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Notes

Synthesis and Characterization of Cyclopentadienyl Titanium(Aryloxide)Sulfide Complexes

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We have been interested in the fundamental nature of the reactivity of early metal−sulfur bonds for some time.[1,2] A variety of group four metal sulfide derivatives are known,[3] including mono and dimetallic compounds such as $(\eta^5\text{-}C_5H_5)_2TiS_5$,[4] 1,5-$((\eta^5\text{-}C_5H_5)_2Ti)_2S_6$, and 1,4-$((\eta^5\text{-}C_5H_5)_2Ti)_2S_4$[5], as well as the higher nuclearity aggregates $[(\eta^5\text{-}C_5H_5)TiS]_4$,[6] $(\eta^5\text{-}C_5H_5)_5Ti_5S_6$,[77] $Zr_3S_3(t\text{-}BuS)_2(BH_4)_4(THF)_2$, $Zr_6S_6(t\text{-}BuS)_4(BH_4)_8(THF)_2$,[8,9] $Zr_3S(S\text{-}t\text{-}Bu)_{10}$,[10] $((\eta^5\text{-}C_5H_5)Ti)_4(\mu^3\text{-}S)_3(\mu^2\text{-}S)(\mu^2\text{-}SEt)_2$, $((\eta^5\text{-}C_5H_5)Ti)_6(\mu^3\text{-}S)_4(\mu^3\text{-}O)_4$, and $[(\eta^5\text{-}C_5H_5)Ti(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu^3\text{-}S)]_3Ti(\eta^5\text{-}C_5H_5)$.[11] In contrast, group four complexes containing terminal-sulfido ligands are much less common, being limited to $[Ti(S)Cl_4]$,[2−12] $(\eta^5\text{-}C_5Me_5)_2M(S)py$ (M = Ti, Zr, Hf),[13,14] $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}S)(S)]_2$,[2−15] and $(PhC(NSiMe_3)_2))_2Ti(S)py$.[16] In our own work, we have been exploring the effects of bulky aryloxide ligands in Ti−sulfide chemistry.[17−20] We have previously reported dimetallic sulfide bridged complexes of the form $[(\eta^5\text{-}C_5H_5)Ti(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}S)]_2$ and $[(\eta^5\text{-}C_5H_5)Ti(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)]_2(\mu\text{-}S)(\mu\text{-}S_2)$.[18] In the present work, we probe several strategies in quest of titanium−terminal-sulfide complexes.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2, employing both Schlenk line techniques and inert atmosphere gloveboxes. Solvents were purified using a Grubb's type column system. All organic reagents were purified by conventional methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in C_6D_6 on a Bruker Avance-300 and -500, operating at 300 and 500 MHz, respectively. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. Guelph Chemical Laboratories Inc. of Guelph, Ontario performed combustion analyses. Li_2S was purchased from the Aldrich Chemical Co. The complexes $(\eta^5\text{-}C_5H_5)Ti(OR)Cl_2$ (R = C_6H_3-2,6-Me_2 **1**; C_6H_3-*i*-Pr_2 **2**) and $(\eta^5\text{-}C_5Me_5)Ti(OR)Cl_2$ (R = C_6H_3-2,6-Me_2 **3**, C_6H_3-*i*-Pr_2 **4**, C_6H_3-2,6-*t*-Bu_2 **5**) were prepared as described in the literature.[17,21]

Synthesis $[(\eta^5\text{-}C_5H_5)Ti(OC_6H_3\text{-}2,6\text{-}Me_2)(\mu\text{-}S)]_2$ 6, $[(\eta^5\text{-}C_5Me_5)Ti(OC_6H_3\text{-}2,6\text{-}Me_2)(\mu\text{-}S)]_2$ 7. These compounds were prepared in a similar fashion. To a solution of **2** (100 mg, 0.28 mmol) in THF was added Li_2S (25 mg, 0.55 mmol). Upon stirring overnight, the solution became brown. The THF was removed in vacuo, and the product was extracted into benzene, filtered, and the solvent removed to give a brown precipitate. **6**. Yield: 50%. ^1H NMR δ: 2.33 (s, 6H, Me), 6.23 (s, 5H, $(\eta^5\text{-}C_5H_5)$), 6.85 (m, 1H, *p*-Ar), 7.03 (d, 2H, *m*-Ar). Anal. Calcd for $C_{13}H_{14}STiO$: C, 58.66; H: 5.30. Found: C, 58.21; H: 5.07. **7**. Yield: 45%. ^1H NMR δ: 1.90 (s, 3H, Me), 1.92 (s, 3H, Me), 2.38 (s, 15H, $(\eta^5\text{-}C_5Me_5)$), 6.67 (tr, 1H, *p*-Ar), 7.04 (d, 2H, *m*-Ar). Anal. Calcd for $C_{18}H_{24}STiO$: C, 64.28; H: 7.19. Found: C, 64.11; H, 7.01.

Synthesis of $(\eta^5\text{-}C_5Me_5)Ti(S)(OR)\cdot LiCl\cdot 2,2'\text{-}bipy$, R = ($C_6H_3$-2,6-$Me_2$) 8, ($C_6H_3$-2,6-*i*-$Pr_2$) 9. A solution of **4** (0.50 g, 1.16 mmol), Li_2S (0.10 g, 2.18 mmol), and 2,2′-bipyridine (0.181 g, 1.16 mmol) in THF (5 mL) was allowed to stir for 2 days. The solvent was removed and the residue extracted into benzene; the solution was filtered and allowed to stand. Light-brown X-ray quality crystals of **9** were deposited in 91% yield. **8**. ^1H NMR δ: 1.91 (s, 3H, Me), 1.93 (s, 3H, Me), 2.40 (s, 15H, $(\eta^5\text{-}C_5Me_5)$), 6.01 (br, 2H, bipy), 6.60 (m, 2H, bipy), 6.90 (m, 3H, Ar), 7.40 (m, 2H, bipy), 8.90 (m, 2H, bipy). Anal. Calcd for $C_{28}H_{32}ClLiN_2STiO$: C, 62.92; H, 5.99; N, 5.24; Found: C, 62.71; H, 5.84; N, 5.09. **9**. Yield: 96%. ^1H NMR δ: 1.43 (d, 6H, $|J_{HH}|$ = 6.8 Hz, $CH(CH_3)_2$), 1.49 (d, 6H, $|J_{HH}|$ = 6.8 Hz, $CH(CH_3)_2$), 2.39 (s, 15H, C_5Me_5), 4.11 (sept, 2H, IJ_{HH}| = 6.8 Hz, $CH(CH_3)_2$), 6.45 (dd, 2H, bipy), 6.90 (trd, 2H, bipy), 7.06 (tr, 1H, $|J_{HH}|$ = 7.5 Hz, *p*-Ar), 7.16 (d, 2H, *m*-Ar), 7.29 (d, 2H, bipy), 8.29 (d, 2H, bipy). $^{13}C\{^1H\}$-NMR δ: 13.3 (C_5Me_5), 24.8 ($CH(CH_3)_2$), 25.3 ($CH(CH_3)_2$), 26.0 ($CH(CH_3)_2$), 119.8 (Ar), 120.4 (Ar), 123.7 (Bipy), 123.9 (C_5Me_5), 124.3 (Bipy), 137.7 (Bipy), 137.9 (*o*-Ar), 150.2 (Bipy), 154.0 (Bipy), 161.6 (ipso-Ar). Anal. Calcd for $C_{32}H_{40}ClLiN_2STiO$: C, 65.03; H, 6.82; N, 4.74. Found: C, 64.81; H, 6.54; N, 4.39.

Generation of $(\eta^5\text{-}C_5Me_5)Ti(S)(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(THF)$ (10) and Benzo-15-crown-5·LiCl To a 5 mL THF solution of **4** (0.200 g, 0.46 mmol) was added Li_2S (0.04 g, 0.87 mmol) and benzo-15-crown-5 (0.124 g, 0.46 mmol). This was allowed to stir for 2 days. The THF was removed in vacuo, and the residue was extracted in benzene and filtered. The extreme sensitivity and propensity for dimerization of this compound precluded isolation, EA, and spectroscopic characterization beyond NMR methods. ^1H NMR(C_6D_6) δ: 1.41 (d, 6H, $|J_{HH}|$ = 6.8 Hz, $CH(CH_3)_2$), 1.45 (d, 6H, $|J_{HH}|$ = 6.8 Hz, $CH(CH_3)_2$), 2.36 (s, 15H, $(\eta^5\text{-}C_5Me_5)$), 3.16 (br, 4H, CH_2), 3.40 (br, 12H, CH_2), 3.56 (m, THF), 4.21 (2H, 2H, $|J_{HH}|$ = 6.8 Hz, $CH(CH_3)_2$), 6.34 (dd, 2H, Ar, crown), 6.73 (dd, 2H, Ar, crown), 6.90 (tr, 1H, *p*-Ar), 7.20 (d, 2H, *m*-Ar). $^{13}C\{^1H\}$-NMR(C_6D_6) δ: 13.8 C_5Me_5, 25.0 ($CH(CH_3)_2$), 26.1 ($CH(CH_3)_2$),

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Table 1. Crystallographic Parameters for **9**[a]

formula	$C_{32}H_{40}ClLiN_2OSTi$
formula weight	591.01
a (Å)	9.589(4)
b (Å)	16.990(6)
c (Å)	19.844(9)
cryst syst	othorhombic
space group	$P2_1/c$
vol (Å^3)	3232.9(23)
D_{calcd} (g cm^{-1})	1.341
Z	4
abs coeff, μ, mm^{-1}	0.438
R (%)	0. 0645
Rw (%)	0.1340

[a] All data collected at 24 C with Mo Kα radiation ($\lambda = 0.71069$ Å), $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = [\Sigma[\omega(F_o^2-F_c^2)^2]/\ \Sigma[\omega F_o^2)^2]]^{0.5}$.

26.2 (CH(CH$_3$)$_2$), 66.7 (CH$_2$), 67.9 (CH$_2$), 69.0 (CH$_2$), 69.1 (CH$_2$), 112.3 (Ar, crown), 121.9 (Ar, crown), 122.4 (Ar), 123.6 (Ar), 128.9 (Me$_5$C$_5$), 138.1 (Ar), 147.5 (Ar, crown), 163.21 (Ar).

X-ray Data Collection and Reduction. The crystal of **9** was manipulated and mounted in capillaries in a glovebox. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer, collecting a hemisphere of data in 1329 frames with 10 s exposure times. Crystal data are summarized in Table 1. A measure of decay was obtained by re-collecting the first 50 frames of each data set. The data were processed using the SAINT, SADABS (empirical absorption correction), XPREP, and SHELXTL packages. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[22] The non-hydrogen atom positions were determined using direct methods and successive difference Fourier map calculations. The refinement was carried out by using full-matrix least squares techniques on *F*, minimizing the function $\omega(|F_o| - |F_c|)^2$, where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$, and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated (C−H: 0.95 Å) and allowed to ride on the carbon to which they are bonded with temperature factors fixed at 1.10 times that of the corresponding carbon atom. Hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. Crystallographic data have been deposited as Supporting Information.

Results and Discussion

In work analogous to our previous reports, reactions of **1** and **4** with Li$_2$S resulted in the isolation of the dimeric complexes [(η^5-C$_5$H$_5$)Ti(OC$_6$H$_3$-2,6-Me$_2$)(μ-S)]$_2$ (**6**) and [(η^5-C$_5$Me$_5$) Ti(OC$_6$H$_3$-2,6-Me$_2$)(μ-S)]$_2$ (**7**), respectively.[18,20] In an effort to intercept a monomeric terminal-sulfide derivative, we examined the reaction of the sterically congested precursor **5** with Li$_2$S. Surprisingly, no reaction was observed, suggesting that steric crowding inhibits the halide/sulfide metathesis. While the reasons for this are not clear, it may be that the steric demands of the ancillary ligands together with aggregation of lithium sulfide in solution contribute to unforeseen steric conflicts.

A second strategy designed to intercept a terminal-sulfide species involved reaction of **3** and **4** with Li$_2$S in the presence of bipyridine (Scheme 1).

NMR spectra of the resulting products **8** and **9,** respectively, were consistent with a 1:1:1 ratio of (η^5-C$_5$Me$_5$), aryloxide, and bipyridine. An X-ray crystallographic study of **9** confirmed the formulation of these species as (η^5-C$_5$Me$_5$)Ti(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(S)·LiCl·(2,2′-bipy) **9** (Figure 1). Sulfur and chlorine atoms bridge the Li and Ti pseudo tetrahedral centers. The Ti−S distance in **9** is 2.227(2) Å, which is slightly longer than the Ti−S distances in the terminal-sulfide species: [PhC(NSiMe$_3$)$_2$)]$_2$-Ti(S)py (2.139(1) Å),[16] (η^5-C$_5$Me$_5$)$_2$Ti(S)py (2.217(1) Å),[13] Na$_2$-[(η^5-C$_5$H$_5$)Ti(μ-S)(S)]$_2$ (2.202(1) Å, 2.187(1) Å)[15] and (NEt$_2$)$_2$-[Ti(S)Cl$_4$] (2.111(1) Å).[12] It is, however, shorter than the Ti−S distances typically seen in sulfido-bridged dimers. Correspondingly, the Ti−Cl distance in **9** is 2.333(2) Å. Thus, species **9** is best viewed as a LiCl adduct of a terminal-sulfide complex.

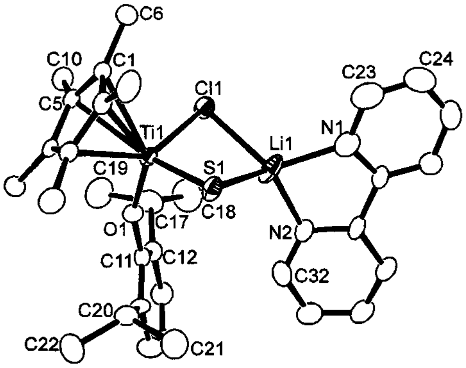
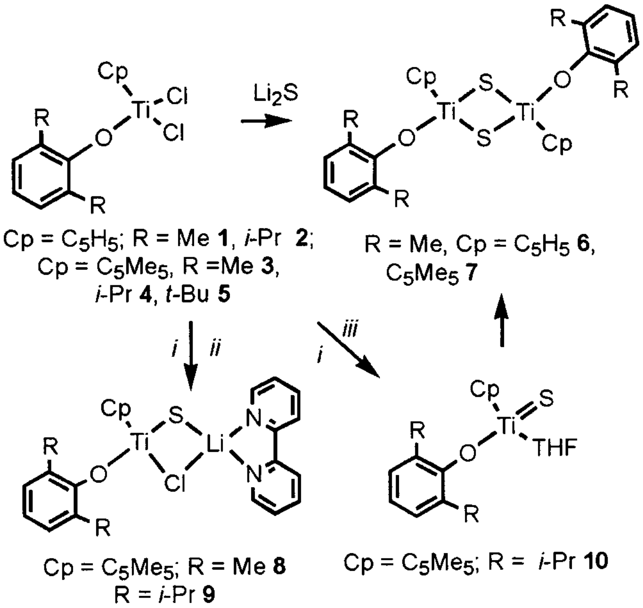


Figure 1. ORTEP drawing of **9**, 20% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity (bond distances in Å, bond angles in deg). Ti(1)−O(1) 1.849(4), Ti(1)−S(1) 2.227(2), Ti(1)−Cl(1) 2.333(2), S(1)−Li(1) 2.465(14), Cl(1)−Li(1) 2.419(13), N(1)−Li(1) 2.00(2), N(2)−Li(1) 2.05(2), O(1)−C(11) 1.355(7) Ti(1)−Li(1) 3.064(14), O(1)−Ti(1)−S(1) 105.50(14), O(1)−Ti(1)−Cl(1) 101.6(2), S(1)−Ti(1)−Cl(1) 98.99(9), Ti(1)−S(1)−Li(1) 81.4(3), Ti(1)−Cl(1)−Li(1) 80.3(4), C(11)−O(1)−Ti(1) 157.1(4), N(1)−Li(1)−N(2) 81.6(5), N(1)−Li(1)−Cl(1) 118.1(8), N(2)−Li(1)−Cl(1) 129.5(7), N(1)−Li(1)−S(1) 123.7(7), N(2)−Li(1)−S(1) 117.8(7), Cl(1)−Li(1)−S(1) 90.5(4).

Scheme 1



i = Li$_2$S, *ii* = bipy, *iii* = benzo-15-crown-5

In a similar vein, the reaction of **4** with Li$_2$S in the presence of benzo-15-crown-5 was allowed to stir for several days in THF/benzene solution. NMR data were consistent with a mixture of two species formulated as (η^5-C$_5$Me$_5$)Ti(OC$_6$H$_3$-2,6-*i*-Pr$_2$)-(S)(THF) (**10**) and benzo-15-crown-5·LiCl. Although these data

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imply the generation of a terminal-sulfide complex **10**, attempts to further characterize or isolate **10** were unsuccessful. Upon concentration of the solution, **10** was observed to dimerize affording the known species $[(\eta^5\text{-}C_5Me_5)Ti(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(\mu\text{-}S)]_2$.[20]

In conclusion, while sulfido-bridged dimers are, in general, readily derived from cyclopentadienyl-Ti-aryloxide complexes, related terminal-sulfide species have been isolated as LiCl adducts. The propensity of terminal-sulfide species for dimerization appears to account for their rather elusive nature.

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Supporting Information Available: Crystallographic X-ray crystallographic files in CIF format for the structure determination of compound **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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