

# Synthesis and molecular structure of titanium complexes containing a reduced TEMPO radical

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Two titanium compounds containing monoanionic ligands derived from TEMPO were synthesized and structurally characterized, demonstrating the flexibility of the coordination modes adopted by the ligand.

TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) enjoys the attention of a variety of chemists due to its stability as a free radical. Applications of this versatile molecule include its use as a mild yet selective oxidant of primary and secondary alcohols,<sup>1,2</sup> as a spin-label in the study of complex chemical environments,<sup>3–6</sup> as a mediator of controlled/living free radical polymerization,<sup>7,8</sup> and in the mechanistic study of radical reactions. Inorganic chemists have extensively studied the fundamental coordination chemistry of the nitroxide moiety to transition metals<sup>9,10</sup> Mn,<sup>11</sup> Co,<sup>12</sup> Cu,<sup>13</sup> Zn,<sup>9</sup> Mo,<sup>14,15</sup> Rh,<sup>14</sup> Pd,<sup>16,17</sup> lanthanides,<sup>18</sup> the *p*-block metalloids such as B<sup>19</sup> and Si,<sup>20</sup> and the *s*-block metals Li, Na, and Mg.<sup>21</sup> A number of these compounds have been investigated in the search for new molecular magnets.<sup>22</sup> TEMPO often serves as an odd-electron Lewis base towards electrophilic metal centers; surprisingly, only a limited number of metal complexes with monoanionic TEMPO ligands have been reported.<sup>11,12,15–18,21,23</sup>

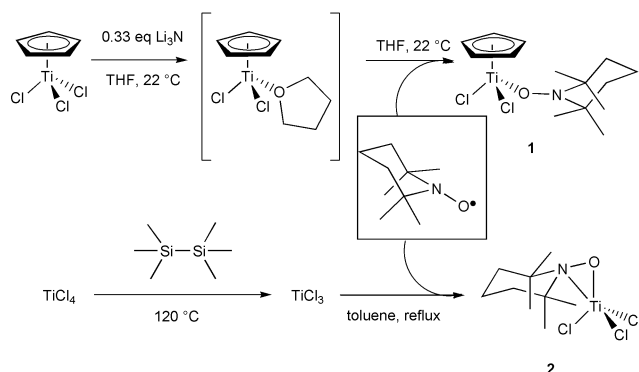
The synthesis of TEMPO and di-*tert*-butylnitroxide complexes of Ti, Zr and Hf was previously reported,<sup>24,25</sup> but little is known about the coordination geometry and oxidation state of the radical-derived ligand. Evans *et al.* recently reported a novel TEMPO complex of Sm containing both  $\eta^1$  and  $\eta^2$ -coordinated TEMPO ligands.<sup>18</sup>  $\eta^2$ -coordination is common for TEMPO complexes of most transition metals;<sup>11–18</sup> for the early metals  $\eta^2$ -coordination was observed for the homoleptic  $\text{Ti}(\text{ONR}_2)_4$  ( $R = \text{Me},^{26} \text{Et}^{27}$ ). In this communication, we report the X-ray structures of two titanium compounds containing anionic TEMPO ligands and demonstrate that the binding mode of these ligands depends sensitively on the ancillary ligation at titanium.

The synthesis of  $\text{CpTiCl}_2(\text{TEMPO})$  (**1**) was achieved by the reaction of TEMPO with  $\text{CpTiCl}_2(\text{THF})$ , generated *in situ* from the  $\text{Li}_3\text{N}$  reduction of  $\text{CpTiCl}_3$  in THF (Scheme 1).<sup>28</sup> Toluene extraction of the reaction product followed by recrystallization at  $-45^\circ\text{C}$  yielded red plates. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1** in  $\text{C}_6\text{D}_6$  reveal a single resonance for the methyl groups of the

TEMPO ligand,<sup>29</sup> implicating an  $\eta^1$ -coordination of TEMPO to Ti, which was confirmed by X-ray analysis of **1**† (Fig. 1). The short Ti–O bond [1.753(3) Å], long N(1)–O(1) bond [1.412(4) Å], and pyramidal geometry of the nitrogen atom [C(6)–N(1)–O(1) 106.8(3)°] indicate that the TEMPO ligand is fully reduced.<sup>9,10,18,30</sup> From this, we formulate **1** as a Ti(IV) complex containing an  $\eta^1$  monoanionic TEMPO ligand, rather than an antiferromagnetically coupled adduct of a metalloradical and the organic radical as proposed for TEMPO adducts of Cu<sup>31</sup> and Rh.<sup>14</sup> The short Ti(1)–O(1) bond distance of 1.753(3) Å and large Ti(1)–O(1)–N(1) angle suggest a large  $p_\pi(\text{O}) \rightarrow d_\pi(\text{Ti})$  contribution, as observed for Ti alkoxides such as  $\text{CpTiCl}_2(\text{OC}_6\text{H}_{11})$ .<sup>32</sup> The similarity of this bonding geometry to Ti alkoxides is also consistent with the formulation as a reduced TEMPO ligand.

To investigate the influence of ancillary ligation on the bonding geometry of Ti–TEMPO complexes, we investigated the solid-state structure of  $(\text{TEMPO})\text{TiCl}_3$  (**2**), whose synthesis was previously reported by Matkovskii and coworkers.<sup>24</sup> Reaction of TEMPO with  $\text{TiCl}_3$  in toluene (generated by the reduction of  $\text{TiCl}_4$  with hexamethyldisilane)<sup>33</sup> followed by recrystallization at  $-30^\circ\text{C}$  yielded yellow–brown crystals of **2** suitable for X-ray diffraction.† The X-ray structure of **2** (Fig. 2) reveals an  $\eta^2$ -O/N chelating coordination mode, analogous to that reported for other hydroxylamide complexes of Ti.<sup>26,27</sup>  $^1\text{H}$  NMR studies of this compound in  $\text{C}_6\text{D}_6$  demonstrate the magnetic inequivalence of the TEMPO methyl groups, indicating that the  $\eta^2$  ligation mode is maintained in non-coordinating solvents at room temperature.<sup>34</sup> The N–O bond distance of 1.433(3) Å, pyramidal geometry at nitrogen (C(1)–N(1)–O(1) 110.6(4)°) and short Ti–O(1) bond distance [1.839(3) Å] are indicative of reduction of the TEMPO radical to generate an  $\eta^2$ -coordinated monoanionic TEMPO ligand.

These results reveal that the coordination geometry of hydroxylamido ligands to Ti depends on the nature of the



Scheme 1

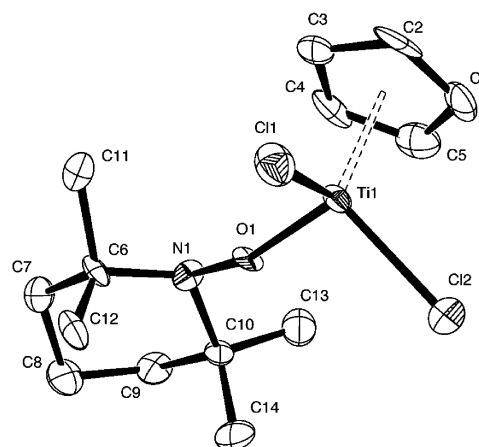
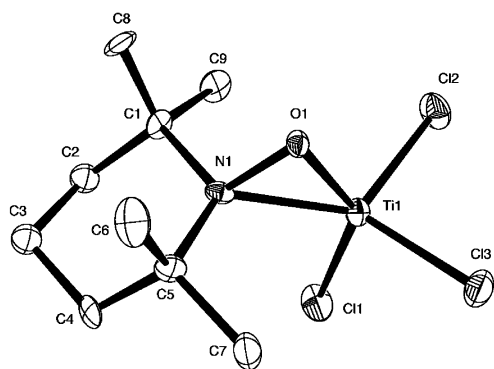


Fig. 1 X-Ray structure of  $\text{CpTiCl}_2(\text{TEMPO})$ . Relevant dimensions (Å and °): Ti(1)–Cp 2.014, Ti(1)–Cl(1) 2.280(2), Ti(1)–O(1) 1.753(3), N(1)–O(1) 1.412(4), N(1)–C(6) 1.486(5); Cl(1)–Ti(1)–Cl(2) 104.1(1), Cl(1)–Ti(1)–O(1) 102.6(1), Ti(1)–O(1)–N(1) 155.7(3), O(1)–N(1)–C(6) 106.8(3), C(6)–N(1)–C(10) 120.3(3).



**Fig. 2** X-Ray structure of (TEMPO)TiCl<sub>3</sub>. Relevant dimensions (Å and °): Ti(1)–O(1) 1.839(3), Ti(1)–N(1) 2.112(4), N(1)–O(1) 1.433(4), Ti(1)–Cl(1) 2.258(2); Ti(1)–O(1)–N(1) 79.4(2), Ti(1)–N(1)–O(1) 58.8(2), Cl(1)–Ti(1)–O(1) 136.6(1), Cl(2)–Ti(1)–O(1) 104.1(1), C(1)–N(1)–O(1) 110.6(4), Cl(1)–Ti(1)–Cl(2) 103.6(1), Cl(1)–Ti(1)–Cl(3) 104.3(1), Cl(2)–Ti(1)–Cl(3) 99.1(1).

hydroxylamine and the ancillary ligation at Ti. The TEMPO ligand of **1** binds  $\eta^1$  to CpTiCl<sub>2</sub> whereas Me<sub>2</sub>NO binds  $\eta^2$  in CpTiCl<sub>2</sub>(ONMe<sub>2</sub>).<sup>35</sup> For the less-sterically hindered TiCl<sub>3</sub> fragment, the TEMPO ligand binds  $\eta^2$ , but appears to cause some distortion as the Cl(1)–Ti(1)–Cl(2) and Cl(1)–Ti(1)–Cl(3) bond angles are expanded at the expense of the the Cl(3)–Ti(1)–Cl(2) angle (Fig. 2). These results, along with those of the groups of Evans<sup>18</sup> and Mulvey<sup>21</sup> imply that TEMPO can be reduced by group 4, lanthanide or s-block elements to form stable and sterically demanding anionic ligands. Investigations of the reactivity of these compounds in catalytic reactions are ongoing and will be reported elsewhere.

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## Notes and references

† Crystal data for CpTiCl<sub>2</sub>(TEMPO) (**1**): C<sub>14</sub>H<sub>23</sub>Cl<sub>2</sub>NOTi, *M* = 340.15, monoclinic, *a* = 7.835(1), *b* = 12.019(2), *c* = 17.930(3) Å, *U* = 1661.3(7) Å<sup>3</sup>, *T* = 180 K, space group *P*2<sub>1</sub>/*n* (no. 14), *Z* = 4,  $\mu$ (Mo–K $\alpha$ ) = 8.29 cm<sup>−1</sup>, 4836 total reflections, 2403 unique reflections (*R*<sub>int</sub> = 0.059) used in all calculations. The final *wR* (*F*<sup>2</sup>) = 0.088 (all data).

Crystal data for (TEMPO)TiCl<sub>3</sub> (**2**): C<sub>9</sub>H<sub>18</sub>Cl<sub>3</sub>NOTi, *M* = 310.51, orthorhombic, *a* = 8.796(1), *b* = 12.266(1), *c* = 12.563(1) Å, *U* = 1355.4(4) Å<sup>3</sup>, *T* = 135 K, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19), *Z* = 4,  $\mu$ (Mo–K $\alpha$ ) = 11.98 cm<sup>−1</sup>, 6067 total reflections, 1328 unique reflections used in all calculations. The final *wR* (*F*<sup>2</sup>) = 0.080 (all data).

CCDC reference numbers 178085 and 178086. See <http://www.rsc.org/suppdata/cc/b1/b110147a/> for crystallographic data in CIF or other electronic format.

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