Ultrasonic Activation of Chalcogen–Chalcogen Bonds: Synthesis of Bis(organyltellurenyl) Selenides and Sulfides, $(RTe)_2(Se,S)$

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Summary: **Ultrasonic activation of diorganyl ditellurides, R_2Te_2, in the presence of selenium or sulfur leads to bis(organyltellurenyl) selenides or sulfides, $(RTe)_2(Se,S)$ (R = Ph, $(Me_3Si)_3C$).**

The lability of the tellurium–tellurium bond in diorganyl ditellurides leads to exchange equilibria with group 15 and 16 alkyls and aryls[1] as shown in eq 1. Also reported have

$$\mathrm{RTeTeR} + \mathrm{R'_2E^{15}E^{15}R'_2} \rightleftharpoons \mathrm{2RTeE^{15}R'_2}$$

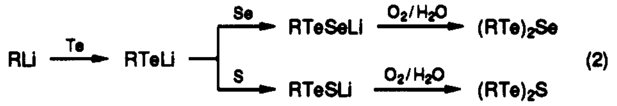
$$\mathrm{RTeTeR} + \mathrm{R'E^{16}E^{16}R'} \rightleftharpoons \mathrm{2RTeE^{16}R'} \qquad (1)$$

$$\mathrm{E^{15}} = \mathrm{P, As, Sb, Bi;}\ \mathrm{E^{16}} = \mathrm{S, Se, Te}$$

been insertion reactions of carbenes,[2] cadmium,[3] or mercury[4] into the tellurium–tellurium bond. Several such compounds have been proposed as single-source precursors to compound semiconductors such as CdTe and HgTe.[3]

Despite the increasing interest in the use of sonochemical methods in synthesis[5] only a few applications to chalcogen reactivity have been reported. One example is the ultrasound-induced electrochemical reduction of Se or Te powder with formation of the Se_2^{2-}, Se^{2-}, Te_2^{2-}, and Te^{2-} anions, which are used as starting materials for the preparation of diorganyl selenides and tellurides.[6]

We report here the use of ultrasound for the insertion of sulfur or selenium into the tellurium–tellurium bond of diorganyl ditellurides and thus a convenient and selective synthesis of bis(organyltellurenyl) sulfides and selenides. A general route to such compounds without ultrasonic activation has been designed previously[7] but is rather intricate and starts out from the corresponding organyllithiums (eq 2).



(2)

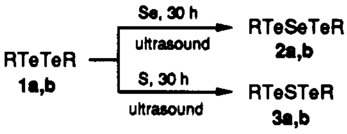
Sonication (35 kHz, 160 W) of a suspension of selenium (0.040 g, 0.51 mmol) in a solution of diphenyl ditelluride

Table I. ^{125}Te NMR Data for Bis(organyltellurenyl) Selenides and Sulfides[a] (300 K)

	^{125}Te chem shift, δ		
	RTeETeR[b]	RTeEETeR[b]	RTeTeR
PhTeSeTePh	1046	981	408
$((Me_3Si)_3CTe)_2Se$	947		
PhTeSTePh	1252	1197	411
$((Me_3Si)_3CTe)_2S$	1139		

[a] Bruker WP 80 FT instrument, THF as solvent, in ppm relative to external Me_2Te. [b] E = Se, S.

Sonication (35 kHz, 160 W) of a suspension of selenium (0.040 g, 0.51 mmol) in a solution of diphenyl ditelluride (**1a**; 0.20 g, 0.49 mmol) or of selenium (0.024 g, 0.30 mmol) in a solution of bis(tris(trimethylsilyl)methyl) ditelluride (**1b**; 0.20 g, 0.28 mmol) in dry tetrahydrofuran (THF) affords bis(phenyltellurenyl) selenide (**2a**) or bis((tris(trimethylsilyl)methyl)tellurenyl) selenide (**2b**),[8] respectively (eq 3).



(3)

a, R = Ph; **b**, R = $(Me_3Si)_3C$

The yields are quantitative with respect to the diorganyl ditellurides. No reaction is observed with tellurium, although the respective diorganyl tritelluride is known, at least in the case of the tris(trimethylsilyl)methyl group.[9] A sample of this compound, however, proved to be stable even to prolonged sonication.

Sonolysis of sulfur (0.20 g, 0.37 mmol) with **1a** (0.20 g, 0.49 mmol) in dry THF only yields about 20% of **3a** within 30 h, whereas **1b** (0.20 g, 0.28 mmol) again quantitatively reacts with sulfur (0.012 g, 0.37 mmol) to form **3b** (eq 3).[10] With this group also minor amounts of polysulfides such as $RTe(S)_{2,3}TeR$ are detected by NMR spectroscopy.[11] Interestingly, sonication of a homogeneous reaction system in carbon disulfide does not enhance the reaction rate or the yield of **3a**, nor does a change of the solvent to toluene to enhance the intensity of cavitation.

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(8) **2a**: purple crystals, mp 56–57 °C, from hexane/benzene (1:1), which slowly decompose in solution with extrusion of selenium. Anal. Calcd for $C_{12}H_{10}Te_2Se$: C, 29.51; H, 2.06. Found: C, 29.1; H, 2.0. MS: *m/e* 494 (5, M), 414 (40, M − Se), 364 (15, M − Te), 284 (50, M − Se, Te), 154 (100, M − TeSeTe). **2b**: red crystals, dec pt 130 °C, from ether/ethanol (1:1). Anal. Calcd for $C_{20}H_{54}Si_6Te_2Se$: C, 30.13; H, 6.83. Found: C, 29.9; H, 6.8. MS: *m/e* 802 (25, M), 722 (10, M − Se), 443 (20, M − TeTsi), 361 (100, TeTsi) (Tsi = $(Me_3Si)_3C$).

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(10) **3a**: not isolated, fractional crystallization failed. **3b**: orange crystals, dec pt 157 °C, from ether/ethanol (1:1). Anal. Calcd for $C_{20}H_{54}Si_6Te_2S$: C, 32.01; H, 7.25. Found: C, 31.8; H, 7.1. MS: *m/e* 754 (10, M), 722 (3, M − S), 393 (10, M − TeTsi), 361 (30, TeTsi), 231 (20, Tsi), 216 (100, Tsi − Me) (Tsi = $(Me_3Si)_3C$).

(11) $((Me_3Si)_3CTe)_2(S)_{2,3}$: $\delta(^{125}Te)$ = 1101 and 1075 ppm.

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No reaction could be observed between the analogous diorganyl diselenides and sulfur, selenium, or tellurium. Also, no reactions occurred in all investigated systems when mechanical stirring was applied instead of ultrasound.

The solution behavior of **2a**, **3a** and **2b**, **3b** is entirely different. **2a**, **3a** establish equilibria as given in eq 4, whereas **2b**, **3b** are kinetically stable, most likely for steric reasons. By addition of **1a** to the mixture both equilibria

$$\mathbf{2a} \rightleftharpoons \mathbf{1a} + \mathrm{PhTeSeSeTePh} \qquad (4)$$

$$\mathbf{3a} \rightleftharpoons \mathbf{1a} + \mathrm{PhTeSSTePh}$$

are shifted almost entirely to the left. The ^{125}Te NMR data for the species involved are given in Table I.

Low-Valent Titanium Porphyrin Complexes: Synthesis and Structural Characterization of the First Titanium(II) Porphyrin Complex, (η^2-Diphenylacetylene)titanium Octaethylporphyrin

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Summary: The anaerobic reduction of the dichlorotitanium(IV) porphyrins (OEP)$TiCl_2$ and (TTP)$TiCl_2$ (OEP = octaethylporphyrinato, TTP = *meso*-tetra-*p*-tolylporphyrinato) with $LiAlH_4$ in the presence of diphenylacetylene in toluene produces the π-alkyne Ti(II) adducts (OEP)Ti(η^2-PhC≡CPh) (**1**) and (TTP)Ti(η^2-PhC≡CPh) (**2**). The structure of **1** has been determined by single-crystal X-ray diffraction analysis. Complex **1** crystallizes in the centrosymmetric space group *C*2/*c* with a = 49.369 (7) Å, b = 13.734 (9) Å, c = 36.042 (5) Å, β = 136.62 (1)°, V = 16784 (9) Å^3, Z = 16, R = 0.061, and R_w = 0.063. The asymmetric unit of **1** contains two molecules. Alkyne C–C distances and Ti–alkyne distances are 1.30 (1) (C_{27}–C_{28}), 2.016 (5) (Ti_1–C_{27}), 2.015 (5) (Ti_1–C_{28}), 1.30 (1) (C_{61}–C_{62}), 2.007 (7) (Ti_2–C_{61}), and 2.028 (7) Å (Ti_2–C_{62}).

Despite the great interest in metalloporphyrins, the chemistry of early-transition-metal porphyrin complexes remains in an undeveloped state. A primary reason for this stems from the fact that syntheses of these complexes thermodynamically lead to the formation of high-valent oxo complexes.[2] The M=O groups in these metalloporphyrins are typically d^0–d^2 and are often extremely difficult to cleave.[3] We have recently examined the metal-centered redox chemistry of titanium oxo and titanium halide porphyrin complexes.[4] As an extension of our work on titanium porphyrins, we have begun to investigate the chemistry of low-valent Ti porphyrin complexes. To date, Ti(III) is the lowest valent state known to exist in a titanium porphyrin complex.[5] We report here the synthesis and structural characterization of the first Ti(II) porphyrin complexes.

As illustrated in eq 1, lithium aluminum hydride reduction of toluene solutions of dichlorotitanium(IV) porphyrins in the presence of diphenylacetylene produces η^2-alkyne complexes of Ti(II). In a typical reaction, 131

$$(\mathrm{POR})\mathrm{TiCl_2} + \mathrm{PhC{\equiv}CPh} \xrightarrow{\mathrm{LiAlH_4}} (\mathrm{POR})\mathrm{Ti}(\eta^2\text{-}\mathrm{PhC{\equiv}CPh}) \qquad (1)$$

$$\mathbf{1},\ \mathrm{POR} = \mathrm{OEP}$$
$$\mathbf{2},\ \mathrm{POR} = \mathrm{TTP}$$

mg of (OEP)$TiCl_2$[6] (0.201 mmol), 141 mg of $LiAlH_4$ (3.67 mmol), and 41 mg of PhC≡CPh (0.23 mmol) were stirred in toluene (40 mL) under N_2 at 22 °C. Over 12 h, the brown solution turned into the ruby red color of the alkyne adduct **1**. Filtering the reaction mixture, concentrating the filtrate to ca. 2 mL, and cooling to −20 °C for 3 days produced 78 mg of purple microcrystals (51% yield) after washing with cold pentane.[7] The TTP[6] analogue **2** can be prepared in a similar manner.[7]

The alkyne adducts **1** and **2** are diamagnetic complexes that exhibit sharp ^{1}H NMR signals. For example, in C_6D_6 the diphenylacetylene protons of **1** appear as two multiplets at 6.29 (6 H, *m*, *p* protons) and 4.37 ppm (4 H, *o* protons). The significant upfield shifts of these resonances are consistent with a structure in which the C≡C triple bond of the alkyne binds to titanium, holding the phenyl substituents above the porphyrin ring current. The porphyrin meso protons resonate as a singlet at 10.33 (4 H) ppm. This indicates that rotation of the alkyne ligand about the axis along the Ti–triple-bond centroid is rapid on the NMR time scale.

Crystals of the OEP complex **1** suitable for single-crystal X-ray diffraction were grown by cooling a toluene solution to −20 °C. Complex **1** crystallizes in the centrosymmetric space group *C*2/*c* with two molecules in the asymmetric unit and 16 molecules per unit cell.[8] The large number of non-hydrogen atoms (110) in the asymmetric unit significantly increased the difficulty and complexity of the

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[6] Abbreviations: OEP is the octaethylporphyrinato dianion and TTP is the *meso*-tetra-*p*-tolylporphyrinato dianion.

[7] Analytical data for (TTP)Ti(PhC≡CPh): ^{1}H NMR (C_6D_6, 300 MHz) 9.06 (s, 8 H, β-H), 7.97 (d, 7.52 Hz, 8 H, $-C_6\mathit{H}_4Me$), 7.28 (m, 8 H, $-C_6\mathit{H}_4Me$), 6.45 (m, 6 H, *m*, *p* H), 4.65 (m, 4 H, *o* H), 2.40 ppm (s, 12 H, $C_6H_4C\mathit{H}_3$); UV–vis (toluene) 426 (Soret), 548, 582 nm; IR (mull) 1666 cm^{-1} ($\nu_{C≡C}$). Anal. Calcd (found) for $C_{62}H_{46}N_4Ti$: C, 83.21 (82.55); H, 5.18 (5.23); N, 6.26 (6.04). Analytical data for (OEP)Ti(PhC≡CPh): ^{1}H NMR (C_6D_6, 300 MHz) 10.33 (s, 4 H, meso H), 6.29 (m, 6 H, *m*, *p* H), 4.37 (m, 4 H, *o* H), 3.92 (q, 7.8 Hz, 16 H, $C\mathit{H}_2CH_3$), 1.84 ppm (t, 7.5 Hz, 24 H, $CH_2C\mathit{H}_3$); UV–vis (toluene) 408 (Soret), 532, 570 nm; IR (mull) 1701 cm^{-1} ($\nu_{C≡C}$). Anal. Calcd (found) for $C_{50}H_{54}N_4Ti$: C, 79.14 (78.59); H, 7.17 (6.77); N, 7.38 (7.09).

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