Oxidative Cleavage of the Te–Te Bond in η^2-Ditellurido Complexes: Syntheses and Structures of $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ (M = Mo, W)

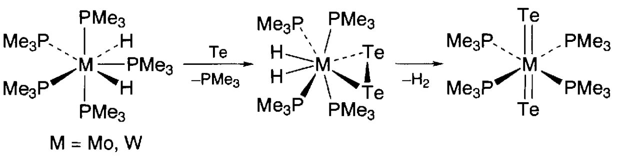
Vincent J. Murphy, Daniel Rabinovich, Shannon Halkyard and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027, USA

The η^2-ditellurido derivatives, $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ (M = Mo, W) are synthesized by the reactions of $M(PMe_3)_5H_2$ with elemental tellurium; the conversion of $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ to the terminal tellurido complexes $M(PMe_3)_4(Te)_2$ provides an unprecedented example of a transformation that involves oxidative cleavage of a ditellurido ligand at a single metal centre.

The coupling and cleavage of ligands at a single transition metal centre represent a class of fundamental transformations in organometallic chemistry. Depending upon the valence nature of both (*a*) the ligands to be coupled and (*b*) the coupled ligand in the product, the coupling reaction may be regarded as either reductive, redox-neutral or oxidative, with respect to the metal.[1] Coupling and cleavage reactions may play an active role in a variety of important transformations,[1,2] including those involving chalcogenido ligands. However, in spite of the potential importance of reactions involving the interconversion of $[M](E)_2$ and $[M](\eta^2\text{-}E_2)$ moieties (E = O, S, Se, Te), relatively few well-characterized examples of such transformations have been described. Here we extend our studies of transition metal tellurido chemistry with the report of transformations that involve the formal oxidative cleavage of a ditellurido ligand at a single metal centre.

We have recently described the first example of the reductive coupling of two terminal tellurido ligands to give the ditellurido complex $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$.[3] To date, however, we have not observed any subsequent reactivity of $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ deriving from the reverse reaction, namely the oxidative cleavage of the η^2-ditellurido ligand. Nevertheless, since the interconversion between $[M](\eta^2\text{-}Te_2)$ and $[M](Te)_2$ moieties is likely to be sensitive to the nature of the metal centre, we have sought to synthesize additional η^2-ditellurido complexes, with the prospect that they may be more susceptible to oxidative cleavage. In this regard, we have discovered that the η^2-ditellurido complexes $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ (M = Mo, W) may be synthesized in good yield by the reactions of $M(PMe_3)_5H_2$[4] with elemental tellurium (Scheme 1).† The molecular structures of $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ (M = Mo, W) have been determined by X-ray diffraction, an ORTEP diagram for $Mo(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ is shown in Fig. 1.‡ The two complexes are isostructural with similar M–Te and Te–Te bond lengths (Table 1). The structural details of the $[W(\eta^2\text{-}Te_2)]$ moiety in $W(PMe_3)_4(\eta^2{=}Te_2)H_2$ are also similar to those in $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$.[3] The M–Te bond lengths in these η^2-ditellurido complexes fall within the range of other M–Te single bonds,[5] but are substantially longer than the corresponding multiple bonds in $M(PMe_3)_4(Te)_2$ [Mo=Te 2.597(1); W=Te 2.596(1) Å].[6] The Te–Te bond lengths in $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ are also comparable to the values reported for other mononuclear ditellurido complexes (2.67–2.69 Å), such as $\{\eta^3\text{-}PhP(CH_2CH_2PPh_2)_2\}Ni(\eta^2\text{-}Te_2)$ [2.668(1) Å], $\{\eta^3\text{-}MeC(CH_2PPh_2)_3\}Ni(\eta^2\text{-}Te_2)$ [2.665(2) Å],[7] $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ [2.680(2) Å],[3] $(C_5Me_5)_2Ta(\eta^2\text{-}Te_2)H$ [2.678(2) Å][8] and $(C_5Me_5)_2Zr(\eta^2\text{-}Te_2)(CO)$ [2.69(2) Å].[9] The hydride ligands in $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ were also located by the X-ray diffraction studies, and their presence is strongly supported by the observation of appropriate signals in the ^1H NMR (δ_{Mo} −4.73, δ_W −3.94) and IR (ν_{Mo-H} = 1855, ν_{W-H} = 1900 cm^{-1}) spectra.§



Scheme 1

Importantly, the reactivity of the ditellurido complexes $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ furnishes good evidence for the unprecedented oxidative cleavage of the ditellurido ligand to give a bis(tellurido) complex. Specifically, solutions of $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ eliminate H_2 to give, *inter alia*, the terminal tellurido complexes $M(PMe_3)_4(Te)_2$.¶ Although the mechanism by which $M(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ converts to $M(PMe_3)_4(Te)_2$ is unknown, the oxidative cleavage of the ditellurido ligand may be conceptually considered to occur within a 16-electron intermediate of the types $[M(PMe_3)_4(\eta^2\text{-}Te_2)]$ or $[M(PMe_3)_3(\eta^2\text{-}Te_2)H_2]$. Indeed, for the molybdenum system, preliminary studies indicate that the decomposition of $Mo(PMe_3)_4(\eta^2\text{-}Te_2)H_2$ is inhibited by the addition of PMe_3, so that a mechanism involving initial dissociation of PMe_3 may operate. For this reason, the presence of PMe_3 is critical in the preparation of $Mo(PMe_3)_4(\eta^2\text{-}Te_2)H_2$.

The observation of both reductive coupling and oxidative cleavage reactions in these molybdenum and tungsten systems is of relevance since well-defined examples of such transformations involving chalcogenido ligands are uncommon. Indeed, such reactions do not generally appear to be kinetically facile. For example, the valence isomers $(\eta^2\text{-}Et_2NCS_2)_2Mo(\eta^2\text{-}ONPh)$ and $(\eta^2\text{-}Et_2NCS_2)_2Mo(O)(NPh)$ do not interconvert under either thermal or photochemical conditions.[10] Similarly, evidence has been presented to suggest that the proposed peroxo

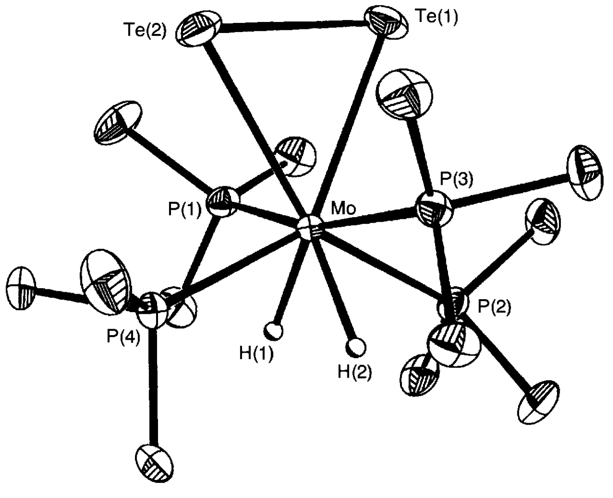


Fig. 1 ORTEP drawing for $Mo(PMe_3)_4(\eta^2\text{-}Te_2)H_2$

Table 1 Bond lengths of $[M(\eta^2\text{-}Te_2)]$ moieties (M = Mo, W)

Compound	M–Te/Å	Te–Te/Å	Ref.
$Mo(PMe_3)_4(\eta^2\text{-}Te_2)H_2$	2.861(1), 2.899(1)	2.698(1)	This work
$W(PMe_3)_4(\eta^2\text{-}Te_2)H_2$	2.856(2), 2.903(2)	2.697(2)	This work
$W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$	2.868(2), 2.877(2)	2.680(2)	3

intermediate {[Tp]Re(O)(η^2-O_2)} does not simply rearrange to the trioxo complex [Tp]Re(O)$_3$, but that a more complicated bimolecular pathway is responsible for its ultimate formation (*[Tp]* = η^3-HBpz$_3$).[11] Nevertheless, pathways that involve oxidative cleavage and reductive coupling have been postulated for several other systems. For example, the reductive coupling of two sulfido ligands may be considered as a possible sequence in several reactions of thiometallate derivatives,[12–16] such as *(a)* the RSSR induced conversion of $[Mo(S)_4]^{2-}$ to $[(\eta^2\text{-}S_2)(S)Mo(\mu\text{-}S)]_2{}^{2-}$,[17] and *(b)* the formation of W(O)(η^2-S_2)$_2$(bipy) by reaction of $[W(S)_4]^{2-}$ with aqueous HCl in the presence of bipy.[18] Similarly, oxidative cleavage and reductive coupling reactions involving oxo ligands include *(a)* the photochemical conversion of (TPP)Mo(η^2-O_2)$_2$ to *cis*-(TPP)Mo(O)$_2$,[19] and *(b)* the photoinduced decomposition of $[Mn(O)_4]^-$.[20]

In summary, the mononuclear molybdenum and tungsten η^2-ditellurido complexes M(PMe$_3$)$_4$(η^2-Te$_2$)H$_2$ (M = Mo, W) have been synthesized by the reactions of M(PMe$_3$)$_5$H$_2$ with elemental tellurium. The conversions of M(PMe$_3$)$_4$(η^2-Te$_2$)H$_2$ to M(PMe$_3$)$_4$(Te)$_2$ provide interesting and unprecedented examples of transformations that involve the oxidative cleavage of a ditellurido ligand at a single metal centre. As such, the transformations provide a valuable complement to our previous observation of the microscopic reverse, *i.e.* the reductive coupling of two tellurido ligands. Hence, by varying the ligand array about a metal centre, the relative favourabilities of [M](η^2-Te$_2$) *vs.* [M](Te)$_2$ moieties may be strongly influenced.

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Footnotes

† Synthesis of Mo(PMe$_3$)$_4$(η^2-Te$_2$)H$_2$: a solution of Mo(PMe$_3$)$_5$H$_2$ (1.00 g, 2.1 mmol) in benzene (25 ml) was treated with tellurium powder (0.54 g, 4.2 mmol) and PMe$_3$ (*ca.* 0.5 ml, 4.9 mmol) at −78 °C. The mixture was allowed to warm to room temp. and stirred for 40 min, producing a dark brown solution. The volatile components were removed under reduced pressure and the residue was extracted into toluene (*ca.* 40 ml) and concentrated to *ca.* 20 ml. Pentane (*ca.* 5 ml) was added and the solution placed at −78 °C, giving black microcrystals of Mo(PMe$_3$)$_4$(η^2-Te$_2$)H$_2$ (0.50 g). A further crop of crystals was obtained by concentrating and cooling the supernatant solution to give a combined yield of 0.82 g (60%). The tungsten complex W(PMe$_3$)$_4$(η^2-Te$_2$)H$_2$ was prepared by an analogous procedure, but in the absence of PMe$_3$.

‡ *Crystal data* for $C_{12}H_{38}MoP_4Te_2$: monoclinic, $P2_1/n$ (no. 14), a = 9.623(2), b = 15.297(3), c = 16.504(2) Å, β = 98.31(2)°, V = 2403(1) Å^3, Z = 4, R = 0.0275, R_w = 0.0392. For $C_{12}H_{38}P_4Te_2W$: monoclinic, $P2_1/n$ (no. 14), a = 9.603(2), b = 15.276(5), c = 16.476(3) Å, β = 98.12(1)°, V = 2400(1) Å^3, Z = 4, R = 0.0522, R_w = 0.0522. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The η^2-ditellurido moieties of M(PMe$_3$)$_4$(η^2-Te$_2$)H$_2$ have also been characterized by ^{125}Te NMR spectroscopy [δ_{Mo} −696, δ_W −884] and the resonances are shifted significantly upfield from the corresponding values for the related terminal tellurido derivatives M(PMe$_3$)$_4$(Te)$_2$ [δ_{Mo} 1507, δ_W 958].[6]

¶ W(PMe$_3$)$_4$(Te)$_2$ is obtained in *ca.* 35% yield by heating M(PMe$_3$)$_4$(η^2-Te$_2$)H$_2$ at 55 °C for 4 h. The molybdenum analogue is considerably less stable and decomposes over a period of 1 h at 40 °C to give Mo(PMe$_3$)$_4$(Te)$_2$ (*ca.* 15%) and other unidentified products.

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