Dithiocarbamate Complexes of Ti(IV) Alkoxides: Synthesis, Characterization, and Electrochemistry

Alberto Donzelli and Pierre G. Potvin*

Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario, Canada M3J 1P3

Isopropoxy- and *tert*-butoxy-*tris*(dithiocarbamato)titanium(IV) complexes of five dithiocarbamate ligands were prepared and characterized by LDI-MS, ^{1}H NMR, ^{13}C NMR, and elemental analysis, as well as by crystallographic determination of two examples. Both showed strongly π-coordinated alkoxy groups and two separate dithiocarbamate coordination environments that, in solution, were in rapid exchange. Cyclic voltammetry in CH_2Cl_2 revealed irreversible but reproducible oxidation peaks between $+1.2$ and $+1.6$ V vs Ag/AgCl, about 1 V positive of those from the free ligands, as well as reduction peaks in the -1.9 to -2.2 V range vs Ag/AgCl assigned to Ti$^{IV/III}$ couples, and second reductions in some cases. The corresponding diisopropoxy-*bis*(dithiocarbamato) analogues were not isolable and slowly transformed to the more stable *tris* species. Indeed, these were shown to be in slow equilibrium.

Introduction

The oxidation of alcohols is a fundamental reaction that has elicited much attention over the decades.[1] Although O_2 is sufficiently strongly oxidizing, its direct reaction with alcohols is impractically slow, in part because of the kinetic and thermodynamic restrictions of one-electron pathways and because of spin considerations (triplet-state O_2 vs singlet-state substrates).[2] Homogeneous catalysts of aerial oxidation,[3] with or without sacrificial additives,[4] alter the electronic structure of O_2 to facilitate the reaction.[5] When involving one-electron couples, such as with the Wieghardt mononuclear Cu$^{II/I}$ catalyst,[6] with other Cu$^{II/I}$ systems that employ *N*-oxyls as additives,[7] and with Co$^{III/II}$ complexes,[8] alcohol oxidation probably proceeds through high-energy ketyl anion radicals in one-electron steps, whereas the Cu$^{II/I}$ system of Markó et al.[9] is said to function via a dinuclear intermediate by a two-electron α-deprotonation process akin to that by Cr^{VI} or Mn^{VIII} laboratory reagents. Some mononuclear Co-based catalysts appear to proceed by a two-electron pathway through a formal Co^{IV}=O species, by employing a sacrificial reductant that, in essence, converts the four-electron oxidant O_2 into a two-electron one.

Electrochemical oxidation is an attractive alternative for industrial scales because it is atom-economical, it obviates transition metal-containing waste, and it can be energetically efficient if conducted at close to the thermodynamic potential. In fuel cells, O_2 drives alcohol oxidation by being reduced at the cathode while the alcohol is oxidized at the anode, with migration of electrons through an external circuit and of H$^+$ in the electrolyte solution. Whereas the cathodic reaction can be fast, the anodic reaction is slow, and much research has been devoted to developing efficient electrode materials for alcohol-fueled cells.[10] Recent work with

* To whom correspondence should be addressed. E-mail: pgpotvin@yorku.ca.

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graphite electrodes covalently modified with Ru[IV/III/II] species[11] has demonstrated the potential utility of surface-grafted molecular electrocatalysts in alcohol oxidation.

As exemplified by the Katsuki–Sharpless catalyst,[12] Ti[IV] alkoxide complexes are capable of rapid alcohol-alkoxide exchanges for reactant loading and product unloading. Because Ti[IV] is not itself oxidizable, a Ti[IV]-based alcohol electro-oxidation catalyst would need to include oxidizable ligands that would reversibly store two oxidation equivalents to drive the α-deprotonation of a Ti-bound alkoxide, as well as sites for alcohol attachment and surface binding. The use of redox-active ligands is not new: the ligands in the Wieghardt catalysts,[13] for instance, cycle between two oxidation states, and porphyrin cation radical complexes of Fe and Ru are suspected intermediates in oxidation catalyzes.[14] Ti[IV] is additionally inexpensive and environmentally benign. While solution-phase complexes aggregate through μ-O linkages upon hydrolysis, surface-chemisorbed Ti[IV] complexes should be relatively insensitive to hydrolysis and unable to aggregate.

We report here our initial exploration in this area, using the well-known dithiocarbamate ligands. These are known to be reversibly oxidized to dimeric thiuram disulfides,[15] which can also act as ligands.[16] We therefore aimed for $L_2Ti(OR)_2$ species in which the dithiocarbamate/thiuram disulfide couple can store two oxidation equivalents, and in which one of the alkoxy groups is available for exchange with a fuel alcohol while the other is used for anchoring to an electrode by exchange with a surface OH group. Dithiocarbamates are easily prepared in situ from amines of varying basicities, and they bind symmetrically as bidentates,[17] yet their coordination chemistry at Ti[IV] alkoxides is essentially undeveloped (only three prior examples of mixed dithiocarbamate-alkoxide Ti[IV] complexes have been reported)[18,19] and their electrochemistry is completely unexplored.

Experimental Section

General Procedures. All reactions were carried out under Ar. All reagents were Sigma-Aldrich products. Titanium tetraisopropoxide, Ti(O[i]Pr)$_4$, was distilled under Ar prior to use. Titanium tetra-*tert*-butoxide, Ti(O[t]Bu)$_4$, was purchased in Aldrich Sure-Seal bottles and used directly. Solvents were from Caledon Laboratories (Georgetown, ON, Canada). Prior to use, tetrahydrofuran (THF) was distilled over K and CH$_2$Cl$_2$ was distilled over P$_2$O$_5$. All NMR spectra were acquired in CDCl$_3$ at 23 °C at 300 or 400 MHz on Bruker ARZ instruments. LDI-MS was carried out on MALDI Voyager-DE spectrometer (PerSeptive Biosystems) equipped with a TOF detector in the positive ion mode. High-resolution EI-MS was performed on a Waters GCT Premier instrument by Dr. Alex Young, University of Toronto. Elemental analyses were performed with weighing under N$_2$ by Guelph Chemical Laboratories (Guelph, ON, Canada). Crystal structure data collection, structural analysis, and refinement were carried out by Dr. Alan Lough at the University of Toronto.

Sample Procedure for Tris(dithiocarbamato) Complexes: Preparation of Isopropoxy-tris(pyrrolidine-*N*-carbodithioato)titanium(IV), Ti(1)$_3$(O[i]Pr). Ti(O[i]Pr)$_4$ (0.33 mL, 1.1 mmol) was added to 40 mL of THF, followed by anhydrous CS$_2$ (0.2 mL, 3.3 mmol) and, subsequently, pyrrolidine (0.28 mL, 3.3 mmol). The resultant yellow mixture was stirred at room temperature for approximately 16 h. The solvent and reaction byproduct were removed under reduced pressure, and the product was recovered as a solid yellow residue in quantitative yield (0.587 g, 97%). ^{1}H NMR: δ 1.24 (d, 6H), 2.00 (bm, 12H), 3.71 (bm, 12H), 4.6 (h, 1H) ppm; ^{13}C NMR: δ 24.72, 25.08, 49.86, 82.29, 201.19 ppm. LDI-MS: m/z 485.9 (100%, M-O[i]Pr), 398.9 (41%, M-**1**). Anal. Calcd for C$_{18}$H$_{31}$N$_3$OS$_6$Ti: 39.62%C, 5.73%H, 7.70%N; Found 39.52%C, 6.05%H, 7.68%N. E_{pa} +1.58 V. E_{pc} −1.89, −2.43 V.

***tert*-Butoxy-tris(pyrrolidine-*N*-carbodithioato)titanium(IV), Ti(1)$_3$(O[t]Bu).** ^{1}H NMR: δ 1.32 (s, 9H), 1.99 (bm, 12H), 3.70 (bm, 12H) ppm; ^{13}C NMR: δ 25.12, 30.37, 49.86, 88.43, 201.34 ppm. LDI-MS: m/z 485.8 (100%, M-O[t]Bu), 412.9 (7%, M-**1**); Anal. Calcd for C$_{19}$H$_{33}$N$_3$OS$_6$Ti: 40.77%C, 5.94%H, 7.51%N; Found 40.55%C, 6.13%H, 7.37%N. E_{pa} +1.54 V. E_{pc} −2.14, −2.59 V.

Isopropoxy-tris(*N*,*N*-diethylamine-*N*-carbodithioato)titanium(IV), Ti(2)$_3$(O[i]Pr). ^{1}H NMR: δ 1.15 (d, 6H), 1.19 (t, 18H), 3.76 (m, 12H), 4.55 (h, 1H) ppm; ^{13}C NMR: δ 12.51, 24.57, 44.60, 81.59, 204.19 ppm. LDI-MS: m/z 491.9 (100%, M-O[i]Pr), 402.9 (94%, M-**2**); Anal. Calcd for C$_{18}$H$_{37}$N$_3$OS$_6$Ti: 39.18%C, 6.76%H, 7.62%N; Found 38.98%C, 6.95%H, 7.43%N. E_{pa} +1.49 V. E_{pc} −2.06, −2.66 V.

***tert*-Butoxy-tris(*N*,*N*-diethylamine-*N*-carbodithioato)titanium(IV), Ti(2)$_3$(O[t]Bu).** ^{1}H NMR: δ 1.18 (bm, 18H), 1.22 (s, 9H), 3.75 (bm, 12H) ppm; ^{13}C NMR: δ 12.57, 30.22, 44.63, 87.62, 204.20 ppm. LDI-MS: m/z 491.9 (100%, M-O[t]Bu), 417.0 (9%, M-**2**); Anal. Calcd for C$_{19}$H$_{39}$N$_3$OS$_6$Ti: 40.33%C, 6.95%H, 7.43%N; Found 39.98%C, 7.23%H, 7.45%N.

Isopropoxy-tris(morpholine-*N*-carbodithioato)titanium(IV), Ti(3)$_3$(O[i]Pr). ^{1}H NMR: δ 1.21 (d, 6H), 3.71 (bm, 12H), 3.97 (bm, 12H), 4.6 (h, 1H) ppm; ^{13}C NMR: δ 24.63, 47.39, 66.90, 82.67, 205.10 ppm. LDI-MS: m/z 533.8 (100%, M-O[i]Pr), 430.9 (48%, M-**3**); Anal. Calcd for C$_{18}$H$_{31}$N$_3$O$_4$S$_6$Ti: 36.41%C, 5.26%H, 7.08%N; Found 36.64%C, 5.36%H, 6.90%N. E_{pa} +1.47 V. E_{pc} −2.17, −2.65 V.

***tert*-Butoxy-tris(morpholine-*N*-carbodithioato)titanium(IV), Ti(3)$_3$(O[t]Bu).** ^{1}H NMR: δ 1.25 (s, 9H), 3.66 (bm, 12H), 3.96 (bm, 12H) ppm; ^{13}C NMR: δ 30.25, 47.45, 66.50, 88.70, 205.15 ppm. LDI-MS: m/z 533.7 (100%, M-O[t]Bu), 444.9 (19%, M-**3**); Anal. Calcd for C$_{19}$H$_{33}$N$_3$O$_4$S$_6$Ti: 37.55%C, 5.47%H, 6.91%N; Found 37.42%C, 5.69%H, 6.64%N.

Isopropoxy-tris(*N*′-methylpiperidine-*N*-carbodithioato)titanium(IV), Ti(4)$_3$(O[i]Pr). ^{1}H NMR: δ 1.16 (d, 6H), 2.26 (s, 9H), 2.40 (bm, 12H), 3.94 (bm, 12H), 4.55 (h, 1H) ppm; ^{13}C NMR: δ 24.64,

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45.78, 46.90, 54.33, 82.35, 204.42 ppm. LDI-MS: *m/z* 572.8 (100%, M-O^{i}Pr), 456.9 (50%, M-**4**); HR-EI-MS: *m/z* 573.0550 (M-O^{i}Pr, C$_{18}$H$_{33}$N$_6$S$_6$Ti requires 573.0570), 457.0692 (M-**4**, C$_{15}$H$_{29}$N$_4$OS$_4$Ti requires 457.0704). E_{pa} +1.32 V. E_{pc} −2.02 V.

tert-Butoxy-tris(N′-methylpiperidine-N-carbodithioato)titanium(IV), Ti(4)$_3$(O^{t}Bu). ^{1}H NMR: δ 1.23 (s, 9H), 2.25 (s, 9H), 2.40 (bm, 12H) 3.93 (bm, 12H) ppm; ^{13}C NMR: δ 30.25, 45.80, 46.92, 54.43, 88.42, 204.44 ppm. LDI-MS: *m/z* 572.8 (100%, M-O^{t}Bu), 470.9 (18%, M-**4**); Anal. Calcd for C$_{22}$H$_{42}$N$_6$OS$_6$Ti: 40.85%C, 6.54%H, 12.99%N; Found 40.80%C, 6.62%H, 12.63%N.

Isopropoxy-tris(N,N′,N′-trimethylethane-1,2-diamine-N-carbodithioato)titanium(IV), Ti(5)$_3$(O^{i}Pr). ^{1}H NMR: δ 1.15 (d, 6H), 2.21 (d, 18H), 2.53 (t, 6H), 3.30 (s, 9H), 3.80 (bm, 6H), 4.55 (h, 1H) ppm; ^{13}C NMR: δ 24.62, 38.63, 45.62, 50.28, 55.99, 82.01, 205.71 ppm. LDI-MS: *m/z* 578.9 (100%, M-O^{i}Pr), 461.0 (11%, M-**5**); Anal. Calcd for C$_{21}$H$_{46}$N$_6$OS$_6$Ti: 39.48%C, 7.26%H, 13.15%N; Found 39.20%C, 6.99%H, 12.87%N. E_{pa} +1.19 V. E_{pc} −2.08 V.

tert-Butoxy-tris(N,N′,N′-trimethylethane-1,2-diamine-N-carbodithioato)titanium(IV), Ti(5)$_3$(O^{t}Bu). ^{1}H NMR: δ 1.23 (s, 9H), 2.21 (s, 18H), 3.28 (s, 9H) 3.85 (bm, 12H) ppm; ^{13}C NMR: δ 30.26, 38.65, 45.62, 50.30, 56.06, 88.07, 205.79 ppm. LDI-MS: *m/z* 578.9 (100%, M-O^{t}Bu), 475.0 (45%, M-**5**); Anal. Calcd for C$_{22}$H$_{48}$N$_6$OS$_6$Ti: 40.47%C, 7.41%H, 12.87%N; Found 40.14%C, 7.12%H, 13.16%N.

Sample Procedure for Bis(dithiocarbamato) Complexes: Preparation of Diisopropoxy-bis(pyrrolidine-N-carbodithioato)titanium(IV), Ti(1)$_2$(O^{i}Pr)$_2$. Ti(O^{i}Pr)$_4$ (0.98 mL, 3.3 mmol) was added to 30 mL of anhydrous CH$_2$Cl$_2$. Pyrrolidine (0.28 mL, 3.3 mmol) was added, and the mixture was left to cool in an ice−water bath for 1 h. Then, CS$_2$ (0.2 mL, 3.3 mmol) dissolved in 10 mL of anhydrous CH$_2$Cl$_2$ was added via a syringe pump over the course of 2 h at 0 °C. The yellow mixture was left to stand overnight at 0 °C. The solvent and reaction byproduct were removed under reduced pressure, and the product was recovered as a yellow oil. ^{1}H NMR: δ 1.25 (d, 6H), 1.96 (m, 4H), 3.65 (m, 4H), 4.94 (h, 1H) ppm. ^{13}C NMR: δ 25.71, 25.08, 50.81, 80.77, 199.41 ppm.

Diisopropoxy-bis(N,N-diethylamine-N-carbodithioato)titanium(IV), Ti(4)$_2$(O^{i}Pr)$_2$. ^{1}H NMR: δ 1.25 (d, 6H), 2.26 (s, 3H), 2.40 (m, 4H), 3.96 (m, 4H), 4.93 (h, 1H) ppm. ^{13}C NMR: δ 26.49, 45.69, 47.80, 54.33, 80.88, 203.03 ppm.

Diisopropoxy-bis(N,N′,N′-trimethylethane-1,2-diamine-N-carbodithioato)titanium(IV), Ti(5)$_2$(O^{i}Pr)$_2$. ^{1}H NMR: δ 1.23 (d, 6H), 2.20 (d, 9H), 2.51 (t, 2H), 3.31 (s, 3H), 3.84 (t, 2H), 4.93 (h, 1H) ppm. ^{13}C NMR: δ 25.68, 39.59, 45.62, 51.29, 55.99, 80.67, 204.13 ppm.

Diisopropoxy-bis(piperidine-N-carbodithioato)titanium(IV), Ti(6)$_2$(O^{i}Pr)$_2$. ^{1}H NMR: δ 1.25 (d, 6H), 2.86 (m, 4H), 3.93 (m, 4H), 4.94 (h, 1H) ppm. ^{13}C NMR: δ 25.71, 45.76, 49.34, 80.88, 202.74 ppm.

Crystallography. Yellow crystals of Ti(**1**)$_3$(O^{i}Pr) were grown over approximately 6 months after layering petroleum ether over a CH$_2$Cl$_2$ solution. Similarly, yellow crystals of Ti(**3**)$_3$(O^{t}Bu) were grown from CDCl$_3$. Diffraction intensities were collected on a Bruker-Nonius Kappa CCD instrument using a fine-focus sealed tube Mo Kα source and graphite monochromator. Unique reflections were corrected for absorption (Denzo-SMN) and used in all calculations. Heavy-atom positions were determined by direct methods (SHELXS-97) and refined anisotropically. The hydrogen atoms were assigned idealized positions according to a riding model and refined isotropically. Structure refinement used full-matrix least-squares on F^2 (SHELXL-97). The Ti(**3**)$_3$(O^{t}Bu) crystal contained a molecule of CDCl$_3$, the non-hydrogen atom positions of which were also refined anisotropically. The ^{t}Bu group of Ti(**3**)$_3$(O^{t}Bu)

Chart 1
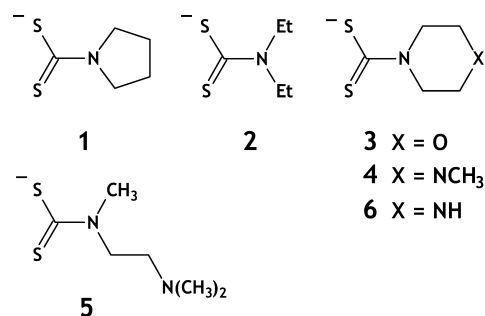
was disordered over two orientations in occupancy ratio 57.4 ± 0.9%:42.6 ± 0.9%. Similarly, the ^{i}Pr group of Ti(**1**)$_3$(O^{i}Pr) was also disordered over two orientations in occupancy ratio 82.3 ± 0.9%:17.7 ± 0.9%, sharing the CH$_3$ carbon positions. In both structures, the disordered C atom positions were refined anisotropically.

Electrochemistry. All the electrochemical analyses were performed in a one-compartment, three-electrode cell with a Pt disk working electrode, a Ag/AgCl pseudo-reference electrode, and a graphite counter-electrode, under an Ar atmosphere, connected to an Obbligato Objectives Faraday MP potentiostat. The sample solutions were 0.03 M in freshly distilled CH$_2$Cl$_2$, containing 0.1 M ^{n}Bu$_4$NPF$_6$ as supporting electrolyte. All scans were performed at a 200 mV s^{-1} sweep rate. They were either limited to oxidation or reduction regimes or covered both in succession and were then initiated in both anodic and cathodic directions. The potentials were internally calibrated with ferrocene and are reported with respect to Ag/AgCl (satd. KCl). To assess the redox potentials of the free ligands, 1:1 mixtures of amine and CS$_2$ were prepared in THF under Ar. After vacuum removal of the volatiles, NMR in CDCl$_3$ showed the solid products to be the ammonium dithiocarbamate salts R$_2$NH$_2^{+-}$SSCNR$_2$, and these were redissolved in CH$_2$Cl$_2$ for analysis as with the complexes.

Results and Discussion

Synthesis. The direct reactions of 3:3:1 ratios of a secondary amine, CS$_2$, and Ti(OR)$_4$ (R = ^{i}Pr or ^{t}Bu) in THF, CH$_2$Cl$_2$, or CDCl$_3$ gave instantaneous color changes and led to the *tris*(dithiocarbamato) complexes L$_3$TiOR as the only detected products, and these could be isolated in quantitative yields (eq 1). These were also the only reaction products at 2:2:1 amine:CS$_2$/Ti stoichiometry, aside from liberated HOR and unreacted Ti(OR)$_4$. Chart 1 lists the ligands L explored. Of these, **3**−**6** presented the possibility of tridentate coordination through the oxygen or free nitrogen atoms, but this was not observed.

$$\text{Ti(O}^i\text{Pr)}_4 \xrightarrow[\text{THF/RT}]{\text{CS}_2} \xrightarrow{\text{amine}} \text{TiL}_3(\text{O}^i\text{Pr}) \quad (1)$$
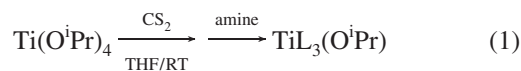
The L$_3$TiOR products were initially identified by ^{1}H NMR. Beyond showing the uptake of amine and the release of HOR when conducted in CDCl$_3$, the reactions showed the appearance of new L and OR ^{1}H NMR signals with integration ratios consistent with a 3:1 L/Ti reaction stoichiometry, as well as signals from unreacted Ti(OR)$_4$ at amine/Ti ratios below 3, or from unreacted amine, at ratios above 3. When R was ^{i}Pr, the new O^{i}Pr methine signals consistently appeared

near 4.6 ppm, some 0.2 ppm downfield of that of Ti(O^{i}Pr)$_4$. ^{13}C NMR confirmed the presence of C=S groups and single O^{i}Pr (or O^{t}Bu) C−O signals shifted some 5−6.5 ppm (or 8−9 ppm) downfield of the corresponding C−O signals with Ti(O^{i}Pr)$_4$ (or Ti(O^{t}Bu)$_4$).[20] In all cases, the single set of ligand NMR signals indicated symmetry or rapid exchange between inequivalent coordination sites. Fast positional exchange has previously been witnessed in *tetrakis*[21] and chloro*tris*(dithiocarbamate)[22] complexes. The only other *tris*(dithiocarbamate) Ti(IV) alkoxide is a Ti(**2**)$_3$(OR) analogue and its NMR spectra (in pyridine-d_5) showed similar ^{13}CS$_2$ and ethyl signals.

The structures were confirmed by ^{13}C NMR, elemental analysis and, in two cases, crystallography (vide infra). LDI-MS showed consistent fragmentations of OR or dithiocarbamate ligands (L) from all L$_3$TiOR. Only Ti(**4**)$_3$(O^{i}Pr) did not provide elemental analyses that were consistent with the formula, indicative instead of possible carbonation and/or partial hydrolysis. However, high-resolution measurements of the EI fragments M-**4** and M-O^{i}Pr were consistent with the compound's identity.

Evidence of a second species, later determined to be *bis*(dithiocarbamato) complexes, was found at 1:1:1 amine/CS$_2$/Ti stochiometry, but this evolved to *tris* product overnight. When CS$_2$ was added last and slowly at 0 °C, this second product was the only detectable product (eq 2), aside from excess Ti(OR)$_4$ (reactions in THF led to ca. 1:1 mixtures with L$_3$Ti(OR) coproducts).

$$Ti(O^iPr)_4 \xrightarrow[CH_2Cl_2/RT]{amine} \xrightarrow[0\ °C]{CS_2} TiL_2(O^iPr)_2 \qquad (2)$$
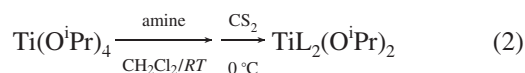
The O^{i}Pr methine signals now appeared at 4.9 ppm (0.5 ppm downfield of that with Ti(O^{i}Pr)$_4$), and integration of the amine and OR signals revealed a 2:2:1 reaction stoichiometry. Again, single sets of signals were found in both ^{1}H- and ^{13}C NMR spectra, that is, without separate signals from bridging alkoxide groups, so they appear to be mononuclear species of formula L$_2$Ti(O^{i}Pr)$_2$ with equivalence through symmetry or rapid positional exchange. A dimer (or other aggregate) would need to undergo fast ligand scrambling to be consistent with the single set of NMR signals. The observation of slow or absent exchange with the liberated HO^{i}Pr, confirmed by the absence of any effect on the NMR signal positions or linewidths upon removal of the HO^{i}Pr, indicates that there is no fast exchange mechanism available. Moreover, we noted no concentration dependence with either the signal positions nor the signal linewidths, which would have been a sign of reversible aggregation. On the weight of the evidence, therefore, we favor the formulation of these products as mononuclear species. Unfortunately, it has proven impossible to prepare or isolate these 2:2:1 products free of either excess Ti(OR)$_4$ or of co-produced L$_3$Ti(OR), and the crude products were oily and failed to grow crystals.

Moreover, the L$_2$Ti(OR)$_2$ species were unstable and slowly transformed to L$_3$Ti(OR). The mass spectrum of the putative Ti(**1**)$_2$(O^{i}Pr)$_2$ was not significantly different from that of Ti(**1**)$_3$(O^{i}Pr), perhaps because of this.

We attempted to obtain L$_2$Ti(OR)$_2$ products in pure state by other means: Not surprisingly, treatment of sodium dithiocarbamate salts with Ti(OR)$_4$ failed to cause the expulsion of sodium alkoxides. *Bis*(dithiocarbamate)diphenoxy complexes have reportedly been prepared from (PhO)$_2$TiCl$_2$.[23] Treatment of Ti(THF)$_2$Cl$_4$ or Ti(OR)$_2$Cl$_2$ (formed in situ from equal amounts of Ti(OR)$_4$ and Ti(THF)$_2$Cl$_4$) with sodium pyrazole-1-carbodithioate, prepared and purified separately, led to the isolation of new species. The spectroscopic data obtained for these products were consistent with L$_2$TiCl$_2$ and L$_2$Ti(OR)$_2$, respectively, but they proved to be too unstable to permit further characterization, possibly because of disproportionation.

In both series of complexes, the alkoxy NMR signal positions were quite independent of the basicity of the amine component. The OC^{1}H signals in the isopropoxy cases were consistently at 4.55−4.60 ppm with the *tris* complexes, compared to 4.93−4.94 ppm with the *bis* complexes. The *tert*-butoxy O^{13}CC signals also appeared in a narrow range (87.6−88.7 ppm), as did the isopropoxy O^{13}CH signals (81.6−82.7 ppm with the *tris* complexes and 80.7−80.9 ppm with the *bis* species). Besides having a diagnostic value, this indicates a poor transmission of the amine electron density through the metal. Conversely, there was little transmission in the opposite direction: The ^{13}CS$_2$ signals were at virtually the same positions in the spectra of the O^{t}Bu complexes as in those of their O^{i}Pr analogues, and this was also the case with the signals from the amine components. Although measured in a different solvent, this was also true of the signals from a Ti(**2**)$_3$(OR) analogue. We earlier noted that the OC^{1}H chemical shifts from TiO^{i}Pr groups were related to the Ti−O bond lengths, which are shortened by π-donation, with shorter bonds associated with more downfield positions.[24] (Unfortunately, there were insufficient data in the literature to draw a correlation with the corresponding ^{13}C NMR chemical shifts.) The chemical shift and bond length measured for Ti(**1**)$_3$(O^{i}Pr) fit within that correlation. In the absence of a crystal structure for a *bis* species, the chemical shift differences between the *tris* and *bis* species' signals are less easily explained.

$$Ti(O^iPr)_4 + HL \rightleftharpoons TiL(O^iPr)_3 + HO^iPr \qquad (3)$$

$$TiL(O^iPr)_3 + HL \rightleftharpoons TiL_2(O^iPr)_2 + HO^iPr \qquad (4)$$

$$TiL_2(O^iPr)_2 + HL \rightleftharpoons TiL_3(O^iPr) + HO^iPr \qquad (5)$$

Substitutions at Ti(OR)$_4$ by an associative mechanism are hindered by interligand repulsions involving the OR alkyl groups, which are evidenced by the fact that Ti(OR)$_4$ is monomeric when R = ^{i}Pr or ^{t}Bu but oligomeric when R =

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Et or Me.[25] As no evidence of monosubstituted product was observed during substitutions of OR with dithiocarbamates L, while $TiL_2(O^iPr)_2$ and $Ti(O^iPr)_4$ can evidently coexist, it appears that the second substitution (eq 4) was easier than the first (eq 3), as that initial substitution relieved some of the steric congestion. This is consistent with the kinetics of analogous substitutions by other monobasic bidentates that produce stable, hexacoordinate $TiL_2(OR)_2$ species without detectable monosubstituted intermediates.[26,27] A relief of steric congestion is also likely the driving force for the ligand redistribution that accompanies the insertion of CS_2 into $Ti(NEt_2)(O^iPr)_3$ to produce $Ti(2)_2(O^iPr)_2$. The third substitution (eq 5) raises the coordination number from six to seven, which the small dithiocarbamate bite angle allows, but it appears to be sufficiently slowed to permit the accumulation of $TiL_2(O^iPr)_2$ under some conditions, although $TiL_3(O^iPr)$ accumulates over time and appears to be more stable, as it suffers no OR-OR repulsions. The fourth substitution, raising the coordination number to eight, appears to be too difficult in these complexes, probably because the consequent build up of congestion at the metal is no longer justified by a relief of interligand repulsions, though other driving forces can be exploited to prepare *tetrakis*(dithiocarbamate) complexes, from $TiCl_4$ and excess sodium dithiocarbamate salts[28,29] or by the insertion of CS_2 into *tetrakis*(dialkylamido) complexes.[30]

We also used the diamines piperidine and *N,N′*-dimethyl ethylenediamine in attempts to form multinuclear variations containing bridging ligands at 1:2:1 and other amine/CS_2/$Ti(OR)_4$ stoichiometries. Unfortunately, much insoluble material was observed, suggestive of oligomerization, as well as only very broad signals in the NMR spectra from what remained in solution. Given the results with non-bridging ligands, 1 equiv of a *bis*(dithiocarbamate) should have given $TiL_2(OR)_2$ and unreacted $Ti(OR)_4$, then either a macrocycle or a polymer with all metals doubly substituted. The observed outcome could mean that the geometry of the $TiL_2(OR)_2$ intermediates was not conducive to macrocyclization, perhaps simply because the L−Ti−L angle was too large. Parallel attempts to combine two disubstituted species with a half-equivalent of a *bis*(dithiocarbamate) also failed.

Equilibration. The formation of $L_2Ti(OR)_2$ to the exclusion of $L_3Ti(OR)$ by addition of the CS_2 last and in the presence of excess $Ti(OR)_4$ could be because the third HL/HOR substitution on $L_2Ti(OR)_2$ was rendered kinetically uncompetitive with the earlier substitutions under these conditions. On the other hand, we found that the proportion of the $L_3Ti(OR)$ co-product increased when the amine was added as the last component, or when an excess of CS_2 was
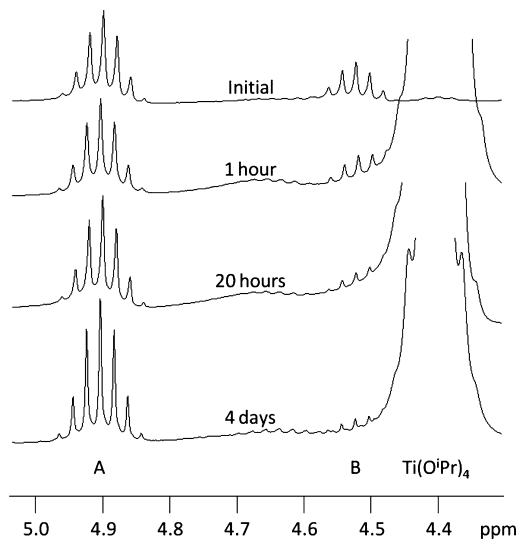
Figure 1. Evolution of a mixture of $Ti(4)_2(O^iPr)_2$ [A] and $Ti(4)_3(O^iPr)$ [B] treated with an excess of $Ti(O^iPr)_4$, followed through the diagnostic ${}^1H$ NMR heptets of the OCH groups.

added, or simply over time. These results might indicate kinetic and thermodynamic control, which requires an equilibration between the two products, with $L_3Ti(OR)$ being more stable. To test this hypothesis, we sought to force a shift in the putative equilibrium. A mixture of $Ti(4)_2(O^iPr)$ and $Ti(4)_3(O^iPr)$ was generated in CH_2Cl_2, then placed in a sealed NMR tube, dried under vacuum, and redissolved in $CDCl_3$. To this was added a large excess of $Ti(O^iPr)_4$, and the time course of the NMR spectra was monitored over a period of 6 days. There was very little sign of decomposition or polymerization over this period. The sample completely converted the $Ti(4)_3(O^iPr)$ component into $Ti(4)_2(O^iPr)_2$ (Figure 1). This is consistent with the two species being in equilibrium (eq 6, a combination of eqs 3−5):

$$3Ti(4)_2(O^iPr)_2 \rightleftharpoons 2Ti(4)_3(O^iPr) + Ti(O^iPr)_4 \qquad (6)$$
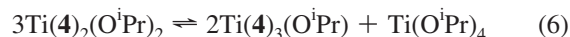
In contrast, a sample treated with excess CS_2 completely converted into $Ti(4)_3(O^iPr)$ in the same time frame, but we do not have a satisfactory explanation for this shift. In another sample treated with excess amine, the proportions of $Ti(4)_3(O^iPr)$ and $Ti(4)_2(O^iPr)_2$ were not much affected, but a new heptet appeared near 4.7 ppm along with a broader multiplet near 4.4 ppm. More work will be needed to identify this new species. Interestingly, these phenomena were only observed in $CDCl_3$. Reactions conducted in THF showed, after transfer to $CDCl_3$, the trisubstituted complex as the exclusive product. Solvent coordination and/or solvent polarity may therefore play a role in these reactions.

Crystal Structures. Diffraction-quality crystals of $Ti(1)_3$-(O^iPr) and $Ti(3)_3(O^tBu)$ were obtained, and Table 1 reports the crystallographic data. As with *tris*(dithiocarbamate) complexes obtained from $TiCl_4$[31] and $(Cp)_2TiCl_2$,[32] these structures (Figures 2 and 3) show a distorted pentagonal pyramidal structure, in these cases with the alkoxy group

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Table 1. Crystallographic Data[a]

	Ti(**1**)$_3$(O^{i}Pr)	Ti(**3**)$_3$(O^{t}Bu)
formula	C$_{18}$H$_{31}$N$_3$OS$_6$Ti	C$_{19}$H$_{33}$N$_3$O$_4$S$_6$Ti·CDCl$_3$
M	545.72	728.12
space group	P2$_1$/c (No. 14)	Pna2$_1$ (No. 33)
a (Å)	11.0462(3)	11.8259(3)
b (Å)	14.5216(5)	23.5185(6)
c (Å)	15.7630(5)	11.6880(3)
β (deg)	98.811(2)	90
V (Å^3)	2498.68(14)	3250.75(14)
Z	4	4
D$_{calc}$ (g cm^{-3})	1.451	1.486
μ(Mo Kα) (mm^{-1})	0.86	0.926
R(F$_o$) [b]	0.0491	0.0383
R$_w$(F$_o^2$) [b]	0.115	0.082

[a] In both cases, T = 150(1) K and λ = 0.71073 Å. Esd's are expressed as uncertainties in the least significant digits in brackets. [b] For reflections where I > 2σ(I). The weights w used in the calculation of R$_w$(F$_o^2$) are given by w = 1/[σ^2(F$_o^2$) + (0.0699P)^2 + 0.7976P] where P = (F$_o^2$ + 2F$_c^2$)/3.
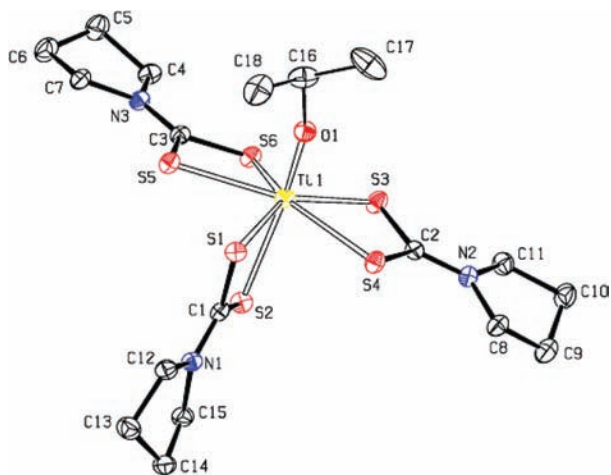
Figure 2. ORTEP plot of the crystal structure of Ti(**1**)$_3$(O^{i}Pr), with the ^{i}Pr group shown in its major orientation. H atoms have been omitted for clarity.
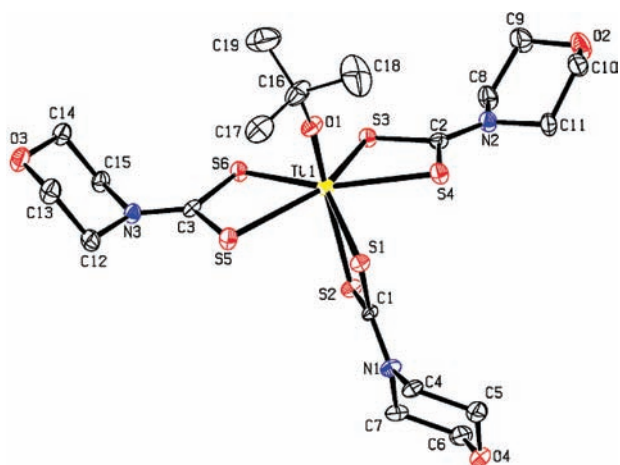
Figure 3. ORTEP plot of the crystal structure of Ti(**3**)$_3$(O^{t}Bu), with the ^{t}Bu group shown in its major orientation. The solvate and H atoms have been omitted for clarity.

located at one of the axial positions while the six sulfur atoms account for the second axial and the five equatorial positions. The ^{i}Pr group in Ti(**1**)$_3$(O^{i}Pr) was disordered between two orientations; the major orientation was associated with a large Ti–O–C angle (164°), but not the minor one (135.5°), while both shared the oxygen at a short Ti–O distance (1.769 Å) indicative of π-bonding. The ^{t}Bu group in Ti(**3**)$_3$(O^{t}Bu) was

Table 2. Selected Bond Lengths (Å) and Angles (deg), with Uncertainties in the Least Significant Digits in Brackets

	Ti(**1**)$_3$(O^{i}Pr)	Ti(**3**)$_3$(O^{t}Bu)
Ti1–O1	1.769(2)	1.742(2)
Ti1–S1	2.5765(9)	2.5780(12)
Ti1–S2	2.5583(10)	2.5556(11)
Ti1–S3	2.5221(10)	2.5242(12)
Ti1–S4	2.5771(10)	2.5460(10)
Ti1–S5	2.5766(10)	2.5566(12)
Ti1–S6	2.5308(9)	2.5313(12)
S1–C1	1.718(3)	1.716(4)
S2–C1	1.711(3)	1.706(4)
S3–C2	1.720(3)	1.714(4)
S4–C2	1.700(3)	1.708(4)
S5–C3	1.707(3)	1.697(4)
S6–C3	1.721(3)	1.714(4)
Ti1–O1–C16	164.0(3)	159.2(4)
Ti1–O1–C16A	135.5(7)	165.2(5)
S1–Ti1–S2	69.27(3)	68.98(3)
S1–Ti1–S4	75.72(3)	74.77(4)
S1–Ti1–S5	75.43(3)	75.14(4)
S2–Ti1–S3	95.02(3)	88.03(4)
S2–Ti1–S4	82.88(3)	84.82(4)
S2–Ti1–S5	85.71(3)	85.36(4)
S2–Ti1–S6	89.33(3)	91.55(4)
S3–Ti1–S4	68.36(3)	68.52(4)
S3–Ti1–S6	71.40(3)	72.05(4)
S5–Ti1–S6	67.93(3)	68.13(3)
S1–C1–S2	116.61(18)	116.3(2)
S3–C2–S4	113.77(18)	113.0(2)
S5–C3–S6	112.71(17)	113.34(19)
S2–Ti1–O1	163.68(8)	167.45(12)

also disordered; both orientations showed large Ti–O–C angles (165° and 167.5°) which, along with an even shorter Ti–O distance (1.742 Å), also indicated π donation. The only other *tris*(dithiocarbamate) Ti(IV) alkoxide complex showed a shorter average Ti–S bond length (2.532 Å vs 2.557 Å in Ti(**1**)$_3$(O^{i}Pr) and 2.549 Å in Ti(**3**)$_3$(O^{t}Bu)) but no sign of π-donation by the primary alkoxide (Ti–O 1.833 Å).

Otherwise, the bond lengths and angles (Tables 2 and 3) and the degrees of distortion were very similar to those measured in the previous dithiocarbamate complexes. Because of these similarities, it appears that the nature of the dithiocarbamate ligand does not much affect the structure of the complex.

Electrochemistry. To our knowledge, no electrochemical studies of Ti^{IV} dithiocarbamate complexes have yet been conducted. The new L$_3$Ti(O^{i}Pr) complexes were therefore examined by standard cyclic voltammetry (CV) in CH$_2$Cl$_2$. For comparisons, we prepared the corresponding ammonium dithiocarbamate salts and examined them under the same conditions. Figure 4 presents typical traces, all involving ligand **1**.

Scanning the complex in the positive direction and then in the negative direction (panel a) showed an oxidation (process I) which gave rise to a re-reduction (process II) that was absent when scanning only in the negative direction (panel b), while the second anodic scan (gray trace in panel a) revealed two new, lower-potential oxidations (processes III and IV). Both this and the negative-only scan (panel b) showed a reduction (process V) that probably does not involve the ligand and which we attribute to the Ti$^{IV/III}$ couple. The free ligands underwent oxidations which differed
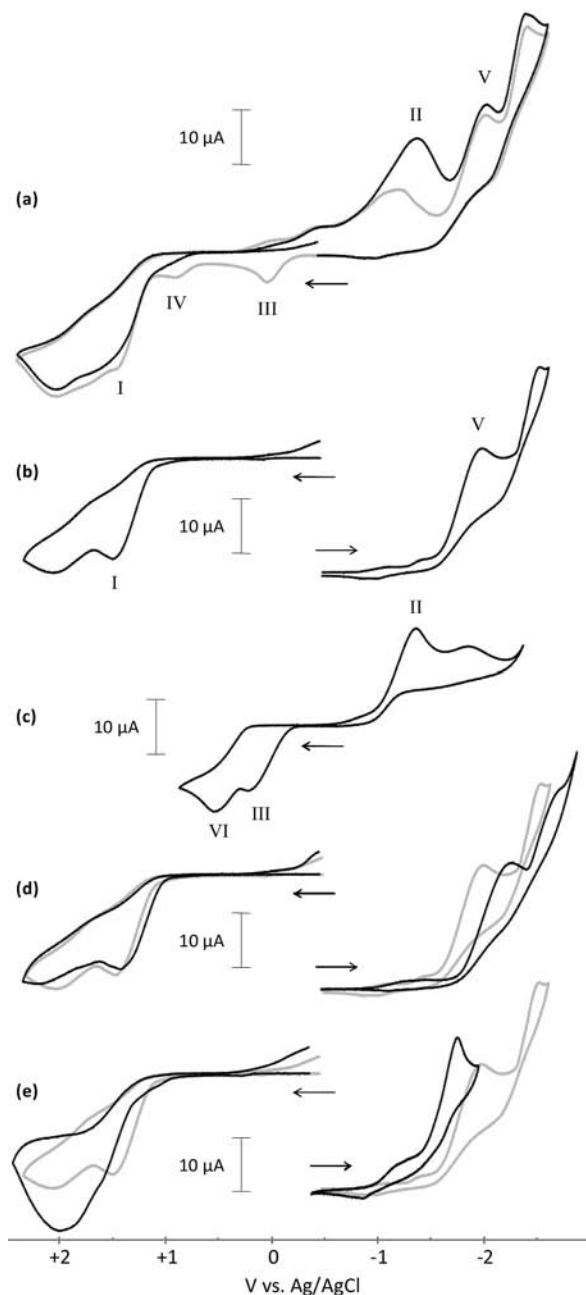
Figure 4. Cyclic voltammograms at 200 mV s^{-1} of 0.03 M solutions in CH$_2$Cl$_2$ containing 0.1 M ^{n}Bu$_4$NPF$_6$: (a) full scan of Ti(**1**)$_3$(O^{i}Pr) (second scan in gray), (b) positive-only and negative-only scans of Ti(**1**)$_3$(O^{i}Pr), (c) free ligand, (d) Ti(**1**)$_3$(O^{t}Bu) and (e) Ti(**1**)$_2$(O^{i}Pr)$_2$. In panels d and e, the corresponding plot with Ti(**1**)$_3$(O^{i}Pr) (panel b) is superposed in gray. Arrows indicate the scan directions.

on the first and subsequent scans. For instance, the pyrrolidinium salt of **1**$^-$ (panel c) showed an oxidation peak at +0.67 V (all potentials vs Ag/AgCl) on the first scan but also a second oxidation peak at +0.32 V on subsequent scans. We attribute the higher-potential process (process VI) to an oxidation of the hydrogen-bonded pyrrolidinium salt which would be absent in panel a and which, after producing the neutral, S—S linked thiuram disulfide, would no longer be associated with a cation until re-reduction occurred on the cathodic scan (process II), whence a more loosely associated ^{n}Bu$_4$N$^+$ salt could then undergo the lower-potential oxidation (process III) on the subsequent anodic scans.

Similar low-potential oxidations have been measured at Pt for Li$^+$ salts of dithiocarbamates in DMSO (scan-rate-dependent values between +0.14 and +0.38 V),[33] where strong solvation of the cation leaves a more naked and more easily oxidized anion. We therefore surmise that oxidation of the complex (process I) formed the thiuram disulfide which, although known to bind in bidentate fashion to otherwise neutral Ti^{IV},[34] dissociated and was reduced back to free dithiocarbamate anion (process II) then reoxidized at a lower potential (process III). On the basis of these low-potential oxidations, the binding to Ti^{IV} apparently retarded the ligand oxidations by about 1.0−1.2 V. Such retardation by coordination to a metal has been earlier noted in organic solvent.[35] Finally, we attribute the second new oxidation (process IV), observed on the second anodic scan in panel a, to an oxidation of pyrrolidine liberated upon reduction of the thiuram disulfide and subsequent fragmentation.

Overall, the L$_3$Ti(O^{i}Pr) complexes underwent a variable and irreversible reduction (peak cathodic currents at −1.87 to −2.17 V) and, in some cases, a second, irreversible reduction near the solvent limit, as well as an irreversible oxidation (peak anodic currents at +1.19 to +1.58 V) that resulted in decomposition. The potentials are reported in the Experimental Section. Similarly irreversible but higher-potential oxidations have been measured with Zn^{II} and Cd^{II} *bis*(dithiocarbamates) in CH$_2$Cl$_2$ solution,[36] also generating thiuram disulfide complexes, but Co^{III}, Rh^{III} and Ir^{III} *tris*-(dithiocarbamate) analogues oxidized at lower potentials in the same solvent ($E_{1/2}$ +0.68 to +1.12 V).[37] It is noteworthy that the complexes of the dithiocarbamates formed from the two most basic amines (**1**, **2**) were counter-intuitively oxidized at higher potentials than those formed from the less basic amines (**3**−**5**). This might be attributed to stronger binding by **1** and **2**, yet the average Ti−S bond lengths in the complexes of **1** and **3** were not statistically significantly different. In particular, those complexes formed from the diamines (with **4** and **5**) were the easiest to oxidize; this may be a consequence of a preferential oxidation at the second nitrogen atom.

With a more electron-rich alkoxy group, Ti(**1**)$_3$(O^{t}Bu) (Figure 4, panel d) underwent a slightly less positive oxidation but a significantly more negative reduction than did the O^{i}Pr analogue. The electronic effect is as expected for the Ti$^{IV/III}$ couple but is poorly transmitted to the dithiocarbamate ligand, in confirmation of this same finding by NMR. The putative *bis*(dithiocarbamate) species Ti(**1**)$_2$(O^{i}Pr)$_2$ oxidized at an even more positive potential, starting with a shoulder near +1.66 V (panel e).

Conclusions

Ten alkoxy-*tris*(dithiocarbamato)titanium(IV) complexes were prepared, isolated, and characterized. The crystal

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structures of two of these were obtained, revealing strongly π-coordinated alkoxy groups. While we have strong NMR evidence that the target diisopropoxy-*bis*(dithiocarbamato) analogues can be prepared, these were not isolable in pure state and were instead prone to transform to the *tris* species. Indeed, equilibria were apparent between the *bis*- and *tris*-substituted complexes. Cyclic voltammetry in homogeneous aprotic solvent revealed irreversible oxidation waves at potentials shifted positive of those from the free dithiocarbamate salts, coupled to loss of the ligand.

Undoubtedly, higher-dielectric and protic media such as would be used in fuel cells would facilitate these oxidations and help stabilize the coordinated disulfide products. For some of our *tris*(dithiocarbamate) complexes, oxidation would perhaps occur at sufficiently low potentials under those conditions as to be driven by O_2 reduction at a cathode.

Although the desired *bis*(dithiocarbamate) complexes proved to be unviable and their oxidation potentials are perhaps too high, these experiments have demonstrated the potential utility of sulfur-bearing Ti^{IV} complexes in storing electrochemical oxidation equivalents. Work with other catalyst designs is underway.

Supporting Information Available: Crystallographic Information Format (CIF) file, NMR signal assignments and coupling constants. This material is available free of charge via the Internet at http://pubs.acs.org.

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