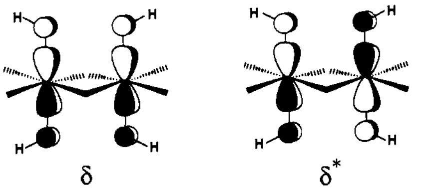
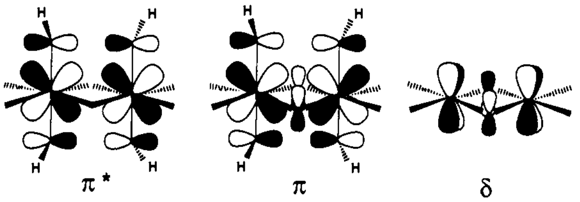
and yields a diamagnetic $\sigma^2\pi^2$ double bond for M = Re. The calculations for M = W yield a similar MO diagram with two fewer electrons and a σ^2 ground-state electronic configuration.

Based on conventional electron counting procedures, each Re atom in $Re_2(OMe)_{10}$ has 16 valence electrons in the absence of M–O π-bonding. Since the M–M σ and π orbitals are occupied by metal d electrons, this leaves the metal δ and δ^* orbitals available for π-bonding interactions. The alkoxide ligand can only form π-bonds with M–M δ-type orbitals by alignment parallel to the metal–metal axis as observed in the crystal structure of $Re_2(OMe)_{10}$. The four π electrons donated into the M–M δ and δ^* orbitals bring each Re atom to an 18-valence-electron count. These important π-bonding interactions are illustrated schematically below.



In $W_2(OMe)_{10}$, each W atom has 14 valence electrons in the absence of M–O π-bonding, and only the M–M σ-bonding orbital is occupied by metal electrons. This leaves the M–M π, δ, δ^*, and π^* orbitals available for M–O π-bonding. In order for the alkoxides to engage in maximum π-bonding, the bridging ligands rehybridize to planar sp^2, making the π lone pairs available for π-bonding interactions in the bridge. The bridging ligands can only interact by symmetry with the bonding M–M π and δ orbitals; the interaction is found to be strongest with the δ orbitals. To avoid a competition between bridge and axial ligand π-bonding with δ orbitals, the axial ligands rotate 90° to form equally strong π-bonds with M–M π and π^* orbitals (Figure 1). The six electrons donated from oxygen π lone pairs into M–M π, π^*, and δ orbitals bring each W atom to 17 valence electrons (34 e^-/dimer). These π-bonding interactions are illustrated schematically below.



Combined with the known $Ta_2(OMe)_{10}$,[22] a fundamental series of third-row decamethoxide dimers has been realized spanning d^0–d^0, d^1–d^1, and d^2–d^2. Full details of the synthetic chemistry, physicochemical properties, and electronic structure calculations will be presented in future publications.[23-25]

Acknowledgment. This work was performed under the auspices of the Division of Chemical Energy Sciences, Office of Energy Sciences, Office of Energy Research, U.S. Department of Energy; financial support is gratefully acknowledged. We also thank Professors B. E. Bursten, M. H. Chisholm, and D. L. Lichtenberger for helpful discussions.

Supplementary Material Available: Analytical, spectroscopic, and crystallographic data for **1** and **2** including tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters (7 pages); listing of observed and calculated structure factors for **1** and **2** (6 pages). Ordering information is given on any current masthead page.

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[24] Wheeler, D. R.; Bryan, J. C.; Jatcko, M.; Lichtenberger, D. L.; Sattelberger, A. P., in preparation.

[25] Bryan, J. C.; Wheeler, D. R.; Jatcko, M.; Schneider, W. F.; Bursten, B. E.; Lichtenberger, D. L.; Sattelberger, A. P., in preparation.

$(Me_3Si)_3SiTeH$: Preparation, Characterization, and Synthetic Utility of a Remarkably Stable Tellurol

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Synthetic routes to metal tellurolates, the tellurium analogues of alkoxides and thiolates, are limited.[1] Interest in these compounds heightened recently following reports that materials such as the oligomeric benzenetellurolates $[M(TePh)_2]_n$ (M = Hg, Cd) may serve as precursors to semiconducting bulk metal tellurides HgTe and CdTe.[2] We are developing tellurolate chemistry supported by large, sterically encumbered ligands in attempts to synthesize atypical metal tellurolates featuring low molecularity and hydrocarbon solubility.[3] At present, the only general route to these compounds involves a metathesis reaction between an alkali-metal tellurolate and a metal halide.[4] Disadvantages include the following: (i) one is limited by the choice of metal halide starting materials; (ii) tellurolate anions are quite reducing; and (iii) the presence of strong donor molecules (either as solvent or ligated to the tellurolate salts) often interferes with product purification. In searching for more versatile routes, we considered the following tellurolysis pathway:

$$L_nMX + HTeR \rightarrow L_nMTeR + HX \qquad (R = \text{alkyl, aryl})$$

Analogous reactivity is well-documented for alcohols,[5] thiols,[6] and selenols,[7] where reactions are extremely flexible with respect to the choice of R and the leaving group X (e.g., X = alkyl, amide, alkoxide, etc.); in addition, these reactions are best carried out in nonpolar solvents. For tellurolysis, however, a major drawback has been that known tellurols are thermally unstable compounds that are difficult to isolate and purify.[8-11]

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[7] For example: Bochmann, M.; Webb, K.; Harman, M.; Hursthouse, M. B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 638.

[8] In situ generated tellurols are useful synthetic reagents. For reactions involving addition of HTeR across C≡C bonds in acetylenes, see: Barros, S. M.; Dabdoub, M. J.; Dabdoub, V. M. B.; Comasseto, J. V. *Organometallics* **1989**, *8*, 1661 and references therein. Reviews of organotellurium reagents in organic synthesis: Engman, L. *Phosphorus Sulfur Relat. Elem.* **1988**, *38*, 105. Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1.

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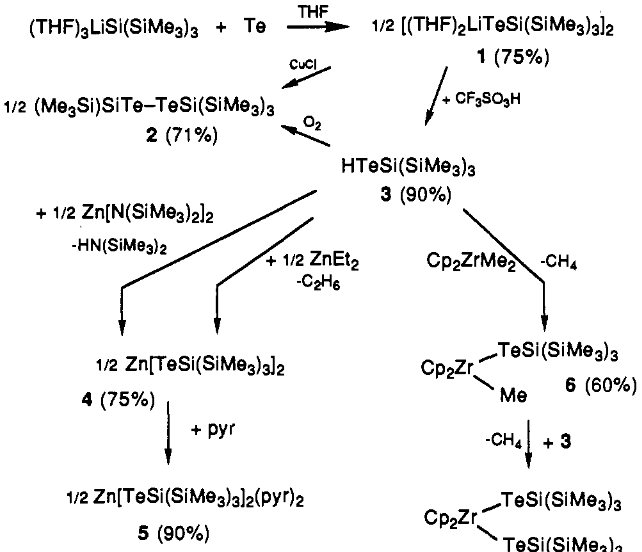
Scheme I



Recently we described several examples of stable sodium and potassium salts of sterically hindered arenetellurolate anions.[3] In common with earlier examples,[11] acidification of these compounds led to formation of thermally unstable tellurols and attempts at isolation and purification led only to decomposition.[12] Further investigations using sterically hindered silyl ligands have been more successful. Here we describe the synthesis and reactivity of a novel silyl tellurolate, its conversion to a stable silyl tellurol, and the first well-defined examples of M–Te bond formation via tellurolysis.

The lithium salt $(THF)_3LiSi(SiMe_3)_3$[13] reacts cleanly with 1 equiv of tellurium powder in THF at room temperature under argon or nitrogen to produce red-brown solutions of the lithium silyl tellurolate **1** as shown in Scheme I. Although tellurium is known to insert into a variety of M–X bonds (X = alkyl, aryl, phosphido, etc.),[14] we are unaware of any examples involving metal–silicon bonds.[15] Large yellow crystals of **1** were obtained from hexane in 75% yield on scales up to ca. 20 g.[16] Evidence for the formulation of **1** is based on elemental analysis and ^1H NMR spectroscopy; X-ray crystallography confirmed the dimeric structure indicated in Scheme I.[17]

Treatment of **1** with excess oxygen in benzene-d_6 quickly leads to quantitative formation of emerald-green ditelluride **2** as determined by ^1H NMR spectroscopy; air-stable crystals were isolated from preparative-scale reactions in hexane. We note that similar oxidations of arenetellurolate anions are often complex, low-yield reactions.[14,18] Cuprous chloride oxidation of **1** is an alternate high-yield route to large quantities of **2**. As monitored by ^1H NMR spectroscopy, benzene-d_6 solutions of **1** were unaffected by addition of 1–4 equiv of weak acids such as water and methanol. Addition of 1 equiv of triflic acid to a hexane solution of **1**, however, immediately produced a gray precipitate and a pale yellow-green solution. After evaporation of volatile components under reduced pressure at room temperature, the remaining residue sublimed at 40 °C (10^{-3} mmHg) onto a dry-ice cooled probe to give colorless crystals of the tellurol $HTeSi(SiMe_3)_3$ (**3**) (mp 128–130 °C) in high yield.

A sharp singlet at unusually high field in the ^1H NMR spectrum is assigned to the tellurol proton (δ −8.81, J_{TeH} = 73 Hz; ^{125}Te, 6.99%); ν_{TeH} appears as a sharp, medium-strength absorption at 2017 cm^{-1} in the infrared spectrum. For PhTeH and MeTeH the tellurol protons are seen at δ −2.4 (J_{TeH} = 50 Hz)[11d,e] and δ −5.5 (no coupling constant reported).[11a–c] IR data for PhTeH were not reported, but for MeTeH, ν_{TeH} occurs at 2053 cm^{-1}.[11a] Compound **3** is stable under EI MS conditions, showing the molecular ion at m/e = 378 (^{130}Te). It is exceedingly soluble in common hydrocarbon or ethereal solvents to give solutions that are stable indefinitely at room temperature under nitrogen or argon and can be heated to 130 °C for at least 1 day without decomposition; however, exposing these solutions to bright sunlight results in formation of a tellurium mirror and uncharacterized $SiMe_3$-containing products. Solid **3** can be stored at room temperature under nitrogen for periods of up to several weeks without affecting analytical or spectroscopic properties. These results highlight the stabilizing effect of the bulky $Si(SiMe_3)_3$ group, particularly when one considers that trimethylsilyl tellurides, which have been known as useful synthetic reagents for some time, are extremely sensitive to protolytic cleavage by reagents such as methanol and water.[11d,e]

The synthetic value of **3** is illustrated by reactions shown in Scheme I. Tellurolysis of Zn–N and Zn–C bonds proceeds rapidly and quantitatively in hydrocarbons to give high yields of the bis-tellurolate **4** as yellow prisms from hexane or hexamethyldisiloxane. NMR tube experiments in benzene-d_6 showed clean formation of $HN(SiMe_3)_2$ in the former reaction. The complex is extremely soluble in nonpolar solvents and is stable for weeks under nitrogen as a solid or in solution. The molecular structure of **4** is presently unknown; however, a tetrahedral bis-pyridine adduct **5** has now been crystallographically characterized.[12] It is important to note that conventional metathesis reactions between $ZnCl_2$ and 2 equiv of **1** in diethyl ether or toluene gave only mixtures of compounds.[19]

Tellurolysis of Zr–Me bonds is an effective pathway to new examples of rare early-transition-metal tellurolates.[20] Reaction between **3** and Cp_2ZrMe_2 is sluggish below −40 °C, but on warming, tellurolysis of a single Zr–Me bond proceeds rapidly around −10 °C; the CH_4 byproduct was detected in NMR tube experiments (δ 0.15). The dark orange-red methyl tellurolate

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(11) Methanetellurol reportedly explodes on contact with oxygen and is unstable above 0 °C;[11a–c] benzenetellurol (generated in situ) decomposes at room temperature.[11d,e] (a) Hamada, K.; Morishita, H. *Jpn. J. Appl. Phys.* **1976**, *15*, 748. (b) Hamada, K.; Morishita, H. *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 355. (c) Sink, C. W.; Harvey, A. B. *J. Chem. Phys.* **1972**, *57*, 4434. (d) Drake, J. E.; Hemmings, R. T. *Inorg. Chem.* **1980**, *19*, 1879. (e) Nagakawa, K.; Osuka, M.; Sasaki, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Chem. Lett.* **1987**, 1331.

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(14) Insertions into metal–carbon bonds are legion; see ref 1 and ref 9, p 26. Sladky has described an in situ preparation of the carbon analogue of **1**, $LiTeC(SiMe_3)_3$, along with di- and tritellurides; the corresponding tellurol was not reported. Sladky, F.; Bildstein, B.; Rieker, C.; Gieren, A.; Betz, H.; Hubner, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1800. Kōllemann, C.; Obendorf, D.; Sladky, F. *Phosphorus Sulfur Relat. Elem.* **1988**, *38*, 69. Giselbrecht, K.; Bildstein, B.; Sladky, F. *Chem. Ber.* **1989**, *122*, 1255. Giselbrecht, K.; Bildstein, B.; Sladky, F. *Chem. Ber.* **1989**, *122*, 2279. Insertion of tellurium into Li–P bonds: Bildstein, B.; Sladky, F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *47*, 341 and references therein.

(15) Te–Si bonds are commonly made by metathesis; see: Armitage, D. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989 and references therein. For Te insertion into a P–Si bond, see: Du Mont, W. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 638.

(16) NMR data (benzene-d_6, 300 MHz, 20 °C): **1** δ 3.75 (m, 8 H), 1.43 (m, 8 H), 0.45 (s, 27 H); **2** δ 0.37 (s); **3** δ 0.23 (s, 27 H), −8.82 (s, 1 H). UV–vis (hexane): **2** λ_{max} 652 nm. Correct elemental analyses were obtained; full characterization data are provided as supplementary material. All (except **2**) are air-sensitive and must be handled under nitrogen.

(17) The structure of **2** is analogous to that for the thiolate $[(THF)_2LiSC(SiMe_3)_3]_2$ (Sigel, G. A.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 2819). A full discussion will be presented shortly.[12]

(18) Engman, L.; Persson, J. *J. Organomet. Chem.* **1990**, *388*, 71.

(19) These mixtures were invariably contaminated with THF from **1**. By contrast, cadmium and mercury analogues were readily prepared by conventional metathesis reactions giving pure $M[TeSi(SiMe_3)_3]_2$ in high yields.[12] This presumably reflects the decreased Lewis acidity of the heavier group 12 elements.

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complex **6** was isolated from preparative-scale reactions between equimolar amounts of reactants at 20 °C. It is intensely soluble in hexane (ca. 1 g/mL), from which it can be crystallized at −80 °C. Tellurolysis of the remaining methyl group with a second equivalent of the tellurol is slow at room temperature, but on warming to 50 °C for 3 h, the maroon bis-tellurolate **7** is produced in high yield.

We are now probing the reactivity of these compounds and attempting to extend the tellurolysis approach to a wider variety of main-group and transition-metal tellurolates.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and the Department of Education for a fellowship (to P.J.B.).

Supplementary Material Available: Spectroscopic and analytical data for new compounds (1 page). Ordering information is given on any current masthead page.

Synthesis and Crystal Structure of a Spherical Polyoxovanadium Organophosphonate Anion: $[H_{12}(VO_2)_{12}(C_6H_5PO_3)_8]^{4-}$

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Several polyoxovanadates have recently been shown to form inclusion compounds with neutral molecules, for example, $[V_{12}O_{36}(CH_3CN)]^{4-}$,[2] $[V_{18}O_{42}(H_2O)]^{12-}$,[3] $[As_6V_{15}O_{42}(H_2O)]^{6-}$,[4] and $[As_8V_{14}O_{42}(0.5H_2O)]^{4-}$,[5] and with anions in $[H_9V_{18}O_{42}(VO_4)]^{6-}$, $[V_{18}O_{42}(SO_4)]^{8-}$, $[H_4V_{18}O_{42}(X)]^{9-}$ (X = Cl, Br, I), and $[V_{15}O_{36}(Y)]^{6-}$ (Y = Cl, Br, CO_3).[6-8] In one case, $[V_{12}O_{36}(CH_3CN)]^{4-}$,[2] the inclusion process is reversible, and consequently this compound can be considered a molecular analogue of the microporous oxides. Very recently, a vanadium organophosphonate anion, $[H_6(VO_2)_{16}(CH_3PO_3)_8]^{8-}$, which includes a tetramethylammonium cation, has been reported.[9] In this communication, the synthesis and structure of a new vanadium organophosphonate, $[N(C_3H_7)_4]_4[H_{12}(VO_2)_{12}(C_6H_5PO_3)_8]\cdot 1.48H_2O$ (**1**), containing a large spherical anion, $\{V_{12}P_8O_{48}\}$, analogous to the $\{V_{18}O_{42}\}$ systems is described.

Blue, parallelepiped crystals of **1** were prepared in ~70% yield by hydrothermal reaction of $C_6H_5PO_3H_2$ (0.952 g), $VOSO_4\cdot 3H_2O$ (0.434 g), and tetra-*n*-propylammonium hydroxide (8.2 g, 1 M in H_2O) at 200 °C for 2 days.[10]

X-ray structural analysis[11] of **1** revealed the presence of discrete TPA^+ (tetra-*n*-propylammonium) cations and disordered water molecules of crystallization in the lattice and inside the two crystallographically independent $[H_{12}(VO_2)_{12}(C_6H_5PO_3)_8]^{4-}$ anions per asymmetric unit (Figure 1). Each anion possesses rigorous crystallographic C_i-$\bar{1}$ symmetry and consists of six condensed vanadium–oxygen dimers covalently connected by eight PO_3C tetrahedra through corner-sharing oxygen atoms. Vanadium atoms are square-pyramidally coordinated by one doubly bonded terminal oxygen atom, two doubly bridging V–(OH)–V hydroxyl oxygens, and two doubly bridging V–O–P oxygen atoms. Each VO_5 unit shares one of its edges to form an O_2–VO–$(OH)_2$–V-O–O_2 dimer, and each $C_6H_5PO_3$ unit is bonded to three vanadium oxygen dimers. The protons of each dimer are positioned favorably to form hydrogen bonds which stabilize the anion structure (Figure 1). The phenyl groups, as well as the terminal (vanadyl) oxygen atoms, protrude from the surface of the "ball" forming a hydrophobic shell. Disordered water molecules were found at four partial occupancy (0.13–0.15) sites inside each anion. Each of these water molecules (O_{3w}, O_{4w}, O_{5w}, and O_{6w}) appears to be weakly coordinated to the vanadium atoms of a O_2–VO–$(OH)_2$–VO–O_2 dimer at bridging sites as shown in Figure 2. The V–O distances and V–O–V angles for these water molecules have ranges of 2.85 (6)–3.37 (6) Å and 57 (6)–60 (6)°, respectively, and the O═V—O(water) angles range from 162 (1)° to 178 (1)°. Since the $O_{3w}\cdots O_{4w}$ and $O_{5w}\cdots O_{6w}$ distances are 2.49 and 2.53 Å, respectively, and each water molecule has a V–O(water)···O(water) angle in the range 102–123°, the included water molecules may exist as hydrogen-bonded and weakly complexed pairs. The 12 vanadium and eight phosphorus atoms of each anion are located at the vertices of a pentagonal dodecahedron (Figure 2); each of its 12 faces is a distorted pentagon consisting of three vanadium atoms and two phosphorus atoms. The V···V and P···V separations have ranges of 3.082 (2)–3.106 (1) Å and 3.295 (2)–3.352 (1) Å, respectively.

Magnetic susceptibility data of **1** measured from 7 to 300 K show a broad maximum at 50 K indicating antiferromagnetic exchange interactions between the d^1 V(IV) ions in the dimers. Similar behavior is observed for the layered compounds $VO(HPO_4)0.5H_2O$, $(VO)_2P_2O_7$, $VOSeO_3H_2O$, and $VOSeO_3$,[12-15] which contain similar structural units.

The $[H_{12}(VO_2)_{12}(C_6H_5PO_3)_8]^{4-}$ cage is a new type of spherical anion structure which resembles the previously reported $\{V_{18}O_{42}\}$ systems in having sufficient internal volume for the inclusion of

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[1] (a) Exxon Research & Engineering Company. (b) Crystalytics Company.

[2] Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 5959.

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[10] Anal. Calcd for $C_{96}H_{167}N_8V_{12}P_8O_{49.5}$: C, 38.08; H, 5.56; N, 1.85; V, 20.19; P, 8.18. Found: C, 37.81; H, 5.47; N, 1.80; V, 20.21; P, 8.52. **1** is only slightly soluble in water but dissolves in mineral acids. Redox titration of **1** in sulfuric acid solution gave an average vanadium oxidation state of 4.00 ± 0.02. IR (solid/KBr): ν (cm^{-1}) 1130 (vs), 1110 (vs), 1030 (vs), 1010 (vs), 990 (vs), 905 (s), 755 (m), 715 (s), 690 (s), 590 (m), 540 (s), 510 (s).

[11] **1**: triclinic, space group $P\bar{1}$ (No. 2) with a = 16.038 (3) Å, b = 16.782 (3) Å, c = 29.345 (5) Å, α = 86.04 (2)°, β = 82.45 (2)°, γ = 63.41 (2)°, V = 7002 (2) $Å^3$, and Z = 2 (d_{calcd} = 1.436 g cm^{-3}; μ_a(Mo Kα) = 0.90 mm^{-1}). A total of 19 255 independent reflections having $2\theta < 45.8°$ were collected on a Nicolet autodiffractometer using ω scans and graphite-monochromated Mo Kα radiation. The structure was solved by using SHELXTL-Plus direct method techniques, and the resulting structural parameters have been refined by using counterweighted block-diagonal least-squares techniques to R_1 (unweighted, based on F) = 0.053 and R_2 (weighted, based on F) = 0.066 for 11 988 independent reflections having $2\theta < 45.8°$ and $I > 3\sigma(I)$. These refinement cycles employed anisotropic thermal parameters for all non-hydrogen atoms (except C_{4a1}–C_{4b4} and O_{2w}–O_{6w}, which were isotropically refined) and isotropic thermal parameters for all anion hydrogen atoms. Hydroxyl hydrogen atoms H_{1m}–H_{1r} and H_{2m}–H_{2r} on anions 1 and 2 were located from a difference Fourier map and refined as independent isotropic atoms. The remaining (phenyl) hydrogen atoms on the anions were fixed at idealized sp^2-hybridized positions.

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