Telluride Ligands

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Tellus in, Tellus out: The Chemistry of the Vanadium Bis(telluride) Functionality**

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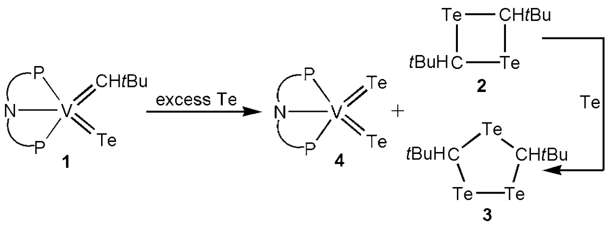
Terminal telluride ligands bound to transition metals still represent a rare functionality,[1–8] the first example (*trans*-$[(Me_3P)_4W(Te)_2]$) being reported by Rabinovich and Parkin in 1991.[1] A terminal telluride on a 3d transition metal, namely the complex $[\{(Me_3SiCH_2CH_2)_3N\}V{=}Te]$ was later reported by Schrock and co-workers in 1994.[2] Even though a few other examples of terminal early-transition-metal tellurides have been documented,[3–8] the only structurally characterized terminal 3d transition metal/telluride complexes consist of $[(\eta^4\text{-}Me_8taa)M'{=}Te]$ (M′ represents Ti and V, Me_8taa^{2-} = octamethyldibenzotetraaza[14]annulene).[7] Therefore it is of no surprise that little is known about the reactivity of the M=Te functionality in question, especially when 3d transition metals are involved.[2,8] For the few 3d examples known,[2,8] it has been proposed that the M=Te linkage decomposes by reductive elimination of Te^0, whereby the fate of the reduced metal complex M^{2-} can sometimes result in formation of dinuclear species.[9,10] Only in the case of $[(\eta^4\text{-}Me_8taa)M'{=}Te]$ or $[Cp^*_2M{=}Te(NC_5H_5)]$, could the terminal Te^{2-} ligand be replaced with O^{2-} (derived from O_2 or N_2O), $Se_2^{\ 2-}$ (derived from elemental Se), and $2\,Cl^-$ from the addition of two equivalents of Me_3SiCl.[7,8] Although not discussed, it can be argued that these transformations proceed by oxidation of the M=Te bond with concurrent Te^0 ejection.

Based on the chemistry known for terminal tellurides, we hypothesized that the $M^n{=}Te$ functionality could be utilized as a labile group by the reductive elimination of the low-valent M^{n-2} fragment with concurrent extrusion of Te^0. This feature is counterintuitive when considering the reactivity of the ubiquitous oxo ligand, given its propensity to stabilize high-valent oxidation states, and would imply that the metal center that has a terminal Te atom should be amenable to substitution and/or redox processes. Herein, we demonstrate that a vanadium alkylidene/telluride complex, $[(PNP)V{=}CHtBu(Te)]$ (**1**) (PNP^- = N(2-P*i*Pr_2-4-methylphenyl)$_2$),[11] prepared from $[(PNP)V(CH_2tBu)_2]$ and Te^0 via the intermediate $[(PNP)V{=}CHtBu]$ (**A**), can reductively eliminate a telluroaldehyde fragment to afford the formation of 2,4-di-*tert*-butyl-1,3-ditelluretane (**2**) and/or 3,5-di-*tert*-butyl-1,2,4-tritellurolane (**3**; Scheme 1). The hypothetical "(PNP)V" fragment can be trapped with excess Te^0 to afford the first 3d transition metal/bis(telluride) complex $(PNP)V(Te)_2$ (**4**).[1,5,6] Through a series of reactivity studies we demonstrated the $[Te{=}V^V{=}Te]$ moiety in **4** to be a synthon of the $[Te{=}V^V{=}X]$ and $[X{=}V^V{=}X]$ scaffolds, which are formed by oxidation of the V=Te bonds with concomitant deposition of Te^0. In addition, we also show the ability of **4** to reductively eliminate one Te ligand to furnish a vanadium(III) complex that contains a terminal telluride moiety.



Scheme 1. Synthesis of complex **2**, and the di- and tritelluroles.

We recently reported that the complex $(PNP)V(CH_2tBu)_2$ could be oxidized by chalcogen sources to promote α-hydrogen abstraction and ultimately form the alkylidene chalcogenides $(PNP)V{=}CHtBu(X)$ (X = O, S, Se, and Te) and CH_3tBu.[11] Complex **1** is remarkably stable in the solid state and in solution, but it was noted that the presence of traces of Te^0 promoted gradual transformation of **1** into another vanadium species together with cyclic ditelluretane $[(TeCHtBu)_2]$ (**2**) and tritellurolane $[Te(TeCHtBu)_2]$ (**3**).[12] Optimization of the reaction to yield these new products involved treatment of $[(PNP)V(CH_2tBu)_2]$ with an excess of Te powder (4–8 equivalents) under a static vacuum over 4 days at 90 °C; this procedure consistently yielded the dark-green insoluble vanadium complex together with the by-products **2** and **3** (Scheme 1). Evacuation of the solution was necessary in order to avoid activation of atmospheric nitrogen, which results in the formation of the known dinitrogen-bridged vanadium dimer $[\{(PNP)V{=}CHtBu\}_2(\mu_2;\eta^1,\eta^1\text{-}N_2)]$.[11a] The reaction mixture was vacuum dried and the organotellurium complexes **2** and **3** were extracted by washing the solids with hexanes or pentane. The identities of compounds **2** and **3** have been confirmed by a combination of ^1H and ^{13}C NMR spectra and chemical ionization (CI) mass

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Supporting information for this article (full synthetic, spectroscopic, and structural details for all new compounds) is available on the WWW under http://dx.doi.org/10.1002/anie.200806022.

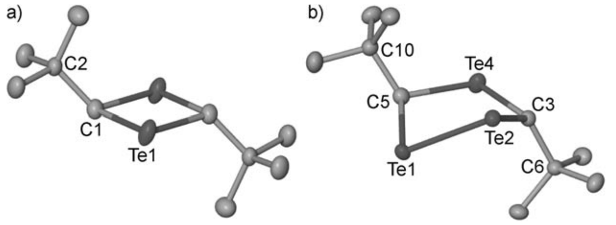


Figure 1. The molecular structures of compounds **2** (a) and **3** (b) showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

spectrometry. Given the rarity of ditelluretane[13] and tritellurolane[14a] derivatives in general, we collected single-crystal X-ray diffraction structures of each compound.[12] Figure 1 shows the head-to-tail isomers of the four- and five-membered rings **2**[15] and **3**,[16] respectively. While the structure of **2** reveals a planar four-membered ring residing on an inversion center, compound **3** incorporates a puckered five-membered ring with a Te1–Te2 distance of 2.7190(3) Å.[17] It was also determined that lower concentrations of Te (ca. 4–5 equivalents) with [(PNP)V(CH$_2$*t*Bu)$_2$] greatly enhanced the yields of **2**, while 6–8 equivalents of the chalcogen facilitated formation of **3**. Previous work has speculated that the analogous 1,2,4-triselenolane formation derives from the insertion of Se^0 into 1,3-diselenetane.[14b] In our case, treatment of the reaction mixture containing **2** and **3** (after removal of the green vanadium-containing precipitate) with Te^0 increased the concentration of **3**, thus supporting the original hypothesis that precursors such as **2** can ring expand by the uptake of elemental chalcogen. A handful of ditelluretanes that originate from transient telluroketones or perfluorinated telluracarbonyl compounds exist; however, to the best of our knowledge, the ditelluretane **2** is the first example of an isolated ditelluretane that originates from a transient telluroaldehyde [Te=CH*t*Bu] monomer.[13,14]

The insoluble green material that resulted from the reaction of **1** with an excess of Te^0 (see above) was extracted with THF, filtered, and dried under reduced pressure to afford a green powder, which was collected in 74% yield. The ^{1}H, ^{31}P ($\delta = 142$ ppm), and ^{51}V ($\delta = 2293$ ppm, triplet, $\Delta\nu_{1/2} = 490$, 299, 460 Hz) NMR spectra of the insoluble green material were consistent with a C_2-symmetric "{(PNP)V^{V}}" scaffold. As expected from the inverse electronegativity dependence of high-valent vanadium complexes, the ^{51}V resonance of this new vanadium product is significantly downfield from that of complex **1** ($\delta = 1249$ ppm, $\Delta\nu_{1/2} = 864$ Hz).[18] Unfortunately, the low solubility of this material in haloarenes and THF (unstable in CHCl$_3$ and CH$_2$Cl$_2$) prevented us from observing a ^{125}Te NMR spectroscopic signal. Crystals suitable for X-ray diffraction could be grown from solution of THF that was heated at reflux, the data confirmed formation of an unprecedented vanadium–bis(telluride) monomeric complex [(PNP)V(Te)$_2$] (**4**, Figure 2).[19] The terminal nature of the V=Te bond is clearly manifested by the short bond lengths of 2.4225(5) and 2.4223(4) Å, which are comparable to the only other crystallographically characterized terminal vanadium–telluride complex [(η^4-Me$_8$taa)V=Te] (2.433(1) and 2.435(1) Å based on two crystallographically independent molecules).[7] In addition, the intramolecular Te⋯Te distance in **4** is too long (4.0190(3) Å) for a η^2-Te$_2^{2-}$-type ligand bound to a vanadium(III) center. Some intermolecular distances of 4.0190(3) Å between Te atoms are observed in the X-ray crystal structure of **4**. The gross geometry about the metal center in **4** closely resembles other Group 5 complexes that have the same ancillary ligand PNP but contain bisalkylidene moieties composed of CH$_2$,[20] CH*t*Bu,[21] and CHSiMe$_3$.[21] It was independently found that complex **4** could be prepared from a one-pot reaction of [(PNP)VCl$_2$][11] with excess Mg and excess Te powder, albeit not in analytically pure form.[12]

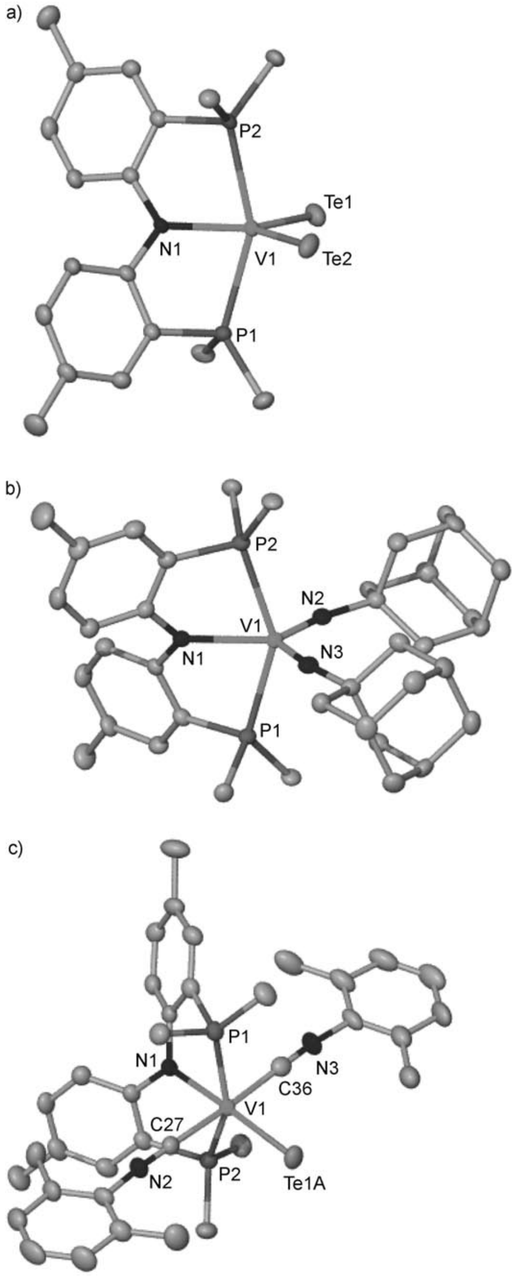
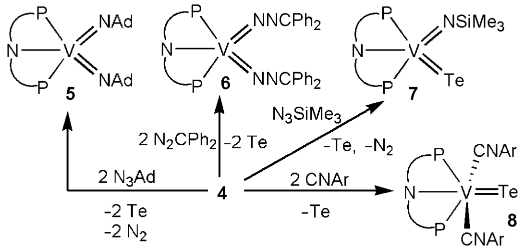


Figure 2. The molecular structures of complexes **4** (a), **5** (b), and **8** (c) with thermal ellipsoids at the 50% probability level. *i*Pr methyl groups on P, solvent, and hydrogen atoms have been excluded for clarity.

Although complex **4** appears to be resistant to thermal decomposition, the choice of reactant can result in the clean substitution of one or two Te ligands. Accordingly, treatment of **4** with two equivalents of N_3Ad (Ad = 1-adamantyl) immediately results in excision of N_2 with concomitant formation of the complex [(PNP)V(NAd)$_2$] (**5**) as yellow crystals in 41 % yield (Scheme 2). The X-ray crystal structure of **5** confirms the existence of a five-coordinate vanadium(V) bisimide complex, which is clearly indicated by the linear V-N-C 159.3(2) and 164.5(2)°) angles and short V=N bond lengths of 1.703(3) and 1.696(3) Å (Figure 2).[22] The V=N metrical parameters are comparable to the few documented monomeric vanadium complexes that have two terminal imide ligands.[23] Likewise, treatment of **4** with N_2CPh_2 also promotes release of two equivalents of Te by forming the bis(diphenylmethylene hydrazido) complex [(PNP)V-(N_2CPh_2)$_2$] (**6**; Scheme 2). Complex **6** was characterized by a combination of multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P, and ^{51}V) and CI mass spectrometry.[12] Much like complex **5**, room-temperature NMR spectroscopic studies of **6** are indicative of a C_2-symmetric system. The CI mass spectrum provides further evidence for the proposed structure, whereby N_2 has not been released, with a peak corresponding to the molecular ion at *m/z* 867.3718.[12]

Treatment of **4** with one equivalent of N_3SiMe_3 resulted in the substitution of one telluride ligand by the trimethysilylimide group to form [(PNP)V=NSiMe$_3$(Te)] (**7**) in 32 % yield (Scheme 2).[12] The addition of excess azide does not promote elimination of a second equivalent of Te, even under forcing conditions (80 °C, 12 h). The formation of compound **7** was confirmed by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P, and ^{51}V) and CI MS and, unlike **5** or **6**, the ^{1}H and ^{13}C NMR spectra are consistent with a C_1-symmetric molecule because of the substitution of only one Te ligand, coupled with the skewing of the aryl moieties in the PNP ligand. The CI mass spectrum of **7** is also consistent with its structure, and shows the molecular ion peak at *m/z* 696.1624 as well as a distinctive isotopic mass distribution that arises from the telluride ligand.[12]



Scheme 2. Synthesis of complexes **5**–**8** from reductive elimination of Te in **4**.

Complex **4** fails to react with a variety of reagents, apart from oxidants, such as P(SiMe$_3$)$_3$, OCNAr (Ar = 2,6-Me$_2$C$_6$H$_3$), B$_2$Pin$_2$ (Pin = pinacol), benzophenone, 2,3-dimethylbutadiene, and diphenylacetylene. However, treatment of **4** with two equivalents of isonitrile CNAr results in the immediate ejection of metallic Te and the simultaneous formation of the first V^{III} terminal telluride complex [(PNP)V=Te(CNAr)$_2$] (**8**) as a dichroic (purple–green) material isolated in 50 % yield. The NMR spectra of **8** are in agreement with a diamagnetic vanadium telluride species (^{51}V NMR: $\delta = 2019$ ppm, $\Delta\nu_{1/2} = 1581$ Hz; ^{125}Te NMR: very broad signal at $\delta = 3966$ ppm), while the IR spectrum of **8** clearly displays two strong ν_{CN} signals (2022 and 2002 cm^{-1}) for the bound isocyanides, which are red-shifted from the ν_{CN} signal of free isocyanide (2116 cm^{-1}). The X-ray crystal structure of **8**[24] predicates a pseudo octahedral V^{III} species (P1-V1-P2 152.58(5)°; N1-V1-Te1A 177.72(10)°; C36-V1-C27 177.23(19)°), which results from one Te^{2-} ligand in precursor **4** being substituted by two neutral isocyanides, presumably by virtue of a reductive elimination step (Figure 2). The most notable feature in the structure of **8** is the V=Te distance of 2.4603(9) Å, which is consistent with that of a terminal chalcogenide ligand.[2] In marked contrast, Parkin and Rabinovich have observed isocyanide-induced reductive coupling of two telluride ligands to form an η^2-ditellurido ligand.[5,6]

The present work illustrates how the chemistry of the alkylidene and telluride functionalities can ultimately afford rare examples of ditelluretane and tritellurolane, as well as the first vanadium–bis(telluride) complex **4**. Ditelluretanes are exceedingly rare, and our work clearly establishes a method of C=Te bond formation and subsequent dimerization of a transient telluroaldehyde [Te=CH*t*Bu], as well as dimerization/Te insertion chemistry to form a ring-expanded tritellurolane. We also demonstrate that one or both telluride ligands in precursor **4** can be readily substituted with oxidants such as azides and diphenyldiazomethane. Likewise, reductive elimination of Te^0 can be instigated with isonitriles to afford a rare example of a vanadium(III)–telluride complex. Therefore, our work has established that terminal telluride ligands have the ability to mask high- or low-valent vanadium fragments, presumably because of the weak bond dissociation enthalpy predicted for Te and 3d early-transition metals.[9]

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[15] Crystal data for **2**: $C_{10}H_{20}Te_2$, $M_r = 395.46$, triclinic, $P\bar{1}$, $a = 6.0203(6)$ Å, $b = 6.1490(6)$ Å, $c = 9.5745(9)$ Å, $\alpha = 101.704(2)°$, $\beta = 90.800(2)°$, $\gamma = 113.446(2)°$, $V = 316.64(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.074$ Mg m^{-3}, $T = 150(2)$ K, $Mo_{K\alpha} = 0.71073$ Å, absorption coefficient 4.563 mm^{-1}, $F(000) = 184$, 5533 reflections collected, 1439 independent reflections, $R_{int} = 0.0304$, GoF = 1.055, $R = 0.0209$ $[I > 2\sigma(I)]$, $wR2 = 0.0522$ $[I > 2\sigma(I)]$. CCDC 706518, 706519, 706520, 706521, 706522 (**2**–**5** and **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] Crystal data for **3**: $C_{10}H_{20}Te_3$, $M = 523.06$, monoclinic, $P21/n$, $a = 12.7214(7)$ Å, $b = 5.9309(3)$ Å, $c = 19.0338(11)$ Å, $\beta = 96.5310(10)°$, $V = 1426.77(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.435$ Mg m^{-3}, $T = 150(2)$ K, $Mo_{K\alpha} = 0.71073$ Å, absorption coefficient 6.058 mm^{-1}, $F(000) = 944$, 24037 reflections collected, 3230 independent reflections, $R_{int} = 0.0195$, GoF = 1.074, $R = 0.0147$ $[I > 2\sigma(I)]$, $wR2 = 0.0319$ $[I > 2\sigma(I)]$.

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[19] Crystal data for **4**: $C_{26}H_{40}NP_2Te_2V$, $M_r = 734.67$, monoclinic, $P21/c$, $a = 7.2758(4)$ Å, $b = 14.7745(10)$ Å, $c = 27.0582(18)$ Å, $\beta = 95.3410(10)°$, $V = 2896.0(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.685$ Mg m^{-3}, $T = 150(2)$ K, $Mo_{K\alpha} = 0.71073$ Å, absorption coefficient 2.442 mm^{-1}, $F(000) = 1440$, 33700 reflections collected, 8801 independent reflections, $R_{int} = 0.0337$, GoF = 1.013, $R = 0.0293$ $[I > 2\sigma(I)]$, $wR2 = 0.0609$ $[I > 2\sigma(I)]$.

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[22] Crystal data for **5**: $C_{46}H_{70}N_3P_2V{\cdot}C_6H_{12}{\cdot}0.5C_6\ H_{14}$, $M_r = 905.17$, monoclinic, $P21/c$, $a = 12.6324(13)$ Å, $b = 36.310(4)$ Å, $c = 11.6032(13)$ Å, $\beta = 101.219(2)°$, $V = 5220.4(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.152$ Mg m^{-3}, $T = 123(2)$ K, $Mo_{K\alpha} = 0.71073$ Å, absorption coefficient 0.289 mm^{-1}, $F(000) = 1972$, 63610 reflections collected, 9229 independent reflections, $R_{int} = 0.0611$, GoF = 1.039, $R = 0.0479$ $[I > 2\sigma(I)]$, $wR2 = 0.0988$ $[I > 2\sigma(I)]$.

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[24] Crystal data for **8**: $C_{44}H_{58}N_3P_2Te_{1.09}V$, $M_r = 880.58$, monoclinic, $P21/c$, $a = 12.439(3)$ Å, $b = 18.092(4)$ Å, $c = 20.004(4)$ Å, $\beta = 106.380(4)°$, $V = 4319.2(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.354$ Mg m^{-3}, $T = 150(2)$ K, $Mo_{K\alpha} = 0.71073$ Å, absorption coefficient 1.056 mm^{-1}, $F(000) = 1810$, 31624 reflections collected, 7713 independent reflections, $R_{int} = 0.0800$, GoF = 1.047, $R = 0.0574$ $[I > 2\sigma(I)]$, $wR2 = 0.1453$ $[I > 2\sigma(I)]$. The crystals of **8** were found to contain co-crystals of complex $C_{44}H_{58}N_3P_2Te_2V$ in a 9:1 ratio. The Te disorder was refined with a set of restraints and constraints.