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Coordination Chemistry of Stable Radicals: Homolysis of a Titanium−Oxygen Bond

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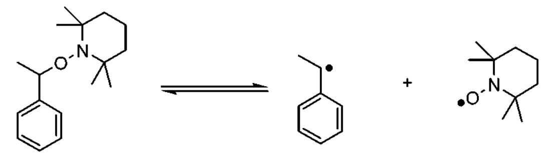
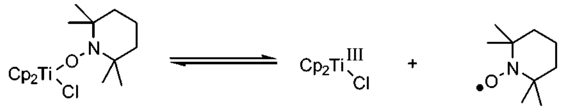
TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) is a persistent radical that reacts with a variety of organic radicals with diffusion-controlled rates to form alkoxyamines with weak carbon−oxygen bonds. The reversible homolysis of these alkoxyamines provides access to controlled concentrations of reactive free radicals and forms the basis of one approach for controlled free radical polymerization reactions mediated by nitroxides.[1]

We recently reported that coordination compounds of TEMPO can be generated by reaction of Ti(III) precursors with TEMPO.[2] Part of our motivation for these studies was to investigate whether these Ti−TEMPO complexes might serve as useful sources of Ti(III) intermediates, in analogy to the formation of radical intermediates for organic alkoxyamines (eqs 1 and 2).[1] Although homolytic dissociation of metal−carbon bonds has been studied extensively,[3] little is known about metal−oxygen bond homolyses, presumably because of the relatively higher bond energies and the unstable nature of the resulting oxygen radicals. Titanium−oxygen bonds are normally quite strong ($\Delta H° = \sim 90$ kcal/mol),[4] but in view of the exceptional stability of the TEMPO radical and the novel η^1 coordination observed for the Ti−TEMPO complex, **1**, we felt that these Ti−TEMPO complexes may serve as a possible source of Ti(III) species by liberation of the stable radical TEMPO.



(1)



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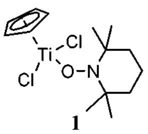

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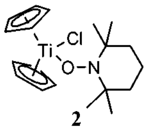
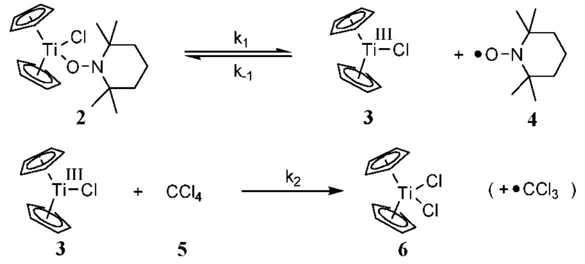


2

The synthesis of Ti−TEMPO complexes can be carried out by mixing TEMPO with a source of Ti(III).[2] Metallocene **1** was prepared as previously described; metallocene **2** was prepared by reduction of $Cp_2TiCl_2$with Zn in THF[5] followed by reaction with TEMPO. Complex **2** was previously reported by Matkovskii and Chernaya as one of the products of the reaction of TEMPO with $Cp_2TiEtCl$.[6] Crystallographic analysis of **1** revealed an η^1-coordinated TEMPO ligand with a short Ti−O bond of 1.75 Å and a relatively long N−O bond of 1.41 Å;[2] these structural data are consistent with the formulation of a reduced TEMPO ligand. The ^1H and ^{13}C NMR spectra of **2** in C_6D_6 at 60 °C possess a single resonance for the methyl groups of the TEMPO ligand.[7] The downfield ^{13}C NMR chemical shift (62.7 ppm) of the piperidine carbon adjacent to N indicates that TEMPO is coordinated to titanium. These results are consistent with the assignment of **2** as a Ti(IV) complex containing a reduced η^1 TEMPO ligand similar to that of **1**.[2]

Scheme 1. Thermolysis of **2** in the Presence of CCl_4



Thermolysis of **1** in the presence of carbon tetrachloride at 60 °C in benzene gave little evidence for Ti−O bond homolysis: there was little change in the ^1H NMR spectra after 4 h and no evidence for the formation of either $CpTiCl_3$ or $(CpTiCl)_2$. In contrast, thermolysis of **2** in benzene at 60 °C in the presence of CCl_4 led to a clean disappearance of **2** and formation of Cp_2TiCl_2.[8,9] The rate of disappearance of **2** increased with increasing concentration of CCl_4 for concentrations of $CCl_4 = 1.00{-}4.00$ M and was strongly inhibited by added TEMPO. The strong inhibition by added TEMPO argues against a heterolytic cleavage of the Ti−O bond and suggests that the Ti−O bond is cleaved homolytically to generate TEMPO (**4**) and a Ti(III) species **3**, which is trapped by CCl_4 (**5**) to generate Cp_2TiCl_2 (**6**) and $^{\bullet}CCl_3$ (Scheme 1).

A rate expression for this process can be derived by assuming a steady-state concentration of **3**,[10]

$$\text{rate} = -\frac{d[\mathbf{2}]}{dt} = \left(\frac{k_2[\mathbf{5}]}{k_{-1}[\mathbf{4}] + k_2[\mathbf{5}]}\right) k_1[\mathbf{2}] \tag{3}$$

In the presence of added TEMPO ($[\mathbf{4}]_0 = 0.010{-}0.100$ M), the rate of disappearance of **2** followed pseudo-first-order kinetics. Plots of $\ln([\mathbf{2}]_0/[\mathbf{2}]_t)$ vs time were linear, with a zero intercept; a plot of the pseudo-first-order rate constant k_{obs} vs $1/[\mathbf{4}]_0$ was linear, revealing the rate to be inverse first order in TEMPO.[10] From the slope of this plot, a value for $(k_1k_2/k_{-1}) = (1.21 \pm 0.02) \times 10^{-7}$ s^{-1} could be calculated (Table 1).[10] This result implies that the rate constant for trapping of the Ti(III) species **3** by TEMPO is larger than that of atom abstraction from CCl_4.[11,12]

Consistent with this analysis, the rate of disappearance of **2** in the absence of TEMPO could not be fit to a simple pseudo-first-

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Table 1. k_{obs} for the Thermolysis of **2** in the Presence of CCl_4[a]

entry	$[\mathbf{4}]_0$ (M)	$[\mathbf{5}]_0$ (M)	k_{obs} ($\times 10^5$ s^{-1})
1[b]	0.010	4.00	4.77 ± 0.02
2[b]	0.030	4.00	1.53 ± 0.06
3[b]	0.050	4.00	0.92 ± 0.04
4[b]	0.100	4.00	0.43 ± 0.02
5[c]	0	4.00	1.78 ± 0.01
6[c]	0	3.00	1.21 ± 0.01
7[c]	0	2.00	0.82 ± 0.01
8[c]	0	1.00	0.40 ± 0.01

[a] $[\mathbf{2}]_0 = 2.98 \times 10^{-2}$ M. [b] Plotting $\ln([\mathbf{2}]_0/[\mathbf{2}]_t)$ vs time. [c] Using eq 4.

order rate expression, implying that even in the absence of added **4**, $k_{-1}[\mathbf{4}] \gg k_2[\mathbf{5}]_0$. However, analysis of the kinetics according to the integrated rate expression of eq 4 gave an excellent fit to the data.[10] Using this expression, a plot of k_{obs}' vs $[\mathbf{5}]_0$ yielded an estimate for $(k_1k_2/k_{-1}) = (1.28 \pm 0.04) \times 10^{-7}$ s^{-1}, in good agreement with that estimated from the TEMPO inhibition studies.

$$\ln\left(\frac{[\mathbf{2}]_0}{[\mathbf{2}]_t}\right) + \frac{[\mathbf{2}]_t}{[\mathbf{2}]_0} - 1 = \frac{k_1k_2[\mathbf{5}]_0}{k_{-1}[\mathbf{2}]_0}t = k_{\mathrm{obs}}'t \qquad (4)$$

The conformance of the kinetic data to eq 4 and the strong inhibition of the rate by added TEMPO favor a mechanism involving Ti−O bond homolysis over heterolytic pathways or free radical chain mechanisms,[10] although we cannot rule out the precoordination of CCl_4 to **2** on the basis of the evidence to date.[13]

The much faster rate of radical recombination ($\mathbf{3} + \mathbf{4}$)[11,12] relative to chlorine atom abstraction prevented an estimation of k_1 using the pseudo-first-order kinetic treatment. However, an estimate for k_1 could be obtained from simulations using the IBM Chemical Kinetics Simulator 1.01 (CKS).[14] For these simulations, it was assumed that escape from the radical cage was rapid; while this assumption may not be completely valid, this analysis provides a lower-limit estimate for k_1.[3a,15,16] The time evolution of the concentration of **2** was simulated by systematically varying k_1, k_{-1}, k_2, and $[\mathbf{2}]_0$ subject to the constraint $(k_1k_2/k_{-1}) = 1.28 \times 10^{-7}$ s^{-1}. These simulations yielded an estimate for $k_1 = 2.05 \times 10^{-3}$ s^{-1} at 60 °C.[14]

The observations that the Ti−TEMPO bond of **2** is readily homolyzed at 60 °C whereas the monocyclopentadienyl complex $CpTiCl_2$(TEMPO) is inert suggest that the strength of the Ti−O bond in these TEMPO complexes depends sensitively on the ancillary ligation at titanium. The use of stable nitroxide radicals as ligands should provide a useful experimental platform to interrogate the influence of ancilliary ligation on the strength of weak bonds derived from stable radicals.

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Supporting Information Available: Synthesis and characterization of **2**, figures and tables giving a summary of kinetic data, and computer kinetics simulation results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The dynamic NMR studies of a series of Ti−TEMPO complexes will be reported elsewhere.

(8) Thermolysis of **2** in the absence of CCl_4 gave no evidence of Cp_2TiCl_2, indicating that conproportionation of **2** is not responsible for the formation of **6**.

(9) Carbon tetrachloride has been used as an excellent trap for metal radicals. For the reaction of CCl_4 with Ti(III) complexes, see: (a) Bruce, A. E.; Bruce, M. R. M.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 6660−6664. For the use of CCl_4 in kinetics studies of metal−metal bond homolyses, see: (b) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187−218.

(10) See Supporting Information for the steady-state treatment, derivation of the rate laws, and the kinetics data and plots.

(11) The rate constant for the *decarbonylative* trapping of $(MeCp)Mo(CO)_3$ radical by the nitroxide radical TMIO is 77 times larger than that of CCl_4 trapping. Tenhaeff, S. C.; Covert, K. J.; Castellani, M. P.; Grunkemeier, J.; Kunz, C.; Weakley, T. J. R.; Keonig, T.; Tyler, D. R. *Organometallics* **1993**, *12*, 5000−5004.

(12) Studies on the atom abstraction of metal radicals also showed that the rate constants for the trapping of $CpM(CO)_3$ (M= Mo, W) radicals by CCl_4 are $\sim 10^4$ M^{-1} s^{-1}, significantly lower than those for radical−radical recombinations. Song, J.-S.; Bullock, R. M.; Creutz, C. *J. Am. Chem. Soc.* **1991**, *113*, 9862−9864.

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(16) If the cage effect is important, k_1 and k_{-1} should be referred to $(k_dk_h/(k_c + k_d))$ and $(k_ck_D/(k_c + k_d))$, respectively.

$$[\text{TEMPO−Ti}] \underset{k_c}{\overset{k_h}{\rightleftharpoons}} \underset{\text{cage pair}}{[\text{TEMPO}^{\bullet}\ {}^{\bullet}\text{Ti}]} \underset{k_D}{\overset{k_d}{\rightleftharpoons}}$$

$$[\text{TEMPO}^{\bullet}] + [{}^{\bullet}\text{Ti}^{\text{III}}] \xrightarrow[CCl_4]{k_2} [\text{Ti−Cl}]$$

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