# (Electronic supplementary information)

# An anionic $\eta^2$ -naphthalene complex of titanium supported by a tripodal $[O_3C]$ ligand

## and its reactions with dinitrogen, anthracene and THF

Yusuke Nakanishi, Yutaka Ishida and Hiroyuki Kawaguchi\*

### **Experimental section**

#### **General considerations**

All operations were performed under argon using standard Schlenk techniques and in an MBraun glovebox unless otherwise stated. Pentane, hexane 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 and DME were purchased from Kanto Chemical Co. and dried by passage through two columns of activated alumina. THF- $d_8$  were dried and degassed over a potassium mirror, vacuum transferred, and then stored in glovebox. NMR spectra were recorded on a JEOL ECX-500 spectrometer. <sup>1</sup>H NMR are reported with reference to solvent resonances of THF- $d_8$  residual protons at  $\delta = 3.62$  ppm, respectively. <sup>13</sup>C{<sup>1</sup>H} NMR were referenced to deuterated solvent peaks  $\delta = 68.0$  (THF- $d_8$ ) ppm. Elemental analyses (C, H, and N) were measured using an Elementar vario MICRO cube apparatus.

**Synthesis of [K<sub>2</sub>(thf){(O<sub>3</sub>C)Ti(C<sub>10</sub>H<sub>8</sub>)K(thf)<sub>2</sub>}<sub>2</sub>] (3-K).** A flask was charged with potassium (22 mg, 0.55 mmol), naphthalene (71 mg, 0.56 mmol) and THF (10 mL). The mixture was stirred until all of the potassium metal was dissolved. The resulting solution of potassium naphthalenide was added dropwise to [(O<sub>3</sub>C)Ti(thf)<sub>2</sub>] (1) (230 mg, 0.28 mmol) in THF (10 mL) at -35 °C. A color of the solution changed from dark brown to black. After stirring at room temperature for 12 h, all volatiles were removed in vacuo. The black residue was washed with hexane (10 mL). The resulting solid was dissolved in THF and layered with hexane to produce black crystals of **3-K** (240 mg, 82%). <sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>, 297 K,  $\delta$ /ppm): 1.22 (s, 27H, 'Bu), 1.37 (s, 27H, 'Bu), 3.85 (m, 2H, H1, H4, for the numbering of proton and carbon atoms, see Fig. S1), 4.67 (m, 2H, H2, H3), 6.01 (m, 2H, H5, H8), 6.08 (m, 2H, H6, H7), 6.81 (s, 6H, Ar), 7.60 (s, 6H, Ar). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, THF-*d*<sub>8</sub>, 297 K,  $\delta$  /ppm): 27.9, 39.8 (C*Me*<sub>3</sub>), 32.0, 32.6 (CMe<sub>3</sub>), n. d. (Ar<sub>3</sub>CTi), 98.0 (C1, C4), 114.4 (C2, C3), 116.3 (OAr), 118.1 (C5, C8), 118.3 (C6, C7), 125.4, 129.8, 135.4, 139.9 (OAr), 145.7 (C9, C10), 163.5 (OAr). Anal. Calcd (%) for C<sub>126</sub>H<sub>176</sub>K<sub>4</sub>O<sub>11</sub>Ti<sub>2</sub>: C, 71.42; H, 8.37. Found: C, 71.29; H, 7.98.



Figure S1. Numbering of carbon atoms in naphthalene and anthracene

Synthesis of Na<sub>2</sub>[(O<sub>3</sub>C)Ti(C<sub>10</sub>H<sub>8</sub>)] (3-Na). A flask was charged with sodium (14 mg, 0.62 mmol), naphthalene (80 mg, 0.63 mmol) and DME (10 mL). The mixture was stirred until all of the sodium metal was dissolved. The resulting solution of sodium naphthalenide was added dropwise to  $[(O_3C)Ti(thf)_2]$  (1) (250 mg, 0.31 mmol) in DME (10 mL) at -35 °C. After stirring at room temperature for 12 h, all volatiles were removed in vacuo. The dark brown residue was washed with hexane (10 mL) to give an inseparable mixture of **3-Na** and unidentified compounds as a dark brown powder (230 mg), in which **3-Na** is a major product. <sup>1</sup>H NMR (500MHz, THF-*d*<sub>8</sub>, 297 K,  $\delta$ /ppm): 1.29 (s, 27H, 'Bu), 1.36 (s, 27H, 'Bu), 3.33, 3.45 (DME), 4.13 (m, 2H, H1, H4), 4.70 (m, 2H, H2, H3), 5.93 (m, 2H, H5, H8), 6.07 (m, 2H, H6, H7), 6.75 (d, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 6H, Ar), 7.69 (d, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 6H, Ar). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, THF-*d*<sub>8</sub>, 297 K,  $\delta$ /ppm): 28.0, 29.9 (*CMe*<sub>3</sub>), 31.9, 32.5 (*CMe*<sub>3</sub>), n. d. (Ar<sub>3</sub>CTi), 95.1 (C1, C4), 113.8 (C2, C3), 115.3 (OAr), 118.47 (C5, C8), 118.51 (C6, C7), 124.7, 129.4, 134.5, 140.9 (OAr), 145.7 (C9, C10), 164.4 (OAr).

Synthesis of  $[{K_2(thf)_2}(O_3C)Ti{O(CH_2)_4}]$  (4-K). A solution of 3-K (48 mg, 0.045 mmol) in THF (5 mL) was stirred at 80 °C for 2 h, during which time a color of the solution changed from dark brown to brown. All removal of volatiles in vacuo, the resulting dark brown solid was washed with pentane (2 mL × 2) to give 4-K as a brown powder in 66% yield (29 mg, 0.030 mmol). <sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>, 297 K,  $\delta$ /ppm): 0.93 (t, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, 2H, O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Ti), 1.26 (s, 27H, 'Bu), 1.48 (s, 27H, 'Bu), 1.66 (m, 2H, O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Ti), 2.03 (m, 2H, O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Ti), 4.22 (t, <sup>3</sup>*J*<sub>HH</sub> = 5.3 Hz, 2H, O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Ti), 6.81 (d, <sup>4</sup>*J*<sub>HH</sub> = 2.4 Hz, 3H, Ar), 7.21 (d, <sup>4</sup>*J*<sub>HH</sub> = 2.4 Hz, 3H, Ar).

<sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, THF, 297 K,  $\delta$ /ppm): 27.7 ('Bu), 28.7 (O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Ti), 29.8, 31.9, 32.7 ('Bu), 37.1 (O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Ti), 63.2 (O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Ti), 69.5 (O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-Ti), 76.6 (TiCAr<sub>3</sub>), 115.8, 122.7, 129.5, 134.0, 143.4, 164.6 (Ar). Anal. calcd (%) for C<sub>55</sub>H<sub>84</sub>K<sub>2</sub>O<sub>6</sub>Ti: C 68.29, H 8.75; found : C 68.76, H 8.75.

**Reaction of 3-K with N<sub>2</sub>.** In a glovebox filled with N<sub>2</sub>, **3-K** (190 mg, 0.18 mmol) was dissolved in THF (5.0 mL). The solution was stood for 12 h at 25 °C, during which time brown crystals of **2** formed. After removing the supernatants and drying in vacuo, **2** was obtained as a right brown solid (140 mg, 73%).

**NMR-scale of 3-K with N<sub>2</sub>.** In a glovebox filled with N<sub>2</sub>, **3-K** (5.0 mg, 4.7  $\mu$ mol) and ferrocene (1.6 mg, 8.6 mmol, for use as an internal integration standard) was dissolved in THF*d*<sub>8</sub> (0.5 mL). After 12 h, all **3-K** was consumed, and formation of **2** was observed in 85% yield according to the <sup>1</sup>H NMR spectrum.

Reduction of 1 with KC<sub>8</sub> under N<sub>2</sub>. A suspension of KC<sub>8</sub> (22 mg, 0.16 mmol) in THF (2.0 mL) was added dropwise to a THF solution of  $[(O_3C)Ti(thf)_2]$  (1) (60 mg, 0.073 mmol, 5.0 mL) at -30 °C under N<sub>2</sub>. A color of the solution immediately changed from dark brown to dark green. Then the solution gradually turned dark brown. After stirring at room temperature for 12 h, formation of 2 and 4-K was observed in approximately 3 : 1 ratio along with other unidentified products according to <sup>1</sup>H NMR spectroscopy.

Synthesis of  $[{K_2(thf)_4}{(O_3C)Ti(C_{14}H_{10})}]$  (5). To a solution of 3-K (69 mg, 0.065 mmol) in THF (5 mL) was added anthracene (20 mg, 0.11 mmol). The mixture was stirred at room temperature for 0.5 h, during which time a color of the solution changed from brown to reddish purple. All volatiles were removed in vacuo, and the residue was washed with hexane (2 mL). The resulting solid was dissolved in 1 mL of THF and layered with pentane (10 mL) to produce 5 as dark purple microcrystals (66 mg, 83%). <sup>1</sup>H-NMR (500 MHz, THF-*d*<sub>8</sub>, 297 K, d/ppm) 1.26 (s, 27H, 'Bu), 1.33 (s, 27H, 'Bu), 3.98 (br, 2H, H1 and H4), 5.22 (br, 2H, H2

and H3), 5.50 (s, 2H, H5 and H10 ), 6.35 (br, 2H, H7 and H8), 6.46 (br, 2H, H6 and H9), 6.80 (d,  ${}^{4}J_{\rm HH} = 1.9$  Hz, 3H, OAr*H*), 7.35 (d,  ${}^{4}J_{\rm HH} = 1.9$  Hz, 3H, OAr*H*). Anal. calcd (%) for C<sub>73</sub>H<sub>102</sub>K<sub>2</sub>O<sub>7</sub>Ti: C 72.01, H 8.44. Found: C 71.58, H 8.09.

X-ray Crystallography. Single crystals were immersed in immersion oil on micromount and transferred to a Rigaku Varimax with Saturn system or XtaLABmini system equipped a Rigaku GNNP low temperature device. Single crystals of 3-K and 5 were obtained by layering hexane and pentane onto THF solutions, while those of 3-K-(cryptand-222) were obtained by layering a toluene solution of cryptand-222 onto a THF solution of 3-K. Crystals of 4-Na was obtained from DME/pentane. Recrystallization of 5 from DME/pentane gave a mixture containing bluish violet crystals of 5-dme and dark brown crystals of 5-dme'. Data were collected under a cold nitrogen stream at 123 K for 3-K, 3-K-(cryptand-222), 4-Na, 5, 5-dme and 5-dme' using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71075$  Å). Equivalent reflections were merged, and the images were processed with the CrysAlis<sup>Pro</sup> Empirical absorption corrections were applied. All structures were solved by software. direct method using SHELXT-2015<sup>1</sup> and refined by full-matrix least-squares method on  $F^2$  for all data using SHELXL-2015.<sup>2</sup> All hydrogen atoms except for those attached to carbons of 1,2,3,4-positions of naphthalene or anthracene ligands in 3-K, 3-K-(cryptand-222), 5, 5-dme and 5-dme' were placed at their geometrically calculated positions.

For **3-K**, two 'Bu groups and one THF molecule were disordered. For **3-K-(cryptand-222)**, two THF molecules are disordered. For **4-Na**, three 'Bu groups are disordered. Moreover, some residual electron density was difficult to model, and therefore the program SQUEEZE<sup>3</sup> was used to remove the contribution of the electron density in the solvent region from the intensity data. A void space contains 174 electrons per unit cell, which could be attributed to distorted pentane molecules (0.5 molecule in the asymmetric unit). For **5**, one 'Bu group and four THF molecules are disordered. For **5-dme**, two crystallographically independent molecules were present in the asymmetric unit. One *tert*-butyl group is disordered. For **5-dme**', two crystallographically independent molecules were present in the asymmetric unit. One *tert*-butyl group is disordered. For **5-dme**', two crystallographically independent molecules were present in the asymmetric unit.

	3-K	3-K-(cryptand-222)	4-Na
formula	C126H176K4O11Ti2	C79H120K2N2O11Ti	C57.5H94Na2O8Ti
mol wt (g mol <sup>-1</sup> )	2118.91	1399.90	1007.22
<i>T</i> (K)	123(2)	123(2)	123(2)
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (#14)	<i>C</i> 2/ <i>c</i> (#15)	<i>C</i> 2/ <i>c</i> (#15)
crystal color	Black	Black	Reddish Brown
crystal size (mm)	$0.41 \times 0.30 \times 0.22$	$0.17 \times 0.14 \times 0.04$	$0.17 \times 0.15 \times 0.02$
<i>a</i> (Å)	23.002(5)	22.0849(6)	42.5729(10)
b (Å)	22.0576(10)	14.9807(4)	15.9089(4)
<i>c</i> (Å)	39.098(8)	47.3336(12)	17.7244(5)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	142.63(4)	91.773(2)	95.135(2)
$\gamma(\text{deg})$	90	90	90
$V(Å^3)$	12041(8)	15652.7(7)	11956.3(5)
Z	4	8	8
$ ho_{ m calc} ({ m g}{ m cm}^{-3})$	1.169	1.188	1.119
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	0.327	0.273	0.206
Abs. Correction type	multi-scan	multi-scan	multi-scan
Reflections collected	126428	65516	47288
Independent reflections (Rint)	27617 (0.1237)	18054 (0.1202)	13671 (0.0502)
$R_1 \left[ I > 2\sigma(I) \right]^a$	0.0669	0.0766	0.0506
w $R_2$ (all data) <sup>b</sup>	0.1523	0.1536	0.1093
Goodness of fit on $F^2$	1.038	1.021	1.014
Largest diff. peak and	0.872 and -0.511	0.474 and -0.418	0.351 and -0.318
hole/e Å-3			

 Table S1. Crystallographic data

(a)  $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ , (b)  $wR_2 = [\Sigma \{w(F_0^2 - F_c^2)^2\} / \Sigma \{w(F_0^2)^2\}]^{0.5}$ 

	5	5-dme	5-dme'
formula	C77H110K2O8Ti	C69H100K2O9Ti	C150H230K4O24Ti2
mol wt (g mol <sup>-1</sup> )	1289.74	1199.61	2669.59
<i>T</i> (K)	123(2)	123(2)	123(2)
crystal system	Monoclinic	orthorhombic	Orthorhombic
space group	P21/c (#14)	P212121 (#19)	<i>Pc</i> (#7)
crystal color	Dark Violet	Bluish Violet	Dark brown
crystal size (mm)	$0.18 \times 0.14 \times 0.14$	$0.20 \times 0.15 \times 0.02$	$0.14 \times 0.02 \times 0.02$
<i>a</i> (Å)	13.6112(9)	17.8325(3)	18.2683(8)
<i>b</i> (Å)	35.8757(6)	18.9575(4)	20.1451(8)
<i>c</i> (Å)	22.0952(15)	40.3110(7)	20.8247(9)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	138.195(13)	90	101.267(4)
$\gamma(\text{deg})$	90	90	90
$V(\text{\AA}^3)$	7192.1(14)	13627.5(4)	7516.1(6)
Z	4	8	2
$\rho_{\text{cale}}$ (g cm <sup>-3</sup> )	1.191	1.169	1.180
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	0.288	0.300	0.281
Abs. Correction type	multi-scan	multi-scan	multi-scan
Reflections collected	81103	155211	91218
Independent reflections (Rint)	16460 (0.0701)	31439 (0.1300)	33702(0.1071)
$R_1 \left[I > 2\sigma(I)\right]^a$	0.0594	0.0716	0.0742
w $R_2$ (all data) <sup>b</sup>	0.1462	0.1450	0.1618
Goodness of fit on $F^2$	1.023	1.017	0.984
Largest diff. peak and	1.385 and -0.748	0.515 and -0.374	1.076 and -0.530
hole/e Å <sup>-3</sup>			

Table S1. Crystallographic data (cont.)

(a)  $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ , (b)  $wR_2 = [\Sigma \{w(F_0^2 - F_c^2)^2\} / \Sigma \{w(F_0^2)^2\}]^{0.5}$ 



**Fig. S2** (a) Structure of **3-K** and (b) structure of one of its dianions with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–O(1) 1.922(2), Ti(1)–O(2) 1.926(2), Ti(1)–O(3) 2.024(2), Ti(1)–C(1) 2.230(4), Ti(1)–C(44) 2.243(4), Ti(1)–C(45) 2.208(4), C(44)–C(45) 1.459(5), C(44)–C(53) 1.446(5), C(45)–C(46) 1.423(5), C(46)–C(47) 1.345(5), C(47)–C(48) 1.428(6), C(48)–C(49) 1.396(6), C(48)–C(53) 1.427(6), C(49)–C(50) 1.356(7), C(50)–C(51) 1.364(7), C(51)–C(52) 1.430(7), C(52)–C(53) 1.414(6), O(1)–Ti(1)–O(2) 142.91(10), O(1)–Ti(1)–O(3) 103.02(10), O(2)–Ti(1)–O(3) 103.29(9), C(1)–Ti(1)–C(44) 166.50(13), C(45)–Ti(1)-C(44) 38.26(13), C(45)–Ti(1)–C(1) 154.67(13)C(45)–C(44)–Ti(1) 69.57(19), C(53)–C(44)–Ti(1) 116.5(3), C(53)–C(44)–C(45) 120.1(4), C(44)–C(45)–Ti(1) 72.17(19), C(46)–C(45)–Ti(1) 115.5(2), C(46)–C(45)–C(44) 116.3(3).



**Fig. S3** Structure of **3-K-(cryptand-222)** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–O(1) 1.919(2), Ti(1)–O(2) 1.985(2), Ti(1)–O(3) 2.001(2), Ti(1)–C(1) 2.226(3), O(1)–Ti(1)–O(2) 123.91(9), O(1)–Ti(1)–O(3) 128.49(9), O(2)–Ti(1)–O(3) 98.08(9), C(1)–Ti(1)–C(44) 157.48(12), C(1)–Ti(1)–C(45) 160.30(13), C(44)–Ti(1)–C(45) 38.38(12), C(45)–C(44)–Ti(1) 71.33(19), C(49)–C(44)–Ti(1) 118.2(2), C(49)–C(44)–C(45) 119.5(3), C(44)–C(45)–Ti(1) 70.29(19), C(46)–C(45)–Ti(1) 107.7(3), C(46)–C(45)–C(44) 116.0(3).



**Fig. S4** Structure of **4-K** with thermal ellipsoids set at 30% probability level. All hydrogen atoms except for those attached to the methylene carbons (C44, C45, C46 and C47) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–O(1) 1.9596(12), Ti(1)–O(2) 2.0579(12), Ti(1)–O(3) 2.0018(12), Ti(1)–C(1) 2.2270(18), Ti(1)–O(4) 1.9040(13), Ti(1)–C(47) 2.1653(19), O(4)–C(44) 1.418(2), C(44)–C(45) 1.504(3), C(45)–C(46) 1.511(3), C(46)–C(47) 1.524(3), O(1)–Ti(1)–O(2) 94.23(5), O(1)–Ti(1)–O(3) 152.24(5), O(3)–Ti(1)–O(2) 93.44(5), O(4)–Ti(1)–O(1) 89.01(5), O(4)–Ti(1)–O(2) 169.89(5), O(4)–Ti(1)–O(3) 88.05(5), C(47)–Ti(1)–C(1) 153.02(7), O(4)–Ti(1)–C(47) 92.23(7), C(44)–O(4)–Ti(1) 126.84(12), O(4)–C(44)–C(45) 112.77(17), C(44)–C(45)–C(46) 114.00(18), C(45)–C(46)–C(47) 114.95(19), C(46)–C(47)–Ti(1) 117.36(14).



**Fig. S5** Structure of **5** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–O(1) 1.9695(17), Ti(1)–O(2) 2.0172(16), Ti(1)–O(3) 1.9647(16), Ti(1)–C(1) 2.247(2), Ti(1)–C(44) 2.515(2), Ti(1)–C(45) 2.361(2), Ti(1)–C(46) 2.393(3), Ti(1)–C(47) 2.583(3), C(44)–C(45) 1.424(3), C(44)–C(49) 1.451(3), C(45)–C(46) 1.380(4), C(46)–C(47) 1.416(4), C(47)–C(48) 1.442(3), C(48)–C(49) 1.445(3), C(48)–C(51) 1.377(3), C(49)–C(50) 1.373(3), C(50)–C(57) 1.434(3), C(51)–C(52) 1.429(4), C(52)–C(53) 1.410(4), C(52)–C(57) 1.421(4), C(53)–C(54) 1.382(4), C(54)–C(55) 1.388(4), C(55)–C(56) 1.380(4), C(56)–C(57) 1.408(3), O(1)–Ti(1)–O(2) 107.05(7), O(3)–Ti(1)–O(1) 131.78(7), O(3)–Ti(1)–O(2) 108.11(7), C(45)–C(44)–C(49) 120.7(2), C(46)–C(47)–C(48) 121.5(2).



**Fig. S6** Structure of **5-dme** with thermal ellipsoids set at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–O(1) 1.915(3), Ti(1)–O(2) 1.952(4), Ti(1)–O(3) 1.996(4), Ti(1)–C(1) 2.256(5), O(1)–Ti(1)–O(2) 123.80(16), O(1)–Ti(1)–O(3) 126.39(15), O(2)–Ti(1)–O(3) 100.07(14), C(1)–Ti(1)–C(44) 158.13(19), C(1)–Ti(1)–C(45) 160.6(2), C(45)–Ti(1)–C(44) 35.7(2), C(45)–C(44)–Ti(1) 67.4(3), C(45)–C(44)–C(49) 123.5(5), C(49)–C(44)–Ti(1) 117.8(4), C(44)–C(45)–Ti(1) 76.8(3), C(46)–C(45)–Ti(1) 99.5(4), C(46)–C(45)–C(44) 114.1(6).



**Fig. S7** Structure of **5-dme'** with thermal ellipsoids set at 30% probability level. There were two crystallographically independent molecules (*Molecular 1* and *Molecular 2*) in the asymmetric unit. The cationic parts ( $[K(dme)_3]^+$  and  $[K(dme)_4]^+$ ) were omitted for clarity. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: (*Molecular 1*): Ti(1)–O(1) 1.958(5), Ti(1)–O(2) 1.968(5), Ti(1)–O(3) 1.986(5), Ti(1)–C(1) 2.252(7), O(1)–Ti(1)–O(2) 115.3(2), O(1)–Ti(1)–O(3) 121.8(2), O(2)–Ti(1)–O(3) 110.76(19), C(30)–C(45)–C(49) 120.2(7), C(46)–C(47)–C(48) 120.8(7), (*Molecular 2*): Ti(2)–O(14) 1.957(5), Ti(2)–O(15) 1.977(5), Ti(2)–O(16) 1.995(5), Ti(2)–C(78) 2.241(7), O(14)–Ti(2)–O(15) 124.4(2), O(14)–Ti(2)–O(16) 116.97(19), O(15)–Ti(2)–O(16) 106.74(19), C(122)–C(121)–C(126) 120.0(7), C(123)–C(124)–C(125) 120.3(7).







**Fig. S9**  $^{13}$ C NMR spectrum of **3-K**.



Fig. S11 <sup>13</sup>C NMR spectrum of **3-Na**.



**Fig. S13**  $^{13}$ C NMR spectrum of **4-K**.







Fig. S15 <sup>13</sup>C NMR spectrum of 4-Na.



**Fig. S16** <sup>1</sup>H NMR spectrum of **5** recorded at 297 K.



**Fig. S17** Variable temperature <sup>1</sup>H NMR spectra of **5**.

### References

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