#### **Supporting Information**

# One-Electron Reduction of Ti(IV) Complex by Dialkylaluminum(I) Anion Giving the Ti(III) Species

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# **Experimental Procedures General Procedure**

All manipulations involving the air- and moisture-sensitive compounds were carried out under an argon atmosphere using glovebox (Korea KIYON) technique. All glasswares were dried for 20 min in the 250 °C oven before use. Toluene and tetrahydrofuran were purified by passing through a solvent purification system (Grass Contour). Hexamethyldisiloxane (TCI) were dried over sodium/potassium alloy, followed by filtering through pad of activated neutral alumina. ESR spectrum was recorded on a JEOL JES-TE200 spectrometer using screw glass tube. ESR simulations were carried out on Isotropic simulation program for JES-X3 series

ESR. Melting points were determined on Optimelt (SRS) and were uncorrected. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer. UV-Vis absorption spectra were recorded on a Shimazu UV-3600 spectrometer using hexane solution of 2 ( $1.52 \times 10^{-2}$  M) with a 1 mm J-young type cell. Tetraalkyldialumane S1 was prepared by according to procedures.<sup>1</sup> Ti(O<sup>*i*</sup>Pr)<sub>4</sub> was purchased (TCI) and used as received.



## Synthesis of 2

In a glovebox, pre-cooled (-35 °C) crystalline tetraalkyldialumane **S1** (40.0 mg, 59.2 µmol) and potassium graphite (41.0 mg, 298 µmol) were placed in a 3 mL vial with a glass stirring bar, then pre-cooled toluene/THF (2.00 mL, v/v = 100/1) was added to the mixture and the resulting suspension was stirred at – 35 °C for 2 days. After the filtration by using a pre-cooled (-35 °C) plastic syringe with glass fiber filter, a red solution of **1** was obtained. To a precooled (-35 °C) toluene (1.00 mL) solution of Ti(O<sup>7</sup>Pr)<sub>4</sub> (51.0 mg, 179 µmol) in a 15 mL vial, the red solution of **1** was added. The resulting dark-green solution was stirred for 3 h at -35 °C. and then volatiles were evaporated under reduced pressure. Recrystallization from hexamethyldisiloxane afforded bright blue crystal of **2** (10.1 mg, 15.3 µmol, 13% yield). Single crystal suitable for X-ray analysis were obtained from hexamethyldisiloxane solution at -35 °C. mp. 100.4-110.2 °C (decomp., the blue color gradually disappeared.); Anal. Calcd for C<sub>28</sub>H<sub>68</sub>AlO<sub>4</sub>Si<sub>4</sub>Ti: C, 51.26; H, 10.45; Found; C, 50.93; H, 10.23.

#### Measurement and simulation of ESR spectrum of 2

In a glovebox, crystals of **2** were dissolved in hexane (1.0 mM) and the resulting solution was pipetted into a quarts ESR tube (5 mm  $\phi$ ). The ESR tube was brought out from glovebox and set to the probe of ESR spectrometer. The spectrum was measured at room temperature. Considering isotopes titanium and aluminum (<sup>47</sup>Ti: *I* = 5/2, g = -1.5105 × 10<sup>7</sup> rad·T<sup>-1</sup>·s<sup>-1</sup>, 7.4%; <sup>49</sup>Ti: I 7/2, g = -1.51095 × 10<sup>7</sup> rad·T<sup>-1</sup>·s<sup>-1</sup>, 5.2%; <sup>27</sup>Al: *I* = 5/2, g = 6.9762715 × 10<sup>7</sup> rad·T<sup>-1</sup>·s<sup>-1</sup>, 100%), the ESR spectral simulation was performed with an assumption of that <sup>47</sup>Ti and <sup>49</sup>Ti have same gyromagnetic ratio and the use of the following spin Hamiltonian.

$$\mathbf{H} = \boldsymbol{\mu}_{\mathbf{B}} \boldsymbol{S} \cdot \boldsymbol{g} \cdot \boldsymbol{B}_{0} + \boldsymbol{A}_{\mathrm{Ti}} \boldsymbol{S} \cdot \boldsymbol{I}_{\mathrm{Ti}} + \boldsymbol{A}_{\mathrm{Al}} \boldsymbol{S} \cdot \boldsymbol{I}_{\mathrm{Al}}$$

where  $\mu_{\rm B}$ , *S*, *g*, and *B*<sub>0</sub> stand for the Bohr magneton, electron spin operator, *g* tensor, and static magnetic field, respectively. *I*<sub>Ti</sub> and *I*<sub>Al</sub> denote the nucleus spin operator. *A*<sub>Ti</sub> and *A*<sub>Al</sub> denote the hyperfine splitting parameter for these nuclei. The hyperfine splitting parameters were estimated by the spectral simulation. The best fitted parameters are shown in caption of Figure 4. The simulated spectrum shown in Figure 4 is in good agreement

with the observed one. The DFT-calculated spin density on Ti and Al atoms (1.12 for Ti, 0.11 for Al; Ti:Al = 0.91:0.09) in **2** supported this observation of ESR spectrum (Ti:Al = 87%:13%).

### **Details for crystallography**

Crystallographic data for **2** are summarized in Table S1. The crystal was coated with Paratone-N (Hampton Research) and put on a MicroMount<sup>TM</sup> (MiTeGen, LLC), and then mounted on diffractometer. Diffraction data were collected on a Rigaku HyPix-6000 detector using MoK $\alpha$  radiation ( $\lambda = 0.7103$  Å). The Bragg spots were integrated using the CrysAlis<sup>Pro</sup> program package.<sup>2</sup> Absorption corrections were applied. All structures were solved by the *SHELXT* program. Refinement on  $F^2$  was carried out by full-matrix least-squares using the *SHELXL* in the *SHELXT* program. Refinement on  $F^2$  was carried out by full-matrix least-squares using the *SHELXL* in the *SHELXT* software package<sup>3</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were assigned to idealized geometric positions and included in the refinement with isotropic thermal parameters. The *SHELXL* was interfaced with Yadokari-XG<sup>4</sup> for most of the refinement steps. The pictures of molecules were prepared using ORTEP-III for Windows.<sup>5</sup> The detailed crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC- 1987277 (**2**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/products/csd/request **Table S1.** Crystallographic data for **2**.

	2
CCDC #	1987277
Empirical formula	C <sub>28</sub> H <sub>68</sub> AlO <sub>4</sub> Si <sub>4</sub> Ti
Formula weight	656.06
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> /c
Т (К)	93(2)
Color	blue
Habit	plate
a (Å)	16.5554(6)
b (Å)	16.4771(6)
c (Å)	14.2768(5)
α (°)	90
β (°)	93.792(3)
γ (°)	90
V (Å <sup>3</sup> )	3886.0(2)
Z	4
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.121
Abs. coeff (mm <sup>-1</sup> )	0.394
F(000)	1436
Crystal size (mm)	0.18×0.12×0.01
heta range (°)	1.746–30.560°
Refins collected	37595
Indep refins/R <sub>int</sub>	9695/0.0695
Parameters	363
GOF on F <sup>2</sup>	1.024
R1, wR2 [ <b>/</b> >2σ( <b>/</b> )]	0.0563, 0.1154
$R_1$ , w $R_2$ (all data)	0.0977, 0.1282

### **Computational Details**

Gaussian 16 (rev. B.01)<sup>6</sup> software package was employed to perform all of the calculations. The full model of **2** was optimized from the crystallographically obtained structure at the UB3LYP<sup>7</sup> level of theory using LanL2DZ<sup>8</sup> (for Ti) and  $6-31+g(d)^9$  (for others) basis sets. The TD-DFT<sup>10</sup> calculations were performed to estimate UV-vis spectrum of **2** with UPBEh1PBE<sup>11</sup> level of theory using LanL2DZ<sup>8</sup> (for Ti) and  $6-31+g(d)^9$  (for others) basis sets.



Figure S1. A simulated UV-Vis spectrum for 2 at UPBEh1PBE level of theory.

 Table S2. Excitation energies and oscillator strength for 2 obtained from TD-DFT calculations

 Excited State
 1:
 2.002-A
 1.1606 eV 1068.23 nm
 f=0.0000
 <S\*\*2>=0.752

 175A ->176A
 0.97844

 175A ->178A
 -0.14512

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -2865.54084671

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State	2:	2.003-A	1.7395 eV	712.74 nm	f=0.0006	<s**2>=0.753</s**2>
175A ->177	7A	0.53515				
175A ->180	)A	-0.15332				
175A ->183	3A	0.74701				
175A ->184	A	0.11480				
175A ->189A		0.12938				
175A ->196	δA	0.14791				
Excited State	3:	2.003-A	1.9653 eV	630.87 nm	f=0.0000	<s**2>=0.753</s**2>
175A ->178A		-0.56322				

## 175A ->179A 0.78595

Excited State 4: 2.004-A 1.9856 eV 624.41 nm f=0.0014 <S\*\*2>=0.754 175A ->177A 0.59280 175A ->180A 0.62548 175A ->182A 0.33856 175A ->183A -0.30360



Figure S2. Transition-related orbitals of 2

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