

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

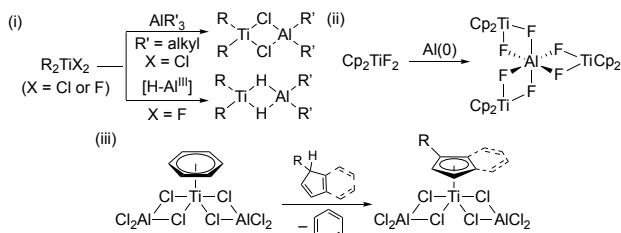
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**ABSTRACT:** A reaction of dialkylaluminumpotassium with Ti(O'Pr)<sub>4</sub> was investigated. The alumanyl anion worked as a reducing reagent to afford the trivalent titanium complex as a contact ion pair with aluminate anion probably via single electron transfer. The ESR spectrum revealed the delocalization of an unpaired electron over Ti and Al atoms. The DFT calculations provided information about the ratio of unpaired electron on Ti and Al atoms and the UV-vis absorption spectrum.

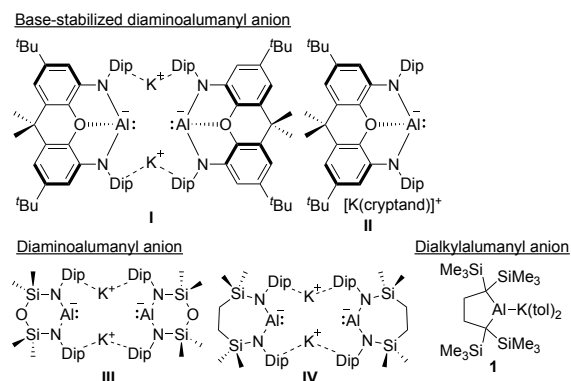
Titanium complexes in low-oxidation state, such as (III) and (II), are widely used for catalytic and stoichiometric reactions in synthetic organic chemistry and polymer chemistry,<sup>1</sup> such as olefin polymerization,<sup>2</sup> exo-olefination of carbonyl compounds,<sup>3</sup> McMurry coupling,<sup>4</sup> and cycloaddition of unsaturated compounds.<sup>5</sup> Although titanium(III) complexes should have an unpaired electron in their d-orbital to lead difficulty of characterization,<sup>6</sup> aluminum-containing titanium(III) complexes have been studied in detail because of their importance as an intermediate for Ziegler-Natta catalysts<sup>2</sup> and Tebbe reagent.<sup>3</sup> These aluminum-containing titanium(III) complexes have been synthesized by the following three methods (Scheme 1): (i) reaction of titanium(IV) dichloride with trialkylaluminum<sup>7</sup> or aluminum hydride,<sup>8</sup> (ii) one-electron reduction of titanocene difluoride by elemental aluminum,<sup>9</sup> and (iii) oxidation of chloride-bridged titanium(II) complex by using cyclopentadiene derivatives.<sup>10</sup>

**Scheme 1.** Synthesis of aluminum-containing titanium(III) complexes.



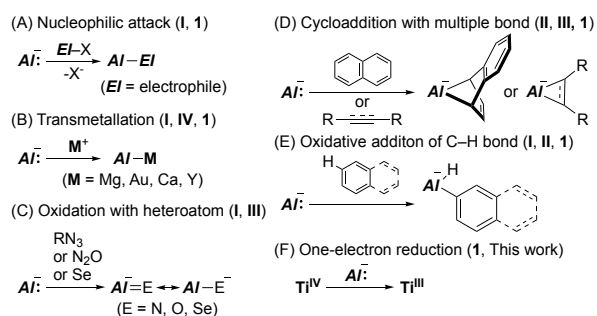
On the other hand, anionic aluminum(I) species I-IV and **1** have emerged in last three years (Figure 1).<sup>11</sup> Confirmed reactivity of these anionic aluminum(I) species can be classified into five types. Based on the lone pair electrons on the Al atom, these species can act as a nucleophile toward electrophiles (Scheme 2A).<sup>11a, 11g, 11i</sup> Nucleophilic transmetalation of alumanyl anion moiety to the other metals afforded the corresponding alumanylmetal species (Scheme 2B).<sup>11a, 11b, 11g, 11k</sup> Because of the low-oxidation state of anionic aluminum(I) species, these anionic alumanyl species can be easily oxidized to form Al-heteroatom bond (Scheme 2C).<sup>11d, 11f, 11h, 11l</sup> They also can undergo (1+2) or (1+4) cycloaddition reaction at the Al center (Scheme 2D).<sup>11c, 11e, 11h, 11j</sup> Oxidative addition with C-H bond at the Al center was also possible to give

(hydrido)(carbyl) species (Scheme 2E).<sup>11a, 11c, 11i</sup> The strongly nucleophilic Al center due to electropositive character of aluminum in these alumanyl anion species would be expected to behave as one-electron reductant. Herein, we report the reaction of dialkylaluminumpotassium **1** with titanium tetraisopropoxide furnishing Ti(III) complex **2** through one-electron transfer reaction (Scheme 2F). The resulting open-shell Ti(III) species was characterized by a single-crystal X-ray diffraction analysis, ESR spectroscopy, and UV-Vis absorption spectroscopy. The unique electronic structure of **2** was also evaluated by DFT calculations.



**Figure 1.** Examples of anionic aluminum(I) species I-IV and **1** (Dip = 2,6-diisopropylphenyl)

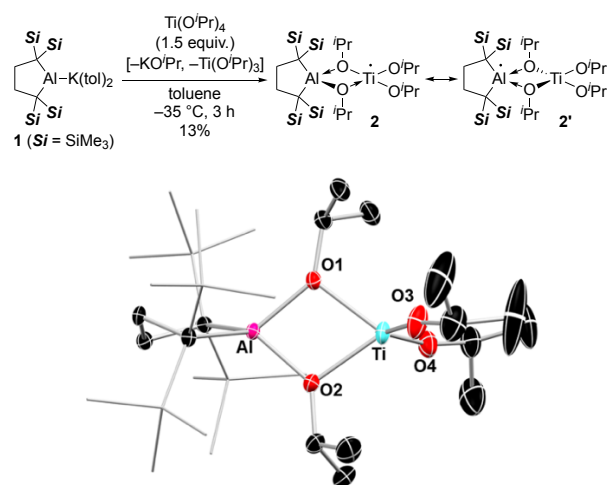
**Scheme 2.** Reactivity of I-IV and **1**



The reaction of *in-situ* generated dialkylaluminumpotassium **1**<sup>11j</sup> with 1.5 equivalent Ti(O'Pr)<sub>4</sub> furnished (dialkoxy)(dialkyl)aluminate-stabilized cationic titanium(III) diisopropoxide **2** as a blue crystalline solid (Scheme 3). It should be noted that the reaction with 2 equivalent of Ti(O'Pr)<sub>4</sub> led to a lower yield probably due to the subsequent reaction giving byproducts. One can speculate that the reaction of **1** with Ti(O'Pr)<sub>4</sub> would induce one-electron reduction of Ti(IV) with no formation of Al-Ti bond to liberate KO'Pr, Ti(O'Pr)<sub>3</sub>, and dialkyl-Al(II)

radical species, which would further react with another  $\text{Ti}(\text{O}^i\text{Pr})_4$  molecule to furnish **2**. As an alternative mechanism, an initial formation of Al–Ti bond followed by its redox reaction with  $\text{Ti}(\text{O}^i\text{Pr})_4$  would also explain the formation of **2**. Since **2** is NMR-silent, the structure of **2** was unambiguously confirmed as a contact ion pair between Ti(III) and aluminate anion by a single-crystal X-ray diffraction analysis (Figure 2). Considering the stoichiometry of the reaction, potassium isopropoxide and titanium(III) isopropoxide would be eliminated from the reaction mixture. Thus, the present reaction would proceed probably via a single electron transfer from anionic aluminum(I) species. In the crystal structure of **2**, the sum of the internal angles in the Al–O–Ti–O four-membered ring is  $359.99^\circ$ , indicating its planarity. Table 1 shows the structural comparison of **2** with known titanium(IV) tetraadamantoxide **3**,<sup>12</sup> six-coordinate titanium(IV) dialkoxide complex **4** coordinated by two four-coordinate aluminum alkoxides,<sup>13</sup> and titanium(IV) tetraisopropoxide-aluminum complex **5**.<sup>14</sup> In the complex **2**, two terminal Ti–O bonds [1.786(2), 1.794(2)] are slightly longer than those of reported Ti(IV) complexes **3–5** [1.737(2)–1.766(2) Å], probably due to smaller  $p\pi$ - $d\pi$  interaction in Ti(III) species **2**. Two Ti–O bonds for the bridging alkoxide [2.0436(18), 2.0434(17) Å] are longer than the terminal Ti–O bond in **2** as expected. These Ti–O bonds for bridging alkoxide in **2** are in the range for those of **4** and an Al–O coordinating bond in **5**. Two O–Al bonds [1.8395(18), 1.8506(18) Å] in **2** are longer than the O–Al bonds for bridging alkoxide in **4** and the O–Al coordination bond in **5**, indicating double Al–O–Ti bridges would lead a larger steric repulsion between substituents. Probably due to the conformational rigidity of the Al-containing five-membered ring in **2**, the O–Ti–O angle for terminal alkoxide are larger than those of **3–5** and the O–Ti–O angle for bridging alkoxide are smaller than that of **4**.

### Scheme 3. Reaction of **1** with titaniumtetraisopropoxide



**Figure 2.** Molecular structure of **2** (thermal ellipsoids set at 50% probability; all hydrogen atoms are omitted and trimethylsilyl groups are displayed in a wireframe view for clarity).

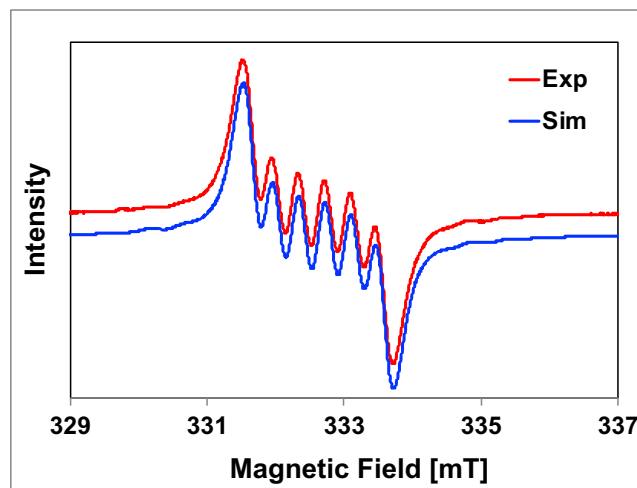
**Table 1.** Selected bond distances (Å) and angles ( $^\circ$ ) of **2** and Ti-containing reference compounds **3–5**.

cpd	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Ti–O	1.786(2)	1.737(2)	1.766(1)	1.739(2)

	1.789(2)	1.766(2)		1.741(2)
Ti–O	2.0436(18) 2.0434(17)	-	2.130(1) 2.039(1)	1.979(2)
O–Al	1.8395(18) 1.8506(18)	-	1.814(1) 1.786(1)	1.834(2)
O–Ti–O	117.31(10)	92.0(7) <sup>a</sup> ~ 117.1(7) <sup>a</sup>	99.39(10)	109.9(1)~ 110.9(1)
O–Ti–O	72.00(7)	-	84.38(6)	-

<sup>a</sup> Positional disorder of oxygen atom prevents accurate comparison.

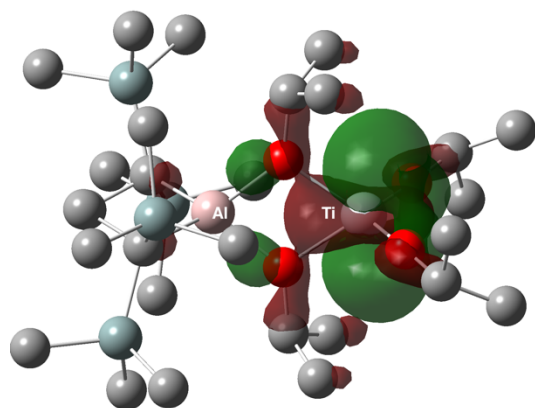
To reveal the property of the unpaired electron in **2**, ESR spectrum was recorded in hexane solution at room temperature (Figure 3). A sextet-like signal was observed at  $g = 1.9635$ . A simulated spectrum with a hyperfine splitting by Ti and Al atoms ( $A[^{47}\text{Ti}] = 0.54$  mT,  $A[^{49}\text{Ti}] = 0.54$  mT,  $A[^{27}\text{Al}] = 0.38$  mT) showed a good agreement with experimental data. The result indicates that the unpaired electron mainly exists on the Ti atom (Ti: 87%, Al: 13%). Considering the distribution of spin density on the Al atom, a minor resonance structure **2'** (Scheme 3) would contribute the electronic property of **2**. The hyperfine coupling with  $^{27}\text{Al}$  nucleus in **2** is close to the lower end of the range of the previously reported values (0.23–2.25 mT) for chloride- or hydride-bridging Ti–Al systems **6–9**.<sup>8a, 10, 15</sup> Strong bridging between Ti and Al nuclei with chloride (two 2c–2e bonds) or hydride (two 2c–3e bonds with a short Ti–Al distance) would contribute to the electron-nuclear spin coupling. In contrast, a similar titanium(III) complex,  $\text{Cp}_2\text{Ti}(\text{Cl}_2\text{AlMe}_2)$ , having dichlorodimethylaluminate anion did not show hyperfine splitting to the  $^{27}\text{Al}$  nucleus in the ESR spectrum.



**Figure 3.** Observed ESR spectrum of **2** in hexane at room temperature (red line) and simulated ESR spectrum (blue) using  $g = 1.9635$ ,  $A[^{47}\text{Ti}] = 0.54$  mT,  $A[^{49}\text{Ti}] = 0.54$  mT,  $A[^{27}\text{Al}] = 0.38$  mT, Line width = 0.33 mT

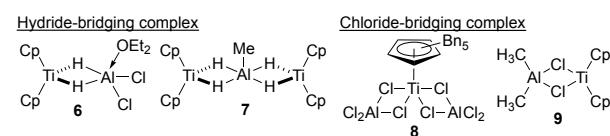
The electronic structure of **2** was also confirmed by DFT calculations. The SOMO is mainly located on the Ti atom with a small contribution of the Al atom (Figure 4). The ratio (Ti: 91%, Al 9%) of the calculated spin density on the Ti (1.12) and the Al (0.11) atoms in **2** is in good agreement with the ratio of the spin density derived from the experimental ESR data (*vide supra*). To clarify the character of SOMO, the UV-Vis absorption spectrum of **2** in hexane was measured (Figure 5). The characteristic absorption at 621 nm ( $\epsilon = 29$ ) and 903 nm ( $\epsilon = 11$ ) with a low intensity were observed to reflect the intense blue color of **2**. The TD-DFT calculations (for details, See SI) provided an assignment of the absorption at 621 nm as transitions from SOMO to LUMO+1, LUMO+4, and LUMO+6 (624 nm,  $f = 0.0014$ ). Although the absorption at 903 nm could not be clearly assigned, one weak absorption (721 nm,  $f = 0.0006$ ) and one forbidden absorption (1068 nm,  $f = 0.0000$ )

were simulated. One can expect the flexibility of alkyl groups in **2** would break a symmetry of molecular orbitals to lead the weak absorption according to the transition from SOMO to LUMO (See SI for details, Table S2).



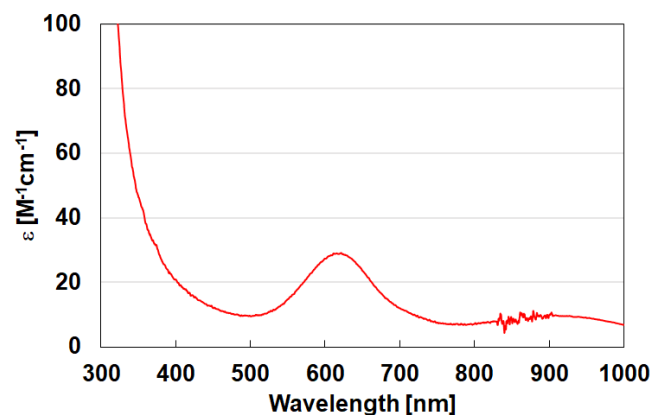
**Figure 4.** SOMO of **2** at the UB3LYP level of theory using LANL2DZ (for Ti) and 6-31+g(d) (all other atoms) basis sets.

**Table 2.** Structural and ESR spectroscopic comparison of **2** with isolated Al-containing Ti(III) complexes showing hyperfine coupling to a  $^{27}\text{Al}$  nucleus ( $A[^{27}\text{Al}]$ ).



cpd	<b>2</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>
Ti---Al (Å)	3.0534(9)	2.745(5)	2.771(4)	3.48(1)	3.1815(8) <sup>a</sup>
$A[^{27}\text{Al}]$ (mT)	0.38	1.04	0.38	0.54	0.23
multiplicity	sextet	- <sup>b</sup>	octet <sup>c</sup>		- <sup>b,c</sup>

<sup>a</sup>disordered with  $\text{CH}_3, \text{Cl}$ -bridging complex, <sup>b</sup>not reported, <sup>c</sup>unresolved



**Figure 5.** The UV-Vis absorption spectra of **2** in hexane [ $\lambda_{\text{max}}(\epsilon) = 621(29), 903(11) \text{ nm}$ ].

In conclusion, the reaction of dialkylaluminumpotassium **1** with titanium tetraisopropoxide was investigated. The aluminyl anion **1** worked as a reducing reagent to afford the trivalent titanium complex **2** as a contact ion pair with aluminate anion via single electron transfer from **1** to titanium tetraisopropoxide. The ESR spectrum of **2** revealed the delo-

calization of an unpaired electron over Ti and Al atoms. The DFT calculations of **2** provided information about the ratio of unpaired electron on Ti and Al atoms and the UV-vis absorption spectrum.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.

Experimental and computational details (PDF)

Crystallographic data (CIF)

Cartesian Coordinates obtained by DFT calculations (XYZ)

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### Notes

The authors declare no competing financial interests.

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