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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.

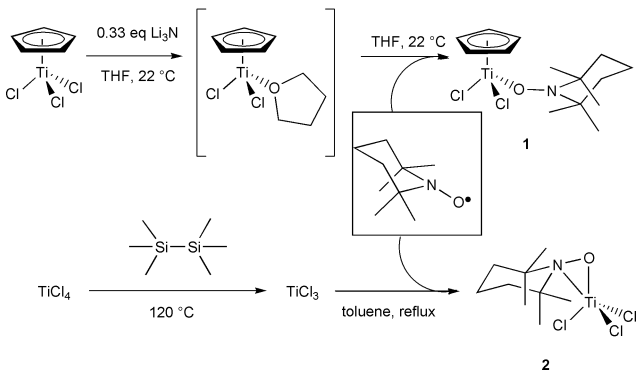
TEMPO (2,2,6,6,-tetramethylpiperidine-*N*-oxyl) enjoys the attention of a variety of chemists due to its stability as a free radical. Applications of this versatile molecule include its use as a mild yet selective oxidant of primary and secondary alcohols,[1,2] as a spin-label in the study of complex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

The synthesis of TEMPO and di-*tert*-butylnitroxide complexes of Ti, Zr and Hf was previously reported,[24,25] 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 η^1 and η^2-coordinated TEMPO ligands.[18] η^2-coordination is common for TEMPO complexes of most transition metals;[11–18] for the early metals η^2-coordination was observed for the homoleptic $Ti(ONR_2)_4$ (R = Me,[26] 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 $CpTiCl_2$(TEMPO) (**1**) was achieved by the reaction of TEMPO with $CpTiCl_2$(THF), generated *in situ* from the Li_3N reduction of $CpTiCl_3$ in THF (Scheme 1).[28] Toluene extraction of the reaction product followed by recrystallization at −45 °C yielded red plates. The ^{1}H and ^{13}C NMR spectra of **1** in C_6D_6 reveal a single resonance for the methyl groups of the TEMPO ligand,[29] implicating an η^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.[9,10,18,30] From this, we formulate **1** as a Ti(IV) complex containing an η^1 monoanionic TEMPO ligand, rather than an antiferromagnetically coupled adduct of a metalloradical and the organic radical as proposed for TEMPO adducts of Cu[31] and Rh.[14] 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 $p_\pi(O) \rightarrow d_\pi(Ti)$ contribution, as observed for Ti alkoxides such as $CpTiCl_2(OC_6H_{11})$.[32] 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 (TEMPO)$TiCl_3$ (**2**), whose synthesis was previously reported by Matkovskii and coworkers.[24] Reaction of TEMPO with $TiCl_3$ in toluene (generated by the reduction of $TiCl_4$ with hexamethyldisilane)[33] followed by recrystallization at −30 °C yielded yellow–brown crystals of **2** suitable for X-ray diffraction.† The X-ray structure of **2** (Fig. 2) reveals an η^2-O/N chelating coordination mode, analogous to that reported for other hydroxylamide complexes of Ti.[26,27] ^{1}H NMR studies of this compound in C_6D_6 demonstrate the magnetic inequivalence of the TEMPO methyl groups, indicating that the η^2 ligation mode is maintained in non-coordinating solvents at room temperature.[34] 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 η^2-coordinated monoanionic TEMPO ligand.

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



Scheme 1

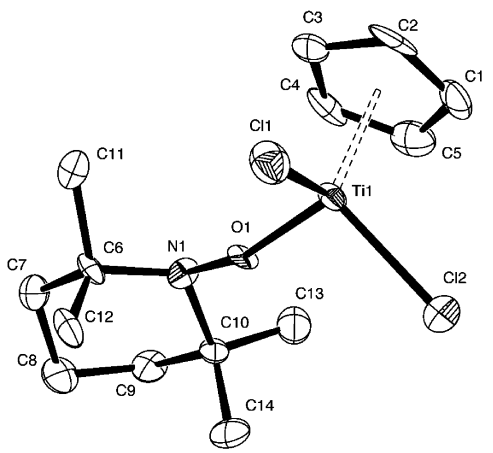


Fig. 1 X-Ray structure of $CpTiCl_2$(TEMPO). Relevant dimensions (Å and °): Ti(1)–Cp 2.014, Ti(1)–Cl(1) 2.280(2), Ti(1)–O(1) 1.753(3), N(1)–O(1) 1.412(4), N(1)–C(6) 1.486(5); Cl(1)–Ti(1)–Cl(2) 104.1(1), Cl(1)–Ti(1)–O(1) 102.6(1), Ti(1)–O(1)–N(1) 155.7(3), O(1)–N(1)–C(6) 106.8(3), C(6)–N(1)–C(10) 120.3(3).

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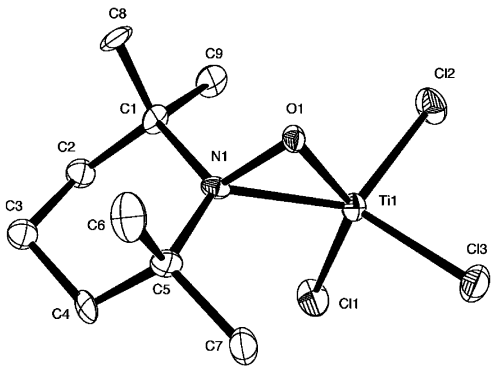

Fig. 2 X-Ray structure of (TEMPO)$TiCl_3$. Relevant dimensions (Å and °): Ti(1)–O(1) 1.839(3), Ti(1)–N(1) 2.112(4), N(1)–O(1) 1.433(4), Ti(1)–Cl(1) 2.258(2); Ti(1)–O(1)–N1(1) 79.4(2), Ti(1)–N(1)–O(1) 58.8(2), Cl(1)–Ti(1)–O(1) 136.6(1), Cl(2)–Ti(1)–O(1) 104.1(1), C(1)–N(1)–O(1) 110.6(4), Cl(1)–Ti(1)–Cl(2) 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 η^1 to $CpTiCl_2$ whereas Me_2NO binds η^2 in $CpTiCl_2(ONMe_2)$.[35] For the less-sterically hindered $TiCl_3$ fragment, the TEMPO ligand binds η^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[18] and Mulvey[21] 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 $CpTiCl_2$(TEMPO) (**1**): $C_{14}H_{23}Cl_2NOTi$, M = 340.15, monoclinic, a = 7.835(1), b = 12.019(2), c = 17.930(3) Å, U = 1661.3(7) Å^3, T = 180 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 8.29 cm^{-1}, 4836 total reflections, 2403 unique reflections (R_{int} = 0.059) used in all calculations. The final wR (F^2) = 0.088 (all data).

Crystal data for (TEMPO)$TiCl_3$ (**2**): $C_9H_{18}Cl_3NOTi$, M = 310.51, orthorhombic, a = 8.796(1), b = 12.266(1), c = 12.563(1) Å, U = 1355.4(4) Å^3, T = 135 K, space group $P2_12_12_1$ (no. 19), Z = 4, μ(Mo-Kα) = 11.98 cm^{-1}, 6067 total reflections, 1328 unique reflections used in all calculations. The final wR (F^2) = 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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