Supporting Information

Crystal Structure Analysis. Addition of hexane to a THF solution of **2a** afforded deep-red crystals of **2a**•$(thf)_2$. X-ray crystal structure analysis gave an ORTEP view of the complex (Figure S-1), in which two THF molecules are coordinated to the octahedral titanium center of **2a** at a distance of 2.16 and 2.20 Å. ^{1}H NMR ($CDCl_3$): δ 1.62 (m, CH_2 (THF)), 3.96 (d, CH_2, J = 13.2 Hz), 3.67 (t, OCH_2 (THF)), 5.09 (d, CH_2, J = 13.2 Hz), 6.88-7.50 (m, Ar). Elemental analysis. Calcd for $C_{33}H_{54}Cl_2O_4Ti$: C, 64.62; H, 5.59. Found: C, 64.54; H, 5.65. The crystal data of **2a**•$(thf)_2$: orthorhombic; *Pbca*; a = 21.801(3), b = 16.983(3), c = 16.399(3) Å; D_{calcd} = 1.342 g/cm^{-3}; Z = 8. A total of 5727 reflections (maximum 2θ of 50°) was collected on a Rigaku AFC7R diffractometer at 23 °C using the ω-2θ scan method. The structure was solved by Patterson methods (DIRDIF 92 PATTY) and refined with 2951 reflections ($|F_0| > 3\sigma$), GOF = 1.93, R = 0.045, R_w = 0.037.

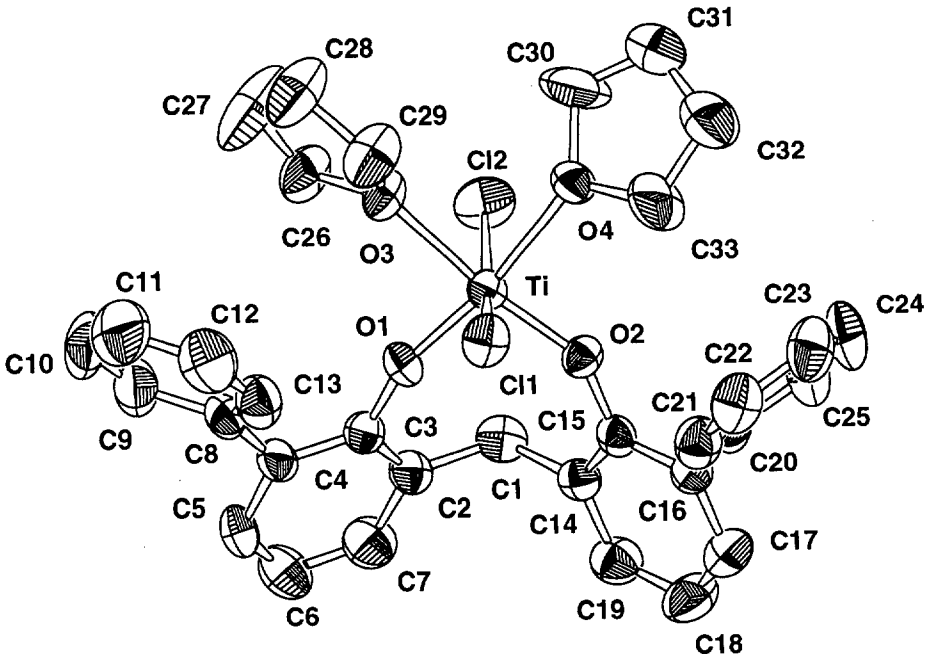

Figure S-1. An ORTEP view of **2a**·$(thf)_2$. Atoms shown with 50% probability ellipsoids. Selected bond lengths (Å): Ti-Cl(1) = 2.341(1); Ti-Cl(2) = 2.367(1); Ti-O(1) = 1.780(3); Ti-O(2) = 1.799(3); Ti-O(3) = 2.203(8); Ti-O(4) = 2.162(3). Selected bond angles (deg): Cl(1)-Ti-Cl(2) = 165.90(5); Cl(1)-Ti-O(1) = 95.99(9); Cl(1)-Ti-O(2) = 93.58(9); Cl(1)-Ti-O(3) = 84.44(8); Cl(1)-Ti-O(4) = 86.08(9); O(1)-Ti-O(2) = 97.8(1); O(1)-Ti-O(3) = 90.2(1); C(2)-C(1)-C(14) = 115.4(4).

Supporting Information
Bulky Titanium Bisphenolate Complexes ...
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Table. Fractional coordinates and isotropic thermal factors for **2a**•$(thf)_2$.

Atom	x/*a*	y/*b*	z/*c*	B_{eq}
Ti	0.57217(3)	0.01538(4)	0.23078(5)	2.85(2)
Cl(1)	0.49929(5)	-0.04158(7)	0.14412(7)	4.08(3)
Cl(2)	0.64159(6)	0.10051(8)	0.29819(7)	4.95(3)
O(1)	0.6281(1)	-0.0603(2)	0.2196(2)	3.21(7)
O(2)	0.5359(1)	-0.0212(2)	0.3218(2)	3.15(7)
O(3)	0.6060(1)	0.0724(2)	0.1189(2)	3.55(7)
O(4)	0.5131(1)	0.1177(2)	0.2316(2)	3.96(8)
C(1)	0.6451(2)	-0.0921(3)	0.3896(3)	3.7(1)
C(2)	0.6745(2)	-0.1393(3)	0.3219(3)	3.6(1)
C(3)	0.6653(2)	-0.1211(3)	0.2393(3)	3.3(1)
C(4)	0.6956(2)	-0.1626(3)	0.1778(3)	3.7(1)
C(5)	0.7337(2)	-0.2246(3)	0.2010(3)	5.4(2)
C(6)	0.7418(2)	-0.2448(3)	0.2808(4)	6.3(2)
C(7)	0.7128(2)	-0.2021(2)	0.3405(3)	5.2(2)
C(8)	0.6894(2)	-0.1417(3)	0.0908(3)	4.1(1)
C(9)	0.7420(2)	-0.1315(3)	0.0427(3)	5.6(2)
C(10)	0.7374(2)	-0.1108(4)	-0.0378(4)	7.1(2)
C(11)	0.6812(4)	-0.1011(4)	-0.0736(4)	7.5(2)
C(12)	0.6288(3)	-0.1112(4)	-0.0277(4)	6.4(2)
C(13)	0.6331(2)	-0.1310(3)	0.0532(3)	4.7(1)
C(14)	0.5802(2)	-0.1163(3)	0.4118(2)	3.2(1)
C(15)	0.5289(2)	-0.0795(3)	0.3774(3)	2.9(1)
C(16)	0.4695(2)	-0.1005(3)	0.4021(3)	3.4(1)
C(17)	0.4629(2)	-0.1582(3)	0.4608(3)	4.9(1)
C(18)	0.5128(3)	-0.1967(3)	0.4932(3)	5.5(2)
C(19)	0.5710(2)	-0.1754(3)	0.4686(3)	4.5(1)
C(20)	0.4134(2)	-0.0634(3)	0.3664(3)	3.5(1)
C(21)	0.3894(2)	-0.0894(3)	0.2930(3)	4.4(1)
C(22)	0.3373(2)	-0.0553(3)	0.2603(3)	5.2(2)

C(23)	0.3089(2)	0.0047(4)	0.3002(4)	5.7(2)
C(24)	0.3321(2)	0.0310(3)	0.3733(4)	6.2(2)
C(25)	0.3839(2)	-0.0026(3)	0.4058(3)	5.2(1)
C(26)	0.6708(2)	0.0805(3)	0.1005(3)	5.2(1)
C(27)	0.6753(3)	0.1216(5)	0.0222(4)	9.6(2)
C(28)	0.6153(3)	0.1353(4)	-0.0079(3)	7.4(2)
C(29)	0.5718(2)	0.0947(3)	0.0467(3)	5.9(2)
C(30)	0.5281(3)	0.1998(3)	0.2293(5)	9.5(2)
C(31)	0.4789(3)	0.2448(3)	0.2542(5)	8.9(2)
C(32)	0.4277(3)	0.1914(3)	0.2715(4)	7.5(2)
C(33)	0.4507(2)	0.1129(3)	0.2574(2)	7.4(2)

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$