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Terminal Sulfido, Selenido, and Tellurido Complexes of Tungsten

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The terminal chalcogenido complexes *trans*-$W(PMe_3)_4(E)_2$ (E = S, Se, Te) have been synthesized by the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with H_2E (E = S, Se) and elemental Te. $W(PMe_3)_4(Te)_2$ is the first example of a transition-metal complex containing a terminal tellurido ligand. Each of the chalcogenido complexes $W(PMe_3)_4(E)_2$ reacts reversibly with RCHO to yield the η^2-aldehyde derivatives $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$, although the equilibrium constants vary strongly as a function of the chalcogen, with $K_S \gg K_{Se} > K_{Te}$. The PMe_3 ligands of $W(PMe_3)_4(S)_2$ and $W(PMe_3)_4(Se)_2$ are readily displaced by Bu^tNC to give $W(PMe_3)_2(CNBu^t)_2(E)_2$. In marked contrast, however, the corresponding reaction of the tellurido derivative $W(PMe_3)_4(Te)_2$ with Bu^tNC results in the unprecedented coupling of the two terminal tellurido ligands, leading to the formation of the η^2-ditellurido derivative $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$. Structural and bonding aspects of the terminal chalcogenido complexes have been probed by X-ray diffraction, while ^{77}Se and ^{125}Te NMR spectroscopies have identified a linear correlation between ^{77}Se and ^{125}Te NMR chemical shifts for structurally analogous selenido and tellurido complexes. $W(PMe_3)_4(S)_2$ is monoclinic, $P2/n$ (No. 13), $a = 15.914(2)$ Å, $b = 9.682(2)$ Å, $c = 15.926(3)$ Å, $\beta = 111.92(2)°$, $Z = 4$. $W(PMe_3)_4(Se)_2$ is monoclinic, $P2/n$ (No. 13), $a = 16.040(5)$ Å, $b = 9.738(2)$ Å, $c = 16.096(3)$ Å, $\beta = 113.27(2)°$, $Z = 4$. $W(PMe_3)_4(Te)_2$ is tetragonal, $I\bar{4}2m$ (No. 121), $a = b = 9.717(1)$ Å, $c = 12.360(2)$ Å, $Z = 2$. $W(PMe_3)_4(Se)H_2$ is monoclinic, Cc (No. 9), $a = 9.580(2)$ Å, $b = 15.757(3)$ Å, $c = 14.860(3)$ Å, $\beta = 98.54(2)°$, $Z = 4$. $W(PMe_3)_2(CNBu^t)_2(S)_2$ is monoclinic, $P2_1/n$ (No. 14), $a = 11.003(2)$ Å, $b = 10.513(3)$ Å, $c = 11.947(3)$ Å, $\beta = 109.87(2)°$, $Z = 2$. $W(PMe_3)_2(CNBu^t)_2(Se)_2$ is monoclinic, $P2_1/n$ (No. 14), $a = 11.147(5)$ Å, $b = 10.617(5)$ Å, $c = 11.973(4)$ Å, $\beta = 110.16(3)°$, $Z = 2$. $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCH_2)$ is orthorhombic, $Pnma$ (No. 62), $a = 10.441(3)$ Å, $b = 11.299(4)$ Å, $c = 13.812(4)$ Å, $Z = 4$. $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHPh)$ is monoclinic, $P2_1/c$ (No. 14), $a = 12.561(3)$ Å, $b = 8.684(1)$ Å, $c = 18.182(3)$ Å, $\beta = 108.57(2)°$, $Z = 4$. $W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHPh)$ is monoclinic, $P2_1/c$ (No. 14), $a = 12.563(5)$ Å, $b = 8.731(4)$ Å, $c = 18.461(6)$ Å, $\beta = 109.22(3)°$, $Z = 4$. $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHPh)$ is monoclinic, $P2_1/n$ (No. 14), $a = 12.661(2)$ Å, $b = 8.931(1)$ Å, $c = 18.779(4)$ Å, $\beta = 108.47(2)°$, $Z = 4$. $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ is orthorhombic, $Pbca$ (No. 61), $a = 18.097(4)$ Å, $b = 18.978(2)$ Å, $c = 19.741(3)$ Å, $Z = 8$.

Introduction

Multiple bonding between atoms has long attracted the attention of synthetic, structural, and theoretical chemists alike. However, despite such intense interest, the development of multiple-bonding to the heavier nonmetals (*i.e.* those of the third and higher periods) has been remarkably slow.[1] For example, whereas multiple bonding is a prominent feature in the chemistry of carbon, the subject of multiple bonding is substantially less developed for its heavier congeners.[2] Indeed, the first stable disilene derivative, $Mes_2Si{=}SiMes_2$, was only discovered 14 years ago.[3] A similar situation is also observed with respect to multiple bonding of the heavier main-group elements to the transition metals. It is, therefore, not surprising that a 1988 monograph on the subject of metal−ligand multiple bonding was devoted almost entirely to complexes with multiple bonds to the second row elements, namely, carbon, nitrogen, and oxygen.[4,5] As a consequence of the paucity of transition-metal complexes that exhibit multiple bonds to the heavier non-metals, a considerable quest for such complexes has ensued over recent years. Some significant recent developments to this area include the syntheses of the first terminal alkyl- and aryl-substituted silylene complexes $[Cp^*Ru(PMe_3)_2(SiR_2)][B(C_6F_5)_4]$ (R = Ph, Me)[6−8] and also the terminal phosphinidine and arsinidene derivatives $Cp_2M[P(C_6H_2Bu^t_3)]$ (M = Mo, W),[9] $W(PMePh_2)_2(CO)Cl_2[P(C_6H_2Bu^t_3)]$,[10] $Cp_2Zr[P(C_6H_2Bu^t_3)](PMe_3)$,[11] [$\eta^4$-

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$N(CH_2CH_2NSiMe_3)_3]TaPCy$,[12] and $(silox)_3TaEPh$ (silox = $Bu^t{}_3SiO$; E = N, P, As).[13,14]

With respect to the chalcogens, interest in transition-metal complexes with [M=E] multiple bonds (E = O, S, Se, Te) derives from the possible roles that such moieties may play in *(i)* metal-based oxidations,[15] *(ii)* hydrodesulfurization,[16-18] *(iii)* biological systems,[19-21] and *(iv)* the formation of solid-state chalcogenides with applications in the electronics industry.[22-24] The metal-oxo moiety is also of interest since it represents the most common class of transition-metal-ligand multiple bond encountered,[25] perhaps not a surprising observation in view of the abundance of O_2 and H_2O in the environment. In contrast, however, surprisingly fewer studies have been reported on the closely related terminal metal-sulfido, -selenido, and -tellurido systems.[26,27] An illustrative example of the distribution of studies on terminal-chalcogenido complexes is provided by a search of the Cambridge Structural Database (Figure 1).[28] Thus, it is evident that few transition-metal complexes containing terminal [M=E] moieties have been structurally characterized for the heavier chalcogens, which is in part a manifestation of the increased difficulty with which the heavier main group elements form multiple *versus* single bonds.[1] Indeed, the heavier chalcogens are commonly found either *(i)* to bridge two or more metal centers[29] or *(ii)* to form polychalcogenide ligands,[30] a reflection of the marked tendency of sulfur, selenium, and tellurium to catenate.[31]

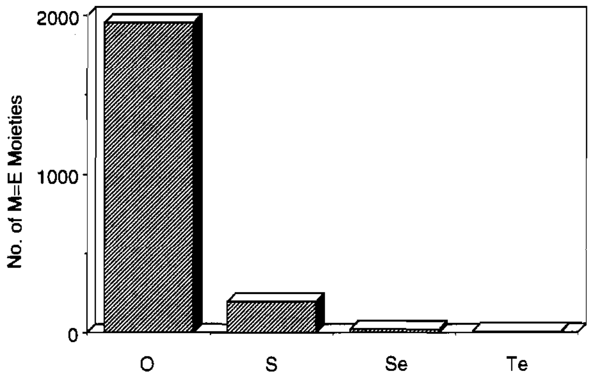

Figure 1. Distribution of structurally characterized complexes with terminal chalcogenido ligands.

In this paper we describe the syntheses of the terminal chalcogenido complexes *trans*-$W(PMe_3)_4(E)_2$ (E = S, Se, Te).

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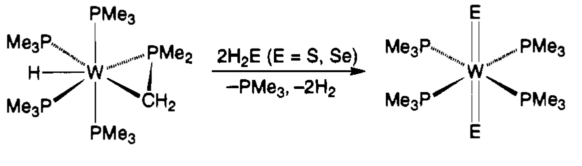
Of most significance, the first example of a terminal tellurido complex of the transition metals, namely, $W(PMe_3)_4(Te)_2$, is reported. A comprehensive account of the chemistry and structures of the first series of terminal sulfido, selenido, and tellurido complexes of tungsten is described, thereby serving to highlight similarities and differences in the chemistry of the system as a function of the chalcogen.[32]

Results and Discussion

1. Tungsten(IV) Bis(chalcogenido) Complexes, *trans*-$W(PMe_3)_4(E)_2$ (E = S, Se, Te). (a) Syntheses of *trans*-$W(PMe_3)_4(E)_2$ (E = S, Se, Te). The relative dearth of terminal sulfido, selenido, and tellurido complexes of the transition metals, in comparison to their oxo analogues, is in part due to the lack of suitable synthetic methods for their preparation.[27b] For example, whereas terminal metal oxo complexes are often obtained by the reactions of transition-metal complexes with either O_2 or H_2O (frequently adventitious!), related reactions of the heavier elemental chalcogens commonly give products in which E—E bonds are present.[33] In view of the facile formation of complexes with E—E bonds, we sought to minimize the opportunity for E—E bond formation by using alternative reagents with only a single chalcogen atom, such as H_2E. However, since the use of H_2E (E = S, Se, Te) in the preparation of terminal chalcogenido derivatives is not well documented, we rationalized that a highly reactive metal complex would be required in order to promote the chalcogen abstraction. In this vein, we have discovered that the electron-rich complex $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$[34] is capable of abstracting chalcogen atoms from both H_2S and H_2Se. Thus, the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with H_2S and H_2Se provide convenient access to the terminal sulfido and selenido complexes $W(PMe_3)_4(S)_2$ and $W(PMe_3)_4(Se)_2$, respectively (eq 1). In each case, the reactions are accompanied by elimination of H_2.



(1)

The preparations of the terminal sulfido and selenido complexes $W(PMe_3)_4(E)_2$ (E = S, Se) by the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with H_2S and H_2Se suggested that the corresponding reaction with H_2Te would provide a plausible approach for the synthesis of the terminal tellurido analogue $W(PMe_3)_4(Te)_2$. However, the inherent instability of H_2Te[35] limits the feasibility of such a method, so that alternative routes to the bis(tellurido) analogue were sought. Significantly, it was discovered that the reaction between $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and elemental tellurium provides a straightforward synthesis for the tellurido analogue $W(PMe_3)_4(Te)_2$ (eq 2).

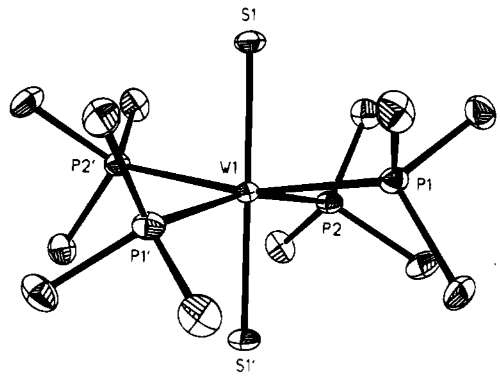
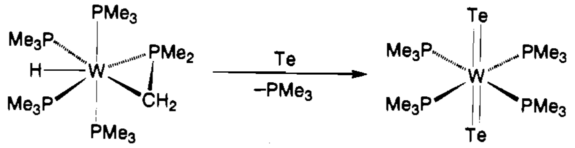


Figure 2. Molecular structure of $W(PMe_3)_4(S)_2$.



(2)

The synthesis of $W(PMe_3)_4(Te)_2$ by such a method is noteworthy since the analogous reaction with elemental sulfur results in the immediate and complete decomposition of the tungsten complex, giving Me_3PS as the only product identifiable by ^1H NMR spectroscopy. However, the corresponding reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with elemental Se does give the selenido complex $W(PMe_3)_4(Se)_2$, albeit contaminated with significant quantities of Me_3PSe. The isolation of the monomeric terminal chalcogenido complexes $W(PMe_3)_4(E)_2$ (E = S, Se, Te) contrasts with the bridging dinuclear cobalt complexes $[(Me_3P)_3Co]_2(\mu\text{-}E)_2$ (E = S, Se, Te) obtained by the reactions of $Co(PMe_3)_4$ with the elemental chalcogens.[36]

Although we have been able to prepare the sulfido, selenido, and tellurido complexes $W(PMe_3)_4(E)_2$, we have not yet been able to isolate the corresponding oxo derivative $W(PMe_3)_4(O)_2$. For example, attempts to prepare $W(PMe_3)_4(O)_2$ by the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with reagents such as H_2O, O_2, and N_2O resulted in substantial decomposition and the formation of Me_3PO. It is noteworthy, however, that related oxo complexes of the type *trans*-$M(CO)_4(O)_2$ (M = Mo, W) have been identified as intermediates during the photolysis of $M(CO)_6$ in O_2-doped Ar or CH_4 matrices at 10 K.[37-39]

(b) Molecular Structures and Spectroscopic Properties of *trans*-$W(PMe_3)_4(E)_2$ (E = S, Se, Te). The molecular structures of the terminal chalcogenido complexes $W(PMe_3)_4(E)_2$ (E = S, Se, Te) have been determined by single crystal X-ray diffraction, as illustrated in Figures 2–4. Selected bond lengths and angles for $W(PMe_3)_4(E)_2$ are presented in Tables 1–3. Although not isomorphous, the molecular structures of

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(32) Portions of this work have been published: (a) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 5904–5905. (b) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 9421–9422. (c) Rabinovich, D., Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 9822–9823. (d) Rabinovich, D.; Parkin, G. *Inorg. Chem.* **1994**, *33*, 2313–2314.

(33) See, for example, references 27b and 30d and: Bruner, H.; Janietz, N.; Meier, W.; Wachter, J.; Herdtweck, E.; Herrmann, W. A.; Serhadli, O.; Ziegler, M. L. *J. Organomet. Chem.* **1988**, *347*, 237–252.

(34) (a) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Bandy, J. A.; Grebenik, P. D.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 2025–2035. (b) Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2227–2236.

(35) H_2Te must be handled in the dark below 0 °C to avoid decomposition. See: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1986; pp 899–900.

(36) Klein, H.-F.; Gass, M.; Koch, U.; Eisenmann, B.; Schäfer, H. *Z. Naturforsch.* **1988**, *43b*, 830–838.

(37) Crayston, J. A.; Almond, M. J.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1984**, *23*, 3051–3056.

(38) In contrast, the corresponding reaction of $Cr(CO)_6$ generates an intermediate that has been identified as four-coordinate tetrahedral $Cr(CO)_2(O)_2$. See: Poliakoff, M.; Smith, K. P.; Turner, J. J.; Wilkinson, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 651–657.

(39) For related studies on photooxidation of $M(CO)_6$, see: (a) Almond, M. J.; Downs, A. J.; Perutz, R. N. *Inorg. Chem.* **1985**, *24*, 275–281. (b) Almond, M. J.; Hahne, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2255–2260. (c) Almond, M. J.; Crayston, J. A.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 19–25. (d) Almond, M. J.; Downs, A. J. *J. Chem. Soc., Dalton Trans.* **1988**, 809–817. (e) Almond, M. J. *Chem. Soc. Rev.* **1994**, *23*, 309–317.

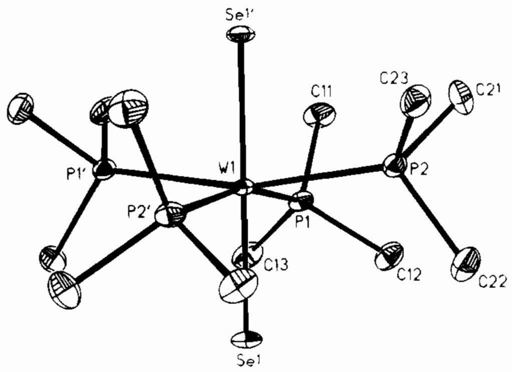

Figure 3. Molecular structure of W(PMe$_3$)$_4$(Se)$_2$.

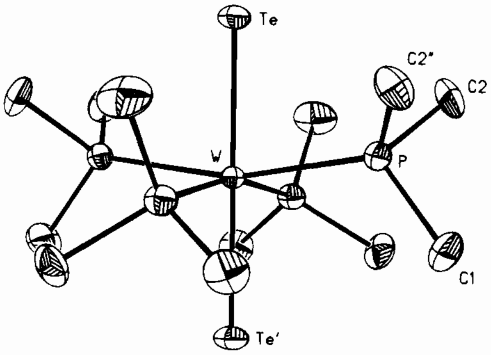

Figure 4. Molecular structure of W(PMe$_3$)$_4$(Te)$_2$.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for W(PMe$_3$)$_4$(S)$_2$

molecule 1		molecule 2	
W(1)−S(1)	2.253(3)	W(2)−S(2)	2.251(3)
W(1)−P(1)	2.503(3)	W(2)−P(3)	2.505(3)
W(1)−P(2)	2.504(3)	W(2)−P(4)	2.497(3)
S(1)−W(1)−S(1′)	179.5(1)	S(2)−W(2)−S(2′)	179.6(1)
S(1)−W(1)−P(1)	82.8(1)	S(2)−W(2)−P(3)	82.8(1)
S(1)−W(1)−P(2)	96.8(1)	S(2)−W(2)−P(4)	97.7(1)
S(1)−W(1)−P(1′)	97.6(1)	S(2)−W(2)−P(3′)	97.5(1)
S(1)−W(1)−P(2′)	82.8(1)	S(2)−W(2)−P(4′)	82.1(1)
P(1)−W(1)−P(2)	90.6(1)	P(3)−W(2)−P(4)	89.8(1)
P(1)−W(1)−P(1′)	90.5(1)	P(3)−W(2)−P(3′)	92.3(1)
P(2)−W(1)−P(2′)	91.8(1)	P(4)−W(2)−P(4′)	92.0(1)
P(1)−W(1)−P(2′)	165.6(1)	P(3)−W(2)−P(4′)	164.9(1)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for W(PMe$_3$)$_4$(Se)$_2$

molecule 1		molecule 2	
W(1)−Se(1)	2.380(1)	W(2)−Se(2)	2.380(1)
W(1)−P(1)	2.502(2)	W(2)−P(3)	2.503(3)
W(1)−P(2)	2.504(3)	W(2)−P(4)	2.495(3)
Se(1)−W(1)−Se(1′)	179.4(1)	Se(2)−W(2)−Se(2′)	179.5(1)
Se(1)−W(1)−P(1)	82.9(1)	Se(2)−W(2)−P(3)	82.5(1)
Se(1)−W(1)−P(2)	96.8(1)	Se(2)−W(2)−P(4)	82.7(1)
Se(1)−W(1)−P(1′)	97.5(1)	Se(2)−W(2)−P(3′)	97.9(1)
Se(1)−W(1)−P(2′)	82.8(1)	Se(2)−W(2)−P(4′)	97.0(1)
P(1)−W(1)−P(2)	90.7(1)	P(3)−W(2)−P(4)	165.2(1)
P(1)−W(1)−P(1′)	90.3(1)	P(3)−W(2)−P(3′)	91.9(1)
P(2)−W(1)−P(2′)	91.7(1)	P(4)−W(2)−P(4′)	91.8(1)
P(1)−W(1)−P(2′)	165.7(1)	P(3)−W(2)−P(4′)	90.0(1)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for W(PMe$_3$)$_4$(Te)$_2$

W−Te	2.596(1)	W−P	2.508(2)
Te−W−Te′	180.0	P−W−P′	91.1(1)
Te−W−P	82.1(1)	P−W−P″	164.2(1)
Te−W−P′	97.9(1)		

W(PMe$_3$)$_4$(E)$_2$ are similar and are based on a distorted octahedron, with two axial *trans* chalcogenido ligands and four PMe$_3$ groups ruffled in the equatorial plane. In this regard, the structures of W(PMe$_3$)$_4$(E)$_2$ resemble those observed for other *trans*-M(PR$_3$)$_4$X$_2$ complexes, *e.g.*, *trans*-Mo(PMe$_3$)$_4$Cl$_2$.[40] As would be expected, the average W=E double bond lengths in W(PMe$_3$)$_4$(E)$_2$ [d(W=S) = 2.253[3] Å, d(W=Se) = 2.380[1] Å, d(W=Te) = 2.596(1) Å] are shorter than the corresponding typical W−E single bond values [d(W−S) = 2.39 Å, d(W−Se) = 2.45 Å, d(W−Te) = 2.82 Å].[41] The W=E bond lengths in W(PMe$_3$)$_4$(E)$_2$ are also very similar to the respective Mo=E bond lengths in the recently reported molybdenum analogues Mo(PMe$_3$)$_4$(E)$_2$.[42]

In view of the fact that chalcogenido and imido ligands are isoelectronic, it is interesting to contrast the stoichiometry and structures of the bis(chalcogenido) complexes W(PMe$_3$)$_4$(E)$_2$ with those of the related bis(imido) complexes W(PMe$_2$Ph)$_2$(NAr)$_2$ and W(PMePh$_2$)$_2$(NAr)$_2$ (Ar = 2,6-Pr$^i_2$C$_6$H$_3$) prepared by Schrock[43] and Mo(PMe$_3$)$_2$(NBu^t)$_2$ and Mo(PMe$_3$)$_2$(NAr)$_2$ (Ar = 2,6-Pr$^i_2$C$_6$H$_3$) prepared by Gibson.[44] Thus, whereas the chalcogenido ligands favor the formation of six-coordinate 18-electron complexes, the imido ligands favor four-coordinate *pseudo*-tetrahedral derivatives. Such an observation may be a consequence of the increased bulk of the NAr moiety and also may reflect an increased preference for the imido, *versus* chalcogenido, ligand to donate its lone pair of electrons to an electron-deficient metal center.

The terminal chalcogenido complexes W(PMe$_3$)$_4$(E)$_2$ (E = S, Se, Te) have been characterized in solution by multinuclear NMR spectroscopy. While the ^{1}H, ^{13}C, and ^{31}P NMR spectra of each of the derivatives W(PMe$_3$)$_4$(E)$_2$ are qualitatively similar, a combination of ^{31}P and ^{125}Te NMR spectroscopies furnishes decisive information concerning the structure of the telluride derivative W(PMe$_3$)$_4$(Te)$_2$ in solution. For example, the relative intensities of the tungsten ($^1J_{W-P}$ = 238 Hz) to tellurium ($^2J_{Te-P}$ = 17 Hz) satellites [1.0(1):1] of the ^{31}P NMR signal at δ −51.2 ppm (Figure 5) compares favorably with that predicted for a molecule of composition W(PMe$_3$)$_4$(Te)$_2$ [1.1:1],[45] thereby providing evidence for the presence of two terminal telluride ligands. Moreover, W(PMe$_3$)$_4$(Te)$_2$ is also characterized by a ^{125}Te NMR signal at δ 950 ppm which exhibits coupling to both tungsten ($^1J_{W-Te}$ = 190 Hz; ^{183}W, I = 1/2, 14.3%) and the four equivalent phosphorus nuclei of the PMe$_3$ groups (quintet, $^2J_{Te-P}$ = 17 Hz), as illustrated in Figure 6.

To our knowledge, W(PMe$_3$)$_4$(Te)$_2$ is the first example of a transition metal complex that possesses a *terminal* metal-tellurium double bond, M=Te. In this regard, it is worth noting

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(40) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *Polyhedron* **1983**, *2*, 185−193.

(41) The W−E bond lengths listed are the mean values obtained from a search of the Cambridge Structural Database (Version 5.09, April 1995) for bonds between tungsten and a two-coordinate chalcogen. The range of W−E bond lengths are d(W−S) = 2.03−2.72 Å, d(W−Se) = 2.32−2.70 Å, and d(W−Te) = 2.67−2.88 Å.

(42) Murphy, V. J.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 3522−3528.

(43) (a) Williams, D. S.; Schofield, M. H.; Schrock, R. R. *Organometallics* **1993**, *12*, 4560−4571. (b) Williams, D. S.; Schofield, M. H.; Anhaus, J. T.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6728−6729.

(44) Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Wilson, C. *J. Organomet. Chem.* **1993**, *462*, C15−C17.

(45) The ratio of the intensities of the tungsten to tellurium satellites in the ^{31}P{1H} NMR spectrum of W(PMe$_3$)$_4$(Te)$_2$ is dependent on the natural abundances of NMR active isotopes, adjusted for the statistical distribution of such isotopes in the molecule. Specifically, the probability of having a single ^{125}Te isotope (abundance = 7%) present in W(PMe$_3$)$_4$(Te)$_2$ is 2 × 0.07 × 0.93 = 0.13 (13%). Thus, the ratio of ^{183}W (abundance = 14.3%) to ^{125}Te satellite intensities is 14.3%/13% = 1.1.

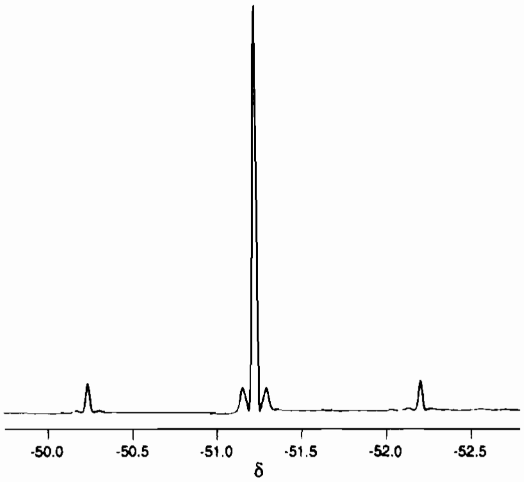


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of $W(PMe_3)_4(Te)_2$.

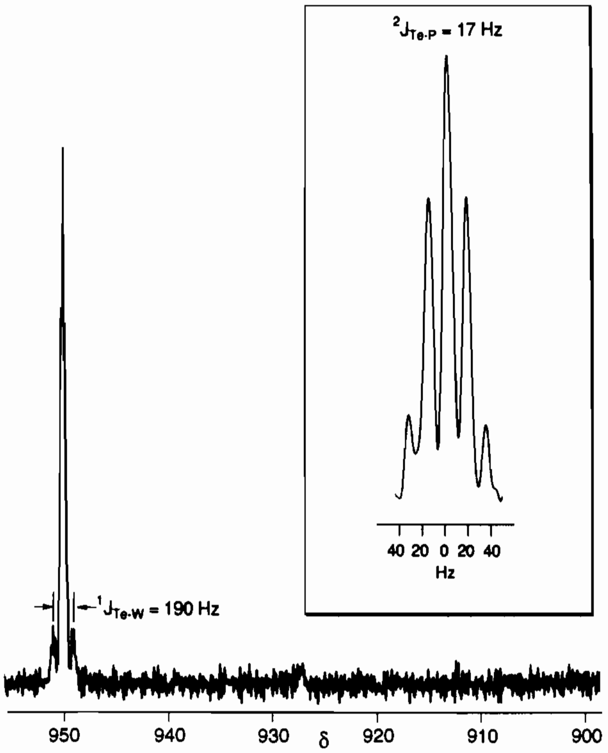


Figure 6. $^{125}Te\{^1H\}$ NMR spectrum of $W(PMe_3)_4(Te)_2$.

that even though the sulfido and selenido complexes of tungsten $[W(S)_4]^{2-}$ and $[W(Se)_4]^{2-}$ are known, attempts to prepare the tellurido analogue $[W(Te)_4]^{2-}$ have so far been unsuccessful.[46] Following the discovery of $W(PMe_3)_4(Te)_2$, however, a number of other terminal tellurido complexes of the transition metals have been prepared, as summarized in Table 4. Also of relevance, several complexes with multiply bonded *bridging* tellurido ligands are known, *e.g.*, $[V(CO)_3(dppe)]_2(\mu_2\text{-}Te)$,[47] $[Cp^*Mn(CO)_2]_2(\mu_2\text{-}Te)$,[48] and $[CpMn(CO)_2]_3(\mu_3\text{-}Te)$.[49]

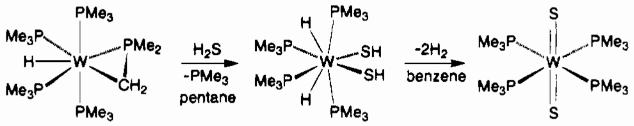
(c) Mechanisms for the Formation of $W(PMe_3)_4(E)_2$ (E = S, Se, Te). An interesting feature of the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with H_2E (E = S, Se) resides in the facile elimination of H_2. Thus, although the formation of bridging sulfido derivatives accompanied by elimination of H_2 has been observed for the reactions of some dinuclear late-transition-metal complexes with H_2S,[50,51] the elimination of H_2 and formation of a terminal sulfido complex at a *single* metal center is very rare. The elimination of H_2 from H_2S also bears some relevance to the proposal that hydrogenation of organic substrates during hydrodesulfurization may involve hydrogen transfer from a -SH group.[17a] In this regard, it was possible to demonstrate that the elimination of dihydrogen from H_2S in the reaction with $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ proceeds *via* the hydrido–hydrosulfido intermediate $W(PMe_3)_4H_2(SH)_2$, which may be isolated if the reaction is carried out in pentane (rather than benzene) in order to aid precipitation of the product (Scheme 1). Although complete characterization of $W(PMe_3)_4H_2(SH)_2$ is precluded by its instability in solution, evidence for its identity is provided by elemental analysis and the observation of both

Table 4. Terminal Tellurido Complexes of the Transition Metals

compound	ref
$Cp^*_2Zr(Te)(NC_5H_5)$	*a*
$Cp^{Et*}_2Zr(Te)(NC_5H_5)$	*a*
$(dmpe)_2Zr[TeSi(SiMe_3)_3]_2(Te)$	*b*
$Cp^*_2Hf(Te)(NC_5H_5)$	*c*
$Cp^{Et*}_2Hf(Te)(NC_5H_5)$	*c*
$(dmpe)_2Hf[TeSi(SiMe_3)_3]_2(Te)$	*b*
$[\eta^4\text{-}N(CH_2CH_2NSiMe_3)_3]V(Te)$	*d*
$Cp^*Nb(PMe_3)(NAr)(Te)$ (Ar = $2,6\text{-}Pr^i_2C_6H_3$)	*e*
$[\eta^4\text{-}N(CH_2CH_2NSiMe_3)_3]Ta(Te)$	*f*
$Cp^*_2Ta(Te)H$	*g*
$Cp^*_2Ta(Te)Me$	*g*
$Mo(PMe_3)_4(Te)_2$	*h*
$W(PMe_3)_4(Te)_2$	this work
$W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$ (R = H, Ph)	this work
$(Ph_4P)_2[W(O)(Te)_3]$	*i*

[a] Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606–615. [b] Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240–6242. [c] Howard, W. A.; Parkin, G. *J. Organomet. Chem.* **1994**, *472*, C1–C4. [d] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448–1457. [e] Siemeling, U.; Gibson, V. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1670–1671. [f] Christou, V.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1450–1452. [g] Shin, J. H.; Parkin, G. *Organometallics* **1994**, *13*, 2147–2149. [h] Murphy, V. J.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 3522–3528. [i] Gardner, D. R.; Fettinger, J. C.; Eichorn, B. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1859–1860.

Scheme 1



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(46) (a) Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1988**, *27*, 1710–1716. (b) Roof, L. C.; Pennington, W. T.; Kolis, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 8172–8174.

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(48) Herrmann, W. A.; Hecht, C.; Ziegler, M. L.; Balbach, B. *J. Chem. Soc., Chem. Commun.* **1984**, 686–687.

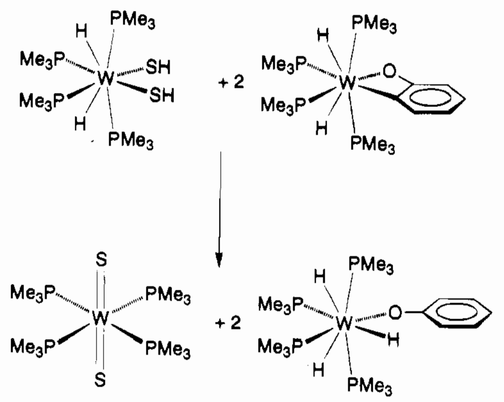
(49) Herberhold, M.; Reiner, D.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 59–60.

(50) (a) Lee, C.-L.; Besenyei, G.; James, B. R.; Neslon, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1175–1176. (b) Besenyei, G.; Lee, C.-L., Gulinski, J.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Inorg. Chem.* **1987**, *26*, 3622–3628. (c) Barnabas, A. F.; Sallin, D.; James, B. R. *Can. J. Chem.* **1989**, *67*, 2009. (d) McDonald, R.; Cowie, M. *Inorg. Chem.* **1993**, *32*, 1671–1680. (e) Wong, T. Y. H.; Barnabas, A. F.; Sallin, D.; James, B. R. *Inorg. Chem.* **1995**, *34*, 2278–2286.

(51) Dinuclear or polynuclear complexes of cobalt, nickel, and palladium with bridging sulfido ligands have also been obtained by reactions with H_2S, but the possibility of H_2 evolution was not commented upon. See: (a) Mealli, C.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1978**, *17*, 632–637. (b) Ghilardi, C. A.; Midollini, S.; Sacconi, L. *Inorg. Chim. Acta* **1978**, *31*, L431–L432. (c) Werner, H.; Bertleff, W. *Inorg. Chim. Acta* **1980**, *43*, L431-L432. (d) Ghilardi, C. A.; Midollini, S.; Sacconi, L. *J. Chem. Soc., Chem. Commun.* **1981**, 47–48. (e) Ghilardi, C. A.; Midollini, S.; Nuzzi, F.; Orlandini, A. *Transition Met. Chem.* **1983**, *8*, 73–75.

ν_{W-H} (1860 cm^{-1}) and ν_{S-H} (2545 cm^{-1}) stretches in the solid-state IR spectrum, assignments that have been confirmed by deuterium labeling studies, *i.e.*, ν_{W-D} = 1337 cm^{-1} (ν_H/ν_D = 1.39) and ν_{S-D} = 1850 cm^{-1} (ν_H/ν_D = 1.38). Additional support for the formulation of the intermediate as $W(PMe_3)_4H_2(SH)_2$ is provided by the observations that other HX reagents react with $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ to give analogous products, *i.e.*, $W(PMe_3)_4H_2X_2$ (X = H, SiH_3, Cl).[34,52]

Consistent with its role as an intermediate in the dehydrogenation reaction, benzene or toluene solutions of mustard-yellow $W(PMe_3)_4H_2(SH)_2$ immediately eliminate 2 equiv of hydrogen at room temperature to give a purple solution of $W(PMe_3)_4(S)_2$ (Scheme 1). The stoichiometry of this reaction has been confirmed by carrying out the reaction in the presence of the oxametallacycle $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$, a hydrogen trap (eq 3).[53]



(3)

It is noteworthy that although there are several reports of mononuclear transition-metal hydrido–hydrosulfido and bis(hydrosulfido) derivatives, these complexes have not been observed to eliminate dihydrogen.[54-56]

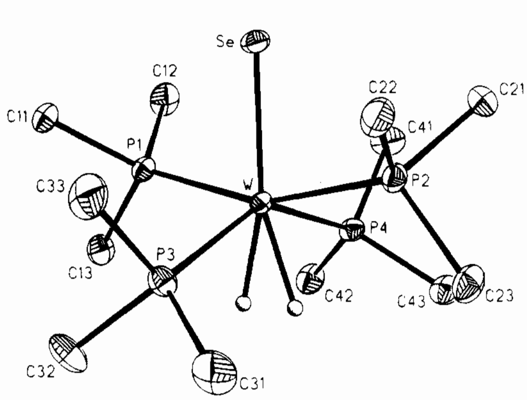


Figure 7. Molecular structure of $W(PMe_3)_4(Se)H_2$.

Scheme 2

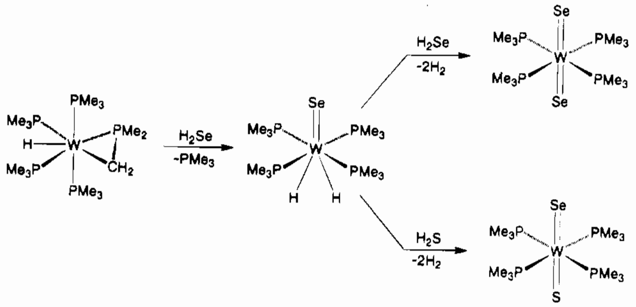


Table 5. Selected Bond Lengths (Å) and Angles (deg) for $W(PMe_3)_4(Se)H_2$

W–Se	2.445(2)	W–P(1)	2.477(5)
W–P(2)	2.484(6)	W–P(3)	2.442(5)
W–P(4)	2.429(5)		
Se–W–P(1)	79.2(1)	Se–W–P(2)	79.7(1)
Se–W–P(3)	111.1(1)	Se–W–P(4)	106.2(1)
P(1)–W–P(2)	158.9(1)	P(2)–W–P(4)	92.4(2)
P(3)–W–P(4)	142.7(2)	P(1)–W–P(3)	93.7(2)
P(1)–W–P(4)	93.8(2)	P(2)–W–P(3)	93.5(2)

An interesting contrast in the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with H_2Se and H_2S resides in the nature of the intermediates that have been isolated. Thus, whereas $W(PMe_3)_4H_2(SH)_2$ has been isolated as an intermediate in the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with H_2S, the emerald-green mono(selenido) derivative $W(PMe_3)_4(Se)H_2$ has been isolated as an intermediate from the corresponding reaction with H_2Se. Successful isolation of $W(PMe_3)_4(Se)H_2$ requires performing the reaction in pentane and using an excess of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, conditions under which $W(PMe_3)_4(Se)H_2$ precipitates (Scheme 2). Bridging selenido–dihydride complexes $[Cp'_2M(H)]_2(\mu\text{-}Se)$ [M = Ti, Zr] and $[Ir(CO)(H)]_2(\mu\text{-}Se)(\mu\text{-}dppm)_2$ have been proposed as intermediates in the formation of $[Cp'_2M(\mu\text{-}Se)]_2$ and $[Ir(CO)(\mu\text{-}dppm)]_2(\mu\text{-}Se)$ by the reactions of H_2Se with $Cp'_2M(CO)_2$[57] and $[Ir_2(CO)_3(dppm)_2]$,[50d] respectively. The molecular structure of $W(PMe_3)_4(Se)H_2$ has been determined by single-crystal X-ray diffraction (Figure 7). Selected bond lengths and angles are listed in Table 5. Although the hydride ligands were not located in the X-ray diffraction study, decisive evidence for their presence includes *(i)* an absorption at 1775 cm^{-1} in the IR spectrum and *(ii)* a 12-line multiplet (due to ^{31}P coupling) at δ 0.31 ppm in the ^1H NMR spectrum. The hydride ligands are presumably located *trans* to the selenido ligand, as suggested in Figure 7.

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(56) Furthermore, $Cp_2Mo(SH)_2$ does not eliminate H_2S to generate $[Cp_2MoS]$. See: Pilato, R. S.; Eriksen, K. A.; Stiefel, E. I.; Rheingold, A. L. *Inorg. Chem.* **1993**, *32*, 3799–3800.

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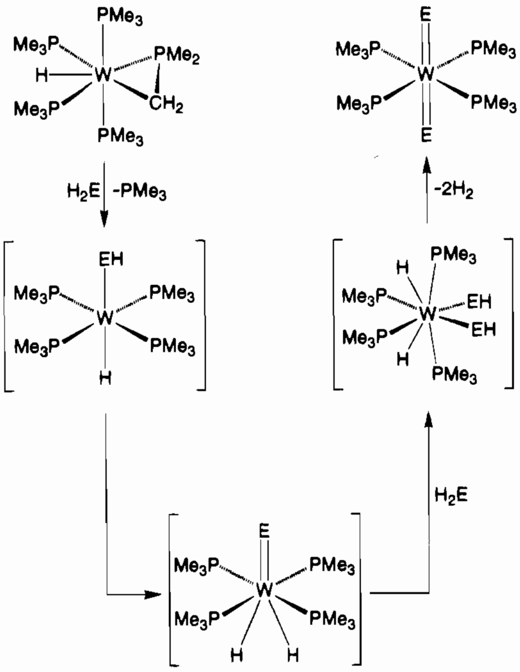
Scheme 3

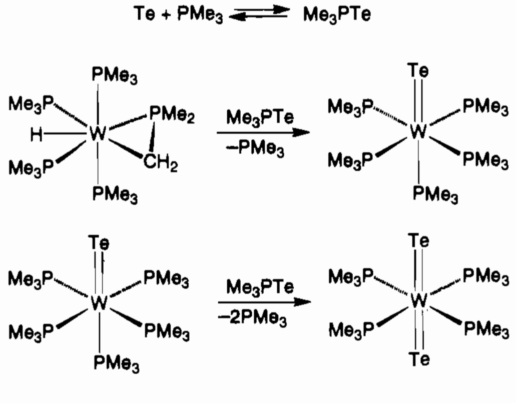


As a consequence of their distinct compositions, $W(PMe_3)_4H_2(SH)_2$ and $W(PMe_3)_4(Se)H_2$ behave very differently with regard to their conversions to $W(PMe_3)_4(E)_2$. Thus, whereas $W(PMe_3)_4H_2(SH)_2$ is extremely unstable in solution and rapidly eliminates H_2 to give $W(PMe_3)_4(S)_2$, the mono(selenido) complex $W(PMe_3)_4(Se)H_2$ is stable under comparable conditions. However, in the presence of a second equivalent of H_2Se, $W(PMe_3)_4(Se)H_2$ is rapidly converted to $W(PMe_3)_4(Se)_2$, accompanied by elimination of H_2 (Scheme 2). Similarly, $W(PMe_3)_4(Se)H_2$ reacts with H_2S to afford the unusual mixed chalcogenido complex $W(PMe_3)_4(S)(Se)$ (Scheme 2).

The isolation of $W(PMe_3)_4H_2(SH)_2$ and $W(PMe_3)_4(Se)H_2$, together with additional studies (*vide infra*), permits a general mechanism for the dehydrogenation of H_2E (E = S, Se) by $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ to be suggested (Scheme 3). The initial steps of the proposed sequence involve *(i)* the direct attack of H_2E at the W–C bond of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, together with loss of PMe_3, thereby generating the 16-electron hydrido–hydrochalcogenido intermediate $[W(PMe_3)_4H(EH)]$[58] and *(ii)* subsequent rapid α-H elimination to give the chalcogenido–dihydrido complex $W(PMe_3)_4(E)H_2$ (isolated for E = Se). In support of this mechanism, ^2H NMR spectroscopy has demonstrated that the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with D_2Se results in the incorporation of deuterium into the PMe_3 ligands of $W(PMe_3)_4(Se)H_2$, as well as at the hydride sites, strongly suggesting that the initial interaction between $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and H_2E occurs at the W–C bond. The final steps of the reaction are proposed to involve the addition of a second equivalent of H_2E to $W(PMe_3)_4(E)H_2$ to afford $W(PMe_3)_4H_2(EH)_2$ (isolated for E = S), followed by elimination of H_2 to give $W(PMe_3)_4(E)_2$.[59]

Several observations have provided some insight into the steps involved in the formation of $W(PMe_3)_4(Te)_2$ by reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with elemental Te. For example, the reaction is autocatalytic in PMe_3. Elemental tellurium is typically less reactive than its lighter congeners,[27b] and PMe_3 would be expected to act as a catalyst for the tellurium atom transfer *via* the intermediacy of Me_3PTe. Consistent with this suggestion, the formation of $W(PMe_3)_4(Te)_2$ from $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ is instantaneous when Me_3PTe, generated *in situ*, is used as a reagent.[60] In effect, PMe_3 acts as a solid–solution phase-transfer catalyst. A plausible sequence of events for the formation of $W(PMe_3)_4(Te)_2$ is illustrated in Scheme 4. Precedence for such a mechanism involving Me_3PTe is provided by the use of R_3PTe derivatives in the synthesis of other tellurium-containing complexes.[61,62] In addition, stable adducts of phosphine tellurides, *e.g.*, $W(CO)_5(TePBu^t_3)$,[63] have been isolated in some cases.

Scheme 4



2. Tungsten (VI) Bis(chalcogenido) Complexes, *cis*-$W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$ (E = S, Se, Te).

(a) Syntheses and Structures of cis-$W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$ (E = S, Se, Te). The trimethylphosphine ligands in *trans*-$W(PMe_3)_4(E)_2$ (E = S, Se, Te) are labile and may be displaced by aliphatic or aromatic aldehydes RCHO to give the η^2-aldehyde complexes $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$ (E = S, R = H, Me, Ph, C_6H_4Me,

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(58) The direct attack at the W–C bond, rather than a sequence involving reductive elimination of the metallacycle–hydride moiety and the intermediacy of 16-electron $[W(PMe_3)_5]$, has also been postulated for the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with other reagents bearing acidic hydrogens.[58a] Furthermore, evidence has also been presented in support of attack at the Fe–C bond in the reaction of $Fe(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H$ with HX (X = Cl, Br).[58b] (a) Reference 53. (b) Karsch, H. H. *Chem. Ber.* **1977**, *110*, 2222–2235.

(59) Several possible mechanisms exist for both of these final transformations but, as a result of isotopic label scrambling, it is not possible at this stage to favor any of the alternatives. However, since $W(PMe_3)_4(Se)H_2$ does not undergo facile exchange with D_2, a mechanism involving direct reductive elimination of H_2 from $W(PMe_3)_4(Se)H_2$ can be excluded.

(60) Tertiary phosphines react with elemental tellurium to give phosphine tellurides R_3PTe. See: (a) Zingaro, R. A.; Steeves, B. H.; Irgolic, K. *J. Organomet. Chem.* **1965**, *4*, 320–323. (b) Steigerwald, M. L.; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245–246.

(61) Some examples include $[(\eta^5\text{-}C_5Me_5)_2Yb]_2(\mu\text{-}Te)$,[61a] $Co_6Te_8(PEt_3)_6$,[61b] $Ni_9Te_6(PEt_3)_8$,[61c] $Ni_{20}Te_{18}(PEt_3)_{12}$,[62c] $[(\eta^5\text{-}C_5H_4Me)_3U]_2(\mu\text{-}Te)$,[61d] $Mn(CO)_3(PEt_3)_2(TeCH_2Ph)$,[61e] $(\eta^5\text{-}C_5Me_5)_2ScTeCH_2Ph$,[61f] $[(\eta^5\text{-}C_5H_4Bu^t)_2Y(\mu\text{-}TeMe)]_2$,[61g] and $[(Et_3P)_2(CO)_3Mn](\mu\text{-}Te_2)$.[61h] (a) Berg, D. J.; Burns, C. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865–1870. (b) Stuczynski, S. M.; Kwon, Y.-U.; Steigerwald, M. L. *J. Organomet. Chem.* **1993**, *449*, 167–172. (c) Brennan, J. G.; Siegrist, T.; Stuczynski, S. M.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 9240–9241. (d) Brennan, J. G.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1986**, *25*, 1761–1765. (e) McGregor, K.; Deacon, G. B.; Dickson, R. S.; Fallon, G. D., Rowe, R. S.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1990**, 1293–1294. (f) Piers, W. E; MacGillivray, L. R.; Zaworotko, M. *Organometallics* **1993**, *12*, 4723–4725. (g) Beletskaya, I. P.; Voskoboynikov, A. Z.; Shestakova, A. K.; Schumann, H. *J. Organomet. Chem.* **1993**, *463*, C1-C2. (h) Steigerwald, M. L.; Rice, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 4228–4233.

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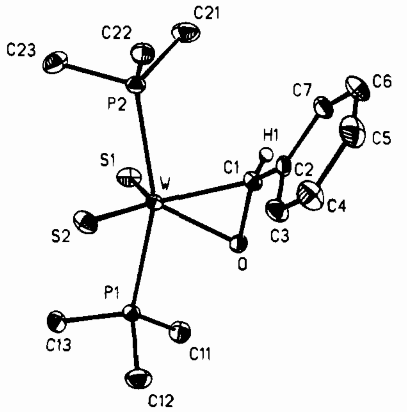


Figure 8. Molecular structure of $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHPh)$.

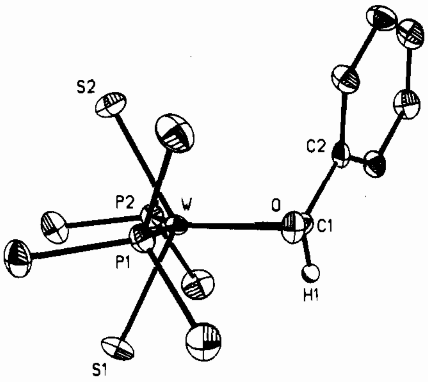


Figure 9. View of $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHPh)$ down the pseudo trigonal axis.

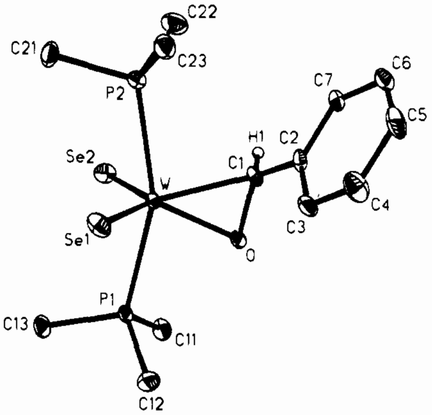


Figure 10. Molecular structure of $W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHPh)$.

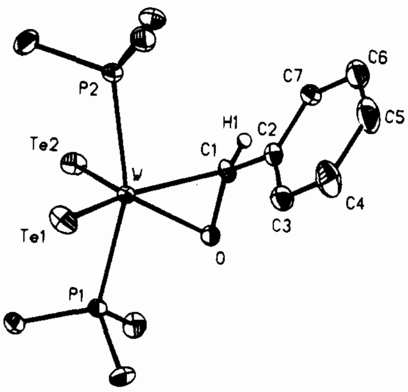


Figure 11. Molecular structure of $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHPh)$.

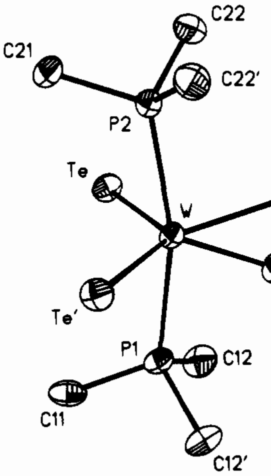
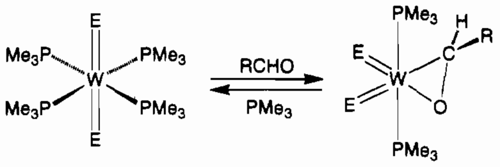


Figure 12. Molecular structure of $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCH_2)$.

C_6H_4OMe; E = Se, R = H, Ph; E = Te, R = H, Ph), as illustrated in eq 4.



(4)

Although η^2-aldehyde complexes of the transition metals are well-known,[64] the substitution of two PR_3 ligands for a single aldehyde moiety is unusual. More commonly, a single aldehyde displaces only one PR_3 ligand, as illustrated in the reactions of $W(PMePh_2)_4Cl_2$[65] and $W(PMe_2Ph)_2(NAr)_2$[43] with aldehydes.

The molecular structures of the three benzaldehyde derivatives $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$ (E = S, Se, Te), as well as that of the tellurido–formaldehyde complex $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCH_2)$, have been determined by X-ray diffraction, as illustrated in Figures 8–12. Selected bond lengths and angles are presented in Tables 6 and 7. If the η^2-aldehyde ligand is viewed as occupying a single coordination site, the structures of $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$ may be considered to be related to a distorted trigonal bipyramid, with axial PMe_3 ligands and equatorial chalcogenido and aldehyde ligands. Accordingly, the E–W–E angles are close to 120° and the P–W–P angles approach linearity, varying from 159.0(1)° in $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$ (E = S, Se) to 165.7(1)° in $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCH_2)$. With the exception of the different W=E bond lengths, the remainder of the bond lengths and angles about tungsten are similar for each of the derivatives, regardless of the chalcogen. Comparison of the C–O bond lengths within the aldehyde ligands [1.363(22)–1.395(11) Å] with those of typical C–O single (1.41 Å) and C=O double (1.20 Å) bond lengths[66] suggests that the complexes are best described as W(VI) metallaoxirane derivatives rather than W(IV) aldehyde adducts.

(b) Equilibrium Studies. The formation of the aldehyde complexes $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$ is reversible and addition of excess PMe_3 regenerates $W(PMe_3)_4(E)_2$. For the case of the benzaldehyde derivatives, ^1H NMR spectroscopy has allowed

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(66) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 19.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$

bond	E = S	E = Se	E = Te
W−E(1)	2.185(2)	2.321(2)	2.534(1)
W−E(2)	2.187(2)	2.313(2)	2.524(1)
W−P(1)	2.543(2)	2.528(3)	2.535(2)
W−P(2)	2.521(2)	2.517(3)	2.521(3)
W−O	1.967(4)	1.962(6)	1.963(7)
W−C(1)	2.130(7)	2.148(9)	2.120(11)
O−C(1)	1.376(9)	1.375(13)	1.395(11)
P(1)−W−P(2)	159.0(1)	159.0(1)	159.8(1)
E(1)−W−E(2)	125.7(1)	125.6(1)	124.5(1)
E(1)−W−P(1)	85.6(1)	86.2(1)	86.5(1)
E(1)−W−P(2)	84.7(1)	84.7(1)	85.0(1)
E(1)−W−O	113.8(2)	116.2(2)	116.4(2)
E(1)−W−C(1)	118.1(2)	119.0(3)	119.7(2)
E(2)−W−P(1)	86.2(1)	85.5(1)	85.1(1)
E(2)−W−P(2)	84.4(1)	84.6(1)	84.7(1)
E(2)−W−O	116.5(1)	114.2(2)	114.7(2)
E(2)−W−C(1)	113.4(2)	112.6(3)	113.0(2)
O−W−C(1)	39.0(2)	38.8(4)	39.7(3)
W−C(1)−O	64.1(3)	63.3(4)	64.1(5)
W−O−C(1)	76.9(3)	77.9(5)	76.2(5)
W−C(1)−C(2)	124.8(4)	124.5(6)	125.4(7)
P(1)−W−O	77.7(2)	77.9(2)	76.9(2)
P(2)−W−O	123.3(2)	123.1(2)	123.3(2)
P(1)−W−C(1)	116.6(2)	116.5(3)	116.4(2)
P(2)−W−C(1)	84.3(2)	84.4(3)	83.6(2)

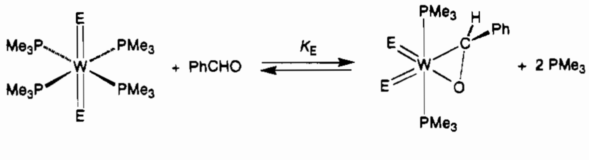
Table 7. Selected Bond Lengths (Å) and Angles (deg) for $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCH_2)$

W−Te	2.531(1)	W−Te′	2.531(1)
W−P(1)	2.553(5)	W−P(2)	2.505(4)
W−O	1.953(11)	W−C	2.115(19)
O−C	1.363(22)		
Te−W−Te′	121.9(1)	P(1)−W−P(2)	165.7(1)
Te−W−P(1)	86.9(1)	Te−W−P(2)	86.2(1)
Te−W−O	117.1(1)	Te−W−C	117.4(1)
Te′−W−P(1)	86.9(1)	Te′−W−P(2)	86.2(1)
Te′−W−O	117.1(1)	Te′−W−C	117.4(1)
O−W−C	38.9(6)	W−C−O	64.1(9)
W−O−C	77.0(8)		

Table 8. Equilibrium Constants for the Reaction between $W(PMe_3)_4(E)_2$ and PhCHO

T/°C	K_S/M	K_{Se}/M	K_{Te}/M
30	8(3)	$7.9(8) \times 10^{-2}$	$4.0(9) \times 10^{-3}$
40	10(2)	$1.2(2) \times 10^{-1}$	$6.8(7) \times 10^{-3}$
50	12(3)	$1.8(3) \times 10^{-1}$	$1.2(2) \times 10^{-2}$
60	17(3)	$2.7(4) \times 10^{-1}$	$2.0(2) \times 10^{-2}$

the equilibrium constants K_E (eq 5) to be determined as a function of the chalcogen.



(5)

Values of ΔH° and ΔS° for the ligand exchange processes have been determined from the temperature dependence of K_E over the range 30−60 °C (Table 8 and Figure 13),[67] from which it is evident that the formation of the aldehyde derivatives is driven entropically by dissociation of the trimethylphosphine ligands.

Examination of Table 8 indicates that the values for K_E vary quite dramatically as a function of the chalcogen. For example, at 30 °C, K_S [8(3) M] is approximately a factor of 100 greater than K_{Se} [$7.9(8) \times 10^{-2}$ M] and approximately a factor of 2000 greater than K_{Te} [$K_{Te} = 4.0(9) \times 10^{-3}$ M]. As would be anticipated, it is apparent from the values of ΔH° and ΔS° listed in Table 9 that the pronounced variation in equilibrium constants is due to enthalpic, rather than entropic, considerations. However, it is not possible with the data available to identify if the origin of the decrease in equilibrium constants across the series S ≫ Se > Te reflects weaker binding of the aldehyde ligands in $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$ or stronger binding of the phosphine ligands in $W(PMe_3)_4(E)_2$. For example, there are no significant bonding changes associated with either the $[W(\eta^2\text{-}OCHPh)]$ moiety in $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$ (see Table 6) or the $W{-}PMe_3$ moieties of $W(PMe_3)_4(E)_2$ (Tables 1−3). Alternatively, the variation in K_E may reflect the preferences for the two chalcogenido ligands in $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$ to adopt a cis-disposition and thereby partake in increased π-bonding (*vide infra*). In support of this latter suggestion, the relative decrease in W≈E bond lengths between $W(PMe_3)_4(E)_2$ and $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$ is greater for the sulfido (2.93%) than the tellurido complexes (2.58%), although the changes are marginal.

The large variation in K_E as a function of the chalcogen is manifested in the conditions required to isolate the aldehyde complexes $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$. For example, whereas the reaction between $W(PMe_3)_4(S)_2$ and PhCHO proceeds readily to completion with only a slight excess of the aldehyde, the corresponding reactions of the selenido and tellurido derivatives require a large excess of reagent and periodic removal of liberated PMe_3 in order to complete the formation of products (see Experimental Section for details).

3. $W(PMe_3)_2(CNBu^t)_2(E)_2$ (E = S, Se) and $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$: Alkyl Isocyanide Derivatives and the Reductive Coupling of Two Tellurido Ligands. Whereas the reactions between RCHO and the chalcogenido complexes $W(PMe_3)_4(E)_2$ (E = S, Se, Te) give analogous η^2-aldehyde derivatives $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$ for each of the chalcogens, the products obtained from the reactions of $W(PMe_3)_4(E)_2$ with alkyl isocyanides depend strongly upon the nature of the chalcogen. For example, the sulfido and selenido complexes $W(PMe_3)_4(E)_2$ react reversibly with alkyl isocyanides to substitute two PMe_3 ligands and give *trans,trans,trans*-$W(PMe_3)_2(CNR)_2(E)_2$ (E = S, R = Pr^i, Bu^t, cyclo-C_6H_{11}; E = Se, R = Bu^t), as illustrated in Scheme 5. The molecular structures of the *tert*-butyl isocyanide derivatives were determined by single-crystal X-ray diffraction, as shown in Figures 14 and 15. Selected bond lengths and angles for the isostructural complexes are summarized in Table 10. The coordination geometries are close to octahedral, with mutually perpendicular pairs of isocyanide, trimethylphosphine, and chalcogenido ligands. The *trans* arrangement of chalcogenido ligands is analogous to that observed for $W(PMe_3)_4(E)_2$, but a noticeable distinction is that the equatorial arrangements of Bu^tNC and PMe_3 ligands in $W(PMe_3)_2(CNBu^t)_2(E)_2$ are reasonably close to planarity and do not form a ruffled array, presumably due to the smaller cone angle of the Bu^tNC *versus* the PMe_3 ligand.[68]

In striking contrast to the formation of the *trans* chalcogenido complexes $W(PMe_3)_2(CNR)_2(E)_2$ (E = S, Se), the corresponding reaction of the tellurido derivative $W(PMe_3)_4(Te)_2$ with Bu^tNC gives the η^2-ditellurido complex $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$, a result of the coupling of the two tellurido ligands. Similar results are also observed in the reactions of the aldehyde

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[67] Standard states of the components are 1 M.

[68] (a) de Lange, P. P. M.; Frühauf, H.-W.; Kraakman, M. J. A.; van Wijnkoop, M.; Kranenburg, M.; Groot, A. H. J. P.; Vrieze, K.; Fraanje, J.; Wang, Y.; Numan, M. *Organometallics* **1993**, *12*, 417−427. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

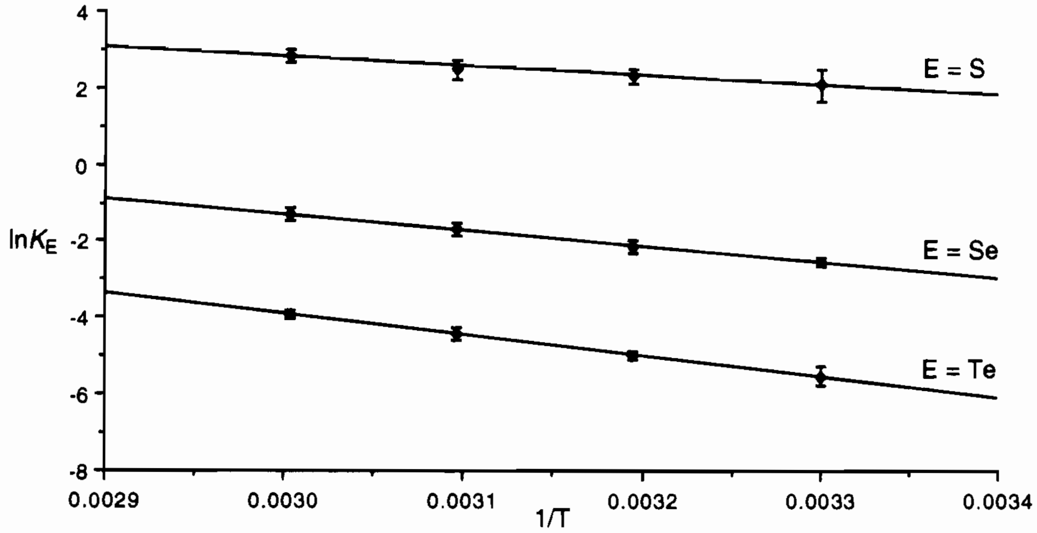


Figure 13. van't Hoff plot for equilibration of $W(PMe_3)_4(E)_2$ and $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$.

Table 9. $\Delta H°$ and $\Delta S°$ for the Equilibrium between $W(PMe_3)_4(E)_2$ and $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$

E	$\Delta H°$/kcal mol^{-1}	$\Delta S°$/eu
S	5(1)	20(4)
Se	8(2)	22(5)
Te	11(2)	25(5)

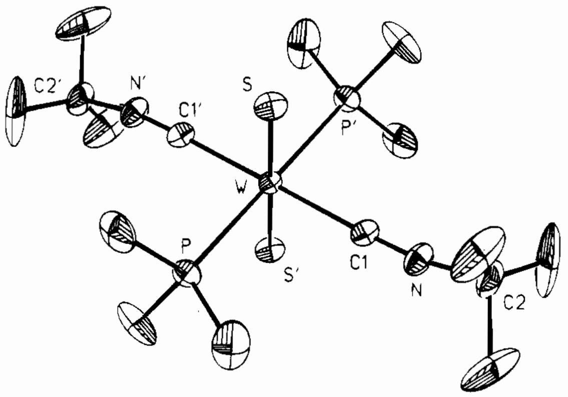
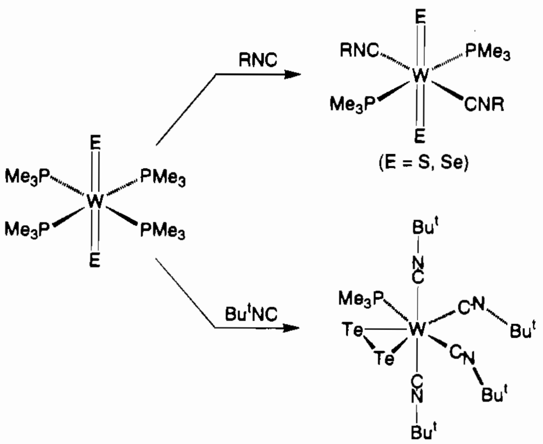


Figure 14. Molecular structure of $W(PMe_3)_2(CNBu^t)_2(S)_2$.

Scheme 5



derivatives $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$ with Bu^{t}NC. Thus, the sulfido and selenido complexes $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$ react with Bu^{t}NC to give the *trans*-chalcogenido derivatives $W(PMe_3)_2(CNBu^t)_2(E)_2$ (E = S, Se), whereas the tellurido analogues $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$ react with Bu^{t}NC to give the η^2-ditellurido complex (Scheme 5).

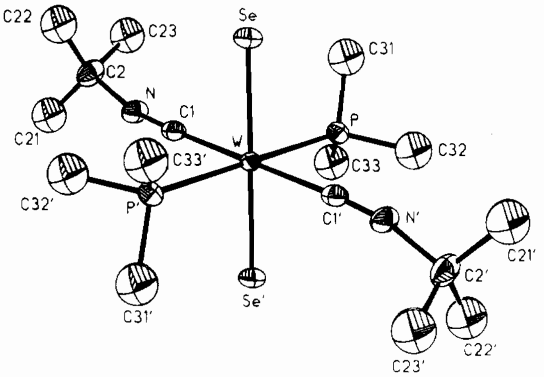


Figure 15. Molecular structure of $W(PMe_3)_2(CNBu^t)_2(Se)_2$.

Table 10. Selected Bond Lengths (Å) and Angles (deg) for $W(PMe_3)_2(CNBu^t)_2(E)_2$ (E = S, Se)

	E = S	E = Se
W−E	2.248(2)	2.375(2)
W−P	2.495(2)	2.489(3)
W−C(1)	2.110(7)	2.126(12)
C(1)−N	1.158(10)	1.152(17)
N−C(2)	1.462(13)	1.438(20)
E−W−E′	180.0	180.0
E−W−P	90.6(1)	90.4(1)
E−W−P′	89.4(1)	89.6(1)
E−W−C(1)	86.6(2)	85.7(3)
E−W−C(1′)	93.4(2)	94.3(3)
P−W−C(1)	91.5(2)	90.6(3)
P−W−C(1′)	88.5(2)	89.4(3)
P−W−P′	180.0	180.0
C(1)−W−C(1′)	180.0	180.0
W−C(1)−N	176.2(6)	175.8(9)
C(1)−N−C(2)	167.2(7)	164.6(12)

The coupling of two tellurido ligands to give an η^2-ditellurido moiety is unprecedented, even though the coupling of other groups, such as CR, CO, RCCR, and CNR, has been studied extensively.[69,70] The observation that coupling of the chalcogenido ligands occurs only for the tellurido system, and not for the sulfido and selenido systems, is consistent with the notion that tellurium exhibits a reduced tendency to partake in multiple bonding. A related effect has also been noted for the permethyltantalocene system $[Cp^*_2TaE_2H]$. Thus, whereas the η^2-diselenido complex $Cp^*_2Ta(\eta^2\text{-}Se_2)H$ is unstable with respect to the terminal selenido complex $Cp^*_2Ta(Se)(SeH)$,[71] the η^2-ditellurido complex $Cp^*_2Ta(\eta^2\text{-}Te_2)H$ is stable with respect to

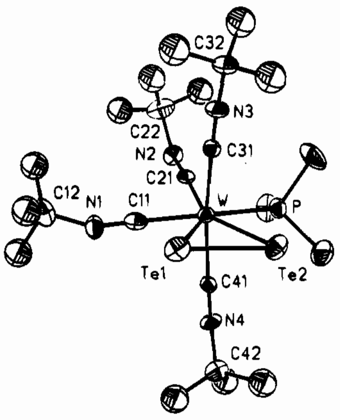


Figure 16. Molecular structure of $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$.

Table 11. Selected Bond Lengths (Å) and Angles (deg) for $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$

W−Te(1)	2.868(2)	W−Te(2)	2.877(2)
Te(1)−Te(2)	2.680(2)	W−P	2.509(5)
W−C(11)	1.974(17)	W−C(21)	1.966(17)
W−C(31)	2.092(14)	W−C(41)	2.082(14)
C(11)−N(1)	1.214(22)	C(21)−N(2)	1.226(21)
C(31)−N(3)	1.164(19)	C(41)−N(4)	1.152(19)
Te(1)−W−Te(2)	55.6(1)	W−Te(1)−Te(2)	62.4(1)
W−Te(2)−Te(1)	62.0(1)	W−C(11)−N(1)	172.8(14)
W−C(21)−N(2)	177.7(13)	W−C(31)−N(3)	177.6(13)
W−C(41)−N(4)	174.4(13)	C(11)−N(1)−C(12)	145.5(15)
C(21)−N(2)−C(22)	138.3(13)	C(31)−N(3)−C(32)	167.1(16)
C(41)−N(4)−C(42)	166.5(15)	Te(1)−W−C(11)	74.0(5)
Te(1)−W−C(21)	143.7(5)	Te(1)−W−C(31)	81.1(4)
Te(1)−W−C(41)	90.7(4)	Te(1)−W−P	137.9(1)
Te(2)−W−C(11)	128.8(5)	Te(2)−W−C(21)	153.7(5)
Te(2)−W−C(31)	82.1(4)	Te(2)−W−C(41)	86.2(4)
Te(2)−W−P	82.4(1)	P−W−C(11)	146.0(5)
P−W−C(21)	77.0(5)	P−W−C(31)	97.6(4)
P−W−C(41)	82.8(4)	C(11)−W−C(21)	75.9(7)
C(11)−W−C(31)	99.8(6)	C(11)−W−C(41)	85.9(6)
C(21)−W−C(31)	84.6(6)	C(21)−W−C(41)	106.9(6)
C(31)−W−C(41)	168.2(6)		

$Cp^*_2Ta(Te)(TeH)$ under comparable conditions.[72] However, although coupling of selenido and sulfido ligands was not observed for the $W(PMe_3)_4(E)_2$ system, it should be noted that the coupling of such ligands has been observed in other systems. For example, the reductive coupling of two sulfido ligands is observed in the formation of $W(O)(\eta^2\text{-}S_2)_2(bipy)$ from $[W(S)_4]^{2-}$ [73] and in the conversion of $[Mo(S)_4]^{2-}$ to $[(\eta^2\text{-}S_2)(S)Mo(\mu\text{-}S)]_2^{2-}$.[74,75]

The molecular structure of $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ has been determined by X-ray diffraction, confirming the presence of an η^2-ditellurido ligand (Figure 16 and Table 11). Although complexes that incorporate ditellurido (Te_2) moieties are well-known, the Te_2 ligand is typically observed to bridge two or more metal centers *via* a large variety of coordination modes.[76] In contrast, mononuclear $\eta^2\text{-}Te_2$ derivatives are not common,[77] with the first structurally characterized examples being the nickel derivatives $L_3Ni(\eta^2\text{-}Te_2)$ [$L_3 = \eta^3\text{-}PhP(CH_2CH_2PPh_2)_2$, $\eta^3\text{-}MeC(CH_2PPh_2)_3$].[78] A summary of structurally-characterized mononuclear complexes containing $\eta^2\text{-}Te_2$ ligands is provided in Table 12. The Te−Te distance in $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ [2.680(2) Å] lies within the relatively narrow range of Te−Te bond lengths (2.67−2.70 Å) observed for $\eta^2\text{-}Te_2$ ligands in other mononuclear complexes. Moreover, the Te−Te distance in $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ is intermediate between those of Te_2 in the gas phase [2.59(2) Å][79] and elemental Te_x in the solid state [2.835(2) Å].[80,81]

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(70) For a theoretical description of some coupling reactions, see, for example: (a) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146−147. (b) Wilker, C. N.; Hoffmann, R.; Eisenstein, O. *Nouv. J. Chim.* **1983**, *7*, 535−544.

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(76) See, for example: (a) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Chem. Commun.* **1986**, 374−375. (b) Eichhorn, B. W.; Haushalter, R. C.; Cotton, F. A.; Wilson, B. *Inorg. Chem.* **1988**, *27*, 4084−4085. (c) Ansari, M. A.; Bollinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3838−3839. (d) Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M. *Inorg. Chem.* **1991**, *30*, 4940−4945. (e) Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 433−435. (f) Herrmann, W. A.; Hecht, C.; Herdtweck, E.; Kneuper, H.-J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 132−134. (g) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Inorg. Chem.* **1989**, *28*, 4614−4619. (h) Huang, S.-P.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 5477−5478. (i) Schreiner, B.; Dehnicke, K.; Fenske, D. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1127−1131. (j) Jutzi, P.; Möhrke, A.; Müller, A.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1518−1519. (k) Leist, A.; Tremel, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1751−1752. (l) Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1981**, *20*, 3583−3585. (m) Eichhorn, B. W.; Haushalter, R. C.; Merola, J. S. *Inorg. Chem.* **1990**, *29*, 728−731. (n) Evans, W. J.; Rabe, G. W.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1994**, *33*, 2719−2726. (o) Dhingra, S. S.; Haushalter, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 3651−3652. (p) Dhingra, S. S.; Haushalter, R. C. *Inorg. Chem.* **1994**, *33*, 2735−2737. (q) Scheidsteger, O.; Huttner, G.; Dehnicke, K.; Pebler, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 428.

(77) However, a number of mononuclear complexes containing $\eta^2\text{-}Se_2$ ligands are known, *e.g.*, $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$,[77a] $[Ir(\eta^2\text{-}Se_2)(dppe)_2]Cl$,[77b] $[K(2.2.2\text{-Kryptand})][CpCr(CO)_2(\eta^2\text{-}Se_2)]$,[77c] $Cp^*Mn(CO)_2(\eta^2\text{-}Se_2)$,[77d] $Et_4N[CpMo(CO)_2(\eta^2\text{-}Se_2)]$,[77e] $K_4[U(\eta^2\text{-}Se_2)_4]$,[77f] $(\eta^2\text{-}Se_2)W(\eta^2\text{-}S_2CNR_2)_3$ ($R = Bu^i$,[77g] Et[77h]), $Cp^*_2Zr(\eta^2\text{-}Se_2)CO$,[77i] and $Cp^*_2Ta(\eta^2\text{-}Se_2)H$.[71] (a) Farrar, D. H.; Grundy, K. R.; Payne, N. C.; Roper, W. R.; Walker, A. *J. Am. Chem. Soc.* **1979**, *101*, 6577−6582. (b) Ginsberg, A. P.; Lindsell, W. E.; Sprinkle, C. R.; West, K. W.; Cohen, R. L. *Inorg. Chem.* **1982**, *21*, 3666−3681. (c) Rohrmann, J.; Herrmann, W. A.; Herdtweck, E.; Riede, J.; Ziegler, M.; Sergeson, G. *Chem. Ber.* **1986**, *119*, 3544−3557. (d) Herberhold, M.; Reiner, D.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1000−1001. (e) Adel, J.; Weller, F.; Dehnicke, K. *J. Organomet. Chem.* **1988**, *347*, 343−348. (f) Sutorik, A. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 7754−7755. (g) Gea, Y.; Greaney, M. A.; Coyle, C. L.; Stiefel, E. I. *J. Chem. Soc., Chem. Commun.* **1992**, 160−161. (h) Fedin, V. P.; Mironov, Yu. V.; Virovets, A. V.; Podberezskaya, N. V.; Fedorov, V. Ye. *Polyhedron* **1992**, *11*, 1959−1963. (i) Howard, W. A.; Parkin, G.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 25−44.

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Table 12. Structurally Characterized Mononuclear Complexes Containing η^2-Te_2 Ligands

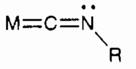
	$d(Te{-}Te)$/Å	ref
$Cp^*{}_2Ti(\eta^2\text{-}Te_2)$	2.703(18)	*a*
$Cp^*{}_2Zr(\eta^2\text{-}Te_2)(CO)$	2.69[2]	*b*
$Cp^*{}_2Ta(\eta^2\text{-}Te_2)H$	2.678(2)	*c*
$Mo(PMe_3)_4(\eta^2\text{-}Te_2)H_2$	2.698(1)	*d*
$W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$	2.680(2)	this work
$W(PMe_3)_4(\eta^2\text{-}Te_2)H_2$	2.697(2)	*d*
$\{\eta^3\text{-}PhP(CH_2CH_2PPh_2)_2\}Ni(\eta^2\text{-}Te_2)$	2.668(1)	*e*
$\{\eta^3\text{-}MeC(CH_2PPh_2)_3\}Ni(\eta^2\text{-}Te_2)$	2.665(2)	*e*

[a] Fischer, J. M.; Piers, W. E.; MacGillivray, L. R.; Zaworotko, M. J. *Inorg. Chem.* **1995**, *34*, 2499−2500. [b] Howard, W. A.; Parkin, G.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 25−44. [c] Shin, J. H.; Parkin, G. *Organometallics* **1994**, *13*, 2147−2149. [d] Murphy, V. J.; Rabinovich, D. R.; Halkyard, S.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1099−1100. [e] Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 916−917.

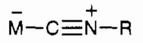
As would be anticipated, the W−Te bond lengths in $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ [2.868(2) Å and 2.877(2) Å] are substantially longer than the corresponding multiple bonds in $W(PMe_3)_4(Te)_2$ [2.596(1) Å] and $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$ [2.524(1)−2.534(1) Å] and are comparable to a typical W−Te single bond length of *ca.* 2.82 Å.[41]

The X-ray structure of $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ also indicates that there are two types of Bu^tNC ligand present in the molecule, namely, *(i)* two mutually trans Bu^tNC ligands that possess essentially linear geometries at nitrogen with $C{-}N{-}Bu^t$ bond angles of 167(2)° and *(ii)* two mutually cis Bu^tNC ligands that are markedly bent at nitrogen, with $C{-}N{-}Bu^t$ bond angles of 138(1)° and 146(2)°. Bent coordination of isocyanide ligands is not as common as linear coordination, although it does have precedence.[82,83]

The presence of bent isocyanide ligands is indicative of extensive donation of electron density from the electron-rich metal center to the isocyanide ligand (π back-bonding) and is therefore associated with a structure having a resonance form of the type $M{=}C{=}\ddot{N}{-}R$ (**A**), in contrast to a resonance form of the type $M^-{-}C{\equiv}N^+{-}R$ (**B**) for linear coordination.


$M{=}C{=}\ddot{N}{\diagdown}R$

(A)


$\overset{-}{M}{-}C{\equiv}\overset{+}{N}{-}R$

(B)

Accordingly, the W−C distances [1.966(17) and 1.974(17) Å] for the two bent isocyanide ligands are slightly shorter than the corresponding values in the two nearly linear isocyanide groups [2.082(14) and 2.092(14) Å] and also those in $W(PMe_3)_2(CNBu^t)_2(S)_2$ [2.110(7) Å] and $W(PMe_3)_2(CNBu^t)_2(Se)_2$ [2.126(12) Å].[84] Similarly, the $C_{ipso}{-}N$ bond lengths are marginally longer in the bent [1.214(22) and 1.226(21) Å] than in the linear [1.152(19) and 1.164(19) Å] isocyanide ligands. A similar trend has been observed in other complexes containing both linear and bent isocyanide ligands.[83a,b,e] Thus, the observation of both relatively short W−C and long $C_{ipso}{-}N$ bonds in bent isocyanide ligands is consistent with resonance form $M{=}C{=}\ddot{N}{-}R$ (**A**) shown.

The ability of the Bu^tNC ligand to induce coupling of the tellurido ligands is most probably a consequence of its strong π-acceptor character, as manifested by the presence of bent $W{=}C{=}\ddot{N}{-}Bu^t$ moieties in $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$. Thus, the π-acceptor nature of the Bu^tNC ligand reduces electron density at the tungsten center, thereby stabilizing the lower valence state and consequently promoting the reductive coupling[85] of the two tellurido ligands. In contrast, PMe_3 ligands, which by comparison to isocyanide ligands are strong σ-donors with little π-acceptor character,[86] stabilize the higher oxidation state, such that there is no tendency for the tellurido ligands in $W(PMe_3)_4(Te)_2$ to couple in a reductive manner.

Although the X-ray structure indicates the presence of inequivalent Bu^tNC groups in $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$, the complex is fluxional in solution, as judged by the observation of only one set of resonances for the four Bu^tNC groups in both the ^1H and ^{13}C NMR spectra. However, despite the fluxional nature of $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ according to ^1H and ^{13}C NMR spectroscopy, two broad signals (δ −480 ppm and −1537 ppm) are nevertheless observed for the ditellurido ligand in the ^{125}Te NMR spectrum. The observation of a static ^{125}Te NMR spectrum, and yet fluxional ^1H and ^{13}C NMR spectra, may be a consequence of either *(i)* the very large frequency difference (*ca.* 10,000 Hz) of the ^{125}Te NMR chemical shifts compared to those of the ^1H and ^{13}C NMR spectra or *(ii)* the possibility that the exchange of Bu^tNC ligands occurs *via* an intermediate in which the asymmetry of the η^2-Te_2 ligand is maintained.

4. Structural and Bonding Aspects of the Terminal Chalcogenido Complexes. The complexes $W(PMe_3)_2(L)_2(E)_2$ (L = PMe_3, E = S, Se, Te; L = CNR, E = S, Se) and $W(PMe_3)_4(Se)H_2$ represent rare examples of structurally-characterized 18-electron tungsten complexes containing terminal chalcogenido ligands. As such, the tungsten−chalcogenido interactions may be aptly represented as "pure" W=E double bonds, with little contribution from the triply bonded resonance form $W^-{\equiv}E^+$. Electronic spectroscopy studies

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(84) For reference, the majority of tungsten−alkylisocyanide complexes listed in the Cambridge Structural Database have W−C bond lengths in the range 2.0−2.2 Å and C−N−C bond angles in the range 160°−180°. Indeed, only two other alkylisocyanide complexes are listed with W−C bond lengths <2.0 Å. See: (a) Dossett, S. J.; Li, S.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1994**, *13*, 822−829. (b) Hahn, F. E.; Tamm, M. *J. Organomet. Chem.* **1991**, *410*, C9−C12.

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on $W(PMe_3)_4(E)_2$ by Thorp[87] and theoretical calculations on the model complexes $W(PH_3)_4(E)_2$ by Kaltsoyannis[88] are also in agreement with such a bonding scheme. In support of this formalism, the presence of "pure" W=S double bonds in $W(PMe_3)_2(L)_2(S)_2$ (L = PMe_3, CNR) is reflected by particularly low $\nu_{W=S}$ stretching frequencies in the range 387−392 cm^{-1}. For reference, $\nu_{W=S}$ stretching frequencies are typically observed in the range 450−570 cm^{-1} for complexes in which the contribution of the resonance form $W^-{\equiv}S^+$ would be expected to be significant.[26,89]

The trans arrangement of the chalcogenido ligands in the W(IV) complexes $W(PMe_3)_4(E)_2$ (E = Se, Te) and $W(PMe_3)_2(CNBu^t)_2(E)_2$ (E = S, Se) is that expected for a formally 18-electron d^2 metal center.[90,91] Specifically, a trans arrangement allows the two d electrons to occupy a nonbonding orbital, rather than an antibonding orbital that would result from a *cis* configuration. In contrast, the chalcogenido ligands in the W(VI) η^2-aldehyde derivatives $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$, with a formally 16-electron d^0 metal center (in the absence of chalcogen lone-pair donation), adopt a cis arrangement which allows for increased π-donation from E to W (*i.e.*, $W^-{\equiv}E^+$).[91] Consequently, an average $W{\approx}E$ bond order of 2.5 results for the tungsten-chalcogenido interactions in $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$. As such, the $W{\approx}E$ bond lengths in $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$ are marginally shorter than the W=E double bonds in the corresponding 18-electron complexes $W(PMe_3)_4(E)_2$, $W(PMe_3)_2(CNBu^t)_2(E)_2$ and $W(PMe_3)_4(Se)H_2$ (Table 13). Furthermore, the W=E bond lengths observed for the 18-electron complexes are indeed longer than the corresponding values for previously reported terminal chalcogenido complexes of tungsten in which the tungsten centers are electronically unsaturated in the absence of lone pair donation, *e.g.*, $W(E)X_4$ (E = S, Se; X = F, Cl, Br) with a formal $W^-{\equiv}E^+$ triple bond (Table 13).[92] Other than the complexes described here, only one other terminal tellurido complex of tungsten has been reported, namely $[Ph_4P]_2[W(O)(Te)_3]$.[93] A formal W=Te bond order of two has also been assigned for this complex, consistent with the average bond length of 2.54(1) Å.

Cundari has performed a series of effective core potential (ECP) calculations on the model complexes $W(PH_3)_4(Se)H_2$ and $W(PH_3)_4(E)_2$ in order to test the applicability of such methods for predicting metal−chalcogen bond lengths.[94] Cundari's calculations were, in fact, found to be in excellent agreement with the experimentally determined structural data for $W(PMe_3)_4(Se)H_2$ and $W(PMe_3)_4(E)_2$ (E = S, Se, Te). For example, the calculated W=Se bond lengths for the model selenido complexes $W(PH_3)_4(Se)H_2$ [2.45 Å] and $W(PH_3)_4(Se)_2$ [2.38 Å] are identical to the experimental values for the trimethylphosphine complexes $W(PMe_3)_4(Se)H_2$ [2.445(2) Å] and $W(PMe_3)_4(E)_2$ [2.380(1) Å].

Table 13. Variation of W=E Bond Length with Bond Order

	bond order	S	Se	Te
$W(PMe_3)_4(E)H_2$	2		2.445(2)	
$W(PMe_3)_4(E)_2$	2	2.253[3]	2.380[1]	2.596(1)
$W(PMe_3)_2(CNBu^t)_2(E)_2$	2	2.248(2)	2.375(2)	
$W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$	2.5	2.186[2]	2.317[4]	2.529[5]
$W(PMe_3)_2(E)_2(\eta^2\text{-}OCH_2)$	2.5			2.531(1)
$W(E)F_4$[a]	3	2.104(7)	2.226(7)	*2.40*[b]
$W(E)Cl_4$[a]	3	2.086(6)	2.203(4)	*2.40*[b]
$W(E)Br_4$[a]	3	2.109(11)	2.220(22)	*2.40*[b]
CSD mean[c]		2.15	2.29	

[a] Data taken from: Page, E. M.; Rice, D. A.; Hagen, K.; Hedberg, L.; Hedberg, K. *Inorg. Chem.* **1991**, *30*, 4758−4761. [b] Theoretically calculated bond lengths. See: Benson, M. T.; Cundari, T. R.; Lim, S. J.; Nguyen, H. D.; Pierce-Beaver, K. *J. Am. Chem. Soc.* **1994**, *116*, 3955−3966. [c] Mean multiply bonded W=E bond lengths determined from a search of the Cambridge Structural Database (Version 5.09, April 1995). The majority of structurally characterized terminal sulfido and selenido complexes have W=E bond lengths in the ranges 2.01−2.25 Å and 2.26−2.32 Å, respectively.

5. ^{77}Se and ^{125}Te NMR Spectroscopy of Terminal Chalcogenido Complexes. The selenido and tellurido complexes reported here have been investigated by ^{77}Se ($I = {}^1/_2$, 7.6%) and ^{125}Te ($I = {}^1/_2$, 7.0%) NMR spectroscopies,[95] as summarized in Table 14. A representative ^{77}Se NMR spectrum, that for $W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHPh)$, is illustrated in Figure 17. As is evident from the data in Table 14, the ^{77}Se and ^{125}Te chemical shifts of the terminal chalcogenido ligands in these series of closely related complexes span the substantial range of more than 1700 ppm and 2500 ppm, respectively! Furthermore, the chemical shifts for $W(PMe_3)_4(Se)_2$, $W(PMe_3)_4(S)(Se)$, and $W(PMe_3)_2(CNBu^t)_2(Se)_2$ (803, 691, and 824 ppm, respectively) are in the range that has been assigned to bridging or "W-bound" selenido ligands.[96] Other terminal tellurido complexes are known to exhibit ^{125}Te NMR resonances at even higher fields than those reported here, *e.g.*, $(dmpe)_2Zr(TeR)_2(Te)$ [δ −706 ppm].[97] Thus, the data currently available suggest that further studies are warranted in order to use ^{77}Se and ^{125}Te NMR spectroscopy with confidence to distinguish between terminal and bridging chalcogenido ligands.

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Table 14. ^{77}Se and ^{125}Te NMR Data[a]

compound	δ_{Se}/ppm	δ_{Te}/ppm
$W(PMe_3)_4(E)H_2$	1955 [qn, $^2J_{Se-P} = 13$]	
$W(PMe_3)_4(E)_2$	803 [qn, $^2J_{Se-P} = 13$]	950 [qn, $^2J_{Te-P} = 17$; $^1J_{W-Te} = 190$]
$W(PMe_3)_4(S)(E)$	691 [qn, $^2J_{Se-P} = 13$]	
$W(PMe_3)_2(CNBu^t)_2(E)_2$	824 [t, $^2J_{Se-P} = 15$]	
$W(PMe_3)_2(E)_2(\eta^2\text{-}OCH_2)$	2312 [t, $^2J_{Se-P} = 12$]	3366 [$^1J_{W-Te} = 312$]
$W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$	2366 [t, $^2J_{Se-P} = 11$] 2397 [t, $^2J_{Se-P} = 13$]	3456 [$^1J_{W-Te} = 319$] 3510 [$^1J_{W-Te} = 312$]
$W(PMe_3)(CNBu^t)_4(\eta^2\text{-}E_2)$		−480 [br s, $\Delta\nu_{1/2} = 199$] −1537 [br s, $\Delta\nu_{1/2} = 205$]

[a] Abbreviations: s = singlet, d = doublet, t = triplet, qn = quintet.

Table 15. ^{1}H NMR Data

compound/assignment	E = S	E = Se	E = Te
$W(PMe_3)_4(E)_2$			
4 $P(CH_3)_3$	1.67 (vt, "J_{P-H}" = 2.7)	1.76 (vt, "J_{P-H}" = 2.7)	1.91 (vt, "J_{P-H}" = 2.8)
$W(PMe_3)_2(E)_2(\eta^2\text{-}OCH_2)$			
2 PMe_3			
1 $P(CH_3)_3$	1.26 (d, $^2J_{P-H} = 7.8$)	1.35 (d, $^2J_{P-H} = 8.6$)	1.46 (d, $^2J_{P-H} = 9.0$)
1 $P(CH_3)_3$	1.34 (d, $^2J_{P-H} = 8.2$)	1.40 (d, $^2J_{P-H} = 8.8$)	1.51 (d, $^2J_{P-H} = 8.5$)
$\eta^2\text{-}OCH_2$	2.97 (d, $^3J_{P-H} = 4.0$; d, $^3J_{P-H} = 1.4$)	2.35 (d, $^3J_{P-H} = 5.1$; d, $^3J_{P-H} = 1.9$)	1.08 (d, $^3J_{P-H} = 6.1$; d, $^3J_{P-H} = 1.9$)
$W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$			
2 PMe_3			
1 $P(CH_3)_3$	1.19 (d, $^2J_{P-H} = 8.4$)	1.29 (d, $^2J_{P-H} = 9.0$)	1.46 (d, $^2J_{P-H} = 8.6$)
1 $P(CH_3)_3$	1.39 (d, $^2J_{P-H} = 8.6$)	1.45 (d, $^2J_{P-H} = 9.8$)	1.51 (d, $^2J_{P-H} = 8.6$)
η^2- OCHPh			
$\eta^2\text{-}OCHC_6H_5$	4.30 (d, $^3J_{P-H} = 4.0$; d, $^3J_{P-H} = 1.4$)	3.79 (d, $^3J_{P-H} = 4.7$; d, $^3J_{P-H} = 2.0$)	2.66 (d, $^3J_{P-H} = 5.4$; d, $^3J_{P-H} = 2.1$)
$\eta^2\text{-}OCHC_6H_5$			
1 H	6.83 (t, $^3J_{H-H} = 7.8$)	6.82 (t, $^3J_{H-H} = 7.5$)	6.83 (t, $^3J_{H-H} = 7.5$)
2 H	7.09 (t, $^3J_{H-H} = 7.8$)	7.07 (t, $^3J_{H-H} = 7.5$)	7.05 (t, $^3J_{H-H} = 7.5$)
2 H	7.22 (d, $^3J_{H-H} = 7.8$)	7.21 (d, $^3J_{H-H} = 7.5$)	7.18 (d, $^3J_{H-H} = 7.5$)
$W(PMe_3)_2(CNBu^t)_2(E)_2$			
2 $P(CH_3)_3$	1.92 (vt, "J_{P-H}" = 3.3)	1.99 (vt, "J_{P-H}" = 3.3)	
2 $CNC(CH_3)_3$	1.13 (s)	1.15 (s)	
$W(PMe_3)(CNBu^t)_4(\eta^2\text{-}E_2)$			
1 $P(CH_3)_3$			1.69 (d, $^2J_{P-H} = 7.9$)
4 $CNC(CH_3)_3$			1.23 (s)
$W(PMe_3)_4(E)H_2$			
4 PMe_3			
2 $P(CH_3)_3$		1.29 (d, "J_{P-H}" = 7.4)	
2 $P(CH_3)_3$		1.89 (vt, "J_{P-H}" = 2.7)	
2 W-H		0.31 (d, $^2J_{P-H} = 47$; d, $^2J_{P-H} = 42$; t, $^2J_{P-H}$ (t) = 38)	

Although examination of Table 14 indicates that there exists no obvious relationship between the chemical shifts of terminal selenido and tellurido ligands with either oxidation state, coordination number, or the nature of the ancillary ligands, a simple correlation does exist between the ^{77}Se and ^{125}Te NMR chemical shifts, as illustrated in Figure 18. A linear relationship between ^{77}Se and ^{125}Te NMR chemical shifts was first noted for a series of closely related organoselenium and organotellurium compounds.[98] Specifically, McFarlane and McFarlane observed a linear relationship in a plot of δ_{Te} *versus* δ_{Se} for a series of structurally-related organoselenium and organotellurium complexes. The observed slope of 1.8 is close to the value of *ca.* 1.55 calculated on the basis of several approximations.[99] However, as the available data on ^{77}Se and ^{125}Te NMR chemical shifts has expanded, the correlation between δ_{Se} and δ_{Te} for organic compounds has been studied by other researchers who have reported a relatively large variation in the slopes in plots of δ_{Te} *versus* δ_{Se}, from at least 1.3 to 2.4, depending upon the specific class of compound under investigation.[99-101] In this regard, the correlation between the ^{77}Se and ^{125}Te NMR chemical shifts for the terminal selenido and tellurido tungsten complexes reported here is $\delta_{Te} = 1.60\delta_{Se} - 338$ ppm. We are

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(96) ^{77}Se chemical shifts in the ranges δ 1000−2500 ppm and δ 600−1000 ppm have been reported for terminal and bridging selenido ligands, respectively, in a variety of anionic polyselenide complexes of tungsten. See, for example: (a) Wardle, R. W. M.; Mahler, C. H.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2790−2795. (b) Wardle, R. W. M.; Bhaduri, S.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 1747−1755. (c) Lu, Y.-J.; Ansari, M. A.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 4049−4050. (d) Ansari, M. A.; Chau, C.-N.; Mahler, C. H.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 650−654. (e) Christuk, C. C.; Ansari, M. A.; Ibers, J. A. *Inorg. Chem.* **1992**, *31*, 4365−4369. (f) Ansari, M. A.; Mahler, C. H.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 2669−2674. (g) Christuk, C. C.; Ibers, J. A. *Inorg. Chem.* **1993**, *32*, 5105−5107.

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Table 16. ^{13}C NMR Data

compound/assignment	E = S	E = Se	E = Te
$W(PMe_3)_4(E)_2$			
4 $P(\textit{C}H_3)_3$	25.1 (m; q, $^1J_{C-H} = 128$)	27.7 (m; q, $^1J_{C-H} = 129$)	33.6 (m; q, $^1J_{C-H} = 130$)
$W(PMe_3)_2(E)_2(\eta^2\text{-}OCH_2)$			
2 PMe_3			
1 $P(\textit{C}H_3)_3$	12.9 (d, $^1J_{P-C} = 26$; q, $^1J_{C-H} = 133$)	14.3 (d, $^1J_{P-C} = 29$; q, $^1J_{C-H} = 130$)	17.5 (d, $^1J_{P-C} = 32$; q, $^1J_{C-H} = 130$)
1 $P(\textit{C}H_3)_3$	16.4 (d, $^1J_{P-C} = 31$; q, $^1J_{C-H} = 132$)	18.3 (d, $^1J_{P-C} = 34$; q, $^1J_{C-H} = 130$)	22.4 (d, $^1J_{P-C} = 38$; q, $^1J_{C-H} = 130$)
$\eta^2\text{-}O\textit{C}H_2$	65.5 (d, $^2J_{P-C} = 12$; t, $^1J_{C-H} = 172$; $^1J_{W-C} = 26$)	67.3 (d, $^2J_{P-C} = 13$; t, $^1J_{C-H} = 172$; $^1J_{W-C} = 26$)	71.8 (d, $^2J_{P-C} = 15$; t, $^1J_{C-H} = 172$; $^1J_{W-C} = 25$)
$W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$			
2 PMe_3			
1 $P(\textit{C}H_3)_3$	12.8 (d, $^1J_{P-C} = 26$; q, $^1J_{C-H} = 130$)	14.3 (d, $^1J_{P-C} = 29$; q, $^1J_{C-H} = 130$)	17.5 (d, $^1J_{P-C} = 32$; q, $^1J_{C-H} = 130$)
1 $P(\textit{C}H_3)_3$	15.8 (d, $^1J_{P-C} = 30$; q, $^1J_{C-H} = 130$)	17.8 (d, $^1J_{P-C} = 33$; q, $^1J_{C-H} = 130$)	21.8 (d, $^1J_{P-C} = 37$; q, $^1J_{C-H} = 130$)
$\eta^2\text{-}OCHPh$			
$\eta^2\text{-}O\textit{C}HC_6H_5$	80.0 (d, $^2J_{P-C} = 11$; d, $^1J_{C-H} = 171$; $^1J_{W-C} = 25$)	81.4 (d, $^2J_{P-C} = 12$; d, $^1J_{C-H} = 171$; $^1J_{W-C} = 25$)	84.5 (d, $^2J_{P-C} = 13$; d, $^1J_{C-H} = 172$; $^1J_{W-C} = 25$)
$\eta^2\text{-}OCH\textit{C}_6H_5$			
2 C	126.6 (d, $^1J_{C-H} = 161$)	126.9 (d, $^1J_{C-H} = 160$)	126.9 (d, $^1J_{C-H} = 161$)
1 C	126.9 (d, $^1J_{C-H} = 161$)	127.0 (d, $^1J_{C-H} = 159$)	127.7 (d, $^1J_{C-H} = 160$)
2 C	127.7 (d, $^1J_{C-H} = 155$)	127.7 (d, $^1J_{C-H} = 159$)	127.5 (d, $^1J_{C-H} = 160$)
1 C	144.6 (s)	143.7 (s)	142.0 (s)
$W(PMe_3)_2(CNBu^t)_2(E)_2$			
2 $P(\textit{C}H_3)_3$	22.5 (vt, "J_{P-C}" = 14; q, $^1J_{C-H} = 128$)	24.9 (vt, "J_{P-C}" = 14; q, $^1J_{C-H} = 129$)	
2 $CNBu^t$			
$CNC(\textit{C}H_3)_3$	30.6 (q, $^1J_{C-H} = 128$)	30.6 (q, $^1J_{C-H} = 128$)	
$CN\textit{C}(CH_3)_3$	55.9 (s)	56.0 (s)	
$\textit{C}NC(CH_3)_3$	161.6 (s)	162.2 (m)	
$W(PMe_3)(CNBu^t)_4(\eta^2\text{-}E_2)$			
1 $P(\textit{C}H_3)_3$			21.5 (d, $^1J_{P-C} = 29$; q, $^1J_{C-H} = 128$)
4 $CNBu^t$			
$CNC(\textit{C}H_3)_3$			31.2 (q, $^1J_{C-H} = 127$)
$CN\textit{C}(CH_3)_3$			57.4 (s)
$\textit{C}NC(CH_3)_3$			not located
$W(PMe_3)_4(E)H_2$			
4 PMe_3			
2 $P(\textit{C}H_3)_3$		27.0 (vt, "J_{P-C}" = 14; q, $^1J_{C-H} = 127$)	
2 $P(\textit{C}H_3)_3$		28.8 (m; q, $^1J_{C-H} = 130$)	

Table 17. ^{31}P NMR Data

compound/assignment	E = S	E = Se	E = Te
$W(PMe_3)_4(E)_2$			
4 $\textit{P}(CH_3)_3$	−44.3 (s, $^1J_{W-P} = 268$)	−48.2 (s, $^1J_{W-P} = 255$)	−51.2 (s, $^1J_{W-P} = 238$; $^2J_{Te-P} = 17$)
$W(PMe_3)_2(E)_2(\eta^2\text{-}OCH_2)$			
2 PMe_3	AB quartet		
1 $\textit{P}(CH_3)_3$	−3.5 ($^2J_{P-P} = 359$; $^1J_{W-P} = 210$)	10.0 (d, $^2J_{P-P} = 327$; $^1J_{W-P} = 206$)	41.2 (d, $^2J_{P-P} = 257$; $^1J_{W-P} = 159$)
1 $\textit{P}(CH_3)_3$	2.3 ($^2J_{P-P} = 359$; $^1J_{W-P} = 210$)	19.6 (d, $^2J_{P-P} = 327$; $^1J_{W-P} = 182$)	62.0 (d, $^2J_{P-P} = 257$; $^1J_{W-P} = 180$)
$W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$			
2 PMe_3	AB quartet		
1 $\textit{P}(CH_3)_3$	−2.6 ($^2J_{P-P} = 365$; $^1J_{W-P} = 215$)	10.9 (d, $^2J_{P-P} = 332$; $^1J_{W-P} = 202$)	42.3 (d, $^2J_{P-P} = 260$; $^1J_{W-P} = 159$)
1 $\textit{P}(CH_3)_3$	2.8 ($^2J_{P-P} = 365$; $^1J_{W-P} = 215$)	20.1 (d, $^2J_{P-P} = 332$; $^1J_{W-P} = 193$)	63.1 (d, $^2J_{P-P} = 260$; $^1J_{W-P} = 180$)
$W(PMe_3)_2(CNBu^t)_2(E)_2$			
2 $\textit{P}(CH_3)_3$	−44.8 (s, $^1J_{W-P} = 271$)	−49.9 (s, $^1J_{W-P} = 258$; $^2J_{Se-P} = 14$)	
$W(PMe_3)(CNBu^t)_4(\eta^2\text{-}E_2)$			
1 $\textit{P}(CH_3)_3$			−49.6 (s, $^1J_{W-P} = 209$; $^2J_{Te-P} = 33$)
$W(PMe_3)_4(E)H_2$			
4 PMe_3			
2 $\textit{P}(CH_3)_3$		−7.2 (t, $^2J_{P-P} = 9$; $^1J_{W-P} = 270$)	
2 $\textit{P}(CH_3)_3$		−12.1 (t, $^2J_{P-P} = 9$; $^1J_{W-P} = 187$)	

not aware of any previous reports of such correlations for other transition-metal tellurium and selenium derivatives. Nevertheless, the molybdenum and tantalum terminal selenido and tellurido complexes, $Mo(PMe_3)_4(E)_2$[42] and $Cp^*{}_2Ta(E)X$ (X = H, Me),[71,72] also exhibit chemical shifts that are consistent with those predicted by the tungsten correlation. However, the tantalum selenido and tellurido complexes $[\eta^4\text{-}N(CH_2CH_2\text{-}NSiMe_3)_3]Ta(E)$[102] do deviate slightly from this correlation.[103] It should, however, be emphasized that the correlation between

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(101) For recent theoretical calculations of some ^{77}Se NMR chemical shifts, see: Nakatsuji, H.; Higashioji, T.; Sugimoto, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3235−3240.

(102) Christou, V.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1450−1452.

(103) The best line fit, constrained to passing through the origin, for all the complexes in Figure 18 is $\delta_{Te} = 1.41\delta_{Se}$.

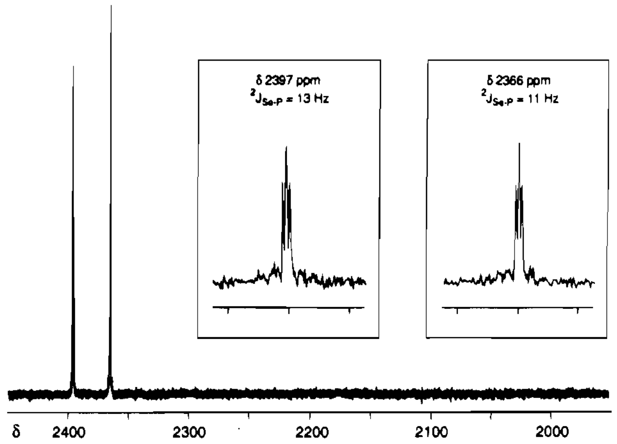

Figure 17. $^{77}Se\{^1H\}$ NMR spectrum of $W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHPh)$.

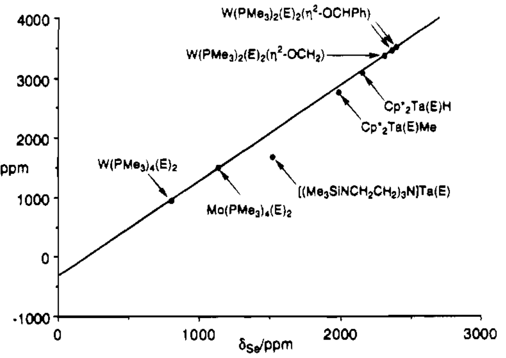

Figure 18. Correlation between ^{77}Se and ^{125}Te NMR chemical shifts for terminal selenido and tellurido complexes.

^{77}Se and ^{125}Te chemical shifts for compounds such as $W(PMe_3)_4(E)_2(\eta^2\text{-}OCHR)$ and $M(PMe_3)_4(E)_2$ (M = Mo, W) is one in which *pairs* of terminal chalcogenido ligands are simultaneously compared. Strictly speaking, for example, rather than comparing the ^{125}Te NMR chemical shift of $W(PMe_3)_4(Te)_2$ with the ^{77}Se chemical shift of $W(PMe_3)_4(Se)_2$, the ^{125}Te NMR chemical shift should be compared with the ^{77}Se NMR chemical shift of $W(PMe_3)_4(Se)(Te)$, in a similar manner to that discussed previously for R_2E_2 derivatives.[98,104] Likewise, the ^{77}Se chemical shift of $W(PMe_3)_4(Se)_2$ should be compared with the ^{125}Te NMR chemical shift of $W(PMe_3)_4(Se)(Te)$. However, regardless of such subtleties, it is evident that a correlation of the type presented in Figure 18 is certainly of use in helping predict the location of the ^{125}Te NMR chemical shift of a complex if the ^{77}Se NMR shift of the selenium analogue is known. Such information is useful in view of both *(i)* the very large range that is presently known for ^{125}Te NMR chemical shifts and *(ii)* the difficulty that is often encountered in locating ^{125}Te NMR signals. The correlation between ^{77}Se and ^{125}Te NMR chemical shifts may also be of use in characterization of transition metal selenido and tellurido complexes. For example, if the ^{77}Se and ^{125}Te NMR chemical shifts of two related selenium and tellurium complexes correlate as illustrated in Figure 18, it would support the notion that they are of the same structural type.[105] Conversely, if the ^{77}Se and ^{125}Te NMR chemical shifts do not correlate, it is likely that the two complexes are not structurally related.[106]

Summary

In summary, the series of terminal chalcogenido complexes $W(PMe_3)_4(E)_2$ (E = S, Se, Te) have been synthesized. Of these complexes, $W(PMe_3)_4(Te)_2$ is the first example of a transition-metal complex containing a terminal tellurido ligand. The terminal sulfido and selenido complexes were synthesized by the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with H_2E (E = S, Se), while the tellurido complex was prepared by the corresponding reaction with elemental Te.

Each of the chalcogenido complexes $W(PMe_3)_4(E)_2$ reacts reversibly with RCHO to yield the η^2-aldehyde derivatives $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$. Thus, by varying the ligand array, the *cis* and *trans* chalcogenido ligands may be interconverted. For the reactions with benzaldehyde, it was demonstrated that the equilibrium constants for the reactions vary strongly as a function of the chalcogen. Thus, the equilibrium constants span the substantial range of more than 3 orders of magnitude, with $K_S \gg K_{Se} > K_{Te}$.

In contrast to the formation of analogous products in the reactions of $W(PMe_3)_4(E)_2$ with aldehydes, the corresponding reactions with Bu^tNC give two types of product, depending upon the chalcogen. Thus, the sulfido and selenido complexes $W(PMe_3)_4(E)_2$ (E = S, Se) react with Bu^tNC to give $W(PMe_3)_2(CNBu^t)_2(E)_2$, whereas the reaction of the tellurido derivative $W(PMe_3)_4(Te)_2$ with Bu^tNC results in coupling of the two tellurido ligands, leading to the formation of the η^2-ditellurido derivative $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$.

The terminal selenido and tellurido complexes have been studied by ^{77}Se and ^{125}Te NMR spectroscopy. From these data it is evident that the NMR chemical shifts of these terminal chalcogenido complexes may span a very large range. For example, a range of more than 1700 ppm and 2500 ppm is observed for the ^{77}Se and ^{125}Te NMR chemical shifts of terminal selenido and tellurido ligands, respectively, in a series of closely related complexes. Moreover, the two ^{125}Te signals for the ditellurido complex $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ (δ −480 ppm and −1537 ppm) differ by more than 1000 ppm. Such a large range in chemical shifts for the W=E moiety indicates that considerable care must be exercised in order to distinguish with confidence between terminal and bridging chalcogenido ligands in other systems on the basis of chemical shifts alone. Finally, the ^{77}Se and ^{125}Te NMR studies have allowed a correlation to be derived for terminal selenido and tellurido complexes which should be of use in the characterization of other systems.

Experimental Details

General Considerations. All manipulations were performed by using a combination of glovebox, high-vacuum or Schlenk techniques.[107] Solvents were purified and degassed by standard procedures and all commercially available reagents were used as received. $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ was prepared as described previously.[53] H_2Se and D_2Se were synthesized by the acid hydrolysis of Al_2Se_3.[108] IR spectra were recorded as KBr pellets on Perkin-Elmer 1430 or 1600 spectrophotometers and are reported in reciprocal centimeters. Mass spectra were

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(104) In this regard, it has been observed that the ^{125}Te NMR chemical shifts of the ditellurides R_2Te_2 (R = Me, Et, Pr^i) are in fact linearly related to the ^{77}Se NMR chemical shifts of the corresponding diselenides R_2Se_2 (see ref 98). Thus, it does not seem unreasonable to include such pairs of complexes in a general correlation of ^{77}Se and ^{125}Te NMR chemical shifts.

(105) Of course, the fact that ^{77}Se and ^{125}Te NMR chemical shifts may correlate does not prove that two compounds are structurally analagous.

(106) As an illustration, it has been observed that for the two most stable complexes of composition $Cp^*_2TaE_2H$ (E = Se, Te), the ^{77}Se and 125Te NMR chemical shifts do not correlate, as a consequence of the fact that in the selenium system $Cp^*_2TaSe_2H$ exists as the terminal selenido isomer $Cp^*_2Ta(Se)(SeH)$, whereas the tellurium complex adopts the form of a ditellurido derivative, *i.e.*, $Cp^*_2Ta(\eta^2\text{-}Te_2)H$. The ^{77}Se NMR chemical shifts of the less stable tautomer of $Cp^*_2TaSe_2H$, *i.e.*, $Cp^*_2Ta(\eta^2\text{-}Se_2)H$, do, however, correlate with the ^{125}Te NMR chemical shifts of $Cp^*_2Ta(\eta^2\text{-}Te_2)H$. See refs 71 and 72.

obtained on a Nermag R10-10 mass spectrometer by using chemical ionization (NH_3 or CH_4) techniques. Elemental analyses were measured on a Perkin-Elmer 2400 CHN elemental analyzer. ^{1}H NMR spectra were recorded on Varian VXR-200 (200.057 MHz), VXR-300 (299.943 MHz), and VXR-400 (399.95 MHz) spectrometers. ^{13}C, ^{31}P, ^{77}Se, and ^{125}Te NMR spectra were recorded on the Varian VXR-300 spectrometer operating at 75.429, 121.421, 57.22, and 94.63 MHz, respectively. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent resonances (^{1}H, $\delta = 7.15$ for C_6D_5H; ^{13}C, $\delta = 128.0$ for C_6D_6). ^{31}P chemical shifts are reported in ppm relative to 85% H_3PO_4 ($\delta = 0$) and were referenced to $P(OMe)_3$ ($\delta = 141.0$) as external standard. ^{77}Se chemical shifts are reported in ppm relative to neat Me_2Se ($\delta = 0$) and were referenced to a solution of Ph_2Se_2 in C_6D_6 ($\delta = 460$) as external standard.[109] ^{125}Te chemical shifts are reported in ppm relative to neat Me_2Te ($\delta = 0$) and were referenced to either a solution of Ph_2Te_2 in $CDCl_3$ ($\delta = 420.8$)[110] or a solution of $Te(OH)_6$ (1.74 M in D_2O, $\delta = 712$)[111,112] as external standards. All coupling constants are reported in hertz. NMR spectroscopic data for selected complexes are presented in Tables 14−17.

Synthesis of $W(PMe_3)_4H_2(SH)_2$. A stirred solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (1.09 g, 1.93 mmol) in pentane (20 mL) was treated with excess H_2S (1 atm), resulting in the rapid formation of a mustard-yellow precipitate. After stirring at room temperature for 5 min, the volume of the mixture was reduced *in vacuo* to *ca.* 10 mL, and $W(PMe_3)_4H_2(SH)_2$ was isolated by filtration at −78 °C and dried *in vacuo* (0.91 g, 86%). Analysis calculated for $C_{12}H_{40}P_4S_2W$: C, 25.9%; H, 7.3%. Found: C, 25.8%; H, 6.8%. IR data: 2972 (vs), 2908 (vs), 2546 (s) (ν_{S-H}), 1862 (vs) [ν_{W-H}], 1415 (vs), 1295 (vs), 1277 (vs), 935 (vs), 847 (vs), 705 (vs), 664 (vs). A sample of $W(PMe_3)_4H_2(SH)_2\text{-}d_4$[113] was prepared similarly from $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and an excess of D_2S. IR data: 1850 (m) (ν_{S-D}), 1337 (s) (ν_{W-D}).

Synthesis of *trans*-$W(PMe_3)_4(S)_2$. Method A. $W(PMe_3)_4H_2(SH)_2$ (0.88 g, 1.61 mmol) was dissolved in benzene (30 mL), rapidly giving a purple solution of $W(PMe_3)_4(S)_2$ accompanied by evolution of H_2. After stirring for 10 min at room temperature, the solution was filtered and the solvent removed under reduced pressure to give a lilac powder, which was washed with pentane (10 mL) and dried *in vacuo* (0.86 g, 97%). Analysis calculated for $C_{12}H_{36}P_4S_2W$: C, 26.1%; H, 6.6%. Found: C, 26.1%; H, 6.4%. IR data: 2968 (m), 2905 (s), 1420 (s), 1294 (m), 1276 (vs), 941 (vs), 855 (m), 720 (m), 708 (s), 662 (s), 390 (s) ($\nu_{W=S}$), 350 (w).

Method B. A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.86 g, 1.52 mmol) in benzene (30 mL) was treated with excess H_2S (1 atm). After stirring at room temperature for 30 min, the resulting purple-brown solution was filtered, and the solvent was removed under reduced pressure to give $W(PMe_3)_4(S)_2$ as a grayish-lilac powder (0.72 g, 86%).

Synthesis of $W(PMe_3)_4(Se)H_2$. A stirred solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (2.32 g, 4.11 mmol) in pentane (30 mL) was treated with H_2Se (*ca.* 2 mmol), resulting in the immediate formation of $W(PMe_3)_4(Se)H_2$ as an emerald-green precipitate. The mixture was concentrated to *ca.* 15 mL and the product was isolated by filtration at −78 °C, washed with pentane (2 × 10 mL), and dried *in vacuo* (0.57 g). Spectroscopically pure (by ^{1}H NMR) $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (*ca.* 1.2 g) was recovered by removing the solvent from the filtrate under reduced pressure. The yield of $W(PMe_3)_4(Se)H_2$ based on consumed $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ is *ca.* 50%. Analysis calculated for $C_{12}H_{38}P_4SeW$: C, 25.3%; H, 6.7%. Found: C, 25.2%; H, 6.4%. IR data: 2965 (s), 2901 (vs), 1775 (vs) (ν_{W-H}), 1423 (s), 1288 (s), 1277 (s), 931 (vs), 850 (s), 711 (vs), 666 (vs). MS: $m/z = 571$ ($M^+ + 1$).

Synthesis of *trans*-$W(PMe_3)_4(Se)_2$. A stirred solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.54 g, 0.96 mmol) in benzene (50 mL) was treated with excess H_2Se (*ca.* 3 mmol), resulting in the rapid formation of a green solution. After stirring at room temperature for 10 min, the solution was filtered and the solvent removed under reduced pressure to give $W(PMe_3)_4(Se)_2$ as a green powder, which was washed with pentane (5 mL) and dried *in vacuo* (0.57 g, 92%). Analysis calculated for $C_{12}H_{36}P_4Se_2W$: C, 22.3%; H, 5.6%. Found: C, 22.4%; H, 5.4%. IR data: 2992 (w), 2968 (m), 2905 (s), 1418 (s), 1292 (m), 1276 (s), 931 (vs), 855 (m), 708 (m), 661 (s).

Synthesis of *trans*-$W(PMe_3)_4(S)(Se)$. A stirred solution of $W(PMe_3)_4(Se)H_2$ (0.30 g, 0.53 mmol) in benzene (20 mL) was treated with excess H_2S (1 atm), resulting in the rapid formation of an olive-green solution. After stirring at room temperature for 5 min, the solution was filtered and the solvent removed under reduced pressure to give $W(PMe_3)_4(S)(Se)$ as an olive-green powder, which was washed with pentane (5 mL) and dried *in vacuo* (0.27 g, 85%). Analysis calculated for $C_{12}H_{36}P_4SSeW$: C, 24.1%; H, 6.1%. Found: C, 24.4%; H, 5.8%. IR data: 2992 (w), 2969 (m), 2906 (s), 1419 (m), 1292 (m), 1276 (s), 936 (vs), 856 (w), 709 (m), 662 (m), 412 (s) ($\nu_{W=S}$). ^{1}H NMR: δ 1.72 [vt, "J_{P-H}" = 2.7, 4 $P(CH_3)_3$]. ^{13}C NMR: δ 26.4 [m, $^{1}J_{C-H}(q) = 128$, 4 $P(CH_3)_3$]. ^{31}P NMR: δ −47.1 [s, $^{1}J_{W-P} = 262$, 4 $P(CH_3)_3$].

Synthesis of *trans*-$W(PMe_3)_4(Te)_2$. Method A. A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (5.12 g, 9.07 mmol) in pentane (30 mL) was stirred with elemental Te powder (2.05 g, 16.1 mmol) for 1 day at room temperature, resulting in the precipitation of *trans*-$W(PMe_3)_4(Te)_2$ as a red-brown solid. The mixture was filtered to separate the product, which was washed with pentane (10 mL) and extracted into benzene (*ca.* 60 mL). The benzene extract was filtered and the solvent removed under reduced pressure to give pure *trans*-$W(PMe_3)_4(Te)_2$ as a red-brown powder (0.62 g). The residue (4.20 g) is sufficiently pure for further reactions. The overall yield is *ca.* 80% (based on Te). Analysis calculated for $C_{12}H_{36}P_4Te_2W$: C, 19.4%; H, 4.9%. Found: C, 19.4%; H, 4.6%. IR data: 2987 (w), 2964 (w), 2902 (s), 1433 (w), 1415 (s), 1292 (s), 1275 (s), 932 (vs), 854 (w), 841 (w), 704 (m), 678 (w), 660 (s), 348 (m), 303 (w).

Method B. Elemental Te (0.33 g, 2.59 mmol) and PMe_3 (*ca.* 1 mL, 9.7 mmol) in benzene (5 mL) were stirred at room temperature for 1 h, resulting in the formation of an off-white solid suspended in a pale yellow solution. The suspension was added to a stirred solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.81 g, 1.44 mmol) in pentane (30 mL), resulting in the rapid formation of $W(PMe_3)_4(Te)_2$ as a red-brown microcrystalline solid. After stirring the mixture for 30 min at room temperature, the product was separated by filtration, washed with pentane (10 mL), and dried *in vacuo* (0.75 g, 78%).

Synthesis of $W(PMe_3)_2(S)_2(\eta^2\text{-}OCH_2)$. A suspension of $W(PMe_3)_4(S)_2$ (0.38 g, 0.69 mmol) and paraformaldehyde (0.30 g, 10.0 mmol) in benzene (20 mL) was stirred at room temperature for 1 day. The solution was filtered and the solvent removed under reduced pressure to give $W(PMe_3)_2(S)_2(\eta^2\text{-}OCH_2)$ as a magenta powder, which was washed with pentane (5 mL) at −78 °C and dried *in vacuo* (0.17 g, 58%). Analysis calculated for $C_7H_{20}OP_2S_2W$: C, 19.6%; H, 4.7%. Found: C, 19.6%; H, 4.5%. IR data: 2970 (s), 2900 (s), 1412 (s), 1297 (m), 1282 (vs), 1116 (s), 1093 (m), 949 (vs), 878 (w), 846 (w), 744 (m), 674 (w), 596 (m), 505 (w), 457 (vs) ($\nu_{W=S}$). MS: $m/z = 431$ ($M^+ + 1$).

Synthesis of $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHMe)$. A solution of $W(PMe_3)_4(S)_2$ (0.40 g, 0.72 mmol) in benzene (15 mL) was treated with excess MeCHO (*ca.* 0.3 mL, 5.4 mmol) and stirred at room temperature for 2 h. The volatile components were removed under reduced pressure, and the oily residue was redissolved in benzene (*ca.* 10 mL) and treated again with MeCHO (*ca.* 0.3 mL). After it was stirred further for 30 min, the solution was filtered and the solvent removed *in vacuo* to

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(112) The ^{125}Te NMR signal for aqueous $Te(OH)_6$ has also been reported to be 707 ppm.[112a] However, we find better internal consistency adopting the value of 712 ppm (as in ref 111). (a) Tötsch, W.; Peringer, P.; Sladky, F. *J. Chem. Soc., Chem. Commun.* **1981**, 841−842.

(113) The sample obtained was not a single isotopomer, *e.g.*, $W(PMe_3)_4D_2(SD)_2$, due to incorporation of deuterium into the PMe_3 groups (*cf.* the analogous reaction with D_2Se, see text).

Table 18. Crystal and Intensity Collection Data

	$\mathrm{W(PMe_3)_4(S)_2}$	$\mathrm{W(PMe_3)_4(Se)_2}$	$\mathrm{W(PMe_3)_4(Te)_2}$
formula	$\mathrm{C_{12}H_{36}P_4S_2W}$	$\mathrm{C_{12}H_{36}P_4Se_2W}$	$\mathrm{C_{12}H_{36}P_4Te_2W}$
formula weight	552.3	646.1	743.4
lattice	monoclinic	monoclinic	tetragonal
cell constants			
a, Å	15.914(2)	16.040(5)	9.717(1)
b, Å	9.682(2)	9.738(2)	9.717(1)
c, Å	15.926(3)	16.096(3)	12.360(2)
α, deg	90.0	90.0	90.0
β, deg	111.92(2)	113.27(2)	90.0
γ, deg	90.0	90.0	90.0
V, Å^3	2276(1)	2310(1)	1167(1)
Z	4	4	2
radiation (*λ*, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
space group	*P*2/*n* (No. 13)	*P*2/*n* (No. 13)	$I\bar{4}2m$ (No. 121)
ρ (calcd), g cm^{-3}	1.61	1.86	2.12
μ (Mo Kα), cm^{-1}	55.3	84.2	76.6
2*θ* range, deg	3–50	3–50	3–60
no. of data	3275 [$F > 4\sigma(F)$]	3009 [$F > 4\sigma(F)$]	499 [$F > 6\sigma(F)$]
no. of params	174	174	29
R^a	0.0420	0.0378	0.0202
$R_w{}^a$	0.0660	0.0464	0.0292

	$\mathrm{W(PMe_3)_4(CNBu^t)_2(S)_2}$	$\mathrm{W(PMe_3)_4(CNBu^t)_2(Se)_2}$	$\mathrm{W(PMe_3)_4(Te)_2(\eta^2\text{-}OCH_2)}$
formula	$\mathrm{C_{16}H_{36}N_2P_2S_2W}$	$\mathrm{C_{16}H_{36}N_2P_2Se_2W}$	$\mathrm{C_7H_{20}OP_2Te_2W}$
formula weight	566.4	660.2	621.2
lattice	monoclinic	monoclinic	orthorhombic
cell constants			
a, Å	11.003(2)	11.147(5)	10.441(3)
b, Å	10.513(3)	10.617(5)	11.299(4)
c, Å	11.947(3)	11.973(4)	13.812(4)
α, deg	90.0	90.0	90.0
β, deg	109.87(2)	110.16(3)	90.0
γ, deg	90.0	90.0	90.0
V, Å^3	1300(1)	1328(1)	1630(1)
Z	2	2	4
radiation (*λ*, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	*Pnma* (No. 62)
ρ (calcd), g cm^{-3}	1.45	1.65	2.53
μ (Mo Kα), cm^{-1}	47.3	72.0	107.7
2*θ* range, deg	3–55	3–52	3–50
no. of data	2032 [$F > 6\sigma(F)$]	1996 [$F > 4\sigma(F)$]	1124 [$F > 6\sigma(F)$]
no. of params	163	69	71
R^a	0.0302	0.0488	0.0390
$R_w{}^a$	0.0389	0.0636	0.0502

give $\mathrm{W(PMe_3)_2(S)_2(\eta^2\text{-}OCHMe)}$ as a red-purple powder (0.18 g, 56%). Analysis calculated for $\mathrm{C_8H_{22}OP_2S_2W}$: C, 21.6%; H, 5.0%. Found: C, 21.1%; H, 4.5%. IR data: 2972 (m), 2902 (s), 1418 (s), 1365 (w), 1339 (w), 1299 (m), 1280 (vs), 1160 (m), 1094 (w), 1066 (m), 948 (vs), 886 (w), 843 (w), 736 (m), 670 (w), 601 (m), 493 (w), 472 (m), 456 (vs) ($\nu_{\mathrm{W=S}}$). MS: $m/z = 445$ ($\mathrm{M}^+ + 1$). ^{1}H NMR: δ 1.35 [9 H, d, $^2J_{\mathrm{P-H}} = 7.6$, 1 $\mathrm{P(C\mathit{H}_3)_3}$], 1.36 [9 H, d, $^2J_{\mathrm{P-H}} = 8.0$, 1 $\mathrm{P(C\mathit{H}_3)_3}$], 2.26 [3 H, dd, $^3J_{\mathrm{H-H}} = 5.0$, $^4J_{\mathrm{P-H}} = 0.9$, η^2-$\mathrm{OCHC\mathit{H}_3}$], 3.64 [1 H, m, η^2-$\mathrm{OC\mathit{H}CH_3}$]. ^{13}C NMR: δ 13.0 [dq, $^1J_{\mathrm{P-C}}(\mathrm{d}) = 24$, $^1J_{\mathrm{C-H}}(\mathrm{q}) = 130$, 1 $\mathrm{P(\mathit{C}H_3)_3}$], 16.9 [dq, $^1J_{\mathrm{P-C}}(\mathrm{d}) = 29$, $^1J_{\mathrm{C-H}}(\mathrm{q}) = 130$, 1 $\mathrm{P(\mathit{C}H_3)_3}$], 24.8 [dq, $^2J_{\mathrm{C-H}}(\mathrm{d}) = 7$, $^1J_{\mathrm{C-H}}(\mathrm{q}) = 126$, η^2-$\mathrm{OCH\mathit{C}H_3}$], 76.8 [dd, $^1J_{\mathrm{C-H}} = 168$, $^2J_{\mathrm{P-C}} = 12$, $^1J_{\mathrm{W-C}} = 29$, η^2-$\mathrm{O\mathit{C}HCH_3}$]. ^{31}P NMR: AB quartet δ −3.1 [$^2J_{\mathrm{P-P}} = 359$, $^1J_{\mathrm{W-P}} = 210$, 1 $\mathrm{\mathit{P}(CH_3)_3}$], 0.8 [$^2J_{\mathrm{P-P}} = 359$, $^1J_{\mathrm{W-P}} = 210$, 1 $\mathrm{\mathit{P}(CH_3)_3}$].

Synthesis of $\mathbf{W(PMe_3)_2(S)_2(\boldsymbol{\eta}^2\text{-}OCHPh)}$. A solution of $\mathrm{W(PMe_3)_4(S)_2}$ (0.53 g, 0.96 mmol) in benzene (20 mL) was treated with PhCHO (*ca.* 0.5 mL, 4.9 mmol) and stirred at room temperature for 4 h. The solution was then filtered and the solvent removed *in vacuo* to give $\mathrm{W(PMe_3)_2(S)_2(\eta^2\text{-}OCHPh)}$ as a bright purple powder (0.41 g, 84%). Analysis calculated for $\mathrm{C_{13}H_{24}OP_2S_2W}$: C, 30.8%; H, 4.8%. Found: C, 32.1%; H, 4.6%. IR data: 3080 (w), 3057 (w), 3030 (w), 2973 (m), 2903 (s), 1598 (m), 1492 (m), 1452 (m), 1413 (s), 1298 (m), 1280 (vs), 1219 (w), 1120 (w), 1106 (w), 1070 (m), 1030 (w), 951 (vs), 847 (w), 821 (w), 757 (s), 738 (m), 720 (w), 697 (s), 670 (w), 629 (s), 595 (m), 500 (w), 470 (s), 459 (vs) ($\nu_{\mathrm{W=S}}$).

Synthesis of $\mathbf{W(PMe_3)_2(S)_2(\boldsymbol{\eta}^2\text{-}OCHC_6H_4Me)}$. A solution of $\mathrm{W(PMe_3)_4(S)_2}$ (0.39 g, 0.71 mmol) in benzene (30 mL) was treated with *p*-$\mathrm{MeC_6H_4CHO}$ (130 μL, 1.10 mmol) and stirred at room temperature for 2 h. The mixture was filtered and the solvent removed under reduced pressure to give $\mathrm{W(PMe_3)_2(S)_2(\eta^2\text{-}OCHC_6H_4Me)}$ as a purple powder, which was washed with pentane (10 mL) and dried *in vacuo* (0.32 g, 87%). Analysis calculated for $\mathrm{C_{14}H_{26}OP_2S_2W}$: C, 32.3%; H, 5.0%. Found: C, 32.6%; H, 5.0%. IR data: 3018 (m), 2973 (m), 2903 (s), 1608 (w), 1511 (s), 1414 (vs), 1371 (w), 1297 (m), 1279 (vs), 1220 (w), 1122 (w), 1096 (m), 1034 (w), 954 (vs), 852 (m), 838 (m), 818 (s), 755 (m), 742 (m), 714 (w), 670 (w), 644 (w), 608 (s), 569 (w), 532 (w), 491 (w), 462 (vs) ($\nu_{\mathrm{W=S}}$). MS: $m/z = 521$ ($\mathrm{M}^+ + 1$). ^{1}H NMR: δ 1.23 [9 H, d, $^2J_{\mathrm{P-H}} = 8.4$, 1 $\mathrm{P(C\mathit{H}_3)_3}$], 1.40 [9 H, d, $^2J_{\mathrm{P-H}} = 8.6$, 1 $\mathrm{P(C\mathit{H}_3)_3}$], 2.17 [3 H, s, η^2-$\mathrm{OCHC_6H_4C\mathit{H}_3}$], 4.35 [1 H, dd, $^3J_{\mathrm{P-H}} = 4.0$, $^3J_{\mathrm{P-H}} = 1.7$, η^2-$\mathrm{OC\mathit{H}C_6H_4CH_3}$], 6.94 [2 H, m, η^2-$\mathrm{OCHC_6\mathit{H}_4CH_3}$], 7.16 [2 H, m, η^2-$\mathrm{OCHC_6\mathit{H}_4CH_3}$]. ^{13}C NMR: δ 12.8 [dq, $^1J_{\mathrm{P-C}}(\mathrm{d}) = 26$, $^1J_{\mathrm{C-H}}(\mathrm{q}) = 130$, 1 $\mathrm{P(\mathit{C}H_3)_3}$], 15.9 [dq, $^1J_{\mathrm{P-C}}(\mathrm{d}) = 30$, $^1J_{\mathrm{C-H}}(\mathrm{q}) = 130$, 1 $\mathrm{P(\mathit{C}H_3)_3}$], 20.8 [q, $^1J_{\mathrm{C-H}} = 126$, η^2-$\mathrm{OCHC_6H_4\mathit{C}H_3}$], 80.3 [dd, $^1J_{\mathrm{C-H}} = 170$, $^2J_{\mathrm{P-C}} = 11$, $^1J_{\mathrm{W-C}} = 25$, η^2-$\mathrm{O\mathit{C}HC_6H_4CH_3}$], 126.7 [d, $^1J_{\mathrm{C-H}} = 158$, η^2-$\mathrm{OCH\mathit{C}_6H_4CH_3}$], 128.5 [d, $^1J_{\mathrm{C-H}} = 158$, η^2-$\mathrm{OCH\mathit{C}_6H_4CH_3}$], 136.5 [s, η^2-$\mathrm{OCH\mathit{C}_6H_4CH_3}$], 141.5 [s, η^2-$\mathrm{OCH\mathit{C}_6H_4CH_3}$]. ^{31}P NMR: AB quartet δ −2.7 [$^2J_{\mathrm{P-P}} = 365$, $^1J_{\mathrm{W-P}} = 215$, 1 $\mathrm{\mathit{P}(CH_3)_3}$], 3.1 [$^2J_{\mathrm{P-P}} = 365$, $^1J_{\mathrm{W-P}} = 215$, 1 $\mathrm{\mathit{P}(CH_3)_3}$].

Synthesis of $\mathbf{W(PMe_3)_2(S)_2(\boldsymbol{\eta}^2\text{-}OCHC_6H_4OMe)}$. A solution of $\mathrm{W(PMe_3)_4(S)_2}$ (0.34 g, 0.62 mmol) in benzene (35 mL) was treated with *p*-$\mathrm{MeOC_6H_4CHO}$ (90 μL, 0.74 mmol) and stirred at room temperature for 1.5 h. The mixture was filtered and the solvent removed under reduced pressure to give $\mathrm{W(PMe_3)_2(S)_2(\eta^2\text{-}OCHC_6H_4OMe)}$ as a purple powder, which was washed with pentane (3 × 10 mL) and dried

Table 18 (Continued)

	$W(PMe_3)_2(S)_2(\eta^2\text{-OCHPh})$	$W(PMe_3)_2(Se)_2(\eta^2\text{-OCHPh})$	$W(PMe_3)_2(Te)_2(\eta^2\text{-OCHPh})$
formula	$C_{13}H_{24}OP_2S_2W$	$C_{13}H_{24}OP_2Se_2W$	$C_{13}H_{24}OP_2Te_2W$
formula weight	506.2	600.0	697.3
lattice	monoclinic	monoclinic	monoclinic
cell constants			
a, Å	12.561(3)	12.563(5)	12.661(2)
b, Å	8.684(1)	8.731(4)	8.931(1)
c, Å	18.182(3)	18.461(6)	18.779(4)
α, deg	90.0	90.0	90.0
β, deg	108.57(2)	109.22(3)	108.47(2)
γ, deg	90.0	90.0	90.0
V, Å^3	1880(1)	1909(1)	2014(1)
Z	4	4	4
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
ρ (calcd), g cm^{-3}	1.79	2.08	2.30
μ (Mo Kα), cm^{-1}	65.3	100.1	87.3
2θ range, deg	3−52	3−50	3−50
no. of data	2820 [$F > 6\sigma(F)$]	3168 [$F > 4\sigma(F)$]	2894 [$F > 6\sigma(F)$]
no. of params	177	177	177
R^a	0.0348	0.0473	0.0387
$R_w{}^a$	0.0479	0.0533	0.0494

	$W(PMe_3)_4(Se)H_2$	$W(PMe_3)_2(CNBu^t)_4(\eta^2\text{-Te}_2)$
formula	$C_{12}H_{38}P_4SeW$	$C_{23}H_{45}N_4PTe_2W$
formula weight	569.1	847.7
lattice	monoclinic	orthorhombic
cell constants		
a, Å	9.580(2)	18.097(4)
b, Å	15.757(3)	18.978(2)
c, Å	14.860(3)	19.741(3)
α, deg	90.0	90.0
β, deg	98.54(2)	90.0
γ, deg	90.0	90.0
V, Å^3	2218(1)	6780(2)
Z	4	8
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
space group	Cc (No. 9)	$Pbca$ (No. 61)
ρ (calcd), g cm^{-3}	1.70	1.66
μ (Mo Kα), cm^{-1}	71.2	51.6
2θ range, deg	3−55	3−45
no. of data	2358 [$F > 6\sigma(F)$]	2298 [$F > 6\sigma(F)$]
no. of params	163	252
R^a	0.0494	0.0441
$R_w{}^a$	0.0601	0.0495

[a] $R = \Sigma|F_o - F_c|/\Sigma|F_o|$; $R_w = \Sigma w^{1/2}|F_o - F_c|/\Sigma w^{1/2}|F_o|$; $w = [\sigma^2(F) + gF^2]^{-1}$.

in vacuo (0.25 g, 75%). Analysis calculated for $C_{14}H_{26}O_2P_2S_2W$: C, 31.4%; H, 4.9%. Found: C, 31.6%; H, 4.9%. IR data: 2970 (m), 2905 (m), 2835 (w), 1685 (w), 1606 (s), 1579 (w), 1508 (vs), 1457 (m), 1443 (m), 1413 (s), 1280 (vs), 1245 (vs), 1169 (m), 1121 (w), 1094 (m), 1031 (s), 947 (vs), 832 (s), 740 (m), 672 (w), 643 (w), 610 (m), 565 (w), 520 (w), 455 (vs) ($\nu_{W=S}$), 408 (w). MS: m/z = 537 (M$^+$ + 1). ^{1}H NMR: δ 1.23 [9 H, d, $^2J_{P-H}$ = 8.5, 1 $P(CH_3)_3$], 1.42 [9 H, d, $^2J_{P-H}$ = 8.6, 1 $P(CH_3)_3$], 3.26 [3 H, s, η^2-$OCHC_6H_4OCH_3$], 4.39 [1 H, dd, $^3J_{P-H}$ = 4.1, $^3J_{P-H}$ = 1.6, η^2-$OCHC_6H_4OCH_3$], 6.72 [2 H, m, η^2-$OCHC_6H_4OCH_3$], 7.15 [2 H, m, η^2-$OCHC_6H_4OCH_3$]. ^{13}C NMR: δ 12.8 [dq, $^1J_{P-C}$(d) = 26, $^1J_{C-H}$(q) = 130, 1 $P(CH_3)_3$], 16.0 [dq, $^1J_{P-C}$(d) = 30, $^1J_{C-H}$(q) = 130, 1 $P(CH_3)_3$], 54.7 [q, $^1J_{C-H}$ = 143, η^2-$OCHC_6H_4OCH_3$], 80.4 [dd, $^1J_{C-H}$ = 170, $^2J_{P-C}$ = 11, $^1J_{W-C}$ = 26, η^2-$OCHC_6H_4OCH_3$], 113.4 [d, $^1J_{C-H}$ = 163, η^2-$OCHC_6H_4OCH_3$], 127.8 [d, $^1J_{C-H}$ = 157, η^2-$OCHC_6H_4OCH_3$], 136.1 [s, η^2-$OCHC_6H_4OCH_3$], 159.5 [s, η^2-$OCHC_6H_4OCH_3$]. ^{31}P NMR: AB quartet δ −2.9 [$^2J_{P-P}$ = 365, $^1J_{W-P}$ = 215, 1 $P(CH_3)_3$], 3.5 [$^2J_{P-P}$ = 365, $^1J_{W-P}$ = 215, 1 $P(CH_3)_3$].

Synthesis of $W(PMe_3)_2(Se)_2(\eta^2\text{-OCH}_2)$. A suspension of $W(PMe_3)_4(Se)_2$ (0.52 g, 0.80 mmol) and excess paraformaldehyde (0.90 g, 30.0 mmol) in benzene (30 mL) was stirred at room temperature for 1 day. The mixture was filtered and the solvent removed under reduced pressure from the filtrate to give a green solid, which was dissolved in benzene (30 mL) and stirred at room temperature for 1 day with a new portion of paraformaldehyde (0.43 g, 14.3 mmol). The mixture was filtered and the solvent removed under reduced pressure to give $W(PMe_3)_2(Se)_2(\eta^2\text{-OCH}_2)$ as a green-blue powder, which was washed with pentane (5 mL) and dried *in vacuo* (0.20 g, 48%). Analysis calculated for $C_7H_{20}OP_2Se_2W$: C, 16.1%; H, 3.9%. Found: C, 16.1%; H, 3.6%. IR data: 2966 (w), 2902 (w), 1408 (s), 1280 (vs), 1156 (w), 1007 (w), 949 (vs), 845 (w), 745 (m), 676 (w), 592 (s), 502 (w). MS: m/z = 525 (M$^+$ + 1).

Synthesis of $W(PMe_3)_2(Se)_2(\eta^2\text{-OCHPh})$. A solution of $W(PMe_3)_4(Se)_2$ (0.77 g, 1.19 mmol) in benzene (30 mL) was treated with excess benzaldehyde (*ca.* 0.6 mL, 5.9 mmol) and stirred at room temperature for 1 day. The mixture was filtered and the solvent removed under reduced pressure to give a dark blue-green oily solid, which was dissolved in benzene (30 mL) and stirred at room temperature for 1 day with additional benzaldehyde (*ca.* 0.3 mL). The solvent was removed *in vacuo* and the resulting residue redissolved in benzene (30 mL) and stirred at room temperature for 14 h. The mixture was filtered and the solvent removed under reduced pressure to give a dark blue-green oily solid, which was extracted into Et_2O (60 mL). The ethereal solution was filtered and its volume reduced *in vacuo* to *ca.* 15 mL. Addition of pentane (30 mL) and cooling to −78 °C for 1 h resulted in crystallization of $W(PMe_3)_2(Se)_2(\eta^2\text{-OCHPh})$ as a blue-green solid, which was separated by filtration, washed with pentane (5 mL), and dried *in vacuo* (0.36 g). A second batch of microcrystalline $W(PMe_3)_2(Se)_2(\eta^2\text{-OCHPh})$ of comparable purity was obtained from the filtrate in an analogous way (0.11 g). Overall yield: 66%. Analysis calculated for $C_{13}H_{24}OP_2Se_2W$: C, 26.0%; H, 4.0%. Found: C, 26.1%; H, 4.0%. IR data: 3078 (w), 3055 (w), 3028 (w), 2971 (m), 2903 (m), 1596 (w), 1491 (w), 1452 (w), 1410 (s), 1276 (s), 1218 (w), 1166 (w), 1067 (w), 1029 (w), 947 (vs), 849 (w), 819 (w), 753 (m), 737 (m), 695 (m), 672 (w), 627 (m), 590 (m), 531 (w), 497 (w). MS: *m/z* = 601 (M^+ + 1).

Synthesis of $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCH_2)$. A suspension of $W(PMe_3)_4(Te)_2$ (0.80 g, 1.08 mmol) and excess paraformaldehyde (0.46 g, 15.3 mmol) in benzene (30 mL) was stirred at room temperature for 4 days. The mixture was filtered and the solvent removed under reduced pressure to give a brown solid, which was redissolved in benzene (30 mL) and stirred for 2 days at room temperature with another portion of paraformaldehyde (0.41 g, 13.7 mmol). The procedure was repeated with a third portion of paraformaldehyde (0.40 g, 13.3 mmol), after which the mixture was filtered and the solvent removed under reduced pressure to give $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCH_2)$ as a brown powder, which was washed with pentane (5 mL) and dried *in vacuo* (0.35 g, 52%). Analysis calculated for $C_7H_{20}OP_2Te_2W$: C, 13.5%; H, 3.3%. Found: C, 13.0%; H, 3.0%. IR data: 2962 (w), 2898 (w), 1408 (s), 1297 (m), 1277 (s), 1113 (m), 1003 (w), 947 (vs), 846 (w), 735 (m), 672 (w), 588 (s), 501 (w). MS: *m/z* = 622 (M^+).

Synthesis of $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHPh)$. A solution of $W(PMe_3)_4(Te)_2$ (0.80 g, 1.08 mmol) in benzene (10 mL) was treated with excess benzaldehyde (*ca.* 1 mL, 9.8 mmol) and stirred at room temperature for *ca.* 10 h. The volatile components were removed under reduced pressure to give a dark brown oily residue, which was redissolved in benzene (*ca.* 10 mL) and stirred with additional benzaldehyde (*ca.* 0.2 mL). This cycle was repeated (typically 5 or 6 times over a 3-day period) until an aliquot taken from the reaction mixture showed (by ^1H NMR spectroscopy) the complete consumption of $W(PMe_3)_4(Te)_2$. The solvent was then removed under reduced pressure and the oily residue extracted into Et_2O (2 × 50 mL). The volume of the combined extracts was reduced *in vacuo* to *ca.* 10 mL and the solution was filtered. Addition of pentane (50 mL) to the filtrate and cooling to −78 °C for 2 h resulted in the separation of $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHPh)$ as a dark purple-red microcrystalline solid, which was isolated by filtration, washed with pentane (5 mL), and dried *in vacuo* (*ca.* 0.10 g, 13%). Analysis calculated for $C_{13}H_{24}OP_2Te_2W$: C, 22.4%; H, 3.5%. Found: C, 22.6%; H, 3.1%. IR data: 2966 (w), 2900 (m), 1595 (m), 1489 (w), 1451 (w), 1409 (s), 1275 (s), 1217 (w), 1066 (w), 946 (vs), 850 (w), 753 (m), 695 (m), 669 (w), 626 (m), 585 (m). MS: *m/z* = 698 (M^+).

Equilibrium Studies for the Reactions between $W(PMe_3)_4(E)_2$ and Benzaldehyde. Procedure A (E = S). In a typical experiment, a gas-tight NMR tube was loaded with $W(PMe_3)_2(S)_2(\eta^2\text{-}OCHPh)$ (6 mg, 0.012 mmol) and C_6D_6 (0.8 mL) containing mesitylene as an internal standard (0.0178 M). The sample was frozen and degassed, and an excess of PMe_3 (*ca.* 0.12 mmol) was condensed into the NMR tube, which was filled with Ar (1 atm.) after allowing the solution to thaw. The sample was placed in a constant-temperature oil bath (±1 °C) and removed periodically to monitor (by ^1H NMR spectroscopy) the formation of the equilibrium mixture with $W(PMe_3)_4(S)_2$. The concentrations of all species were determined directly by ^1H NMR spectroscopy, being placed on an absolute scale relative to the concentration of the mesitylene internal standard (0.0178 M). The equilibrium constant

$$K_S = [W(PMe_3)_2(S)_2(\eta^2\text{-OCHPh})][PMe_3]^2/[W(PMe_3)_4(S)_2][PhCHO]$$

was measured over the temperature range 30−60 °C (Table 8) and a plot of ln K_S *vs* $1/T$ (Figure 13) yielded $\Delta H°$ and $\Delta S°$ (Table 9).

Procedure B (E = Se, Te). In a typical experiment, a gas-tight NMR tube was loaded with $W(PMe_3)_4(E)_2$ (8 mg, *ca.* 0.012 mmol) and C_6D_6 (0.8 mL) containing mesitylene as an internal standard (0.0178 M). Benzaldehyde (10 μL, 0.098 mmol) was added to the samples, which were placed in a constant-temperature oil bath (±1 °C) and removed periodically to monitor (by ^1H NMR spectroscopy) the formation of the equilibrium mixtures with the derivatives $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh)$. Additional samples were prepared by using different amounts of PhCHO (in the range 5−15 μL). The concentrations of all species were determined directly by ^1H NMR spectroscopy, being placed on an absolute scale relative to the concentration of the mesitylene internal standard (0.0178 M). The equilibrium constants

$$K_E = [W(PMe_3)_2(E)_2(\eta^2\text{-OCHPh})][PMe_3]^2/[W(PMe_3)_4(E)_2][PhCHO]$$

were measured over the temperature range 30−60 °C (Table 8) and a plot of ln K_E *vs* $1/T$ (Figure 13) yielded $\Delta H°$ and $\Delta S°$ (Table 9).

Synthesis of *trans,trans,trans*-$W(PMe_3)_2(CNBu^t)_2(S)_2$. A stirred solution of $W(PMe_3)_4(S)_2$ (0.33 g, 0.60 mmol) in benzene (15 mL) was treated with Bu^tNC (155 μL, 1.37 mmol). After stirring for 1 h at room temperature, the solution was filtered and the solvent removed under reduced pressure, giving $W(PMe_3)_2(CNBu^t)_2(S)_2$ as a red-brown powder (0.27 g, 80%). Analysis calculated for $C_{16}H_{36}N_2P_2S_2W$: C, 33.9%; H, 6.4%; N, 5.0%. Found: C, 32.9%; H, 6.0%; N, 4.7%. IR data: 2976 (s), 2932 (m), 2900 (m), 2088 (vs), 2054 (vs), 1420 (m), 1368 (m), 1276 (s), 1231 (m), 1201 (s), 952 (vs), 859 (m), 731 (m), 671 (m), 522 (m), 407 (m), 387 (s) ($\nu_{W=S}$), 332 (w).

Synthesis of *trans,trans,trans*-$W(PMe_3)_2(CNPr^i)_2(S)_2$. $W(PMe_3)_2(CNPr^i)_2(S)_2$ was prepared from the reaction of $W(PMe_3)_4(S)_2$ with Pr^iNC and isolated as a brown powder in 80% yield, using a procedure analogous to the preparation of $W(PMe_3)_2(CNBu^t)_2(S)_2$ described above. Analysis calculated for $C_{14}H_{32}N_2P_2S_2W$: C, 31.2%; H, 6.0%; N, 5.2%. Found: C, 30.3%; H, 5.7%; N, 4.7%. IR data: 2980 (m), 2933 (w), 2900 (m), 2096 (vs), 2031 (m), 1454 (w), 1420 (w), 1380 (w), 1363 (w), 1323 (m), 1276 (s), 1166 (w), 1118 (s), 950 (vs), 858 (w), 730 (w), 670 (w), 528 (w), 389 (vs) ($\nu_{W=S}$), 335 (w). ^1H NMR: δ 1.92 [18 H, vt, "J_{P-H}" = 3.3, 2 $P(CH_3)_3$], 0.94 [12 H, d, $^3J_{H-H}$ = 6.6, 2 $CNCH(CH_3)_2$], 3.65 [2 H, spt, $^3J_{H-H}$ = 6.6, 2 $CNCH(CH_3)_2$]. ^{13}C NMR: δ 22.6 [vt, "J_{P-C}" = 13, $^1J_{C-H}(q)$ = 128, 2 $P(CH_3)_3$], 23.6 [q, $^1J_{C-H}$ = 128, 2 $CNCH(CH_3)_2$], 48.0 [d, $^1J_{C-H}$ = 145, 2 $CNCH(CH_3)_2$], 162.6 [s, 2 $CNCH(CH_3)_2$]. ^{31}P NMR: −44.3 [s, $^1J_{W-P}$ = 272, 2 $P(CH_3)_3$].

Synthesis of *trans,trans,trans*-$W(PMe_3)_2(CNC_6H_{11})_2(S)_2$. $W(PMe_3)_2(CNC_6H_{11})_2(S)_2$ was synthesized from the reaction of $W(PMe_3)_4(S)_2$ with cyclo-$C_6H_{11}NC$ and isolated as a pale brown powder in 39% yield, using a procedure analogous to the preparation of $W(PMe_3)_2(CNBu^t)_2(S)_2$ described above. Analysis calculated for $C_{20}H_{40}N_2P_2S_2W$: C, 38.8%; H, 6.5%; N, 4.5%. Found: C, 38.7%; H, 6.4%; N, 4.5%. IR data: 2975 (w), 2935 (s), 2902 (m), 2857 (m), 2096 (vs), 1449 (w), 1428 (w), 1416 (s), 1366 (m), 1350 (m), 1330 (m), 1275 (m), 1128 (w), 950 (vs), 860 (w), 729 (m), 669 (w), 653 (m), 536 (w), 494 (w), 432 (w), 392 (vs) ($\nu_{W=S}$), 333(w). ^1H NMR: δ 1.96 [18 H, vt, "J_{P-H}" = 3.3, 2 $P(CH_3)_3$], 1.0−1.7 [20 H, m, 2 CNC_6H_{11}], 3.54 [2 H, qn, $^3J_{H-H}$ = 5.5, H(α) in 2 CNC_6H_{11}]. ^{13}C NMR: δ 22.7 [vt, "J_{P-C}" = 14, $^1J_{C-H}(q)$ = 130, 2 $P(CH_3)_3$], 23.1 [t, $^1J_{C-H}$ = 128, 2 CNC_6H_{11}], 25.3 [t, $^1J_{C-H}$ = 128, 2 CNC_6H_{11}], 33.5 [t, $^1J_{C-H}$ = 132, 2 CNC_6H_{11}], 53.7 [d, $^1J_{C-H}$ = 138, 2 CNC_6H_{11}], 162.3 [s, 2 CNC_6H_{11}]. ^{31}P NMR: −44.2 [s, $^1J_{W-P}$ = 269, 2 $P(CH_3)_3$].

Synthesis of *trans,trans,trans*-$W(PMe_3)_2(CNBu^t)_2(Se)_2$. A stirred solution of $W(PMe_3)_4(Se)_2$ (0.72 g, 1.11 mmol) in benzene (30 mL) was treated with Bu^tNC (*ca.* 0.3 mL, 2.7 mmol), resulting in the rapid formation of a brown-green solution. After stirring for 20 min at room temperature, the solution was filtered and the solvent removed under reduced pressure, giving $W(PMe_3)_2(CNBu^t)_2(Se)_2$ as a green powder (0.68 g, 93%). Analysis calculated for $C_{16}H_{36}N_2P_2Se_2W$: C, 29.1%; H, 5.5%; N, 4.2%. Found: C, 29.2%; H, 5.8%; N, 4.2%. IR data: 2973 (s), 2928 (m), 2899 (m), 2079 (vs), 2049 (vs), 1459 (w), 1418 (m), 1367 (m), 1275 (m), 1201 (s), 949 (vs), 858 (w), 728 (w), 671 (w), 522 (w), 427 (w). MS: *m/z* = 661 (M^+ + 1).

Reaction of $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$ (E = S, Se) with Bu^tNC. A solution of $W(PMe_3)_2(E)_2(\eta^2\text{-}OCHR)$ (*ca.* 10 mg) in C_6D_6 (*ca.* 0.8

mL) was treated with Bu^{t}NC (*ca.* 10 μL). W(PMe$_3$)$_2$(CNBu^t)$_2$(E)$_2$ was formed within *ca.* 10 min at room temperature, as judged by ^{1}H NMR spectroscopy.

Synthesis of W(PMe$_3$)(CNBu^t)$_4$(η^2-Te$_2$). A solution of W(PMe$_3$)$_4$(Te)$_2$ (1.63 g, 2.19 mmol) in benzene (50 mL) was treated with excess Bu^{t}NC (*ca.* 1.8 mL, 16 mmol) and stirred at room temperature for 7 h. The solution was filtered and the solvent removed under reduced pressure to give pure W(PMe$_3$)(CNBu^t)$_4$(η^2-Te$_2$) as a dark green-brown powder (1.52 g, 82%). Analysis calculated for $C_{23}H_{45}N_4PTe_2W$: C, 32.6%; H, 5.4%; N, 6.6%. Found: C, 32.8%; H, 5.3%; N, 5.8%. IR data: 2975 (vs), 2928 (m), 2902 (m), 2034 (vs, br), 1849 (vs, br), 1458 (m), 1418 (m), 1394 (w), 1366 (s), 1281 (m), 1232 (s), 1203 (vs), 1037 (w), 952 (s), 857 (w), 735 (w), 672 (w), 586 (w), 530 (m), 437 (m). MS: m/z = 849 (M$^+$ + 1).

Reaction of W(PMe$_3$)$_2$(Te)$_2$(η^2-OCH$_2$) with Bu^{t}NC. A solution of W(PMe$_3$)$_2$(Te)$_2$(η^2-OCH$_2$) (10 mg, 0.016 mmol) in C$_6$D$_6$ (0.8 mL) was treated with Bu^{t}NC (8 μL, 0.071 mmol). W(PMe$_3$)(CNBu^t)$_4$(η^2-Te$_2$) was formed within *ca.* 12 h at room temperature, as judged by ^{1}H NMR spectroscopy.

Reaction of W(PMe$_3$)$_2$(Te)$_2$(η^2-OCHPh) with Bu^{t}NC. A solution of W(PMe$_3$)$_2$(Te)$_2$(η^2-OCHPh) (10 mg, 0.014 mmol) in C$_6$D$_6$ (0.8 mL) was treated with Bu^{t}NC (11 μL, 0.098 mmol). W(PMe$_3$)(CNBu^t)$_4$(η^2-Te$_2$) was formed within *ca.* 3 h at room temperature, as judged by ^{1}H NMR spectroscopy.

X-ray Structure Determinations. Crystal data, data collection, and refinement parameters for all structurally characterized complexes are summarized in Table 18, and a typical procedure is described for W(PMe$_3$)$_4$(Te)$_2$. A single crystal of W(PMe$_3$)$_4$(Te)$_2$, grown from benzene at room temperature, was mounted in a glass capillary and placed on a Nicolet R3M diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected by using graphite monochromated Mo Kα X-radiation (λ = 0.710 73 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. Systematic absences were consistent with several space groups, of which the choice $I\bar{4}2m$ (No. 121) was made on the basis that this is the space group for the isostructural complex *trans*-Mo(PMe$_3$)$_4$Cl$_2$[40] and subsequently confirmed by the success of the solution. Hydrogen atoms were refined in calculated positions. Least-squares refinement converged to R = 0.0202 (R_w = 0.0292). Inversion of configuration established the correct absolute structure.

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Supporting Information Available: Additional ORTEP diagrams and tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for W(PMe$_3$)$_4$(S)$_2$ (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. Tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for all other structurally characterized complexes are provided in the supplementary material of the communications.[32]

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