A Mononuclear and High-Spin Tetrahedral TiII Complex

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ABSTRACT: A high-spin, mononuclear TiII complex, [(TpBu,Me)TiCl] with a linear Ti topology, established by single-crystal X-ray diffraction. The N2 complex was characterized using XAS and IR and Raman spectroscopies, thus establishing this complex to possess two TiIII centers covalently bridged by an N2 group.

INTRODUCTION

Divalent Ti compounds have been widely used in C–C bond coupling reactions, such as the Kulinkovich or McMurry type reactions, and recently in catalytic C–N bond coupling reactions by Tonks. However, the coordination chemistry of TiII complexes is largely restricted to octahedral systems of the type [TiX2(L)] {X = Cl, CH3, BH4, and OPh and L = 2 dmpe [1,2-bis(dimethylphosphino)ethane], 4 pyridines; 4 X2 = porphyrin, 5 L = 2 THF (tetrahydrofuran), 2 phosphines, or bulky Cp−based ligands}. Other strategies to stabilize the high and highly reducing TiII ion are to coordinatively saturate it with soft or π acids, such as N2, CO3, isonitriles, bipyridine, 1,10-phenanthroline, alkynes, olefins, cyclooctatetraene, phosphines, or bulky Cp−based ligands. Common to these strategies is the reliance on maximizing the coordination number and, notably, low-coordinate TiII complexes continue to elude isolation. In particular, we found that no example of a four-coordinate, high-spin TiII d3 complex exists. Despite the aforementioned cases all being formally categorized as TiII, the strongly π-accepting nature of one or more of the ligands means that the metal does not typically behave as a diradical or powerful π base. Perhaps only in the case of trans-[TiCl2(TMEDA)] could one argue that the TiII ion represents a bona fide example of a high-spin d2 configuration, given the more inherent nature of the chloride and chelating diamine ligands. However, this complex is highly unstable in solution, undergoing dinuclearization or disproportionation reactions. More recently, Lin, Tilley, Ye, and co-workers as well as Deng and co-workers have used sterically bulky, cyclic (alkyl)(amino)carbene (cAAC) ligands to stabilize C2−symmetric TiII and HfII centers of the type [(cAAC)2MCl2], wherein a combination of π-accepting properties of the ligand and/or low symmetry electronically favors closed-shell ground states.

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Given the propensity for mononuclear TiIII to disproportionate, especially if bearing halide or pseudohalide ligands, we decided to reinvestigate its chemistry with the ubiquitous Tp− ligand. Lee and co-workers established that two Tp− ligands can be substituted onto TiII, with each being κ1 (vide supra). However, the use of more sterically encumbering groups on the pyrazoles should allow one to isolate and stabilize tetrahedral geometries with divalent ions, which has been observed for most of the 3d metals. In fact, Petrov and co-workers recently reported the synthesis of a tetrahedral divalent VII complex, [(TpBu2)Cl2][Cl2]−, showing distortion of one pyrazolyl arm of the TpBu2− ligand. Thermal ellipsoids are at 50% probability. Solvent and H atoms (except on B) are omitted.

RESULTS AND DISCUSSION

Synthesis of Mononuclear TiIII Complexes with a Sterically Encumbering Trispyrazolylborate Ligand. Lee and co-workers reported how [TiCl3(TMEDA)]2− could be cleanly transmetalated with 2 equiv of [KTP] to afford the octahedral TiII complex [TTiP]. Intuitively, one would expect this reaction to proceed via the mononeric intermediate [TPCl2]. Surprisingly, we found that no examples of mono-Tp-based TiII complexes exist, despite the VII complex [(TpBu2)VCl]− having been recently reported by Petrov and co-workers. An initial investigation of salt metathesis between mer-[TiCl3(THF)]4+ and [KTP] led to isolation of the TiIII complex [(κ1,κ1,η2-TpBu2)TiCl2]−, albeit in low (∼10%) yield and with the presence of impurities (Scheme 1).

Single-crystal X-ray diffraction (XRD; Figure 1) studies revealed a highly distorted system where the TpBu2− ligand coordinates in an unusual κ1,κ1,η2 mode, which has been observed only in coordination polymers and for large metal ions that favor high coordination numbers, such as BuIII, SmIII,22 YbIII,33 and UIII.34 Here, the severe skewing of one pyrazolyl arm results in an almost side-on interaction between both of its N atoms and the metal ion. A moderate degree of elongation for one of the B−N bonds [1.973(3), 1.924(3), 1.848(3) Å] compared to the other two [1.382(2) and 1.385(2) Å]. Distortion of one of the sterically encumbered pyrazolyl arms in [(κ1,κ1,η2-TpBu2)−TiCl2]− implies the possibility of decomposition reactions, involving B−N and N−N bond activation, especially in subsequent reduction chemistry, leading to the large and strongly reducing TiIII ion. Not surprisingly, attempts to prepare pure samples of [(κ1,κ1,η2-TpBu2)−TiCl2]− invariably resulted in impure bulk material containing traces of other species, including free pyrazole. Given the larger ionic radius of TiIII (100 pm) versus VII (93 pm), we decided to reduce some of the steric congestion in TpBu2− by replacing the tert-butyl group in the 5 position of each pyrazolyl arm with a methyl group. Theopol and co-workers have popularized this ligand scaffold with various 3d metals, including the early-transition-metal Cr in the formal oxidation states I−V.25,35

Following a modified recipe to prepare [(κ1,κ1,η2-TpBu2)−TiCl2]−, treatment of mer-[TiCl3(THF)]4+ with 1 equiv of [Ti(TpBu2)Cl]− in toluene over 13 h at 70 °C resulted in the smooth formation of [(κ1,κ1,η2-TpBu2)−TiCl2]− (1), which was isolated in 72% yield as blue crystals (Scheme 2). The use of [Ti(TpBu2)Cl]− as opposed to the K+ salt improves the overall isolated yield because of the lower content of residual pyrazole that remains from synthesis of the alkali salt X− and Q-band EPR spectroscopic studies of I in toluene glass afford typical S = 1/2 rhombic spectra, indicative of low symmetry around the TiIII ion (X band, g = [1.973, 1.923, 1.848], 12 K; Q band, g = [1.973, 1.924, 1.848], 2 K; Figure 2). Likewise, solution Evans (μeff = 1.70 μB, 27 °C, CD2Cl2), IR (νHH = 2569 cm−1), and UV−vis (d = 648 nm; ε = 35 M−1 cm−1) spectral studies are all in accordance with a mononeric d1 species. While the starting material, mer-[TiCl3(THF)]4+, shows a UV−vis absorption spectrum with two transitions due to a Jahn−Teller-distorted excited E state (668 and 763 nm, ε = 7 and 4 M−1 cm−1, respectively), complex I shows a single transition at 648 nm with a 5-fold increase in intensity in accord with the lower

Scheme 1. Synthesis of [(κ1,κ1,η2-TpBu2)−TiCl2]−
symmetry about the Ti$^{	ext{III}}$ ion (Figure S51). XRD studies also confirmed a five-coordinate monomer more in line with a square-pyramidal geometry at the Ti$^{	ext{III}}$ ion ($\tau_5 = 0.27$; Figure 3). Moreover, no isomeric species resulting from borotropic shifts have been observed for 1, and significant twisting of the pyrazolyl arms is no longer as noticeable when judged by the B−N and N−N metrical parameters. The view down the Ti−B−H axis (Figure 3, right) clearly shows how twisting of the pyrazole arms in 1 is minimized compared to [(κ$^1$,κ$^1$,η$^2$-Tp$^\text{Bu}_2$)TiCl$_2$].

**Synthesis of a High-Spin, Tetrahedral Ti$^{	ext{II}}$ Complex and Exploration of Its Electronic Structure.** A cyclic voltammogram of 1 revealed an irreversible one-electron anodic process with an anodic peak at 0.44 V (referenced to FeCp$_2$ as 0.0 V), while a reversible one-electron cathodic process could be observed at −1.85 V (Figure 4). In Lee’s [Tp$_2$Ti]PF$_6$ complex, reversible one-electron oxidation and reduction processes occur at 1.20 and −1.28 V versus SCE, i.e., at 0.65 and −1.83 V versus FeCp$_2$ as 0.0 V. These features indicate that reduction potentials are largely conserved between five-coordinate 1 and pseudooctahedral [Tp$_2$Ti]PF$_6$, and, importantly, both Ti$^{	ext{III}}$ complexes provide access to the corresponding Ti$^{	ext{II}}$ ions in a reversible manner. In the case of 1, the nonreversible electrochemical features are likely due to significant structural distortion upon reduction, whereas the irreversible anodic feature might be due to the instability of a hypothetical four-coordinate [1]$^+$ species, especially in the presence of electrolyte. Encouraged by the facile electrochemical reduction chemistry, we conducted a chemical reduction of 1 under Ar with KC$_8$ in THF over 10 min, which resulted in an immediate color change from blue to
intense green. Subsequent workup of the reaction mixture resulted in the formation of [(Tp\textsuperscript{Bu,bn,Me})TiCl] (2) as light-green crystals in a respectable yield (78%; \( \tau \text{hit} = 2554 \text{ cm}^{-1} \); Scheme 2). XRD studies revealed a slightly distorted tetrahedral TiII ion in each of the two crystallographically independent molecules (Table 1 and Figure 5, top). The chlorido ligand resulted in the formation of [(Tp\textsuperscript{int})TiCl\textsuperscript{3}] with a high-spin Ti II d\textsubscript{2} ion. Specifically, the SQUID magnetization measurements of 2 in the temperature range 2–300 K are consistent with an \( S = 1 \) species (for two independently isolated samples). Below 10 K, the magnetic moment drastically decreases to 2.24 \( \mu \text{B} \) (at 2 K), as shown in Figure 6, due to zero-field splitting (ZFS, vide infra). Variable-temperature and -field (VTVF) magnetization measurements in the temperature range 1 and 5 T were also measured and simulated using a \( g_{\text{eff}} \) value of 1.85 (Figure 6, inset, and Table 2). Being confined to a tetrahedral coordination geometry, complex 2 shows ligand-field transitions at lower energies than those in 1, extending into the near-IR (NIR) region of the UV–vis spectrum (\( \lambda = 391, 701, 857, 889, \text{ and } 925 \text{ nm} \); \( \epsilon = 1500, 180, 340, 320, \text{ and } 230 \text{ M}^{-1} \text{ cm}^{-1} \), respectively; Figure S52).

Given the unique geometry of 2 and the even number of unpaired electrons resulting in an integer electronic spin, we carried out HFEPR spectroscopic measurements of powdered samples of 2 at low temperatures (Figure 7, top, 216 GHz; spectra at additional frequencies are shown in Figures S59–S62). The spectra are characteristic powder patterns for a triplet spin state (\( S = 1 \)) and reveal the presence of two independent \( S = 1 \) species. The number and intensity of turning points in the spectra could be readily simulated at various frequencies using two sets of spin-Hamiltonian parameters (Table 2). These parameters were obtained from 2D maps of field versus frequency (Figure 7, bottom), with a tunable-frequency methodology applied.\textsuperscript{41} The sign of \( D \) was obtained from the simulation of single-frequency spectra such as those shown in Figure 7 and was found to be negative for one species, hence designated as 2-neg and positive for the other, hence 2-pos (\( E \) was assigned the same sign as that of \( D \) by convention). The spectroscopically determined \( D \) values compare well with the average value of the same parameter extracted from SQUID magnetometry (\( -5.08 \text{ cm}^{-1} \); Table 2), and the presence of two crystallographically independent molecules in the asymmetric unit of the crystal structure of 2 readily explains the two \( S = 1 \) species observed by HFEPR. Apparently, the sign and magnitude of \( D \) is highly sensitive to the geometry of the TiII ion in 2. Ligand-field-theory (LFT) analysis using the angular overlap model provides an explanation for 2-neg and 2-pos having different magnitudes and signs of ZFS (Supporting Information, section 13).

Conformer 2-li, which more closely approximates trigonal (C\textsubscript{3v}) symmetry, is assigned to 2-pos, whereas the more distorted conformer 2-ben is assigned to 2-neg.

The dependence of \( D \) on molecular structure was further explored by quantum-chemistry computational means. The \( g \) and \( D \) tensors were calculated for 2 by employing hybrid density functional theory (DFT) calculations using the B3LYP
hybrid density functional with the CP(PPP) basis set on the Ti atom and the ZORA-def2-TZVP(-f) basis set on all other atoms; the calculations were based on the atomic coordinates from the crystal structures. The two conformers of 2 (cf. Table 1) each gave a unique set of parameters, in accord with the appearance of two spin systems in the HFEPR data. Notably, as with classical LFT (Supporting Information, section 13), the calculations reproduce the oppositely signed D values, although the magnitudes of D and E/D poorly match the experimental data (Table 3), which was also the case using LFT. In light of this, complete-active-space self-consistent-field (CASSCF) calculations with the strongly contracted N-electron valence perturbation theory 2 (NEVPT2)42 dynamical correlation correction were undertaken. Multiconfigurational approaches, including CASSCF/NEVPT2, predict ZFS for transition-metal complexes more accurately than DFT.43 This is partially attributable to multiconfigurational methods giving a more accurate prediction of d→d excited-state energies, which are essential to accurately determining the spin–orbit coupling (SOC) contribution to the ZFS. The present calculations used the effective Hamiltonian theory and included both contributions from SOC and spin–spin coupling (SSC);44 the SSC contribution is not directly accounted for in the classical LFT model.

The CASSCF/NEVPT2 calculations were based on the quasi-restricted orbitals (QROs)43 generated by the B3LYP calculation. The active spaces comprised two electrons and five orbitals [CAS(5,2)] and were averaged over all singlet (1S) and triplet (1T) ligand-field states expected for a d5 ion in C3v symmetry. State energies and ground-state configurations are included in the Supporting Information. The spin-Hamiltonian parameters (g, D, and E/D) calculated using this approach conform better with values calculated using DFT (Table 3). Importantly, species 2-neg observed by HFEPR can be plausibly assigned to conformer 2-ben, while 2-pos can be assigned to conformer 2-lin, exactly as proposed from LFT.

Reactivity of Complex 2 toward N2, THF, and an Isocyanide. Transient TiII species are known to activate N2, but reports of isolable and well-defined TiII species that can activate this inert gas remain quite rare.8c,45 Potential synthetic applications of this activation chemistry include reductive splitting of N2.46 In order to prepare complex 2, manipulations must be carried out under a strictly pure Ar atmosphere, and solvents must be sparged thoroughly in order to avoid

| species | SQUID | HFEPR |
|---------|-------|-------|
|         | D (cm⁻¹) | E/D | g_y | g_x | g_z |
| dc, 1 T | −5.08 | 0 | 1.85 | 1.85 | 1.85 |
| VTVF    | −4.86 | 0 | 1.85 | 1.85 | 1.85 |

Table 2. Electronic Structure Parameters for Complex 2 Extracted with SQUID Magnetometry and HFEPR Spectroscopy
reduction of 1 with KC₈ in THF under a N₂ (as opposed to Ar) atmosphere, and with workup carried out essentially identically with that for 2, resulted in the clean formation of a new diamagnetic product. Moreover, exposure of 2 in a pentane solution to an atmosphere of N₂ afforded the same species, quantitatively, over the course of minutes as a dark-green crystalline material. We should stress that, even in an Ar-filled glovebox, complex 2 gradually converts, in solution, to this new diamagnetic species, making it a potent scavenger of N₂! By contrast, crystalline 2 shows no signs of conversion into this new species when stored under N₂ over at least 24 h, reflecting the energetic penalties associated with structural changes in the solid state. The ¹H and ¹³C NMR, in addition to IR (νBH = 2559 cm⁻¹), spectral data of this new species feature a single pyrazolyl chemical environment, indicating that the new five-coordinate species undergoes rapid Berry pseudorotations in solution. XRD studies established formation of the bridged N₂ species [(Tp⁵Bu,Me)TiCl₂(η⁴-N=C=N=N=C-Ti₂-N₂)] (3) having a linear Ti≡N≡N≡Ti topology (Scheme 2 and Figure 8). The intense-green solution, the color of which matches neither the light-green color of 2 nor the dark-green color of 3. In both syntheses, removal of the volatiles produces an intense-green film, and the addition of pentane induces crystallization of 2 (under Ar) and 3 (under N₂) over the course of minutes. Surprisingly, an initial attempt at generating the ¹⁵N isotopeologue of 3 by exposing 2 to ¹⁵N₂ in THF over 1 h resulted in the isolation of only unconverted 2. Likewise, a complementary experiment involving the reduction of 1 with KC₈ in THF under N₂ followed by removal of the volatiles in vacuo and subsequent workup under Ar, afforded a mixture of 2 and 3 in a 70:30% proportion. To better understand the apparent inhibition of N₂ binding to 2 in THF, we turned to UV–vis spectroscopic studies. Upon going from toluene to a THF solution, absorption from 2 at 391 nm (1500 M⁻¹ cm⁻¹) undergoes a slight redshift to 412 nm (380 M⁻¹ cm⁻¹). More importantly, the intense absorptions extending into the NIR region (λ = 701, 857, 889, and 925 nm and ε = 180, 340, 320, and 230 M⁻¹ cm⁻¹, respectively) disappear altogether and are replaced by a weaker and broad absorption at 606 nm (38 M⁻¹ cm⁻¹; Figure S53). Thus, titration of toluene solutions of 2 with THF (0–0.70 M) indicates that an equilibrium takes place between 2 and the Lewis base with an association constant in the range of 5–8 M⁻¹ (Figure 9, left). In neat THF

Table 3. Calculated Spin-Hamiltonian Parameters for Conformers of Complex 2

| geometry         | τ₂ | method       | g₁  | g₂  | g₃  | D (cm⁻¹) | E/D |
|------------------|----|--------------|-----|-----|-----|----------|-----|
| 2-lin/2-pos      | 0.75| DFT          | 1.966 | 1.971 | 1.973 | −5.58 | 0.029 |
|                  |    | CASSCF/NEVPT2⁺ | 1.792 | 1.829 | 1.916 | +2.87 | 0.19  |
| 2-ben/2-neg      | 0.69| DFT          | 1.953 | 1.970 | 1.979 | +7.59 | 0.020 |
|                  |    | CASSCF/NEVPT2⁺ | 1.668 | 1.888 | 1.940 | −7.77 | 0.068 |

*Calculated using CAS(2,5) with an effective Hamiltonian SOC contribution and including a SSC contribution. CASSCF calculations are state-averaged over all d–d states of the d⁵ configuration.

Figure 8. Solid-state structure of 3. Thermal ellipsoids are at 50% probability. Solvent and H atoms (except on B) are omitted. Disorder in two ‘Bu groups and CI1’ is not shown.

Figure 9. Left: UV–vis absorption spectra of 2 (1.6 mM) in toluene with increasing concentrations of THF. Right: Solid-state structure of 2-THF. Thermal ellipsoids are at 50% probability. Solvent and H atoms (except on B) are omitted.

(12.3 M), this corresponds to 98–99% of 2 being present as the five-coordinate [(Tp⁵Bu,Me)TiCl(THF)] (2-THF; Scheme 2 and Figure 9, right). Eventually, we isolated crystalline 2-THF (in the strict absence of N₂) by prolonged storage of 2 in pentane containing low concentrations of THF (~35 °C). XRD studies verify that 2-THF is a rare example of a five-coordinate, mononuclear, and high-spin Ti²⁺ ion (τ₂ = 0.46). Moreover, the Ti–Cl [2.414(1) Å] and Ti–O THF [2.251(2) Å] distances in 2-THF fall in the longest decile of crystallographically characterized Ti–Cl and Ti–O THF distances in the CSD (version 2020.1), again reflecting the size of the Ti²⁺ ion in 2-THF. Importantly, the reactivity and spectroscopic and structural data provide evidence that the
reduction of 1 to ultimately produce 2 or 3 proceeds with 2-THF as a common intermediate (Scheme 2). It is apparent from our studies that THF blocks the binding site for N₂ activation. This finding is quite influential because it suggests that reductions of metal ions, often conducted in polar solvents such as THF, might actually disfavor binding of N₂ if the association constant of THF is large. In addition to this feature, the lability of the THF ligand is central for the TiII ion in subsequently attaining the tetrahedral geometry that is characteristic of complex 2.

Exposing complex 2 to isotopically enriched ¹⁵N₂ in pentane afforded [(Tp²H₃Me)₂(N₂)₂(TiCl)[η₁,η₂,η₂,η₂-15N₂)] (3-¹⁵N₂), and collecting ¹⁵N NMR spectroscopic data revealed a downfield chemical shift at 309 ppm [vs NH₃(l) referenced at 0.0 ppm; top right in Figure 10]. The ¹⁵N NMR data indicate a strongly red-shifted N vibration (14N/15N at 1401.1/1346.3 cm⁻¹; Figure 11) along with a difference spectrum (blue). Resonance Raman (405 nm excitation) data for 3 (black) and 3-¹⁵N (red) along with a difference spectrum (blue).

![Figure 10](https://dx.doi.org/10.1021/acs.inorgchem.0c02586)

**Figure 10.** Top left: IR spectral data for 3 (black) and 3-¹⁵N (red) along with a difference spectrum (blue). Top right: ¹⁵N NMR spectrum of 3-¹⁵N [with an external standard, AdC₁⁵N, referenced at 0.0 ppm]). Bottom: Resonance Raman (405 nm excitation) data for 3 (black) and 3-¹⁵N (red) along with a difference spectrum (blue).

TiCl([CNAd]) (2-CNAd) in 66% yield as a dark-maroon crystalline material. The ¹H NMR spectrum of 2-CNAd covers a ∼50 ppm chemical shift range (∼8 to +40 ppm), similar to the range found for 2 (∼2 to +46 ppm). Likewise, the magnetic moment extracted with Evans’ method (μₑffective = 2.72 μ₆) 28 °C, C₈D₈) attests to 2-CNAd still being high spin, consistent with the persistence of a TiII ion. Akin to 2-THF, an XRD study reaffirmed the connectivity in 2-CNAd, showing a rare example of a five-coordinate high-spin TiII complex (Figure 11). The linear Ti–C–N geometry [174.2(1)°] in 2-CNAd and the modest redshift of the C≡N stretching frequency versus free CNAd (2096 vs 2124 cm⁻¹; Figure 11) reflect a moderate degree of π-back-bonding, in line with the high-spin nature of 2-CNAd. However, the isonitrile ligand is not entirely spectroscopically innocent because the UV–vis spectrum of 2-CNAd displays much more intense charge-transfer bands (λ < 450 nm and ε > 3000 M⁻¹ cm⁻¹; Figure S56) than complexes 2 and 2-THF.

**XAS Spectra of Complexes 1–3 and 2-CNAd.** Ti K-edge XAS spectra were obtained for compounds 1–3 and the titanium(II) isocyanide adduct, 2-CNAd (Scheme 2 and Figure 12). The rising-edge energies obtained from the first

![Figure 12](https://dx.doi.org/10.1021/acs.inorgchem.0c02586)

**Figure 12.** Ti K-edge XAS data for complexes 1 (blue), 2 (black), 2-CNAd (gray), and 3 (red).

derivatives of the spectra are presented in Table 4. Compounds 1 and 3 exhibit inflection points at 4974.5 and 4973.9 eV, respectively, while 2 and 2-CNAd have inflection points at 4971.6 and 4971.1 eV, respectively. The ca. 3 eV gap between the pairs of rising-edge energies accords with the assignment of 2 and 2-CNAd as bona fide TiII species, whereas 1 and 3 are
physically defined Ti\textsuperscript{III} species. The XAS spectra also display prominent preedge absorption features, which were assigned with aid from time-dependent density functional theory (TDDFT) calculations (vide infra).

**Electronic Structure Calculations.** Hybrid DFT calculations using the B3LYP hybrid density functional with the CP(PPP) basis set on the Ti atom and the ZORA-def2-TZVP(-f) basis set on all other atoms were carried out using atomic coordinates from the crystal structures. The calculations were used as starting points for TDDFT calculations of the Ti K-edge XAS data. Calculated excitation energies correlated strongly and linearly with the experimental data (Figure S66; $R^2 = 0.97$). The linear fit was used to shift the calculated energies such that the calculated and experimental spectra overlap (Figures 13 and 14). Spectra for 2 were calculated for both independent conformers in the crystal structure (2-lin and 2-ben; Table 1) but were found to be effectively superimposable.

Table 4. Ti K-Edge XAS Preedge and Rising-Edge Energies for 1–3 and 2-CNAd

| complex  | preedge energy (eV) | rising-edge energy (eV) |
|----------|---------------------|------------------------|
| 1        | 4968.0              | 4974.5                 |
| 2        | 4966.8              | 4971.6                 |
| 2-CNAd   | 4966.6              | 4971.1                 |
| 3        | 4967.3              | 4973.9                 |

Assignments of the preedge features in the Ti K-edge XAS data of 2 and 3 were facilitated using molecular orbital (MO) diagrams produced by the initial single-point DFT calculations. Complex 2 exhibits a $2 + 1 + 2$ d–d splitting diagram, as would be expected for an effectively $C_3v$ system (Figure 15). The two d electrons reside within an effectively degenerate (e) level comprised of MOs of ca. 80% d character in accordance with the physical Ti\textsuperscript{III} d\textsuperscript{2} assignment suggested by the XAS data. Preedge excitations thus comprise several quadrupole-allowed Ti 1s $\rightarrow$ 3d excitations that gain intensity due to 4p mixing in the $C_3v$ environment.

The MO diagram of 3 (Figure 16) resulting from a spin-restricted hybrid DFT calculation depicts four electrons in two pseudodegenerate MOs of $\sim$50% Ti 3d and $\sim$30% N 2p
Reactivity of Complexes 2 and 3 toward Small Molecules. Complex 2 is stable in the solid state at room temperature and can be stored over months without showing signs of decomposition. In a toluene or benzene solution, 2 is stable over several hours at room temperature, after which it displays rich chemistry; for example, it rapidly reacts with \( \text{N}_2 \text{SiMe}_3(\text{Cl}) \) to form the imide \([(\text{Tp}^{\text{BuMe}})\text{Ti}\equiv\text{NSiMe}_3(\text{Cl})] \) in 80% isolated yield along with \( \text{N}_2 \) extrusion (Scheme 2). Complex 4 is diamagnetic and has been characterized by a combination of IR and \(^1\text{H}\) and \(^1\text{C}\) NMR spectra in addition to solid-state structural studies (Figure 17, top left). \(^{39}\text{Si}\) NMR spectroscopy reveals an upfield resonance (~13.5 ppm, vs SiMe\(_4\) referenced at 0.0 ppm), indicating that the \([(\text{Tp}^{\text{BuMe}})\text{Ti}\equiv\text{N}](\text{Cl})]\) fragment in 4 is more electron-donating than a methyl group. The structure shows short Ti–N distances for the imide ligand [1.692(1)–1.700(2) Å] in accordance with metal–ligand multiple-bond character, whereas the Ti–N–Si angles [158.9(10)–160.2(9)°] indicate that the imide N is best described as an sp-hybridized motif. In contrast, when 2 is treated with \( \text{N}_2\text{CPh}_2\) \( \text{N}_2 \) is not expelled, and instead of the hypothetical carbene \([(\text{Tp}^{\text{BuMe}})\text{Ti}\equiv\text{CPh}_2(\text{Cl})]\), the diamagnetic diazoalkane adduct \([(\text{Tp}^{\text{BuMe}})\text{Ti}\equiv\text{N}](\text{NCCPh}_2)(\text{Cl})]\) is isolated in 91% yield. Neither thermolysis (100 °C, overnight) nor photolysis (full spectrum from a Xe lamp, 1 h) promotes \( \text{N}_2 \) extrusion from 5. Thus, 5 behaves like Herberhold’s prototypical \([\text{Cp}_2\text{Ti}(\text{N}_2\text{CPh}_2)(\text{PMe}_3)]\) complex \(^{31}\) but shows marked contrast to the more reactive \([\text{Cp}_2\text{Ti}(\text{diazoalkane})]\) systems studied by Bergman, Andersen, and Chirik. \(^{32}\) While 4 shows \( \text{C}_2\) symmetry in solution (two sets of pyrazole resonances), 5 displays a symmetry similar to that of 3 in solution, based on multinuclear NMR spectral studies, reflecting the larger separation between the CPh\(_2\) and Bu groups in 5 compared to the SiMe\(_3\) and Bu groups in 4. A solid-state structure confirmed retention of the \( \text{N}_2 \) unit in 5, as well as the presence of a short Ti–N multiple bond [1.722(1) Å; Figure 17, top right]. Bond distances within the diazoalkane ligand in 5 \([\text{C–N}, 1.297(2) Å; \text{N–N}, 1.327(2) Å]\) correspond reasonably well with bond distances in the hydrazone, \( \text{Ph}_2\text{C(NH)NH}_2 \) \([\text{C–N}, 1.286(2) Å; \text{N–N}, 1.371(3) Å]\). \(^{53}\) This hints at a dianionic diazoalkane ligand; notably, free diaryldiazoalkanes display much shorter N–N bond distances (1.12–1.16 Å). \(^{54}\)

We also explored the reactivity of the high-spin, tetrahedral Ti\(^{III}\) ion in 2 with other small molecules. \( \text{N}_2\text{O} \) reacts immediately upon contact with a benzene solution of 2 to form the terminal oxo \([(\text{Tp}^{\text{BuMe}})\text{Ti}≡\text{O}(\text{Cl})]\) along with 3 (Scheme 2), due to the concomitant release of \( \text{N}_2 \) and trapping by 2 equiv of the azophile 2. The greater affinity of 2 for \( \text{N}_2 \) compared to \( \text{N}_2\text{O} \) most likely results in capture of the former. However, one could also argue for a bimolecular mechanism involving a \( \text{N}_2\text{O} \) complex, \(^{55}\) “\([(\text{Tp}^{\text{BuMe}})\text{Ti}(\text{N}_2\text{O})(\text{Cl})]\),” reacting with 2. Regardless, the reaction mixture progresses over 18 h to eventually form the oxo complex in quantitative spectroscopic yield, and workup results in colorless crystals of 6 in 75% isolated yield (Scheme 2). Independently, treating 3 with 1 atm of \( \text{N}_2\text{O} \) cleanly produces 6, thus rendering the former species a masked form of Ti\(^{III}\) ion. \(^{56}\) The Ti≡O bond in 6 is remarkably short [1.621(1) Å; Figure 17, bottom left], possibly in line with triple-bond character; this is also manifested in the \(^1\text{H}\) NMR spectrum of 6, where the Me and Bu groups display broad resonances because of restricted rotation (e.g., via a Berry pseudorotation) around the central Ti≡O unit. This feature might contribute to the more restricted rotation in 4 compared to 3 and 5, but it is noteworthy that the \(^1\text{H}\) NMR spectrum of 7 (a titanium imide akin to 4, vide infra) shows only a single pyrazole environment.

The bicyclic imine 2,3,5,6-dibenzo-7-azabicyclo[2.2.1]-hepta-2,5-diene (Hdbabh)\(^{58}\) delivers a parent imide moiety to the Ti\(^{III}\) ion of 2 by forming \([(\text{Tp}^{\text{BuMe}})\text{Ti}≡\text{N}](\text{Cl})]\).
near-quantitative spectroscopic yield (Scheme 2). Separation of 7 from the side product anthracene can be achieved via filtration of the reaction mixture through activated charcoal, providing yellow crystals of 7 in 32% isolated yield. The \(^{1}H-^{15}N\) HSQC NMR spectrum of 7 unambiguously identifies the parent imide group through a cross-peak between a \(^{1}H\) triplet (4.97 ppm) and a downfield \(^{15}N\) nucleus (458 ppm; Figure S36). The same conclusion can be derived from the IR spectrum of 7, which exhibits a strong NH stretching vibration (3296 cm\(^{-1}\)). Whereas terminal titanium–oxo ligands are not uncommon, terminal parent imides are quite a rare motif for group 4 transition metals.\(^{59}\) A solid-state structural study of 7 (Figure 17, bottom right) confirms the terminal parent imide motif and a geometry similar to that of 4 and 6. The imide H for both independent molecules was located in the difference Fourier map, and the Ti–N bond distances [1.674(4) – 1.680(4) Å] fall within the range for terminal titanium imide complexes [1.627(8) – 1.747(2) Å].\(^{59a-d}\) The transfer of a parent imide group to low-valent Ti, thereby forming a mononuclear group 4 transition-metal imide, is unprecedented. In a few instances, this type of reaction has been reported for group 5 metals, via NH group transfer from 2-methylaziridine to V\(^{III}\) and Ta\(^{III}\) ions.\(^{60}\) Moreover, NH transfer reactions from aziridines or Hdbkbh are known to generate transient imide functionalities, which are implicated in the formation of amide and nitride complexes of Ti, W, and Fe.\(^{61}\) The few known examples of titanium complexes having the parent imide group have been reported by several routes: deprotonation of NH\(_{2}\),\(^{59d}\) protonation of a nitride salt,\(^{59d}\) or via a nitridyl radical that effects H-atom abstraction.\(^{59b,c}\) Along these lines, an alternative, nitridyl-mediated, route to 7 consists of treatment of the Ti\(^{III}\) precursor 1 with NaN\(_{3}\) in THF. However, this reaction suffers from the sacrificial use of the \([\text{Tp}^{\text{Bu,Me}}\text{Ti}]\) fragment as a H-atom source as well as the partial substitution of chloride for azide, thus giving mixtures of the corresponding azide and chloride imide complexes \([\text{Tp}^{\text{Bu,Me}}\text{N}]{\text{X}}\) \([\text{X} = \text{N}_{3}\) or Cl (7)\] as well as other poorly defined decomposition products. The azide imide complex was identified via the characteristic \(^{1}H\) NMR resonance from the NH group (triplet at 3.58 ppm; Figure S33).

With the availability of structural and vibrational data for the new complexes 1, 2, adducts of 2, and the derived products (3–7), some general conclusions about their geometries and electronic structure can be inferred (Table 5). With 1 as the exception \((r_{e} = 0.27)\), the values of \(r_{e}\) fall closely around 0.5, such that complexes 2-THF, 2-CNAd, and 3–7 do not lend themselves to a classification as being either trigonal-bipyramidal or square-pyramidal. The divalent nature of 2-THF and 2-CNAd can be directly seen from the long Ti–E and Ti–Cl distances compared to complexes 3–7, both reflecting the single-bond character of the Ti–E bonds and the large size of the Ti\(^{II}\) ion. Complexes 2-THF, 2-CNAd, and 3–7 underline the strong tendency for complex 2 to undergo reactions that render the Ti ion five-coordinate. As the reverse to this, complexes 4 and 7 might, in principle, eliminate small molecules (Me\(_{3}\)SiCl and HCl) to generate a neutral titanium nitride functionality, but this mode of reactivity is not operational for the \((\text{Tp}^{\text{Bu,Me}}\text{Ti} = \text{E}(\text{Cl}))\) scaffold. Finally, inspection of the molecular structures of all complexes reported herein shows that the Ti\(^{II}\) complexes have Ti–Cl and B–H vectors oriented in an antiparallel fashion, whereas the Ti\(^{IV}\) complexes have the same vectors aligned nearly perpendicular. Indeed, the average B–Ti–Cl angles correlate well with the average Ti–B separations, as shown in Figure 18, revealing that all complexes group into three distinct regions when judged by their formal oxidation states. The link between metric variation and the formal oxidation state likely reflects the increasing ionic radius encountered upon going from Ti\(^{IV}\) to Ti\(^{II}\); thus, a reduced Ti center tends to slide out of the \(\text{Tp}^{\text{Bu,Me}}\text{N}^{-}\) ligand, accounting for the increase in Ti–B separations and the straightening of B–Ti–Cl angles. Importantly, complex 3 falls between the Ti\(^{II}\) and Ti\(^{III}\) regions in Figure 18, augmenting support for the assignment of 3 as consisting of two Ti\(^{III}\) centers covalently bound through an \(\text{N}_{3}^{2-}\) ligand.

### CONCLUSIONS

In summary, we have demonstrated the use of a sterically encumbering tris(4-pyrazolyl)borate ligand, \(\text{Tp}^{\text{Bu,Me}}^{-}\), to generate the Ti\(^{III}\) precursor, 1. Tuning of the steric profile of the Tp ligand (replacement of the S\(^{5}\)Bu group with Me) proved essential for obtaining a Ti\(^{III}\) precursor with sufficient purity and stability for subsequent chemistry. Reduction of 1 under Ar furnishes a new geometry with a unique electronic structure: a stable tetrahedral Ti\(^{II}\) ion, 2, having two unpaired electrons. The Ti K-edge XAS spectrum of 2 is shifted to lower energy relative to structurally similar complexes bearing.
formally TiIII centers, consistent with 2 having a more reduced metal center. Complex 2 exhibits a \(^3\)A_2\(^g\) electronic ground state because of its confinement to a tetrahedral coordination geometry, as demonstrated by the magnetic moments extracted from SQUID magnetometric studies; the spin-only \(^d^2\) behavior of 2 persists to temperatures as low as 10 K, whereupon ZFS results in a drastically lowered magnetic moment. HFPEPR spectroscopic studies corroborate that 2 is a bona fide example of an \(S = 1\) TiIII ion via the observation of two spin triplet systems (ZFS parameters: \(D = -5.91\) and \(+1.55\) \(\text{cm}^{-1}\), respectively). The origin of two \(S = 1\) systems can be traced to the two crystallographically independent molecules (conformers) in 2, which display geometric distortions around the tetrahedral TiIII ion, e.g., B–Ti–Cl angles spanning 162.9(1)–174.6(1)°. This assertion is supported by classical LFT and by CASSCF/NEVPT2 calculations, which closely reproduce these ZFS parameters and depict excited-state manifolds consistent with \(d^2\) ions in an effective \(C_{3v}\) environment. Complex 2 is a potent scavenger of \(N_2\) thus producing the dinuclear dianionic complex 3, where the \(N_2\) unit coordinates in a linear fashion between two Ti centers. The use of \(^{15}\)N to generate isotopically labeled 3–\(^{15}\)N confers atmospheric \(N_2\) as the source of the bridging \(N_2\) ligand. Labeling studies further identify a N–N stretching frequency by IR vibrational spectroscopy (\(^{14}\)N\(^{15}\)N at 1401.1/1366.3 \(\text{cm}^{-1}\)), a Ti–N stretching frequency by IR vibrational spectroscopy (\(^{14}\)N\(^{13}\)N at 769/749 \(\text{cm}^{-1}\)), and a \(^{15}\)N NMR resonance at 309 ppm. Ti K-edge XAS supported by TDDFT calculations accord with these complexes bearing physically formal TiIII \(d^1\) centers. Taken together, these results show that the bonding in 3 can be viewed as a covalent interaction between two Ti centers and \(N_2\), producing a TiIII\(^{2-}\)–TiIII core. A combination of electrochemical, reactivity, spectroscopic, and structural studies demonstrate that THF coordinates reversibly to 2 with a fairly high association constant on the order of \(5–8\) \(\text{M}^{-1}\); the so-formed \(2\)-THF adduct is impervious to \(N_2\) binding, implying the intermediacy of a four-coordinate geometry in reactions, where 1 is reduced to generate 2 as well as 3. Even when using a strong-field ligand, such as CNad, complex 2 forms a five-coordinate adduct, 2-CNad, while preserving the high-spin nature of the TiIII ion, owing to only a moderate degree of \(\pi\)-back-bonding, as seen from the linear Ti–C–N geometry \([174.2(1)^\circ]\) and slight redshift of \(\nu(C=N)\) (28 \(\text{cm}^{-1}\)). The availability of an open coordination site as well as two energetically high-lying \(d\) electrons renders tetrahedral 2 a versatile precursor to a family of five-coordinate TiIV complexes of the type \([\{\text{Tp}^{Bu,Me}\}\text{Ti}\equiv E(\text{Cl})\}]\), with \(E^{2-} = \text{O, NH, NSiMe}_3\), and \(N_2\text{CPh}_3\). These products result from O-atom transfer from \(N_2O\) and NH group transfer from the bicyclic amine Hdbbh to generate respectively the corresponding terminal oxide and parent terminal imide complexes. While \(N_2\)SiMe\(_3\) reacts with 2 under \(N_2\) extrusion, \(N_2\text{CPh}_3\) retains an intact N≡N≡C spine up to 100 °C.

We are presently scrutinizing the unique electronic structure of additional tetrahedral TiIII complexes, as well as examining their potential for generating unusual metal–ligand multiple bonds.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02586.

### Accession Codes

CCDC: 2005728–2005738 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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