# *Articles*

# Density Functional Theory Calculations of Ti−TEMPO Complexes: Influence of Ancillary Ligation on the Strength of the Ti−O Bond

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A series of mono(cyclopentadienyl)titanium TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) complexes were investigated by density functional theory (DFT) calculations to study the influence of the ligands on the Ti−O bond energies. Mono-Cp complexes with pendant amino groups were found to possess significantly weaker Ti−O bonds than those lacking pendant donor ligands. On the basis of DFT predictions, a novel mono-Cp pendant dimethylamino complex, $Cp^NTiCl_2$(TEMPO) (**12**; $Cp^N = C_5H_4CH_2CH_2N(CH_3)_2$), was identified as a mono-Cp titanium TEMPO complex with a weak Ti−O bond (25 kcal/mol). The calculated bond energy of this complex is comparable to that of $Cp_2TiCl$(TEMPO) (**3**; 17 kcal/mol). Thermolysis of **12** in the presence of $CCl_4$ at 100 °C resulted in the formation of $Cp^NTiCl_3$, consistent with the predicted low Ti−O bond energy.

## Introduction

An understanding of the energetics of metal−ligand bonds is central to the use of these complexes in stoichiometric and catalytic applications.[1,2] The stability of coordination complexes depends on both the thermodynamic and kinetic stability of the metal−ligand bonds. In addition, for covalent bonds metal−ligand bond homolysis results in the formal reduction of the metal to a lower formal oxidation state. We sought to exploit this latter behavior as a strategy for generating reactive Ti(III) complexes for use in both epoxide opening[3−8] and polymerization reactions.[9−11] To this end, we initiated a study on the coordination chemistry of the stable nitroxyl radical TEMPO with titanium complexes.[7,12−14] This effort was motivated by the possibility of using these Ti−TEMPO complexes as a source of Ti(III) species by homolysis of the Ti−O bond, in analogy to the reversible homolysis of weak C−O bonds of alkoxyamines derived from TEMPO in controlled free-radical polymerization reactions (Figure 1).[15]

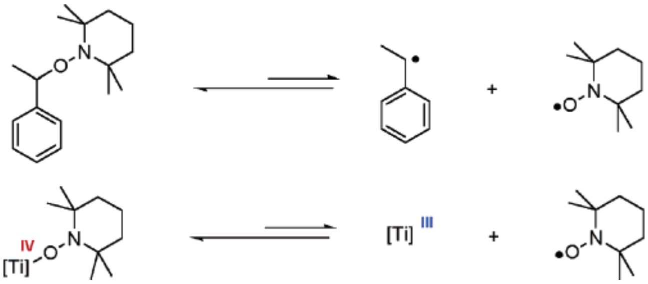

**Figure 1.** Generating a Ti(III) species through homolysis of a Ti−O bond.

The coordination geometry and bonding energetics of stable nitroxyl radicals, such as TEMPO, depend sensitively on the ligation environment at titanium.[7,8,12] In the absence of other sterically demanding ligands, TEMPO adopts an $\eta^2$ coordination geometry for $TiCl_3$(TEMPO) (**1**) in the solid state, but in solution the TEMPO ligand is labile and undergoes an $\eta^1-\eta^2$ interconversion.[13] The presence of cyclopentadienyl ligands enforces an $\eta^1$ coordination geometry on the TEMPO ligand for $CpTiCl_2$(TEMPO) (**2**), $Cp_2TiCl$(TEMPO) (**3**), and $Cp_2TiCl$(4-MeO-TEMPO) (**4**) (Figure 2).[7,8,12] The short Ti−O bonds (1.839 Å in **1**, 1.753 Å in **2**, and 1.824 Å in **4**) and relatively long N−O bonds (1.433 Å in **1**, 1.412 Å in **2**, and 1.406 Å in **4**) are consistent with the formulation of Ti(IV) complexes with a reduced TEMPO ligand.[8,12]

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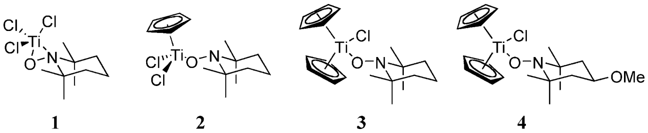

**Figure 2.** Titanium TEMPO complexes.

The most interesting feature of the coordination chemistry of these TEMPO ligands is the remarkably low homolytic bond energies for the Ti−O bonds for the bis(cyclopentadienyl) complexes **3** and **4**. Thermolysis of **3** or **4** in the presence of $CCl_4$ or other nitroxyl radicals reveals that the Ti−O bond cleaves readily at 60 °C with a Ti−O bond energy on the order of approximately 25 kcal/mol.[7,8] This is the weakest Ti−O bond known for neutral complexes.[16] In contrast, the mono(cyclopentadienyl) complex **2** is stable for days at 100 °C in $CCl_4$. DFT calculations indicate that the Ti−O bond of **2** is 26 kcal/mol stronger than that of **3** or **4**.[8] These results suggest that not only is the coordination geometry of the TEMPO ligand sensitive to ancillary ligation at titanium but also the bonding energetics of the Ti−O bonds depend sensitively on the ligation environment as well.

Our original goal was to exploit the homolysis of weak Ti−O bonds to generate mono(cyclopentadienyl) Ti(III) complexes, which have been implicated as active species in syndiospecific styrene polymerization.[9,17,18] We have demonstrated that the Ti−O bond in the bis-Cp complexes **3** and **4** can be homolyzed to afford Ti(III) species and that the lifetime of the Ti(III) species is sufficient to undergo subsequent chemistry, such as the ring opening of epoxides.[8] However, experimental and theoretical studies revealed that the Ti−O bond for the mono-Cp complex **2** is too strong (43 kcal/mol) to be cleaved at reasonable rates.[8] These observations prompted us to apply modern theoretical methods[19−26] as a predictive tool to identify ancillary environments that would facilitate the homolysis of Ti−O bonds.

We have previously shown that density functional theory (DFT) calculations at the B3LYP/6-31G* level of theory are suitable for predicting the structures of titanium−TEMPO complexes and estimating the Ti−O bond strengths.[8] Our calculations revealed that the remarkable weakening of the Ti−O bond by the addition of strongly donating cyclopentadienyl (Cp) ligands (43 kcal/mol for **2** and 17 kcal/mol for both **3** and **4**) is mainly due to an electronic effect of adding the second Cp ligand,[27] with only a partial contribution from steric effects (4−6 kcal/mol).[8] On the basis of these encouraging preliminary DFT results,[8] we further extended our studies to investigate the effects of other electron-donating ancillary ligands on the strength of Ti−O bonds. In particular, here we report the dramatic influence of pendant donors appended to cyclopentadienyl ligands on the strength of Ti−O bonds derived from stable radicals. Pendant donor ligands have been widely investigated as hemilabile ligands to stabilize reactive coordinatively unsaturated intermediates;[28−34] the results reported herein implicate a more fundamental role for pendant donors on the electronic properties of metal complexes in that, for mono(cyclopentadienyl)titanium complexes, they exhibit a significant influence (up to 25 kcal/mol!) on the thermodynamic stability of Ti−O bonds derived from nitroxyl radicals.

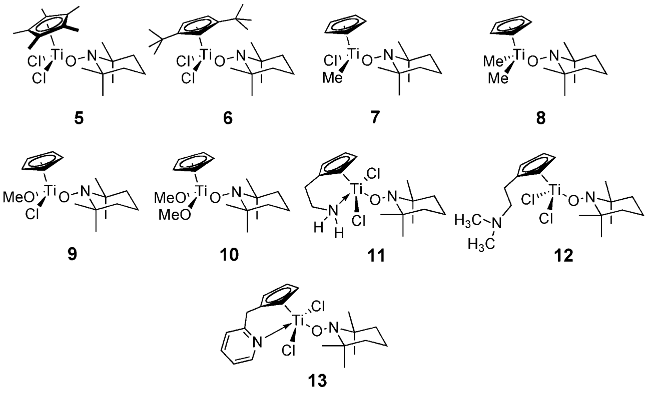

**Figure 3.** Mono(cyclopentadienyl) Ti−TEMPO complexes.

## Computational Details

Density functional theory (DFT) calculations were performed using the Gaussian 98 program.[19] The B3LYP[20] gradient-corrected exchange hybrid DFT method was used for all calculations. This hybrid functional has been shown to have relatively good accuracy at moderate computational cost and has been used previously to investigate titanium−oxygen bonds.[35,36] The exchange functional is a linear combination of Slater's local spin density, Becke's 1988 nonlocal, and exact (Hartree−Fock) exchange terms. The correlation functional is a combination of Lee−Yang−Parr and VWN local spin density correlation functionals.[21] We have used the unrestricted method (UB3LYP) for all calculations. Geometry optimizations of the structures were performed using the default convergence criteria without any geometric constraints. All atoms were described using the all-electron Pople 6-31G* basis set.[22,26,37,38] Frequency calcula-

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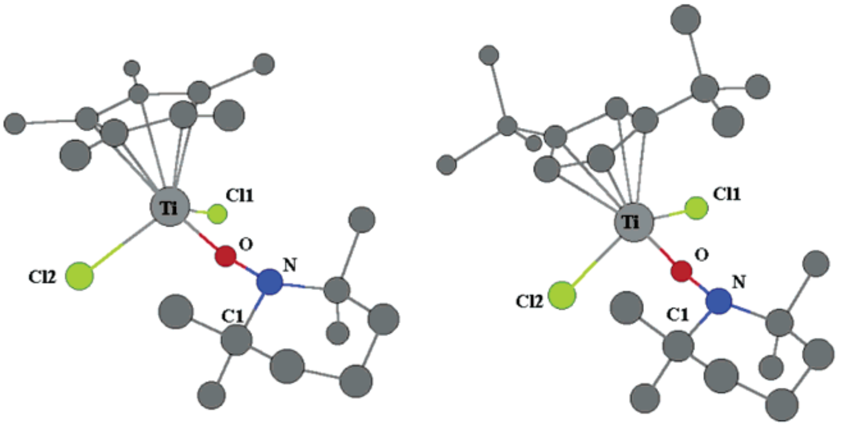
**Table 1. Geometrical Parameters and Bond Dissociation Energies at the B3LYP/6-31G* Level**[a]

| | Ti−O | N−O | Ti−O−N | Ti−Cl | Cl−Ti−Cl | Ti-Me | Ti−OMe | C−N−C | Ti−N | Ti−O BDE | Δ*S* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2**[b] | 1.758 | 1.403 | 154.3 | 2.279 | 104.6 | | | 120.8 | | 43 | 51 |
| **3**[b] | 1.842 | 1.426 | 144.8 | 2.404 | | | | 118.8 | | 17 | 55 |
| **5**[c] | 1.760 | 1.401 | 166.7 | 2.295 | 103.3 | | | 120.4 | | 40 | 54 |
| **6**[c] | 1.758 | 1.402 | 168.3 | 2.286 | 101.9 | | | 120.1 | | 36 | 56 |
| **7**[c] | 1.770 | 1.407 | 153.4 | 2.285 | | 2.106 | | 120.5 | | 50 | 53 |
| **8**[c] | 1.780 | 1.409 | 154.7 | | | 2.115 | | 120.5 | | 56 | 55 |
| **9**[c] | 1.784 | 1.405 | 151.8 | 2.311 | | | 1.790 | 120.2 | | 41 | 52 |
| **10**[c] | 1.817 | 1.409 | 147.3 | | | | 1.815 | 119.5 | | 40 | 48 |
| **11**[c] | 1.775 | 1.410 | 157.3 | 2.388 | 127.4 | | | 120.1 | 2.414 | 21 | 54 |
| **12**[c] | 1.761 | 1.403 | 154.0 | 2.286 | 104.4 | | | 120.8 | | 25 | 40 |
| **13**[c] | 1.775 | 1.407 | 153.1 | 2.334 | 121.5 | | | 120.3 | 2.703 | 18 | 53 |

[a] Bond lengths and angles are given in Å and deg, respectively. Ti−O BDEs are reported in kcal/mol at 0 K. Δ*S* is the entropic change for the corresponding Ti−O homolysis process at 298.15 K, reported in eu. [b] From ref 8. [c] This work.



$Cp^*TiCl_2(TEMPO)$ (**5**) $Cp^{tt}TiCl_2(TEMPO)$ (**6**)

**Figure 4.** B3LYP/6-31G* optimized bond lengths and angles for **5** and **6** (Å and deg): **5**, Ti−O = 1.760, Ti−Cl = 2.295 (average), N−O = 1.401, Ti−O−N = 166.7, Cl1−Ti−O = 101.2, Cl1−Ti−Cl2 = 103.3, O−N−C = 108.9, C−N−C = 120.4, (Cl2−Ti−N)−(Ti−N−C1) = 12.1; **6**, Ti−O = 1.758, Ti−Cl1 = 2.286, Ti−Cl2 = 2.298, N−O = 1.402, Ti−O−N = 168.3, Cl1−Ti−O = 102.2, Cl1−Ti−Cl2 = 101.9 O−N−C = 108.7, C−N−C = 120.1, (Cl2−Ti−N)−(Ti−N−C1) = 38.5.

tions were performed to confirm that the geometries are at energy minima. The unscaled frequencies obtained from these calculations were also used to determine the zero-point energies (ZPE). All reported bond energies have been zero-point corrected and represent the energy at 0 K.

## Results and Discussion

**Effects of Ancillary Ligation on Ti−O Bond Energies.** To investigate the influence of ancillary ligation on the strength of Ti−O bonds for mono(cyclopentadienyl) Ti−TEMPO complexes, DFT calculations were carried out for a variety of mono(cyclopentadienyl) complexes, **5**−**13** (Figure 3). The influence of the nature of the cyclopentadienyl group was studied by replacement of the cyclopentadienyl ligands of **2** by the pentamethylcyclopentadienyl (Cp* = **5**) or the 1,3-di-*tert*-butylcyclopentadienyl ligand ($Cp^{tt}$ = **6**). The influence of the ancillary monodentate ligands was investigated by replacement of the chloride ligands of **2** with methyl (**7** and **8**) or methoxide ligands (**9** and **10**). Finally, the influence of donor ligands appended to the cyclopentadienyl ligands[28,30−34] was studied (**11**−**13**).

Full geometry optimizations of the Ti(IV)−TEMPO complexes and the Ti(III) and TEMPO products were performed to assess the bond energies. Solvent effects were not included in this study. Thus, while these energies might not be directly compared to experimental measures of the bond-energies, comparisons among the different mono(cyclopentadienyl) complexes **5**−**13** provide a measure of the steric and electronic influences of ancillary ligation on the Ti−O bond strengths. A summary of these calculations is provided in Table 1.

The structure of $Cp^*TiCl_2(TEMPO)$ (**5**) predicted using B3LYP/6-31G* yielded geometric parameters in good agreement with the X-ray crystal structure (Ti−O bond, 1.760 Å calculated vs 1.7596 Å experimental; Ti−Cl bond, 2.295 Å calculated vs 2.298 Å experimental).[14] The molecular structure of the Cp* derivative **5** is similar to that of **2**, but the substitution of the Cp ligand with the Cp* ligand (Figure 3) results in some slight differences in the bonding geometry of **5** relative to that of **2**: the crystallographic Ti−O−N and the Cp(centroid)−Ti−O angles in **5** (165.3 and 122.5°, respectively) are larger than those for **2** (155.7 and 117.6° for **2**). These differences are also reflected in the DFT-optimized structures (Figure 4). The agreement between the calculated and crystallographically determined bonding geometries provide good evidence that the B3LYP/6-31G* level of theory is appropriate to capture the key structural properties of these complexes.

The calculated Ti−O bond energy of **5** is 40 kcal/mol, 3 kcal/mol weaker than that of **2**. This result suggests that replacement of Cp with the more sterically demanding and electron-rich Cp* ligand[39−41] has only a modest influence on the Ti−O bond strength, not nearly as dramatic as the effect of adding an

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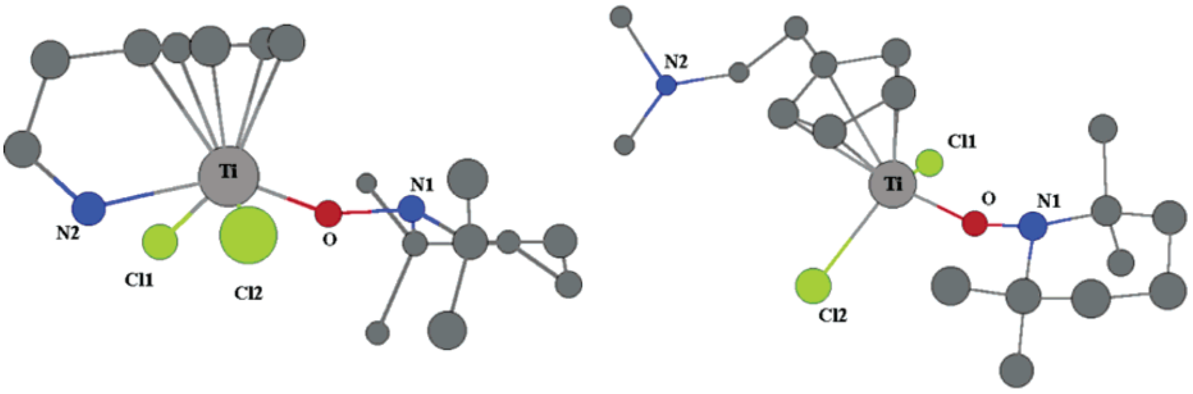
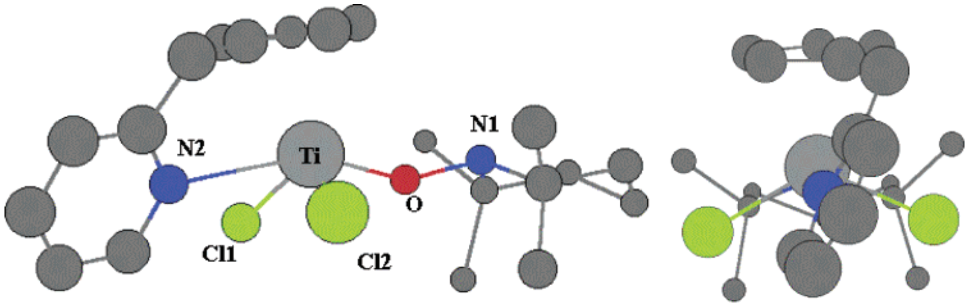


$Cp^{NH2}TiCl_2$(TEMPO) (**11**) $Cp^{N}TiCl_2$(TEMPO) (**12**)

**Figure 5.** B3LYP/6-31G* optimized bond lengths and angles for **11** and **12** (Å and deg): **11**, Ti−O = 1.775, Ti−Cl1 = 2.387, Ti−Cl2 = 2.391, Ti−N2 = 2.414, N1−O = 1.410, Cl1−Ti−Cl2 = 127.4, Ti−O1−N1 = 157.3, O−N1−C = 108.8, C−N1−C = 120.1; **12**, Ti−O = 1.761, Ti−Cl1 = 2.283, Ti−Cl2 = 2.289, N1−O = 1.403, Ti−O1−N1 = 154.0, Cl1−Ti−Cl2 = 104.4, O−N1−C = 108.6, C−N1−C = 120.8.



**View I** **View II**

**Figure 6.** B3LYP/6-31G* optimized bond lengths and angles for **13** (Å and deg): Ti−O = 1.775, Ti−N2 = 2.703, Ti−Cl1 = 2.332, Ti−Cl2 = 2.337, N1−O = 1.407, Ti−O1−N1 = 153.1, Cl1−Ti−Cl2 = 121.5, O−N1−C = 108.7, C−N1−C = 120.3.

additional Cp group (from 43 kcal/mol in **2** to 17 kcal/mol in **3**; Table 1). In contrast, replacement of the Cp ligand with the $Cp^{tt}$ ligand has a more pronounced effect on the Ti−O bond energy: the Ti−O bond energy of **6** is 36 kcal/mol, 7 kcal/mol weaker than that of **2** and 4 kcal/mol weaker than that of **5**. We attribute this largely to a steric effect,[42] because the $Cp^{tt}$ ligand is slightly less electron donating than Cp*[41] but is sterically more demanding. This is also evidenced by the DFT-calculated structure of **6**, where the TEMPO ligand is tilted by approximately 26° to accommodate one of the *tert*-butyl groups (the Cl2−Ti−N−C1 torsion angle is 12.1° for **5** but 38.5° for **6**, Figure 4).

Replacement of the ancillary chloride ligands by methyl ligands (**7** and **8**) results in an increase in the Ti−O bond energy relative to **2** (Table 1), whereas replacement of the chloride ligands by methoxide, a better $\pi$-donor, results in a slight lengthening of the Ti−O bond (1.817 Å for **10** vs 1.758 Å for **2**) but only a modest decrease in the bond energy (**9** and **10**, 40−41 kcal/mol, Table 1). Taken together, these results imply that modulating the electron-donating ability of the Cp ligand or varying the nature of monodentate ancillary ligands at titanium is not likely to weaken the Ti−O bond as dramatically as that observed by replacing one of the chloride ligands with the cyclopentadienyl ligand (cf. **3**, Table 1). These calculations reveal that substitution of the cyclopentadienyl or chloride ligands of **2** has a slight to modest influence on the Ti−O bond energies.

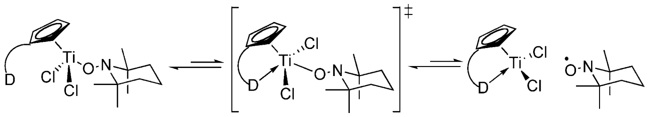


**Figure 7.** Stabilization of the Ti(III) intermediate by a pendant donor.

As our previous investigations had implicated that the dramatic weakening of the Ti−O bond in the bis(cyclopentadienyl) complexes **3** and **4** relative to that of the mono(cyclopentadienyl) complexes **2** was due to the stabilization of Ti(III) by the six-electron-donor Cp ligand,[8] we investigated the influence of pendant donors[28,30−34] on the Ti−O bond energies.

To evaluate the effects of additional donor ligands, we calculated the structure and Ti−O bond energy of the complex $Cp^{NH2}TiCl_2$(TEMPO) (**11**). In the optimized structure of **11,** the $NH_2$ donor coordinates to the Ti with a Ti−N bond distance of 2.414 Å. The addition of the amine donor results in a slight distortion of the bonding geometry (Cl−Ti−Cl = 127.4°, O−Ti−Cl = 91.5°) but very little change in the Ti−O, Ti−Cl,

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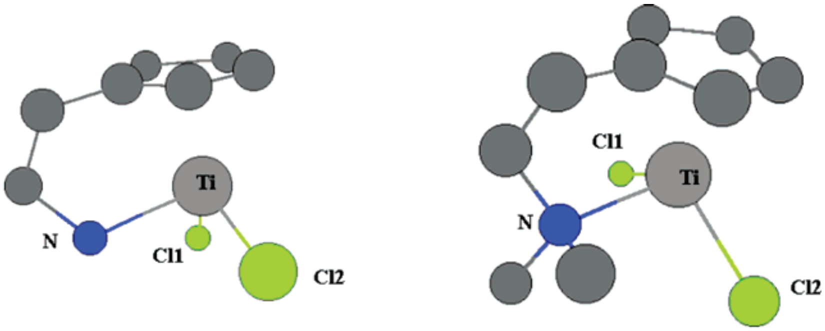


$Cp^{NH2}Ti(III)Cl_2$ (**14**) $Cp^{N}Ti(III)Cl_2$ (**15**)

**Figure 8.** B3LYP/6-31G* optimized bond lengths and angles for **14** and **15** (Å and deg): **14**, Ti−N = 2.229, Cp-Ti = 2.041, Ti−Cl1 = 2.311, Ti−Cl2 = 2.315, Cl1−Ti−Cl2 = 107.7, Cl1−Ti−N = 90.9, Cl2−Ti−N = 93.2; **15**, Ti−N = 2.310, Cp−Ti = 2.043, Ti−Cl1 = 2.318, Ti−Cl2 = 2.314, Cl1−Ti−Cl2 = 105.9, Cl1−Ti−N = 99.1, Cl2−Ti−N = 94.7.

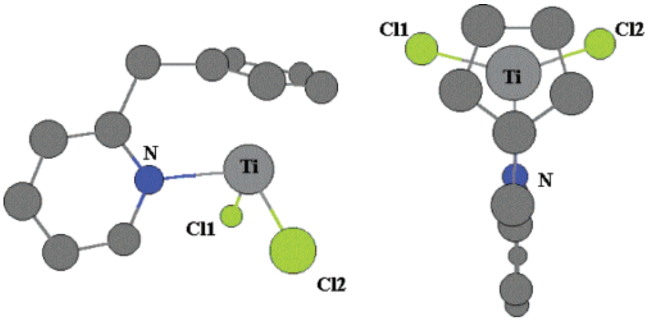
and O−N bonds and the Ti−O−N bond angle (Figure 5). These parameters can be compared to those recently reported for the $Cp^{N}Ti(CH_3)Cl_2$ complex (Ti−N = 2.445 Å, Cl−Ti−Cl = 125.18°)[34] and $Cp^{N'}TiCl_3$ ($Cp^{N'}$ = $C_5H_4$ $CH_2CH_2N(CH_2)_4$) (Ti−N = 2.357 Å, Cl(1)−Ti−Cl(3) = 128.55°)[33]

The addition of the $CH_2CH_2NH_2$ group to the Cp ring caused a significant decrease in the Ti−O bond energy to 21 kcal/mol, 22 kcal/mol weaker than that of **2**! This is a telling observation and implies that the coordination of the additional electron donors to the $CpTiCl_2(ONR_2)$ fragment leads to a substantial weakening of the Ti−O bond.[43]

Similar calculations with the pendant dimethylamino substituent **12** revealed that, for this pendant donor, the amine remains uncoordinated to the titanium. Esteruelas had reported that the dimethylamino substituent binds weakly to Ti ($\Delta H°$ = 2.4 kcal/mol) for $Cp^{N}Ti(CH_3)Cl_2$.[34] The greater steric demands of the TEMPO ligand (relative to the methyl ligand in $Cp^{N}Ti(CH_3)Cl_2$) and the dimethylamino substituent (relative to that of the $NH_2$ substituent in **11**) might explain the differences in the bonding geometry. While the bonding geometry and Ti−O bond length for **12** are calculated to be very similar to those of **2**, the Ti−O bond energy is 26 kcal/mol, much lower than that calculated for **2** and comparable to the 22 kcal/mol bond energy calculated for **11**.

Simulation of the pendant pyridine donor $(CpCH_2Pyr)TiCl_2$-TEMPO (**13**) reveals that the pyridine coordinates to the titanium center with a Ti−N bond distance of 2.703 Å (Figure 6). This coordination is likely a consequence of a smaller repulsive interaction between the planar pyridine moiety and the chloride ligands, in comparison to that between the dimethylamino substituent and the chloride ligands in **12**. The calculated Ti−O bond energy for this complex is 18 kcal/mol, 25 kcal/mol weaker than that of **2** and comparable to that observed for the bis(cyclopentadienyl) complexes **3** and **4**.

The much lower Ti−O bond energies for the bis(cyclopentadienyl) complexes **3** and **4** and the mono(cyclopentadienyl) complexes **11**−**13**, containing pendant donors, relative to those for complexes **2** and **5**−**10** imply that increasing the electron density at Ti facilitates the homolytic cleavage of Ti−O bonds derived from stable nitroxyl radicals. To the extent that the Ti−O bond homolysis is a formal reduction of the Ti(IV) to Ti(III), it is at first glance surprising that the addition of an electron donor should facilitate this formal reduction of the titanium center. Nevertheless, it should be appreciated that homolysis of the titanium−oxygen bond results not only in the formal reduction of the titanium center but also the loss of a ligand. The homolysis of the Ti−O bond of **2** (a 12-electron species if $\pi$-donor interactions are ignored) yields an 11-electron, highly unsaturated Ti(III) metal fragment. As $CpTi^{III}X_2$ species are known to bind Lewis bases avidly,[43,44] it is expected that pendant donors will stabilize these intermediates. Nadasdi and Stephan previously observed that the addition of donor ligands such as trimethylphosphine to $CpTiCl_3$ induces the formation of approximately 2% of a paramagnetic mono-Cp Ti(III) phosphine adduct by losing a chlorine atom.[43] Thus, we propose that the pendant donor leads to the stabilization of the Ti(III) fragment, leading to a lower Ti−O bond energy (Figure 7).



**View I** **View II**

**Figure 9.** B3LYP/6-31G* optimized bond lengths and angles for **16** (Å and deg): Ti−N = 2.193, Cp-Ti = 2.036, Ti−Cl1 = 2.306, Ti−Cl2 = 2.307, Cl1−Ti−Cl2 = 105.8, Cl1−Ti−N = 96.6, Cl2−Ti−N = 96.4.

Evidence for the stabilization of the highly unsaturated Ti(III) species through the coordination of the pendant amino ligand to Ti is provided by the fully optimized gas-phase structures of the corresponding Ti(III) complexes. For $Cp^{NH2}Ti^{III}Cl_2$ (**14**) (Figure 8) the calculated Ti−N bond distance is 2.229 Å, shorter than that in **11** (2.414 Å). A similar interaction was also confirmed for $Cp^{N}Ti^{III}Cl_2$ (**15**) (Ti−N = 2.310 Å, Figure 8), despite the fact that the dimethylamino group was not bound to the titanium center in **12**. The lower $\Delta S$ value calculated for the homolysis of **12** (Table 1) is consistent with the intramolecular coordination of the pendant donor upon homolysis of the Ti−O bond. These observations imply that the dramatic influence of the pendant donors on the strength of the Ti−O bonds in complexes **11**−**13** is a consequence of the stabilization of the resulting Ti(III) products.

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(44) Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1971**, *24*(12), 2533−2540.

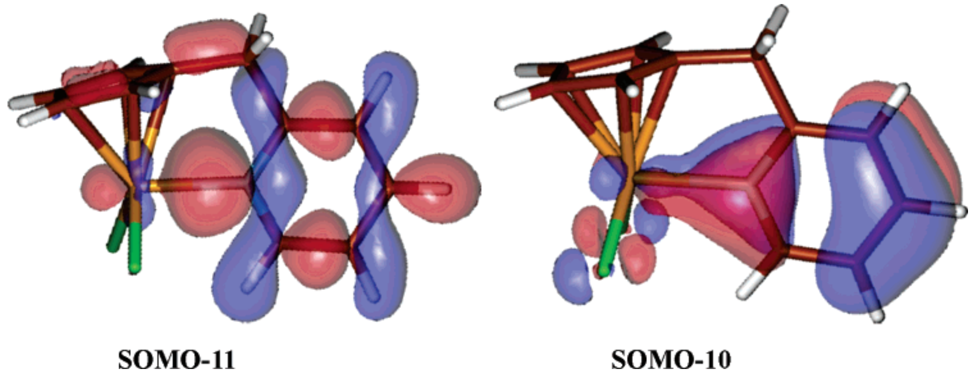
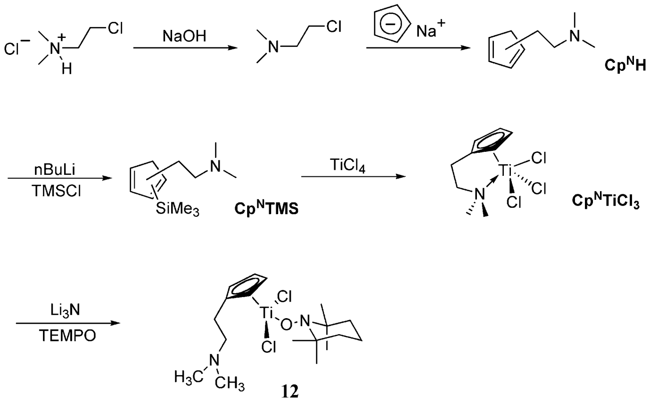

**SOMO-11** **SOMO-10**

**Figure 10.** Selected molecular orbitals of **16** showing $\sigma$ (SOMO-11) and $\pi$ (SOMO-10) interactions. Surfaces indicate a contour value of 0.03.

**Scheme 1. Synthesis of Complex 12**



The structure of $(CpCH_2Pyr)Ti^{III}Cl_2$ (**16**) provides additional support for this hypothesis (Figure 9). The Ti−N bond distance for **16** is the shortest among complexes **14**−**16** (2.193 Å). The pyridine ring is perpendicular to the Cp group, providing optimal overlap between the $\pi$ orbitals of the pyridine with the $d_\pi$ orbital of titanium (SOMO-10, Figure 10). This $\pi$-donation may provide additional stabilization of the Ti(III) fragment, implicating that pendant donors capable of both $\sigma$ and $\pi$ donation might provide even better ancillary ligands for modulating the energy of the Ti−O bond.

On the basis of DFT predictions that pendant donors should weaken the Ti−O bond, the synthesis of complex **12** was carried out. $Li_3N$ reduction[45] of $Cp^NTiCl_3$[30] in THF followed by the addition of TEMPO afforded $Cp^NTiCl_2$(TEMPO) in 27% isolated yield (Scheme 1). This compound can be dissolved in warm pentane and recrystallized at −30 °C as fine pale yellow needles.

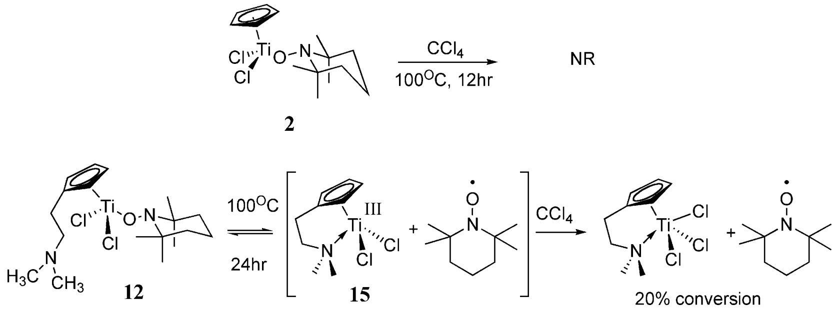
Thermolysis of **12** in a 1:1 $CCl_4$/$d_6$-benzene solution at 100 °C for 24 h yielded ∼20% of $Cp^NTiCl_3$ (∼80% of **12** remained unreacted) (Scheme 2). Under the same reaction conditions, complex **2** showed no evidence of formation of $CpTiCl_3$. These results suggest that at 100 °C the Ti−O bond of **12** undergoes homolysis to generate the Ti(III) complex **15**, which is trapped by $CCl_4$ in competition with re-formation of **12**.[7,8]

The chlorination of **12** with $CCl_4$ is slower (20% conversion after 24 h at 100 °C) than that of **3** with $CCl_4$ (60% conversion after 1.6 h at 60 °C),[7,8] consistent with the higher Ti−O bond strength calculated for **12** (Table 1). Moreover, the chlorination of **12** with $CCl_4$ and the stability of **2** to extended thermolysis in the presence of $CCl_4$ are also consistent with the much higher calculated trends in the Ti−O bond strength for **2** relative to that of **12**. These results suggest that pendant donor ligands can have a significant influence on the thermodynamics of M−X bonds. Pendant donor ligands have been widely investigated as hemilabile ligands to stabilize reactive coordinatively unsaturated intermediates;[28−34] the results reported here suggest that pendant donor ligands may exhibit a more fundamental electronic influence—to modulate the thermodynamic stabilities of M−X bonds involved in key bond-forming steps.

## Conclusion

The strengths of Ti−O bonds derived from the stable nitroxyl species TEMPO range from 17 to 56 kcal/mol and are remarkably sensitive to the ancillary ligation at titanium. DFT calculations at the B3LYP/6-31G* level of theory have provided important insights into the role of ancillary ligation in modulating the strength of Ti−O bonds. For mono(cyclopentadienyl)titanium complexes, ancillary chloride, alkoxide, or alkyl ligands exert only a modest influence on the strength of the Ti−O bond. In contrast, pendant donor ligands have a significant influence (up to 25 kcal/mol!) on the thermodynamic stability of Ti−O bonds derived from nitroxyl radicals. To the extent that the trends observed for Ti−O bonds derived from nitroxyl radicals are generalizable to other M−X bonds, these results imply that pendant donor ligands may have a significant influence on the

**Scheme 2. Thermolysis of Complex 12 in the Presence of $CCl_4$**



energetics of catalytic reactions mediated by this class of coordination compounds.

## Experimental Details

**General Considerations.** Nitrogen gloveboxes and standard Schlenk techniques were applied in handling all oxygen- and moisture-sensitive compounds. Pentane and toluene were purchased from Aldrich and purified through towers containing alumina and Q5 prior to use. Tetrahydrofuran and $d_6$-benzene were vacuum-transferred from purple sodium/benzophenone solutions. $CCl_4$ was dried over $CaH_2$ prior to use. $Cp^NTiCl_3$ was synthesized according to the literature procedure.[30] $Li_3N$ was purchased from Aldrich and stored under $N_2$ prior to use. TEMPO was purchased from Aldrich and sublimed in vacuo prior to use.

$^1H$ NMR spectra were recorded at 400 MHz on a Varian Mercury 400. $^{13}C$ NMR spectra were recorded at 100 MHz on the same instrument. $^1H$ and $^{13}C$ chemical shifts were referenced relative to tetramethylsilane by internal residual solvent peaks. Elemental analyses were carried out at Desert Analytics Laboratory (Tucson, AZ).

**$Cp^NTiCl_2$(TEMPO) (12).** $Cp^NTiCl_3$ (220 mg, 0.76 mmol) and $Li_3N$ (8.9 mg, 0.26 mmol) were mixed in 10 mL of THF and stirred for 10 min until the color changed to yellow-green. To this mixture was added TEMPO (120 mg, 0.77 mmol) in 10 mL of THF. The color of the reaction mixture changed to brown-red immediately. This mixture was stirred for another 8 h. THF was then removed in vacuo. The residue was extracted with 5 mL of toluene and diluted with 15 mL of pentane. The solution was filtered, and the solvent was removed in vacuo. The residue was extracted with 30 mL of pentane. Recrystallization at −30 °C gave fine pale yellow needles (81 mg; 27%). $^1H$ NMR ($C_6D_6$): $\delta$ 1.02−1.22 (m, 6H), 1.21 (*s*, 12H), 2.04 (s, 6H), 2.36 (t, $J = 7.2$ Hz, 2H), 2.93 (t, $J = 7.2$ Hz, 2H), 6.10 (t, $J = 2.8$ Hz, 2H), and 6.29 (t, $J = 2.8$ Hz, 2H); $^{13}C$ NMR ($C_6D_6$): 120.1, 119.4, 63.2, 59.5, 45.2, 39.5, 29.0, 26.7, and 16.7. Anal. Calcd: C, 52.57; H, 7.84; N, 6.81. Found: C, 52.41; H, 7.83; N, 6.54.

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**Supporting Information Available:** Tables giving Cartesian coordinates for the optimized structures of **5**−**16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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