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Titanium(IV) Complexes of Disulfide-Linked Schiff Bases

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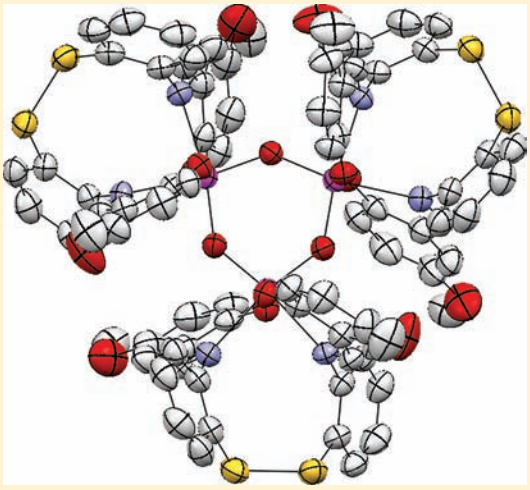
Supporting Information

ABSTRACT: With the goal of preparing Ti(IV) complexes bearing a sulfur-based redox function of possible use in electrocatalytic oxidations of alcohols at electrode surfaces, a series of seven 2,2′-dithiodianiline Schiff-base derivatives, including two new variations, were tested in reactions with $Ti(OR)_4$ (R = ^{i}Pr, ^{t}Bu). Instead of the expected dimetallic products of general formula $[LTi(OR)_2]_2$, mononuclear species $LTi(OR)_2$ were obtained, confirmed by crystallographic determinations to have an unprecedented, symmetrical, and macrocyclic arrangement with four-point binding to the metal center and with the disulfide moieties remaining uncoordinated. Cyclic voltammetry performed in CH_2Cl_2 displayed oxidations at potentials useful for fuel cells (+1.1−1.5 V vs Ag/AgCl), but despite the uncoordinated disulfide moieties, the complexes were reticent to engage in reduction processes.



INTRODUCTION

In pursuit of an efficient electrocatalyst of alcohol oxidation for possible use in direct methanol fuel cells, we chose to base our design on a dialkoxytitanium(IV) center carrying a redox-active multidentate ligand. One alkoxide site would be used for anchoring to an electrode surface, and the other would enable rapid fuel loading and product unloading through alcohol−alkoxide exchanges, while the redox-active ligand would store up oxidation equivalents. We chose to examine a few families of sulfur-containing ligands for redox activity, specifically for oxidations that could be driven by O_2 reduction at the cathode of a fuel cell.

We first explored the coordination chemistry at Ti(IV) of dithiocarbamates,[1] which are known to reversibly oxidize to thiurams. However, the dithiocarbamates prefentially formed $L_3Ti(OR)$ complexes and the onsets of their oxidations were too far positive to be driven by O_2 reduction (i.e., above +1.24 V vs SHE) and up to 1.2 V more positive than the free dithiocarbamates themselves. The more π-delocalized Schiff bases derived from 2-aminothiophenol and various salicylaldehydes are dibasic tridentates that would oxidize to quinonoid forms. They more usefully formed the desired $L_2Ti(OR)_2$ species or dimeric forms thereof. Relative to the free ligands, the complexes' oxidations were less positively shifted (by 0.5 V or less) and were even easier in the presence of an alcohol.[2]

To further reduce the impact of the metal on the onset of oxidation, we chose to segregate the redox function from the metal-coordination function. This paper reports our exploration of the coordination at Ti(IV) of salicylaldehyde-derived Schiff bases of 2,2′-dithiodianiline (DTDA), with a view toward their possible utility as two-electron stores in electrocatalytic oxidation. Disulfide-containing molecules such as DTDA have been widely investigated because of their easy participation in reversible redox processes[3] and because of the important role played by the RS-SR/RSH equilibrium in biological systems.[4] DTDA has been considered for energy-storage devices,[5] with its oxidation occurring at a readily accessible +0.27 V vs Ag/AgCl, but the large separation between oxidation and reduction events indicated that the kinetics involved are relatively slow and, hence, not suitable for practical storage applications. DTDA-derived Schiff bases have also been used in coordination chemistry, in particular as synthons of the anil forms of the 2-aminothiophenol Schiff bases in complexes of Cu(II),[6] Ni(II),[7] Zn(II),[8] Cd(II),[9] Sn(II),[10] V(III),[11] and Fe(III).[12] In direct reactions, salicylaldehyde derivatives of DTDA could potentially behave as doubly monobasic bis(O,N,S-tridentates) or bis(O,N-bidentates) and could therefore potentially accommodate two metal centers. Only one example of this coordination mode has been proposed for a di-Ru(II) species, but it was not well characterized.[13] In most cases, they behave as pentadentates, with a metal−sulfur bond always present.[11−14] Prior to this work, the reactivity of salicylaldehyde-DTDA Schiff bases toward Ti(IV) was completely unknown. With the possibility of isolating dimetallic products, we investigated the reactions of seven examples (Chart 1) with two $Ti(OR)_4$ species (R = ^{i}Pr, ^{t}Bu) and report the electrochemical behavior of the products in aprotic media.

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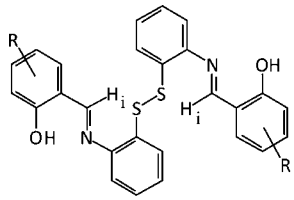
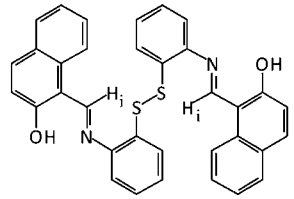
Chart 1



H_2**1** R = H
H_2**2** R = 3-OMe
H_2**3** R = 4-OMe
H_2**4** R = 5-OMe
H_2**5** R = 5-NO_2
H_2**6** R = 4-NEt_2



H_2**7**

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under Ar. 2,2′-Dithiodianiline (DTDA) was prepared by the literature procedure.[15] All other reagents were Sigma-Aldrich products. Titanium tetraisopropoxide, $Ti(O^iPr)_4$, was distilled under Ar prior to use. Titanium tetra-*tert*-butoxide, $Ti(O^tBu)_4$, was purchased in Aldrich Sure-Seal bottles and used directly. Solvents were from Caledon Laboratories (Georgetown, ON, Canada). Prior to use, $CHCl_3$ was dried and kept over $MgSO_4$ and CH_2Cl_2 was distilled over P_2O_5. HO^iPr was kept over molecular sieves. NMR spectra were acquired in $CDCl_3$ or DMSO-d_6 (Cambridge Isotope Laboratories) at 23 °C on a Bruker ARZ 300 MHz instrument. Signal assignments were made with the help of COSY, HMQC, and HMBC spectra. Relative integrations were obtained after careful baseline and phase corrections on spectra acquired with a relaxation delay of 5 s. Elemental analyses were performed with weighing under N_2 by Guelph Chemical Laboratories (Guelph, ON, Canada).

Ligand Synthesis. All ligands were prepared according to the general literature procedure[14f] by reaction of DTDA with 2 equiv of the corresponding salicylaldehyde in absolute EtOH. The reaction mixture was heated to reflux for 3 h under a blanket of Ar. The yellow solid precipitates were filtered, washed with cold absolute EtOH, and dried under reduced pressure. The products were recovered in 82–98% yields and used without further purification.

*H_2**1**.*[14f] ^{1}H NMR (DMSO-d_6): δ 12.57 (s, 1H), 9.03 (s, 1H), 7.73 (d, 1H), 7.58 (d, 1H), 7.50 (m, 2H), 7.37 (t, 1H), 7.30 (t, 1H), 7.04 (m, 2H) ppm. ^{13}C NMR (DMSO-d_6): δ 163.4, 160.0, 145.8, 133.8, 132.6, 130.2, 128.0, 127.8, 126.0, 119.3 (2C), 118.3, 116.6 ppm.

*H_2**2**.*[11] ^{1}H NMR (DMSO-d_6): δ 12.66 (s, 1H), 9.03 (s, 1H), 7.57 (d, 1H), 7.52 (d, 1H), 7.36 (t, 1H), 7.29 (m, 2H), 7.19 (d, 1H), 6.96 (t, 1H), 3.84 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6): δ 163.6, 150.1, 147.8, 145.7, 130.2, 128.0, 127.8, 126.0, 123.8, 119.2, 118.8, 118.3, 115.9, 55.8 ppm.

*H_2**3**.* ^{1}H NMR (DMSO-d_6): δ 13.07 (s, 1H), 8.93 (s, 1H), 7.60 (d, 1H), 7.54 (d, 1H), 7.48 (d, 1H), 7.34 (t, 1H), 7.26 (t, 1H), 6.61 (d, 1H), 6.55 (s, 1H), 3.83 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6): δ 164.0, 162.8, 162.5, 145.8, 134.3, 129.9, 127.9, 127.3, 125.8, 118.1, 113.0, 107.1, 100.7, 55.5 ppm. Mp: 197–199 °C. Anal. Calcd for $C_{28}H_{24}N_2O_4S_2$: C, 65.09; H, 4.68; N, 5.42. Found: C, 63.87; H, 4.92; N, 5.41.

*H_2**4**.*[14a] ^{1}H NMR (DMSO-d_6): δ 11.99 (s, 1H), 8.99 (s, 1H), 7.58 (d, 1H), 7.48 (d, 1H), 7.36 (t, 1H), 7.30 (m, 2H), 7.10 (d, 1H), 6.96 (d, 1H), 3.76 (s, 3H) ppm. ^{13}C NMR (DMSO-d_6): δ 162.9, 154.2, 151.9, 146.0, 130.3, 128.0, 127.8, 125.9, 121.1, 119.2, 118.2, 117.5, 115.0, 55.4 ppm.

*H_2**5**.*[16] ^{1}H NMR (DMSO-d_6): δ 13.57 (s, 1H), 9.14 (s, 1H), 8.72 (s, 1H), 8.31 (d, 1H), 7.65 (d, 1H), 7.50 (d, 1H), 7.36 (m, 2H), 7.19 (d, 1H) ppm. NMR (DMSO-d_6): δ 165.2, 161.2, 145.7, 139.6, 130.5, 128.6, 128.5, 128.3, 127.7, 127.2, 119.2, 118.6, 117.8 ppm.

*H_2**6**.* ^{1}H NMR (DMSO-d_6): δ 13.03 (s, 1H), 8.76 (s, 1H), 7.48 (d, 1H), 7.40 (m, 2H), 7.29 (t, 1H), 7.18 (t, 1H), 6.36 (d, 1H), 6.13 (s, 1H), 3.41 (q, 4H), 1.13 (t, 6H) ppm. ^{13}C NMR (DMSO-d_6): δ 162.6, 161.6, 151.8, 146.2, 134.5, 129.4, 127.6, 126.2, 125.2, 117.4, 108.4, 104.0, 96.6, 43.9, 12.4 ppm. Mp: 181–183 °C. Anal. Calcd for $C_{34}H_{38}N_4O_2S_2$: C, 68.19; H, 6.40; N, 9.36. Found: C, 66.73; H, 6.81; N, 9.25.

*H_2**7**.*[16] ^{1}H NMR (DMSO-d_6): δ 15.04 (s, 1H), 9.75 (s, 1H), 8.69 (d, 1H), 8.01 (d, 1H), 7.86 (d, 1H), 7.80 (d, 1H), 7.61 (m, 2H), 7.40 (m, 2H), 7.27 (t, 1H), 7.15 (d, 1H) ppm. ^{13}C NMR (DMSO-d_6): δ 164.8, 158.7, 145.1, 136.1, 132.6, 129.4, 128.9, 128.6, 128.0, 127.6, 127.4, 127.2, 123.7, 120.8, 119.9, 119.0, 109.4 ppm.

Sample Complexation Procedure: Preparation of (1)Ti-(O^iPr)$_2$. With Ar protection, ligand H_2**1** (0.107 g, 0.23 mmol) was suspended in 1 mL of anhydrous $CHCl_3$, the suspension was stirred for 1 min, and subsequently, $Ti(O^iPr)_4$ (0.07 mL, 0.23 mmol) was added. The resultant dark red solution was stirred in a vortex mixer for a few seconds and then in a sonicator for approximately 10 min at room temperature. The solvent and reaction byproduct were removed under reduced pressure, and the product was recovered as a red solid in quantitative yield (0.142 g, 100%). All other complexes were prepared on the same scale in quantitative yields. ^{1}H NMR ($CDCl_3$): δ 7.94 (s, 1H), 7.71 (d, 1H), 7.43 (d, 1H), 7.29 (t, 1H), 7.17 (t, 1H), 7.05 (d, 1H), 6.84 (t, 1H), 6.64 (m, 2H), 4.86 (h, 1H), 1.21 (d, 6H) ppm. ^{13}C NMR ($CDCl_3$): δ 168.6, 164.1, 153.4, 136.7, 134.8, 134.2, 129.1 (2C), 128.0, 125.3, 120.7, 119.1, 116.9, 78.5, 25.3 ppm. Anal. Calcd for $C_{32}H_{32}N_2O_4S_2Ti$: C, 61.93; H, 5.20; N, 4.51. Found: C, 61.65; H, 5.34; N, 4.16.

*(**1**)Ti(O^tBu)$_2$.* ^{1}H NMR ($CDCl_3$): δ 7.90 (s, 1H), 7.83 (d, 1H), 7.46 (d, 1H), 7.28 (bt, 1H), 7.20 (bt, 1H), 7.04 (d, 1H), 6.87 (bt, 1H), 6.60 (m, 2H), 1.29 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 168.4, 165.0, 153.8, 136.6, 134.5, 134.1, 129.1, 128.7, 128.4, 125.1, 120.9, 118.8, 116.2, 83.9, 31.5 ppm. Anal. Calcd for $C_{34}H_{36}N_2O_4S_2Ti$: C, 62.96; H, 5.59; N, 4.32. Found: C, 63.14; H, 5.33; N, 3.98.

*(**2**)Ti(O^iPr)$_2$.* ^{1}H NMR ($CDCl_3$): δ 7.90 (s, 1H), 7.76 (d, 1H), 7.40 (d, 1H), 7.08 (bt, 1H), 6.90 (d, 1H), 6.81 (t, 1H), 6.69 (d, 1H), 6.54 (t, 1H), 4.94 (h, 1H), 3.94 (s, 3H), 1.20 (d, 6H) ppm. ^{13}C NMR ($CDCl_3$): δ 168.5, 156.4, 153.4, 149.0, 136.4, 129.0 (2C), 127.8, 126.7, 125.3, 121.3, 119.3, 119.3, 78.7, 57.5, 25.3 ppm. Anal. Calcd for $C_{34}H_{36}N_2O_6S_2Ti$: C, 60.00; H, 5.33; N, 4.12. Found: C, 59.60; H, 5.10; N, 4.14.

*(**2**)Ti(O^tBu)$_2$.* ^{1}H NMR ($CDCl_3$): δ 7.90 (m, 2H), 7.45 (d, 1H), 7.14 (t, 1H), 6.96 (d, 1H), 6.85 (t, 1H), 6.74 (d, 1H), 6.53 (t, 1H), 4.07 (s, 3H), 1.31 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 168.4, 157.1, 153.7, 148.8, 136.5, 129.0, 128.8, 128.2, 127.3, 125.2, 121.8, 121.0, 115.8, 84.0, 58.4, 31.6 ppm. Anal. Calcd for $C_{36}H_{40}N_2O_6S_2Ti$: C, 61.01; H, 5.69; N, 3.95. Found: C, 60.77; H, 5.42; N, 4.23.

*(**3**)Ti(O^tBu)$_2$.* ^{1}H NMR ($CDCl_3$): δ 7.77 (d, 1H), 7.74 (s, 1H), 7.44 (d, 1H), 7.19 (t, 1H), 6.89 (m, 2H), 6.19 (d, 1H), 6.02 (s, 1H), 3.82 (s, 3H), 1.29 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 166.9, 165.3, 154.2, 136.7, 135.2, 129.2, 128.6 (2C), 124.8, 115.4, 105.3, 101.3, 83.8, 55.2, 31.6 ppm; Anal. Calcd for $C_{36}H_{40}N_2O_6S_2Ti$: 61.01; H, 5.69; N, 3.95. Found: C, 60.77; H, 5.50; N, 4.02.

*(**4**)Ti(O^iPr)$_2$.* ^{1}H NMR ($CDCl_3$): δ 7.89 (s, 1H), 7.70 (d, 1H), 7.41 (d, 1H), 7.16 (t, 1H), 6.92 (d, 1H), 6.83 (t, 1H), 6.59 (d, 1H), 6.51 (s, 1H), 4.83 (h, 1H), 3.69 (s, 3H), 1.19 (d, 6H) ppm. ^{13}C NMR ($CDCl_3$): δ 168.2, 159.1, 153.4, 150.5, 136.7, 129.1, 129.0, 128.0, 125.3, 123.3, 119.9 (2C), 115.5, 78.1, 55.7, 25.3 ppm. Anal. Calcd for $C_{34}H_{36}N_2O_6S_2Ti$: 60.00; H, 5.33; N, 4.12. Found: C, 60.24; H, 5.15; N, 4.35.

*(**4**)Ti(O^tBu)$_2$.* ^{1}H NMR ($CDCl_3$): δ 7.83 (s, 1H), 7.78 (d, 1H), 7.44 (d, 1H), 7.17 (t, 1H), 6.88 (m, 2H), 6.50 (m, 2H), 3.71 (s, 3H), 1.32 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 168.0, 160.3, 153.9, 150.0, 136.6, 129.0, 128.7, 128.5, 125.1, 123.2, 119.7 (2C), 115.4, 83.6, 55.8, 32.2 ppm. Anal. Calcd for $C_{36}H_{40}N_2O_6S_2Ti$: 61.01; H, 5.69; N, 3.95. Found: C, 60.84; H, 5.42; N, 3.70.

*(**5**)Ti(O^iPr)$_2$.* ^{1}H NMR ($CDCl_3$): δ 8.16 (d, 1H), 8.10 (s, 1H), 8.02 (s, 1H), 7.59 (d, 1H), 7.48 (d, 1H), 7.23 (t, 1H), 6.92 (t, 1H), 6.67 (d, 1H), 4.86 (h, 1H), 1.20 (2d, 6H) ppm. ^{13}C NMR ($CDCl_3$): δ 168.8, 168.0, 152.3, 138.0, 137.2, 131.2, 129.9, 129.3, 129.0, 127.2, 126.3, 119.8, 119.3, 81.0, 25.3, 25.2 ppm. Anal. Calcd for $C_{32}H_{30}N_4O_8S_2Ti$: 54.09; H, 4.26; N, 7.88. Found: C, 54.24; H, 3.96; N, 8.07.

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(5)Ti(O^{t}Bu)$_2$. ^{1}H NMR ($CDCl_3$): δ 8.16 (d, 1H), 8.09 (s, 1H), 7.98 (s, 1H), 7.68 (d, 1H), 7.49 (d, 1H), 7.23 (t, 1H), 6.92 (t, 1H), 6.63 (d, 1H), 1.29 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 169.2, 167.8, 152.4, 137.7, 137.3, 131.2, 129.9, 129.1, 129.0, 127.5, 126.2, 119.7, 119.4, 86.4, 31.3 ppm. Anal. Calcd for $C_{34}H_{34}N_4O_8S_2Ti$: 55.28; H, 4.64; N, 7.58. Found: C, 54.96; H, 4.48; N, 7.24.

(6)Ti(O^{i}Pr)$_2$. ^{1}H NMR ($CDCl_3$): δ 7.63 (d, 1H), 7.52 (s, 1H), 7.30 (d, 1H), 7.01 (t, 1H), 6.67 (m, 2H), 5.88 (d, 1H), 5.75 (s, 1H), 4.77 (h, 1H), 3.26 (2q, 4H), 1.09 (m, 12H) ppm. ^{13}C NMR ($CDCl_3$): δ 165.6, 165.0, 154.6, 153.1, 136.7, 135.6, 129.2, 128.8, 128.6, 124.1, 111.6, 102.8, 99.0, 76.9, 44.3, 25.5, 25.2, 12.7 ppm. Anal. Calcd for $C_{40}H_{50}N_4O_4S_2Ti$: 62.98; H, 6.61; N, 7.34. Found: C, 62.80; H, 6.86; N, 7.31.

X-ray Crystallography. Red crystals of (**6**)Ti(O^{i}Pr)$_2$ were grown overnight after layering petroleum ether over a $CDCl_3$ solution. Yellow plates of [(**4**)TiO]$_3$ were similarly grown over several months from a solution of (**4**)Ti(O^{t}Bu)$_2$. Crystal structure data collection, structural analysis, and refinement were carried out by Dr. Alan Lough at the University of Toronto. 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 C(CH$_3$)$_2$ groups of (**6**)Ti(O^{i}Pr)$_2$ were disordered (52%:48%) over two sets of correlated positions, both refined anisotropically. During the refinement of [(**4**)TiO]$_3$, electron density peaks corresponding to approximately 47 electrons were located within the 318 Å^3 of void volume within the unit cell (PLATON), believed to be due to highly disordered solvent molecules (possibly chloroform) on a $\bar{3}$ axis. Attempts to model these were not successful. Following the literature treatments of disordered solvent molecules,[17] this contribution to the electron density was removed from the observed data in the final cycles of refinement. The reported density, F(000) value, molecular weight, and formula are given without taking into account the results using the SQUEEZE option of PLATON.[18]

Electrochemistry. All 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 0.05 M in freshly distilled CH_2Cl_2 (10 mL) containing 0.1 M nBu_4NPF_6 as supporting electrolyte. All scans were performed at a 100 mV s^{-1} sweep rate. They were limited to either oxidation or reduction regimes or covered both in succession and were then initiated in both anodic and cathodic directions. Selected examples (2,2′-dithioaniline, H$_2$**1**, H$_2$**2**, and H$_2$**4**) were also tested in protic solvent (20% water in CH_3CN), keeping all concentrations unchanged. The potentials were internally calibrated with ferrocene and are reported with respect to Ag/AgCl (saturated KCl).

RESULTS AND DISCUSSION

Ligand Synthesis. The new examples of DTDA-derived Schiff bases, H$_2$**3** and H$_2$**6**, were prepared in high yields by condensations of DTDA with 2 equiv of the appropriate, commercially available salicylaldehydes, and their ^{1}H and ^{13}C NMR spectra were consistent with their formulations. Combustion analyses showed lower than expected carbon contents, but these ligands nevertheless produced complexes that analyzed as pure (vide infra). All of the other ligands were previously reported but had been characterized mainly by IR spectroscopy, elemental analysis,[11,14f,16] and X-ray crystallography.[11,14e,19] For comparisons with their complexes, ^{1}H and ^{13}C NMR spectra were acquired and fully assigned for the known ligands as well (Supporting Information). With the exception of H$_2$**1**[13] and H$_2$**4**,[14a] detailed NMR spectroscopy was missing due to a reported lack of solubility in deuterated solvents. Indeed, we found them to be scarcely soluble in $CDCl_3$ but soluble at room temperature in DMSO-d_6 after warming the samples. Ligand H$_2$**5** was soluble only in hot DMSO-d_6, presumably because of strong intermolecular H bonding or zwitterion formation. In all cases, the ^{1}H NMR spectra confirmed the ligands' 2-fold symmetry, with diagnostic singlets for the aldimino hydrogens (labeled H$_i$ in Chart 1) in the 8.7−9.8 ppm range, at positions consistent with the expected electronic effects of their substituents.

Complex Synthesis. Direct reactions of 1:1 ratios of the ligands with Ti(O^{i}Pr)$_4$ in anhydrous $CHCl_3$ gave instantaneous color changes, turning the thick, yellow suspensions of the ligands into clear, dark orange-red solutions. All cases except that of H$_2$**7** led to complexes of apparent formulas LTi(O^{i}Pr)$_2$ as the only NMR-detectable products. With ligands L^{2-} acting as bis(bidentates), either surrounding a single metal or bridging pairs of metals, the S−S moieties were evidently not participating in the coordination. The analogous reactions with Ti(O^{t}Bu)$_4$ were generally slower, requiring longer reaction times, but led to the same results, except that neither H$_2$**6** nor H$_2$**7** gave a clear result. Even with H$_2$**4**, the reaction was not clean, and the desired product was accompanied by one or more side products. Nevertheless, NMR assignments for (**4**)Ti(O^{t}Bu)$_2$ were possible by comparisons with the spectra from (**4**)Ti(O^{i}Pr)$_2$ and through 2D experiments. In any case, elemental analysis supported the LTi(OR)$_2$ formulation, as was the case with the other ligands. The combination of H$_2$**3** with Ti(O^{i}Pr)$_4$ produced an impure product, though the main NMR signals could readily be assigned to (**3**)Ti(O^{i}Pr)$_4$ by analogy with the O^{t}Bu analogue (see the Supporting Information). Mass spectral analysis of the complexes (EI, MALDI) has proven fruitless, showing no molecular ions and too much fragmentation.

When a 1:2 ratio of ligand to Ti was instead used, 1 equiv of unreacted Ti(OR)$_4$ always remained, indicating the impossibility of isolating a dimetallic complex and confirming the preference for 1:1 stoichiometries. The formation of the complexes produced a general change in the NMR signal patterns in the aromatic region. The ligand symmetry was preserved, as the number of ligand signals remained the same. There was a consistent upfield shift of the H$_i$ signal (by 1.1−1.2 ppm from free ligand positions in DMSO-d_6) to fall in the 7.5−8.0 ppm range (Figure 1) in all cases. This differs from what we had found for complexes of 2-aminothiophenol-derived Schiff bases,[2] where the thiazoline forms of the starting ligands underwent ring opening to engage in tridentate coordination and the corresponding H$_i$ signals understandably shifted upon

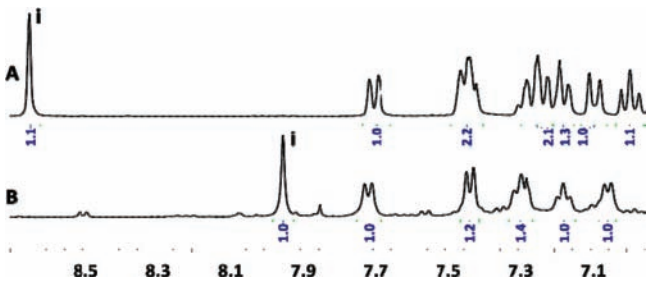

Figure 1. Aromatic regions of the ^{1}H NMR spectra in $CDCl_3$ of (A) ligand H$_2$**1** and (B) (**1**)Ti(O^{i}Pr)$_2$.

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complexation, but to positions further downfield into the 8.6–8.8 ppm range. The H_i magnetic environment here is consistent with bidentate ligation and the nonparticipation of the S atoms in coordination in the present series, since the aminothiophenol moiety needs to be more or less coplanar with the salicylidene portion to enable S coordination in the previous series, but must become noncoplanar for bidentate coordination in the present cases.

Pairs of ^{i}Pr $^{13}CH_3$ signals were detected for three of the $LTi(O^{i}Pr)_2$ complexes, indicating diastereotopicity and a chiral metal center given by a cis disposition of two salicylidene units in, moreover, a C_2-symmetric fashion that preserves the ligands' internal symmetry. Given the C_2 symmetry and the spectral similarities between these three cases and the others, with no reason to anticipate different behaviors, this arrangement is very probably common to all five examples observed. Furthermore, the close spectral similarities displayed by the 5 $LTi(O^{t}Bu)_2$ complexes and their $O^{i}Pr$ analogues suggests that all 10 complexes have identical ligand arrangements. NMR cannot a priori distinguish between 1:1 and higher-order, closed *n*:*n* assemblies that two independent bidentate sites make possible. However, entropic considerations favor a 1:1 assembly. This requires the ligands to loop back onto the same metal, and the preferred conformation about the S–S bond in disulfides, with an approximate 90° dihedral angle,[20] makes this possible, as confirmed by X-ray diffraction (vide infra). Although the earlier literature reports two analogous but dinuclear complexes with Cu(II)[14a] and Mn(II),[14d] these were merely dimeric, looped-back 1:1 complexes, linked through phenoxy bridges.

We used several differently substituted salicylaldehydes to gauge substituent effects. The substituents will influence not only the ligand oxidizability, as revealed by electrochemistry (see below), but also the ease with which ligated alkoxides will become oxidized. The effects of the salicylaldehyde substituents on the acidities of Ti–O–C–H groups can be gauged by the TiOC^{1}H positions in the $O^{i}Pr$ complexes and the TiO^{13}C chemical shifts in the $O^{i}Pr$ and $O^{t}Bu$ complexes, relative to their positions in the unsubstituted complexes of $\mathbf{1}^{2-}$. The signals for all three kinds of signals spanned limited ranges, but they were nevertheless consistent with the anticipated inductive and resonance effects. Not surprisingly, the 4-NEt_2 group in $\mathbf{6}^{2-}$ exerted the strongest upfield shifts, and the 5-NO_2 group in $\mathbf{5}^{2-}$ exerted strong downfield shifts, but the 3-OMe group in $\mathbf{2}^{2-}$ was more interesting in that this π-donating group also caused the strongest deshielding on the TiOC^{1}H signal and also deshielded the TiO^{13}C signals, an effect that probably has a steric origin.

In those cases where no clean $LTi(OR)_2$ product was obtained (L = $\mathbf{6}^{2-}$ with R = ^{t}Bu and L = $\mathbf{7}^{2-}$ with R = ^{i}Pr, ^{t}Bu), NMR showed only broad signals that did not resolve over time, yet we see no evident source of product destabilization within these ligands. In reactions with monobasic bidentates, such as Hacac, the second substitution step is usually faster than the first, owing to a relief of the steric congestion about Ti(IV), and such ligands tend to quickly form hexacoordinate $L_2Ti(OR)_2$ complexes even at 1:1 metal–ligand ratios. In the present heterogeneous reactions between insoluble free ligands and soluble $Ti(OR)_4$, however, where the metal was present in relative excess over dissolved ligand throughout, the process may have been biased toward multinuclear intermediates that would need to, then, in a second phase, disproportionate to 1:1 products through exchange reactions involving liberated alcohol. The three unclear cases encountered here may have produced slowly evolving mixtures of multinuclear or even polymeric products, where the requisite exchanges were particularly slow, mixtures of coordination isomers, products involving S coordination, or a combination of these.

X-ray Crystallography. Diffraction-quality crystals were obtained with $(\mathbf{6})Ti(O^{i}Pr)_2$ (Figure 2) and $[(\mathbf{4})TiO]_3$ (Figure 3). Tables 1 and 2 report the crystallographic data and selected bond metrics. The latter crystal was obtained from a solution of $(\mathbf{4})Ti(O^{t}Bu)_2$ and evidently arose by preferential crystallization after adventitious hydrolysis, occurring over the months of crystal growth, and trimerization of a complex analogous to $(\mathbf{6})Ti(O^{i}Pr)_2$. Unfortunately, we were unsuccessful in deliberately preparing $[(\mathbf{4})TiO]_3$. The unit cell of $(\mathbf{6})Ti(O^{i}Pr)_2$ was composed of a pair of molecules of one enantiomeric form next to a pair of the opposite enantiomers. One of the diethylamino groups is coplanar with the attached benzene rings, with both ethyl groups falling to the same side. The other is twisted out of coplanarity, with an ethyl group falling on each side of the nitrogen plane. The difference is no doubt packing-induced, but as a result, the ligand halves and the two $O^{i}Pr$ groups are not quite crystallographically equivalent. Nevertheless, this structure completely supported the NMR analysis. Both alkoxy groups of $(\mathbf{6})Ti(O^{i}Pr)_2$ were found to occupy two disordered positions to nearly equal extents. The Ti–O bond lengths were virtually the same and were in line with those found in similar Schiff base and dithiocarbamate complexes of Ti(IV) alkoxides,[1,2] and as expected, they were shorter than the

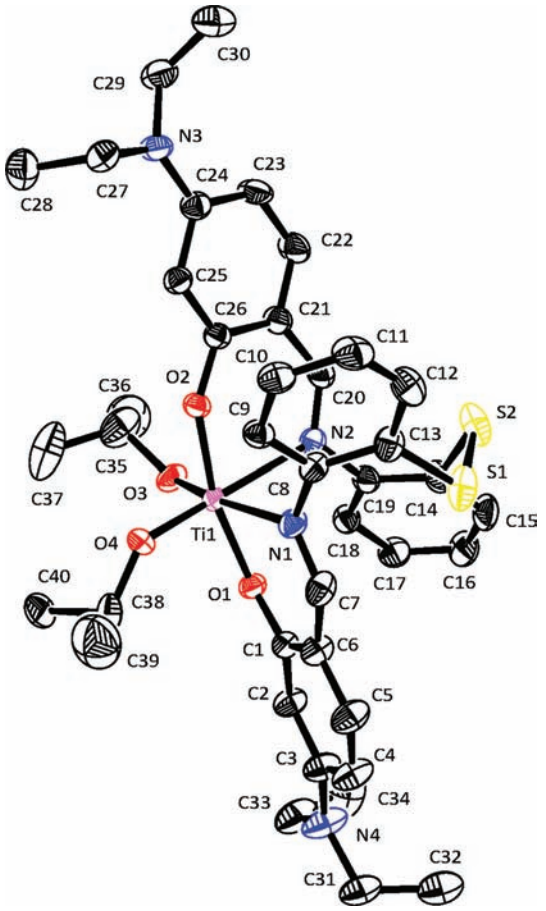

Figure 2. ORTEP plot of the crystal structure of $(\mathbf{6})Ti(O^{i}Pr)_2$, with H atoms and disordered alkoxy positions omitted for clarity.

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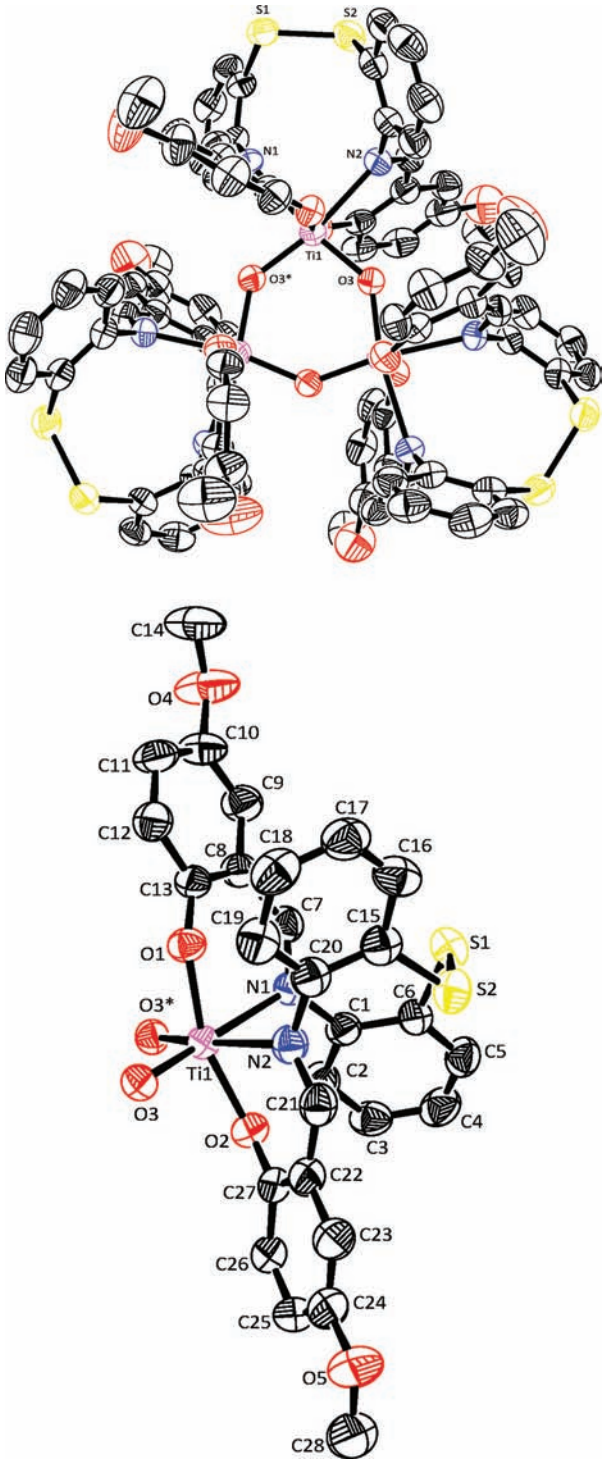

Figure 3. ORTEP plots of the crystal structure of $[(4)TiO]_3$, with H atoms omitted for clarity: (top) view of the propeller-shaped trimer down the C_3 axis; (bottom) side view of one metallic center.

average phenolic O−Ti bond length. The Ti−O−CCH_3 angles fell in the 132−142° range and, along with the short Ti−O bonds, are evidence of modest π donation. The unit cell of $[(4)TiO]_3$ also includes both enantiomers. Each of those molecules contains crystallographically equivalent metal centers but inequivalent ligand halves and inequivalent Ti−oxo bonds.

Both structures confirm the four-point binding deduced by NMR, with no involvement of sulfur and with the looped ligand conformation. The absence of coordination by neutral sulfur at relatively hard Ti(IV) centers is perhaps not surprising but contrasts with most of the DTDA-derived Schiff base complexes previously reported.[14c−f,21] On the assumption that the coordination sphere of $(4)Ti(O^tBu)_2$ was preserved in

Table 1. Crystallographic Data for $(6)Ti(O^iPr)_2$ and $[(4)TiO]_3$[a]

	$(6)Ti(O^iPr)_2$	$[(4)TiO]_3$
formula	$C_{40}H_{50}N_4O_4S_2Ti$	$C_{84}H_{66}N_6O_{15}S_6Ti_3$
M_r	762.86	1735.49
space group	$P2_1/c$	$R\bar{3}$
a (Å)	16.3908(7)	21.2378(3)
b (Å)	11.9907(4)	21.2378(3)
c (Å)	20.1174(8)	31.7593(7)
α (deg)	90	90
β (deg)	91.946(2)	90
γ (deg)	90	120
V (Å^3)	3951.5(3)	12 405.7(4)
Z	4	6
D_{calcd} (g cm^{-3})	1.282	1.394
λ(Mo Kα) (mm^{-1})	0.367	0.502
$R(F_o)^b$	0.0635	0.0543
$R_w(F_o^2)^b$	0.1547[c]	0.1541[d]

[a]In both cases, T = 150(1) K and λ = 0.710 73 Å. Esd's are expressed as uncertainties in the least significant digits in brackets. [b]For reflections where $I > 2\sigma(I)$. [c]The weights w used in the calculation of $R_w(F_o^2)$ are given by $w = 1/[\sigma^2(F_o^2) + (0.0831P)^2 + 6.523P]$, where $P = (F_o^2 + 2F_c^2)/3$. [d]The weights are given by $w = 1/[\sigma^2(F_o^2) + (0.0751P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

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

$(6)Ti(O^iPr)_2$			
Ti_1-O_1	1.911(2)	$O_3-C_{35/38}$	1.435(5)
Ti_1-O_2	1.911(2)	O_4-C_{35A}/C_{38A}	1.434(5)
Ti_1-O_3	1.820(3)	S_1-C_{13}	1.777(4)
Ti_1-O_4	1.811(3)	S_1-S_2	2.059(2)
Ti_1-N_1	2.260(3)	S_2-C_{14}	1.788(4)
Ti_1-N_2	2.282(3)		
$Ti_1-O_2-C_{26}$	140.5(2)	$O_1-Ti_1-O_2$	166.8(1)
$Ti_1-O_3-C_{35}$	133.1(6)	$O_2-Ti_1-O_3$	95.8(1)
$Ti_1-O_3-C_{35A}$	140.0(5)	$O_3-Ti_1-N_1$	167.1(1)
$Ti_1-O_4-C_{38}$	131.5(5)	$S_1-S_2-C_{14}$	105.7(1)
$Ti_1-O_4-C_{38A}$	142.4(6)	$S_2-S_1-C_{13}$	105.8(1)
$[(4)TiO]_3$			
Ti_1-O_1	1.915(2)	Ti_1-N_2	2.300(3)
Ti_1-O_2	1.909(2)	S_2-C_6	1.780(4)
Ti_1-O_3	1.817(2)	S_2-S_3	2.064(2)
Ti_1-O_3*	1.807(2)	S_3-C_{15}	1.776(4)
Ti_1-N_1	2.279(3)		
$O_1-Ti_1-O_2$	161.5(1)	$N_1-Ti_1-O_3$	84.8(1)
$O_3-Ti_1-O_3$*	103.1(1)	$N_1-Ti_1-O_3$*	171.7(1)
$O_2-Ti_1-O_3$	96.3(1)	$N_2-Ti_1-O_1$	84.2(1)
$O_2-Ti_1-O_3$*	95.0(1)	$N_2-Ti_1-O_2$	80.6(1)
$O_1-Ti_1-O_3$	96.9(1)	$N_2-Ti_1-O_3$	169.2(1)
$O_1-Ti_1-O_3$*	94.7(1)	$N_2-Ti_1-O_3$*	87.6(1)
$N_1-Ti_1-N_2$	84.7(1)	$C_6-S_2-S_3$	104.6(1)
$N_1-Ti_1-O_1$	81.8(1)	$C_{15}-S_3-S_2$	105.9(1)
$N_1-Ti_1-O_2$	86.5(1)		

[a]The labels marked with an asterisk refer to symmetry equivalents.

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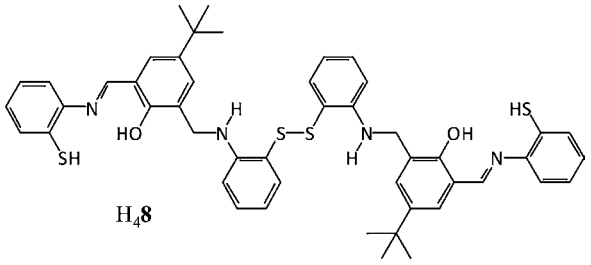
forming $[(\mathbf{4})TiO]_3$, the same was therefore true with $(\mathbf{4})Ti(O^tBu)_2$. One previously reported example, a V(III) complex of a symmetrical disulfide,[11] similarly lacked S coordination. On the other hand, the two nitrogen atoms in the V(III) case were inequivalent, whereas the structures of both of our crystalline Ti(IV) complexes are consistent with the single sets of ^1H and ^{13}C NMR signals detected, in which the internal ligand symmetry was preserved in the complexes. The exception was a Ti(IV) complex of ligand $H_4\mathbf{8}$ which we reported earlier,[2] a 2:2 assembly of a bis(dibasic tridentate) that arose by postcomplexation modifications.



$H_4\mathbf{8}$

Monobasic bidentate ligands such as $acac^-$ normally form 2:1 ligand−Ti complexes, adopting cis arrangements with chiral metal centers.[22] The same arrangement has been reported for *N*-phenylsalicylidenimine[23] with, moreover, cis nitrogen atoms. This arrangement is retained in the trinuclear product of its partial hydrolysis, analogous to the case for $[(\mathbf{4})TiO]_3$, and is replicated with the present ligands. Planar (equatorial or meridional) arrangements are more usual with salen-type tetradentate ONNO ligands[24] (except with bidentate auxiliary ligands and bridging ligands),[25] but the present ligands are twisted out of coplanarity, resulting in cis coordination of the alkoxide ligands. The looped conformations of the ligands in $(\mathbf{6})Ti(O^iPr)_2$ and $[(\mathbf{4})TiO]_3$ evidently allowed for entropically favored 1:1 complexation in preference over bridged species but necessitated somewhat strained S−S linkages. In comparison to the average S−S bond length reported for similar ligands in their free states (2.02 ± 0.03 Å),[11,18,27] the S−S bonds in the present complexes were somewhat elongated (2.059 Å in $(\mathbf{6})Ti(O^iPr)_2$ and 2.064 Å in $[(\mathbf{4})TiO]_3$). While these fall in line with the values measured in those metal complexes that do include sulfur coordination, one exception being the Fe(III) complex,[12] they were nevertheless noticeably shorter than in the comparable V(III) species,[11] which also lacked S coordination but may have been strained, and in $[(\mathbf{8})Ti]_2$ (2.086 Å on average),[2] in which the S−S linkages were perhaps more relaxed but which were also engaged in H bonding. The C−S−S−C torsion angles (106.9° in $(\mathbf{6})Ti(O^iPr)_2$ and 109.5° in $[(\mathbf{4})TiO]_3$) are among the largest reported. In $[(\mathbf{8})Ti]_2$,[2] these angles were significantly smaller (77.6° on average) and more acute than is ideal but are more in line with those found in the literature. The torsional distortions from coplanarity between the two aromatic rings in each bidentate half of $(\mathbf{6})Ti(O^iPr)_2$ (averaging about 67°) were stronger than those previously found in the analogous ONS ligands,[2] and that distortion appears to be required for coordination of the bidentate halves to the same metal. In $[(\mathbf{4})TiO]_3$, the average angle was about 79°. These torsions move the aldimino hydrogens out of the deshielding regions of the thiophenol rings and account for the upfield shifts of the H_i NMR signals upon complexation.

Several complexes showing a $Ti_3(\mu\text{-}O)_3$ core have been previously reported and, as in the case of $[(\mathbf{4})TiO]_3$, resulted from partial hydrolyses of complexes with salicylidenimine,[23] cyclopentadiene,[26] or tripodal tertiary amine ligands.[27] Within the annular core of $[(\mathbf{4})TiO]_3$, the almost identical $Ti-O_3$ and $Ti-O_3$* bond lengths and the $Ti_1-O_3-Ti_2-O_3$* angle of 5.39° account for the unusually planar six-membered ring, while all the other reported $Ti_3(\mu\text{-}O)_3$ compounds showed a chairlike configuration and inequivalence between the three units. Because the Ti−O bond lengths are consistent, on average, across all the structures reported, the electronic densities and the steric demands of the different ligands are not apparently affecting the $Ti_3(\mu\text{-}O)_3$ core.

Electrochemistry. All of the isolated complexes were tested by standard cyclic voltammetry (CV) in comparisons with the corresponding free ligands. All scans were obtained at the same concentrations and scan rates under identical conditions, but the free ligands were examined in two different solvents. The redox processes were all essentially irreversible, but barring small differences in kinetics that one would expect within a family of complexes, the steady-state peak potentials (Table 3)

Table 3. Peak Anodic (E_{pa}) and Cathodic (E_{pc}) Potentials (in V vs Ag/AgCl) for H_2L and $LTi(OR)_2$ Complexes in CH_2Cl_2 (0.1 M in $^nBu_4NPF_6$)[a]

	E_{pa}	E_{pc}
	Ligands	
DTDA	(+0.77)	(nd)[a]
$H_2\mathbf{1}$	+1.79, +2.03	−1.57, −1.87
$H_2\mathbf{2}$	+1.37, +1.62	nd
$H_2\mathbf{3}$	+1.40, +1.61	−1.71, −2.11
$H_2\mathbf{4}$	nd	nd
$H_2\mathbf{5}$	nd	−1.25, −1.72
$H_2\mathbf{6}$	+1.22, +1.90	−1.92, −2.48
$H_2\mathbf{7}$	+1.61	−1.21, −1.65
	$LTi(O^iPr)_2$ Complexes	
$H_2\mathbf{1}$	nd	nd
$H_2\mathbf{2}$	+1.52	−1.68
$H_2\mathbf{3}$	+1.54, +1.94	ca. −1.83
$H_2\mathbf{4}$	+1.31	nd
$H_2\mathbf{5}$	nd	−1.28, −2.09
$H_2\mathbf{6}$	+1.13, +1.25	nd
	$LTi(O^tBu)_2$ Complexes	
$H_2\mathbf{1}$	nd	−1.72, −2.38
$H_2\mathbf{2}$	+1.33	−1.74
$H_2\mathbf{3}$	+1.31	−1.84
$H_2\mathbf{4}$	+1.26	nd
$H_2\mathbf{5}$	+1.39	−1.26

[a]nd = no clear wave detected. [a]Values measured in 1:4 H_2O-CH_3CN are given in parentheses.

are nevertheless useful points of comparison. Figure 4 presents representative steady-state traces in the positive direction, all involving the new ligand $H_2\mathbf{3}$, but scans were also initiated in the negative direction with the same result. Unfortunately, few species showed activity in both oxidation and reduction regimes and some showed none at all, allowing for few useful comparisons.

The oxidizable $LTi(OR)_2$ complexes showed one or two distinct and irreversible processes when scanning in the positive direction, as exemplified by Figure 4b,c. These had been previously identified[14a] as being due to oxidations of the phenolic moiety (process I) and of the sulfur atoms (process II), and those processes seem to coalesce in the case of the free

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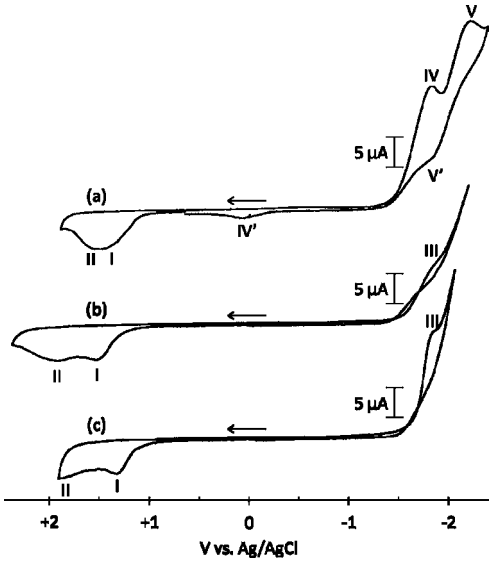

Figure 4. Full cyclic voltammometric scans at 100 mV s^{-1} of 0.04 M solutions in CH_2Cl_2 containing 0.1 M nBu_4NPF_6 of (a) H_2**3**, (b) (**3**)Ti(O^iPr)$_2$, and (c) (**3**)Ti(O^tBu)$_2$.

ligand (Figure 4a). In the case of H_2**6** and its complex, the lower-potential oxidation (Table 3) was no doubt due to an easy oxidation of the anilino nitrogen.

Our earlier work with oxidizable ligands had revealed a pronounced retardation of the ligand oxidations once attached to Ti(IV).[1,2] Setting aside the anilino oxidations of H_2**6** and its complex, the remaining available comparisons with LTi(O^iPr)$_2$ in this series show only a small retardation of the oxidation, while the two comparable LTi(O^tBu)$_2$ complexes oxidized at slightly *lower* potentials than the free ligands. It is therefore unlikely that process I involves the Schiff base itself. Instead, the ordering is perhaps reversed from that reported earlier,[14a] with process I associated with sulfur oxidation and process II with a retarded Schiff-base oxidation. The difference in oxidation behavior between LTi(O^tBu)$_2$ and LTi(O^iPr)$_2$ species has been noted before,[1,2] owing to the greater electron-donating effect of O^tBu groups, but the only two comparable cases here show larger differences. A steric, rather than electronic, effect may be responsible for the easier oxidation at sulfur.

Several of the free ligands were also tested in 20:80 H_2O–CH_3CN, whence the first oxidations were detected at potentials up to 0.8 V less positive than in CH_2Cl_2, which is consistent with the formation of charged species upon oxidation. Unfortunately, water sensitivity precluded similar measurements with the complexes. When they were scanned in the negative direction, H_2**3** (Figure 4a) and most of the other free ligands (Table 3) showed a first irreversible reduction (process IV), associated with the cleavage of the disulfide bond, followed by a more reversible reduction (processes V/V′), reportedly that of the aldimino functionality.[14a] Process IV′ (Figure 4a), not detected during the first positive scan, was evidently associated with the re-formation of the disulfide bond. However, half of the complexes did not show such waves. The few available comparisons reveal more negative waves with the complexes than with the free ligands, with no reoxidation waves, but we cannot ascertain whether these are due to electrostatically retarded S–S bond reductions, to aldimine reductions, or to $Ti^{IV/III}$ couples. In the case of H_2**5** and its complexes, however, the lower-potential waves were probably instead due to reductions of the nitro group, as had been the case with the nitro-substituted salicylaldehyde-2-aminothiophenol Schiff base.[2]

CONCLUSIONS

Seven DTDA-derived Schiff-base ligands, including two new variations, formed ten mononuclear Ti(IV) complexes of novel architecture, while three other combinations were ill-defined and perhaps oligomeric. As revealed in two hitherto-unprecedented crystal structures, the mononuclear species feature a C_2-symmetrical cis ligation of the two monobasic bidentate portions that take advantage of the preference for right-angle conformations about the noncoordinated S–S linkages. These mononuclear complexes then uniquely present a redox function independent of the coordination function. However, the products were less redox active in aprotic solvent than anticipated, showing difficult reductions with no detectable reoxidation waves. The diethylamino-substituted complex showed a potentially useful oxidation at +1.13 V vs Ag/AgCl. We will reinvestigate their electrochemical behavior after chemisorption on electrode surfaces.

ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data and text and tables giving NMR signal assignments and coupling constants for all species and ^1H and ^{13}C NMR spectra for H_2**3**, (**3**)Ti(O^iPr)$_2$, and H_2**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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