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Syntheses, Structures, and Reactivities of Terminal Selenido Complexes of Tungsten

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Our interest in metal–ligand multiple bonding[1] has recently centered on complexes that exhibit terminal multiple bonds between the transition metals and the chalcogens, as exemplified by the complexes *trans*-$W(PMe_3)_4(E)_2$ (E = S,[2] Te[3]) and $Cp^{\dagger}_2M(E)(NC_5H_5)$ ($Cp^{\dagger} = Cp^*$ or Cp^{Et*}; E = O, S, Se, Te; M = Zr,[4] Hf[5]).[6] In this paper we report the syntheses, structures, and reactivities of some terminal selenido complexes of tungsten and comment upon both the similarities to and differences from their sulfido and tellurido analogues.

We have previously described the facile dehydrogenation of H_2S by $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ to give the purple bis(sulfido) complex *trans*-$W(PMe_3)_4(S)_2$.[2] In a similar fashion, the green bis(selenido) complex *trans*-$W(PMe_3)_4(Se)_2$ is readily obtained in *ca.* 90% yield by the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with excess H_2Se (Scheme 1).[7,8] However, although the final products $W(PMe_3)_4(S)_2$ and $W(PMe_3)_4(Se)_2$ are analogous, an interesting difference in the reactions of H_2S and H_2Se with $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ is manifested by the compositions of the intermediates that have been isolated, namely the yellow bis(hydrosulfido) complex $W(PMe_3)_4(SH)_2H_2$ and the emerald-green mono(selenido) complex $W(PMe_3)_4(Se)H_2$, respectively.[9,10] 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. Similarly, $W(PMe_3)_4(Se)H_2$ reacts with H_2S to give cleanly the novel mixed-chalcogenido complex $W(PMe_3)_4(S)(Se)$ (Scheme 1).[8]

As with $W(PMe_3)_4(S)_2$[2] and $W(PMe_3)_4(Te)_2$,[3] the trimethylphosphine ligands in $W(PMe_3)_4(Se)_2$ are labile and may be displaced by aldehydes to give the blue-green complexes $W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHR)$ (R = H, Ph) in 45–65% isolated yields (Scheme 1).[8] The formation of the derivatives $W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHR)$ is reversible, and addition of excess PMe_3 regenerates $W(PMe_3)_4(Se)_2$.

Equilibrium measurements of the reactions of $W(PMe_3)_4(E)_2$ (E = S, Se, Te) with PhCHO at 30 °C (eq 1) indicate that the

$$W(PMe_3)_4(E)_2 + PhCHO \overset{K_E}{\rightleftarrows} W(PMe_3)_2(E)_2(\eta^2\text{-}OCHPh) + 2PMe_3 \quad (1)$$

equilibrium constants K_E span a substantial range of more than 3 orders of magnitude.[11] However, although the trend is monotonic, K_{Se} is much more comparable to K_{Te} than to K_S; *i.e.*, $K_S \gg K_{Se} > K_{Te}$.

The PMe_3 ligands in $W(PMe_3)_4(Se)_2$ may also be displaced by Bu^tNC to give $W(PMe_3)_2(CNBu^t)_2(Se)_2$ (Scheme 1).[8] In this respect, the selenido complex $W(PMe_3)_4(Se)_2$ resembles much more its sulfido rather than its tellurido analogue, since $W(PMe_3)_4(Te)_2$ undergoes reductive coupling of the two terminal tellurido ligands to give an η^2-ditellurido derivative, $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$.[12]

The molecular structures of $W(PMe_3)_4(Se)H_2$,[13] $W(PMe_3)_4(Se)_2$,[14] $W(PMe_3)_2(CNBu^t)_2(Se)_2$,[15] and $W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHPh)$[16] have been determined by X-ray diffraction, and their respective W=Se bond lengths are summarized in Table 1.

Of the complexes listed in Table 1, $W(PMe_3)_4(Se)H_2$, $W(PMe_3)_4(Se)_2$, and $W(PMe_3)_2(CNBu^t)_2(Se)_2$ represent rare examples of 18-electron terminal selenido complexes. As such, the tungsten–selenido interaction may be aptly represented as a

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(2) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 5904–5905.

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(6) For other recent reports of terminal selenido and tellurido complexes see: (a) Siemeling, U.; Gibson, V. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1670–1671. (b) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240–6242. (c) Christou, V.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1450–1452. (d) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448–1457.

(7) A stirred solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.54 g, 0.96 mmol) in benzene (*ca.* 50 mL) was treated with excess H_2Se, resulting in the rapid formation of a green solution. The mixture was filtered after 10 min, and the solvent was removed under reduced pressure, giving a green solid, which was washed with pentane (5 mL) and dried *in vacuo*. Yield of $W(PMe_3)_4(Se)_2$: 0.57 g (92%).

(8) All new compounds have been characterized analytically and spectroscopically (see supplementary material).

(9) $W(PMe_3)_4(Se)H_2$ was isolated by 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.

(10) The *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 $Cp'_2M(CO)_2$[10a] and $[Ir_2(CO)_3(dppm)_2]$,[10b] respectively. (a) Bottomley, F.; Chin, T.-T.; Egharevaba, G. O.; Kane, L. M.; Pataki, D. A.; White, P. S. *Organometallics* **1988**, *7*, 1214–1221. (b) McDonald, R.; Cowie, M. *Inorg. Chem.* **1993**, *32*, 1671–1680.

(11) K_S = 8(3) M, $K_{Se} = 7.9(8) \times 10^{-2}$ M, and $K_{Te} = 4.0(9) \times 10^{-3}$ M at 30 °C.

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(13) Crystal data for $W(PMe_3)_4(Se)H_2$: monoclinic, *Cc* (No. 9), a = 9.580(2) Å, b = 15.757(3) Å, c = 14.860(3) Å, β = 98.54(2)°, V = 2218(1) Å^3, Z = 4.

(14) Crystal data for $W(PMe_3)_4(Se)_2$: monoclinic, $P2/n$ (No. 13), a = 16.040(5) Å, b = 9.738(2) Å, c = 16.096(3) Å, β = 113.27(2)°, V = 2310(1) Å^3, Z = 4.

(15) Crystal data for $W(PMe_3)_2(CNBu^t)_2(Se)_2$: monoclinic, $P2_1/n$ (No. 14), a = 11.147(5) Å, b = 10.617(5) Å, c = 11.973(4) Å, β = 110.16(3)°, V = 1328(1) Å^3, Z = 2.

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Scheme 1

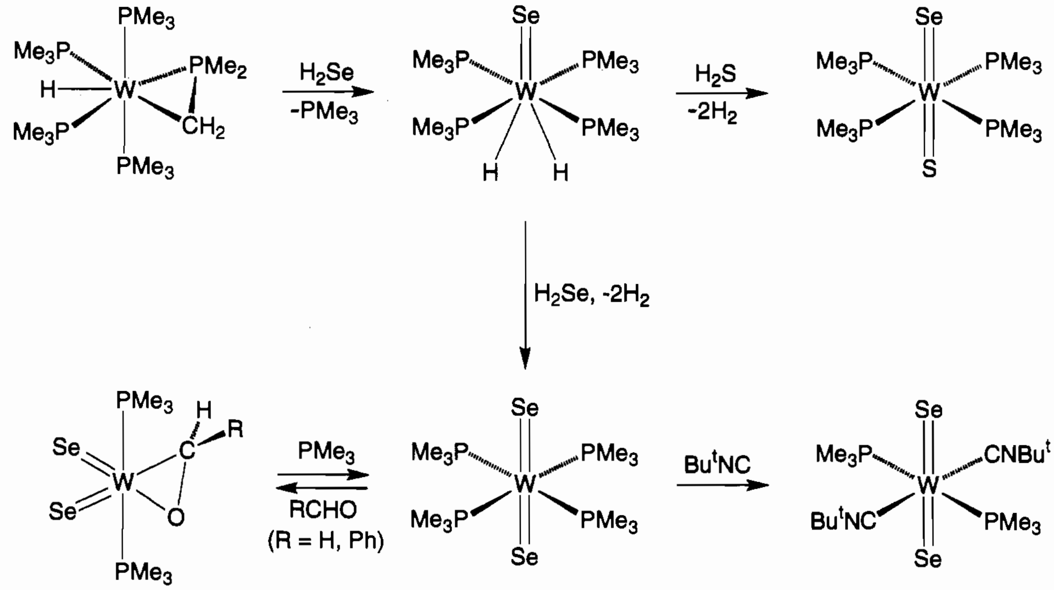

Table 1. W═Se Bond Length and ^{77}Se NMR Data for Terminal Selenido Complexes of Tungsten

	d(W═Se)/Å	$\delta(^{77}\mathrm{Se})$/ppm	$^2J_{\mathrm{Se-P}}$/Hz
$\mathrm{W(PMe_3)_4(Se)H_2}$	2.445(2)	1955	13 (quintet)
$\mathrm{W(PMe_3)_4(Se)_2}$	2.380(1)	803	13 (quintet)
$\mathrm{W(PMe_3)_4(S)(Se)}$		691	13 (quintet)
$\mathrm{W(PMe_3)_2(CNBu^t)_2(Se)_2}$	2.375(2)	824	15 (t)
$\mathrm{W(PMe_3)_2(Se)_2(\eta^2\text{-}OCH_2)}$		2312	12 (t)
$\mathrm{W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHPh)}$	2.317[4][a]	2366	11 (t)
		2397	13 (t)

[a] Average value for the two independent bond lengths [2.313(2) and 2.321(2) Å].

W═Se double bond, with little contribution from the triply bonded resonance structure $\mathrm{W^-{\equiv}Se^+}$. Thus, it is notable that each of these 18-electron complexes possesses W═Se bond lengths [2.375(2)–2.445(2) Å] that are longer than the values that have been reported previously for terminal selenido complexes (2.15-2.34 Å),[17,18] in which the tungsten centers are electronically unsaturated in the absence of lone-pair donation. Moreover, the formally 16-electron complex $\mathrm{W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHPh)}$, with an average bond order of 2.5 for each of the selenido ligands, also exhibits slightly shorter W═Se bond lengths [2.313(2) and 2.321(2) Å] than those observed for the above 18-electron complexes.

The terminal selenido complexes have also been studied by ^{77}Se NMR spectroscopy, as summarized in Table 1. These data complement the ^{77}Se NMR studies of Ibers on tungsten complexes,[19] but of particular interest in the present study is that a range of more than 1700 ppm is observed for the chemical shifts of terminal selenido ligands in a series of closely related complexes. Indeed, the ^{77}Se NMR chemical shifts for $\mathrm{W(PMe_3)_4(Se)_2}$, $\mathrm{W(PMe_3)_4(S)(Se)}$, and $\mathrm{W(PMe_3)_2(CNBu^t)_2(Se)_2}$ are in the range that is commonly assigned to bridging selenido ligands.[19,20] As such, this suggests that further studies are warranted in order to use ^{77}Se NMR spectroscopy with confidence to distinguish between terminal and bridging selenido ligands.

In summary, the mono- and bis(selenido) complexes $\mathrm{W(PMe_3)_4(Se)H_2}$ and $\mathrm{W(PMe_3)_4(Se)_2}$ have been prepared by the reaction of $\mathrm{W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H}$ with $\mathrm{H_2Se}$. In terms of its reactivity, $\mathrm{W(PMe_3)_4(Se)_2}$ exhibits features by which it may be regarded to resemble more closely either its sulfido or its tellurido analogue, depending upon the reagent. Thus, the formation of the bis(selenido) complex $\mathrm{W(PMe_3)_2(CNBu^t)_2(Se)_2}$ rather than the diselenido complex $\mathrm{W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Se_2)}$ indicates a closer similarity to its sulfido analogue, whereas in terms of the magnitude of the equilibrium constants for the reactions with benzaldehyde, $\mathrm{W(PMe_3)_4(Se)_2}$ more closely resembles the tellurido analogue.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences (Contract #DE-FG02-93ER14339) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. G.P. is the recipient of an A. P. Sloan Research Fellowship (1991–1993), a Camille and Henry Dreyfus Teacher-Scholar Award (1991–1996), and a Presidential Faculty Fellowship Award (1992–1997).

Supplementary Material Available: Table S1, giving analytical and spectroscopic data for all new complexes, Tables S2-S24, giving crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters, and ORTEP drawings for $\mathrm{W(PMe_3)_4(Se)_2}$, $\mathrm{W(PMe_3)_4(Se)H_2}$, $\mathrm{W(PMe_3)_2(CNBu^t)_2(Se)_2}$, and $\mathrm{W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHPh)}$ (27 pages). Ordering information is given on any current masthead page.

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(16) Crystal data for $\mathrm{W(PMe_3)_2(Se)_2(\eta^2\text{-}OCHPh)}$: monoclinic, $P2_1/c$ (No. 14), $a = 12.563(5)$ Å, $b = 8.731(4)$ Å, $c = 18.461(6)$ Å, $\beta = 109.22(3)^\circ$, $V = 1909(1)$ Å^3, $Z = 4$.

(17) W═Se double bond lengths have been observed in the range 2.15–2.34 Å, either by single-crystal X-ray diffraction for a variety of electron-deficient selenides[17a–e] or by gas-phase electron diffraction for the selenido tetrahalides $\mathrm{W(Se)X_4}$.[17f] (a) Wardle, R. W. M.; Bhaduri, S.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 1747–1755. (b) O'Neal, S. C.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 1971–1973. (c) Lu, Y.-J.; Ansari, M. A.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 4049–4050. (d) O'Neal, S. C.; Pennington, W. T.; Kolis, J. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1486–1488. (e) Britnell, D.; Drew, M. G. B.; Fowles, G. W. A.; Rice, D. A. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 415–417. (f) Page, E. M.; Rice, D. A.; Hagen, K.; Hedberg, L.; Hedberg, K. *Inorg. Chem.* **1991**, *30*, 4758–4761.

(18) W–Se single-bond lengths are typically in the range 2.38–2.59 Å, but it must be noted that some *formal* single bonds may also be shortened by lone-pair donation from Se to W. See: (a) Chisholm, M. H.; Parkin, I. P.; Huffman, J. C.; Streib, W. B. *J. Chem. Soc., Chem. Commun.* **1990**, 920–921. (b) Wardle, R. W. M.; Mahler, C. H.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2790–2795. (c) Endrich, K.; Guggolz, E.; Serhadle, O.; Ziegler, M. L.; Korswagen, R. P. *J. Organomet. Chem.* **1988**, *349*, 323–351. (d) Rettenmeier, A.; Weidenhammer, K.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1981**, *473*, 91–100. (e) Drew, M. G. B.; Fowles, G. W. A.; Page, E. M.; Rice, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5827–5828. (f) Boorman, P. M.; Kraatz, H.-B.; Parvez, M. *J. Chem. Soc., Dalton Trans.* **1982**, 3281–3282.

(19) See refs 17a and 18b and: (a) Christuk, C. C.; Ansari, M. A.; Ibers, J. A. *Inorg. Chem.* **1992**, *31*, 4365–4369. (b) Ansari, M. A.; Chau, C.-N.; Mahler, C. H.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 650–654. (c) Wardle, R. W. M.; Chau, C.-N.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1859–1860. (d) Ansari, M. A.; Mahler, C. H.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 2669–2674. (e) Christuk, C. C.; Ibers, J. A. *Inorg. Chem.* **1993**, *32*, 5105–5107.

(20) For example, $\mathrm{[W_3Se_9]^{2-}}$ (δ 889 ppm), $\mathrm{[W_2Se_9]^{2-}}$ (δ 859 ppm), and $\mathrm{[W_3Se_8O]^{2-}}$ (δ 731 ppm).[17a]