Supporting Information for: Lewis acid mediated β-hydride abstraction reactions of divalent $M(C(SiHMe_2)_3)_2THF_2$ (M = Ca, Yb).

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Experimental procedures for compounds $Ca(C(SiHMe_2)_3)_2THF_2$ (**1a**), $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**), $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2a**), $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2b**), $Ca(HB(C_6F_5)_3)_2THF_2$ (**3a**), $Yb(HB(C_6F_5)_3)_2THF_2$ (**3b**), $Yb(HBPh_3)_2THF_2$ (**5**), and $Zn(C(SiHMe_2)_3)_2$.

X-ray crystallographic data for $Ca(C(SiHMe_2)_3)_2THF_2$ (**1a**), $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**), $CaC(SiHMe_2)_3HB(C_6F_5)_3THF_2$ (**2a**), $YbC(SiHMe_2)_3HB(C_6F_5)_3THF_2$ (**2b**), $Ca(HB(C_6F_5)_3)_2THF_2$ (**3a**), $Yb(HBPh_3)_2THF_2$ (**5**), and $(Me_2SiC(SiHMe_2)_2)_2$.

Experimental.

General Procedures All reactions were performed under a dry argon atmosphere using standard Schlenk techniques, or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Dry, oxygen-free solvents were used throughout. Benzene, toluene, pentane, and tetrahydrofuran were degassed by sparging with nitrogen, filtered through activated alumina columns, and stored under N_2. Benzene-d_6, toluene-d_8, THF-d_8 were vacuum transferred from Na/K alloy and stored under N_2 in the glovebox. Anhydrous CaI_2 was purchased from Aldrich and used as received. All organic reagents were purchased from Aldrich. Anhydrous YbI_2,[1] $KC(SiHMe_2)_3$,[2] and $B(C_6F_5)_3$[3] were prepared as described in literature procedures. 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(dimethylsilyl)-1,3-disilacyclobutane was identified by comparison with previous preparation[4] and X-ray crystallography (see below). ^1H and $^{13}C\{^1H\}$ NMR spectra were collected on Bruker DRX-400 spectrometer. $^{29}Si\{^1H\}$ NMR spectra were recorded using DEPT experiments, and assigments were verified by ^1H COSY, ^1H-^{13}C HMQC, ^1H-^{13}C HMBC, and ^1H-^{29}Si HMBC experiments. Elemental analysis was performed using a Perkin-Elmer 2400 Series II CHN/S by the Iowa State Chemical Instrumentation Facility.

$Ca(C(SiHMe_2)_3)_2(THF)_2$ (1a). THF (12 mL) was added to a Schlenk flask containing $KC(SiHMe_2)_3$ (0.463 g, 2.03 mmol) and CaI_2 (0.298 g, 1.01 mmol) at room temperature to yield a deep reddish orange suspension. The solution turned light orange and cloudy after 1 h, and the mixture was stirred for 12 h. Upon standing, a clear yellow solution and a brown precipitate was obtained. The solvent was evaporated to dryness under reduced pressure, and the residue was extracted with pentane. The yellow extract was concentrated and recrystallized overnight at -30

°C to obtain yellow crystals of $Ca(C(SiHMe_2)_3)_2(THF)_2$ (0.335 g, 0.594 mmol, 58.7%). ^1H NMR (benzene-d_6, 400 MHz, 25 °C): δ 4.78 (m, 6 H, $^1J_{SiH}$ = 152.1 Hz, Si*H*Me$_2$), 3.64 (m, 8 H, OC*H*$_2$), 1.32 (m, 8 H, C*H*$_2$), 0.50 (d, 36 H, $^3J_{HH}$ = 2.8 Hz, CaC(SiH*Me*$_2$)$_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 125 MHz, 25 °C): δ 70.3 (O*C*H$_2$CH$_2$), 25.4 (OCH$_2$*C*H$_2$), 6.3 (Ca*C*(SiHMe$_2$)$_3$), 4.2 (CaC(SiH*Me*$_2$)$_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 79.5 MHz, 25 °C): δ -20.0 (*Si*HMe$_2$). IR (KBr, cm^{-1}): 2955 s, 2897 m, 2107 m (SiH), 2066 m (SiH), 1905 m (SiH), 1423 w, 1247 s, 1177 w, 1023 s, 894 s, 768 s, 668 m. Anal. Calcd for $C_{22}H_{58}Si_6O_2Ca$: C, 46.9; H, 10.4. Found: C, 46.5; H, 10.0. mp 111-113 °C.

Yb(C(SiHMe$_2$)$_3$)$_2$THF$_2$ (1b). THF (12 mL) was added at room temperature to $KC(SiHMe_2)_3$ (0.463 g, 2.03 mmol) and YbI_2 (0.432 g, 1.01 mmol) giving a deep red-orange suspension. This mixture was stirred for 12 h to yield a reddish brown solution and a brown precipitate upon standing. Solvent was evaporated to dryness under reduced pressure, and the solid was extracted with pentane. The deep red pentane extract was concentrated and recrystallized overnight at -30 °C to obtain dark red crystalline blocks of $Yb(C(SiHMe_2)_3)_2THF_2$ (0.350 g, 0.502 mmol, 49.6 %). ^1H NMR (benzene-d_6, 400 MHz, 25 °C): δ 4.78 (m, 6 H, $^1J_{SiH}$ = 150.4 Hz, Si*H*Me$_2$), 3.65 (s, 8 H, OC*H*$_2$CH$_2$), 1.32 (s, 8 H, OCH$_2$C*H*$_2$), 0.49 (d, 18 H, $^3J_{HH}$ = 3.3 Hz, CaC(SiH*Me*$_2$)$_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 125 MHz, 25 °C): δ 70.5 (O*C*H$_2$CH$_2$), 20.4 (OCH$_2$*C*H$_2$), 11.4 (Yb*C*(SiHMe$_2$)$_3$), 4.1 (C(SiH*Me*$_2$)$_3$). $^{29}Si\{^1H\}$ NMR (benzene-d_6, 79.5 MHz, 25 °C): δ -19.5 (*Si*HMe$_2$). IR (KBr, cm^{-1}): 2951 s, 2895 m, 2101 m (SiH), 2065 m (SiH), 1890 w (SiH), 1458 w, 1420 w, 1247 s, 1023 s, 886 vs, 833 s, 766 s, 668 s. Anal. Calcd for $C_{22}H_{58}Si_6O_2Yb$: C, 38.0; H, 8.4. Found: C, 38.3; H, 8.5. mp 115-119 °C.

CaC(SiHMe$_2$)$_3$(HB(C$_6$F$_5$)$_3$)THF$_2$ (2a). In the glovebox, $Ca(C(SiHMe_2)_3)_2THF_2$ (0.134 g, 0.238 mmol), $B(C_6F_5)_3$ (0.134 g, 0.261 mmol), and toluene (5 mL) were placed in a 20 mL scintillation vial. The mixture was shaken well and allowed to stand at room temperature for 15 min to give a slightly cloudy solution. This mixture was cooled to -30 °C overnight to produce colorless crystals of the byproduct disilacyclobutane $(Me_2SiC(SiHMe_2)_2)_2$, which were removed by filtration. The colorless mother liquor was placed at -30 °C overnight to obtain a second crop of colorless crystals of $(Me_2SiC(SiHMe_2)_2)_2$. The mother liquor was isolated and the solvent was evaporated under reduced pressure to give a white solid that contained <5% $(Me_2SiC(SiHMe_2)_2)_2$

(as determined by ^{1}H NMR spectroscopy). The resulting white solid was dissolved in 5 mL of pentane and cooled to -30 °C overnight to yield colorless crystals of $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (0.107 g, 0.121 mmol, 50.7%). ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 4.55 (m, 3 H, $^1J_{SiH}$ = 148.9 Hz, Si*H*Me$_2$), 3.43 (m, 8 H, OC*H*$_2$CH$_2$), 1.15 (m, 8 H, OCH$_2$C*H*$_2$), 2.27-2.96 (br q, 1 H, *H*B(C$_6$F$_5$)$_3$), 0.35 (d, 18 H, $^3J_{HH}$ = 3.4 Hz, CaC(SiH*Me*$_2$)$_3$). ^{1}H{^{11}B} NMR (benzene-d_6, 125 MHz, 25 °C): δ 2.6 (s, br, *H*B(C$_6$F$_5$)$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 25 °C): δ 150.1 (br, *C*$_6$F$_5$), 147.8 (br, *C*$_6$F$_5$), 141.0 (br, *C*$_6$F$_5$), 139.1 (br, *C*$_6$F$_5$), 138.6 (br, *C*$_6$F$_5$), 136.7 (br, *C*$_6$F$_5$), 70.3 (O*C*H$_2$CH$_2$), 25.3 (OCH$_2$*C*H$_2$), 12.0 (Ca*C*(SiHMe$_2$)$_3$), 3.3 (CaC(SiH*Me*$_2$)$_3$). ^{11}B NMR (benzene-d_6, 79.5 MHz, 25 °C): δ -21.3 (d, $^1J_{BH}$ = 76.2 Hz). ^{19}F NMR (benzene-d_8, 376 MHz, 25 °C): δ -137.0 (br, 6 F, *ortho*-C$_6$F$_5$), -158.7 (br, 3 F, *para*-C$_6$F$_5$), -163.3 (6 F, *meta*-C$_6$F$_5$). ^{29}Si{^{1}H} NMR (benzene-d_6, 79.5 MHz, 25 °C): δ -19.0 (*Si*HMe$_2$). IR (KBr, cm^{-1}): 2958 m, 2899 m, 2329 m (BH), 2109 w (SiH, residual (Me$_2$SiC(SiHMe$_2$)$_2$)$_2$), 2077 m (SiH), 2042 w (SiH), 1957 br (SiH), 1645 m, 1604 w, 1516 vs, 1467 vs, 1373 m, 1361 w, 1282 m, 1253 m, 1110 vs, 1086 s, 1077 s, 1024 s, 966 vs br, 875 vs br, 837 s, 771 w, 685 m, 673 w. Anal. Calcd for $C_{33}H_{38}Si_3O_2BF_{15}Ca$: C, 44.7; H, 4.3. Found: C, 44.5; H, 3.9. mp 125-135 °C.

$YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (2b). A similar procedure was employed as described above for the calcium analog, substituting $Yb(C(SiHMe_2)_3)_2THF_2$ (0.592 g, 0.850 mmol) for $Ca(C(SiHMe_2)_3)_2THF_2$. $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ was obtained in reasonable yield (0.542 g, 0.532 mmol, 62.5%). ^{1}H NMR (benzene-d_6, 600 MHz, 25 °C): δ 4.61 (m, br, 3 H, $^1J_{SiH}$ = 146.4 Hz, Si*H*Me$_2$), 3.43 (m, br, 8 H, OC*H*$_2$), 1.16 (m, br, 8 H, C*H*$_3$), 0.34 (d, 18 H, $^3J_{HH}$ = 3.7 Hz, SiC*H*$_3$). The HB resonance overlaps with THF. ^{13}C{^{1}H} NMR (benzene-d_6, 150 MHz, 25 °C): δ 149.2 (br, *C*$_6$F$_5$), 147.6 (br, *C*$_6$F$_5$), 140.1 (br, *C*$_6$F$_5$), 138.2 (br, *C*$_6$F$_5$), 136.5 (br, *C*$_6$F$_5$), 120.8 (br, *C*$_6$F$_5$), 114.8 (br, *C*$_6$F$_5$), 69.9 (O*C*H$_2$CH$_2$), 24.7 (OCH$_2$*C*H$_2$), 2.5 ($^3J_{SiC}$ = 50.1 Hz, SiH*Me*$_2$), -1.8 (Yb*C*(SiHMe$_2$)$_3$). ^{11}B NMR (benzene-d_6, 79.5 MHz, 25 °C): δ -20.8 (d, $^1J_{BH}$ = 72.8 Hz). ^{19}F NMR (benzene-d_8, 376 MHz, 25 °C): δ -134.5 (br, 6 F, *ortho*-C$_6$F$_5$), -160.8 (t, $^3J_{FF}$ = 21.4 Hz, 3 F, *para*-C$_6$F$_5$), -163.3 (6 F, *meta*-C$_6$F$_5$). ^{29}Si{^{1}H} NMR (benzene-d_6, 79.5 MHz, 25 °C): δ -19.0 (*Si*HMe$_2$). IR (KBr, cm^{-1}): 2959 m, 2899 w, 2310 w (BH), 2110 w (SiH, residual (Me$_2$SiC(SiHMe$_2$)$_2$)$_2$), 2074 w (SiH), 1921 br (SiH), 1645 m, 1604 w, 1516 s, 1466 s, 1373 w, 1326 vw, 1282 m, 1254 m, 1108 m, 1086 m, 1024 m, 966 s, 875 s, 837 s, 770 w. Calcd for

$C_{33}H_{38}Si_3O_2BF_{15}Yb$: C, 38.9; H, 3.8. Found: C, 39.3; H, 3.9. mp 115-119 °C.

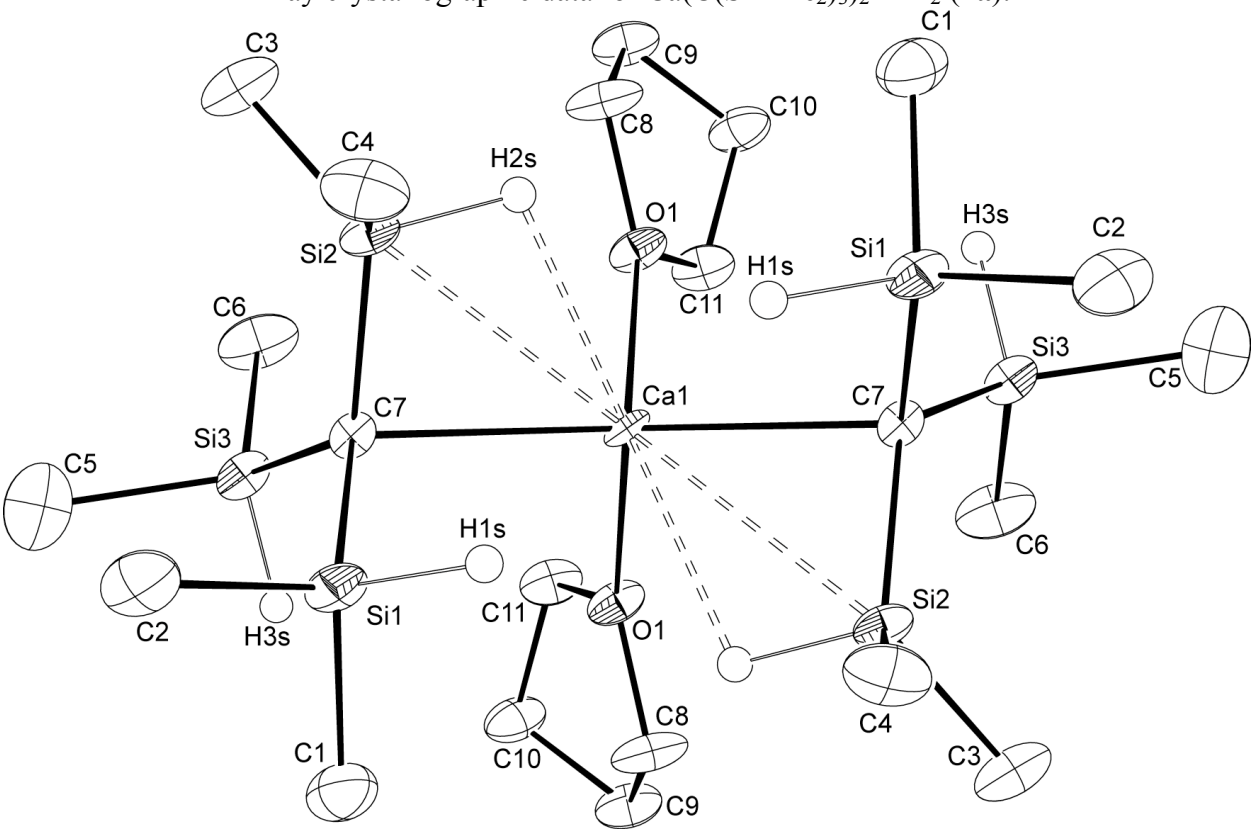
$Ca(HB(C_6F_5)_3)_2THF_2$ (3a). In the glovebox, $Ca(C(SiHMe_2)_3)_2(THF)_2$ (0.185 g, 0.328 mmol), $B(C_6F_5)_3$ (0.354 g, 0.691 mmol) and toluene (10 mL) were placed in a 20 mL scintillation vial. The mixture was thoroughly shaken and allowed to stand at room temperature for 15 min. The resulting pale yellow solution was cooled to -30 °C overnight to yield colorless crystals of $(Me_2SiC(SiHMe_2)_2)_2$ and toluene insoluble **3a**. To separate the disilacyclobutane and **3a**, the solid was washed with toluene (2 × 5 mL) and pentane (1 × 5 mL), and dried under reduced pressure to obtain pure **3a** as an off-white crystalline solid. (0.275 g, 0.228 mmol, 69.5%). ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ 3.62 (m, 8 H, OCH_2CH$_2$), 1.78 (m, 8 H, OCH$_2$CH_2), HB resonance overlaps with THF. ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz, 25 °C): δ 150.4 (br, C_6F_5), 148.1 (br, C_6F_5), 139.9 (br, C_6F_5), 138.5 (br, C_6F_5), 137.5 (br, C_6F_5), 136.2 (br, C_6F_5), 68.4 (OCH$_2$CH$_2$), 26.4 (OCH$_2$$CH_2$). ^{11}B NMR (THF-$d_8$, 79.5 MHz, 25 °C): δ -26.5 (d, $^1J_{BH}$ = 90.8 Hz). ^{19}F NMR (THF-d_8, 376 MHz, 25 °C): δ -135.9 (d, $^3J_{FF}$ = 21.4 Hz, 6 F, *ortho*-C_6F_5), -168.2 (t, $^3J_{FF}$ = 19.9 Hz, 3 F, *para*-C_6F_5), -170.9 (t, $^3J_{FF}$ = 19.6 Hz, 6 F, *meta*-C_6F_5). IR (KBr, cm^{-1}): 2981 w, 2904 w, 2308 (m, BH), 1648 s, 1608 m, 1517 vs, 1467 vs, 1375 s, 1281 s, 1123 s, 1084 s, 1012 m, 961 vs, 900 m, 864 m, 790 w, 769 w, 756 w, 729 m. Anal. Calcd for $C_{49}H_{30}O_2B_2F_{30}Ca$: C, 45.9; H, 2.4. Found: C, 45.9; H, 2.3. M.p: 177-182 °C.

$Yb(HB(C_6F_5)_3)_2THF_2$ (3b). A similar procedure was employed as for **3a**, with $Yb(C(SiHMe_2)_3)_2THF_2$ (0.266 g, 0.382 mmol) and $B(C_6F_5)_3$ (0.410 g, 0.801 mmol). Yield 0.420 g, 0.312 mmol, 81.8%. ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ 3.79 (m, 8 H, OCH_2CH$_2$), 1.94 (m, 8 H, CH$_2$CH_2); HB resonance overlaps with THF. ^{13}C{^{1}H} NMR (THF-d_8, 175 MHz, 25 °C): δ 150.5 (br, C_6F_5), 148.1 (br, C_6F_5), 139.9 (br, C_6F_5), 138.5 (br, C_6F_5), 137.5 (br, C_6F_5), 136.2 (br, C_6F_5), 68.4 (OCH$_2$), 26.4 (CH$_2$). ^{11}B NMR (THF-d_8, 79.5 MHz, 25 °C): δ -26.4 (d, $^1J_{BH}$ = 79.0 Hz). ^{19}F NMR (THF-d_8, 376 MHz, 25 °C): δ -134.0 (d, $^3J_{FF}$ = 20.3 Hz, 6 F, *ortho*-C_6F_5), -166.3 (t, $^3J_{FF}$ = 19.9 Hz, 3 F, *para*-C_6F_5), -169.0 (t, $^3J_{FF}$ = 18.3 Hz, 6 F, *meta*-C_6F_5). IR (KBr, cm^{-1}): 2984 m, 2901 m, 2377 (w, BH), 1642 m, 1604 w, 1511 vs, 1464 vs, 1376 m, 1274 m, 1101 s, 1078 m, 1019 s, 969 vs, 913 m, 862 s, 760 w, 725 w. Anal. Calcd for $C_{49}H_{30}O_2B_2F_{30}Yb$: C, 41.6; H, 2.1. Found: C, 41.7; H, 1.9. mp: 85-90 °C.

$Yb(HBPh_3)_2THF$ (5). In the glovebox, $Yb(C(SiHMe_2)_3)_2THF_2$ (0.208g, 0.299 mmol), BPh_3 (0.152 g, 0.628 mmol) and benzene (7 mL) were placed into a 20 mL scintillation vial. The mixture was thoroughly shaken and allow to stand at room temperature for 6 h. The resulting deep red solution was evaporated to dryness to provide an orange solid. The solid was washed with pentane (3 × 7 mL), and residual solvent was removed under vacuum to yield **5** as bright orange solid. X-ray quality single crystals can be obtained by slow diffusion of pentane into a toluene solution of **5** (5:1 v/v) at -30 °C. Yield: 0.190 g, 0.260 mmol, 86.8%. ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 7.49 (br, 12 H, *meta*-C_6H_5), 7.2 (br, 12 H, *ortho*-C_6H_5), 7.1 (br, 6 H, *para*-C_6H_5), 3.29 (m, 4 H, CH_2CH_2O), 1.24 (m, br, 4 H, CH_2CH_2O). ^{1}H{^{11}B} NMR (benzene-d_6, 125 MHz, 25 °C): δ 3.7 (br, *H*B). ^{13}C{^{1}H} NMR (benzene-d_6, 125 MHz, 25 °C): δ 135.5 (*meta*-C_6H_5), 129.4 (*ortho*-C_6H_5), 126.3 (*para*-C_6H_5), 69.1 (CH_2CH_2O), 25.7 (CH_2CH_2O). ^{11}B NMR (benzene-d_6, 79.5 MHz, 25 °C): δ -4.0 (d, br, $^1J_{BH}$ = 56.4 Hz). IR (KBr, cm^{-1}): 3059 s, 2993 s, 2003 m (BH), 1591 m, 1481 m, 1263 m, 1240 s, 1130 m, 1170 m, 1081 m, 1026 m, 998 m, 884 m, 740 s, 703 vs. Anal. Calcd for $C_{40}H_{40}O B_2Yb$: C, 65.7; H, 5.5. Found: C, 65.4; H, 5.4. mp: 165-182 °C.

$Zn(C(SiHMe_2)_3)_2$. In the glovebox, $KC(SiHMe_2)_3$ (1.40 g, 6.13 mmol) and $ZnCl_2$ (0.418 g, 3.06 mmol) were placed in a 100 mL Schlenk flask with a stir bar. At -78°C, THF (35 mL) was added to the mixture with vigorous stirring. After addition, the reaction mixture was warmed to room temperature and stirred for 8.5 h to yield a pale yellow cloudy solution. THF was evaporated under reduced pressure to obtain a pale yellow gel, which was extracted with pentane (25 mL). After removing the pentane under reduced pressure, $Zn(C(SiHMe_2)_3)_2$ was obtained as spectroscopically and analytically pure colorless oil. Microcrystalline solid is isolated from concentrated pentane solution of $Zn(C(SiHMe_2)_3)_2$ at -80 °C. (0.890 g, 2.00 mmol, 65.3%). ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 4.60 (m, 6 H, $^1J_{SiH}$ = 181.6 Hz, Si*H*Me_2), 0.34 (d, 36 H, $^3J_{HH}$ = 3.7 Hz, SiH*Me*$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, 125 MHz, 25 °C): δ 9.6 (Zn*C*$(SiHMe_2)_3$), 1.8 ($^3J_{SiC}$ = 51 Hz, ZnC(SiH*Me*$_2)_3$). ^{29}Si{^{1}H} NMR (benzene-d_6, 79.5 MHz, 25 °C): δ -20.3 (*Si*HMe_2). IR (KBr, cm^{-1}): 2953 vs, 2901 m, 2087 vs (SiH), 1415 m, 1250 vs, 890 vs, br, 688 s, 668 s. Anal. Calcd for $C_{14}H_{42}Si_6Zn$: C, 37.8; H, 9.5. Found: C, 38.0; H, 9.5.

X-ray crystallographic data for $Ca(C(SiHMe_2)_3)_2THF_2$ (**1a**).



Data Collection for $Ca(C(SiHMe_2)_3)_2THF_2$ (1a).

A yellow crystal was selected under ambient conditions. The crystal was mounted and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed at 173K on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the detector to crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3º in a 10º range about ω with the exposure time of 10 seconds per frame. The obtained reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of strong reflections from the actual data collection. The data were collected using the full sphere routine by collecting four sets of frames with 0.3º scans in ω with an exposure time 10 sec per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was based on a fit of a spherical harmonic function to the empirical transmission surface as sampled by multiple equivalent measurements using SADABS software.[5,6]

Structure Solution and Refinement for $Ca(C(SiHMe_2)_3)_2THF_2$ (1a).

The systematic absences in the diffraction data were consistent for the space groups *C2*/c[6] yielded chemically reasonable and computationally stable results of refinement. The position of almost all non-hydrogen atoms were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions (except hydrogen atoms belonged to Si atoms which were found objectively in the fourier difference map) and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

Table S1. Crystal data and structure refinement for $Ca(C(SiHMe_2)_3)_2THF_2$ (**1a**).

Empirical formula	$C_{22}H_{58}CaO_2Si_6$	
Formula weight	563.30	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.185(7) Å	α= 90°.
	b = 9.352(3) Å	β= 121.49(2)°.
	c = 18.826(6) Å	γ = 90°.
Volume	3481(2) $Å^3$	
Z	4	
Density (calculated)	1.075 Mg/m^3	
Absorption coefficient	0.403 mm^{-1}	
F(000)	1240	
Crystal size	0.40 x 0.30 x 0.20 mm^3	
Theta range for data collection	2.06 to 21.97°.	
Index ranges	$-24 \le h \le 24$, $-9 \le k \le 9$, $-19 \le l \le 19$	
Reflections collected	8916	
Independent reflections	2119 [R(int) = 0.1322]	
Completeness to theta = 21.97°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9238 and 0.8555	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2119 / 0 / 156	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0804, wR2 = 0.1921	
R indices (all data)	R1 = 0.1185, wR2 = 0.2165	
Largest diff. peak and hole	0.695 and -0.633 $e.Å^{-3}$	

$R1 = \Sigma \, | |F_o| - |F_c| | \, / \, \Sigma \, |F_o|$ and $wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for $Ca(C(SiHMe_2)_3)_2THF_2$ (**1a**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

atom	x	y	z	U(eq)
Ca(1)	5000	7036(2)	2500	13(1)
Si(1)	3616(1)	4482(2)	1469(1)	21(1)

Si(2)	4304(1)	5279(2)	3325(1)	19(1)
Si(3)	3270(1)	7423(2)	1898(1)	20(1)
C(1)	3261(4)	5167(9)	368(5)	35(2)
C(2)	2965(4)	3182(8)	1400(5)	33(2)
C(3)	4010(5)	5935(9)	4027(5)	37(2)
C(4)	4407(4)	3297(8)	3493(5)	33(2)
C(5)	2373(4)	6972(9)	1560(6)	47(3)
C(6)	3503(5)	8947(8)	2665(5)	37(2)
C(7)	3872(3)	5919(7)	2242(4)	13(2)
C(8)	5509(4)	8619(8)	4396(4)	31(2)
C(9)	5736(4)	10044(9)	4833(5)	30(2)
C(10)	6117(4)	10675(8)	4449(5)	30(2)
C(11)	5664(4)	10262(8)	3542(4)	26(2)
O(1)	5381(2)	8853(5)	3553(3)	22(1)

Table S3. Bond lengths [Å] for $Ca(C(SiHMe_2)_3)_2THF_2$ (**1a**).

Ca(1)-O(1)	2.402(5)	Si(3)-H(3S)	1.46(6)	C(6)-H(6A)	0.9800
Ca(1)-C(7)	2.616(7)	C(1)-H(1A)	0.9800	C(6)-H(6B)	0.9800
Ca(1)-Si(2)	3.216(2)	C(1)-H(1B)	0.9800	C(6)-H(6C)	0.9800
Ca(1)-Si(3)	3.571(2)	C(1)-H(1C)	0.9800	C(8)-O(1)	1.469(8)
Ca(1)-H(2S)	2.53(6)	C(2)-H(2A)	0.9800	C(8)-C(9)	1.509(11)
Si(1)-C(7)	1.838(7)	C(2)-H(2B)	0.9800	C(8)-H(8A)	0.9900
Si(1)-C(2)	1.889(8)	C(2)-H(2C)	0.9800	C(8)-H(8B)	0.9900
Si(1)-C(1)	1.897(8)	C(3)-H(3A)	0.9800	C(9)-C(10)	1.523(11)
Si(1)-H(1S)	1.42(6)	C(3)-H(3B)	0.9800	C(9)-H(9A)	0.9900
Si(2)-C(7)	1.840(7)	C(3)-H(3C)	0.9800	C(9)-H(9B)	0.9900
Si(2)-C(4)	1.874(7)	C(4)-H(4A)	0.9800	C(10)-C(11)	1.514(10)
Si(2)-C(3)	1.878(8)	C(4)-H(4B)	0.9800	C(10)-H(10A)	0.9900
Si(2)-H(2S)	1.39(6)	C(4)-H(4C)	0.9800	C(10)-H(10B)	0.9900
Si(3)-C(7)	1.844(7)	C(5)-H(5A)	0.9800	C(11)-O(1)	1.477(9)
Si(3)-C(5)	1.877(9)	C(5)-H(5B)	0.9800	C(11)-H(11A)	0.9900
Si(3)-C(6)	1.896(8)	C(5)-H(5C)	0.9800	C(11)-H(11B)	0.9900

Table S4. Bond angles [°] for $Ca(C(SiHMe_2)_3)_2THF_2$ (**1a**).

O(1)-Ca(1)-C(7)	109.6(2)	Si(2)-Ca(1)-Si(3)	56.03(5)	C(3)-Si(2)-Ca(1)	129.1(3)
O(1)#1-Ca(1)-C(7)	103.2(2)	Si(2)#1-Ca(1)-Si(3)	131.48(6)	C(7)-Si(2)-H(2S)	103(3)
C(7)-Ca(1)-C(7)#1	132.9(3)	Si(3)#1-Ca(1)-Si(3)	168.37(9)	C(4)-Si(2)-H(2S)	105(3)
O(1)-Ca(1)-Si(2)	91.3(1)	O(1)-Ca(1)-H(2S)	76(1)	C(3)-Si(2)-H(2S)	106(3)
O(1)#1-Ca(1)-Si(2)	134.4(1)	O(1)#1-Ca(1)-H(2S)	151(1)	Ca(1)-Si(2)-H(2S)	49(3)
C(7)-Ca(1)-Si(2)	34.9(2)	C(7)-Ca(1)-H(2S)	59(1)	C(7)-Si(3)-C(5)	116.6(4)
C(7)#1-Ca(1)-Si(2)	114.3(2)	C(7)#1-Ca(1)-H(2S)	98(1)	C(7)-Si(3)-C(6)	116.3(3)
O(1)-Ca(1)-Si(2)#1	134.4(1)	Si(2)-Ca(1)-H(2S)	24(1)	C(5)-Si(3)-C(6)	104.6(4)
O(1)#1-Ca(1)-Si(2)#1	91.3(1)	Si(2)#1-Ca(1)-H(2S)	116(1)	C(7)-Si(3)-Ca(1)	45.0(2)
C(7)-Ca(1)-Si(2)#1	114.3(2)	Si(3)#1-Ca(1)-H(2S)	108(1)	C(5)-Si(3)-Ca(1)	161.1(3)
C(7)#1-Ca(1)-Si(2)#1	34.9(2)	Si(3)-Ca(1)-H(2S)	77(1)	C(6)-Si(3)-Ca(1)	90.5(3)
Si(2)-Ca(1)-Si(2)#1	118.5(1)	C(7)-Si(1)-C(2)	116.1(3)	C(7)-Si(3)-H(3S)	117(3)
O(1)-Ca(1)-Si(3)#1	78.4(1)	C(7)-Si(1)-C(1)	113.2(4)	C(5)-Si(3)-H(3S)	97(2)
O(1)#1-Ca(1)-Si(3)#1	93.3(1)	C(2)-Si(1)-C(1)	105.4(4)	C(6)-Si(3)-H(3S)	102(2)
C(7)-Ca(1)-Si(3)#1	161.4(2)	C(7)-Si(1)-H(1S)	101(2)	Ca(1)-Si(3)-H(3S)	90(2)
C(7)#1-Ca(1)-Si(3)#1	29.9(2)	C(2)-Si(1)-H(1S)	114(3)	Si(1)-C(1)-H(1A)	109.5
Si(2)-Ca(1)-Si(3)#1	131.48(6)	C(1)-Si(1)-H(1S)	107(2)	Si(1)-C(1)-H(1B)	109.5
Si(2)#1-Ca(1)-Si(3)#1	56.03(5)	C(7)-Si(2)-C(4)	117.1(3)	H(1A)-C(1)-H(1B)	109.5
O(1)-Ca(1)-Si(3)	93.3(1)	C(7)-Si(2)-C(3)	119.0(4)	Si(1)-C(1)-H(1C)	109.5
O(1)#1-Ca(1)-Si(3)	78.4(1)	C(4)-Si(2)-C(3)	105.4(4)	H(1A)-C(1)-H(1C)	109.5
C(7)-Ca(1)-Si(3)	29.9(2)	C(7)-Si(2)-Ca(1)	54.4(2)	H(1B)-C(1)-H(1C)	109.5
C(7)#1-Ca(1)-Si(3)	161.4(2)	C(4)-Si(2)-Ca(1)	122.3(3)	Si(1)-C(2)-H(2A)	109.5

Si(1)-C(2)-H(2B)	109.5	H(5B)-C(5)-H(5C)	109.5	C(8)-C(9)-H(9B)	111.4
H(2A)-C(2)-H(2B)	109.5	Si(3)-C(6)-H(6A)	109.5	C(10)-C(9)-H(9B)	111.4
Si(1)-C(2)-H(2C)	109.5	Si(3)-C(6)-H(6B)	109.5	H(9A)-C(9)-H(9B)	109.3
H(2A)-C(2)-H(2C)	109.5	H(6A)-C(6)-H(6B)	109.5	C(11)-C(10)-C(9)	101.7(6)
H(2B)-C(2)-H(2C)	109.5	Si(3)-C(6)-H(6C)	109.5	C(11)-C(10)-H(10A)	111.4
Si(2)-C(3)-H(3A)	109.5	H(6A)-C(6)-H(6C)	109.5	C(9)-C(10)-H(10A)	111.4
Si(2)-C(3)-H(3B)	109.5	H(6B)-C(6)-H(6C)	109.5	C(11)-C(10)-H(10B)	111.4
H(3A)-C(3)-H(3B)	109.5	Si(1)-C(7)-Si(2)	113.8(4)	C(9)-C(10)-H(10B)	111.4
Si(2)-C(3)-H(3C)	109.5	Si(1)-C(7)-Si(3)	114.1(4)	H(10A)-C(10)-H(10B)	109.3
H(3A)-C(3)-H(3C)	109.5	Si(2)-C(7)-Si(3)	120.8(4)	O(1)-C(11)-C(10)	105.3(6)
H(3B)-C(3)-H(3C)	109.5	Si(1)-C(7)-Ca(1)	108.4(3)	O(1)-C(11)-H(11A)	110.7
Si(2)-C(4)-H(4A)	109.5	Si(2)-C(7)-Ca(1)	90.7(3)	C(10)-C(11)-H(11A)	110.7
Si(2)-C(4)-H(4B)	109.5	Si(3)-C(7)-Ca(1)	105.1(3)	O(1)-C(11)-H(11B)	110.7
H(4A)-C(4)-H(4B)	109.5	O(1)-C(8)-C(9)	105.9(6)	C(10)-C(11)-H(11B)	110.7
Si(2)-C(4)-H(4C)	109.5	O(1)-C(8)-H(8A)	110.6	H(11A)-C(11)-H(11B)	108.8
H(4A)-C(4)-H(4C)	109.5	C(9)-C(8)-H(8A)	110.6	C(8)-O(1)-C(11)	107.9(5)
H(4B)-C(4)-H(4C)	109.5	O(1)-C(8)-H(8B)	110.6	C(8)-O(1)-Ca(1)	124.5(4)
Si(3)-C(5)-H(5A)	109.5	C(9)-C(8)-H(8B)	110.6	C(11)-O(1)-Ca(1)	126.4(4)
Si(3)-C(5)-H(5B)	109.5	H(8A)-C(8)-H(8B)	108.7		
H(5A)-C(5)-H(5B)	109.5	C(8)-C(9)-C(10)	101.9(6)		
Si(3)-C(5)-H(5C)	109.5	C(8)-C(9)-H(9A)	111.4		
H(5A)-C(5)-H(5C)	109.5	C(10)-C(9)-H(9A)	111.4		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

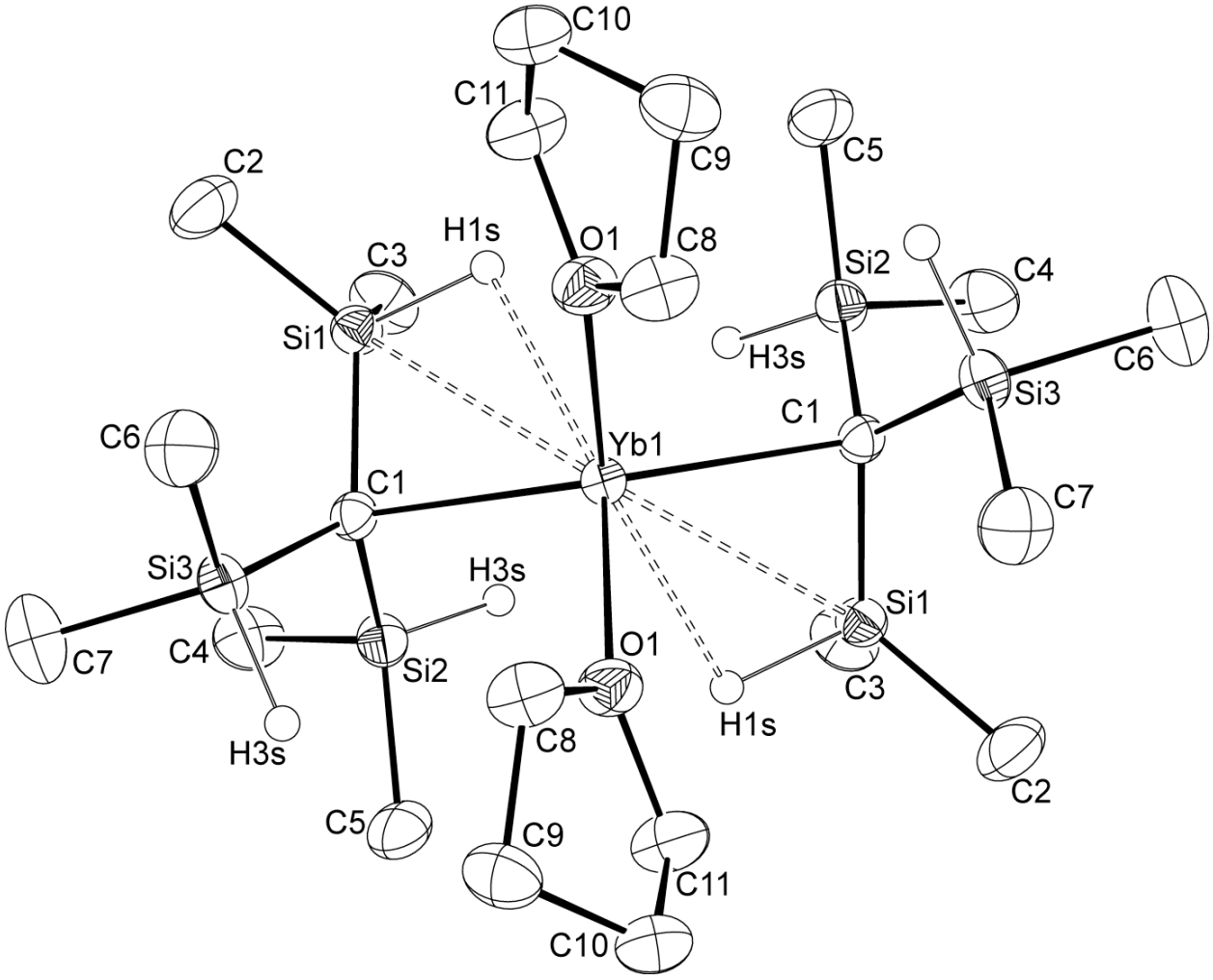
Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Ca(C(SiHMe_2)_3)_2THF_2$ (**1a**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca(1)	23(1)	10(1)	14(1)	0	15(1)	0
Si(1)	32(1)	17(1)	21(1)	-8(1)	17(1)	-2(1)
Si(2)	31(1)	12(1)	17(1)	0(1)	16(1)	-2(1)
Si(3)	30(1)	12(1)	24(1)	2(1)	19(1)	3(1)
C(1)	44(5)	37(6)	30(5)	-9(4)	23(4)	-13(4)
C(2)	48(6)	22(5)	33(5)	-11(4)	25(4)	-11(4)
C(3)	58(6)	34(6)	34(5)	2(4)	35(5)	-2(4)
C(4)	46(5)	19(5)	27(5)	9(4)	13(4)	2(4)
C(5)	47(6)	34(6)	67(7)	4(5)	36(5)	4(5)
C(6)	66(6)	19(5)	35(5)	-7(4)	33(5)	4(4)
C(7)	21(4)	3(4)	19(4)	-4(3)	13(3)	-5(3)
C(8)	59(6)	19(5)	20(5)	-2(4)	25(4)	-7(4)
C(9)	48(5)	27(5)	21(5)	-12(4)	21(4)	-2(4)
C(10)	43(5)	27(5)	24(5)	-8(4)	21(4)	-10(4)
C(11)	42(5)	15(5)	24(5)	-6(3)	19(4)	-5(4)
O(1)	36(3)	14(3)	22(3)	-6(2)	20(3)	-5(2)

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $Ca(C(SiHMe_2)_3)_2THF_2$ (**1a**).

	x	y	z	U(eq)
H(1S)	4250(30)	3850(70)	1730(40)	16
H(2S)	4960(30)	5800(70)	3670(40)	22
H(3S)	3130(30)	8180(70)	1150(40)	23
H(1A)	2843	5701	191	53
H(1B)	3163	4357	-8	53
H(1C)	3592	5797	354	53
H(2A)	3151	2670	1929	49
H(2B)	2848	2495	951	49
H(2C)	2559	3707	1283	49
H(3A)	4014	6983	4035	55
H(3B)	4313	5573	4593	55
H(3C)	3549	5592	3820	55
H(4A)	3977	2877	3371	50
H(4B)	4757	3099	4073	50
H(4C)	4540	2880	3122	50
H(5A)	2196	6268	1108	70
H(5B)	2096	7840	1363	70
H(5C)	2360	6572	2032	70
H(6A)	3408	8668	3097	56
H(6B)	3235	9794	2372	56
H(6C)	3985	9166	2925	56
H(8A)	5866	7889	4693	37
H(8B)	5093	8293	4370	37
H(9A)	6035	9923	5443	36
H(9B)	5345	10647	4716	36
H(10A)	6160	11726	4518	36
H(10B)	6573	10248	4694	36
H(11A)	5299	10974	3243	31
H(11B)	5928	10196	3266	31

X-ray crystallographic data for $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**).



Data Collection $Yb(C(SiHMe_2)_3)_2THF_2$ (1b).

A well-shaped crystal was selected under ambient conditions. The crystal was mounted and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed at 173 K on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the detector to crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3º in a 10º range about ω with the exposure time of 10 seconds per frame. The obtained reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of strong reflections from the actual data collection. The data were collected using the full sphere routine by collecting four sets of frames with 0.3º scans in ω with an exposure time 10 sec per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was

based on a fit of a spherical harmonic function to the empirical transmission surface as sampled by multiple equivalent measurements using SADABS software.[5,6]

Structure Solution and Refinement $Yb(C(SiHMe_2)_3)_2THF_2$ (1b).

The systematic absences in the diffraction data were consistent for the space groups *Cc and C2*/c.[6] Data statistics strongly recommended non-centrosymmetrical space-group CC yielded chemically reasonable and computationally stable results of refinement. The position of almost all non-hydrogen atoms were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. The atomic coordinates strongly indicated the existence of inversion center, therefore further calculations were performed in C2/c space group. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. Almost all hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The hydrogen atoms belonged to Si atoms were found objectively on a difference Fourier map and were refined in an isotropic approximation.

Table S7. Crystal data and structure refinement for $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**).

Empirical formula	$C_{22}H_{58}O_2Si_6Yb$	
Formula weight	696.26	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 22.792(12) Å	α= 90°.
	b = 9.284(4) Å	β= 121.189(16)°.
	c = 18.655(10) Å	γ = 90°.
Volume	3377(3) $Å^3$	
Z	4	
Density (calculated)	1.370 Mg/m^3	
Absorption coefficient	2.999 mm^{-1}	
F(000)	1440	
Crystal size	0.41 × 0.36 × 0.15 mm^3	
Theta range for data collection	2.09 to 28.42°.	
Index ranges	-29≤h≤29, -12≤k≤12, -24≤l≤24	
Reflections collected	14537	
Independent reflections	4044 [R(int) = 0.0566]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.74 and 0.45	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4044 / 0 / 159	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0627	
R indices (all data)	R1 = 0.0480, wR2 = 0.0684	
Largest diff. peak and hole	1.548 and -1.056 $e.Å^{-3}$	

$R1 = \Sigma \, | \, |F_o| - |F_c| \, | \, / \, \Sigma \, |F_o|$ and $wR2 = \{ \, \Sigma \, [\, w(F_o^2 - F_c^2)^2 \,] \, / \, \Sigma \, [\, w(F_o^2)^2 \,] \, \}^{1/2}$

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Yb(1)	10000	2950(1)	7500	19(1)
Si(1)	9302(1)	4708(1)	8326(1)	24(1)
Si(2)	8615(1)	5525(1)	6473(1)	26(1)
Si(3)	8268(1)	2590(1)	6893(1)	26(1)
C(1)	8870(2)	4098(4)	7249(2)	21(1)
C(2)	8990(2)	4050(5)	9016(3)	44(1)
C(3)	9420(2)	6697(4)	8509(3)	39(1)
C(4)	7963(2)	6842(4)	6413(3)	44(1)
C(5)	8262(2)	4854(5)	5381(2)	39(1)
C(6)	8509(2)	1076(4)	7662(3)	41(1)
C(7)	7359(2)	3034(5)	6543(3)	49(1)
C(8)	9329(2)	-290(4)	6451(2)	33(1)
C(9)	8883(2)	-716(4)	5547(2)	37(1)
C(10)	9259(2)	-68(4)	5161(2)	34(1)
C(11)	9488(2)	1356(4)	5594(2)	37(1)
O(1)	9608(1)	1114(3)	6430(2)	29(1)

Table S9. Bond lengths [Å] for $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**).

Yb(1)-O(1)	2.417(3)	Si(3)-H(3S)	1.42(4)	C(7)-H(7A)	0.9600
Yb(1)-C(1)	2.596(4)	C(2)-H(2A)	0.9600	C(7)-H(7B)	0.9600
Yb(1)-Si(1)	3.180(1)	C(2)-H(2B)	0.9600	C(7)-H(7C)	0.9600
Yb(1)-Si(3)	3.515(2)	C(2)-H(2C)	0.9600	C(8)-O(1)	1.460(4)
Yb(1)-H(1S)	2.50(3)	C(3)-H(3A)	0.9600	C(8)-C(9)	1.504(5)
Si(1)-C(1)	1.810(4)	C(3)-H(3B)	0.9600	C(8)-H(8A)	0.9700
Si(1)-C(2)	1.866(4)	C(3)-H(3C)	0.9600	C(8)-H(8B)	0.9700
Si(1)-C(3)	1.872(4)	C(4)-H(4A)	0.9600	C(9)-C(10)	1.502(5)
Si(1)-H(1S)	1.48(3)	C(4)-H(4B)	0.9600	C(9)-H(9A)	0.9700
Si(2)-C(1)	1.821(3)	C(4)-H(4C)	0.9600	C(9)-H(9B)	0.9700
Si(2)-C(5)	1.869(4)	C(5)-H(5A)	0.9600	C(10)-C(11)	1.496(5)
Si(2)-C(4)	1.883(4)	C(5)-H(5B)	0.9600	C(10)-H(10A)	0.9700
Si(2)-H(2S)	1.36(4)	C(5)-H(5C)	0.9600	C(10)-H(10B)	0.9700
Si(3)-C(1)	1.828(4)	C(6)-H(6A)	0.9600	C(11)-O(1)	1.454(4)
Si(3)-C(7)	1.866(4)	C(6)-H(6B)	0.9600	C(11)-H(11A)	0.9700
Si(3)-C(6)	1.876(4)	C(6)-H(6C)	0.9600	C(11)-H(11B)	0.9700

Table S10. Bond angles [°] for $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**).

O(1)-Yb(1)-O(1)#1	90.3(1)	O(1)#1-Yb(1)-Si(3)#1	78.10(6)	C(2)-Si(1)-Yb(1)	129.2(2)
O(1)-Yb(1)-C(1)#1	110.26(9)	C(1)#1-Yb(1)-Si(3)#1	30.33(8)	C(3)-Si(1)-Yb(1)	122.2(2)
O(1)-Yb(1)-C(1)	103.5(1)	C(1)-Yb(1)-Si(3)#1	160.24(8)	C(1)-Si(1)-H(1S)	104(1)
O(1)#1-Yb(1)-C(1)	110.26(9)	Si(1)#1-Yb(1)-Si(3)#1	56.23(3)	C(2)-Si(1)-H(1S)	105(1)
C(1)#1-Yb(1)-C(1)	131.5(2)	Si(1)-Yb(1)-Si(3)#1	130.79(3)	C(3)-Si(1)-H(1S)	104(1)
C(1)#1-Yb(1)-Si(1)#1	34.70(8)	Si(3)-Yb(1)-Si(3)#1	169.11(4)	Yb(1)-Si(1)-H(1S)	49(1)
C(1)-Yb(1)-Si(1)#1	113.62(8)	O(1)-Yb(1)-H(1S)	152.0(7)	C(1)-Si(2)-C(5)	113.9(2)
O(1)-Yb(1)-Si(1)	134.31(7)	O(1)#1-Yb(1)-H(1S)	75.0(7)	C(1)-Si(2)-C(4)	115.9(2)
O(1)#1-Yb(1)-Si(1)	91.45(7)	C(1)#1-Yb(1)-H(1S)	96.5(7)	C(5)-Si(2)-C(4)	105.7(2)
C(1)#1-Yb(1)-Si(1)	113.62(8)	C(1)-Yb(1)-H(1S)	61.6(7)	C(1)-Si(2)-H(2S)	107(2)
C(1)-Yb(1)-Si(1)	34.70(8)	Si(1)#1-Yb(1)-H(1S)	115.9(7)	C(5)-Si(2)-H(2S)	109(2)
Si(1)#1-Yb(1)-Si(1)	118.25(5)	Si(1)-Yb(1)-H(1S)	26.9(7)	C(4)-Si(2)-H(2S)	104(2)
O(1)-Yb(1)-Si(3)	78.10(6)	Si(3)-Yb(1)-H(1S)	79.3(7)	C(1)-Si(3)-C(7)	116.5(2)
C(1)#1-Yb(1)-Si(3)	160.24(8)	Si(3)#1-Yb(1)-H(1S)	105.6(7)	C(1)-Si(3)-C(6)	115.4(2)
C(1)-Yb(1)-Si(3)	30.33(8)	C(1)-Si(1)-C(2)	118.7(2)	C(7)-Si(3)-C(6)	105.4(2)
Si(1)#1-Yb(1)-Si(3)	130.79(3)	C(1)-Si(1)-C(3)	117.1(2)	C(1)-Si(3)-Yb(1)	45.8(1)
Si(1)-Yb(1)-Si(3)	56.23(3)	C(2)-Si(1)-C(3)	105.5(2)	C(7)-Si(3)-Yb(1)	161.7(2)
O(1)-Yb(1)-Si(3)#1	94.14(6)	C(1)-Si(1)-Yb(1)	54.7(1)	C(6)-Si(3)-Yb(1)	89.4(1)

C(1)-Si(3)-H(3S)	107(2)	Si(2)-C(4)-H(4C)	109.5	C(9)-C(8)-H(8B)	110.8
C(7)-Si(3)-H(3S)	103(2)	H(4A)-C(4)-H(4C)	109.5	H(8A)-C(8)-H(8B)	108.9
C(6)-Si(3)-H(3S)	108(2)	H(4B)-C(4)-H(4C)	109.5	C(10)-C(9)-C(8)	102.1(3)
Yb(1)-Si(3)-H(3S)	81(2)	Si(2)-C(5)-H(5A)	109.5	C(10)-C(9)-H(9A)	111.3
Si(1)-C(1)-Si(2)	114.9(2)	Si(2)-C(5)-H(5B)	109.5	C(8)-C(9)-H(9A)	111.3
Si(1)-C(1)-Si(3)	121.1(2)	H(5A)-C(5)-H(5B)	109.5	C(10)-C(9)-H(9B)	111.3
Si(2)-C(1)-Si(3)	113.5(2)	Si(2)-C(5)-H(5C)	109.5	C(8)-C(9)-H(9B)	111.3
Si(1)-C(1)-Yb(1)	90.6(1)	H(5A)-C(5)-H(5C)	109.5	H(9A)-C(9)-H(9B)	109.2
Si(2)-C(1)-Yb(1)	108.7(2)	H(5B)-C(5)-H(5C)	109.5	C(11)-C(10)-C(9)	102.7(3)
Si(3)-C(1)-Yb(1)	103.9(2)	Si(3)-C(6)-H(6A)	109.5	C(11)-C(10)-H(10A)	111.2
Si(1)-C(2)-H(2A)	109.5	Si(3)-C(6)-H(6B)	109.5	C(9)-C(10)-H(10A)	111.2
Si(1)-C(2)-H(2B)	109.5	H(6A)-C(6)-H(6B)	109.5	C(11)-C(10)-H(10B)	111.2
H(2A)-C(2)-H(2B)	109.5	Si(3)-C(6)-H(6C)	109.5	C(9)-C(10)-H(10B)	111.2
Si(1)-C(2)-H(2C)	109.5	H(6A)-C(6)-H(6C)	109.5	H(10A)-C(10)-H(10B)	109.1
H(2A)-C(2)-H(2C)	109.5	H(6B)-C(6)-H(6C)	109.5	O(1)-C(11)-C(10)	105.2(3)
H(2B)-C(2)-H(2C)	109.5	Si(3)-C(7)-H(7A)	109.5	O(1)-C(11)-H(11A)	110.7
Si(1)-C(3)-H(3A)	109.5	Si(3)-C(7)-H(7B)	109.5	C(10)-C(11)-H(11A)	110.7
Si(1)-C(3)-H(3B)	109.5	H(7A)-C(7)-H(7B)	109.5	O(1)-C(11)-H(11B)	110.7
H(3A)-C(3)-H(3B)	109.5	Si(3)-C(7)-H(7C)	109.5	C(10)-C(11)-H(11B)	110.7
Si(1)-C(3)-H(3C)	109.5	H(7A)-C(7)-H(7C)	109.5	H(11A)-C(11)-H(11B)	108.8
H(3A)-C(3)-H(3C)	109.5	H(7B)-C(7)-H(7C)	109.5	C(11)-O(1)-C(8)	108.9(3)
H(3B)-C(3)-H(3C)	109.5	O(1)-C(8)-C(9)	104.8(3)	C(11)-O(1)-Yb(1)	124.1(2)
Si(2)-C(4)-H(4A)	109.5	O(1)-C(8)-H(8A)	110.8	C(8)-O(1)-Yb(1)	125.9(2)
Si(2)-C(4)-H(4B)	109.5	C(9)-C(8)-H(8A)	110.8		
H(4A)-C(4)-H(4B)	109.5	O(1)-C(8)-H(8B)	110.8		

Table S11. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \ldots + 2 h k a^* b^* U^{12}]$

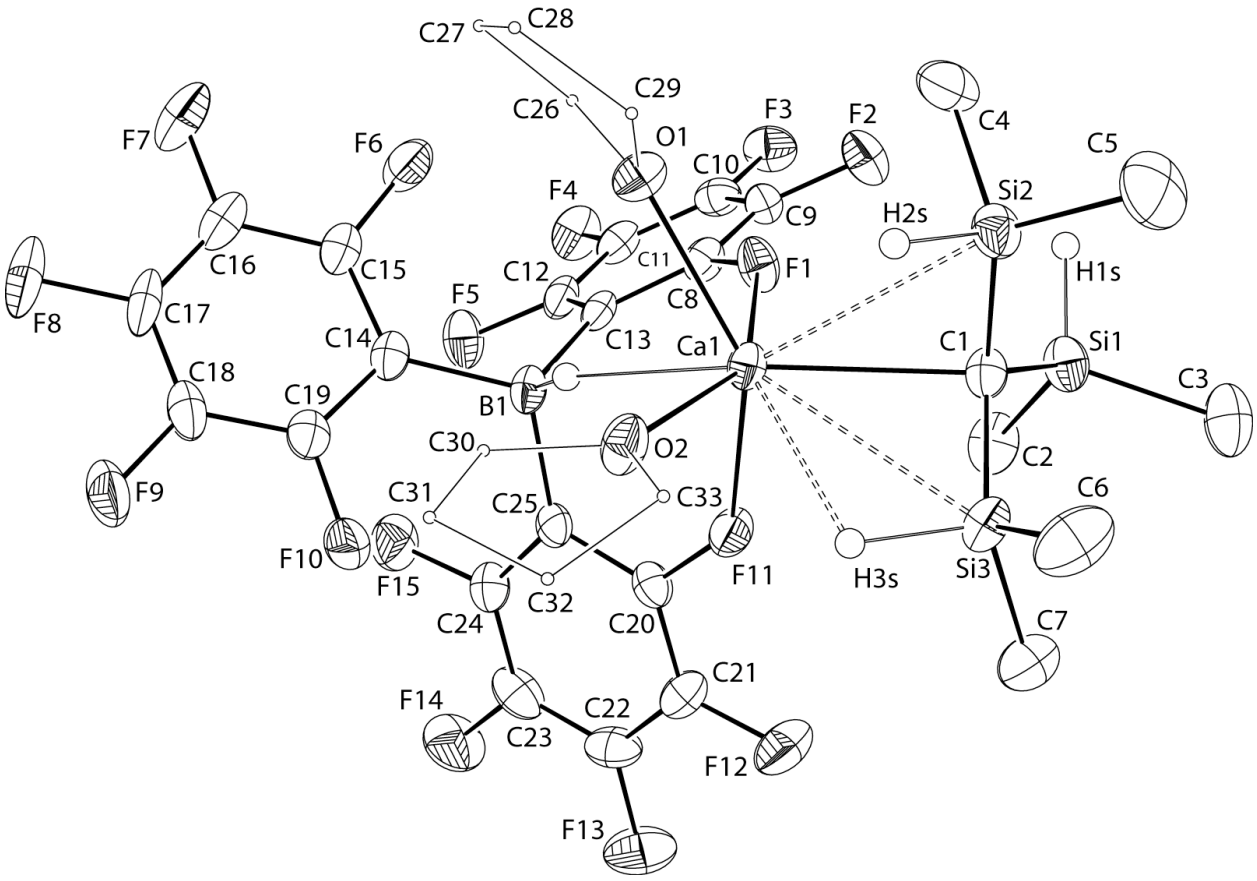
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Yb(1)	18(1)	19(1)	19(1)	0	9(1)	0
Si(1)	24(1)	24(1)	22(1)	-1(1)	11(1)	2(1)
Si(2)	24(1)	27(1)	27(1)	8(1)	12(1)	3(1)
Si(3)	21(1)	24(1)	30(1)	-1(1)	12(1)	-3(1)
C(1)	21(2)	22(2)	21(2)	3(1)	12(2)	2(1)
C(2)	53(3)	55(3)	36(2)	-4(2)	32(2)	-2(2)
C(3)	39(2)	30(2)	40(2)	-8(2)	14(2)	-2(2)
C(4)	46(3)	40(3)	41(3)	8(2)	19(2)	15(2)
C(5)	41(3)	50(3)	29(2)	13(2)	20(2)	11(2)
C(6)	46(3)	31(2)	46(3)	2(2)	25(2)	-7(2)
C(7)	30(2)	47(3)	68(3)	1(2)	24(2)	-1(2)
C(8)	44(2)	26(2)	31(2)	-1(2)	20(2)	-2(2)
C(9)	37(2)	34(2)	31(2)	-6(2)	12(2)	-8(2)
C(10)	42(2)	34(2)	26(2)	-5(2)	17(2)	0(2)
C(11)	51(3)	34(2)	30(2)	-4(2)	23(2)	-8(2)
O(1)	33(2)	29(1)	27(1)	-6(1)	15(1)	-4(1)

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $Yb(C(SiHMe_2)_3)_2THF_2$ (**1b**).

	x	y	z	U(eq)
H(2A)	8517	4312	8776	66
H(2B)	9258	4479	9560	66
H(2C)	9034	3021	9065	66
H(3A)	9562	7108	8150	59
H(3B)	9764	6878	9083	59
H(3C)	8995	7126	8387	59
H(4A)	7565	6328	6323	66
H(4B)	7834	7497	5957	66

H(4C)	8157	7373	6928	66
H(5A)	8604	4293	5355	59
H(5B)	8134	5658	5005	59
H(5C)	7866	4266	5221	59
H(6A)	8993	901	7935	61
H(6B)	8263	221	7371	61
H(6C)	8393	1330	8072	61
H(7A)	7339	3456	7000	73
H(7B)	7089	2170	6365	73
H(7C)	7182	3704	6086	73
H(8A)	9062	-223	6720	40
H(8B)	9695	-985	6753	40
H(9A)	8851	-1754	5482	44
H(9B)	8425	-315	5303	44
H(10A)	9648	-658	5269	41
H(10B)	8959	52	4561	41
H(11A)	9905	1672	5622	45
H(11B)	9136	2081	5301	45
H(2S)	9181(19)	6330(40)	6700(20)	38(11)
H(3S)	8220(20)	2030(40)	6150(30)	42(12)
H(1S)	10007(17)	4140(30)	8700(20)	21(9)

X-ray crystallographic data for $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2a**).



Data Collection for $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (2a).

A colorless crystal was selected under ambient conditions. The crystal was mounted and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed at 123K on a Bruker APEX2 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the detector to crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3º in a 10º range about ω with the exposure time of 10 seconds per frame. The obtained reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of strong reflections from the actual data collection. The data were collected using the full sphere routine by collecting four sets of frames with 0.3º scans in ω with an exposure time 10 sec per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was

based on a fit of a spherical harmonic function to the empirical transmission surface as sampled by multiple equivalent measurements using SADABS software.[5,6]

Structure Solution and Refinement of $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (2a).

The systematic absences in the diffraction data were consistent for the space groups $P2_1/n$[6] yielded chemically reasonable and computationally stable results of refinement. The position of almost all non-hydrogen atoms were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. Almost all hydrogen atoms were placed in the structure factor calculation at idealized positions. The H-atoms belonged to Si and B atoms were found objectively on a difference Fourier map. All hydrogens were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

Table S13. Crystal data and structure refinement for $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2a**).

Empirical formula	$C_{33}H_{38}BCaF_{15}O_2Si_3$	
Formula weight	886.79	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.0485(15) Å	α= 90°.
	b = 23.131(3) Å	β= 96.616(2)°.
	c = 15.359(2) Å	γ = 90°.
Volume	3898.9(9) $Å^3$	
Z	4	
Density (calculated)	1.511 Mg/m^3	
Absorption coefficient	0.356 mm^{-1}	
F(000)	1816	
Crystal size	0.27 × 0.27 × 0.14 mm^3	
Theta range for data collection	1.60 to 23.25°.	
Index ranges	-12≤h≤12, -25≤k≤25, -17≤l≤17	
Reflections collected	26308	
Independent reflections	5604 [R(int) = 0.0732]	
Completeness to theta = 23.25°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.85	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5604 / 0 / 514	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.0990	
R indices (all data)	R1 = 0.0626, wR2 = 0.1093	
Largest diff. peak and hole	0.341 and -0.305 $e.Å^{-3}$	

$R1 = \Sigma \, | \, |F_o| - |F_c| \, | \, / \, \Sigma \, |F_o|$ and $wR2 = \{ \, \Sigma \, [\, w(F_o^2 - F_c^2)^2 \,] \, / \, \Sigma \, [\, w(F_o^2)^2 \,] \, \}^{1/2}$

Table S14. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2a**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ca(1)	1920(1)	8657(1)	3017(1)	23(1)
Si(1)	-532(1)	8462(1)	4639(1)	31(1)
Si(2)	195(1)	7623(1)	3223(1)	31(1)
Si(3)	2105(1)	7955(1)	4745(1)	30(1)
C(1)	679(3)	8136(1)	4093(2)	26(1)
C(2)	-256(3)	9226(1)	5010(2)	39(1)
C(3)	-912(4)	8055(2)	5634(2)	48(1)
C(4)	-978(3)	7915(2)	2363(2)	46(1)
C(5)	-326(4)	6892(2)	3507(3)	60(1)
C(6)	2548(4)	7177(2)	4868(2)	52(1)
C(7)	2410(3)	8306(2)	5840(2)	43(1)
C(8)	-89(3)	9876(1)	2630(2)	24(1)
C(9)	-1294(3)	10012(1)	2685(2)	25(1)
C(10)	-1661(3)	10575(1)	2554(2)	28(1)
C(11)	-822(3)	10979(1)	2368(2)	27(1)
C(12)	375(3)	10821(1)	2326(2)	26(1)
C(13)	807(3)	10260(1)	2455(2)	22(1)
C(14)	2888(3)	10298(1)	1613(2)	25(1)
C(15)	2272(3)	10435(1)	799(2)	30(1)
C(16)	2839(3)	10594(1)	83(2)	37(1)
C(17)	4088(4)	10616(1)	158(2)	37(1)
C(18)	4749(3)	10471(1)	928(2)	33(1)
C(19)	4148(3)	10316(1)	1631(2)	28(1)
C(20)	2971(3)	9969(1)	4152(2)	25(1)
C(21)	3458(3)	10128(1)	4985(2)	32(1)
C(22)	3948(3)	10666(2)	5107(2)	34(1)
C(23)	3935(3)	11032(1)	4407(2)	36(1)
C(24)	3445(3)	10851(1)	3588(2)	29(1)
C(25)	2933(3)	10311(1)	3415(2)	24(1)
C(26)	885(4)	8944(2)	858(2)	54(1)
C(27)	1268(6)	8772(3)	3(3)	106(2)
C(28)	1723(6)	8201(3)	90(3)	107(2)
C(29)	1685(4)	8022(2)	1009(2)	49(1)
C(30)	4539(3)	8692(2)	2146(2)	45(1)
C(31)	5707(4)	8382(2)	2122(3)	69(1)
C(32)	5754(3)	7941(2)	2808(3)	60(1)
C(33)	4490(3)	7820(2)	2927(3)	46(1)
F(1)	199(2)	9302(1)	2767(1)	30(1)
F(2)	-2092(2)	9606(1)	2863(1)	38(1)
F(3)	-2813(2)	10730(1)	2613(1)	37(1)
F(4)	-1174(2)	11531(1)	2211(1)	38(1)
F(5)	1143(2)	11244(1)	2137(1)	37(1)
F(6)	1040(2)	10412(1)	666(1)	40(1)
F(7)	2181(2)	10721(1)	-688(1)	53(1)
F(8)	4660(2)	10776(1)	-536(1)	54(1)
F(9)	5970(2)	10479(1)	989(1)	47(1)
F(10)	4852(2)	10165(1)	2371(1)	37(1)
F(11)	2488(2)	9419(1)	4082(1)	32(1)
F(12)	3452(2)	9758(1)	5660(1)	45(1)
F(13)	4444(2)	10834(1)	5908(1)	54(1)
F(14)	4414(2)	11565(1)	4523(1)	52(1)
F(15)	3493(2)	11234(1)	2928(1)	42(1)
O(1)	1447(2)	8540(1)	1484(1)	30(1)
O(2)	3820(2)	8349(1)	2685(1)	32(1)

B(1)	2249(3)	10093(2)	2467(2)	24(1)

Table S15. Bond lengths [Å] for $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2a**).

Ca(1)-O(2)	2.328(2)	C(6)-H(6B)	0.9800	C(22)-C(23)	1.367(5)
Ca(1)-O(1)	2.368(2)	C(6)-H(6C)	0.9800	C(23)-F(14)	1.346(4)
Ca(1)-F(1)	2.412(2)	C(7)-H(7A)	0.9800	C(23)-C(24)	1.376(5)
Ca(1)-F(11)	2.438(2)	C(7)-H(7B)	0.9800	C(24)-F(15)	1.351(3)
Ca(1)-C(1)	2.566(3)	C(7)-H(7C)	0.9800	C(24)-C(25)	1.385(4)
Ca(1)-Si(2)	3.097(1)	C(8)-F(1)	1.377(3)	C(25)-B(1)	1.640(5)
Ca(1)-Si(3)	3.097(1)	C(8)-C(13)	1.379(4)	C(26)-O(1)	1.430(4)
Ca(1)-H(2S)	2.73(3)	C(8)-C(9)	1.379(4)	C(26)-C(27)	1.480(6)
Ca(1)-H(3S)	2.38(3)	C(9)-F(2)	1.338(3)	C(26)-H(26A)	0.9900
Ca(1)-H(1G)	2.45(3)	C(9)-C(10)	1.372(4)	C(26)-H(26B)	0.9900
Si(1)-C(1)	1.823(3)	C(10)-F(3)	1.335(3)	C(27)-C(28)	1.415(7)
Si(1)-C(2)	1.870(3)	C(10)-C(11)	1.369(4)	C(27)-H(27A)	0.9900
Si(1)-C(3)	1.883(3)	C(11)-F(4)	1.349(3)	C(27)-H(27B)	0.9900
Si(1)-H(1S)	1.38(3)	C(11)-C(12)	1.381(4)	C(28)-C(29)	1.475(6)
Si(2)-C(1)	1.821(3)	C(12)-F(5)	1.349(3)	C(28)-H(28A)	0.9900
Si(2)-C(5)	1.854(4)	C(12)-C(13)	1.390(4)	C(28)-H(28B)	0.9900
Si(2)-C(4)	1.866(4)	C(13)-B(1)	1.637(5)	C(29)-O(1)	1.441(4)
Si(2)-H(2S)	1.46(3)	C(14)-C(15)	1.389(4)	C(29)-H(29A)	0.9900
Si(3)-C(1)	1.816(3)	C(14)-C(19)	1.390(4)	C(29)-H(29B)	0.9900
Si(3)-C(7)	1.863(3)	C(14)-B(1)	1.630(4)	C(30)-O(2)	1.449(4)
Si(3)-C(6)	1.870(4)	C(15)-F(6)	1.354(4)	C(30)-C(31)	1.480(5)
Si(3)-H(3S)	1.48(3)	C(15)-C(16)	1.376(5)	C(30)-H(30A)	0.9900
C(2)-H(2A)	0.9800	C(16)-F(7)	1.349(4)	C(30)-H(30B)	0.9900
C(2)-H(2B)	0.9800	C(16)-C(17)	1.372(5)	C(31)-C(32)	1.463(6)
C(2)-H(2C)	0.9800	C(17)-F(8)	1.352(4)	C(31)-H(31A)	0.9900
C(3)-H(3A)	0.9800	C(17)-C(18)	1.359(5)	C(31)-H(31B)	0.9900
C(3)-H(3B)	0.9800	C(18)-F(9)	1.341(4)	C(32)-C(33)	1.457(5)
C(3)-H(3C)	0.9800	C(18)-C(19)	1.378(4)	C(32)-H(32A)	0.9900
C(4)-H(4A)	0.9800	C(19)-F(10)	1.347(4)	C(32)-H(32B)	0.9900
C(4)-H(4B)	0.9800	C(20)-F(11)	1.378(3)	C(33)-O(2)	1.455(4)
C(4)-H(4C)	0.9800	C(20)-C(25)	1.378(4)	C(33)-H(33A)	0.9900
C(5)-H(5A)	0.9800	C(20)-C(21)	1.380(4)	C(33)-H(33B)	0.9900
C(5)-H(5B)	0.9800	C(21)-F(12)	1.343(4)	B(1)-H(1G)	1.10(3)
C(5)-H(5C)	0.9800	C(21)-C(22)	1.363(5)		
C(6)-H(6A)	0.9800	C(22)-F(13)	1.346(4)		

Table S16. Bond angles [°] for $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2a**).

O(2)-Ca(1)-O(1)	81.28(7)	F(1)-Ca(1)-Si(3)	115.69(5)	Si(3)-Ca(1)-H(3S)	27.5(8)
O(2)-Ca(1)-F(1)	150.29(7)	F(11)-Ca(1)-Si(3)	79.47(5)	H(2S)-Ca(1)-H(3S)	77.9(10)
O(1)-Ca(1)-F(1)	80.39(7)	C(1)-Ca(1)-Si(3)	35.86(7)	O(2)-Ca(1)-H(1G)	89.0(7)
O(2)-Ca(1)-F(11)	101.51(7)	Si(2)-Ca(1)-Si(3)	59.24(3)	O(1)-Ca(1)-H(1G)	77.6(7)
O(1)-Ca(1)-F(11)	139.53(7)	O(2)-Ca(1)-H(2S)	84.8(7)	F(1)-Ca(1)-H(1G)	64.3(7)
F(1)-Ca(1)-F(11)	78.30(6)	O(1)-Ca(1)-H(2S)	73.3(7)	F(11)-Ca(1)-H(1G)	62.2(7)
O(2)-Ca(1)-C(1)	123.99(9)	F(1)-Ca(1)-H(2S)	111.7(7)	C(1)-Ca(1)-H(1G)	142.4(7)
O(1)-Ca(1)-C(1)	120.88(9)	F(11)-Ca(1)-H(2S)	147.0(7)	Si(2)-Ca(1)-H(1G)	152.1(7)
F(1)-Ca(1)-C(1)	85.59(8)	C(1)-Ca(1)-H(2S)	59.6(7)	Si(3)-Ca(1)-H(1G)	141.2(7)
F(11)-Ca(1)-C(1)	91.30(8)	Si(2)-Ca(1)-H(2S)	28.2(7)	H(2S)-Ca(1)-H(1G)	151(1)
O(2)-Ca(1)-Si(2)	111.53(6)	Si(3)-Ca(1)-H(2S)	67.7(7)	H(3S)-Ca(1)-H(1G)	126(1)
O(1)-Ca(1)-Si(2)	86.84(6)	O(2)-Ca(1)-H(3S)	68.2(8)	C(1)-Si(1)-C(2)	115.3(2)
F(1)-Ca(1)-Si(2)	90.59(5)	O(1)-Ca(1)-H(3S)	139.5(8)	C(1)-Si(1)-C(3)	114.3(2)
F(11)-Ca(1)-Si(2)	127.14(5)	F(1)-Ca(1)-H(3S)	137.6(8)	C(2)-Si(1)-C(3)	105.6(2)
C(1)-Ca(1)-Si(2)	35.98(7)	F(11)-Ca(1)-H(3S)	74.7(8)	C(1)-Si(1)-H(1S)	107(1)
O(2)-Ca(1)-Si(3)	93.14(6)	C(1)-Ca(1)-H(3S)	63.3(8)	C(2)-Si(1)-H(1S)	105(1)
O(1)-Ca(1)-Si(3)	140.98(6)	Si(2)-Ca(1)-H(3S)	80.7(8)	C(3)-Si(1)-H(1S)	109(1)

C(1)-Si(2)-C(5)	119.6(2)	H(7A)-C(7)-H(7B)	109.5	O(1)-C(26)-C(27)	106.0(3)
C(1)-Si(2)-C(4)	113.9(2)	Si(3)-C(7)-H(7C)	109.5	O(1)-C(26)-H(26A)	110.5
C(5)-Si(2)-C(4)	106.7(2)	H(7A)-C(7)-H(7C)	109.5	C(27)-C(26)-H(26A)	110.5
C(1)-Si(2)-Ca(1)	55.9(1)	H(7B)-C(7)-H(7C)	109.5	O(1)-C(26)-H(26B)	110.5
C(5)-Si(2)-Ca(1)	156.0(2)	F(1)-C(8)-C(13)	119.5(3)	C(27)-C(26)-H(26B)	110.5
C(4)-Si(2)-Ca(1)	91.9(1)	F(1)-C(8)-C(9)	114.8(3)	H(26A)-C(26)-H(26B)	108.7
C(1)-Si(2)-H(2S)	106(1)	C(13)-C(8)-C(9)	125.8(3)	C(28)-C(27)-C(26)	107.5(4)
C(5)-Si(2)-H(2S)	106(1)	F(2)-C(9)-C(10)	120.4(3)	C(28)-C(27)-H(27A)	110.2
C(4)-Si(2)-H(2S)	103(1)	F(2)-C(9)-C(8)	121.0(3)	C(26)-C(27)-H(27A)	110.2
Ca(1)-Si(2)-H(2S)	62(1)	C(10)-C(9)-C(8)	118.6(3)	C(28)-C(27)-H(27B)	110.2
C(1)-Si(3)-C(7)	117(2)	F(3)-C(10)-C(9)	120.9(3)	C(26)-C(27)-H(27B)	110.2
C(1)-Si(3)-C(6)	118.5(2)	F(3)-C(10)-C(11)	120.3(3)	H(27A)-C(27)-H(27B)	108.5
C(7)-Si(3)-C(6)	108.1(2)	C(9)-C(10)-C(11)	118.8(3)	C(27)-C(28)-C(29)	107.7(4)
C(1)-Si(3)-Ca(1)	55.9(1)	F(4)-C(11)-C(10)	119.7(3)	C(27)-C(28)-H(28A)	110.2
C(7)-Si(3)-Ca(1)	122.2(1)	F(4)-C(11)-C(12)	120.0(3)	C(29)-C(28)-H(28A)	110.2
C(6)-Si(3)-Ca(1)	125.6(1)	C(10)-C(11)-C(12)	120.3(3)	C(27)-C(28)-H(28B)	110.2
C(1)-Si(3)-H(3S)	103(1)	F(5)-C(12)-C(11)	116.6(3)	C(29)-C(28)-H(28B)	110.2
C(7)-Si(3)-H(3S)	105(1)	F(5)-C(12)-C(13)	119.6(3)	H(28A)-C(28)-H(28B)	108.5
C(6)-Si(3)-H(3S)	102(1)	C(11)-C(12)-C(13)	123.8(3)	O(1)-C(29)-C(28)	106.2(3)
Ca(1)-Si(3)-H(3S)	48(1)	C(8)-C(13)-C(12)	112.7(3)	O(1)-C(29)-H(29A)	110.5
Si(3)-C(1)-Si(2)	114.7(2)	C(8)-C(13)-B(1)	124.5(3)	C(28)-C(29)-H(29A)	110.5
Si(3)-C(1)-Si(1)	118.5(2)	C(12)-C(13)-B(1)	122.6(3)	O(1)-C(29)-H(29B)	110.5
Si(2)-C(1)-Si(1)	116.0(2)	C(15)-C(14)-C(19)	113.4(3)	C(28)-C(29)-H(29B)	110.5
Si(3)-C(1)-Ca(1)	88.2(1)	C(15)-C(14)-B(1)	125.3(3)	H(29A)-C(29)-H(29B)	108.7
Si(2)-C(1)-Ca(1)	88.1(1)	C(19)-C(14)-B(1)	121.2(3)	O(2)-C(30)-C(31)	106.7(3)
Si(1)-C(1)-Ca(1)	125.24(1)	F(6)-C(15)-C(16)	115.6(3)	O(2)-C(30)-H(30A)	110.4
Si(1)-C(2)-H(2A)	109.5	F(6)-C(15)-C(14)	120.4(3)	C(31)-C(30)-H(30A)	110.4
Si(1)-C(2)-H(2B)	109.5	C(16)-C(15)-C(14)	124.0(3)	O(2)-C(30)-H(30B)	110.4
H(2A)-C(2)-H(2B)	109.5	F(7)-C(16)-C(15)	120.7(3)	C(31)-C(30)-H(30B)	110.4
Si(1)-C(2)-H(2C)	109.5	F(7)-C(16)-C(17)	120.0(3)	H(30A)-C(30)-H(30B)	108.6
H(2A)-C(2)-H(2C)	109.5	C(15)-C(16)-C(17)	119.3(3)	C(32)-C(31)-C(30)	106.1(3)
H(2B)-C(2)-H(2C)	109.5	F(8)-C(17)-C(18)	120.0(3)	C(32)-C(31)-H(31A)	110.5
Si(1)-C(3)-H(3A)	109.5	F(8)-C(17)-C(16)	120.1(3)	C(30)-C(31)-H(31A)	110.5
Si(1)-C(3)-H(3B)	109.5	C(18)-C(17)-C(16)	119.9(3)	C(32)-C(31)-H(31B)	110.5
H(3A)-C(3)-H(3B)	109.5	F(9)-C(18)-C(17)	119.5(3)	C(30)-C(31)-H(31B)	110.5
Si(1)-C(3)-H(3C)	109.5	F(9)-C(18)-C(19)	121.4(3)	H(31A)-C(31)-H(31B)	108.7
H(3A)-C(3)-H(3C)	109.5	C(17)-C(18)-C(19)	119.1(3)	C(33)-C(32)-C(31)	105.6(3)
H(3B)-C(3)-H(3C)	109.5	F(10)-C(19)-C(18)	116.4(3)	C(33)-C(32)-H(32A)	110.6
Si(2)-C(4)-H(4A)	109.5	F(10)-C(19)-C(14)	119.3(3)	C(31)-C(32)-H(32A)	110.6
Si(2)-C(4)-H(4B)	109.5	C(18)-C(19)-C(14)	124.3(3)	C(33)-C(32)-H(32B)	110.6
H(4A)-C(4)-H(4B)	109.5	F(11)-C(20)-C(25)	119.4(3)	C(31)-C(32)-H(32B)	110.6
Si(2)-C(4)-H(4C)	109.5	F(11)-C(20)-C(21)	115.1(3)	H(32A)-C(32)-H(32B)	108.7
H(4A)-C(4)-H(4C)	109.5	C(25)-C(20)-C(21)	125.5(3)	O(2)-C(33)-C(32)	105.9(3)
H(4B)-C(4)-H(4C)	109.5	F(12)-C(21)-C(22)	120.9(3)	O(2)-C(33)-H(33A)	110.6
Si(2)-C(5)-H(5A)	109.5	F(12)-C(21)-C(20)	120.6(3)	C(32)-C(33)-H(33A)	110.6
Si(2)-C(5)-H(5B)	109.5	C(22)-C(21)-C(20)	118.5(3)	O(2)-C(33)-H(33B)	110.6
H(5A)-C(5)-H(5B)	109.5	F(13)-C(22)-C(21)	120.2(3)	C(32)-C(33)-H(33B)	110.6
Si(2)-C(5)-H(5C)	109.5	F(13)-C(22)-C(23)	120.5(3)	H(33A)-C(33)-H(33B)	108.7
H(5A)-C(5)-H(5C)	109.5	C(21)-C(22)-C(23)	119.3(3)	C(8)-F(1)-Ca(1)	141.7(2)
H(5B)-C(5)-H(5C)	109.5	F(14)-C(23)-C(22)	119.6(3)	C(20)-F(11)-Ca(1)	141.9(2)
Si(3)-C(6)-H(6A)	109.5	F(14)-C(23)-C(24)	120.5(3)	C(26)-O(1)-C(29)	107.0(2)
Si(3)-C(6)-H(6B)	109.5	C(22)-C(23)-C(24)	119.9(3)	C(26)-O(1)-Ca(1)	128.5(2)
H(6A)-C(6)-H(6B)	109.5	F(15)-C(24)-C(23)	116.2(3)	C(29)-O(1)-Ca(1)	124.5(2)
Si(3)-C(6)-H(6C)	109.5	F(15)-C(24)-C(25)	119.9(3)	C(30)-O(2)-C(33)	108.0(2)
H(6A)-C(6)-H(6C)	109.5	C(23)-C(24)-C(25)	123.9(3)	C(30)-O(2)-Ca(1)	121.7(2)
H(6B)-C(6)-H(6C)	109.5	C(20)-C(25)-C(24)	112.8(3)	C(33)-O(2)-Ca(1)	130.3(2)
Si(3)-C(7)-H(7A)	109.5	C(20)-C(25)-B(1)	121.4(3)	C(14)-B(1)-C(13)	115.7(3)
Si(3)-C(7)-H(7B)	109.5	C(24)-C(25)-B(1)	125.7(3)	C(14)-B(1)-C(25)	115.3(3)

C(13)-B(1)-C(25)	106.6(2)	C(13)-B(1)-H(1G)	110(2)
C(14)-B(1)-H(1G)	103(2)	C(25)-B(1)-H(1G)	106(2)

Table S17. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2a**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \ldots + 2 h k a^* b^* U^{12}]$

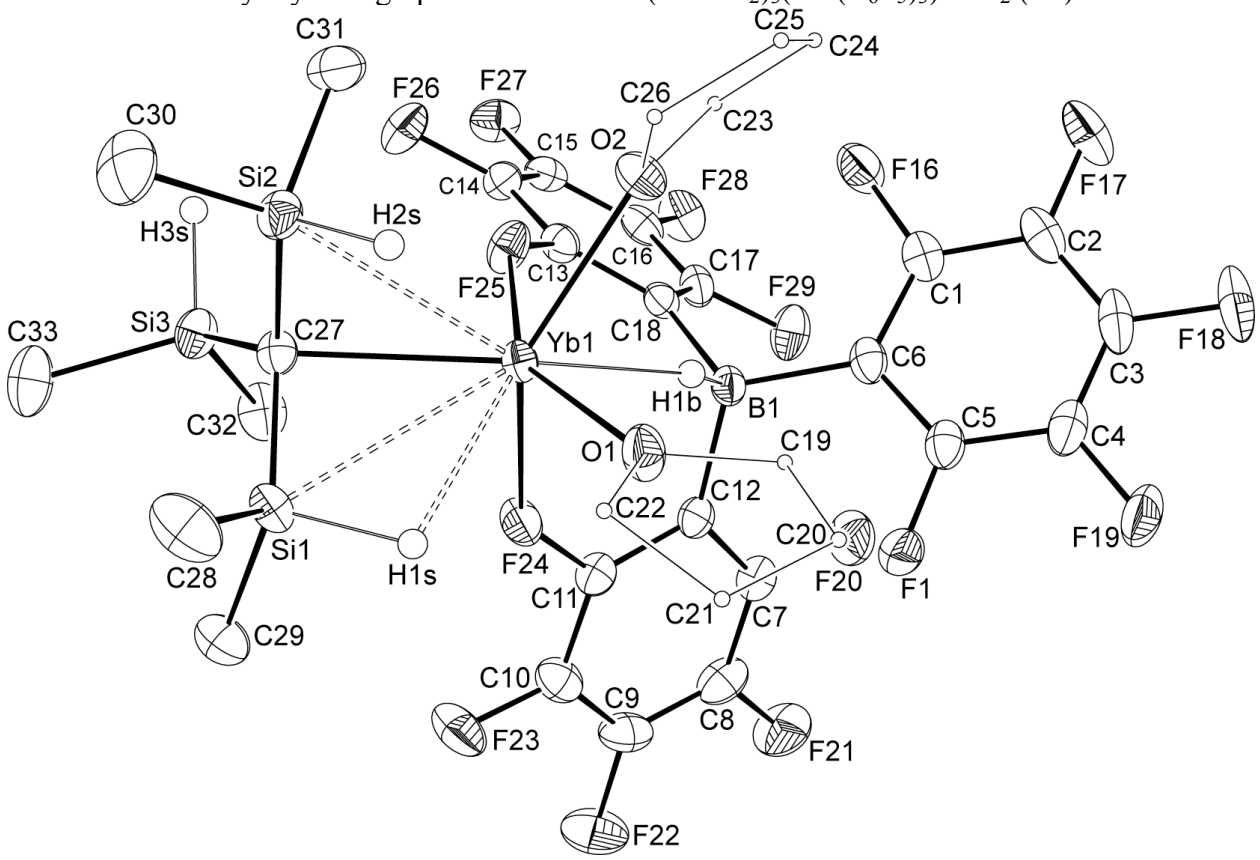
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca(1)	26(1)	22(1)	21(1)	1(1)	8(1)	1(1)
Si(1)	31(1)	27(1)	36(1)	-1(1)	12(1)	1(1)
Si(2)	37(1)	26(1)	33(1)	-4(1)	8(1)	-6(1)
Si(3)	36(1)	29(1)	24(1)	5(1)	7(1)	6(1)
C(1)	31(2)	21(2)	26(2)	0(1)	9(1)	-1(1)
C(2)	49(2)	30(2)	39(2)	-2(2)	17(2)	7(2)
C(3)	52(2)	44(2)	52(2)	3(2)	27(2)	-4(2)
C(4)	40(2)	54(2)	45(2)	-10(2)	0(2)	-16(2)
C(5)	84(3)	32(2)	65(3)	-7(2)	12(2)	-20(2)
C(6)	71(3)	42(2)	41(2)	2(2)	-1(2)	21(2)
C(7)	52(2)	43(2)	32(2)	0(2)	0(2)	3(2)
C(8)	32(2)	19(2)	22(2)	2(1)	5(1)	3(1)
C(9)	23(2)	28(2)	25(2)	0(1)	4(1)	-4(2)
C(10)	24(2)	36(2)	24(2)	-4(2)	1(1)	5(2)
C(11)	40(2)	22(2)	20(2)	0(1)	4(2)	6(2)
C(12)	36(2)	26(2)	18(2)	2(1)	7(1)	-3(2)
C(13)	30(2)	24(2)	14(2)	1(1)	5(1)	0(1)
C(14)	33(2)	19(2)	24(2)	-1(1)	10(1)	-1(1)
C(15)	37(2)	28(2)	26(2)	1(2)	10(2)	1(2)
C(16)	55(3)	33(2)	23(2)	6(2)	11(2)	7(2)
C(17)	60(3)	26(2)	30(2)	1(2)	28(2)	-7(2)
C(18)	36(2)	29(2)	38(2)	-8(2)	20(2)	-9(2)
C(19)	35(2)	20(2)	28(2)	-4(1)	8(2)	-6(1)
C(20)	25(2)	22(2)	29(2)	-4(1)	7(1)	-4(1)
C(21)	39(2)	35(2)	21(2)	0(2)	5(2)	4(2)
C(22)	31(2)	39(2)	31(2)	-14(2)	-2(2)	3(2)
C(23)	32(2)	25(2)	51(2)	-12(2)	7(2)	-6(2)
C(24)	33(2)	26(2)	31(2)	2(2)	9(2)	-2(2)
C(25)	20(2)	28(2)	24(2)	0(1)	9(1)	1(1)
C(26)	78(3)	49(2)	32(2)	0(2)	-8(2)	20(2)
C(27)	159(6)	125(5)	36(3)	26(3)	27(3)	85(4)
C(28)	174(6)	119(5)	30(3)	-4(3)	17(3)	79(4)
C(29)	72(3)	44(2)	32(2)	-11(2)	11(2)	17(2)
C(30)	34(2)	60(3)	43(2)	19(2)	14(2)	4(2)
C(31)	42(3)	66(3)	107(4)	33(3)	37(3)	18(2)
C(32)	35(2)	36(2)	107(4)	6(2)	0(2)	5(2)
C(33)	48(2)	41(2)	54(2)	11(2)	20(2)	19(2)
F(1)	27(1)	21(1)	43(1)	5(1)	10(1)	1(1)
F(2)	26(1)	34(1)	54(1)	2(1)	9(1)	-4(1)
F(3)	29(1)	41(1)	41(1)	-2(1)	0(1)	9(1)
F(4)	48(1)	26(1)	40(1)	5(1)	9(1)	12(1)
F(5)	43(1)	23(1)	46(1)	5(1)	16(1)	-3(1)
F(6)	40(1)	56(1)	25(1)	7(1)	5(1)	8(1)
F(7)	75(2)	60(1)	27(1)	14(1)	16(1)	14(1)
F(8)	80(2)	48(1)	42(1)	6(1)	41(1)	-6(1)
F(9)	42(1)	58(1)	46(1)	-14(1)	26(1)	-18(1)
F(10)	28(1)	50(1)	33(1)	-3(1)	9(1)	-6(1)
F(11)	45(1)	27(1)	23(1)	1(1)	4(1)	-7(1)
F(12)	65(1)	46(1)	24(1)	1(1)	1(1)	2(1)
F(13)	65(2)	54(1)	40(1)	-19(1)	-13(1)	-1(1)
F(14)	58(1)	38(1)	60(1)	-16(1)	2(1)	-16(1)

F(15)	55(1)	31(1)	42(1)	1(1)	9(1)	-14(1)
O(1)	36(1)	28(1)	24(1)	-1(1)	2(1)	6(1)
O(2)	31(1)	38(1)	30(1)	8(1)	12(1)	9(1)
B(1)	31(2)	20(2)	24(2)	2(2)	9(2)	-1(2)

Table S18. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $CaC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2a**).

	x	y	z	U(eq)
H(1S)	-1550(30)	8483(14)	4030(20)	46
H(2S)	1250(30)	7531(14)	2740(20)	47
H(3S)	3040(30)	8185(14)	4230(20)	44
H(2A)	515	9248	5394	58
H(2B)	-923	9354	5331	58
H(2C)	-214	9475	4498	58
H(3A)	-1052	7647	5483	71
H(3B)	-1650	8219	5835	71
H(3C)	-233	8087	6102	71
H(4A)	-1743	7977	2615	70
H(4B)	-1112	7638	1878	70
H(4C)	-695	8283	2145	70
H(5A)	301	6708	3920	91
H(5B)	-470	6658	2974	91
H(5C)	-1084	6925	3778	91
H(6A)	2004	6981	5233	78
H(6B)	3390	7148	5145	78
H(6C)	2482	6994	4289	78
H(7A)	2207	8718	5788	64
H(7B)	3274	8262	6060	64
H(7C)	1910	8122	6249	64
H(26A)	1159	9342	1012	65
H(26B)	-13	8927	839	65
H(27A)	566	8789	-459	127
H(27B)	1908	9037	-161	127
H(28A)	2570	8186	-60	129
H(28B)	1216	7938	-309	129
H(29A)	1032	7734	1050	59
H(29B)	2473	7849	1250	59
H(30A)	4685	9082	2400	54
H(30B)	4110	8732	1546	54
H(31A)	5740	8201	1541	83
H(31B)	6402	8653	2236	83
H(32A)	6163	7588	2626	72
H(32B)	6205	8087	3359	72
H(33A)	4172	7496	2546	56
H(33B)	4417	7718	3544	56
H(1G)	2350(30)	9620(13)	2457(19)	29

X-ray crystallographic data for $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2b**).



Data Collection $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (2b).

A yellow crystal was selected under ambient conditions. The crystal was mounted and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed at 123K on a Bruker APEX II diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the detector to crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3º in a 10º range about ω with the exposure time of 10 seconds per frame. The obtained reflections were successfully indexed by an automated indexing routine built in the APEX2 program. The final cell constants were calculated from a set of strong reflections from the actual data collection. The data were collected using the full sphere routine by collecting four sets of frames with 0.3º scans in ω with an exposure time 10 sec per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was

based on a fit of a spherical harmonic function to the empirical transmission surface as sampled by multiple equivalent measurements using SADABS software.[5,6]

Structure Solution and Refinement of $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (2b).

The systematic absences in the diffraction data were consistent for the space groups $P2_1/n$[6] yielded chemically reasonable and computationally stable results of refinement. The position of almost all non-hydrogen atoms were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. Almost all hydrogen atoms were placed in the structure factor calculation at idealized positions. H-atoms belonged to Si atoms were found objectively on a difference Fourier map. All H-atoms were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

Table S19. Crystal data and structure refinement for $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2b**).

Empirical formula	$C_{33}H_{38}BF_{15}O_2Si_3Yb$	
Formula weight	1019.75	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.0583(7) Å	α= 90°.
	b = 23.1942(14) Å	β= 97.0320(10)°.
	c = 15.3710(9) Å	γ = 90°.
Volume	3912.8(4) $Å^3$	
Z	4	
Density (calculated)	1.731 Mg/m^3	
Absorption coefficient	2.584 mm^{-1}	
F(000)	2016	
Crystal size	0.30 × 0.30 × 0.15 mm^3	
Theta range for data collection	1.60 to 26.45°.	
Index ranges	-13≤h≤13, -28≤k≤29, -19≤l≤19	
Reflections collected	34431	
Independent reflections	8062 [R(int) = 0.0269]	
Completeness to theta = 26.45°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6979 and 0.5111	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8062 / 14 / 514	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0215, wR2 = 0.0526	
R indices (all data)	R1 = 0.0262, wR2 = 0.0549	
Largest diff. peak and hole	1.310 and -0.389 $e.Å^{-3}$	

$R1 = \Sigma \, | \, |F_o| - |F_c| \, | \, / \, \Sigma \, |F_o|$ and $wR2 = \{ \, \Sigma \, [\, w(F_o^2 - F_c^2)^2 \,] \, / \, \Sigma \, [\, w(F_o^2)^2 \,] \, \}^{1/2}$

Table S20. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2b**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Yb(1)	6972(1)	1344(1)	8017(1)	19(1)
B(1)	7242(2)	-98(1)	7481(2)	20(1)
C(1)	7249(2)	-450(1)	5818(2)	28(1)
C(2)	7819(3)	-601(1)	5094(2)	33(1)
C(3)	9063(3)	-614(1)	5168(2)	35(1)
C(4)	9729(3)	-463(1)	5944(2)	31(1)
C(5)	9133(2)	-311(1)	6649(2)	26(1)
C(6)	7873(2)	-307(1)	6630(2)	23(1)
C(7)	8445(2)	-867(1)	8588(2)	27(1)
C(8)	8947(3)	-1052(1)	9410(2)	33(1)
C(9)	8972(3)	-690(1)	10120(2)	33(1)
C(10)	8482(2)	-145(1)	10003(2)	29(1)
C(11)	7983(2)	14(1)	9172(2)	23(1)
C(12)	7932(2)	-324(1)	8426(2)	21(1)
C(13)	4900(2)	118(1)	7630(2)	21(1)
C(14)	3696(2)	-18(1)	7677(2)	24(1)
C(15)	3325(2)	-580(1)	7556(2)	24(1)
C(16)	4173(2)	-986(1)	7381(2)	25(1)
C(17)	5369(2)	-828(1)	7346(2)	24(1)
C(18)	5800(2)	-268(1)	7467(2)	20(1)
C(19)	9586(3)	1324(1)	7112(2)	38(1)
C(20)	10765(3)	1622(2)	7102(3)	66(1)
C(21)	10848(3)	2067(1)	7776(3)	55(1)
C(22)	9572(3)	2186(1)	7930(2)	39(1)
C(23)	5949(4)	1040(2)	5828(2)	50(1)
C(24)	6350(6)	1205(2)	4989(3)	100(2)
C(25)	6774(6)	1787(2)	5058(2)	96(2)
C(26)	6700(3)	1978(1)	5979(2)	42(1)
C(27)	5705(2)	1868(1)	9090(2)	21(1)
C(28)	7457(3)	1691(1)	10836(2)	35(1)
C(29)	7589(3)	2822(1)	9867(2)	44(1)
C(30)	4732(4)	3109(1)	8472(2)	50(1)
C(31)	4072(3)	2075(1)	7338(2)	38(1)
C(32)	4768(3)	780(1)	10004(2)	34(1)
C(33)	4116(3)	1950(1)	10621(2)	43(1)
F(1)	9842(1)	-156(1)	7386(1)	34(1)
F(16)	6021(2)	-433(1)	5682(1)	37(1)
F(17)	7155(2)	-732(1)	4328(1)	48(1)
F(18)	9634(2)	-771(1)	4479(1)	49(1)
F(19)	10951(2)	-462(1)	6001(1)	43(1)
F(20)	8487(2)	-1245(1)	7932(1)	40(1)
F(21)	9424(2)	-1585(1)	9521(1)	46(1)
F(22)	9482(2)	-860(1)	10916(1)	49(1)
F(23)	8490(2)	216(1)	10682(1)	42(1)
F(24)	7504(2)	562(1)	9110(1)	30(1)
F(25)	5186(1)	693(1)	7753(1)	29(1)
F(26)	2894(1)	391(1)	7842(1)	35(1)
F(27)	2177(1)	-733(1)	7614(1)	32(1)
F(28)	3820(2)	-1537(1)	7234(1)	34(1)
F(29)	6133(2)	-1251(1)	7166(1)	34(1)
O(1)	8894(2)	1665(1)	7671(1)	29(1)
O(2)	6474(2)	1458(1)	6457(1)	27(1)

Si(1)	7143(1)	2045(1)	9745(1)	24(1)
Si(2)	5241(1)	2371(1)	8207(1)	26(1)
Si(3)	4497(1)	1541(1)	9628(1)	26(1)

Table S21. Bond lengths [Å] for $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2b**).

Yb(1)-O(1)	2.374(2)	C(11)-C(12)	1.385(3)	C(26)-O(2)	1.449(3)
Yb(1)-O(2)	2.409(2)	C(13)-F(25)	1.378(3)	C(26)-H(26A)	0.9900
Yb(1)-F(25)	2.480(1)	C(13)-C(14)	1.379(3)	C(26)-H(26B)	0.9900
Yb(1)-F(24)	2.493(1)	C(13)-C(18)	1.384(3)	C(27)-Si(2)	1.815(2)
Yb(1)-C(27)	2.593(2)	C(14)-F(26)	1.343(3)	C(27)-Si(3)	1.821(2)
Yb(1)-Si(2)	3.0925(7)	C(14)-C(15)	1.374(4)	C(27)-Si(1)	1.822(3)
Yb(1)-Si(1)	3.1016(7)	C(15)-F(27)	1.331(3)	C(28)-Si(1)	1.860(3)
Yb(1)-H(1B)	2.40(3)	C(15)-C(16)	1.379(4)	C(28)-H(28A)	0.9800
Yb(1)-H(1S)	2.41(3)	C(16)-F(28)	1.347(3)	C(28)-H(28B)	0.9800
Yb(1)-H(2S)	2.60(3)	C(16)-C(17)	1.379(4)	C(28)-H(28C)	0.9800
B(1)-C(6)	1.630(4)	C(17)-F(29)	1.347(3)	C(29)-Si(1)	1.872(3)
B(1)-C(18)	1.640(4)	C(17)-C(18)	1.387(3)	C(29)-H(29A)	0.9800
B(1)-C(12)	1.642(4)	C(19)-O(1)	1.452(3)	C(29)-H(29B)	0.9800
B(1)-H(1B)	1.16(3)	C(19)-C(20)	1.477(4)	C(29)-H(29C)	0.9800
C(1)-F(16)	1.349(3)	C(19)-H(19A)	0.9900	C(30)-Si(2)	1.862(3)
C(1)-C(2)	1.389(4)	C(19)-H(19B)	0.9900	C(30)-H(30A)	0.9800
C(1)-C(6)	1.390(4)	C(20)-C(21)	1.458(5)	C(30)-H(30B)	0.9800
C(2)-F(17)	1.344(3)	C(20)-H(20A)	0.9900	C(30)-H(30C)	0.9800
C(2)-C(3)	1.366(4)	C(20)-H(20B)	0.9900	C(31)-Si(2)	1.872(3)
C(3)-F(18)	1.348(3)	C(21)-C(22)	1.485(4)	C(31)-H(31A)	0.9800
C(3)-C(4)	1.368(4)	C(21)-H(21A)	0.9900	C(31)-H(31B)	0.9800
C(4)-F(19)	1.343(3)	C(21)-H(21B)	0.9900	C(31)-H(31C)	0.9800
C(4)-C(5)	1.381(4)	C(22)-O(1)	1.452(3)	C(32)-Si(3)	1.871(3)
C(5)-F(1)	1.346(3)	C(22)-H(22A)	0.9900	C(32)-H(32A)	0.9800
C(5)-C(6)	1.391(4)	C(22)-H(22B)	0.9900	C(32)-H(32B)	0.9800
C(7)-F(20)	1.341(3)	C(23)-O(2)	1.440(3)	C(32)-H(32C)	0.9800
C(7)-C(8)	1.386(4)	C(23)-C(24)	1.464(5)	C(33)-Si(3)	1.888(3)
C(7)-C(12)	1.391(4)	C(23)-H(23A)	0.9900	C(33)-H(33A)	0.9800
C(8)-F(21)	1.347(3)	C(23)-H(23B)	0.9900	C(33)-H(33B)	0.9800
C(8)-C(9)	1.374(4)	C(24)-C(25)	1.429(6)	C(33)-H(33C)	0.9800
C(9)-F(22)	1.343(3)	C(24)-H(24A)	0.9900	Si(1)-H(1S)	1.53(3)
C(9)-C(10)	1.378(4)	C(24)-H(24B)	0.9900	Si(2)-H(2S)	1.48(3)
C(10)-F(23)	1.336(3)	C(25)-C(26)	1.495(5)	Si(3)-H(3S)	1.42(3)
C(10)-C(11)	1.378(4)	C(25)-H(25A)	0.9900		
C(11)-F(24)	1.377(3)	C(25)-H(25B)	0.9900		

Table S22. Bond angles [°] for $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2b**).

O(1)-Yb(1)-O(2)	81.05(6)	C(27)-Yb(1)-Si(2)	35.89(5)	O(1)-Yb(1)-H(1S)	68.4(7)
O(1)-Yb(1)-F(25)	150.66(5)	O(1)-Yb(1)-Si(1)	93.72(4)	O(2)-Yb(1)-H(1S)	141.1(7)
O(2)-Yb(1)-F(25)	79.84(6)	O(2)-Yb(1)-Si(1)	141.08(5)	F(25)-Yb(1)-H(1S)	137.1(7)
O(1)-Yb(1)-F(24)	103.60(6)	F(25)-Yb(1)-Si(1)	115.05(4)	F(24)-Yb(1)-H(1S)	73.6(7)
O(2)-Yb(1)-F(24)	139.24(5)	F(24)-Yb(1)-Si(1)	79.58(4)	C(27)-Yb(1)-H(1S)	64.8(7)
F(25)-Yb(1)-F(24)	77.58(5)	C(27)-Yb(1)-Si(1)	35.93(6)	Si(2)-Yb(1)-H(1S)	82.7(7)
O(1)-Yb(1)-C(27)	124.30(7)	Si(2)-Yb(1)-Si(1)	59.22(2)	Si(1)-Yb(1)-H(1S)	28.9(7)
O(2)-Yb(1)-C(27)	120.42(7)	O(1)-Yb(1)-H(1B)	90.5(6)	H(1B)-Yb(1)-H(1S)	124.7(9)
F(25)-Yb(1)-C(27)	84.74(6)	O(2)-Yb(1)-H(1B)	77.3(6)	O(1)-Yb(1)-H(2S)	83.9(6)
F(24)-Yb(1)-C(27)	90.77(6)	F(25)-Yb(1)-H(1B)	63.6(6)	O(2)-Yb(1)-H(2S)	73.5(6)
O(1)-Yb(1)-Si(2)	111.15(5)	F(24)-Yb(1)-H(1B)	62.3(6)	F(25)-Yb(1)-H(2S)	111.4(6)
O(2)-Yb(1)-Si(2)	86.62(5)	C(27)-Yb(1)-H(1B)	141.3(7)	F(24)-Yb(1)-H(2S)	146.8(6)
F(25)-Yb(1)-Si(2)	89.73(4)	Si(2)-Yb(1)-H(1B)	150.7(6)	C(27)-Yb(1)-H(2S)	59.7(6)
F(24)-Yb(1)-Si(2)	126.46(4)	Si(1)-Yb(1)-H(1B)	141.6(6)	Si(2)-Yb(1)-H(2S)	28.5(6)

Si(1)-Yb(1)-H(2S)	67.6(6)	F(29)-C(17)-C(18)	119.7(2)	Si(1)-C(27)-Yb(1)	87.43(9)
H(1B)-Yb(1)-H(2S)	150.8(9)	C(16)-C(17)-C(18)	124.0(2)	Si(1)-C(28)-H(28A)	109.5
H(1S)-Yb(1)-H(2S)	79.7(9)	C(13)-C(18)-C(17)	112.7(2)	Si(1)-C(28)-H(28B)	109.5
C(6)-B(1)-C(18)	115.4(2)	C(13)-C(18)-B(1)	124.1(2)	H(28A)-C(28)-H(28B)	109.5
C(6)-B(1)-C(12)	114.6(2)	C(17)-C(18)-B(1)	123.0(2)	Si(1)-C(28)-H(28C)	109.5
C(18)-B(1)-C(12)	106.3(2)	O(1)-C(19)-C(20)	106.4(2)	H(28A)-C(28)-H(28C)	109.5
C(6)-B(1)-H(1B)	103(1)	O(1)-C(19)-H(19A)	110.5	H(28B)-C(28)-H(28C)	109.5
C(18)-B(1)-H(1B)	110(1)	C(20)-C(19)-H(19A)	110.5	Si(1)-C(29)-H(29A)	109.5
C(12)-B(1)-H(1B)	107(1)	O(1)-C(19)-H(19B)	110.5	Si(1)-C(29)-H(29B)	109.5
F(16)-C(1)-C(2)	115.5(2)	C(20)-C(19)-H(19B)	110.5	H(29A)-C(29)-H(29B)	109.5
F(16)-C(1)-C(6)	120.7(2)	H(19A)-C(19)-H(19B)	108.6	Si(1)-C(29)-H(29C)	109.5
C(2)-C(1)-C(6)	123.7(3)	C(21)-C(20)-C(19)	107.6(3)	H(29A)-C(29)-H(29C)	109.5
F(17)-C(2)-C(3)	120.3(2)	C(21)-C(20)-H(20A)	110.2	H(29B)-C(29)-H(29C)	109.5
F(17)-C(2)-C(1)	120.4(3)	C(19)-C(20)-H(20A)	110.2	Si(2)-C(30)-H(30A)	109.5
C(3)-C(2)-C(1)	119.3(3)	C(21)-C(20)-H(20B)	110.2	Si(2)-C(30)-H(30B)	109.5
F(18)-C(3)-C(2)	120.3(3)	C(19)-C(20)-H(20B)	110.2	H(30A)-C(30)-H(30B)	109.5
F(18)-C(3)-C(4)	120.0(3)	H(20A)-C(20)-H(20B)	108.5	Si(2)-C(30)-H(30C)	109.5
C(2)-C(3)-C(4)	119.7(2)	C(20)-C(21)-C(22)	105.4(3)	H(30A)-C(30)-H(30C)	109.5
F(19)-C(4)-C(3)	119.2(2)	C(20)-C(21)-H(21A)	110.7	H(30B)-C(30)-H(30C)	109.5
F(19)-C(4)-C(5)	121.3(3)	C(22)-C(21)-H(21A)	110.7	Si(2)-C(31)-H(31A)	109.5
C(3)-C(4)-C(5)	119.4(3)	C(20)-C(21)-H(21B)	110.7	Si(2)-C(31)-H(31B)	109.5
F(1)-C(5)-C(4)	116.4(2)	C(22)-C(21)-H(21B)	110.7	H(31A)-C(31)-H(31B)	109.5
F(1)-C(5)-C(6)	119.6(2)	H(21A)-C(21)-H(21B)	108.8	Si(2)-C(31)-H(31C)	109.5
C(4)-C(5)-C(6)	124.0(3)	O(1)-C(22)-C(21)	105.7(2)	H(31A)-C(31)-H(31C)	109.5
C(1)-C(6)-C(5)	113.8(2)	O(1)-C(22)-H(22A)	110.6	H(31B)-C(31)-H(31C)	109.5
C(1)-C(6)-B(1)	125.3(2)	C(21)-C(22)-H(22A)	110.6	Si(3)-C(32)-H(32A)	109.5
C(5)-C(6)-B(1)	120.8(2)	O(1)-C(22)-H(22B)	110.6	Si(3)-C(32)-H(32B)	109.5
F(20)-C(7)-C(8)	115.9(2)	C(21)-C(22)-H(22B)	110.6	H(32A)-C(32)-H(32B)	109.5
F(20)-C(7)-C(12)	120.6(2)	H(22A)-C(22)-H(22B)	108.7	Si(3)-C(32)-H(32C)	109.5
C(8)-C(7)-C(12)	123.5(2)	O(2)-C(23)-C(24)	106.0(3)	H(32A)-C(32)-H(32C)	109.5
F(21)-C(8)-C(9)	119.5(2)	O(2)-C(23)-H(23A)	110.5	H(32B)-C(32)-H(32C)	109.5
F(21)-C(8)-C(7)	120.4(3)	C(24)-C(23)-H(23A)	110.5	Si(3)-C(33)-H(33A)	109.5
C(9)-C(8)-C(7)	120.1(2)	O(2)-C(23)-H(23B)	110.5	Si(3)-C(33)-H(33B)	109.5
F(22)-C(9)-C(8)	120.5(3)	C(24)-C(23)-H(23B)	110.5	H(33A)-C(33)-H(33B)	109.5
F(22)-C(9)-C(10)	120.3(3)	H(23A)-C(23)-H(23B)	108.7	Si(3)-C(33)-H(33C)	109.5
C(8)-C(9)-C(10)	119.2(2)	C(25)-C(24)-C(23)	108.3(3)	H(33A)-C(33)-H(33C)	109.5
F(23)-C(10)-C(9)	120.5(2)	C(25)-C(24)-H(24A)	110.0	H(33B)-C(33)-H(33C)	109.5
F(23)-C(10)-C(11)	121.4(2)	C(23)-C(24)-H(24A)	110.0	C(11)-F(24)-Yb(1)	140.8(1)
C(9)-C(10)-C(11)	118.1(3)	C(25)-C(24)-H(24B)	110.0	C(13)-F(25)-Yb(1)	141.0 (1)
F(24)-C(11)-C(10)	114.7(2)	C(23)-C(24)-H(24B)	110.0	C(22)-O(1)-C(19)	108.9(2)
F(24)-C(11)-C(12)	119.3(2)	H(24A)-C(24)-H(24B)	108.4	C(22)-O(1)-Yb(1)	130.3(2)
C(10)-C(11)-C(12)	126.0(2)	C(24)-C(25)-C(26)	107.1(3)	C(19)-O(1)-Yb(1)	120.0(2)
C(11)-C(12)-C(7)	113.0(2)	C(24)-C(25)-H(25A)	110.3	C(23)-O(2)-C(26)	107.5(2)
C(11)-C(12)-B(1)	121.3(2)	C(26)-C(25)-H(25A)	110.3	C(23)-O(2)-Yb(1)	128.3(2)
C(7)-C(12)-B(1)	125.6(2)	C(24)-C(25)-H(25B)	110.3	C(26)-O(2)-Yb(1)	124.3(2)
F(25)-C(13)-C(14)	114.8(2)	C(26)-C(25)-H(25B)	110.3	C(27)-Si(1)-C(28)	116.9(1)
F(25)-C(13)-C(18)	119.5(2)	H(25A)-C(25)-H(25B)	108.6	C(27)-Si(1)-C(29)	118.3(1)
C(14)-C(13)-C(18)	125.6(2)	O(2)-C(26)-C(25)	105.4(3)	C(28)-Si(1)-C(29)	108.5(1)
F(26)-C(14)-C(15)	120.2(2)	O(2)-C(26)-H(26A)	110.7	C(27)-Si(1)-Yb(1)	56.64(8)
F(26)-C(14)-C(13)	120.9(2)	C(25)-C(26)-H(26A)	110.7	C(28)-Si(1)-Yb(1)	121.7(1)
C(15)-C(14)-C(13)	118.9(2)	O(2)-C(26)-H(26B)	110.7	C(29)-Si(1)-Yb(1)	125.3(1)
F(27)-C(15)-C(14)	121.0(2)	C(25)-C(26)-H(26B)	110.7	C(27)-Si(1)-H(1S)	106(1)
F(27)-C(15)-C(16)	120.6(2)	H(26A)-C(26)-H(26B)	108.8	C(28)-Si(1)-H(1S)	102(1)
C(14)-C(15)-C(16)	118.5(2)	Si(2)-C(27)-Si(3)	116.8(1)	C(29)-Si(1)-H(1S)	103(1)
F(28)-C(16)-C(15)	119.3(2)	Si(2)-C(27)-Si(1)	114.6(1)	Yb(1)-Si(1)-H(1S)	49(1)
F(28)-C(16)-C(17)	120.4(2)	Si(3)-C(27)-Si(1)	118.8(1)	C(27)-Si(2)-C(30)	119.5(1)
C(15)-C(16)-C(17)	120.2(2)	Si(2)-C(27)-Yb(1)	87.22(9)	C(27)-Si(2)-C(31)	113.9(1)
F(29)-C(17)-C(16)	116.2(2)	Si(3)-C(27)-Yb(1)	125.3(1)	C(30)-Si(2)-C(31)	107.0(2)

C(27)-Si(2)-Yb(1)	56.88(8)	C(31)-Si(2)-H(2S)	103(1)	C(27)-Si(3)-H(3S)	109(1)
C(30)-Si(2)-Yb(1)	159.4(1)	Yb(1)-Si(2)-H(2S)	57(1)	C(32)-Si(3)-H(3S)	107(1)
C(31)-Si(2)-Yb(1)	91.8(1)	C(27)-Si(3)-C(32)	115.7(1)	C(33)-Si(3)-H(3S)	105(1)
C(27)-Si(2)-H(2S)	103(1)	C(27)-Si(3)-C(33)	114.0(1)		
C(30)-Si(2)-H(2S)	109(1)	C(32)-Si(3)-C(33)	105.5(1)		

Table S23. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2b**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Yb(1)	20(1)	19(1)	17(1)	-1(1)	5(1)	-1(1)
B(1)	23(1)	19(1)	19(1)	-2(1)	5(1)	2(1)
C(1)	34(2)	24(1)	26(1)	-2(1)	8(1)	-2(1)
C(2)	51(2)	26(1)	23(1)	-5(1)	10(1)	-4(1)
C(3)	53(2)	24(1)	31(2)	0(1)	25(1)	7(1)
C(4)	34(2)	27(1)	35(2)	8(1)	17(1)	10(1)
C(5)	31(1)	22(1)	26(1)	3(1)	10(1)	5(1)
C(6)	31(1)	18(1)	22(1)	0(1)	8(1)	3(1)
C(7)	25(1)	27(1)	30(1)	0(1)	7(1)	1(1)
C(8)	30(1)	25(1)	44(2)	12(1)	5(1)	6(1)
C(9)	31(1)	38(2)	28(1)	11(1)	-3(1)	0(1)
C(10)	32(1)	32(1)	24(1)	1(1)	4(1)	-6(1)
C(11)	23(1)	21(1)	26(1)	3(1)	5(1)	1(1)
C(12)	18(1)	24(1)	23(1)	1(1)	7(1)	-1(1)
C(13)	26(1)	18(1)	20(1)	-2(1)	1(1)	-1(1)
C(14)	22(1)	25(1)	23(1)	1(1)	3(1)	3(1)
C(15)	22(1)	31(1)	19(1)	3(1)	0(1)	-4(1)
C(16)	35(1)	21(1)	18(1)	1(1)	2(1)	-7(1)
C(17)	30(1)	22(1)	20(1)	-2(1)	6(1)	3(1)
C(18)	23(1)	22(1)	15(1)	0(1)	2(1)	1(1)
C(19)	28(2)	51(2)	37(2)	-17(1)	12(1)	-2(1)
C(20)	41(2)	57(2)	106(3)	-30(2)	40(2)	-15(2)
C(21)	31(2)	35(2)	100(3)	-10(2)	10(2)	-4(1)
C(22)	37(2)	36(2)	48(2)	-11(1)	18(1)	-15(1)
C(23)	79(3)	42(2)	25(2)	-3(1)	-9(2)	-15(2)
C(24)	155(4)	115(3)	36(2)	-28(2)	31(2)	-78(3)
C(25)	158(4)	106(3)	28(2)	-5(2)	26(2)	-68(3)
C(26)	61(2)	38(2)	28(2)	10(1)	8(1)	-14(2)
C(27)	25(1)	16(1)	22(1)	1(1)	5(1)	1(1)
C(28)	42(2)	38(2)	24(1)	1(1)	1(1)	-2(1)
C(29)	60(2)	34(2)	38(2)	-4(1)	1(2)	-19(2)
C(30)	75(2)	26(2)	52(2)	6(1)	15(2)	18(2)
C(31)	31(2)	49(2)	34(2)	6(1)	-1(1)	8(1)
C(32)	43(2)	26(1)	35(2)	3(1)	14(1)	-6(1)
C(33)	45(2)	39(2)	49(2)	-3(1)	27(2)	2(1)
F(1)	25(1)	47(1)	30(1)	3(1)	6(1)	4(1)
F(16)	35(1)	51(1)	24(1)	-7(1)	4(1)	-9(1)
F(17)	68(1)	54(1)	24(1)	-12(1)	12(1)	-12(1)
F(18)	71(1)	45(1)	37(1)	-4(1)	35(1)	7(1)
F(19)	36(1)	55(1)	42(1)	14(1)	23(1)	17(1)
F(20)	51(1)	30(1)	41(1)	-2(1)	8(1)	12(1)
F(21)	50(1)	33(1)	55(1)	14(1)	2(1)	16(1)
F(22)	58(1)	51(1)	35(1)	18(1)	-11(1)	4(1)
F(23)	60(1)	43(1)	21(1)	-1(1)	0(1)	-1(1)
F(24)	43(1)	26(1)	21(1)	-1(1)	4(1)	7(1)
F(25)	24(1)	20(1)	44(1)	-5(1)	8(1)	-1(1)
F(26)	22(1)	31(1)	52(1)	-2(1)	8(1)	4(1)
F(27)	23(1)	37(1)	37(1)	4(1)	1(1)	-9(1)
F(28)	43(1)	23(1)	38(1)	-4(1)	7(1)	-11(1)

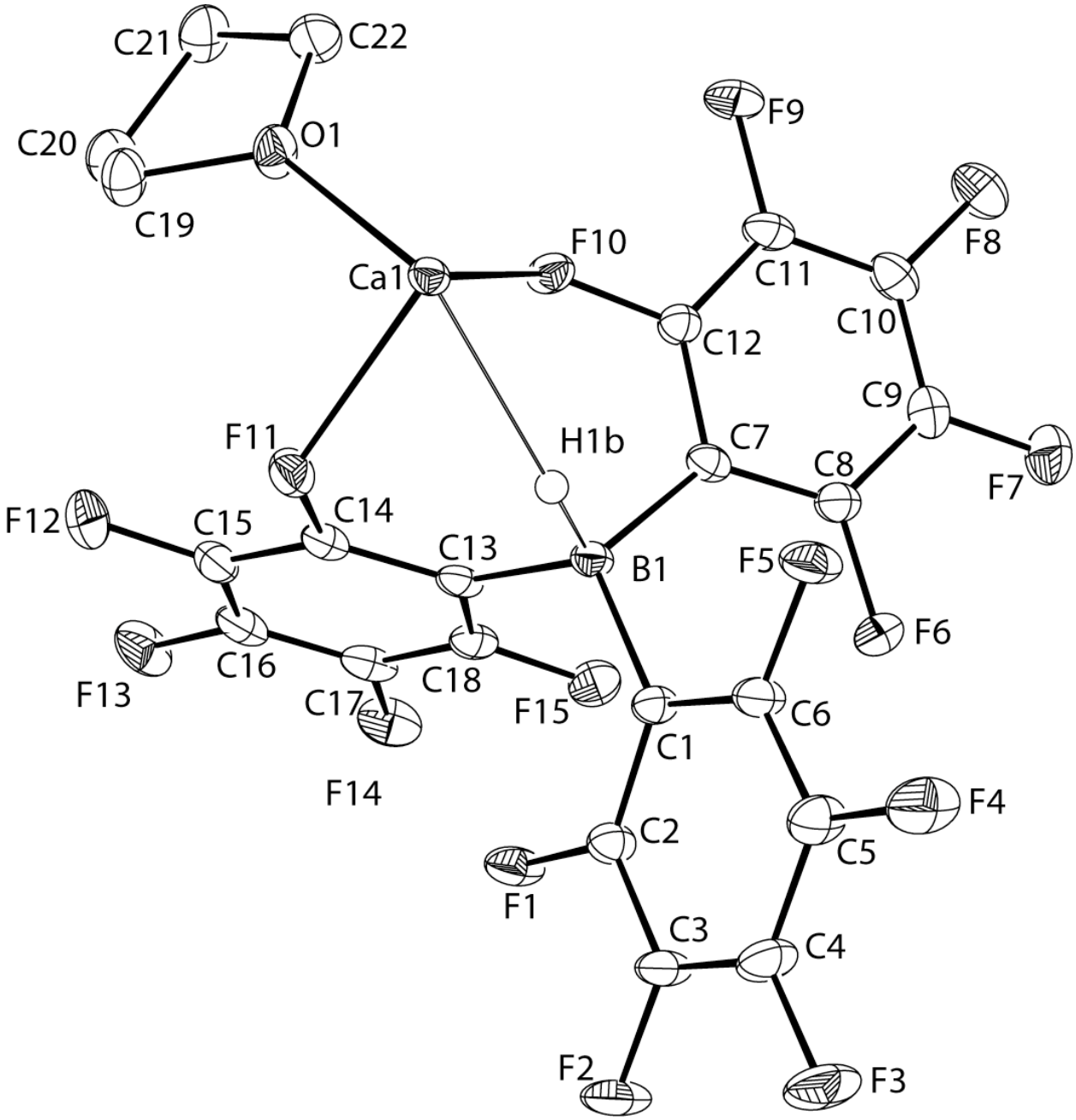
F(29)	38(1)	22(1)	44(1)	-5(1)	15(1)	2(1)
O(1)	25(1)	34(1)	29(1)	-8(1)	10(1)	-6(1)
O(2)	33(1)	26(1)	21(1)	2(1)	3(1)	-5(1)
Si(1)	29(1)	24(1)	19(1)	-3(1)	5(1)	-5(1)
Si(2)	30(1)	22(1)	26(1)	4(1)	6(1)	6(1)
Si(3)	25(1)	24(1)	30(1)	1(1)	10(1)	-1(1)

Table S24. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $YbC(SiHMe_2)_3(HB(C_6F_5)_3)THF_2$ (**2b**).

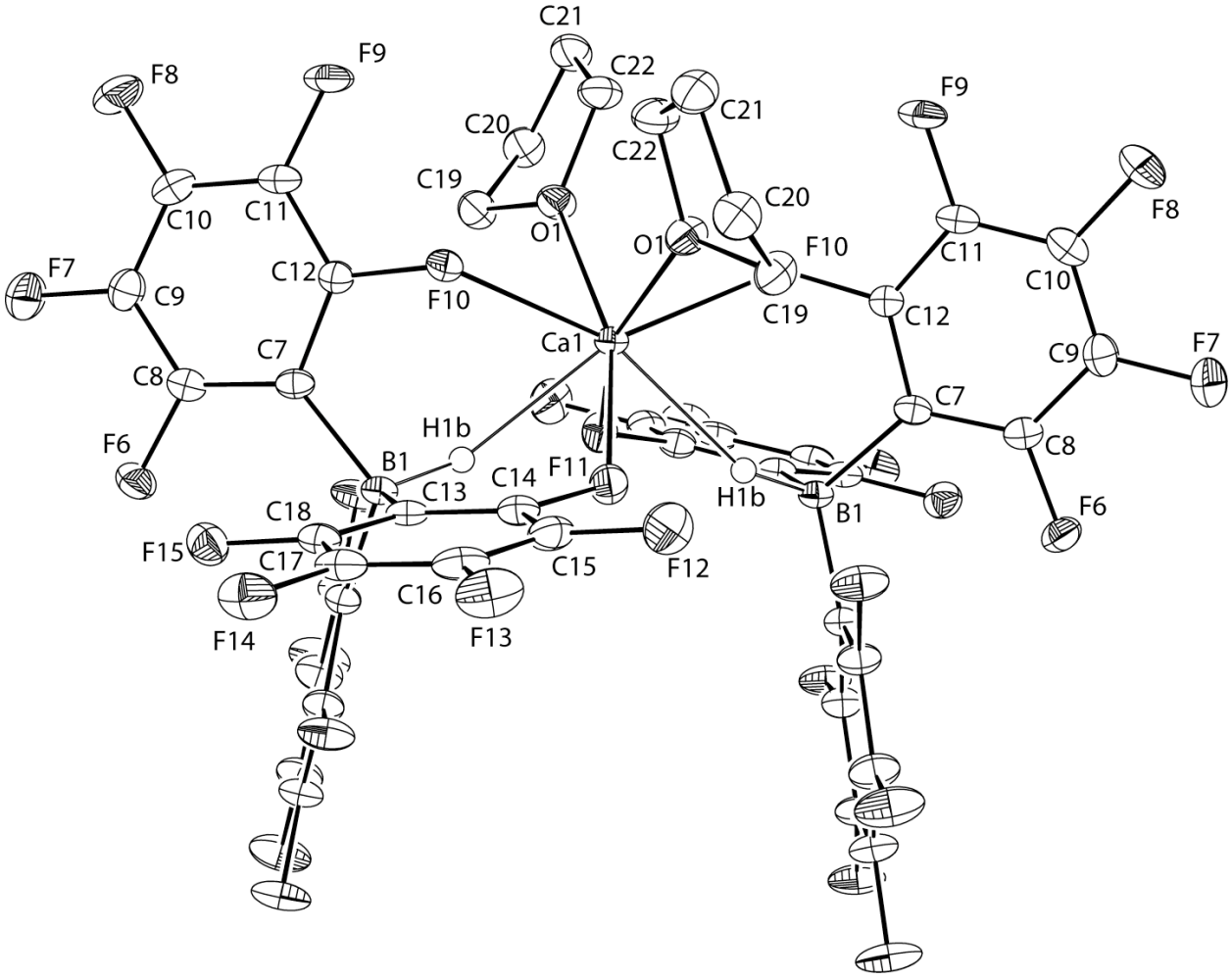
	x	y	z	U(eq)
H(1B)	7350(20)	400(12)	7471(18)	24
H(19A)	9147	1300	6512	45
H(19B)	9714	929	7348	45
H(20A)	11445	1345	7224	79
H(20B)	10811	1798	6520	79
H(21A)	11236	2419	7574	66
H(21B)	11333	1929	8320	66
H(22A)	9530	2273	8556	47
H(22B)	9241	2518	7572	47
H(23A)	5049	1047	5787	60
H(23B)	6238	647	5998	60
H(24A)	7014	946	4852	120
H(24B)	5665	1171	4514	120
H(25A)	6260	2036	4640	115
H(25B)	7625	1810	4922	115
H(26A)	7473	2161	6231	51
H(26B)	6027	2257	6000	51
H(28A)	6955	1870	11245	52
H(28B)	8321	1737	11059	52
H(28C)	7261	1280	10778	52
H(29A)	7520	3004	9287	67
H(29B)	8433	2851	10146	67
H(29C)	7049	3019	10231	67
H(30A)	3987	3083	8755	76
H(30B)	4569	3334	7930	76
H(30C)	5372	3298	8868	76
H(31A)	4365	1710	7120	57
H(31B)	3931	2352	6854	57
H(31C)	3309	2009	7586	57
H(32A)	4792	528	9494	51
H(32B)	4108	656	10332	51
H(32C)	5547	755	10382	51
H(33A)	4800	1923	11089	64
H(33B)	3386	1783	10824	64
H(33C)	3965	2356	10466	64
H(1S)	8150(20)	1790(12)	9258(18)	29
H(2S)	6340(30)	2416(12)	7753(19)	31
H(3S)	3400(30)	1543(13)	9038(19)	31

X-ray crystallographic data for $Ca(HB(C_6F_5)_3)_2THF_2$ (**3a**).

ORTEP diagram of asymmetric unit of 3a, with non-bridging hydrogen and benzene solvent not shown form clarity.



ORTEP diagram of full molecule of 3a, excluding hydrogen on THF and a benzene solvent molecule.



Data Collection for $Ca(HB(C_6F_5)_3)_2THF_2$ (3a).

A colorless block was selected under ambient conditions. The crystal was mounted and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed at 123K on a Bruker APEX2 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the detector to crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3º in a 10º range about ω with the exposure time of 10 seconds per frame. The obtained reflections were successfully indexed by an automated indexing routine

built in the SMART program. The final cell constants were calculated from a set of strong reflections from the actual data collection. The data were collected using the full sphere routine by collecting four sets of frames with 0.3º scans in ω with an exposure time 10 sec per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was based on a fit of a spherical harmonic function to the empirical transmission surface as sampled by multiple equivalent measurements using SADABS software.[5,6]

Structure Solution and Refinement of $Ca(HB(C_6F_5)_3)_2THF_2$ (3a).

The systematic absences in the diffraction data were consistent for the space groups C*2*/c[6] yielded chemically reasonable and computationally stable results of refinement. The position of almost all non-hydrogen atoms were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The H-atom belonged to boron was found objectively on a difference Fourier map.

One half of a cluster and disordered by symmetry benzene solvent were found in an asymmetric unit of C-centered monoclinic cell. The solvent molecule geometry and displacement parameters were constrained during refinement.

Table S25. Crystal data and structure refinement for $Ca(HB(C_6F_5)_3)_2THF_2$ (**3a**).

Empirical formula	$C_{50}H_{24}B_2CaF_{30}O_2$	
Formula weight	1288.39	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 15.9249(9) Å	α= 90°.
	b = 15.7207(9) Å	β= 107.8530(10)°.
	c = 20.7711(12) Å	γ = 90°.
Volume	4949.7(5) $Å^3$	
Z	4	
Density (calculated)	1.729 Mg/m^3	
Absorption coefficient	0.283 mm^{-1}	
F(000)	2560	
Theta range for data collection	1.87 to 28.33°.	
Index ranges	-21≤h≤21, -20≤k≤20, -27≤l≤27	
Reflections collected	24707	
Independent reflections	6149 [R(int) = 0.0265]	
Completeness to theta = 28.33°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	6149 / 48 / 403
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.1177
R indices (all data)	R1 = 0.0556, wR2 = 0.1293
Largest diff. peak and hole	1.306 and -0.613 e.Å^{-3}

Table S26. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2\times 10^3$) for $Ca(HB(C_6F_5)_3)_2THF_2$ (**3a**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ca(1)	0	10475(1)	2500	15(1)
B(1)	1837(1)	9288(1)	3066(1)	16(1)
F(1)	2464(1)	7593(1)	2636(1)	26(1)
F(2)	2471(1)	6127(1)	3238(1)	32(1)
F(3)	1895(1)	5994(1)	4342(1)	37(1)
F(4)	1323(1)	7417(1)	4833(1)	37(1)
F(5)	1353(1)	8931(1)	4252(1)	28(1)
F(6)	3463(1)	9166(1)	4331(1)	25(1)
F(7)	4203(1)	10489(1)	5102(1)	33(1)
F(8)	3585(1)	12096(1)	4763(1)	37(1)
F(9)	2211(1)	12354(1)	3619(1)	29(1)
F(10)	1482(1)	11042(1)	2820(1)	20(1)
F(11)	487(1)	9565(1)	1734(1)	23(1)
F(12)	771(1)	9553(1)	536(1)	32(1)
F(13)	2413(1)	9255(1)	441(1)	33(1)
F(14)	3794(1)	9036(1)	1587(1)	31(1)
F(15)	3532(1)	9066(1)	2804(1)	25(1)
C(1)	1923(1)	8354(1)	3420(1)	17(1)
C(2)	2190(1)	7605(1)	3190(1)	19(1)
C(3)	2190(1)	6819(1)	3492(1)	22(1)
C(4)	1902(1)	6749(1)	4048(1)	26(1)
C(5)	1621(2)	7474(1)	4298(1)	26(1)
C(6)	1644(1)	8246(1)	3986(1)	21(1)
C(7)	2417(1)	10036(1)	3551(1)	17(1)
C(8)	3129(1)	9942(1)	4132(1)	19(1)
C(9)	3529(1)	10617(1)	4540(1)	23(1)
C(10)	3218(1)	11433(1)	4368(1)	24(1)
C(11)	2531(1)	11568(1)	3789(1)	21(1)
C(12)	2166(1)	10874(1)	3399(1)	18(1)
C(13)	2003(1)	9307(1)	2330(1)	17(1)
C(14)	1342(1)	9428(1)	1730(1)	19(1)
C(15)	1456(1)	9425(1)	1096(1)	22(1)
C(16)	2287(2)	9287(1)	1051(1)	24(1)
C(17)	2983(1)	9178(1)	1632(1)	22(1)
C(18)	2835(1)	9196(1)	2252(1)	19(1)
C(19)	-396(1)	11257(1)	915(1)	25(1)
C(20)	241(1)	11725(1)	635(1)	27(1)
C(21)	405(2)	12549(1)	1051(1)	28(1)
C(22)	270(2)	12297(1)	1722(1)	26(1)
C(23)	5123(3)	680(2)	2369(3)	52(2)
C(24)	4902(3)	1217(3)	2824(2)	61(2)
C(25)	4921(4)	2094(3)	2742(3)	94(3)
C(26)	5160(4)	2434(2)	2206(4)	100(3)
C(27)	5381(3)	1896(3)	1751(3)	91(2)
C(28)	5363(3)	1020(2)	1833(2)	58(2)
O(1)	-55(1)	11420(1)	1641(1)	23(1)

Table S27. Bond lengths [Å] for $Ca(HB(C_6F_5)_3)_2THF_2$ (**3a**)

Ca					
(1)-O(1)#1	2.304(1)	F(13)-C(16)	1.344(2)	C(19)-H(19A)	0.9900
Ca(1)-O(1)	2.304(1)	F(14)-C(17)	1.342(2)	C(19)-H(19B)	0.9900
Ca(1)-F(10)	2.418(1)	F(15)-C(18)	1.344(2)	C(20)-C(21)	1.534(3)
Ca(1)-F(10)#1	2.418(1)	C(1)-C(2)	1.386(2)	C(20)-H(20A)	0.9900
Ca(1)-F(11)	2.435(1)	C(1)-C(6)	1.387(3)	C(20)-H(20B)	0.9900
Ca(1)-F(11)#1	2.435(1)	C(2)-C(3)	1.385(3)	C(21)-C(22)	1.526(3)
Ca(1)-H(1B)	2.32(2)	C(3)-C(4)	1.371(3)	C(21)-H(21A)	0.9900
B(1)-C(1)	1.628(3)	C(4)-C(5)	1.383(3)	C(21)-H(21B)	0.9900
B(1)-C(13)	1.631(3)	C(5)-C(6)	1.382(3)	C(22)-O(1)	1.464(2)
B(1)-C(7)	1.638(3)	C(7)-C(12)	1.384(2)	C(22)-H(22A)	0.9900
B(1)-H(1B)	1.16(2)	C(7)-C(8)	1.388(3)	C(22)-H(22B)	0.9900
F(1)-C(2)	1.353(2)	C(8)-C(9)	1.386(3)	C(23)-C(24)	1.3900
F(2)-C(3)	1.344(2)	C(9)-C(10)	1.381(3)	C(23)-C(28)	1.3900
F(3)-C(4)	1.337(2)	C(10)-C(11)	1.373(3)	C(23)-H(23A)	0.9500
F(4)-C(5)	1.340(2)	C(11)-C(12)	1.377(3)	C(24)-C(25)	1.3900
F(5)-C(6)	1.356(2)	C(13)-C(14)	1.376(3)	C(24)-H(24A)	0.9500
F(6)-C(8)	1.343(2)	C(13)-C(18)	1.394(3)	C(25)-C(26)	1.3900
F(7)-C(9)	1.336(2)	C(14)-C(15)	1.383(3)	C(25)-H(25A)	0.9500
F(8)-C(10)	1.343(2)	C(15)-C(16)	1.373(3)	C(26)-C(27)	1.3900
F(9)-C(11)	1.341(2)	C(16)-C(17)	1.375(3)	C(26)-H(26A)	0.9500
F(10)-C(12)	1.378(2)	C(17)-C(18)	1.381(3)	C(27)-C(28)	1.3900
F(11)-C(14)	1.382(2)	C(19)-O(1)	1.460(2)	C(27)-H(27A)	0.9500
F(12)-C(15)	1.343(2)	C(19)-C(20)	1.506(3)	C(28)-H(28A)	0.9500

Table S28. Bond angles [°] for $Ca(HB(C_6F_5)_3)_2THF_2$ (**3a**).

O(1)#1-Ca(1)-O(1)	99.65(7)	C(2)-C(1)-B(1)	127.1(2)	F(9)-C(11)-C(12)	121.2(2)
O(1)#1-Ca(1)-F(10)	75.35(5)	C(6)-C(1)-B(1)	119.2(2)	C(10)-C(11)-C(12)	118.2(2)
O(1)-Ca(1)-F(10)	77.13(4)	F(1)-C(2)-C(3)	114.6(2)	C(11)-C(12)-F(10)	116.0(2)
O(1)#1-Ca(1)-F(10)#1	77.13(4)	F(1)-C(2)-C(1)	121.3(2)	C(11)-C(12)-C(7)	125.5(2)
O(1)-Ca(1)-F(10)#1	75.35(5)	C(3)-C(2)-C(1)	124.1(2)	F(10)-C(12)-C(7)	118.5(2)
F(10)-Ca(1)-F(10)#1	136.73(5)	F(2)-C(3)-C(4)	120.1(2)	C(14)-C(13)-C(18)	113.8(2)
O(1)#1-Ca(1)-F(11)	160.18(4)	F(2)-C(3)-C(2)	120.0(2)	C(14)-C(13)-B(1)	123.6(2)
O(1)-Ca(1)-F(11)	79.44(5)	C(4)-C(3)-C(2)	119.9(2)	C(18)-C(13)-B(1)	122.6(2)
F(10)-Ca(1)-F(11)	85.23(4)	F(3)-C(4)-C(3)	120.6(2)	C(13)-C(14)-F(11)	119.9(2)
F(10)#1-Ca(1)-F(11)	121.07(4)	F(3)-C(4)-C(5)	120.7(2)	C(13)-C(14)-C(15)	125.1(2)
O(1)#1-Ca(1)-F(11)#1	79.44(5)	C(3)-C(4)-C(5)	118.7(2)	F(11)-C(14)-C(15)	115.1(2)
O(1)-Ca(1)-F(11)#1	160.18(4)	F(4)-C(5)-C(6)	121.0(2)	F(12)-C(15)-C(16)	120.6(2)
F(10)-Ca(1)-F(11)#1	121.07(4)	F(4)-C(5)-C(4)	119.7(2)	F(12)-C(15)-C(14)	121.0 (2)
F(10)#1-Ca(1)-F(11)#1	85.23(4)	C(6)-C(5)-C(4)	119.4(2)	C(16)-C(15)-C(14)	118.4(2)
F(11)-Ca(1)-F(11)#1	108.09(6)	F(5)-C(6)-C(5)	116.4(2)	F(13)-C(16)-C(15)	119.7(2)
O(1)#1-Ca(1)-H(1B)	104.7(5)	F(5)-C(6)-C(1)	119.1(2)	F(13)-C(16)-C(17)	120.6(2)
O(1)-Ca(1)-H(1B)	126.6(5)	C(5)-C(6)-C(1)	124.5(2)	C(15)-C(16)-C(17)	119.7(2)
F(10)-Ca(1)-H(1B)	64.7(5)	C(12)-C(7)-C(8)	113.7(2)	F(14)-C(17)-C(16)	119.6(2)
F(10)#1-Ca(1)-H(1B)	156.1(5)	C(12)-C(7)-B(1)	118.3(2)	F(14)-C(17)-C(18)	120.7(2)
F(11)-Ca(1)-H(1B)	62.3(5)	C(8)-C(7)-B(1)	127.9(2)	C(16)-C(17)-C(18)	119.6(2)
F(11)#1-Ca(1)-H(1B)	72.0(5)	F(6)-C(8)-C(9)	116.3(2)	F(15)-C(18)-C(17)	117.4(2)
C(1)-B(1)-C(13)	115.2(1)	F(6)-C(8)-C(7)	120.4(2)	F(15)-C(18)-C(13)	119.1(2)
C(1)-B(1)-C(7)	114.6(2)	C(9)-C(8)-C(7)	123.3(2)	C(17)-C(18)-C(13)	123.4(2)
C(13)-B(1)-C(7)	109.9(1)	F(7)-C(9)-C(10)	119.6(2)	O(1)-C(19)-C(20)	103.4(2)
C(1)-B(1)-H(1B)	106(1)	F(7)-C(9)-C(8)	120.9(2)	O(1)-C(19)-H(19A)	111.1
C(13)-B(1)-H(1B)	106(1)	C(10)-C(9)-C(8)	119.5(2)	C(20)-C(19)-H(19A)	111.1
C(7)-B(1)-H(1B)	104(1)	F(8)-C(10)-C(11)	119.7(2)	O(1)-C(19)-H(19B)	111.1
C(12)-F(10)-Ca(1)	127.8(1)	F(8)-C(10)-C(9)	120.6(2)	C(20)-C(19)-H(19B)	111.1
C(14)-F(11)-Ca(1)	127.4(1)	C(11)-C(10)-C(9)	119.8(2)	H(19A)-C(19)-H(19B)	109.1
C(2)-C(1)-C(6)	113.5(2)	F(9)-C(11)-C(10)	120.6(2)	C(19)-C(20)-C(21)	102.4(2)

C(19)-C(20)-H(20A)	111.3	C(21)-C(22)-H(22A)	110.4	C(25)-C(26)-C(27)	120.0
C(21)-C(20)-H(20A)	111.3	O(1)-C(22)-H(22B)	110.4	C(25)-C(26)-H(26A)	120.0
C(19)-C(20)-H(20B)	111.3	C(21)-C(22)-H(22B)	110.4	C(27)-C(26)-H(26A)	120.0
C(21)-C(20)-H(20B)	111.3	H(22A)-C(22)-H(22B)	108.6	C(28)-C(27)-C(26)	120.0
H(20A)-C(20)-H(20B)	109.2	C(24)-C(23)-C(28)	120.0	C(28)-C(27)-H(27A)	120.0
C(22)-C(21)-C(20)	104.3(2)	C(24)-C(23)-H(23A)	120.0	C(26)-C(27)-H(27A)	120.0
C(22)-C(21)-H(21A)	110.9	C(28)-C(23)-H(23A)	120.0	C(27)-C(28)-C(23)	120.0
C(20)-C(21)-H(21A)	110.9	C(25)-C(24)-C(23)	120.0	C(27)-C(28)-H(28A)	120.0
C(22)-C(21)-H(21B)	110.9	C(25)-C(24)-H(24A)	120.0	C(23)-C(28)-H(28A)	120.0
C(20)-C(21)-H(21B)	110.9	C(23)-C(24)-H(24A)	120.0	C(19)-O(1)-C(22)	106.9(1)
H(21A)-C(21)-H(21B)	108.9	C(26)-C(25)-C(24)	120.0	C(19)-O(1)-Ca(1)	126.9(1)
O(1)-C(22)-C(21)	106.5(2)	C(26)-C(25)-H(25A)	120.0	C(22)-O(1)-Ca(1)	126.2(1)
O(1)-C(22)-H(22A)	110.4	C(24)-C(25)-H(25A)	120.0		

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Table S29. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Ca(HB(C_6F_5)_3)_2THF_2$ (**3a**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

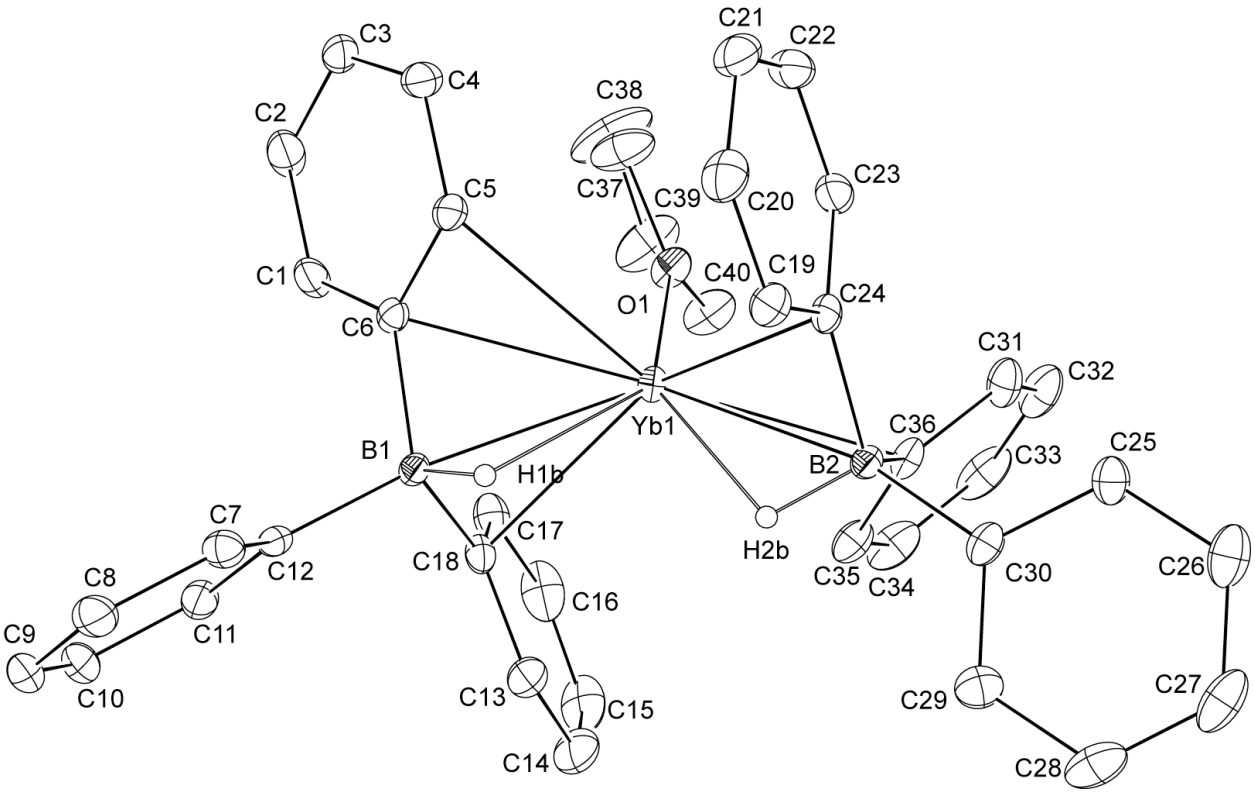
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca(1)	18(1)	12(1)	14(1)	0	6(1)	0
B(1)	20(1)	12(1)	17(1)	0(1)	8(1)	0(1)
F(1)	43(1)	15(1)	28(1)	1(1)	24(1)	4(1)
F(2)	51(1)	13(1)	41(1)	2(1)	26(1)	7(1)
F(3)	61(1)	17(1)	44(1)	14(1)	31(1)	8(1)
F(4)	62(1)	27(1)	37(1)	11(1)	36(1)	9(1)
F(5)	45(1)	18(1)	30(1)	1(1)	24(1)	7(1)
F(6)	28(1)	20(1)	25(1)	4(1)	4(1)	6(1)
F(7)	32(1)	36(1)	24(1)	-3(1)	-3(1)	-2(1)
F(8)	43(1)	26(1)	36(1)	-12(1)	3(1)	-9(1)
F(9)	38(1)	11(1)	37(1)	-2(1)	11(1)	0(1)
F(10)	21(1)	14(1)	24(1)	3(1)	4(1)	0(1)
F(11)	22(1)	26(1)	20(1)	-5(1)	6(1)	3(1)
F(12)	41(1)	37(1)	16(1)	-4(1)	6(1)	3(1)
F(13)	52(1)	31(1)	25(1)	-6(1)	25(1)	-5(1)
F(14)	32(1)	28(1)	42(1)	-4(1)	25(1)	-1(1)
F(15)	22(1)	24(1)	29(1)	2(1)	9(1)	2(1)
C(1)	19(1)	13(1)	19(1)	1(1)	7(1)	1(1)
C(2)	25(1)	16(1)	20(1)	1(1)	11(1)	1(1)
C(3)	30(1)	12(1)	28(1)	1(1)	12(1)	4(1)
C(4)	35(1)	15(1)	30(1)	8(1)	14(1)	3(1)
C(5)	36(1)	21(1)	26(1)	6(1)	18(1)	3(1)
C(6)	28(1)	14(1)	23(1)	0(1)	12(1)	3(1)
C(7)	21(1)	14(1)	18(1)	-1(1)	10(1)	-1(1)
C(8)	23(1)	16(1)	20(1)	1(1)	9(1)	2(1)
C(9)	22(1)	28(1)	18(1)	-2(1)	4(1)	-2(1)
C(10)	28(1)	20(1)	25(1)	-6(1)	9(1)	-6(1)
C(11)	27(1)	12(1)	27(1)	-1(1)	12(1)	-1(1)
C(12)	19(1)	15(1)	19(1)	1(1)	6(1)	0(1)
C(13)	24(1)	9(1)	20(1)	-1(1)	10(1)	-1(1)
C(14)	24(1)	14(1)	21(1)	-4(1)	10(1)	0(1)
C(15)	32(1)	16(1)	18(1)	-4(1)	7(1)	-1(1)
C(16)	40(1)	14(1)	23(1)	-4(1)	19(1)	-3(1)
C(17)	29(1)	13(1)	32(1)	-3(1)	19(1)	-2(1)
C(18)	24(1)	12(1)	24(1)	1(1)	10(1)	0(1)
C(19)	30(1)	26(1)	17(1)	2(1)	5(1)	-5(1)
C(20)	30(1)	29(1)	23(1)	4(1)	11(1)	-2(1)

C(21)	34(1)	24(1)	24(1)	6(1)	7(1)	-6(1)
C(22)	36(1)	18(1)	25(1)	2(1)	9(1)	-2(1)
C(23)	35(3)	32(2)	83(5)	-4(3)	8(3)	11(2)
C(24)	20(2)	73(4)	86(4)	-19(3)	8(2)	1(3)
C(25)	40(3)	50(4)	150(6)	-59(3)	-34(4)	21(3)
C(26)	41(4)	31(3)	178(7)	-13(3)	-37(4)	6(3)
C(27)	31(3)	71(4)	147(6)	20(4)	-9(3)	10(3)
C(28)	16(2)	39(3)	112(5)	16(3)	12(3)	19(2)
O(1)	30(1)	20(1)	16(1)	3(1)	6(1)	-5(1)

Table S30. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $Ca(HB(C_6F_5)_3)_2THF_2$ (**3a**).

	x	y	z	U(eq)
H(1B)	1111(14)	9503(13)	2973(11)	14(5)
H(19A)	-1002	11482	723	30
H(19B)	-398	10640	817	30
H(20A)	-23	11844	147	32
H(20B)	794	11399	706	32
H(21A)	1012	12760	1121	33
H(21B)	-19	12996	822	33
H(22A)	834	12333	2093	31
H(22B)	-164	12678	1828	31
H(23A)	5111	81	2425	63
H(24A)	4739	985	3191	74
H(25A)	4770	2461	3053	113
H(26A)	5173	3033	2150	119
H(27A)	5545	2129	1385	109
H(28A)	5514	653	1522	69

X-ray crystallographic data for $Yb(HBPh_3)_2THF$ (**5**).



Data Collection for $Yb(HBPh_3)_2THF$ (5).

A specimen of $C_{47}H_{48}B_2OYb$, approximate dimensions 0.14 mm x 0.23 mm x 0.31 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured using BRUKER APEX2 CCD diffractometer.

The integration of the data using an orthorhombic unit cell yielded a total of 40159 reflections to a maximum θ angle of 28.37° (0.75 Å resolution), of which 9665 were independent (average redundancy 4.155, completeness = 99.7%, R_{int} = 3.91%, R_{sig} = 3.81%) and 9010 (93.22%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.2093(8) Å, b = 15.3491(11) Å, c = 24.679(2) Å, volume = 3867.2(5) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5168 and 0.7252.

Structure solution for $Yb(HBPh_3)_2THF$ (5).

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{47}H_{48}B_2OYb$. The final anisotropic full-matrix least-squares refinement on F^2 with 467 variables converged at R1 = 2.40%, for the observed data and wR2 = 5.59% for all data. The goodness-of-fit was 1.006. The largest peak in the final difference electron density synthesis was 0.846 $e^-/Å^3$ and the largest hole was -0.476 $e^-/Å^3$ with an RMS deviation of 0.068 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.414 g/cm^3 and F(000), 1672 e^-. H-atoms belonged to B atoms were found objectively on a different Fourier map.

Table S31. Crystal data and structure refinement for $Yb(HBPh_3)_2THF$ (**5**).

Empirical formula	$C_{47}H_{48}B_2OYb$	
Formula weight	823.51	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.2093(8) Å	α= 90°.
	b = 15.3491(12) Å	β= 90°.
	c = 24.6786(19) Å	γ = 90°.
Volume	3867.2(5) $Å^3$	
Z	4	
Density (calculated)	1.414 Mg/m^3	
Absorption coefficient	2.453 mm^{-1}	
F(000)	1672	
Crystal size	0.31 × 0.23 × 0.14 mm^3	
Theta range for data collection	1.56 to 28.37°.	
Index ranges	-13≤h≤13, -20≤k≤20, -32≤l≤32	
Reflections collected	40159	
Independent reflections	9665 [R(int) = 0.0391]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7252 and 0.5168	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9665 / 0 / 467	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0240, wR2 = 0.0544	
R indices (all data)	R1 = 0.0279, wR2 = 0.0559	
Absolute structure parameter	0.042(7)	
Largest diff. peak and hole	0.846 and -0.476 e.$Å^{-3}$	

Table S32. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$× 10^3) for $Yb(HBPh_3)_2THF$ (**5**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	5278(4)	582(2)	49(1)	23(1)
B(2)	2725(3)	-620(2)	1413(1)	24(1)
C(1)	6620(4)	2047(2)	237(1)	37(1)
C(2)	6732(5)	2905(3)	395(1)	54(1)
C(3)	5667(4)	3329(2)	628(1)	46(1)
C(4)	4525(4)	2892(2)	696(1)	39(1)
C(5)	4415(3)	2017(2)	532(1)	29(1)
C(6)	5459(3)	1570(2)	293(1)	25(1)
C(7)	4465(3)	683(2)	-968(1)	31(1)
C(8)	4662(4)	657(2)	-1530(1)	40(1)
C(9)	5889(4)	501(2)	-1733(1)	42(1)
C(10)	6918(4)	371(3)	-1386(1)	40(1)
C(11)	6717(3)	400(2)	-832(1)	33(1)
C(12)	5485(3)	559(2)	-606(1)	25(1)
C(13)	5922(4)	-1047(2)	220(1)	41(1)
C(14)	6688(5)	-1724(3)	413(2)	59(1)
C(15)	7761(5)	-1547(3)	732(2)	65(1)
C(16)	8088(4)	-701(3)	851(2)	60(1)
C(17)	7337(3)	-19(3)	643(1)	41(1)
C(18)	6229(3)	-165(2)	322(1)	29(1)
C(19)	1295(3)	616(2)	987(1)	34(1)
C(20)	796(4)	1450(2)	932(2)	43(1)

C(21)	1162(4)	2093(2)	1294(2)	48(1)
C(22)	2013(4)	1891(2)	1700(2)	44(1)
C(23)	2506(3)	1048(2)	1758(1)	34(1)
C(24)	2166(3)	381(2)	1403(1)	26(1)
C(25)	674(3)	-1306(2)	1888(1)	33(1)
C(26)	-158(4)	-1992(3)	2007(1)	46(1)
C(27)	-76(3)	-2757(3)	1722(2)	50(1)
C(28)	824(4)	-2830(3)	1317(2)	51(1)
C(29)	1671(3)	-2143(2)	1193(1)	39(1)
C(30)	1629(3)	-1363(2)	1486(1)	29(1)
C(31)	3686(4)	-645(2)	2419(1)	40(1)
C(32)	4596(5)	-881(2)	2807(2)	53(1)
C(33)	5744(5)	-1295(3)	2650(2)	60(1)
C(34)	5969(4)	-1463(2)	2117(2)	53(1)
C(35)	5052(3)	-1221(2)	1727(2)	38(1)
C(36)	3872(3)	-804(2)	1869(1)	29(1)
C(37)	6343(5)	1950(3)	1808(2)	65(1)
C(38)	7602(6)	2106(3)	2066(3)	106(2)
C(39)	8236(5)	1262(3)	2133(2)	81(2)
C(40)	7197(5)	611(3)	2046(2)	56(1)
C(41)	1532(7)	8840(4)	8724(3)	89(2)
C(42)	2227(7)	9020(3)	9147(3)	86(2)
C(43)	1747(5)	9109(3)	9672(2)	68(1)
C(44)	455(6)	9023(3)	9754(2)	84(2)
C(45)	-366(6)	8845(3)	9283(3)	92(2)
C(46)	190(10)	8742(3)	8789(3)	111(3)
C(47)	-398(13)	8586(4)	8263(3)	227(8)
O(1)	6170(2)	1039(1)	1738(1)	38(1)
Yb(1)	4713(1)	397(1)	1101(1)	24(1)

Table S33. Bond lengths [Å] for $Yb(HBPh_3)_2THF$ (**5**).

B(1)-C(12)	1.630(4)	C(9)-C(10)	1.371(5)	C(23)-C(24)	1.391(4)
B(1)-C(6)	1.642(4)	C(9)-H(9)	0.9500	C(23)-H(23)	0.9500
B(1)-C(18)	1.647(4)	C(10)-C(11)	1.383(4)	C(25)-C(26)	1.385(5)
B(1)-Yb(1)	2.675(3)	C(10)-H(10)	0.9500	C(25)-C(30)	1.392(4)
B(1)-H(1B)	1.16(3)	C(11)-C(12)	1.397(4)	C(25)-H(25)	0.9500
B(2)-C(30)	1.608(4)	C(11)-H(11)	0.9500	C(26)-C(27)	1.370(6)
B(2)-C(24)	1.640(4)	C(13)-C(14)	1.385(5)	C(26)-H(26)	0.9500
B(2)-C(36)	1.648(4)	C(13)-C(18)	1.413(5)	C(27)-C(28)	1.364(6)
B(2)-Yb(1)	2.675(3)	C(13)-H(13)	0.9500	C(27)-H(27)	0.9500
B(2)-H(2B)	1.14(3)	C(14)-C(15)	1.375(7)	C(28)-C(29)	1.397(5)
C(1)-C(2)	1.379(5)	C(14)-H(14)	0.9500	C(28)-H(28)	0.9500
C(1)-C(6)	1.399(4)	C(15)-C(16)	1.373(7)	C(29)-C(30)	1.400(5)
C(1)-H(1)	0.9500	C(15)-H(15)	0.9500	C(29)-H(29)	0.9500
C(2)-C(3)	1.391(6)	C(16)-C(17)	1.395(5)	C(31)-C(32)	1.384(5)
C(2)-H(2)	0.9500	C(16)-H(16)	0.9500	C(31)-C(36)	1.392(5)
C(3)-C(4)	1.356(5)	C(17)-C(18)	1.399(5)	C(31)-H(31)	0.9500
C(3)-H(3)	0.9500	C(17)-H(17)	0.9500	C(32)-C(33)	1.388(6)
C(4)-C(5)	1.407(4)	C(19)-C(20)	1.385(5)	C(32)-H(32)	0.9500
C(4)-H(4)	0.9500	C(19)-C(24)	1.405(4)	C(33)-C(34)	1.361(6)
C(5)-C(6)	1.399(4)	C(19)-H(19)	0.9500	C(33)-H(33)	0.9500
C(5)-H(5)	0.9500	C(20)-C(21)	1.381(5)	C(34)-C(35)	1.393(5)
C(7)-C(12)	1.385(4)	C(20)-H(20)	0.9500	C(34)-H(34)	0.9500
C(7)-C(8)	1.402(4)	C(21)-C(22)	1.362(6)	C(35)-C(36)	1.408(5)
C(7)-H(7)	0.9500	C(21)-H(21)	0.9500	C(35)-H(35)	0.9500
C(8)-C(9)	1.370(5)	C(22)-C(23)	1.395(5)	C(37)-O(1)	1.421(4)
C(8)-H(8)	0.9500	C(22)-H(22)	0.9500	C(37)-C(38)	1.454(7)

C(37)-H(37A)	0.9900	C(40)-H(40B)	0.9900	C(45)-C(46)	1.353(9)
C(37)-H(37B)	0.9900	C(41)-C(42)	1.292(8)	C(45)-H(45)	0.9500
C(38)-C(39)	1.457(7)	C(41)-C(46)	1.387(10)	C(46)-C(47)	1.450(9)
C(38)-H(38A)	0.9900	C(41)-H(41)	0.9500	C(47)-H(47A)	0.9800
C(38)-H(38B)	0.9900	C(42)-C(43)	1.392(8)	C(47)-H(47B)	0.9800
C(39)-C(40)	1.473(6)	C(42)-H(42)	0.9500	C(47)-H(47C)	0.9800
C(39)-H(39A)	0.9900	C(43)-C(44)	1.341(8)	O(1)-Yb(1)	2.378(2)
C(39)-H(39B)	0.9900	C(43)-H(43)	0.9500	Yb(1)-H(1B)	2.45(3)
C(40)-O(1)	1.452(4)	C(44)-C(45)	1.460(8)	Yb(1)-H(2B)	2.22(3)
C(40)-H(40A)	0.9900	C(44)-H(44)	0.9500		

Table S34. Bond angles [°] for $Yb(HBPh_3)_2THF$ (**5**).

C(12)-B(1)-C(6)	111.6(2)	C(10)-C(9)-H(9)	120.1	C(26)-C(25)-C(30)	122.2(3)
C(12)-B(1)-C(18)	108.3(2)	C(9)-C(10)-C(11)	120.0(3)	C(26)-C(25)-H(25)	118.9
C(6)-B(1)-C(18)	115.2(2)	C(9)-C(10)-H(10)	120.0	C(30)-C(25)-H(25)	118.9
C(12)-B(1)-Yb(1)	171.1(2)	C(11)-C(10)-H(10)	120.0	C(27)-C(26)-C(25)	120.4(4)
C(6)-B(1)-Yb(1)	76.5(1)	C(10)-C(11)-C(12)	122.2(3)	C(27)-C(26)-H(26)	119.8
C(18)-B(1)-Yb(1)	69.9(1)	C(10)-C(11)-H(11)	118.9	C(25)-C(26)-H(26)	119.8
C(12)-B(1)-H(1B)	107(1)	C(12)-C(11)-H(11)	118.9	C(28)-C(27)-C(26)	119.2(3)
C(6)-B(1)-H(1B)	107(2)	C(7)-C(12)-C(11)	116.3(3)	C(28)-C(27)-H(27)	120.4
C(18)-B(1)-H(1B)	107(2)	C(7)-C(12)-B(1)	122.6(3)	C(26)-C(27)-H(27)	120.4
Yb(1)-B(1)-H(1B)	67(1)	C(11)-C(12)-B(1)	121.0(3)	C(27)-C(28)-C(29)	121.1(4)
C(30)-B(2)-C(24)	115.1(2)	C(14)-C(13)-C(18)	122.1(4)	C(27)-C(28)-H(28)	119.5
C(30)-B(2)-C(36)	107.2(2)	C(14)-C(13)-H(13)	119.0	C(29)-C(28)-H(28)	119.5
C(24)-B(2)-C(36)	114.7(2)	C(18)-C(13)-H(13)	119.0	C(28)-C(29)-C(30)	120.9(3)
C(30)-B(2)-Yb(1)	167.1(2)	C(15)-C(14)-C(13)	120.0(4)	C(28)-C(29)-H(29)	119.6
C(24)-B(2)-Yb(1)	73.3(1)	C(15)-C(14)-H(14)	120.0	C(30)-C(29)-H(29)	119.6
C(36)-B(2)-Yb(1)	75.9(2)	C(13)-C(14)-H(14)	120.0	C(25)-C(30)-C(29)	116.3(3)
C(30)-B(2)-H(2B)	113(2)	C(14)-C(15)-C(16)	120.2(4)	C(25)-C(30)-B(2)	121.5(3)
C(24)-B(2)-H(2B)	102(2)	C(14)-C(15)-H(15)	119.9	C(29)-C(30)-B(2)	121.8(3)
C(36)-B(2)-H(2B)	104(2)	C(16)-C(15)-H(15)	119.9	C(32)-C(31)-C(36)	122.5(4)
Yb(1)-B(2)-H(2B)	55(2)	C(15)-C(16)-C(17)	119.8(4)	C(32)-C(31)-H(31)	118.8
C(2)-C(1)-C(6)	122.8(4)	C(15)-C(16)-H(16)	120.1	C(36)-C(31)-H(31)	118.8
C(2)-C(1)-H(1)	118.6	C(17)-C(16)-H(16)	120.1	C(31)-C(32)-C(33)	119.6(4)
C(6)-C(1)-H(1)	118.6	C(16)-C(17)-C(18)	122.1(4)	C(31)-C(32)-H(32)	120.2
C(1)-C(2)-C(3)	120.0(4)	C(16)-C(17)-H(17)	118.9	C(33)-C(32)-H(32)	120.2
C(1)-C(2)-H(2)	120.0	C(18)-C(17)-H(17)	118.9	C(34)-C(33)-C(32)	119.9(4)
C(3)-C(2)-H(2)	120.0	C(17)-C(18)-C(13)	115.8(3)	C(34)-C(33)-H(33)	120.0
C(4)-C(3)-C(2)	119.4(3)	C(17)-C(18)-B(1)	126.7(3)	C(32)-C(33)-H(33)	120.0
C(4)-C(3)-H(3)	120.3	C(13)-C(18)-B(1)	117.5(3)	C(33)-C(34)-C(35)	120.3(4)
C(2)-C(3)-H(3)	120.3	C(20)-C(19)-C(24)	122.8(3)	C(33)-C(34)-H(34)	119.8
C(3)-C(4)-C(5)	120.4(3)	C(20)-C(19)-H(19)	118.6	C(35)-C(34)-H(34)	119.8
C(3)-C(4)-H(4)	119.8	C(24)-C(19)-H(19)	118.6	C(34)-C(35)-C(36)	121.6(4)
C(5)-C(4)-H(4)	119.8	C(19)-C(20)-C(21)	119.8(3)	C(34)-C(35)-H(35)	119.2
C(6)-C(5)-C(4)	121.9(3)	C(19)-C(20)-H(20)	120.1	C(36)-C(35)-H(35)	119.2
C(6)-C(5)-H(5)	119.1	C(21)-C(20)-H(20)	120.1	C(31)-C(36)-C(35)	116.1(3)
C(4)-C(5)-H(5)	119.1	C(22)-C(21)-C(20)	119.0(3)	C(31)-C(36)-B(2)	122.5(3)
C(5)-C(6)-C(1)	115.5(3)	C(22)-C(21)-H(21)	120.5	C(35)-C(36)-B(2)	121.1(3)
C(5)-C(6)-B(1)	121.5(3)	C(20)-C(21)-H(21)	120.5	O(1)-C(37)-C(38)	108.9(4)
C(1)-C(6)-B(1)	122.9(3)	C(21)-C(22)-C(23)	121.1(3)	O(1)-C(37)-H(37A)	109.9
C(12)-C(7)-C(8)	121.8(3)	C(21)-C(22)-H(22)	119.5	C(38)-C(37)-H(37A)	109.9
C(12)-C(7)-H(7)	119.1	C(23)-C(22)-H(22)	119.5	O(1)-C(37)-H(37B)	109.9
C(8)-C(7)-H(7)	119.1	C(24)-C(23)-C(22)	121.9(3)	C(38)-C(37)-H(37B)	109.9
C(9)-C(8)-C(7)	119.9(3)	C(24)-C(23)-H(23)	119.0	H(37A)-C(37)-H(37B)	108.3
C(9)-C(8)-H(8)	120.1	C(22)-C(23)-H(23)	119.0	C(37)-C(38)-C(39)	107.3(4)
C(7)-C(8)-H(8)	120.1	C(23)-C(24)-C(19)	115.3(3)	C(37)-C(38)-H(38A)	110.3
C(8)-C(9)-C(10)	119.8(3)	C(23)-C(24)-B(2)	126.5(3)	C(39)-C(38)-H(38A)	110.3
C(8)-C(9)-H(9)	120.1	C(19)-C(24)-B(2)	118.1(3)	C(37)-C(38)-H(38B)	110.3

C(39)-C(38)-H(38B)	110.3	C(41)-C(42)-C(43)	125.5(6)	H(47A)-C(47)-H(47B)	109.5
H(38A)-C(38)-H(38B)	108.5	C(41)-C(42)-H(42)	117.3	C(46)-C(47)-H(47C)	109.5
C(38)-C(39)-C(40)	105.4(4)	C(43)-C(42)-H(42)	117.3	H(47A)-C(47)-H(47C)	109.5
C(38)-C(39)-H(39A)	110.7	C(44)-C(43)-C(42)	118.5(6)	H(47B)-C(47)-H(47C)	109.5
C(40)-C(39)-H(39A)	110.7	C(44)-C(43)-H(43)	120.8	C(37)-O(1)-C(40)	107.0(3)
C(38)-C(39)-H(39B)	110.7	C(42)-C(43)-H(43)	120.8	C(37)-O(1)-Yb(1)	124.5(2)
C(40)-C(39)-H(39B)	110.7	C(43)-C(44)-C(45)	117.6(5)	C(40)-O(1)-Yb(1)	127.6(2)
H(39A)-C(39)-H(39B)	108.8	C(43)-C(44)-H(44)	121.2	O(1)-Yb(1)-B(2)	121.75(9)
O(1)-C(40)-C(39)	106.8(3)	C(45)-C(44)-H(44)	121.2	O(1)-Yb(1)-B(1)	117.58(9)
O(1)-C(40)-H(40A)	110.4	C(46)-C(45)-C(44)	119.9(6)	B(2)-Yb(1)-B(1)	120.3(1)
C(39)-C(40)-H(40A)	110.4	C(46)-C(45)-H(45)	120.1	O(1)-Yb(1)-H(1B)	141.6(8)
O(1)-C(40)-H(40B)	110.4	C(44)-C(45)-H(45)	120.1	B(2)-Yb(1)-H(1B)	96.5(8)
C(39)-C(40)-H(40B)	110.4	C(45)-C(46)-C(41)	120.4(6)	B(1)-Yb(1)-H(1B)	25.6(7)
H(40A)-C(40)-H(40B)	108.6	C(45)-C(46)-C(47)	131(1)	O(1)-Yb(1)-H(2B)	142.4(8)
C(42)-C(41)-C(46)	118.1(7)	C(41)-C(46)-C(47)	108.9(9)	B(2)-Yb(1)-H(2B)	24.8(8)
C(42)-C(41)-H(41)	120.9	C(46)-C(47)-H(47A)	109.5	B(1)-Yb(1)-H(2B)	97.0(8)
C(46)-C(41)-H(41)	120.9	C(46)-C(47)-H(47B)	109.5	H(1B)-Yb(1)-H(2B)	75(1)

Table S35. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Yb(HBPh_3)_2THF$ (**5**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	24(1)	20(2)	24(1)	3(1)	2(1)	0(1)
B(2)	25(2)	21(2)	25(2)	2(1)	0(1)	-1(1)
C(1)	40(2)	41(2)	31(2)	-9(2)	10(2)	-14(2)
C(2)	76(3)	49(2)	37(2)	-12(2)	15(2)	-34(2)
C(3)	80(3)	27(2)	30(2)	-5(1)	10(2)	-16(2)
C(4)	60(3)	28(2)	30(2)	-1(1)	-2(2)	8(2)
C(5)	37(2)	26(1)	24(1)	4(1)	-3(1)	4(1)
C(6)	30(2)	25(1)	21(1)	2(1)	-3(1)	-2(1)
C(7)	32(2)	29(1)	31(2)	-2(1)	-4(1)	1(1)
C(8)	56(2)	35(2)	29(2)	-3(1)	-11(2)	1(2)
C(9)	66(2)	34(2)	24(1)	-1(1)	7(2)	5(2)
C(10)	48(2)	39(2)	34(2)	-1(2)	15(1)	5(2)
C(11)	33(2)	31(2)	35(2)	3(2)	3(1)	1(2)
C(12)	32(2)	18(1)	26(1)	0(1)	-1(1)	-1(1)
C(13)	52(2)	32(2)	40(2)	6(2)	4(2)	7(2)
C(14)	75(3)	34(2)	68(3)	14(2)	16(3)	18(2)
C(15)	60(3)	67(3)	67(3)	33(2)	12(2)	39(2)
C(16)	36(2)	91(4)	52(2)	21(2)	0(2)	20(2)
C(17)	29(2)	56(2)	38(2)	8(2)	5(2)	5(2)
C(18)	28(2)	33(2)	25(1)	7(1)	5(1)	6(1)
C(19)	35(2)	32(2)	34(2)	4(1)	-2(1)	0(1)
C(20)	38(2)	43(2)	50(2)	14(2)	0(2)	8(2)
C(21)	48(2)	30(2)	68(3)	7(2)	17(2)	7(2)
C(22)	48(2)	34(2)	52(2)	-10(2)	13(2)	-4(2)
C(23)	34(2)	36(2)	33(2)	-4(1)	6(1)	-4(1)
C(24)	22(1)	28(1)	29(1)	3(1)	5(1)	-6(1)
C(25)	27(2)	42(2)	31(2)	6(1)	-1(1)	-4(1)
C(26)	30(2)	60(2)	47(2)	18(2)	-7(2)	-11(2)
C(27)	35(2)	47(2)	69(2)	21(2)	-18(2)	-21(2)
C(28)	58(2)	33(2)	63(2)	-2(2)	-24(2)	-9(2)
C(29)	38(2)	36(2)	44(2)	-3(2)	-4(2)	-1(1)
C(30)	25(2)	28(2)	34(2)	9(1)	-5(1)	-1(1)
C(31)	42(2)	47(2)	30(2)	12(1)	-5(1)	-9(2)
C(32)	70(3)	50(2)	39(2)	18(2)	-22(2)	-18(2)
C(33)	68(3)	43(2)	70(3)	25(2)	-43(2)	-12(2)
C(34)	40(2)	39(2)	81(3)	16(2)	-23(2)	0(2)

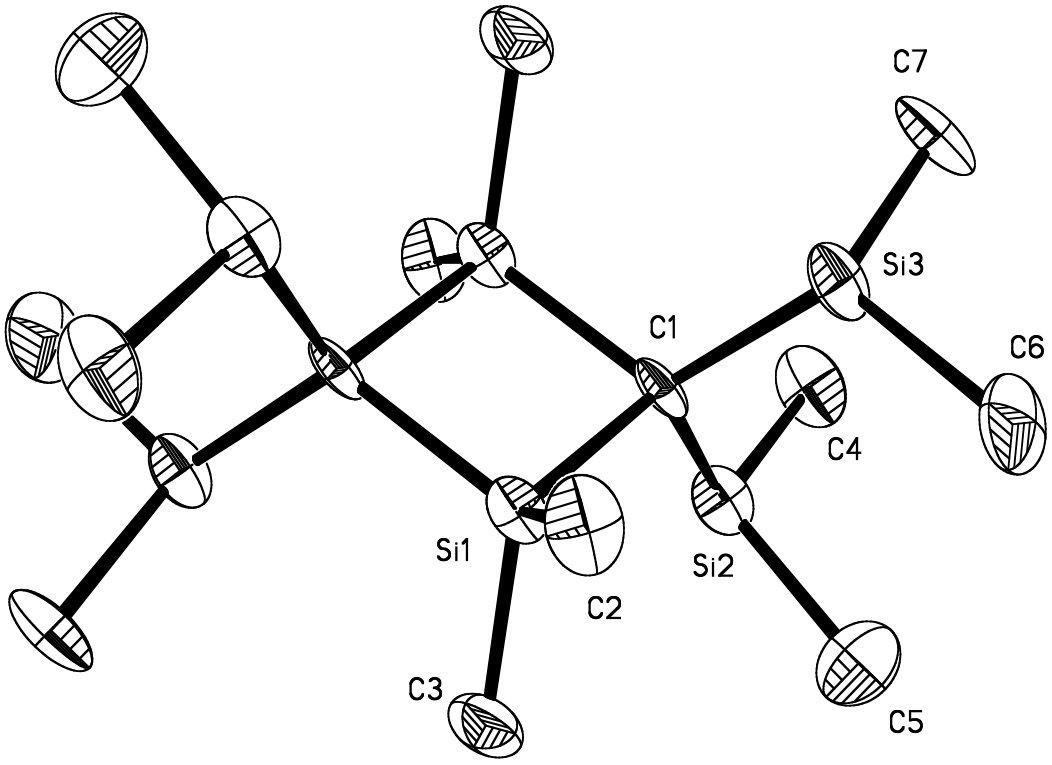
C(35)	34(2)	30(2)	50(2)	11(2)	-8(1)	-2(1)
C(36)	28(2)	28(2)	33(2)	10(1)	-5(1)	-8(1)
C(37)	91(4)	36(2)	69(3)	-7(2)	-45(3)	4(2)
C(38)	98(4)	39(3)	182(7)	5(3)	-71(5)	-18(3)
C(39)	64(3)	58(3)	121(5)	16(3)	-43(3)	-16(3)
C(40)	64(3)	44(2)	61(3)	4(2)	-25(2)	-6(2)
C(41)	90(4)	60(3)	117(5)	22(4)	12(4)	19(3)
C(42)	101(5)	47(3)	110(5)	-12(3)	36(4)	-17(3)
C(43)	68(3)	57(3)	80(3)	-6(2)	-4(3)	-12(2)
C(44)	77(4)	77(3)	99(4)	-32(3)	23(3)	-3(3)
C(45)	49(3)	61(3)	167(6)	-38(4)	-18(4)	21(3)
C(46)	199(9)	38(2)	95(4)	-15(3)	-65(5)	39(4)
C(47)	500(20)	51(3)	130(6)	-16(4)	-138(11)	47(7)
O(1)	44(1)	34(1)	35(1)	4(1)	-12(1)	-6(1)
Yb(1)	23(1)	26(1)	22(1)	4(1)	0(1)	-2(1)

Table S36. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $Yb(HBPh_3)_2THF$ (**5**).

	x	y	z	U(eq)
H(1B)	4200(30)	370(20)	129(11)	28
H(2B)	3260(30)	-666(19)	1007(12)	28
H(1)	7363	1767	84	45
H(2)	7535	3207	345	65
H(3)	5740	3920	739	55
H(4)	3795	3179	855	47
H(5)	3608	1721	587	35
H(7)	3609	788	-832	37
H(8)	3947	748	-1770	48
H(9)	6026	484	-2114	50
H(10)	7769	261	-1525	48
H(11)	7441	309	-597	39
H(13)	5166	-1181	11	50
H(14)	6472	-2309	326	71
H(15)	8277	-2012	870	78
H(16)	8825	-580	1073	71
H(17)	7585	564	723	49
H(19)	1037	184	733	41
H(20)	203	1580	646	52
H(21)	826	2667	1259	58
H(22)	2274	2331	1948	53
H(23)	3090	927	2047	41
H(25)	591	-779	2087	40
H(26)	-790	-1932	2287	55
H(27)	-640	-3231	1807	61
H(28)	876	-3356	1115	62
H(29)	2283	-2206	906	47
H(31)	2904	-363	2531	48
H(32)	4436	-762	3179	64
H(33)	6372	-1461	2915	73
H(34)	6755	-1746	2010	64
H(35)	5226	-1341	1356	46
H(37A)	5630	2188	2035	78
H(37B)	6315	2246	1451	78
H(38A)	7474	2388	2423	127
H(38B)	8148	2492	1838	127
H(39A)	8611	1206	2501	97
H(39B)	8947	1188	1864	97
H(40A)	7544	105	1843	67

H(40B)	6851	403	2398	67
H(41)	1929	8778	8378	106
H(42)	3141	9097	9096	103
H(43)	2322	9228	9966	82
H(44)	87	9077	10106	101
H(45)	-1290	8800	9322	111
H(47A)	-858	8026	8268	341
H(47B)	287	8574	7985	341
H(47C)	-1022	9054	8181	341

X-ray crystallographic data for $(Me_2SiC(SiHMe_2)_2)_2$.



Data Collection for $(Me_2SiC(SiHMe_2)_2)_2$.

A colorless prismatic crystal was selected under ambient conditions. The crystal was mounted and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed at 173K on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the detector to crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3º in a 10º range about ω with the exposure time of 30 seconds per frame. The obtained reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of strong reflections from the actual data collection. The data were collected using the full sphere routine by collecting four sets of frames with 0.3º scans in ω with an exposure time 30 sec per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was

based on a fit of a spherical harmonic function to the empirical transmission surface as sampled by multiple equivalent measurements using SADABS software.[5,6]

Structure Solution and Refinement for $(Me_2SiC(SiHMe_2)_2)_2$.

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ [6] yielded chemically reasonable and computationally stable results of refinement. The position of almost all non-hydrogen atoms were found by direct methods. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in full-matrix anisotropic approximation. Almost all hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The H-atoms belonged to Si atoms were found objectively on a Fourier map and were refined in an isotropic approximation.

Table S37. Crystal data and structure refinement for $(Me_2SiC(SiHMe_2)_2)_2$.

Empirical formula	$C_{14}H_{40}Si_6$	
Formula weight	377.00	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.512(7) Å	α= 104.555(19)°.
	b = 8.569(7) Å	β= 91.47(2)°.
	c = 9.253(9) Å	γ = 114.49(2)°.
Volume	588.0(9) $Å^3$	
Z	1	
Density (calculated)	1.065 Mg/m^3	
Absorption coefficient	0.348 mm^{-1}	
F(000)	208	
Crystal size	0.35 x 0.35 x 0.19 mm^3	
Theta range for data collection	2.30 to 21.00°.	
Index ranges	-8≤h≤8, -8≤k≤8, -9≤l≤9	
Reflections collected	3026	
Independent reflections	1275 [R(int) = 0.3013]	
Completeness to theta = 21.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.78	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1275 / 0 / 105	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0771, wR2 = 0.1992	
R indices (all data)	R1 = 0.1016, wR2 = 0.2429	
Largest diff. peak and hole	0.641 and -0.763 $e.Å^{-3}$	

$R1 = \Sigma \, | \, |F_o| - |F_c| \, | \, / \, \Sigma \, |F_o|$ and $wR2 = \{ \, \Sigma \, [\, w(F_o^2 - F_c^2)^2 \,] \, / \, \Sigma \, [\, w(F_o^2)^2 \,] \, \}^{1/2}$

Table S38. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(Me_2SiC(SiHMe_2)_2)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)

Si(1)	5791(2)	11075(2)	9191(2)	23(1)
Si(2)	4023(2)	6925(2)	7369(2)	29(1)
Si(3)	1668(2)	8944(2)	8257(2)	29(1)
C(1)	3766(7)	8816(7)	8752(7)	22(2)
C(2)	5343(9)	12956(7)	8893(8)	39(2)
C(3)	7587(8)	11071(8)	8090(8)	38(2)
C(4)	2247(8)	4617(7)	7196(8)	43(2)
C(5)	4123(10)	7122(9)	5396(8)	52(2)
C(6)	1417(9)	9344(10)	6392(8)	53(2)
C(7)	-340(7)	6886(9)	8276(9)	47(2)

Table S39. Bond lengths [Å] for $(Me_2SiC(SiHMe_2)_2)_2$.

Si(1)-C(3)	1.859(7)	Si(3)-C(1)	1.886(5)	C(4)-H(4C)	0.9800
Si(1)-C(2)	1.883(5)	Si(3)-H(3S)	1.25(6)	C(5)-H(5A)	0.9800
Si(1)-C(1)#1	1.902(6)	C(1)-Si(1)#1	1.902(6)	C(5)-H(5B)	0.9800
Si(1)-C(1)	1.920(5)	C(2)-H(2A)	0.9800	C(5)-H(5C)	0.9800
Si(1)-Si(1)#1	2.623(3)	C(2)-H(2B)	0.9800	C(6)-H(6A)	0.9800
Si(2)-C(5)	1.876(7)	C(2)-H(2C)	0.9800	C(6)-H(6B)	0.9800
Si(2)-C(1)	1.892(6)	C(3)-H(3A)	0.9800	C(6)-H(6C)	0.9800
Si(2)-C(4)	1.890(6)	C(3)-H(3B)	0.9800	C(7)-H(7A)	0.9800
Si(2)-H(2S)	1.40(6)	C(3)-H(3C)	0.9800	C(7)-H(7B)	0.9800
Si(3)-C(6)	1.865(7)	C(4)-H(4A)	0.9800	C(7)-H(7C)	0.9800
Si(3)-C(7)	1.885(6)	C(4)-H(4B)	0.9800		

Table S40. Bond angles [°] for $(Me_2SiC(SiHMe_2)_2)_2$.

C(3)-Si(1)-C(2)	105.2(3)	Si(3)-C(1)-Si(2)	113.1(3)	H(4A)-C(4)-H(4C)	109.5
C(3)-Si(1)-C(1)#1	114.4(3)	Si(3)-C(1)-Si(1)#1	113.6(3)	H(4B)-C(4)-H(4C)	109.5
C(2)-Si(1)-C(1)#1	114.7(3)	Si(2)-C(1)-Si(1)#1	113.8(2)	Si(2)-C(5)-H(5A)	109.5
C(3)-Si(1)-C(1)	115.1(3)	Si(3)-C(1)-Si(1)	113.5(3)	Si(2)-C(5)-H(5B)	109.5
C(2)-Si(1)-C(1)	114.4(3)	Si(2)-C(1)-Si(1)	113.6(3)	H(5A)-C(5)-H(5B)	109.5
C(1)#1-Si(1)-C(1)	93.3(2)	Si(1)#1-C(1)-Si(1)	86.7(2)	Si(2)-C(5)-H(5C)	109.5
C(3)-Si(1)-Si(1)#1	127.6(2)	Si(1)-C(2)-H(2A)	109.5	H(5A)-C(5)-H(5C)	109.5
C(2)-Si(1)-Si(1)#1	127.2(3)	Si(1)-C(2)-H(2B)	109.5	H(5B)-C(5)-H(5C)	109.5
C(1)#1-Si(1)-Si(1)#1	46.93(17)	H(2A)-C(2)-H(2B)	109.5	Si(3)-C(6)-H(6A)	109.5
C(1)-Si(1)-Si(1)#1	46.37(19)	Si(1)-C(2)-H(2C)	109.5	Si(3)-C(6)-H(6B)	109.5
C(5)-Si(2)-C(1)	114.1(3)	H(2A)-C(2)-H(2C)	109.5	H(6A)-C(6)-H(6B)	109.5
C(5)-Si(2)-C(4)	105.8(3)	H(2B)-C(2)-H(2C)	109.5	Si(3)-C(6)-H(6C)	109.5
C(1)-Si(2)-C(4)	114.7(3)	Si(1)-C(3)-H(3A)	109.5	H(6A)-C(6)-H(6C)	109.5
C(5)-Si(2)-H(2S)	112(3)	Si(1)-C(3)-H(3B)	109.5	H(6B)-C(6)-H(6C)	109.5
C(1)-Si(2)-H(2S)	103(3)	H(3A)-C(3)-H(3B)	109.5	Si(3)-C(7)-H(7A)	109.5
C(4)-Si(2)-H(2S)	108(2)	Si(1)-C(3)-H(3C)	109.5	Si(3)-C(7)-H(7B)	109.5
C(6)-Si(3)-C(7)	107.0(3)	H(3A)-C(3)-H(3C)	109.5	H(7A)-C(7)-H(7B)	109.5
C(6)-Si(3)-C(1)	114.9(3)	H(3B)-C(3)-H(3C)	109.5	Si(3)-C(7)-H(7C)	109.5
C(7)-Si(3)-C(1)	113.2(3)	Si(2)-C(4)-H(4A)	109.5	H(7A)-C(7)-H(7C)	109.5
C(6)-Si(3)-H(3S)	103(3)	Si(2)-C(4)-H(4B)	109.5	H(7B)-C(7)-H(7C)	109.5
C(7)-Si(3)-H(3S)	107(3)	H(4A)-C(4)-H(4B)	109.5		
C(1)-Si(3)-H(3S)	111(3)	Si(2)-C(4)-H(4C)	109.5		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+2

Table S41. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $(Me_2SiC(SiHMe_2)_2)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	20(1)	16(1)	37(1)	14(1)	1(1)	7(1)

Si(2)	28(1)	22(1)	44(1)	12(1)	2(1)	15(1)
Si(3)	21(1)	25(1)	47(2)	14(1)	-2(1)	14(1)
C(1)	9(3)	16(3)	40(4)	17(3)	0(3)	1(3)
C(2)	42(4)	23(3)	54(4)	22(3)	-5(4)	11(3)
C(3)	24(3)	37(4)	49(4)	21(3)	8(3)	4(3)
C(4)	38(4)	16(3)	61(5)	-1(3)	-3(4)	6(3)
C(5)	70(5)	45(4)	41(4)	5(4)	8(4)	30(4)
C(6)	43(4)	73(5)	59(5)	30(4)	-5(4)	34(4)
C(7)	13(3)	45(4)	80(6)	20(4)	7(4)	8(3)

Table S42. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $(Me_2SiC(SiHMe_2)_2)_2$

	x	y	z	U(eq)
H(2A)	4896	12675	7828	58
H(2B)	6426	14068	9179	58
H(2C)	4475	13104	9519	58
H(3A)	8631	12205	8504	57
H(3B)	7229	10929	7032	57
H(3C)	7847	10076	8154	57
H(4A)	2037	4489	8206	64
H(4B)	2611	3711	6659	64
H(4C)	1171	4454	6635	64
H(5A)	4545	6289	4810	77
H(5B)	4921	8349	5426	77
H(5C)	2955	6830	4920	77
H(6A)	2531	10240	6248	80
H(6B)	523	9781	6363	80
H(6C)	1065	8222	5585	80
H(7A)	-1381	7076	8108	71
H(7B)	-278	6655	9256	71
H(7C)	-406	5856	7474	71
H(3S)	1580(70)	10250(70)	9160(70)	38(16)
H(2S)	5580(80)	7030(80)	8020(70)	44(17)

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