

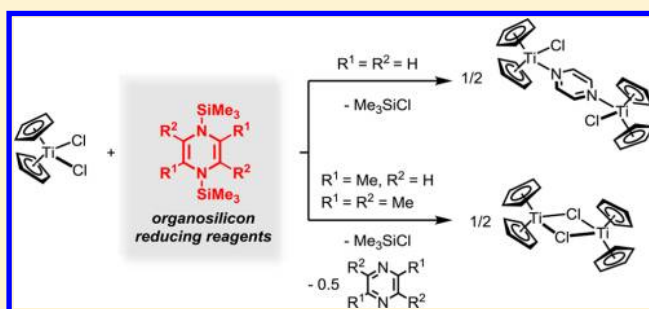
# 1,4-Bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadienes as Strong Salt-Free Reductants for Generating Low-Valent Early Transition Metals with Electron-Donating Ligands

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## S Supporting Information

**ABSTRACT:** Electron-rich organosilicon compounds, such as 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**2a**), 2,5-dimethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**2b**), 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**2c**), and 1,1'-bis(trimethylsilyl)-1,1'-dihydro-4,4'-bipyridine (**4**), served as versatile reducing reagents of group 4–6 metal chloride complexes, such as  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{Cp}^*\text{TiCl}_2$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ),  $\text{Cp}^*\text{TiCl}_3$ ,  $\text{Cp}^*\text{TaCl}_4$ , and  $\text{WCl}_4(\text{PMe}_2\text{Ph})_2$ , to generate the corresponding low-valent metal species in a salt-free manner. Nitrogen-containing reductants, such as **2a–c** and **4**, had stronger reducing ability than the parent organosilicon reductants, 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (**1a**) and 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (**1b**), as well as a pyridine-derived reductant, 1,4-bis(trimethylsilyl)-1-aza-2,5-cyclohexadiene (**3**). These greater effects of **2a–c** and **4** are likely due to their negative one-electron redox potentials, as typically demonstrated in the reduction of  $\text{Cp}_2\text{TiCl}_2$ , for which compounds **2a** and **4** gave the corresponding one-electron reduced products, pyrazine-bridged and 4,4'-bipyridyl-bridged dimeric Ti(III) complexes **5** and **6**, and compounds **2b** and **2c** afforded the same double chloride-bridged dimeric Ti(III) complex,  $[\text{Cp}_2\text{Ti}]_2(\mu\text{-Cl})_2$  (**7**), though **1a** and **1b** could not reduce  $\text{Cp}_2\text{TiCl}_2$ . Application of the organosilicon compounds as reducing agents for catalytic reactions revealed that the combination of **2c** and a catalytic amount of  $\text{Cp}_2\text{TiCl}_2$  assisted a Reformatsky reaction of nonanal and ethyl 2-bromoisobutyrate and its derivatives to give ethyl 3-hydroxy-2,2-dimethylundecanoate and its derivatives. In this coupling reaction, **2c** served as the best reductant among **2a–c** and **4** due to the suppression of an undesired reaction between **2c** and ethyl 2-bromoalkanoates.

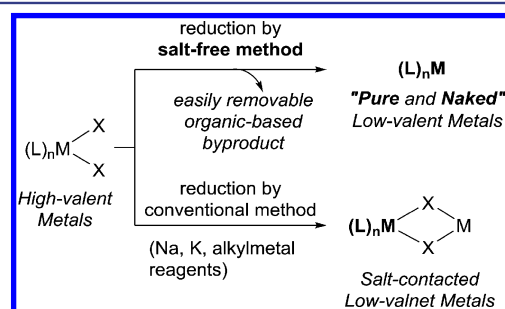


## INTRODUCTION

Low-valent species of early transition metals continue to attract great interest due to their high versatility as stoichiometric reagents and catalysts that mediate various bond-forming reactions as well as small-molecule activations.<sup>1–7</sup> Because early transition metals favorably accept their highest oxidation state and have a potentially Lewis acidic and oxophilic nature, powerful reducing reagents such as alkaline and alkaline-earth metal amalgams, alloys, and naphthalenides, along with their alkyl reagents, are required to generate low-valent early transition metal species.<sup>8</sup> A long-standing practical problem, however, is that contamination by reductant-derived salts and over-reduced impurities hampers the isolation of the desired low-oxidation state compounds in pure form and often retards their intrinsic reactivity as reagents and catalysts due to the formation of salt-contacted coordinatively saturated species.<sup>9</sup> In particular, typical low-oxidation state titanocene-catalyzed pinacol coupling reactions are affected by the interaction of low-valent titanocene with reductant-derived metal salts.<sup>3e,10</sup> Thus, to elucidate the original and intrinsic reactivity of “pure” naked metal centers with a controlled low-oxidation state, the development of a

reduction method without concomitant reductant-derived metal salts is highly desired (Figure 1).

Various approaches were developed to eliminate reductant-derived metal waste contamination, the most effective of which is



**Figure 1.** Reduction of high-valent metal species of early transition metals.

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the use of organic compounds as reductants for early transition metal complexes due to easy removal of the byproducts during the reduction process by washing with organic solvents or evaporating under high vacuum. Notably, unsaturated hydrocarbons, such as internal alkynes and alkenes are used for the reduction of  $WCl_6$  and  $MoCl_5$ , in which easily removable chloroalkenes or chloroalkanes are generated in the reduction process.<sup>11,12</sup> Theopold and Schrock reported the synthesis of alkyne- $W(IV)$  complexes,  $W(C_2R_2)Cl_4$ , in which alkynes function as both the ligand and reductant.<sup>12</sup> This methodology, however, is limited to only group 6 metals. In addition, although hexamethyldisilane is used as a one-electron reductant for  $TiCl_4$  with generation of an easily removable  $Me_3SiCl$ , other early transition metal halides were inactive to  $Me_3Si-SiMe_3$ .<sup>13</sup>

As a new approach to the organic-based reduction of early transition metals, we recently reported that 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (BTCD, **1a**, Figure 2) and 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (MBTCD, **1b**, Figure 2) serve as unique reducing reagents of early transition metal chlorides,<sup>14</sup> reductions in which the byproducts are easily removable  $Me_3SiCl$  and the corresponding aromatic compounds, e.g., benzene and toluene. Although these organosilicon reagents are effective for generating highly reactive low-valent species of tantalum, niobium, and tungsten from the corresponding metal chlorides, they do not reduce any halide complexes of early transition metals bearing electron-donating  $\pi$ -ligands, such as cyclopentadienyl (Cp) and trialkylphosphines, which are mostly reliable  $\pi$ -ligands for stabilizing early transition metals in a low oxidation state. Herein, we report a new family of organosilicon compounds, 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**2a**) and its derivatives as strong reducing reagents, by which  $Cp_2TiCl_2$ ,  $Cp^*_2TiCl_2$  ( $Cp^* = \eta^5-C_5Me_5$ ),  $Cp^*TiCl_3$ ,  $Cp^*TaCl_4$ , and  $WCl_4(PMe_2Ph)_2$  were reduced in a salt-free manner. We further describe an attractive application for generating low-valent titanocene species upon combination with silicon reagents to a catalytic Reformatsky reaction of nonanal and ethyl 2-bromoalkanoates without forming reductant-derived metal waste. In this coupling reaction, sterically hindered tetramethylpyrazine-derived reductant **2c** served as the best reductant due to the suppression of an undesired reaction between **2c** and ethyl 2-bromoalkanoates.

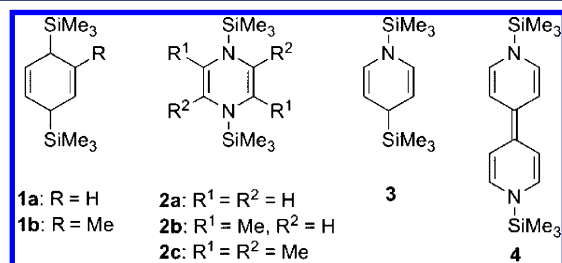


Figure 2. Series of organosilicon compounds 1–4.

## RESULTS AND DISCUSSION

**Redox Potential and Ionization Energy of Organosilicon Reagents 1–4.** In our search for organosilicon compounds with the same advantages (no salt formation) of **1a,b** and that overcome their limitation of being unable to reduce halide complexes bearing any electron-donating ligands, we modified these organosilicon compounds **1a,b** based on the first vertical ionization energies ( $IE_v$ ),<sup>15</sup> which is a good indicator of reducing ability. Because the highest occupied molecular orbital

levels of 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadienes (**2a**) and its derivatives **2b,c**, 1,4-bis(trimethylsilyl)-1-aza-2,5-cyclohexadiene (**3**), and 1,1'-bis(trimethylsilyl)-1,1'-dihydro-4,4'-bipyridine (**4**) are higher than that of **1a,b**, we reasoned that these compounds would act as strong reducing reagents capable of generating low-valent species of early transition metals with electron-donating ligands. Compounds **2a–c**, **3**, and **4** were prepared by reducing the corresponding heteroaromatic compounds with appropriate alkali metals in the presence of excess amounts of  $Me_3SiCl$  according to a protocol modified from the literature.<sup>16</sup> In association with such a one-electron reduction pathway, we measured the oxidation potential of **1–4** with cyclic voltammetry in  $CH_2Cl_2$  containing  $[^nBu_4N][PF_6]$  (0.1 M) as an electrolyte at room temperature, revealing that the single-electron redox potentials ( $E_{1/2}$ ) of **2a–c** and **4** were negatively shifted compared with those of **1a,b** and **3** (Figure 3).

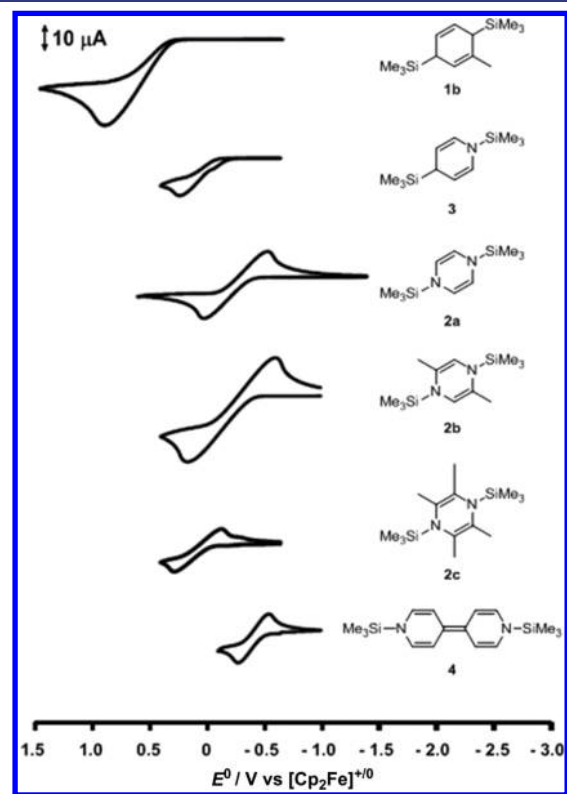
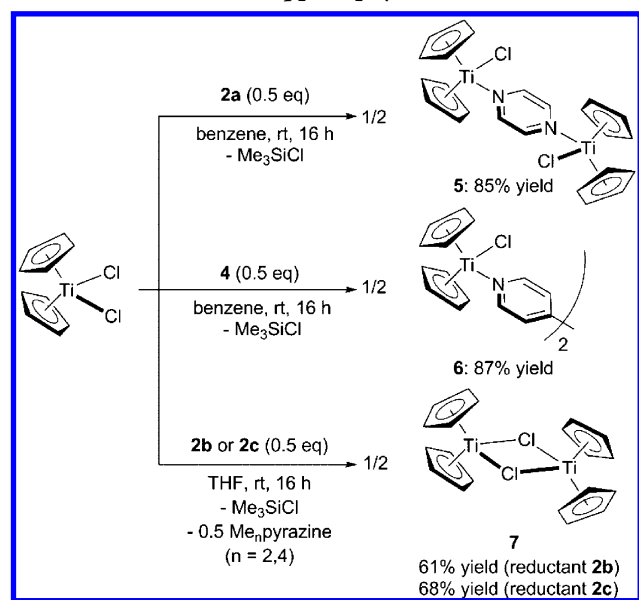


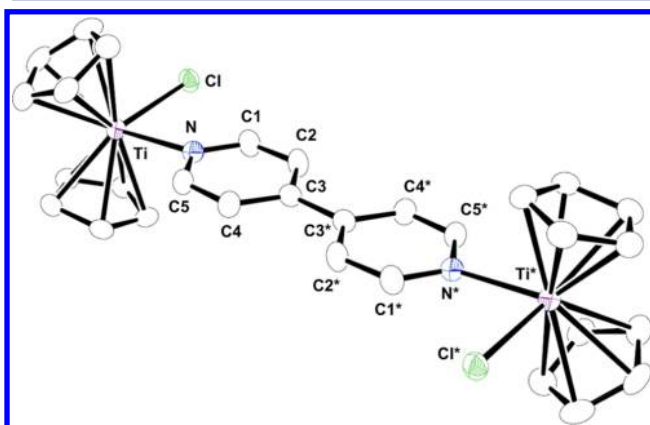
Figure 3. Cyclic voltammogram of organosilicon compounds **1b**, **2a–c**, **3**, and **4** in  $CH_2Cl_2$  ( $[organosilicon] = 5$  mM,  $[^nBu_4N][PF_6] = 0.1$  M, scan rate = 100 mV/s). Redox potential ( $E_{1/2}$ ) of the organosilicon compounds: + 0.83 V (**1b**, anodic peak potential), − 0.24 V (**2a**), − 0.21 V (**2b**), + 0.10 V (**2c**), + 0.25 V (**3**, anodic peak potential), and − 0.40 V (**4**).

Among **2a–c**, cyclic voltammetry measurements showed almost equal redox potentials of **2a** (−0.24 V vs  $Fc^+/Fc$ ) and **2b** (−0.21 V vs  $Fc^+/Fc$ ); however, that of **2c** was observed as an reversible wave at +0.10 V vs  $Fc^+/Fc$ , positive by ~0.3 V compared to **2a** and **2b**. Compound **4** showed the most negative redox-potential value at −0.40 V vs  $Fc^+/Fc$  as a reversible wave.

**Reduction of Titanocene and Half-Titanocene Complexes.** We examined nitrogen-containing cyclohexadiene derivatives **2a–c** and **4** for their ability to reduce a widely used early transition metal complex, titanocene dichloride ( $Cp_2TiCl_2$ ), and the results are summarized in Scheme 1. In benzene solution, compounds **2a** and **4** reacted with  $Cp_2TiCl_2$  in

Scheme 1. Reduction of  $\text{Cp}_2\text{TiCl}_2$  by 2a–c and 4

a one-electron reduction, as evidenced by the amounts of  $\text{Me}_3\text{SiCl}$  (1.0 equiv to Ti) and coordinated heteroaromatic compounds (0.5 equiv to Ti), to respectively give a pyrazine-bridged dimeric Ti(III) complex 5 in 85% yield and a 4,4'-bipyridyl-bridged dimeric Ti(III) complex 6 in 87% yield.<sup>17</sup> The structure of complex 6 was confirmed by X-ray diffraction analysis (Figure 4). Both titanium centers adopt an oxidation

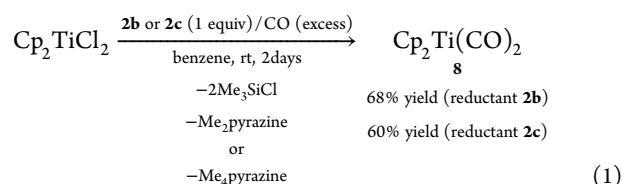


**Figure 4.** Molecular structure of complex 6 with 30% thermal ellipsoids. The hydrogen atoms and solvent are omitted for clarity. Selected bond distances (Å) and angles (deg.): Ti–Cl, 2.5047(13); Ti–N, 2.339(4); N–C1, 1.335(5); C1–C2, 1.391(8); C2–C3, 1.394(7); C3–C3\*, 1.494(7); C3–C4, 1.401(5); C4–C5, 1.371(8); C5–N1, 1.359(6); N–Ti–Cl, 85.80(9).

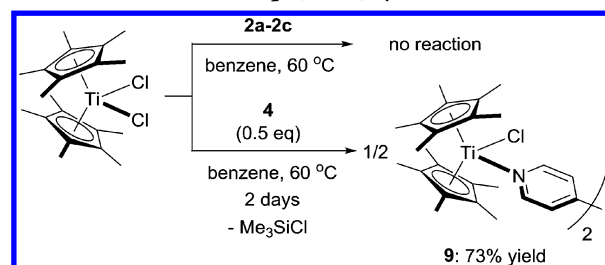
state of +3. The bond distance of Ti–N (2.339(4) Å) is almost the same as that of Ti(III)–nitrogen dative bonds.<sup>18</sup> In addition, because the C3–C3\* bond length (1.494(7) Å) is assignable to a C–C single bond, the pyridine moieties of 4,4'-bipyridyl are fully aromatized, and two titanium centers are bridged by a neutral 4,4'-bipyridyl ligand. When two and four methyl groups were introduced into the 1,4-diazacyclohexadiene rings of 2b and 2c, reduction under the same condition was very slow compared with reduction using 2a and 4 because of the steric repulsion between approaching 2b and 2c and the metal center of  $\text{Cp}_2\text{TiCl}_2$ . In an aprotic polar solvent, such as THF, to enhance

the electron transfer process from the reductants to the metal center, the reduction of  $\text{Cp}_2\text{TiCl}_2$  by 2b or 2c smoothly proceeded to give a double chloride-bridged dimeric Ti(III) species,  $[\text{Cp}_2\text{Ti}]_2(\mu\text{-Cl})_2$  (7),<sup>19</sup> in 61% and 68% yield, respectively. The methylated pyrazine, i.e. 2,5-dimethylpyrazine ( $\text{Me}_2\text{pyrazine}$ ) and 2,3,5,6-tetramethylpyrazine ( $\text{Me}_4\text{pyrazine}$ ), could not coordinate to the metal center due to steric hindrance around the nitrogen atom. Cyclohexadiene- and azacyclohexadiene-derived reductants 1a,b and 3 were completely inactive for the reduction of  $\text{Cp}_2\text{TiCl}_2$ .

We further applied nitrogen-containing organosilicon reductants to the synthesis of a carbonyl complex of titanocene. Treatment of  $\text{Cp}_2\text{TiCl}_2$  with 1 equiv of 2b and 2c under atmospheric pressure of CO resulted in the formation of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  (8) in 68% and 60% yield, respectively, as a consequence of the disproportionation of  $\text{Cp}_2\text{TiCl}(\text{CO})$  in the mixture of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  and  $\text{Cp}_2\text{TiCl}_2$ ,<sup>20</sup> while reactions with 2a and 4 did not afford 8 under the same conditions due to the formation of 5 and 6 (eq 1).

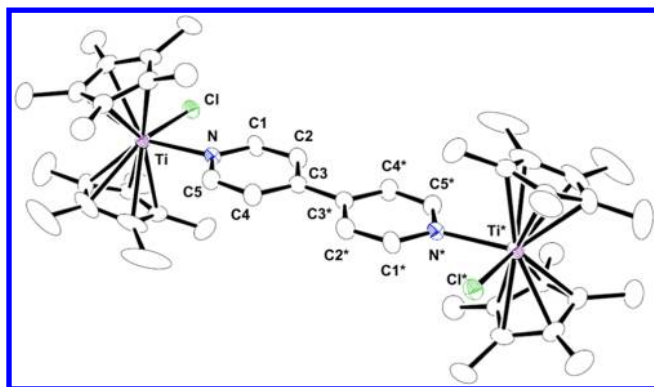


Redox potentials of the metal complexes are an important factor for the applicability of 2–4 as reductants. Decamethyltitanocene dichloride,  $\text{Cp}^*\text{TiCl}_2$ , is more difficult to reduce to the Ti(III) species because of the negatively shifted redox potentials compared to  $\text{Cp}_2\text{TiCl}_2$  ( $E_{1/2}(+/+3) = -1.62$  V for  $\text{Cp}^*\text{TiCl}_2$  vs  $-1.33$  V for  $\text{Cp}_2\text{TiCl}_2$ ).<sup>21</sup> When  $\text{Cp}^*\text{TiCl}_2$  was treated with 2a–c in  $\text{C}_6\text{D}_6$ , the reduction did not proceed even by heating the reaction mixture at 60 °C for 2 days. On the other hand, compound 4, which showed the most negative redox potential among 2–4, could reduce  $\text{Cp}^*\text{TiCl}_2$  upon heating at 60 °C for 2 days to form a 4,4'-bipyridyl-bridged dimeric Ti(III) complex 9 as blue crystals (Scheme 2 and Figure 5), suggesting that the redox potential of the organosilicon compounds strongly influenced the reducing ability, and electron transfer from the organosilicon compounds to the metal center is crucial for the reduction. The structure of complex 9 was essentially the same as that of complex 6, indicating that the structural feature of the 4,4'-bipyridyl bound to two titanium centers is the same as that of 6, typically a C3–C3\* bond length (1.494(7) Å) being equal, and the oxidation state of each titanium center was +3.

Scheme 2. Reduction of  $\text{Cp}^*\text{TiCl}_2$  by 2a–c and 4

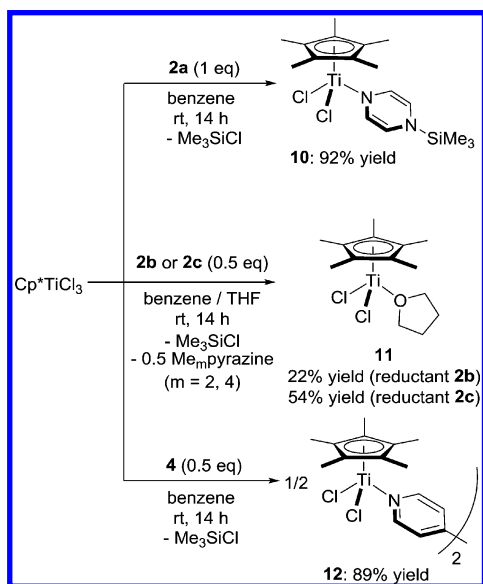
We examined the reduction of half-titanocene titanium complex,  $\text{Cp}^*\text{TiCl}_3$ . As outlined in Scheme 3, the reaction of  $\text{Cp}^*\text{TiCl}_3$  with 2a did not afford any Ti(III) complex; however, a Ti(IV) complex 10 was isolated in 92% yield. Around the titanium center of 10, one  $\text{Cp}^*$ , two chlorides, and an amido ligand derived from 2a were attached. Relevant to the reaction mechanism, complex 10 was a unique product where a one-electron





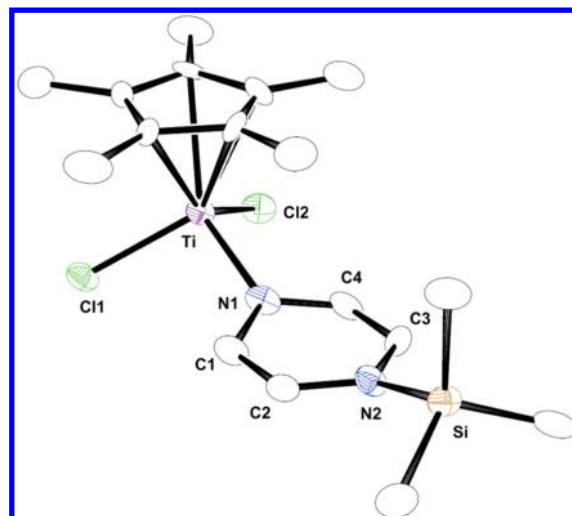
**Figure 5.** Molecular structure of complex **9** with 30% thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg); Ti–Cl, 2.4872(9); Ti–N, 2.278(3); N–C1, 1.351(4); C1–C2, 1.387(5); C2–C3, 1.393(4); C3–C3\*, 1.494(7); C3–C4, 1.389(5); C4–C5, 1.378(5); C5–N1, 1.352(4); N–Ti–Cl, 85.32(7).

**Scheme 3. Reactions of Half-Titanocene Trichloride,  $\text{Cp}^*\text{TiCl}_3$ , with **2a–c** and **4****



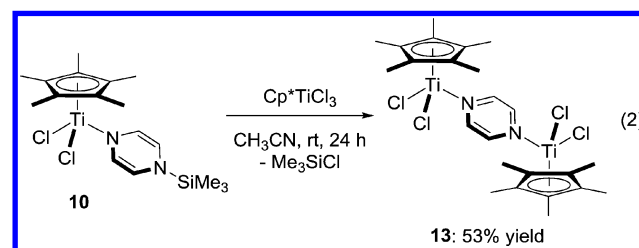
reduced species  $\text{Cp}^*\text{TiCl}_2$  was trapped by a 1-trimethylsilyldiazacyclohexadienyl radical derived from **2a**, which was a potent intermediate species (*vide infra*). When compounds **2b** and **2c** were used for the reduction of  $\text{Cp}^*\text{TiCl}_3$  in a mixture of benzene and THF,  $\text{Cp}^*\text{TiCl}_2(\text{THF})$  (**11**) was isolated in 22% and 54% yield, respectively.<sup>22</sup> In the reaction of  $\text{Cp}^*\text{TiCl}_3$  with **4**, we obtained a 4,4'-bipyridyl bridged Ti(III) complex **12** in 89% yield.

The structure of complex **10** determined by X-ray analysis indicated that **10** adopts a three-legged piano stool geometry with two chloride atoms and one 1-trimethylsilyldiazacyclohexadienyl as the legs (Figure 6). The bond distance of Ti–N1 is 1.949(6) Å, which is in the normal range typically observed for Ti–NR<sub>2</sub> bonds.<sup>23</sup> In addition, the C–C bonds were shorter than the N–C bonds in the six-membered ring (C1–C2 = 1.338(9) Å and C3–C4 = 1.333(9) Å; N1–C1 = 1.406(9) Å, N1–C4 = 1.383(9) Å, N2–C2 = 1.365(8) Å, and N2–C3 = 1.383(8) Å), and a similar tendency was observed in the diazacyclohexadiene ring of **2a**.<sup>24</sup> Based on such geometrical parameters, the six-membered ring in **10** possesses a 1,4-disubstituted-1,4-diaza-2,5-cyclohexadiene structure, and the nitrogen atom coordinates as an amide ligand to the

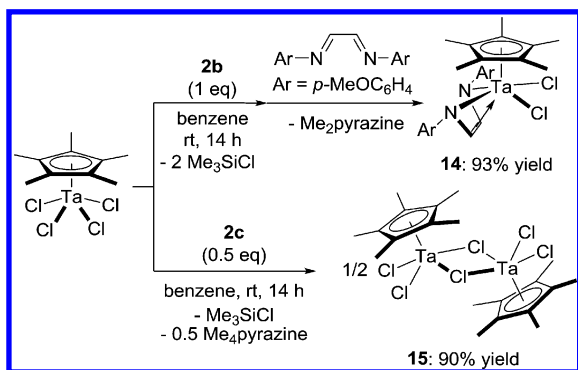


**Figure 6.** Molecular structure of complex **10** with 30% thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg); Ti–N1, 1.949(6); N1–C1, 1.406(9); N1–C4, 1.383(9); C1–C2, 1.338(9); C3–C4, 1.333(9); N2–C2, 1.365(8); N2–C3, 1.383(8); Si–N2, 1.776(5); Cl1–Ti–Cl2, 108.31(7); Cl1–Ti–N1, 98.28(17); Cl2–Ti–N1, 98.33(16).

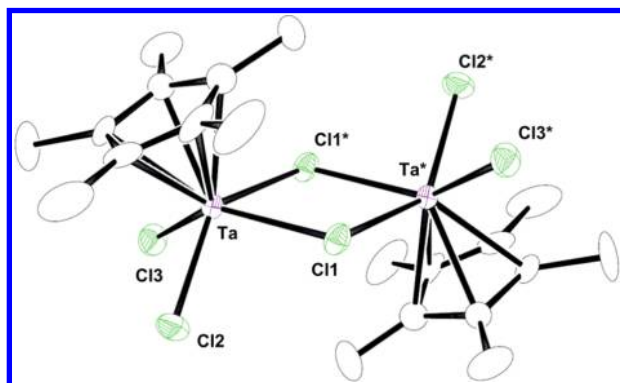
titanium center whose oxidation state is +4. The Ti(IV) complex **10** was stable in benzene and  $\text{CH}_3\text{CN}$  solution; however, treatment of **10** in the presence of  $\text{Cp}^*\text{TiCl}_3$  (1 equiv to **10**) in  $\text{CH}_3\text{CN}$  afforded  $[\text{Cp}^*\text{TiCl}_2]_2(\mu\text{-pyrazine})$  (**13**) in 53% isolated yield with a release of  $\text{Me}_3\text{SiCl}$  (1 equiv to **10**) (eq 2).



**Reduction of  $\text{Cp}^*\text{TaCl}_4$ .** With the better reducing reagents **2a–c** and **4** in hand, we examined the reduction of a tantalum complex  $\text{Cp}^*\text{TaCl}_4$  bearing an electron-donating  $\text{Cp}^*$  ligand, which could not be reduced by the reductants **1a,b**. When  $\text{Cp}^*\text{TaCl}_4$  was treated with **2b** (1 equiv), the corresponding two-electron-reduced product  $[\text{Cp}^*\text{TaCl}_2(\text{L})]_n$  (L =  $\text{Me}_6\text{pyrazine}$ ) was obtained as the product of an *in situ*-generated  $\text{Cp}^*\text{TaCl}_2$  species trapped by the *in situ*-generated  $\text{Me}_6\text{pyrazine}$  (Scheme 4). The coordinated 2,5-dimethylpyrazine was labile upon treatment of  $[\text{Cp}^*\text{TaCl}_2(\text{L})]_n$  with an equimolar amount of *N,N'*-bis(4-methoxyphenyl)-1,4-diaza-1,3-butadiene ( $\alpha$ -diimine), giving  $\text{Cp}^*\text{TaCl}_2(\alpha\text{-diimine})$  (**14**) in 93% yield.<sup>25</sup> We also observed a two-electron reduction for the reactions of **2a** and **4** with  $\text{Cp}^*\text{TaCl}_4$ ; a similar trapping experiment with the  $\alpha$ -diimine ligand, however, resulted in a complicated mixture from which we could not isolate **14**, but did obtain unidentified solids containing pyrazine- and 4,4'-bipyridyl-coordinated Ta(III) species, probably due to the strong coordination nature of sterically less-hindered pyrazine and 4,4'-bipyridyl, preventing the introduction of the  $\alpha$ -diimine ligand to the tantalum center of these compounds. In sharp contrast to the reduction by **2b**, the lower reduction ability of **2c** compared with that of **2b** with  $\text{Cp}^*\text{TaCl}_4$  proceeded in only a one-electron reduction to afford a chloride-bridged tantalum(IV)

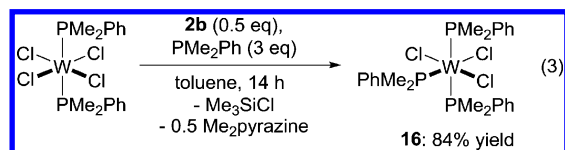
Scheme 4. Reduction of  $\text{Cp}^*\text{TaCl}_4$  by **2b** and **2c**

complex,  $[\text{Cp}^*\text{TaCl}_2]_2(\mu\text{-Cl})_2$  (**15**), in 90% yield,<sup>26</sup> to which the *in situ* generated  $\text{Me}_4\text{pyrazine}$  could not coordinate due to steric congestion at the nitrogen site (Scheme 4). X-ray diffraction studies showed that complex **15** existed in a solid state as a dinuclear Ta(IV) complex with two bridging chloride atoms (Figure 7). The long distance between the two tantalum centers (3.925(1) Å) suggested a nonbonding interaction between them.



**Figure 7.** Molecular structure of complex **15** with 30% thermal ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ta–Cl1, 2.502(4); Ta–Cl2, 2.364(4); Ta–Cl3, 2.379(4); Ta–Ta\*, 3.925(1); Cl1–Ta–Cl1\*, 76.66(13); Ta–Cl1–Ta\*, 103.34(13).

**Reduction of  $\text{WCl}_4(\text{PMe}_2\text{Ph})_2$ .** We conducted a reduction of  $\text{WCl}_4(\text{PMe}_2\text{Ph})_2$  as a typical tungsten phosphine complex. We recently reported the salt-free reduction of  $\text{WCl}_6$  by **1b** to form low-valent tungsten aggregates after a 3.5-electron reduction corresponding to the chloride-bridged aggregated species of W(II) and W(III), from which  $\text{W}_3\text{Cl}_7(\text{THF})_3$  was isolated upon extraction with THF.<sup>14c</sup> Similar to the reduction of  $\text{Cp}^*\text{TaCl}_4$  by **1–4**, the stronger reducing ability of the nitrogen-containing reductant **2b** compared with that of **1a** and **1b** was clearly observed for the phosphine-coordinating tungsten complex,  $\text{WCl}_4(\text{PMe}_2\text{Ph})_2$ . The reaction of **2b** with  $\text{WCl}_4(\text{PMe}_2\text{Ph})_2$  in the presence of  $\text{PMe}_2\text{Ph}$  (3 equiv) provided  $\text{mer-WCl}_3(\text{PMe}_2\text{Ph})_3$  (**16**) in good yield (84% yield),<sup>27</sup> in sharp contrast to the lack of reduction of  $\text{WCl}_4(\text{PMe}_2\text{Ph})_2$  by **1a** and **1b** due to their weaker reduction ability (eq 3). Although compound



**2c** could reduce  $\text{WCl}_4(\text{PMe}_2\text{Ph})_2$  to give **16**, a long reaction time (7 days) was necessary to complete the reduction due to the weaker reducing ability of **2c**. Compounds **2a** and **4** also underwent a one-electron reduction of  $\text{WCl}_4(\text{PMe}_2\text{Ph})_2$  to form **16** with contamination of pyrazine/4,4'-bipyridyl-coordinated W(III) complexes, which were not separated from **16**. Thus, organosilicon compound **2b** was the best reducing reagent for generating low-valent metal complexes with electron-donating ligands due to the strong reducing power and low coordination ability of the generated  $\text{Me}_2\text{pyrazine}$  to the metal center.

**Reaction Pathway for the Reduction of Metal Complexes by Organosilicon Reagents.** Scheme 5 shows a proposed pathway of the reduction of metal complexes with 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (**2a**) and its derivatives. The first step was an electronic interaction between the electron-deficient metal center and the electron-rich diazacyclohexadienes to form intermediate **A**, in association with similar electron transfer processes between 1,4-bis-(triisopropylsilyl)-1,4-diaza-2,5-cyclohexadienes and electron-accepting organic molecules such as TCNE, TCNQ, and  $\text{C}_{60}$ , which are reported to give the corresponding radical ion pairs.<sup>15a,b,g,i</sup> To elucidate the structure of the reductants after the electronic interaction process, we calculated the optimized structure of the radical cation of **2a** using density calculation theory,<sup>28,29</sup> and the N–Si bond was elongated with aromatization of the central six-membered ring as a release of one-electron from **2a** (Figure 8). Accordingly, the *N*-trimethylsilyl moiety was ready to react with a metal–chloride bond (**B**), and subsequent elimination of  $\text{Me}_3\text{SiCl}$  led to the formation of (4-trimethylsilyl-1,4-diazacyclohexadien-1-yl)metal species **C**. Complex **10**, derived from the reaction of  $\text{Cp}^*\text{TiCl}_3$  with **2a**, provides additional evidence for **C**. Due to stabilization of the organic radical **D** through delocalization of the unpaired electron in the six-membered ring, the high-valent metal species **C**, reduced metal species  $\text{L}_n\text{MCl}$ , and the organic radical **D** are in equilibrium. A similar equilibrium between the metal species and organic radicals was typically observed for the interaction between  $\text{CpTiCl}_2$  and a stable organic radical, TEMPO, to form Ti(IV) species,  $\text{CpTiCl}_2(\text{TEMPO})$ , as reported by Waymouth et al.<sup>30</sup> The liberated radical **D** further reacted with  $\text{L}_n\text{MCl}_2$  via transition state **E** to produce high-valent intermediate **F** with the liberation of  $\text{Me}_3\text{SiCl}$ . Subsequent aromatization of the six-membered radical moiety in **F** afforded another low-valent metal species along with the corresponding heteroaromatic compound.

**Application of Organosilicon Reagents 1–4 to the Titanocene-Catalyzed Reformatsky Reaction.** We found that **2c** served as the most convenient reagent for mediating a titanocene(III)-assisted Reformatsky reaction of ethyl 2-bromoisobutyrate (**17**) as the model substrate with various aldehydes (**18a–d**),<sup>31</sup> and the results are summarized in Scheme 6(a). The preference of reductant **2c** in this coupling reaction was due to the inertness of **2c** to substrate **17**; when compound **17** was treated with reductants **2a**, **2b**, and **4**,  $\text{Me}_3\text{SiBr}$  was generated even in the absence of a titanium species, probably due to the high nucleophilicity of the nitrogen atom of **2a**, **2b**, and **4**.<sup>32</sup> The optimized reaction condition was as follows: dropwise addition of **17** (1.0 M in THF) to the mixture of nonanal (**18a**) and **2c** in the presence of  $\text{Cp}_2\text{TiCl}_2$  (10 mol %) in THF afforded the corresponding Reformatsky coupling product, 3-hydroxy-2,2-dimethylundecanoate (**19a**), in 92% yield after hydrolysis of the reaction mixture. Not only aldehydes with a primary alkyl group, such as 3-phenylpropanal (**18b**), but also isobutyraldehyde (**18c**) and benzaldehyde (**18d**) were applicable, and the corresponding

Scheme 5. Plausible Mechanism for Reduction by 1,4-Bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene and Its Derivatives; Si Designates SiMe<sub>3</sub>

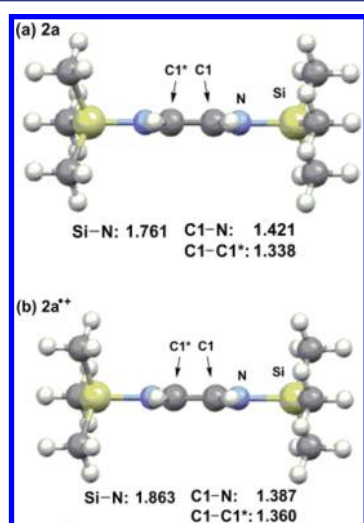
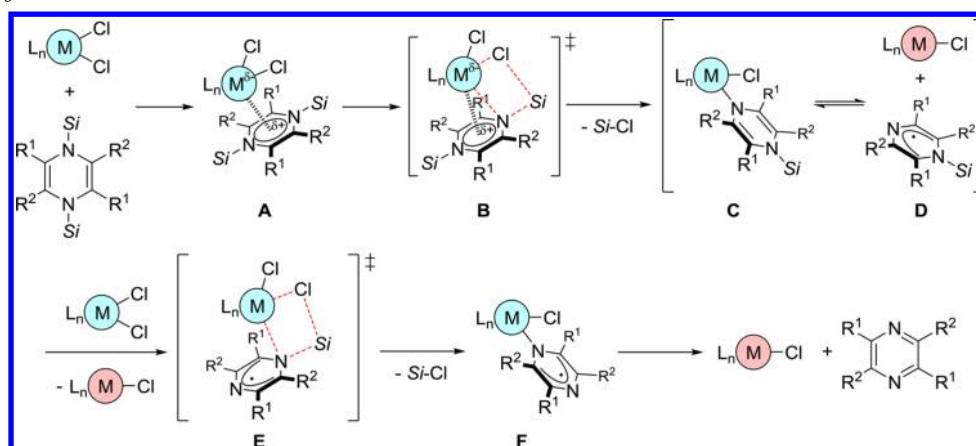
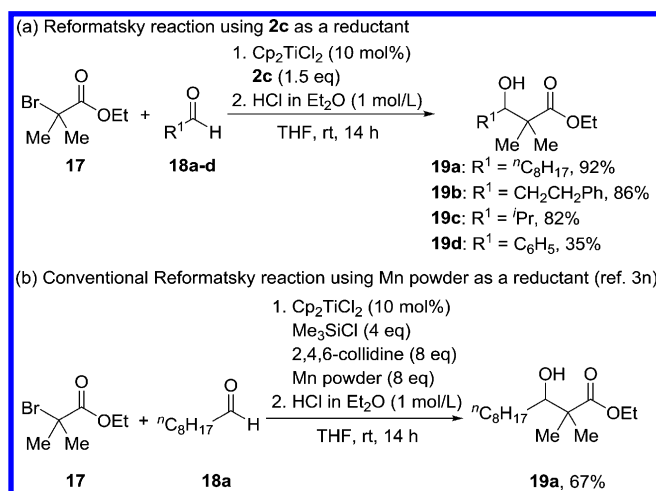


Figure 8. Optimized structures of (a) **2a** and (b) its radical cation, **[2a]<sup>•+</sup>** along with the selected bond lengths (Å).

Scheme 6. Reformatsky Reactions Catalyzed by (a) Cp<sub>2</sub>TiCl<sub>2</sub>/2c and (b) Reported System of Cp<sub>2</sub>TiCl<sub>2</sub>/Mn/Me<sub>3</sub>SiCl/2,4,6-Collidine<sup>3n</sup>



coupling products **19b-d** were obtained in good yields. Compared with the most useful catalytic system of Cp<sub>2</sub>TiCl<sub>2</sub> and Mn/Me<sub>3</sub>SiCl/2,4,6-collidine for the Reformatsky reaction

between **17** and **18a** (Scheme 6(b)),<sup>3n</sup> our catalytic system afforded a higher product yield (92% yield), presumably due to the homogeneity of the reaction mixture. This coupling system was further applicable to the Reformatsky reactions of ethyl 2-bromopropanoate with **18a-c** and that of ethyl 2-bromoacetate with **18a**.<sup>33</sup>

## CONCLUSION

In summary, we demonstrated that 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene derivatives **2a-c** and 1,1'-bis(trimethylsilyl)-1,1'-dihydro-4,4'-bipyridine (**4**) functioned as unique reducing reagents for various groups 4–6 metal chloride complexes bearing electron-donating ligands such as Cp, Cp\*, and phosphines, taking advantage of a salt-free reduction protocol. Methyl substitutes adjacent to the nitrogen atom in the six-membered rings of **2a-c** are important for controlling the coordination ability of the resulting free heteroaromatic compounds generated during the reduction: typically, reactions of **2a** and **4** with Cp<sub>2</sub>TiCl<sub>2</sub> produced titanocene(III) species, [Cp<sub>2</sub>TiCl]<sub>2</sub>(μ-L) (L = pyrazine (**5**), and 4,4'-bipyridyl (**6**)), whereas treatments of **2b** and **2c** with Cp<sub>2</sub>TiCl<sub>2</sub> afforded [Cp<sub>2</sub>Ti]<sub>2</sub>(μ-Cl)<sub>2</sub> (**7**). The negative oxidation potentials of **2a-c** and **4** compared with those of **1a,b** and **3**, as observed in their cyclic voltammetry measurements, indicated that compounds **2a-c** and **4** were preferable for the strong electronic interaction between the metal complexes and the reductants. Density functional theory analyses of the radical cation species **[2a]<sup>•+</sup>** as well as **2a** revealed that the Si–N bond distances were significantly elongated due to aromatization of the heteroaromatic moiety, increasing the reactivity of the N–Si bond toward a metal–halide bond. The reducing ability of **2c** toward Cp<sub>2</sub>TiCl<sub>2</sub> was further applicable to a low-valent titanocene-mediated Reformatsky reaction of nonanal and ethyl 2-bromoalkanoates without forming reductant-derived metal waste in the reaction mixture. Based on the advantages of the salt-free protocol, synthesis and catalytic application of various low-valent early transition metal complexes are in progress.

## EXPERIMENTAL SECTION

**General.** All manipulations involving air- and moisture-sensitive organometallic compounds were performed under argon using the standard Schlenk technique or an argon-filled glovebox. 3,6-Bis(trimethylsilyl)-1,4-cyclohexadiene (**1a**) and 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (**1b**) were prepared according to the literature.<sup>34</sup> 1,4-Bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene



(2a), 2,5-dimethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (2b), 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene (2c), 1,4-bis(trimethylsilyl)-1-aza-2,5-cyclohexadiene (3), and 1,1'-bis(trimethylsilyl)-1,1'-dihydro-4,4'-bipyridine (4) were prepared according to the modified procedure of the literature by replacing potassium metal by sodium metal except for the synthesis of 2c that needed the use of potassium.<sup>16</sup> Cp\*TiCl<sub>3</sub>,<sup>35</sup> Cp\*TaCl<sub>4</sub>,<sup>36</sup> WCl<sub>6</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>,<sup>37</sup> and N,N'-bis(4-methoxyphenyl)-1,4-diaza-1,3-butadiene<sup>38</sup> were prepared according to the literature. Cp<sub>2</sub>TiCl<sub>2</sub> was purchased from TCI Co. Ltd. Cp\*<sub>2</sub>TiCl<sub>2</sub> was obtained from Alfa Aesar and used as received. Anhydrous hexane, toluene, THF, and dichloromethane were purchased from Kanto Chemical and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.<sup>39</sup> Benzene, benzene-*d*<sub>6</sub>, toluene-*d*<sub>8</sub>, and THF-*d*<sub>8</sub> were distilled over CaH<sub>2</sub> and degassed before use. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were measured on BRUKER AVANCEIII-400 spectrometers. Assignment of <sup>1</sup>H and <sup>13</sup>C NMR peaks for some of the complexes was facilitated by 2D <sup>1</sup>H–<sup>1</sup>H COSY, 2D <sup>1</sup>H–<sup>1</sup>H NOESY, 2D <sup>1</sup>H–<sup>13</sup>C HMQC, and 2D <sup>1</sup>H–<sup>13</sup>C HMBC spectra. Cyclic voltammograms were recorded in a glovebox at room temperature in CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M [n-Bu<sub>4</sub>N][PF<sub>6</sub>] as the supporting electrolyte. GC-MS measurements were performed using a DB-1 capillary column (0.25 mm × 30 m) on a Shimadzu GCMS-QP2010Plus. All melting points were measured in sealed tubes under argon atmosphere. Elemental analyses were recorded by using Perkin-Elmer 2400 at the Faculty of Engineering Science, Osaka University.

**Synthesis of [Cp<sub>2</sub>TiCl<sub>2</sub>](μ-L) [L = pyrazine (5); L = 4,4'-bipyridyl (6)].**<sup>17</sup> To a solution of Cp<sub>2</sub>TiCl<sub>2</sub> (100 mg, 0.406 mmol) in benzene (2 mL) at room temperature was added a solution of 2a (0.241 mmol) in benzene (2 mL). After the reaction mixture was stirred for 16 h, all volatiles were removed under reduced pressure. The resulting residue was washed with hexane (10 mL × 3) to afford 5 (62.8 mg, 61% yield) as green powders. Complex 5 was characterized by combustion analysis.<sup>17</sup> Anal. Calcd for C<sub>30</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>2</sub>Ti<sub>2</sub>: C, 56.84; H, 4.77; N, 5.52. Found: C, 56.42; H, 5.08; N, 5.56.

In a similar manner, [Cp<sub>2</sub>TiCl<sub>2</sub>](μ-4,4'-bipyridyl) (6) was obtained as green powders in 68% yield by the reduction of Cp<sub>2</sub>TiCl<sub>2</sub> by 4. Complex 6 was characterized by X-ray diffraction analysis (*vide infra*) and combustion analysis.<sup>17</sup> Anal. Calcd for C<sub>30</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>2</sub>Ti<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>: C, 68.22; H, 5.45; N, 3.79. Found: C, 67.72; H, 6.02; N, 3.55.

**Synthesis of [Cp<sub>2</sub>Ti](μ-Cl)<sub>2</sub> (7).**<sup>19</sup> A solution of 2b (0.241 mmol) in THF (5 mL) was added to a solution of Cp<sub>2</sub>TiCl<sub>2</sub> (100 mg, 0.406 mmol) in THF (10 mL), and then the reaction mixture was stirred for 16 h. All volatiles were evaporated under reduced pressure to give green solids, which were washed with hexane (10 mL × 3). By drying in vacuo, green powders of 7 were obtained in 61% yield. The same reaction was conducted for 2c, and the same product 7 was obtained in 68% yield. The <sup>1</sup>H NMR spectral data of complex 7 displayed one broad resonance at δ<sub>H</sub> 30.4, and the resonance was almost identical to the reported data (broad resonance at δ<sub>H</sub> 31.0 in C<sub>6</sub>D<sub>6</sub>).<sup>19</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K) δ 30.4 (br, Cp).

**Synthesis of Cp<sub>2</sub>Ti(CO)<sub>2</sub> (8).** A reaction mixture of Cp<sub>2</sub>TiCl<sub>2</sub> (500 mg, 2.01 mmol) and 2b (542 mg, 2.01 mmol) in THF (15 mL) was stirred at room temperature. After the color of the solution turned to deep green, carbon monoxide (1 atm) was introduced to immediately give a red-colored solution. The solution was stirred for 2 days under CO atmosphere. After the solvent was removed under reduced pressure, the resulting residue was extracted with hexane (20 mL) under atmospheric pressure of CO, and the filtrate was cooled overnight at –30 °C to give 8 (320 mg, 68% yield) as red-brown microcrystals. In a similar manner, complex 8 (282 mg) was obtained in 60% yield for 2c. Complex 8 was characterized by <sup>1</sup>H NMR spectroscopy and IR. The <sup>1</sup>H NMR spectrum of 8 was in good agreement with the reported data.<sup>40</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K) δ 4.58 (s, Cp). IR (nujol, cm<sup>–1</sup>) ν<sub>CO</sub> = 1895 (s), 1974 (s).

**Synthesis of [Cp\*<sub>2</sub>TiCl<sub>2</sub>](μ-L) (L = 4,4'-bipyridyl) (9).** A solution of Cp\*<sub>2</sub>TiCl<sub>2</sub> (200 mg, 0.812 mmol) and 4 (123 mg, 0.406 mmol) in benzene (10 mL) was stirred for 2 days at 60 °C. The solvent was removed under reduced pressure to afford green precipitates, which

were washed with hexane (10 mL × 5). Removal of all volatiles under reduced pressure afforded complex 9 (256 mg, 73% yield) as green powders, mp 198–200 °C dec. Complex 9 was characterized by X-ray diffraction analysis (*vide infra*) and elemental analysis. Anal. Calcd for C<sub>30</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>2</sub>Ti<sub>2</sub>: C, 69.53; H, 7.94; N, 3.24. Found: C, 69.31; H, 8.28; N, 3.29.

**Synthesis of Cp\*TiCl<sub>2</sub>(1-trimethylsilyldiazacyclohexadienyl) (10).** To a solution of Cp\*TiCl<sub>3</sub> (100 mg, 0.346 mmol) in benzene (1 mL), was added a solution of 2a (101 mg, 0.444 mmol) in benzene (4 mL) at room temperature. The color of the reaction mixture immediately turned to purple. After the reaction mixture was stirred for 14 h, all volatiles were removed under reduced pressure to give purple solids, which were washed with hexane (10 mL × 3) to give complex 10 (130 mg, 92% yield) as purple powders, mp 184–190 °C dec. Complex 10 was characterized by <sup>1</sup>H NMR spectral data, X-ray analysis (*vide infra*), and combustion analysis. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K): δ 0.29 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.94 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 4.43 (d, *J* = 6.0 Hz, 2H, CHNSi), 7.24 (d, *J* = 6.0 Hz, 2H, TiNCH) <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K): δ –2.25 (Si(CH<sub>3</sub>)<sub>3</sub>), 11.7 (C<sub>5</sub>Me<sub>5</sub>), 115.3 (CHNSi), 121.4 (TiNCH), 126.8 (C<sub>5</sub>Me<sub>5</sub>). Anal. Calcd for C<sub>17</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>2</sub>SiTi: C, 50.13; H, 6.93; N, 6.88. Found: C, 49.99; H, 7.52; N, 6.84.

**Synthesis of Cp\*TiCl<sub>2</sub>(THF) (11).**<sup>22</sup> A solution of Cp\*TiCl<sub>3</sub> (100 mg, 0.346 mmol) and 2b (113 mg, 0.444 mmol) in THF (5 mL) at room temperature was stirred for 14 h. The color of the mixture gradually turned to green. After the reaction mixture was concentrated to ~3 mL, the reaction mixture was cooled to –18 °C to give 11 as blue crystals. Then a second crop of blue crystals was collected from the mother liquor, totally giving 11 (30.0 mg, 22% yield). In a similar manner, complex 11 (78.1 mg, 54% yield) was obtained from the reaction with 2c. During drying of the blue crystals, the coordinated THF was too liberated to be lost, affording green powders of Cp\*TiCl<sub>2</sub>, which was characterized by combustion analysis.<sup>22</sup> Anal. Calcd for C<sub>10</sub>H<sub>15</sub>Cl<sub>2</sub>Ti: C, 47.29; H, 5.95. Found: C, 47.41; H, 6.32.

**Synthesis of [Cp\*TiCl<sub>2</sub>]<sub>2</sub>(μ-4,4'-bipyridyl) (12).** A solution of Cp\*TiCl<sub>3</sub> (100 mg, 0.346 mmol) and 4 (134 mg, 0.444 mmol) in benzene (2 mL) was stirred for 14 h at room temperature. The color of the mixture immediately changed to be dark brown, from which green precipitates were formed gradually. The green powders were filtered and then washed with hexane (10 mL × 3), and dried to give 12 (102 mg, 89% yield), mp 246–250 °C dec. Anal. Calcd for C<sub>30</sub>H<sub>38</sub>Cl<sub>4</sub>N<sub>2</sub>Ti<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>): C, 58.25; H, 5.97; N, 3.77. Found: C, 57.83; H, 6.26; N, 3.90.

**Reaction of Complex 10 with Cp\*TiCl<sub>3</sub> in CH<sub>3</sub>CN.** A solution of Cp\*TiCl<sub>3</sub> (68.5 mg, 0.236 mmol) in CH<sub>3</sub>CN (4 mL) was added to a solution of complex 10 (100 mg, 0.236 mmol) in CH<sub>3</sub>CN (1 mL) at room temperature by a syringe. The color of the solution gradually turned to brown with precipitation of green powders. After stirring the reaction mixture for 24 h, the green powders were filtered and washed with CH<sub>3</sub>CN (1 mL × 5). The green powders were dried under reduced pressure to give [Cp\*TiCl<sub>2</sub>]<sub>2</sub>(μ-pyrazine) (13) in 53% yield (78 mg, 0.126 mmol). mp 149–151 °C dec. During drying process, the coordinated pyrazine was lost, affording deep-green powders which contained [Cp\*TiCl<sub>2</sub>]<sub>2</sub>. Low nitrogen content for combustion analysis of 13 was consistent with the contamination of [Cp\*TiCl<sub>2</sub>]<sub>2</sub>. Anal. Calcd for C<sub>24</sub>H<sub>36</sub>Cl<sub>4</sub>N<sub>2</sub>Ti<sub>2</sub>: C, 48.85; H, 6.15; N, 4.75. Found: C, 48.35; H, 5.73; N, 3.85. The low nitrogen value is presumably due to loss of pyrazine (15%) from complex 13 under vacuum. Anal. Calcd for (C<sub>24</sub>H<sub>34</sub>Cl<sub>4</sub>N<sub>2</sub>Ti<sub>2</sub>)<sub>0.85</sub>(C<sub>20</sub>H<sub>30</sub>Ti<sub>2</sub>Cl<sub>4</sub>)<sub>0.15</sub>: C, 48.71; H, 5.85; N, 3.92. Found: C, 48.35; H, 5.73; N, 3.85.

**Synthesis of Cp\*TaCl<sub>2</sub>(α-diimine) (α-diimine = N,N'-bis(4-methoxyphenyl)-1,4-diaza-1,3-butadiene) (14).** To a solution of Cp\*TaCl<sub>4</sub> (110 mg, 0.242 mmol) in benzene (3 mL) at room temperature, was added a solution of 2b (67.7 mg, 0.266 mmol) in benzene (2 mL). The color of the solution turned to brown within 10 min, and N,N'-bis(4-methoxyphenyl)-1,4-diaza-1,3-butadiene (100 mg, 0.266 mmol) was added to the reaction mixture. After the reaction mixture was stirred for 14 h, all volatiles were removed under reduced pressure to give yellow solids, which was washed with hexane (15 mL × 3) to afford 14 (172 mg, 93% yield) as yellow powders. Complex 14 was characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy,

whose spectral data were superimposed with the reported data.<sup>25</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K):  $\delta$  2.16 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 3.38 (s, 6H, OCH<sub>3</sub>), 5.96 (s, 2H, N–CH=), 6.82 (m, 4H, *m*-C<sub>6</sub>H<sub>4</sub>), 7.35 (m, 4H, *o*-C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K):  $\delta$  12.6 (C<sub>5</sub>Me<sub>5</sub>), 55.2 (OCH<sub>3</sub>), 110.9 (N–CH=), 113.7 (*m*-C<sub>6</sub>H<sub>4</sub>), 121.9 (s, C<sub>5</sub>Me<sub>5</sub>), 127.1 (*o*-C<sub>6</sub>H<sub>4</sub>), 144.0 (*ipso*-C<sub>6</sub>H<sub>4</sub>), 158.4 (*p*-C<sub>6</sub>H<sub>4</sub>).

**Synthesis of [Cp\*TaCl<sub>2</sub>]<sub>2</sub>( $\mu$ -Cl)<sub>2</sub> (15).** A solution of Cp\*TaCl<sub>4</sub> (303 mg, 0.662 mmol) and 2c (112 mg, 0.397 mmol) in benzene (10 mL) was stirred for 14 h. The resulting green solution was concentrated under reduced pressure, and the resulting solid was washed with hexane (15 mL  $\times$  3) and dried under vacuum to afford 15 (227 mg, 90% yield) as green powders, mp 238–242 °C dec. Complex 15 was characterized by <sup>1</sup>H NMR spectroscopy,<sup>26</sup> X-ray diffraction analysis (*vide infra*), and elemental analysis. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K):  $\delta$  47.9 (s, C<sub>5</sub>Me<sub>5</sub>). Anal. Calcd for C<sub>20</sub>H<sub>30</sub>Cl<sub>6</sub>Ta<sub>2</sub>: C, 28.43; H, 3.58. Found: C, 28.44; H, 3.27.

**Synthesis of mer-WCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> (16).** WCl<sub>6</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (200 mg, 0.330 mmol) was placed in an Ar-filled Schlenk tube, and toluene (5 mL) was added to the Schlenk via a syringe. A solution of PMe<sub>2</sub>Ph (138 mg, 1.00 mmol) in toluene (5 mL) was added to the solution containing the tungsten complex. To the reaction mixture, a solution of 2b (84.0 mg, 0.330 mmol) in toluene (5 mL) was added at room temperature. The color of the solution changed to deep brown. After the reaction mixture was stirred for 14 h at room temperature, all the volatiles were removed under reduced pressure. The residue was washed with hexane (10 mL  $\times$  3), and the resulting brown solid was dried in vacuo to give 16 as brown powders (197 mg, 84% yield). Complex 16 was characterized by <sup>1</sup>H NMR spectroscopy, and the <sup>1</sup>H NMR spectral data was superimposed with the reported data.<sup>27</sup> <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 303 K):  $\delta$  –23.8 (br, 12H, CH<sub>3</sub>), –15.6 (br, 6H, CH<sub>3</sub>), 4.18 (brt, 1H, *p*-Ph), 6.30 (t, 2H, *p*-Ph), 8.65 (brs, 2H, *o*-Ph), 8.92 (d, *J* = 6.2 Hz, 4H, *m*-Ph), 9.03 (d, *J* = 6.2 Hz, 2H, *m*-Ph), 12.0 (br, 4H, *o*-Ph).

**General Procedure for Catalytic Reformatsky Reaction of Aldehydes and  $\alpha$ -Bromoesters by Cp<sub>2</sub>TiCl<sub>2</sub> and Organosilicon Compounds.** After a mixture of Cp<sub>2</sub>TiCl<sub>2</sub> (12.5 mg, 50.0  $\mu$ mol) and organosilicon compounds (750  $\mu$ mol) in THF (2.5 mL) was stirred for 15 min, aldehyde (500  $\mu$ mol) was added to the reaction mixture via a syringe. A solution of ethyl 2-bromoalkanoate (1.00 mmol) in THF (1.0 mL) was slowly added over a period of 15 min. The reaction mixture was stirred for 14 h, quenched with hydrogen chloride (~1 mol/L in diethyl ether), and neutralized with Na<sub>2</sub>CO<sub>3</sub> aq. Reformatsky coupling products were extracted with EtOAc from the reaction mixture. The organic layer was dried, and the solvent was evaporated to dryness. The products were purified by flash chromatography on silica gel (hexane/EtOAc) and characterized by NMR spectroscopy.

**Electrochemical Analyses of Compounds 1b, 2a–c, 3 and 4.** In an argon-filled glovebox, compound 2a (4.6 mg, 2.0  $\times$  10<sup>–2</sup> mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (4 mL), and an electrolyte ([<sup>1</sup>Bu<sub>4</sub>N][PF<sub>6</sub>], 155 mg, 4.0  $\times$  10<sup>–1</sup> mmol) was added. The solution which contained 5 mM of 2a and 0.1 M of [<sup>1</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] was used for measurement of cyclic voltammogram with a glassy carbon working electrode, a platinum wire auxiliary electrode, a silver wire reference electrode, and scan rate of 100 mV/s. In a similar manner, cyclic voltammograms of the organosilicon compounds 1b, 2b, c, 3, and 4 were measured, and the results are shown in Figure 3.

**X-ray Crystallographic Analysis.** All crystals were handled similarly. The crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(1) K. Measurements were made on Rigaku R-Axis RAPID imaging plate area detector or Rigaku AFC7R/Mercury CCD detector with graphite-monochromated Mo K $\alpha$  (0.71075 Å) radiation. Crystal data and structure refinement parameters are listed in SI (Table S16).

The structures of complexes 6, 9, 10, and 15 were solved by direct methods (SHELXS-97).<sup>41</sup> The structures were refined on F<sup>2</sup> by full-matrix least-squares method, using SHELXL-97.<sup>42</sup> Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was  $\sum w(F_o^2 - F_c^2)^2$  ( $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ ), where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$  with  $\sigma^2(F_o^2)$  from counting statistics. The function R1 and wR2 were  $(\sum ||F_o| - |F_c||)/\sum |F_o|$  and

$[\sum w(F_o^2 - F_c^2)^2/\sum (wF_o^4)]^{1/2}$ , respectively. The ORTEP-3 program was used to draw the molecule.<sup>43</sup>

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Experimental details, NMR spectra, and summary of the DFT calculation; CIF file giving data for complexes 6, 9, 10 and 15. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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