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Balance between Metal and Ligand Reduction in Diiminepyridine Complexes of Ti

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Supporting Information

ABSTRACT: Reaction of the diiminepyridine ligand EtDIP (2,6-Et2-C6H3N=CMe3)(C5H3N) with TiCl3(THF)3 gave the corresponding Ti(III) complex (EtDIP)TiCl3 (1). Reduction of 1 with 1 equiv of KC8 produced the formally Ti(II) complex (EtDIP)TiCl2 (2). From this, (EtDIP)TiClR complexes (R = Me (3a), Me3SiCH2 (3b), Ph (3c)) were obtained by addition of 1 equiv of RLi. Similarly, dialkyl complexes (EtDIP)TiR2 (R = Me (4a), Me3SiCH2 (4b)) were obtained with 2 equiv of RLi. All new complexes except 3b were characterized by single-crystal X-ray diffraction. EPR studies indicate that complex 1 is best regarded as a true Ti(III) complex with an “innocent” DIP ligand. Complexes 2−4 are all diamagnetic. In contrast to DIP complexes of the late transition metals Fe and Co, the new complexes 2−4 show strong upfield 1H NMR shifts for the pyridine β and γ protons caused by transfer of negative charge to the DIP ligand. On the basis of this and the C=N and Cimine−Cpy bond lengths, a description involving Ti(IV) and a dianionic ligand seems most appropriate, and DFT calculations support this interpretation. This means that reduction of Ti(III) complex 1 results in oxidation of the metal center to Ti(IV). VT-NMR studies of 4a suggest a small and temperature-dependent thermal population of a triplet state, and indeed calculations indicate that 4a has the lowest singlet−triplet energy difference of the systems studied.

INTRODUCTION

Next to the choice of a metal itself, the metal oxidation state is one of the key determinants of reactivity of metal complexes. Low-valent metals may undergo oxidative addition, and high-valent metals tend toward reductive elimination and/or Lewis acid catalysis. The introduction of redox-active ligands has blurred this simple picture. In a combination of a metal with such a ligand, the formal oxidation state of the metal may be deceptive. In addition, the ligand may serve as an electron reservoir, supporting chemistry that would not happen with the same metal and a redox-innocent ligand. Finally, the combination of redox-active ligands and non-noble metals has been reported to lead to chemistry more typical of noble-metal catalysis.1−3

Within this context, the diiminepyridine (DIP) ligand (Scheme 1) occupies a pre-eminent position. It stabilizes metals in low formal oxidation states, often in electronic structures that have ligand-centered electrons antiferromagnetically coupled to metal-centered electrons. The DIP ligand has been documented to accept up to three electrons in its π* orbitals,4 and once it has accepted one or more electrons, it preferentially stabilizes lower-spin states of the metal, such as intermediate-spin Fe(II),5 low-spin Mn(III),6 and low-spin Co(II).7,8

Scheme 1. 8DIP Ligand
species \([\text{DIP}]\text{TiCl}_3^+\). Heating \([\text{iPrDIP}]\text{TiCl}_3^+\text{Cl}^-\) in toluene resulted in spontaneous reduction to the neutral Ti(III) complex \([\text{iPrDIP}]\text{TiCl}_3\) (characterized by XRD and IR), which could also be prepared directly from \([\text{iPrDIP}]\text{TiCl}_3\text{(THF)}_3\). In addition, they reported the formation of diamagnetic \([\text{iPrDIP}]\text{TiCl}_2\) (characterized by elemental analysis and IR) from \([\text{iPrDIP}]\text{TiCl}_3\text{(THF)}_2\). The authors do not appear to have considered the possible noninnocence of the DIP ligand in these formally Ti(III) and Ti(II) complexes. In contrast, recent work by the group of Panda on Ti complexes of the potentially redox active \(\alpha\)-diimine (ADI) ligand indicates that in \((\text{ADI})\text{TiCl}_2\), \((\text{ADI})\text{Ti(Cp)}\text{Cl}\), and \((\text{ADI})\text{Ti(Cp)}\text{CH}_2\text{SiMe}_3\), the \(\sigma^2,\pi\)-bound ADI ligand is in the doubly reduced state. In the present work, we report the synthesis and characterization of \((\text{EtDIP})\text{TiCl}_3\) and \((\text{EtDIP})\text{TiCl}_2\) complexes and probe the spectroscopic oxidation state of the metal using NMR, EPR, XRD, XPS, and computational methods. The EtDIP ligand was chosen because it offers a nice compromise in terms of solubility and steric shielding of the metal center.

## RESULTS AND DISCUSSION

### Syntheses

Syntheses of formally Ti(III) and Ti(II) complexes are summarized in Scheme 2. The "spontaneous reduction" route toward \((\text{EtDIP})\text{TiCl}_3\) (1) was found to be rather messy. In contrast, the reaction of \((\text{EtDIP})\text{TiCl}_3\) in THF cleanly yields 1. This dark green compound has low solubility in common organic solvents. X-ray-quality crystals were obtained by layering THF solutions of \(\text{EtDIP}\) and \(\text{TiCl}_3\). Reduction of 1 with \(\text{KCl}_2\) in THF afforded \((\text{EtDIP})\text{TiCl}_2\) (2) in high yield. This complex shows much higher solubility in common solvents, giving deep green solutions. Alkylation of 2 with 1 equiv of \(\text{RLi} (R = \text{Me}, \text{Me}_3\text{SiCH}_2, \text{Ph})\) produced the mixed alkyl–chloro complexes \((\text{EtDIP})\text{Ti(R)Cl}\) (3a–c). Use of 2 equiv of \(\text{MeLi}\) or \(\text{Me}_3\text{SiCH}_2\text{Li}\) gave the dialkyls \((\text{EtDIP})\text{TiR}_2\) (4a, b); curiously, reaction with 2 equiv or an excess of \(\text{PhLi}\) did not yield any isolable \((\text{EtDIP})\text{TiPh}_2\), producing instead mixtures of uncharacterized compounds. Attempted syntheses of monalkyl compounds bearing \(\beta\)-hydrogens were unsuccessful.

All of the aforementioned formally Ti(II) complexes (2, 3a–c, 4a, b) are dark green solids, air-sensitive but thermally rather stable. For example, \((\text{EtDIP})\text{TiMe}_2\) survives prolonged heating at 85 °C.

The above synthetic procedures represent the standard approach to low-valent iminepyridine complexes. However, alternative routes have been reported, such as deprotonation/oxidation of coordinated picolylamine ligands.

### X-ray Structural Characterization

The molecular structures of all new compounds except 3b were determined by single-crystal X-ray diffraction. Unfortunately, we find that complexes of \(\text{EtDIP}\) have a high tendency to crystallize with disorder in the orientation of one or more Et substituents, reducing the precision of the resulting geometric parameters. Selected bond lengths are collected in Table 1.

The structure of 1 (Figure 1) shows a distorted-octahedral environment around Ti, with three rather different Ti–Cl bond lengths (2.3418(12), 2.2547(13), and 2.4154(11) Å); one of the chlorides is bent back over the DIP ligand (\(\angle\)N2–Ti–Cl41

### Table 1. Selected Bond Lengths (Å) for \((\text{EtDIP})\text{Ti}\) Complexes

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3a</th>
<th>3c</th>
<th>4a</th>
<th>4b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–N1</td>
<td>2.202(3)</td>
<td>2.040(2)</td>
<td>2.155(2)</td>
<td>2.059(2)</td>
<td>2.119(2)</td>
<td></td>
</tr>
<tr>
<td>Ti–N2</td>
<td>2.107(4)</td>
<td>2.152(2)</td>
<td>2.014(2)</td>
<td>2.002(2)</td>
<td>1.990(2)</td>
<td>2.014(2)</td>
</tr>
<tr>
<td>Ti–N3</td>
<td>2.107(4)</td>
<td>2.152(2)</td>
<td>2.014(2)</td>
<td>2.002(2)</td>
<td>1.990(2)</td>
<td>2.014(2)</td>
</tr>
<tr>
<td>Ti–X41</td>
<td>2.254(1)</td>
<td>2.288(2)</td>
<td>2.299(9)</td>
<td>2.227(8)</td>
<td>2.109(4)</td>
<td>2.093(3)</td>
</tr>
<tr>
<td>Ti–X61</td>
<td>2.342(1)</td>
<td>2.394(3)</td>
<td>2.436(3)</td>
<td>2.389(3)</td>
<td>2.341(4)</td>
<td>2.305(4)</td>
</tr>
<tr>
<td>N1–C12</td>
<td>1.298(5)</td>
<td>1.332(7)</td>
<td>1.360(3)</td>
<td>1.317(3)</td>
<td>1.355(4)</td>
<td>1.347(4)</td>
</tr>
<tr>
<td>C12–C13</td>
<td>1.459(6)</td>
<td>1.411(7)</td>
<td>1.398(3)</td>
<td>1.429(3)</td>
<td>1.386(4)</td>
<td>1.418(4)</td>
</tr>
<tr>
<td>C17–C18</td>
<td>1.471(6)</td>
<td>1.411(1)</td>
<td>1.424(3)</td>
<td>1.392(3)</td>
<td>1.421(4)</td>
<td>1.404(4)</td>
</tr>
<tr>
<td>C18–N3</td>
<td>1.298(4)</td>
<td>1.333(8)</td>
<td>1.326(3)</td>
<td>1.369(4)</td>
<td>1.339(4)</td>
<td>1.355(4)</td>
</tr>
</tbody>
</table>
molecules in the unit cell of (iPrDIP)ScCl3° 2.298(1), 2.429(1) Å; 80.79(9)°. The three independent molecules in the unit cell of (iPrDIP)ScCl3° also show such a “bent-back” chloride, with a longer M–Cl bond; therefore, this deformation is likely due to steric rather than caused by the presence of a single 3d electron.

The formally Ti(II) complexes 2–4 all have a distorted-square-pyramidal Ti environment. The structures of 3a, 3c, and 4b are shown in Figures 2–4, respectively, and those of 3a and 22.5°. In the highly sterically hindered complex 4b, the apical Me3SiCH2 group is folded back toward the pyridine ring of the DIP ligand, while the equatorial alkyl group is stretched out away from the DIP ligand.

Bond lengths have been used as indicators of the amount of charge absorbed by the DIP ligand. Electron transfer from metal to ligand results in the population of low-lying ligand π* orbitals which are C=N antibonding but Cimine–Cpy bonding, resulting in elongation of the former and contraction of the latter bonds. Table 2 compares relevant bond length changes.

Table 2. DIP Ligand Bond Length Changes (Å)°

<table>
<thead>
<tr>
<th></th>
<th>av C=N</th>
<th>av Cim–Cpy</th>
<th>av deform</th>
</tr>
</thead>
<tbody>
<tr>
<td>0e transfer</td>
<td>1.280</td>
<td>1.437</td>
<td>0.053</td>
</tr>
<tr>
<td>1e transfer</td>
<td>1.330</td>
<td>1.425</td>
<td>0.063</td>
</tr>
<tr>
<td>2e transfer</td>
<td>1.298</td>
<td>1.465</td>
<td>0.023</td>
</tr>
<tr>
<td>(iPrDIP)TiCl3°44</td>
<td>1.286</td>
<td>1.478</td>
<td>0.011</td>
</tr>
<tr>
<td>2</td>
<td>1.329</td>
<td>1.411</td>
<td>0.066</td>
</tr>
<tr>
<td>3a</td>
<td>1.343</td>
<td>1.411</td>
<td>0.073</td>
</tr>
<tr>
<td>3c</td>
<td>1.343</td>
<td>1.411</td>
<td>0.073</td>
</tr>
<tr>
<td>4a</td>
<td>1.347</td>
<td>1.404</td>
<td>0.078</td>
</tr>
<tr>
<td>4b</td>
<td>1.351</td>
<td>1.411</td>
<td>0.077</td>
</tr>
<tr>
<td>av over 2–4</td>
<td>1.343</td>
<td>1.409</td>
<td>0.073</td>
</tr>
</tbody>
</table>

°For a complete list of reference data used, see Table S2 in the Supporting Information. °See text for explanation. °See eq 1.

Reference bond lengths were obtained as follows from structures in the Cambridge Structural Database [35] (see the Supporting Information for details):

For no electron transfer (0e): averages over several (DIP)MnCl2 and (DIP)CoCl2 complexes
For 1e transfer: averages over several (DIP)Co(alkyl) complexes
For 2e transfer: averages over several (DIP)Fe(N2), (DIP)Fe(N2)2, and [(DIP)Fe(N2)]2(μ-N2) complexes

As an aggregate measure we use \( \Delta d \), the average of elongations of the C=N bonds and contractions of the Cimine–Cpy bonds relative to their 0e reference values:

\[
\Delta d = \frac{1}{2} \left[ (d_{C=N}(av) - d_{C=N}^{0e}(av)) + (d_{Cim-Cpy}^{0e}(av) - d_{Cim-Cpy}(av)) \right]
\]

(1)

The average \( \Delta d(1e) \) for the reference set of 1e transfer molecules is 0.053 Å. The \( \Delta d \) values for our complex 1 (0.023 Å) and Calderazzo’s (iPrDIP)TiCl3 (0.011 Å) are much smaller, indicating little electron transfer in these complexes and supporting a description involving Ti(III) bound to a neutral DIP ligand. The average \( \Delta d(2e) \) for the set of reference 2e transfer molecules (0.063 Å) is much smaller than twice the value of \( \Delta d(1e) \), suggesting that bond length changes may not be linear in the amount of electron transfer.

In any case, the average \( \Delta d \) value for our complexes 2–4 (0.073 Å) is larger than the \( \Delta d(2e) \) reference, which we take as indicating the presence of Ti(IV) bound to a dianionic DIP ligand, i.e. a dominant contribution of resonance structures B and C in eq 2, rather than the perhaps to be expected Ti(III)–ligand radical anion combination.

One final comment on bond lengths involves the (lack of) symmetry of the DIP skeleton. While complexes 1, 2, and 4b each show two basically identical C=N and Cim–Cpy bonds,

4a (very similar to 2) are provided in the Figures S4 and S7 in the Supporting Information. In the mixed alkyl–chloro complexes 3a,c, the alkyl group occupies the apical position, which might be due to trans influence. The highest possible symmetry for 3c is C3v, but we find that the phenyl group (C41–C46) has rotated out of the potential mirror plane through Ti1, N2, Cl51, and C41, with \( \angle(\text{Ti1N2Cl51C41})_{(C41-C46)} = 79.38(8)° \). These deformations are very similar to those reported by Calderazzo°44 for (iPrDIP)TiCl3 (2.344(1), 2.429(1) Å; 80.79(9)°).
those in 3a,c differ considerably, with rms left–right differences of 0.03–0.04 Å. This could be interpreted as partial localization of the negative charge on the ligand: i.e., unequal contributions of structures B and C. However, all complexes show left–right equivalence in solution on the NMR time scale, and calculations (vide infra) consistently produce symmetric structures. We therefore attribute the considerable asymmetry in the solid state of 3a,c (and the lesser asymmetry of 4a) to packing forces, which would mean that the energy difference between symmetric and more localized structures is very small.\(^5\)

One problem with the analysis of DIP ligand bond lengths is that the changes due to electron transfer are not very large, while at the same time the presence of Et group disorder in virtually all of our \(^{10}\)DIP complexes reduces the precision with which skeleton bond lengths are determined. Ti–Cl bond lengths suffer less from this problem. For a closely related Ti Cp–phosphinimide complexes, Stephan\(^51\) reported Ti–Cl bond lengths of ∼2.31 Å for Ti(IV) and ∼2.38 Å for Ti(III). There are not many Ti(II) halides, but a reasonable range appears to be 2.4–2.5 Å.\(^32,53\) The observed range of 2.27–2.30 Å for complexes 2 and 3 is highly suggestive of a Ti(IV) assignment. For complex 1 the situation is less clear, since the three Ti–Cl bonds have rather different lengths; the average of 2.34 Å suggests a situation somewhere between Ti(III) and Ti(IV). Ti–C bond lengths are also sensitive to the oxidation state of the metal. Our Ti–C bond lengths for 3 and 4 (2.08–2.11 Å) are much shorter than the Ti–Me bond of 2.219(2) Å in the true Ti(II) complex Ti(CH\(_3\))\(_2\)(dmpe),\(^54\) and closer to the bond length observed for e.g. Ti(IV) in (BDMP)TiBr–(CH\(_2\)CMe\(_2\)Ph) (2.121(7) Å).\(^55\)

**EPR of 1.** The reported magnetic moments for \((^{10}\)DIP)TiCl\(_3\) (1.67 \(\mu_B\)) and \((^{10}\)DIP)TiCl\(_4\) (1.72 \(\mu_B\))\(^55\) establish the presence of a single unpaired electron but do not provide information on the location (ligand or metal) of that electron. The low solubility of 1 in most solvents presented a problem for EPR measurements: only CH\(_2\)Cl\(_2\) dissolved enough to allow recording of meaningful X-band EPR spectra, but this solvent often gives a poor glass on cooling, leading to aggregation behavior and preferred orientation effects of the paramagnetic solutes. Indeed, in pure CH\(_2\)Cl\(_2\) the EPR spectrum of 1 is very broad and asymmetric. In an attempt to reduce such preferred orientation/aggregation effects, we added \([^{10}\text{Bu}_4\text{N}]\text{PF}_6\) to the solution. The EPR spectrum of this frozen mixture (Figure 5) is indeed sharper but otherwise shows peak positions overall identical with those of the spectrum in pure CH\(_2\)Cl\(_2\). Some aggregation/preferred orientation effects remain, and as a result a satisfactory simulation of the experimental spectrum could only be obtained by assuming the presence of two species (ratio ∼1:4) with very similar g tensors but differing widely in their line width parameters (Table 3). This behavior is best ascribed to remaining “bad glass” effects and probably does not mean that there are really two different EPR-active species in the sample.

The rhombicity of the \(g\) tensor and the significant deviations of the \(g\) values from \(g_z\) (2.0023) demonstrate that the unpaired electron is substantially or even predominantly metal centered, suggesting a formulation of 1 as \((^{10}\text{DIP})\text{Ti}^{\text{III}}\text{Cl}_3\). Computational studies are in reasonable agreement, although the calculated \(g\) values are all slightly higher than the observed values, indicating a somewhat more extensive delocalization of spin density over the DIP ligand in these calculations (for details see the Supporting Information).

**NMR Studies.** Complexes 2–4 all show fairly similar NMR spectra. Resonances are mostly sharp and in the normal 0–10 ppm range, indicative of diamagnetic complexes.

Reported \(^1\)H chemical shifts for the backbone of DIP complexes show remarkable variations in chemical shift as a function of the metal fragment bound to it (Table 4). DIP complexes of formally Co(I), which are proposed to actually contain low-spin Co(II) antiferromagnetically coupled
to a ligand-centered electron, show a strong low-field shift for pyridine H4 (9.5–10.5 ppm), a normal shift for H3/S, and a high-field shift for the imine methyl group (−1 to 0 ppm).7 In contrast, (EIPI)Fe(N2)2, which likely contains intermediate-coalescence to a single set of CH2SiMe3 resonances and 40, and these should be strongly hindered by the ligand side related iron dialkyls,24 as well as for (iPrDIP)Zn(CH2C6H5)2,58 which would be observed around 454.7 eV.64,65 Alkylation to give 3 or 4 results in a very small decrease of the Ti 2p binding energy, which remains in the range typical of Ti(IV). The XPS data thus agree with the formulation of 1 as containing (DIP)TiII and indicate the “more reduced” complexes 2–4 actually contain Ti in a higher oxidation state: (DIP)TiIV.

**Computational Studies.** Complexes 1’–4’, containing the MeDIP model ligand instead of EtDIP, were studied by DFT methods (TurboMole, TPSSH functional, def-TZVP basis set), starting from the solid-state structures but replacing the original DIP Et groups by Me groups. The final optimized ligand geometries agree well with the X-ray structures, be it that the optimized structures for 2’–4’ are all left-right symmetric within error margins. A spin density plot for complex 1’ (Figure 7) shows that the single unpaired electron is mostly concentrated on Ti, but with evident delocalization to the ligand π system, consistent with the X-ray, EPR, and XPS results.

For structures 2’–4’, broken-symmetry solutions were explored, but with very few exceptions (vide infra) the SCF calculations converged to closed-shell solutions. This is in marked contrast to low-valent Co and Fe DIP complexes, where broken-symmetry solutions are often preferred. Electronically and geometrically, 2’–4’ are all rather similar. The HOMO has little Ti character and basically corresponds to one of the two DIP π* orbitals, while the LUMO is the second π* orbital; Figure 8 shows these orbitals for 4a’. The singlet–triplet energy difference is rather small and varies somewhat with the computational method used. In agreement with NMR data mentioned earlier, 4a’ is predicted to have the smallest singlet–triplet separation of the studied complexes. In fact, TPSSH/def-TZVP seems to overestimate the stability of the triplet, making it 0.1 kcal/mol more stable than the singlet, while the NMR data for 4a (clearly mostly diamagnetic) indicate the triplet to be −2 to −3 kcal/mol less stable.

**Triplet 4a’** is predicted to prefer a trigonal-bipyramidal (TPB) C3v geometry, unlike the square-pyramidal (SP) C2v structure preferred by the singlet. The path for apical/equatorial exchange of Me groups in singlet 4a’ was briefly investigated (eq 5). At the SP geometry, a closed-shell solution
is preferred. However, deformation toward the TBP structure costs less than 1 kcal/mol. For structures close to TBP, a broken-symmetry solution becomes lower in energy, and its energy at its optimized TBP geometry is only ∼0.5 kcal/mol above the SP closed-shell singlet. Interestingly, the broken-symmetry solution has the two antiferromagnetically coupled electrons occupying π*-type SOMOs concentrated on the left and right sides of the DIP ligand (Figure 9), rather than the metal/π* orbital combination usually found in formally Co(I) and Fe(0) complexes.7,30

As mentioned earlier, the difference in ligand 1H NMR chemical shifts between our new "Ti(II)" complexes and formally low-valent Co and Fe complexes is remarkable. To investigate this further, we also calculated 1H NMR chemical shifts for 2′−4′ using the GIAO method. Unlike the case for low-valent Co and Fe complexes, these predictions are reasonable, including the high-field shift of the pyridine ring protons (Table 4). This means that no contributions of thermally populated or spin-admixed triplet states are needed to explain these shifts, and it is only for complex 4a that we have any indication of a thermally populated triplet state.

**Conclusions.** True Ti(II) complexes are rare, and Ti(II) is a strong reductant. It is therefore not surprising that in the reported new formally low-valent Ti DIP complexes the diiminepyridine ligand is noninnocent, accepting two electrons. It seems complex 1 is perhaps closest to (DIP(0))TiIII, while 2−4 are probably best regarded as containing (DIP 2−)TiIV. Experimental data establish a diamagnetic ground state for 2−4, although the NMR data for 4a indicate the presence of a thermally populated triplet state. Calculations indicate the presence of a low-lying triplet state for all formally Ti(II) complexes. Nevertheless, the mono- and dialkyl complexes 3 and 4 are surprisingly thermally stable, with both 4a and 4b surviving temperatures up to 85 °C in solution. However, alkyl derivatives bearing β-hydrogens could not be isolated, likely due to easy β-elimination.

Perhaps the most surprising outcome of this work is the observation that reduction of 1 to 2 results in oxidation of
Ti(III) to Ti(IV). The situation is somewhat analogous to the one-electron reduction of $\text{[DIP}^{(0)}\text{]}\text{Mn}^{\text{IV}}$, which produces $\text{[DIP}^-\text{]}\text{Mn}^{\text{III}}$; i.e., oxidation of the metal center. However, this Mn case involves a spin state change at the metal (high spin to low spin), which is not possible for Ti.

**EXPERIMENTAL SECTION**

**General Considerations.** All air- and moisture-sensitive manipulations were carried out under argon using standard Schlenk techniques or in an MBraun drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using sodium/benzophenone. Benzene-$d_6$ and toluene-$d_6$ were purchased from Cambridge Isotope Laboratories, distilled from sodium/benzophenone, and stored in the drybox. TiCl$_3$(THF)$_3$ was isolated from reagents by filtration and washing with a minimum of THF.

**Data Collection.** The crystal system was elucidated using a Bruker SMART APEXII area detector or a Bruker D8 QUEST ECO diffractometer. Data collection was optimized for low spin), which is not possible for Ti.

**Energy of Charge on the Samples.** All spectra were collected with a pass energy of 160 eV, and high-resolution scans were collected with a pass energy of 20 eV. Peak fitting of the high-resolution XPS spectra was performed using CasaXPS software (casaxps.com). All peak positions were normalized with respect to the C 1s peak with a binding energy of 285 eV.

**EPR Spectra.** EPR spectra of $\text{[DIP}^{-}\text{]}\text{TiCl}_3$ (1) were recorded at 10 K using a Bruker EMX spectrometer (Bruker BioSpin) equipped with a He temperature control cryostat system (Oxford Instruments). Simulations of the EPR spectra were performed using the Spinach package of Dr. Frank Neese. 

**XPS Spectra.** XPS spectra were collected on a Kratos Axis Ultra DLD XPS spectrometer in a vacuum environment at a base pressure of 10$^{-9}$ Torr. Al K$_\alpha$ (1486.6 eV) monochromatic X-rays at 10 mA emission current and 15 kV anode voltage were used for photoexcitation. Samples were transferred from a nitrogen glovebox to the instrument in a sealed container designed to mate with the sample loading arm of the spectrometer so that the samples were not exposed to air/moisture. A coaxial charge neutralizer was utilized to prevent buildup of charge on the samples. All spectra were collected with a fixed analyzer transmission mode. Survey scans were collected with a pass energy of 160 eV, and high-resolution scans were collected with a pass energy of 20 eV. Peak fitting of the high-resolution XPS spectra was performed using CasaXPS software (casaxps.com). All peak positions were normalized with respect to the C 1s peak with a binding energy of 285 eV.

**EPR Spectra.** EPR spectra of $\text{[DIP}^{-}\text{]}\text{TiCl}_3$ (1) were recorded at 10 K using a Bruker EMX spectrometer (Bruker BioSpin) equipped with a He temperature control cryostat system (Oxford Instruments). Simulations of the EPR spectra were performed using the Spinach package of Dr. Frank Neese. 

**XPS Spectra.** XPS spectra were collected on a Kratos Axis Ultra DLD XPS spectrometer in a vacuum environment at a base pressure of 10$^{-9}$ Torr. Al K$_\alpha$ (1486.6 eV) monochromatic X-rays at 10 mA emission current and 15 kV anode voltage were used for photoexcitation. Samples were transferred from a nitrogen glovebox to the instrument in a sealed container designed to mate with the sample loading arm of the spectrometer so that the samples were not exposed to air/moisture. A coaxial charge neutralizer was utilized to prevent buildup of charge on the samples. All spectra were collected with a fixed analyzer transmission mode. Survey scans were collected with a pass energy of 160 eV, and high-resolution scans were collected with a pass energy of 20 eV. Peak fitting of the high-resolution XPS spectra was performed using CasaXPS software (casaxps.com). All peak positions were normalized with respect to the C 1s peak with a binding energy of 285 eV.
Crystallization at ~35 °C gave 0.127 g (55%) of dark green crystals. X-ray-quality crystals were obtained from benzene.

Anal. Calcd for C_{31}H_{41}N_{3}Ti: C, 73.94; H, 8.21; N, 8.34. Found (1): C, 72.69; H, 8.21; N, 8.17; (2): C, 69.63; H, 7.50; N, 7.95; (2): C, 72.5 (C, 2), 72.69; H, 8.21; N, 8.17. Py 3 not detected.

For examination of the SP-TBP path for 4a, as well as prediction of NMR data, geometry optimizations for 1−4 were performed with Turbomole 6.5 (V6.3) coupled to the PQS Baker optimizer75,76 at the TPSSH/def-TZVP83 level. Vibrational analyses were used to confirm the nature of the stationary points (no imaginary frequencies). Free energies were obtained by combining electronic energy, enthalpy, and entropy corrections (298 K, entropy scaled by 0.6794). Configurational entropy corrections were taken from DFT-D3 (options “func=tpsh-zero”)-NMR chemical shifts (TPSSH functional, GIAO method; 96,97 IGLO-II basis set98) were calculated using Gaussian 09. 99 MO and spin density plots were generated with the program Molden.100

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00239.

Crystallographic and spectroscopic details and computational results (PDF)

Ceramic coordinates of optimized structures (XYZ)

**ACCESSION CODES**

CCDC 1545713-1545718 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 360333.

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Notes

The authors declare no competing financial interest.

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