

(Supplementary Information)

**Synthesis and structures of titanium complexes bearing tetradentate tripodal
[O₂XC] ligands (X = C, P)**

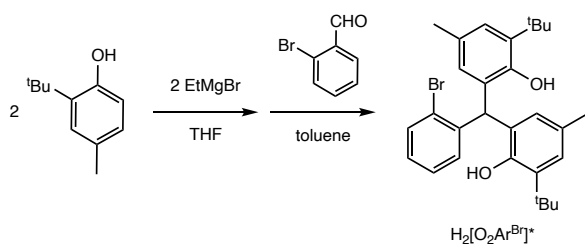
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Experimental section

General considerations

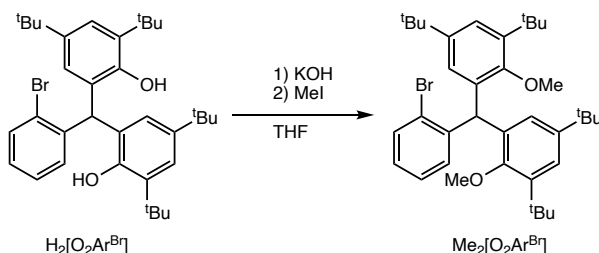
All operations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk techniques and in an MBraun glovebox. Pentane and toluene were purchased from Kanto Chemical Co. and dried by passage through two columns of activated alumina and a Q-5 column, while stabilizer-free THF was purchased from Kanto Chemical Co. and dried by passage through two columns of activated alumina. Benzene-*d*₆ and THF-*d*₈ were dried and degassed over a potassium mirror, vacuum transferred, and then stored in glovebox. (2-Br-C₆H₄)(2,4-*t*Bu₂-C₆H₂OH)₂CH was prepared using the literature procedures.¹ NMR spectra were recorded on a JEOL ECX-500 spectrometer. ¹H NMR are reported with reference to solvent resonances of chloroform-*d*₁, benzene-*d*₆ and THF-*d*₈ residual protons at 7.25, 7.15 and 3.62 ppm, respectively. ¹³C{¹H} NMR were referenced to deuterated solvent peaks 77.1 (chloroform-*d*₁), 127.6 (C₆D₆) and 68.0 (THF-*d*₈) ppm, respectively. ³¹P{¹H} NMR were referenced to liquid H₃PO₄ (δ = 0) as an external standard. Elemental analyses (C, H, and N) were measured using an Elementar vario MICRO cube apparatus.

Synthesis of (2-Br-C₆H₄)(2-^tBu-4-Me-C₆H₂OH)₂CH (H₂[O₂Ar^{Br}]^{*})



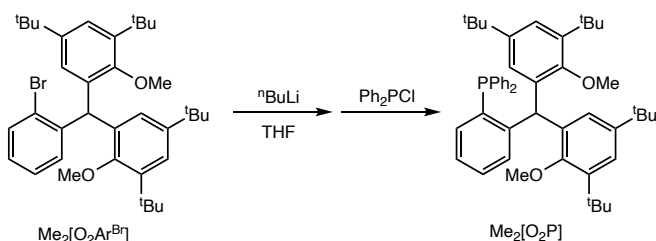
Addition of bromoethane (12 mL, 17 g, 0.16 mol) in THF (40 mL) was added dropwise to magnesium (3.7 g, 0.15 mol) in THF. The reaction mixture was stirred for 1 h and then added dropwise to a THF (50 mL) solution of 2-*tert*-butyl-4-methylphenol (23 g, 0.15 mol). After the resulting solution was stirred for 1 h, the solvent was removed under vacuum. To the residue was added toluene (150 mL) and 2-bromobenzaldehyde. The mixture was heated to 100 °C for 12 h. After allowing the mixture to cool to 0 °C, hydrochloric acid (2 M) was added, and the product was extracted into ethyl acetate. The organic layer was washed with brine, followed by drying over MgSO₄. Removal of the solvent followed by washing with hexane produced H₂[O₂Ar^{Br}]^{*} as a white crystalline solid (32 g, 90% yield). ¹H NMR (400 MHz, CDCl₃, 297 K, δ/ppm) 1.36, (s, 18H, ^tBu), 2.17, (s, 6H, OArMe), 4.69 (brs, 2H, ArOH), 5.90 (s, 1H, HCAr₃), 6.41 (s, 2H, OArH), 7.00 (dd, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.2 Hz, 1H, BrArH), 7.05 (s, 2H, OArH), 7.17 (ddd, ³J_{HH} = 7.6 Hz, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.2 Hz, 1H, BrArH), 7.25 (overlap, 1H, BrArH), 7.63 (d, ³J_{HH} = 7.6 Hz, 1H, BrArH). Anal. calcd (%) for C₂₉H₃₅O₂Br : C 70.30, H 7.12 ; found : C 70.18, H 7.10.

Synthesis of (2-Br-C₆H₄)(2,4-^tBu₂-C₆H₂OMe)₂CH (Me₂[O₂Ar^{Br}])



A solution of H₂[O₂Ar^{Br}] (20 g, 35 mmol) KOH (5.0 g, 130 mmol) in THF (60 mL) was stirred at room temperature for 2 h. After iodomethane (23 mL, 370 mmol) was added, the mixture was stirred for additional 12 h. The mixture was filtered to remove an insoluble material and evaporated to dryness. The residue was extracted into toluene, and the solution was washed with water. After the organic layer was dried over MgSO₄, removal of the solvent under vacuum followed by washing with hexane produced Me₂[O₂Ar^{Br}] as a white crystalline solid (12 g, 59% yield). ¹H NMR (500 MHz, CDCl₃, 297 K, δ/ppm) 1.15, 1.35, (s, 18H, ^tBu), 3.55 (s, 6H, ArOCH₃), 6.38 (s, 1H, HCAr₃), 6.80 (d, ⁴J_{HH} = 2.0 Hz, 2H, OArH), 7.00–7.06 (m, 2H), (ddd, ³J_{HH} = 7.5 Hz, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.2 Hz, 1H, BrArH), 7.19 (d, ⁴J_{HH} = 2.0 Hz, 2H, OArH), 7.49 (dd, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.2 Hz, 1H, BrArH).

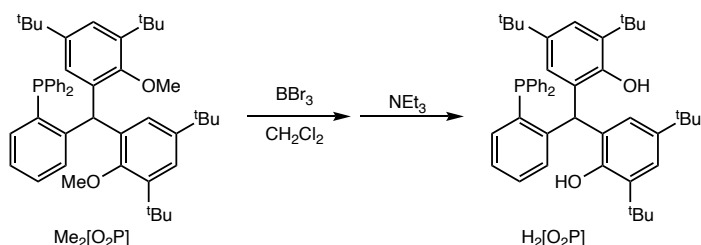
Synthesis of Me₂[O₂P]



A solution of ⁿBuLi (1.5 M in *n*-hexane, 7.6 mL, 12 mmol) was added dropwise to Me₂[O₂Ar^{Br}] (7.1 g, 12 mmol) at -98 °C. After stirring for 10 min, Ph₂PCl (2.1 mL, 13

mmol) was added. The mixture was allowed to warm to room temperature and stirred for additional 12 h. After removal of all volatiles, the residue was extracted into toluene. The solution was evaporated to dryness, and the residue was washed with pentane to provide $\text{Me}_2[\text{O}_2\text{P}]$ as a white powder (7.4 g, 88% yield). ^1H NMR (500 MHz, C_6D_6 , 297 K, δ/ppm) 1.24, 1.43 (s, 18H, ^tBu), 3.70 (s, 6H, *OMe*), 6.88-7.50 (Ar-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6 , 297 K, δ/ppm) -18.0. Anal. calcd (%) for $\text{C}_{49}\text{H}_{61}\text{O}_2\text{P}$: C 82.54, H 8.62; found: C 82.42, H 8.51.

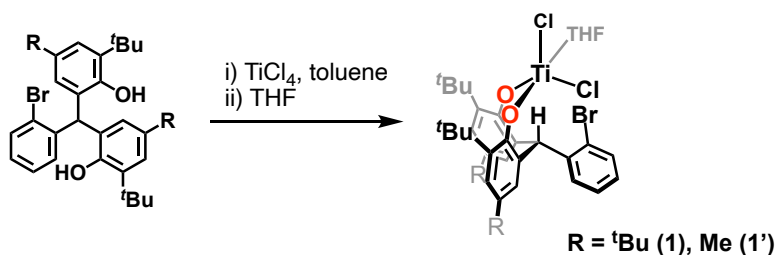
Synthesis of $\text{H}_2[\text{O}_2\text{P}]$



A solution of BBr_3 (1.0 M in CH_2Cl_2 , 30 mL) was added to $\text{Me}_2[\text{O}_2\text{P}]$ (5.3 g, 7.4 mmol) in CH_2Cl_2 (40 mL) at -98 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The solution was poured into a solution of trimethylamine (15 mL) in water (120 mL) at 0 °C. The water layer was separated, and the water layer was extracted with CH_2Cl_2 . The combined organic layers were dried over MgSO_4 . The solution was concentrated to produce a white solid, which was washed with methanol, yielding $\text{H}_2[\text{O}_2\text{P}]$ as a white powder (4.4 g, 87% yield).

^1H NMR (500 MHz, CDCl_3 , 297 K, δ/ppm) 1.11/1.33 (s, 18H, ^tBu), 4.95 (brs, 2H, *OH*), 6.41 (d, $^4J_{\text{PH}} = 9.4$ Hz, Ar_3CH), 6.52, 7.14 (d, $^4J_{\text{PH}} = 2.2$ Hz, Ar), 7.08-7.25 (Ar-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 297 K, δ/ppm) -16.8. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 297 K, δ/ppm) 30.0, 31.5, 34.3, 35.0 (^tBu), 44.6 (d, $^3J_{\text{CP}} = 27.5$ Hz, Ar_3CH), 122.7-150.5 (Ar). Anal. calcd (%) for $\text{C}_{47}\text{H}_{57}\text{O}_2\text{P}$: C 82.42, H 8.39; found: C 82.17, H 8.41.

Synthesis of $[\text{O}_2\text{Ar}^{\text{Br}}]\text{TiCl}_2(\text{thf})$ (1)



A solution of TiCl_4 (0.5 M in toluene, 6.0 mL, 3.0 mmol) was added dropwise to $\text{H}_2[\text{O}_2\text{Ar}^{\text{Br}}]$ (1.7 g, 3.0 mmol) in toluene (20 mL) at room temperature. The solution immediately turned red and was stirred for 12 h. Removal of all volatiles under vacuum provided an orange solid. The residue was extracted with THF (20 mL), and the supernatant was evaporated to dryness. The residue was washed with pentane to yield **1** as a brown crystalline material in 94% yield (2.14 g).

^1H NMR (500 MHz, C_6D_6 , 297 K, δ/ppm) 1.21, (s, 18H, 'Bu), 1.35 (brs, 4H, THF), 1.58, (s, 18H, 'Bu) 4.12 (brs, 4H, THF), 6.68 (ddd, $^3J_{\text{HH}} = 7.9$ Hz, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H, Ar), 6.69 (s, 1H, HCAr_3), 6.94 (ddd, $^3J_{\text{HH}} = 7.9$ Hz, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H, Ar), 7.36 (d, $^4J_{\text{HH}} = 2.4$ Hz, 2H, Ar), 7.45 (d, $^4J_{\text{HH}} = 2.4$ Hz, 2H, Ar), 7.49 (dd, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H, Ar), 7.77 (dd, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 297 K, δ/ppm) 25.4 (THF), 30.9, 31.4, 34.7, 35.7 ('Bu), 45.9 (HCAr_3), 73.0 (THF), 121.6, 124.7 (OAr), 126.7, 127.0, 128.6, 131.4, 135.0 ($\text{C}_6\text{H}_4\text{Br}$), 136.8, 138.8 (OAr), 141.0 ($\text{C}_6\text{H}_4\text{Br}$), 145.8, 164.9 (OAr). Anal. calcd (%) for $\text{C}_{39}\text{H}_{53}\text{BrCl}_2\text{O}_3\text{Ti}\cdot(\text{C}_5\text{H}_{12})_{0.5}$: C 61.95, H 7.39; found: C 62.20, H 6.99.

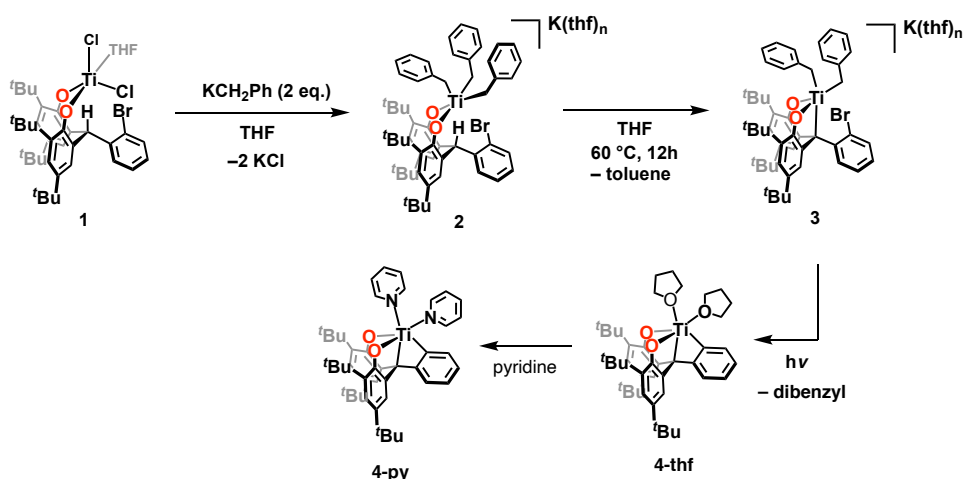
Synthesis of **1'**

The same procedure as used for **1** was followed. Reaction of TiCl_4 (0.5 M in toluene, 9.2 mL, 4.6 mmol) with the ligand precursor $\text{H}_2[\text{O}_2\text{Ar}^{\text{Br}}]^*$ (2.3 g, 4.6 mmol) in toluene (20 mL) afforded **1'** as brown crystals (3.22 g).

^1H NMR (500 MHz, C_6D_6 , 297 K, δ/ppm) 1.34 (4H, THF), 1.56 (s, 18H, 'Bu), 2.00 (s, 6H, PhCH_3), 4.06 (4H, THF), 6.66 (dd, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 1H, ArH), 6.73 (s, 1H, HCAr_3), 6.89 (dd, $^3J_{\text{HH}} = 6.6$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 1H, BrArH), 6.98 (d, $^4J_{\text{HH}} = 1.6$ Hz,

2H, OArH), 7.14 (d, $^4J_{\text{HH}} = 1.6$ Hz, 2H, OArH), 7.46 (d, $^3J_{\text{HH}} = 6.6$ Hz, 1H, BrArH), 7.77 (d, $^3J_{\text{HH}} = 6.6$ Hz, 1H, BrArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 297 K, δ/ppm) 21.3 (PhCH₃), 25.5 (THF), 31.0, 35.4 (^tBu), 45.3 (HCAr₃), 72.2 (THF), 125.9 (OAr), 126.8, 127.2 ($\text{C}_6\text{H}_4\text{Br}$), 128.0 (OAr, overlapping with solvent), 128.5, 131.4 ($\text{C}_6\text{H}_4\text{Br}$), 132.9 (OAr), 135.0 ($\text{C}_6\text{H}_4\text{Br}$), 137.4, 138.5 (OAr), 140.7 ($\text{C}_6\text{H}_4\text{Br}$), 165.7 (OAr). Anal. calcd (%) for $\text{C}_{33}\text{H}_{41}\text{BrCl}_2\text{O}_3\text{Ti}\cdot\text{C}_5\text{H}_{12}$: C 60.33, H 7.06; found: C 60.12, H 6.51.

Synthesis of $[\text{O}_2\text{CC}]\text{Ti}(\text{py})_2$ (**4-py**)



A THF (10 mL) solution of PhCH_2K (520 mg, 4.0 mmol) was added dropwise to **1** (1.0 g, 1.3 mmol) in THF (20 mL). A color of the solution gradually turned from dark brown to reddish brown, yielding $\text{K}[(\text{O}_2\text{Ar}^{\text{Br}})\text{Ti}(\text{CH}_2\text{Ph})_3]$ (**2**). The solution was shielded from light because the product is light-sensitive. The mixture was heated to $60\text{ }^\circ\text{C}$ and stirred for 12 h to give $\text{K}[(\text{O}_2\text{CAr}^{\text{Br}})\text{Ti}(\text{CH}_2\text{Ph})_2]$ (**3**). The resulting solution was irradiated with a xenon lamp at room temperature for additional 12 h. The reaction mixture included **4-thf** according to ^1H NMR spectroscopy. After removal of an insoluble material by centrifugation, pyridine (0.5 mL) was added to the supernatant. The solution was stirred at room temperature for 30 min. Evaporation of the solution under vacuum followed by washing the residue with pentane afforded **4-py** as a purple powder in 29% yield (270 mg).

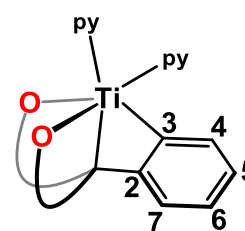
Data for 2: ^1H NMR (500 MHz, THF- d_8 , 297 K, δ/ppm) 1.18, 1.44 (s, 18H, $t\text{Bu}$), 3.12 (brs, 6H, CH_2Ph), 5.31 (s, 1H, CH), 6.79 (d, $^4J_{\text{HH}} = 2.0$ Hz, 2H, Ar), 6.88 (brs, 3H), 6.91 (brs, 3H), 6.93 (d, $^4J_{\text{HH}} = 2.0$ Hz, 2H, Ar), 6.98 (t, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.12 (t, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 7.15–7.30 (m, 4H), 7.42 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.59 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H). Some aromatic protons are not detected because of broadening or overlapping.

Data for 3: ^1H NMR (500 MHz, THF- d_8 , 297 K, δ/ppm) 1.24, 1.49 (s, 18H, $t\text{Bu}$), 2.07, 2.41 (s, 2H, CH_2). Aromatic protons are not detected because of broadening or overlapping.

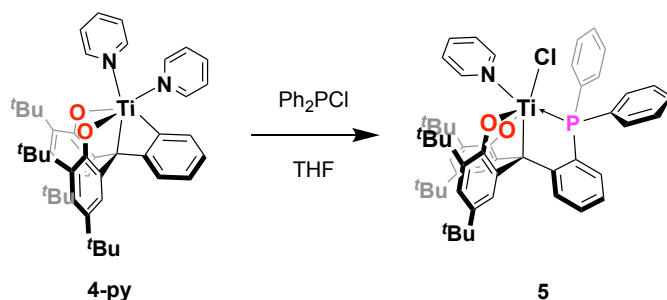
Data for 4-thf: ^1H NMR (500 MHz, THF, 297 K, δ/ppm) 1.26 (s, 18H, $t\text{Bu}$), 1.33 (s, 18H, $t\text{Bu}$), 6.75 (dd, $^3J_{\text{HH}} = 7.2$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 1H, Ar), 6.87 (d, 2H, $^4J_{\text{HH}} = 2.0$ Hz, Ar), 7.336 (d, 2H, $^4J_{\text{HH}} = 2.0$ Hz, Ar), 7.342 (d, $^3J_{\text{HH}} = 7.2$ Hz, 1H, Ar), 7.50 (d, $^3J_{\text{HH}} = 7.2$ Hz, 1H, Ar). One aromatic resonance could not be detected because of overlap with dibenzyl. Complex **4-thf** was obtained as brown powder, contaminated with inseparable side-products, which failed to give satisfactory combustion analytical data.

Data for 4-py: ^1H NMR (500 MHz, THF- d_8 , 297 K, δ/ppm)

1.36 (s, 18H, $t\text{Bu}$), 1.43 (s, 18H, $t\text{Bu}$), 6.68 (dd, $^3J_{\text{HH}} = 7.6$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 1H, H5), 6.97 (d, 2H, $^4J_{\text{HH}} = 2.3$ Hz, OArH), 7.02 (dd, $^3J_{\text{HH}} = 7.2$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 1H, H6), 7.16 (d, 1H, $^3J_{\text{HH}} = 7.2$ Hz, H7), 7.40 (d, $^3J_{\text{HH}} = 7.6$ Hz, 1H, H4), 7.42 (br, 4H, py), 7.47 (d, $^4J_{\text{HH}} = 2.3$ Hz, 2H, OArH), 7.72 (brs, 2H, py), 8.63 (brs, 4H, py). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, THF- d_8 , 297 K, δ/ppm) 21.5, 23.2, 25.6, 26.0 ($t\text{Bu}$), 98.0 (Ti-CAr₃), 110.1 (OAr), 113.2 (C5), 114.9 (OAr), 118.6 (C7), 120.6 (C6), 123.0 (C4), 123.3 (OAr), 130.5 (C2), 131.1, 139.2, 158.5 (OAr), 201.0 (C3). Anal. calcd (%) for $\text{C}_{45}\text{H}_{54}\text{N}_2\text{O}_2\text{Ti}$: C 76.91, H 7.74, N 3.99; found : C 77.23, H 7.70, N 3.47.



Synthesis of [O₂PC]TiCl(py) (**5**).



To a solution of **4-py** (153 mg, 0.21 mmol) in THF (10 mL) was added Ph₂PCl (65 mg, 0.29 mmol) at room temperature. The solution was stirred at room temperature for 20 min. After centrifugation, the solvent was removed under vacuum. The residue was washed with pentane to afford **5** as a brown powder in 85% (151 mg).

¹H NMR (500 MHz, C₆D₆, 297 K, δ/ppm) 1.18 (s, 18H, ^tBu), 1.26 (s, 18H, ^tBu), 6.35 (m, 2H, -PPhPh), 6.65 (m, 1H, -PPhPh), 6.75 (m, 1H, -PPhPh), 6.99 (m, 2H, Ti-C-C₆H₄-PPh₂), 7.10-7.06 (four signals overlapping, total 7H, -PPhPh, Ti-C-C₆H₄-PPh₂, OArH and py), 7.16 (overlap with solvent, 2H, OArH), 7.19 (m, 2H, -PPhPh), 7.87~7.91 (two signals overlapping, 4H, py), 8.33 (m, 2H, -PPhPh). ³¹P NMR (202 MHz, C₆D₆, 297 K, δ/ppm) 44.3. ¹³C {¹H} NMR (125 MHz, C₆D₆, 297 K, δ/ppm) 30.0, 31.9, 34.6, 35.0 (^tBu), 114.2 (d, ³J_{CP} = 13.8 Hz, Ti-CAr₃), 123.0 (-PPhPh), 123.9 (br, -PPhPh), 126.0 (br, -PPhPh), 127.2 (d, ⁴J_{CP} = 5.3 Hz, -PPhPh), 127.5~128.5 (overlapping with solvent, Ti-C-C₆H₄-PPh₂, OAr and py ring carbons), 129.5, 129.6 (Ti-C-C₆H₄-PPh₂), 129.7 (OAr), 130.8, 133.0 (Ti-C-C₆H₄-PPh₂ or OAr or py ring carbons), 133.9, 134.0 (py), 137.8 (-PPhPh), 150.7 (-PPhPh). Anal. calcd (%) for C₅₂H₅₉ClNO₂PTi : C 73.97, H 7.04, N 1.66 ; found : C 72.53, H 6.90, N 1.56. Combustion analysis tested low in carbon content possibly due to poor combustion properties.

X-ray Crystallography. Single crystals were immersed in immersion oil on micromount and transferred to a Rigaku Varimax with Saturn system equipped a Rigaku GNNP low temperature device. Data were collected under a cold nitrogen stream at 123

K using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Equivalent reflections were merged, and the images were processed with the CrysAlis^{Pro} software. Empirical absorption corrections were applied. All structures were solved by direct method using SHELXT-2015² and refined by full-matrix least-squares method on F^2 for all data using SHELXL-2015³ with the Olex2 program⁴. All hydrogen atoms were placed at their geometrically calculated positions.

For **1'**, two crystallographically independent molecules were present in the asymmetric unit. One *tert*-butyl group and one THF molecule were disordered. Some residual electron density was difficult to model, and therefore the program SQUEEZE⁵ was used to remove the contribution of the electron density in the solvent region from the intensity data. A void space contains 86 electrons per unit cell, which could be attributed to distorted THF molecules (two molecules in the asymmetric unit). For **5**, one *tert*-butyl group and one toluene molecule were disordered.

Table S1. Crystallographic data

	1'	4-thf	5
Formula	C ₃₃ H ₄₁ BrCl ₂ O ₃ Ti, 0.5 (C ₄ H ₈ O)	C ₄₃ H ₆₀ O ₄ Ti	C ₅₂ H ₅₉ ClNO ₂ PTi, (C ₇ H ₈)
Formula Mass (g mol ⁻¹)	720.42	688.81	936.45
Temperature (K)	123	123	123
Crystal system	<i>Triclinic</i>	<i>Monoclinic</i>	<i>Triclinic</i>
Space group	P-1 (#2)	<i>P2₁/n</i> (#14)	P-1 (#2)
Crystal color	Reddish brown	Brown	Reddish brown
Crystal size (mm)	0.15 × 0.12 × 0.02	0.19 × 0.05 × 0.05	0.12 × 0.08 × 0.08
<i>a</i> (Å)	11.1016(2)	9.8645(2)	11.9944(2)
<i>b</i> (Å)	13.3903(3)	17.6446(5)	13.2152(2)
<i>c</i> (Å)	24.3259(5)	21.7498(5)	17.0702(3)
α (°)	78.765(2)	90	79.141(1)
β (°)	80.424(2)	89.382(2)	80.483(1)
γ (°)	89.325(2)	90	84.749(1)
<i>V</i> (Å ³)	3496.62(13)	3785.45(16)	2615.65(8)
<i>Z</i>	4	4	2
ρ_{calc} (g cm ⁻³)	1.369	1.209	1.189
μ (Mo K α) (cm ⁻¹)	1.574	0.266	0.287
Reflections collected	57804	31095	32698
Independent reflections	16124	8740	12066
<i>R</i> _{int}	0.0637	0.0368	0.0280
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.05	0.0433	0.0407
<i>wR</i> ₂ (all data) ^b	0.1043	0.1080	0.1083
Goodness of fit on <i>F</i> ²	1.013	1.025	1.036
Largest diff. peak/hole (e Å ⁻³)	0.447/-0.479	0.316/-0.394	0.389/-0.283

(a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, (b) $wR_2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)\}]^{0.5}$

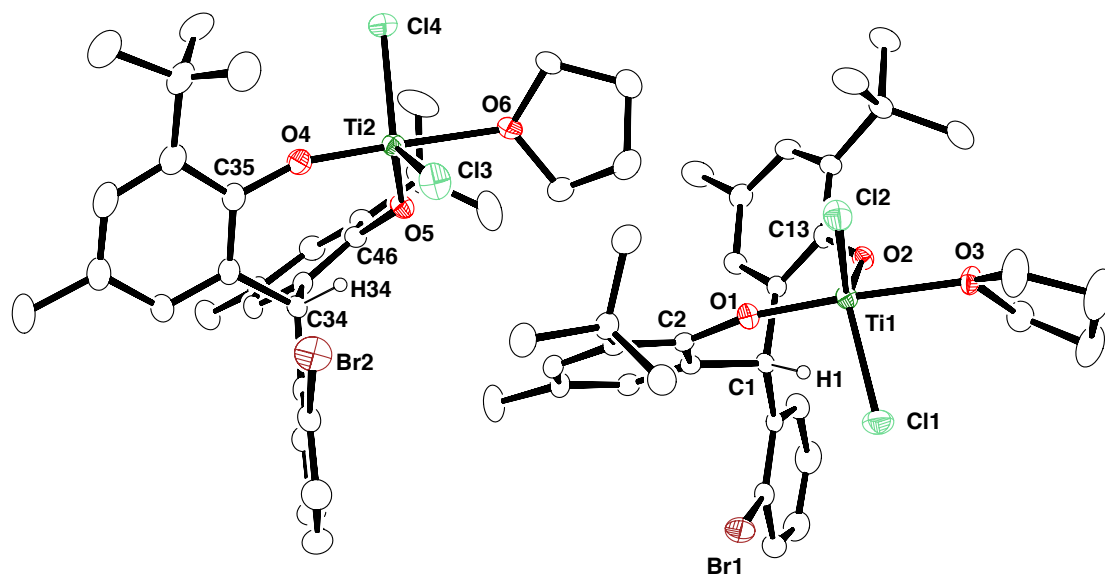


Fig. S1 Molecular structure of **1'** with thermal ellipsoids set at 50% probability level. All hydrogen atoms are omitted for clarity except for the methine proton. Selected bond lengths [Å] and angles [°]: Ti(1)–O(1) 1.773(2), Ti(1)–O(2) 1.819(2), Ti(1)–O(3) 2.181(2), Ti(1)–Cl(1) 2.2835(9), Ti(1)–Cl(2) 2.244(1), O(1)–Ti(1)–O(2) 97.36(9), O(1)–Ti(1)–O(3) 176.22(9), Cl(1)–Ti–Cl(2) 116.01(4), Cl(1)–Ti(1)–O(2) 121.50(7), Cl(2)–Ti–O(2) 118.60(7), Ti(1)–O(1)–C(2) 159.4(2), Ti(1)–O(2)–C(13) 138.7(2).
 Ti(2)–O(4) 1.779(2), Ti(2)–O(5) 1.820(2), Ti(2)–O(6) 2.186(2), Ti(2)–Cl(3) 2.275(1), Ti(2)–Cl(4) 2.2514(9), O(4)–Ti(2)–O(5) 97.7(1), O(4)–Ti(1)–O(6) 176.78(9), Cl(3)–Ti(2)–Cl(4) 117.74(4), Cl(3)–Ti(2)–O(5) 119.91(7), Cl(4)–Ti(2)–O(5) 118.91(7), Ti(2)–O(4)–C(35) 162.1(2), Ti(2)–O(5)–C(46) 135.2(2).

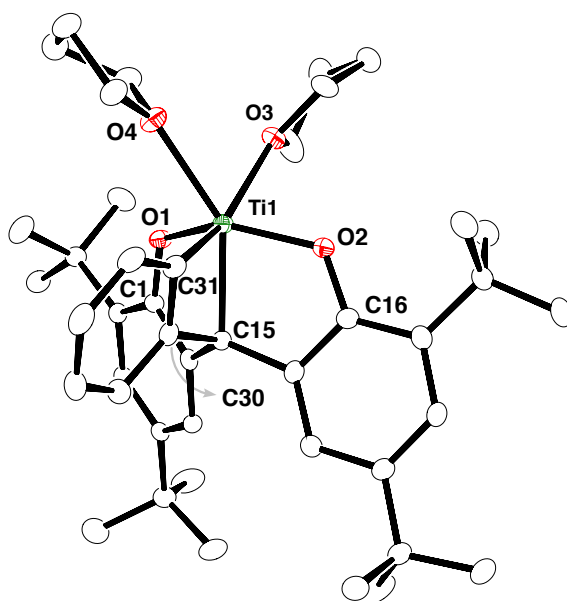


Fig. S2 Molecular structure of **4-thf** with thermal ellipsoids set at 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–O(1) 1.929(1), Ti(1)–O(2) 1.908(1), Ti(1)–O(3) 2.161(1), Ti(1)–O(4) 2.301(1), Ti(1)–C(15) 2.143(2), O(1)–Ti(1)–O(2) 133.69(5), O(1)–Ti(1)–C(15) 78.03(5), O(2)–Ti(1)–C(15) 78.20(5), C(15)–Ti(1)–C(31) 71.68(6), Ti(1)–C(15)–C(30) 81.04(9), Ti(1)–C(31)–C(30) 86.6(1), C(15)–C(30)–C(31) 115.3(1), Ti(1)–O(1)–C(1) 121.7(1), Ti(1)–O(2)–C(16) 122.9(1).

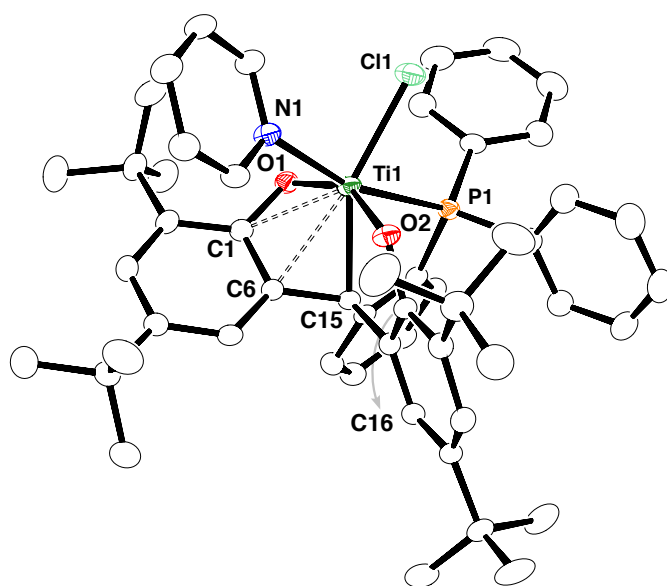


Fig. S3 Molecular structure of **5** with thermal ellipsoids set at 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Ti(1)–O(1) 1.929(1), Ti(1)–O(2) 1.897(1), Ti(1)–P(1) 2.565(5), Ti(1)–Cl(1) 2.3786(4), Ti(1)–N(1) 2.259(2), Ti(1)–C(15) 2.245(1), Ti(1)–C(1) 2.423(2), Ti(1)–C(6) 2.448(2), O(1)–C(1) 1.358(2), O(2)–C(16) 1.356(2), C(1)–C(6) 1.419(2), C(6)–C(15) 1.493(2), O(1)–Ti(1)–O(2) 150.23(5), Cl(1)–Ti(1)–C(6) 170.87(4), P(1)–Ti(1)–N(1) 165.12(4), O(1)–Ti(1)–C(6) 63.66(5), O(2)–Ti(1)–C(6) 86.60(5), P(1)–Ti(1)–C(6) 102.80(4), Ti(1)–O(1)–C(1) 93.34(9), Ti(1)–O(2)–C(16) 124.7(1).

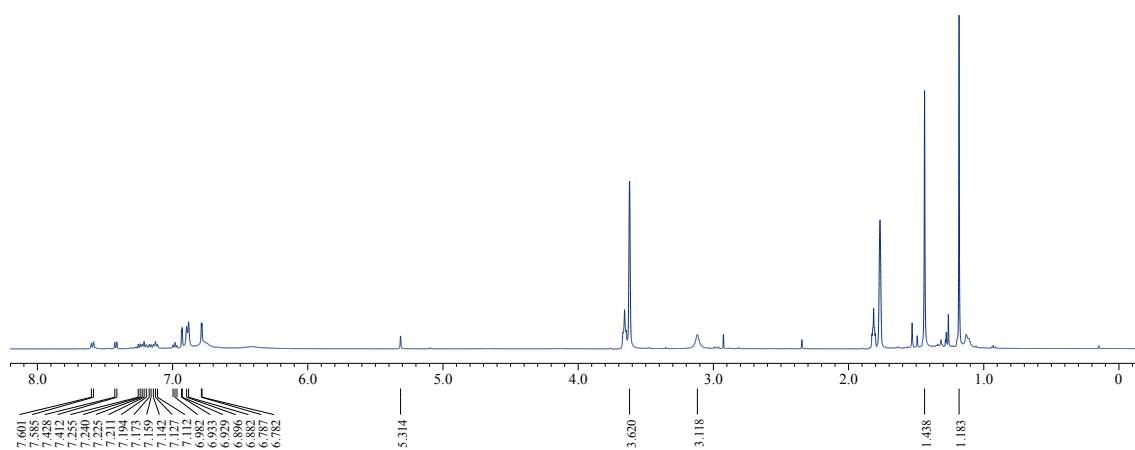


Fig. S4 ^1H NMR spectrum of **2** in-situ prepared by the reaction of **1** with PhCH_2K (3 eq.) in $\text{THF-}d_8$.

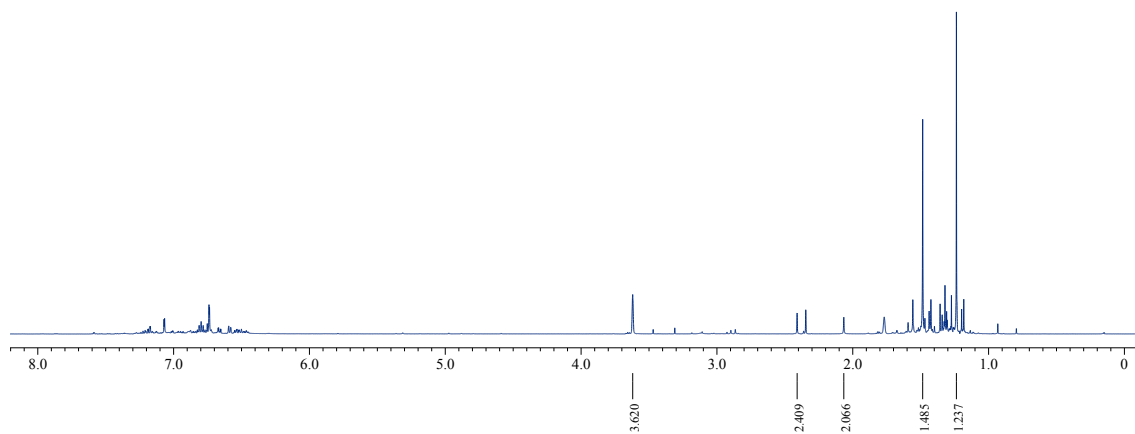


Fig. S5 ^1H NMR spectrum recorded after heating a solution of **2** in $\text{THF-}d_8$. The spectrum indicates formation of **3** as a major Ti-containing product.

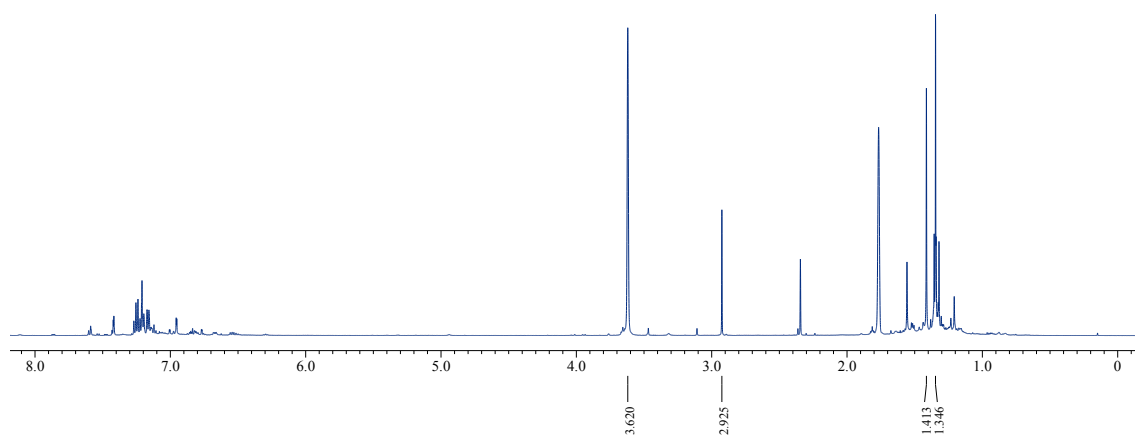


Fig. S6 ^1H NMR spectrum recorded after heating a solution of **2** in $\text{THF-}d_8$ and subsequent irradiation of light.

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