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# Synthesis and Structures of $Ti^{III}$ and $Ti^{IV}$ Complexes Supported by a Bulky Guanidinate Ligand

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**Abstract:** In this work, titanium complexes of the bidentate bulky guanidine ligand $[\{(Dip)N\}_2CNR_2]H$ (where Dip = $C_6H_3iPr_2$-2,6 and R = $CH(CH_3)_2$) (LH) were prepared. Reaction of LH with one equivalent of $[(CH_3)_2NTiCl_3]$ underwent amine elimination to afford the monomeric complex $[LTiCl_3]$ (**1**) in high yield. Attempts to reduce **1** with potassium graphite ($KC_8$) in tetrahydrofuran (THF) were unsuccessful. However, reacting **1** with 3.3 equivalents of $KC_8$ in hexane led to the first example of structurally characterized mono-guanidinate ligand stabilized dimeric $Ti^{III}$ complex $[LTiCl(\mu\text{–}Cl)]_2$ (**2**). The synthesized complexes were characterized by NMR spectroscopy and the structures were further confirmed by X-ray crystallography.

**Keywords:** guanidinate; N-ligands; single crystal; titanium; X-ray analysis

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## 1. Introduction

Stabilization of highly reactive low coordinate and low valent early transition metal complexes has long been an area of interest for chemists, not only from a structural point of view but also due to their reactivity pattern. The strategy that has been widely sought is the application of steric bulk and the mono-anionic nature of the stabilizing ligands. In this regard, N-containing chelating bidentate ligands such as amidinate [1–3], guanidinate [1,2,4,5], β-diketiminate [6–8], and aminopyridinate [9–11] have recently attracted enormous attention (Figure 1).

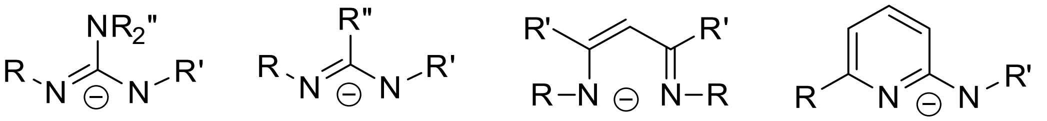


**Figure 1.** Guanidinate ligands (left) and other related bidentate monoanionic N-Ligands (R, R′ and R″, for instance, alkyl or aryl substituents).

The unusual oxidation state of +1 is known for all members of first row early transition metals except titanium, and these complexes are mainly stabilized by N-containing ligands [12–16]. Compared to other N-containing bidentate ligands, bulky guanidine ligands seem to be more suitable due to the possibility of varying steric bulk on the NCN moiety that may push the phenyl rings down towards each other to stabilize (to form metal-metal bond) and protect metals in unusually low oxidation states [4,17,18]. Thus, we became interested to explore the possible isolation of titanium (I) species by applying guanidine ligands. Divalent titanium has already been widely used for a variety of metal-promoted organic transformations, which shows that $Ti^{I}$ species might be very interesting in terms of reactivity studies [19]. The chemistry of $Ti^{II}$ complexes is mainly dominated by cyclopentadiene (Cp) ligands, however, N-containing ligands (aminopyridine) have also been successfully applied for Cp-free $Ti^{II}$ species [20]. In comparison to $Ti^{II}$, isolation of $Ti^{I}$ species is a challenge to chemists [21]. Here, we describe our attempt to isolate $Ti^{I}$ species using the steric bulk and the mono-anionic nature of the guanidinate ligands, and report the synthesis and structures of $Ti^{IV}$ guanidinate and its reduction to $Ti^{III}$ instead of $Ti^{I}$ complex.

## 2. Materials and Methods

### 2.1. General Information

All manipulations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or in $N_2$ filled glove box (mBraun 120-G) with a high-capacity recirculator (<0.1 ppm $O_2$). Solvents were dried by distillation from sodium wire/benzophenone. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried, and distilled prior to use. $[(CH_3)_2NTiCl_3]$ and guanidine ligand [LH] were prepared according to the published procedures [22,23]. Commercial $TiCl_4$ (Acros) was used as received. NMR spectra were recorded on Varian 300 and Varian 400 MHz at ambient temperature. The chemical shifts are reported in ppm relative to the internal TMS. Elemental analyses (CHN) were determined using a Vario EL III instrument. The effective magnetic moments were determined using Sherwood Scientific Magnetic Susceptibility Balance. X-ray crystal structure analyses were performed using a STOE IPDSII equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement was accomplished using SIR97 [24], SHELXL97 [25] and WinGX [26]. Data collection and cell refinement by X-AREA-STOE. The single crystal was irradiated with Mo-Kα at 133 K. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were added at calculated positions and refined using a riding model. No absorption correction was applied to the data. Some of the reflections at certain angles were omitted in the refinement of **2** and that might be the reason for the B-alert in the checkcif. Selected crystallographic data are gathered in Table 1.

**Table 1.** Crystallographic data of the compounds **1** and **2**.

| **Compound** | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{31}H_{48}Cl_3N_3Ti$ | $C_{68}H_{110}Cl_4N_6Ti_2$ |
| Formula weight | 616.97 | 1249.22 |
| crystal system | orthorhombic | monoclinic |
| space group | Pna2(1) | C2/c |
| a [Å] | 19.4050(9) | 36.6350(15) |
| b [Å] | 10.5550(4) | 11.2480(8) |
| c [Å] | 16.1720(7) | 19.9120(15) |
| α [deg] | 90.00 | 90.00 |
| β [deg] | 90.00 | 120.746(6) |
| γ [deg] | 90.00 | 90.00 |
| V, [$Å^3$] | 3312.3(2) | 7051.8(8) |
| crystal size, [$mm^3$] | 0.43 × 0.32 × 0.25 | 0.38 × 0.36 × 0.33 |
| $\varrho_{calcd}$, [g $cm^{-3}$] | 1.237 | 1.177 |
| μ, [$mm^{-1}$] (Mo Kα) | 0.524 | 0.420 |
| T, [K] | 133(2) | 133(2) |
| 2θ range, [deg] | 2.52–52.06 | 2.59–45.42 |
| no. of reflections unique | 6232 | 6661 |
| no. of reflections obs. [I > 2σ (I)] | 5081 | 2099 |
| no. of parameters | 343 | 374 |
| $wR^2$ (all data) | 0.0687 | 0.1999 |
| R value [I > 2σ (I)] | 0.0351 | 0.0747 |

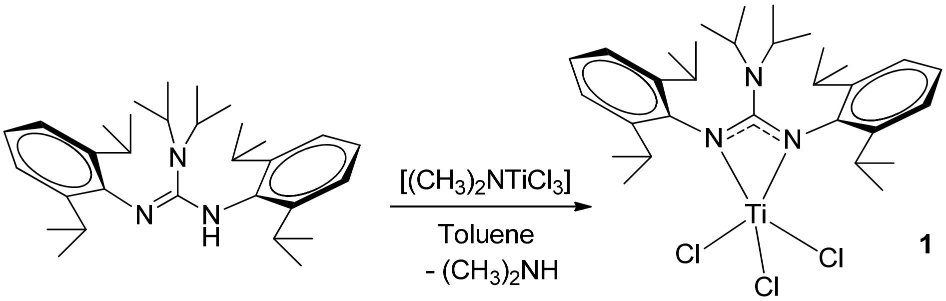
### 2.2. Syntheses

Synthesis of **1:** LH (0.928 g, 2 mmol) was added to $[(CH_3)_2NTiCl_3]$ (0.397 g, 2 mmol) in toluene (50 mL) at room temperature. The resulting brown–red solution mixture was then heated overnight at 80 °C. After cooling to room temperature, the solution was filtered. Volume of the filtrate was reduced to ca. 20 mL under vacuum. After standing at room temperature the solution afforded red crystals of **1**. Yield: 1.01 g (82%). $C_{31}H_{48}Cl_3N_3Ti$ (616.96): Calcd. C 60.35 H 7.84 N 6.81; found C 59.95 H 7.79 N 6.77. $^1$H NMR: ($C_6D_6$, 400 MHz): $\delta$ = 0.66 (d, $J$ = 6.9 Hz, 12 H, CH($CH_3$)$_2$), 1.20 (d, $J$ = 6.9 Hz, 12 H, CH($CH_3$)$_2$), 1.58 (d, $J$ = 6.9 Hz, 12 H, CH($CH_3$)$_2$), 3.60 (sep, 4 H, $J$ = 6.9 Hz, $CH$($CH_3$)$_2$), 3.86 (sep, 2 H, $J$ = 6.9 Hz, $CH$($CH_3$)$_2$), 7.01–7.11 (m, 6 H, $C_6H_3$) ppm. $^{13}$C NMR (100 MHz, $C_6D_6$, 298 K): $\delta$ = 23.0 (NCH$CH_3$), 23.1 (NCH$CH_3$), 24.0 (CH($CH_3$)$_2$), 24.1 (CH($CH_3$)$_2$), 26.5 ($CH$($CH_3$)$_2$), 26.5 ($CH$($CH_3$)$_2$), 29.2 ($CH$($CH_3$)$_2$), 51.1 (N$CH$), 124.8 ($C^{meta}$), 143.2 ($C^{ipso}$), 145.3 ($C^{ortho}$), 170.2 (NCN) ppm.

Synthesis of **2:** Hexane (50 mL) was added to **1** (3.040 g, 4.93 mmol) and potassium graphite (16.27 mmol) at −30 °C. The suspension was then allowed to come to room temperature and stirred overnight. The resulting green solution was then filtered. The volume of the filtrate was reduced to ca. 10 mL as green crystalline material of **2** started to precipitate. Filtrate was kept at room temperature to afford further material of **2**. Yield: 0.850 g (28 %). $C_{64}H_{96}Cl_4N_6Ti_2.C_6H_{14}$ (1249.22): Calcd. C 64.03 H 8.32 N 7.23; found C 63.86 H 8.6 N 7.78. $^1$H NMR: ($C_6D_6$, 300 MHz): $\delta$ = −1.98 (br s), 0.47 (d), 0.56 (d), 1.16–1.25 (m), 1.48 (d), 1.57 (d), 1.87 (s), 2.09 (s), 3.11–3.30 (m), 3.48 (sep), 4.09 (s), 6.35 (br tr), 7.33 (d) ppm. μeff(298 K) = 0.95 μB.

## 3. Results

Reacting one equivalent of the bulky guanidine ligand [{(Dip)N}$_2$CNR$_2$]H (where Dip = $C_6H_3iPr_2$-2,6 and R = CH($CH_3$)$_2$) (LH) with [($CH_3$)$_2$NTiCl$_3$] in toluene at 80 °C afforded selectively red crystalline material of mono(guanidinate) Ti$^{IV}$ complex [{(Dip)N}$_2$CNR$_2$]TiCl$_3$] (**1**) in 82% yield (Scheme 1). Compound **1** was characterized using $^1$H and $^{13}$C NMR spectroscopy along with elemental analysis. The $^1$H-NMR data was in accordance with the nature of the compound formed, showing three doublets for the isopropyl $CH_3$ protons and two septets for the isopropyl CH protons of the guanidinate ligand.



**Scheme 1.** Synthesis of mono(guanidinate) titanium(IV) complex (**1**).

The molecular structure of **1** was confirmed by single crystal structure analysis. The structure analysis revealed the expected mono(guanidinate)titanium(IV) trichloride complex. A distorted trigonal bi-pyramidal coordination around titanium was observed (Figure 2). Titanium is coordinated by two nitrogen and three chlorine atoms. The Ti-N [Ti-N1 2.008 (2) and Ti-N2 2.049 (2) Å] and Ti-Cl [Cl1-Ti1 2.2461(9), Cl2-Ti1 2.2565(9) and Cl3-Ti1 2.2185(8) Å] bond lengths were comparable to values in the literature [27,28]. The nearly identical C-N bond lengths [C1-N2-1.350(3), C1-N3-1.353(3), C1-N1 1.373(3) Å] and the sum of the bond angles around N3 and C1 was approximately 360°, confirm sp$^2$-hybridized nitrogen and carbon atoms. This shows the role of the lone pair of the non-coordinating N-atom in the π system of the ligand that can lead to an increased electron density at the metal center and may result in stronger bonding of the guanidinate ligand.

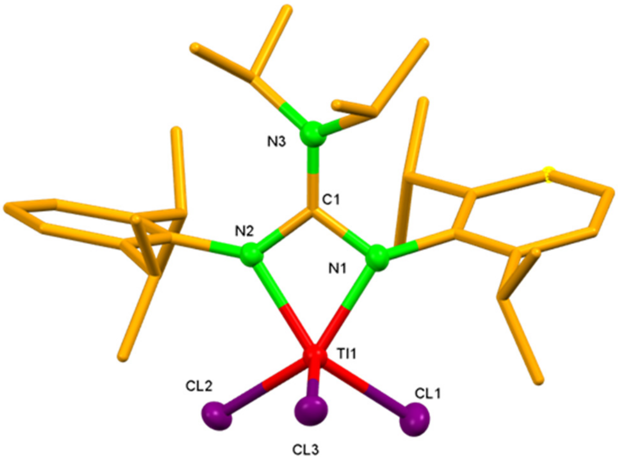
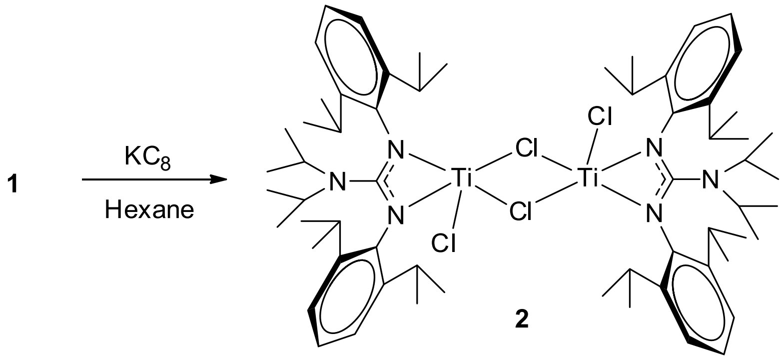


**Figure 2.** Molecular structure of **1**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N2-1.350(3), C1-N3-1.353(3), C1-N1 1.373(3), N1-Ti1 2.008(2), N2-Ti1 2.049(2), Cl1-Ti1 2.2461(9), Cl2-Ti1 2.2565(9), Cl3-Ti1 2.2185(8); N2-C1-N3 129.1(2), N2-C1-N1 105.9(2), N3-C1-N1 124.9(2), N2-C1-Ti1 54.14(13), N3-C1-Ti1 168.93(19), N1-C1-Ti1 52.48(12), N1-Ti1-N2 64.76(9), N1-Ti1-Cl3 103.70(7), N2-Ti1-Cl3 111.02(7), N1-Ti1-Cl1 93.51(7), N2-Ti1-Cl1 142.38(7), Cl3-Ti1-Cl1 103.59(3), N1-Ti1-Cl2 146.75(7), N2-Ti1-Cl2 88.39(6), Cl3-Ti1-Cl2 104.15(3), Cl1-Ti1-Cl2 97.25(3), N1-Ti1-C1 32.84(9), N2-Ti1-C1 32.27(9), Cl3-Ti1-C1 107.11(6), Cl1-Ti1-C1 122.74(7), Cl2-Ti1-C1 119.69(7).

To explore the possible reduction of 1 to $Ti^{I}$ species, we analyzed its reaction with $KC_8$ in THF and found that it didn't lead to the isolation of any characterizable product. However, in hexane its reaction with 3.3 equivalents of $KC_8$ (Scheme 2) led to a green solution. Filtration and reducing the volume of solvent led to the isolation of green crystalline material in a 28% yield. The low yield may be attributed to the low solubility of the product in hexane.



**Scheme 2.** Synthesis of mono(guanidinate) titanium(III) complex (**2**).

X-ray analysis showed **2** to be dimeric $Ti^{III}$ complex (Figure 3) where guanidinate ligand is $\eta^2$-coordinated. Compare to $Ti^{IV}$, $Ti^{III}$ guanidinates are rare [29–31] and dimeric structures of $Ti^{III}$ guanidinates are not known, to the best of our knowledge. The geometry around titanium can be best described as distorted triangular bi-pyramidal with two N-atoms of the chelating guanidinate and three halide ligands (Figure 2). The distortion is mainly caused by the NCN moiety of the ligand. The N-Ti-N bond angle [64.08(19)°] in **2** is comparable to that in **1** [64.76(7)°]. The Ti-N bonds are slightly longer than those in **1**. As expected, the Cl-Ti bond for the bridging chloride ligand [Cl1-Ti1 2.403(2) Å] is longer than the terminal chloride ligand [Cl2-Ti1 2.276(2) Å]. The long Ti-Ti distance of 3.127(2) Å rules out any possible metal-metal bonding interaction. The magnetic susceptibility experiments show the magnetic moment of μeff(298 K) of 0.95 μB which is comparable to values found in the literature [32,33]. The purity of the compounds was further confirmed by elemental analysis.

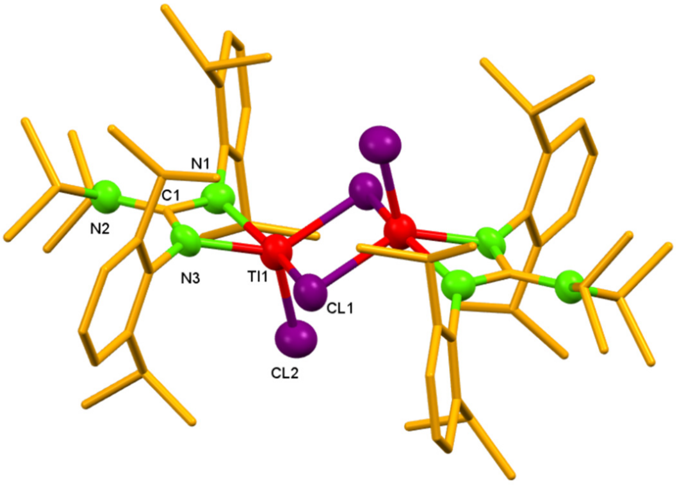


**Figure 3.** Molecular structure of **2**. Ellipsoids are set at 50% probability; hydrogen atoms and one hexane molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-N3 1.347(7), C1-N1 1.355(7), C1-N2 1.374(7), N1-Ti1 2.026(5), N3-Ti1 2.078(5), Cl1-Ti1 2.368(2), Cl1A-Ti1 2.403(2), Cl2-Ti1 2.276(2), Ti1-Ti1 3.127(2); N3-C1-N1 107.4(5), N3-C1-N2 128.3(5), N1-C1-N2 124.2(5), Ti1-Cl1-Ti1 81.90(7), N1-Ti1-N3 64.08(19), N1-Ti1-Cl2 105.83(15), N3-Ti1-Cl2 117.88(15), N1-Ti1-Cl1A 93.73(15), N3-Ti1-Cl1A 139.54(15), Cl2-Ti1-Cl1 100.07(8), N1-Ti1-Cl1 151.10(16), N3-Ti1-Cl1 90.46(14), Cl2-Ti1-Cl1A 97.96(8), Cl1-Ti1-Cl1A 98.10(7).

To satisfy our curiosity as to whether **2** can be reduced further it was reacted with two equivalents of $KC_8$ in THF. Despite a color change from green to red, all attempts to produce isolatable material for characterization were unsuccessful.

## 4. Conclusions

To isolate titanium in the unusual oxidation state of +1, the reduction of monomeric titanium$^{IV}$ and subsequently isolated dimeric Ti$^{III}$ complexes, supported by a bulky guanidine ligand, were studied using THF and hexane as reaction solvents. Despite the fact that in the present study the reduction of T$^{III/IV}$ complexes didn't lead to the desired Ti$^{I}$ species, it nevertheless highlights the challenges faced in search of the isolation of these complexes. One possibility might be the use of aromatic solvents, as the highly reactive Ti$^{I}$ complexes (if formed) might lead to arene sandwiched Ti$^{I}$ complexes. During these studies the first example of structurally characterized dimeric mono(guanidinate) Ti$^{III}$ complex has been isolated and structurally characterized.

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**Data Availability Statement:** Supplementary crystallographic data can be obtained online free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html ((or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)), deposition numbers CCDC-2073975 (**1**) and CCDC-2073976 (**2**).

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**Conflicts of Interest:** The author declares no conflict of interest.

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