	0.6475–0.5353
data/restraints/parameters	5782 / 0 / 42d
goodness-of-fit (*S*)[e] [all data]	1.093
final *R* indices[e]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0405
wR_2 [all data]	0.1016
largest difference peak and hole	0.865 and -2.362 e Å^{-3}

[a] Obtained from least-squares refinement of 430 reflections with $3.00° < 2\theta < 46.56°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Siemens

[c] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

[d] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0515P)^2 + 17.9241P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

[(Tp^{tBu,Me})SmCH(SiMe$_3$)$_2$]•1.5PhMe 5-Sm CCDC 776646
(structure determined by R. McDonald)

Table S5. Crystallographic Experimental Details on [{κ^3–HB(3-^{t}Bu-5 Me-pyrazolyl)$_3$}Sm{CH(SiMe$_3$)$_2$}]•1.5PhMe (**5-Sm**)

A. Crystal Data

formula	$C_{41.5}H_{71}BN_6Si_2Sm$
formula weight	871.38
crystal dimensions (mm)	0.51 × 0.24 × 0.14
crystal system	monoclinic
space group	*P*2/*n* (an alternate setting of *P*2/*c* [No. 13])
unit cell parameters[a]	
a (Å)	17.8391 (18)
b (Å)	11.9006 (12)
c (Å)	24.176 (3)
β (deg)	106.6876 (17)
V (Å^3)	4916.4 (9)
Z	4
ρ_{calcd} (g cm^{-3})	1.177
μ (mm^{-1})	1.275

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.2°) (20 s exposures)
data collection 2θ limit (deg)	52.80
total data collected	32605 ($-22 \le h \le 22$, $-13 \le k \le 14$, $-30 \le l \le 30$)
independent reflections	10069 (R_{int} = 0.0647)
number of observed reflections (*NO*)	7249 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d,e])
absorption correction method	multi-scan (*SADABS*)
range of transmission factors	0.8417–0.5626
data/restraints/parameters	10069 [$F_o^2 \ge -3\sigma(F_o^2)$] / 6[f] / 397
goodness-of-fit (*S*)[g]	1.052 [$F_o^2 \ge -3\sigma(F_o^2)$]
final *R* indices[h]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0510
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.1347
largest difference peak and hole	0.976 and –0.547 e Å^{-3}

[a] Obtained from least-squares refinement of 4300 reflections with 4.90° < 2θ < 51.70°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[d] Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993.

[e] Attempts to refine peaks of residual electron density as carbon atoms of a second full-occupancy molecule of solvent toluene were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure (Sluis, P. van der; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194–201) as implemented in *PLATON* (Spek, A.L. *Acta Crystallogr.* **1990**, *A46*, C34. *PLATON* - a multipurpose crystallographic tool. Utrecht University, Utrecht, The Netherlands). A total solvent-accessible void volume of 983.5 A^3 with a total electron count of 271 (consistent with four molecules of solvent toluene, or one molecule per formula unit of the samarium complex) was found in the unit cell.

[f] Restraints were imposed upon distances involving the minority-occupancy carbons (C38B, C39B, C40B) of the disordered *t*-butyl group: d(C37–C38B) = d(C37–C39B) = d(C37–C40B) = 1.54 Å; d(C38B···C39B) = d(C38B···C40B) = d(C39B···C40B) = 2.52 Å.

[g] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0678P)^2 + 0.9449P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[h] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

The final values of the positional and thermal parameters, and bond distances and angles can be found in the deposited cif; CCDC

==

[(Tp^{tBu,Me})SmCH(SiMe$_3$)$_2$(THF)]• 2CH$_3$C$_6$H$_{11}$ 5a-Sm CCDC 776645
(structure determined by M.J. Feguson)

Table S6. Crystallographic Experimental Details on [(HB{3-^{t}Bu-5-Me-pyrazolyl}$_3$)Sm(CH{SiMe$_3$}$_2$)(OC$_4$H$_8$)]• 2CH$_3$C$_6$H$_{11}$ (**5a-Sm**)

A. Crystal Data	
formula[a]	$C_{49}H_{95}BN_6OSi_2Sm$
formula weight	1001.65
crystal dimensions (mm)	0.24 × 0.18 × 0.06
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[b]	
a (Å)	12.1033 (9)
b (Å)	16.3329 (13)
c (Å)	16.7012 (13)
α (deg)	65.7920 (10)
β (deg)	70.6740 (10)
γ (deg)	89.696 (2)
V (Å^3)	2808.7 (4)
Z	2
ρ_{calcd} (g cm^{-3})	1.184
μ (mm^{-1})	1.125
B. Data Collection and Refinement Conditions	
diffractometer	Bruker PLATFORM/SMART 1000 CCD[c]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.3°) (25 s exposures)
data collection 2θ limit (deg)	52.92
total data collected	21176 ($-15 \le h \le 15$, $-20 \le k \le 20$, $-20 \le l \le 19$)
independent reflections	11447 (R_{int} = 0.0588)
number of observed reflections (*NO*)	8354 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	Patterson search/structure expansion (*DIRDIF–99*[d])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[e])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9356–0.7740
data/restraints/parameters	11447 [$F_o^2 \ge -3\sigma(F_o^2)$] / 0 / 433
goodness-of-fit (S)[f]	0.954 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[g]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0532
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.1175
largest difference peak and hole	1.246 and –0.849 e Å^{-3}

[a] The SQUEEZE routine (Sluis, P. van der; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194–201) of the program *PLATON* (Spek, A. L. *Acta Crystogr.* **1990**, *A46*, C-34) was used to remove the contributions of the two disordered solvent methylcyclohexane molecules to the observed structure factors. A large 934 Å^3 void centered at (0.036, 0.456, 0.500) with scattering associated with a total density equivalent to 218 electrons was found and attributed to the four molecules of methylcyclohexane located within in the unit cell. The ratio of $[(\mathrm{Tp}^{\mathrm{tBu,Me}})\mathrm{SmCH(SiMe_3)_2(THF)}]$ to C_7H_{14} was 1:2.

[b] Obtained from least-squares refinement of 5146 reflections with $4.77° < 2\theta < 51.75°$.

[c] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[d] Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. (1999). The *DIRDIF-99* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

[e] Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted R-factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional R-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. R-factors based on F_o^2 are statistically about twice as large as those based on F_o, and R-factors based on ALL data will be even larger.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0506P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

The final values of the positional and thermal parameters, and bond distances and angles can be found in the deposited cif; CCDC

==

[(Tp^{tBu,Me})YbCH$_2$SiMe$_3$(THF)] **6a-Yb**

(structure determined by R. McDonald)

Table S7. Crystallographic Experimental Details on [(HB{3-^{t}Bu-5-Me-pyrazolyl}$_3$)Yb(CH$_2$SiMe$_3$)(OC$_4$H$_8$)] (**6a-Yb**)

A. Crystal Data	
formula	$C_{32}H_{59}BN_6OSiYb$
formula weight	755.79
crystal dimensions (mm)	0.48 × 0.33 × 0.26
crystal system	triclinic
space group	$P\overline{1}$ (No. 2)
unit cell parameters^a	
a (Å)	10.9336 (11)
b (Å)	13.1957 (13)
c (Å)	14.0307 (12)
α (deg)	83.721 (7)
β (deg)	71.087 (8)
γ (deg)	86.607 (8)
V (Å^3)	1902.9 (3)
Z	2
ρ_{calcd} (g cm^{-3})	1.319
μ (mm^{-1})	2.519
B. Data Collection and Refinement Conditions	
diffractometer	Enraf-Nonius CAD4^b
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–50
scan type	ω scans (0.6+[0.34tanθ]°, 6.67–1.54°/min)
data collection 2θ limit (deg)	49.94
total data collected	6962 ($-12 \le h \le 12$, $-15 \le k \le 15$, $0 \le l \le 16$)
independent reflections	6660 (R_{int} = 0.0313)
number of observed reflections (*NO*)	5849 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–86*^{c})
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*^{c})
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.5604–0.3776
data/restraints/parameters	6660 / 0 / 382
goodness-of-fit (S)^d [all data]	1.032
final R indices^e	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0329
wR_2 [all data]	0.0840

largest difference peak and hole	2.131 and –1.428 e Å^{-3}

[a] Obtained from least-squares refinement of 24 reflections with $20.14° < 2\theta < 24.62°$.

[b] Data acquisition and initial processing software: (a) diffractometer operation and data collection: *CAD4-PC* (Enraf-Nonius [1993]. Delft, The Netherlands); (b) data reduction: *XCAD4* (Harms, K; Wocadlo, S. [1995]. University of Marburg, Germany); (c) absorption correction: Bruker *XPREP* v.2008/2 (Bruker AXS [2008]. Madison, WI, U.S.A.).

[c] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

[d] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0576P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

The final values of the positional and thermal parameters, and bond distances and angles can be found in the deposited cif; CCDC

==