

# Syntheses of Mo(PMe<sub>3</sub>)<sub>6</sub> and *trans*-Mo(PMe<sub>3</sub>)<sub>4</sub>(E)<sub>2</sub> (E = S, Se, Te): The First Series of Terminal Sulfido, Selenido, and Tellurido Complexes of Molybdenum

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Received October 18, 1994<sup>⊗</sup>

**Abstract:** Mo(PMe<sub>3</sub>)<sub>6</sub> has been synthesized by the reduction of MoCl<sub>5</sub> with Na(K) alloy using PMe<sub>3</sub> as a reactive solvent. In solution, Mo(PMe<sub>3</sub>)<sub>6</sub> exists in equilibrium with Mo(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H and PMe<sub>3</sub>. At 30 °C, the equilibrium constant is a factor of ca. 2 × 10<sup>3</sup> less than that for the analogous tungsten system. The reactions of Mo(PMe<sub>3</sub>)<sub>6</sub> and Mo(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H with H<sub>2</sub>S, H<sub>2</sub>Se, Se, and Te/PMe<sub>3</sub> have provided convenient syntheses of Mo(PMe<sub>3</sub>)<sub>4</sub>(E)<sub>2</sub> (E = S, Se, Te), the first series of terminal sulfido, selenido, and tellurido derivatives of molybdenum. Mo(PMe<sub>3</sub>)<sub>4</sub>(S)<sub>2</sub> is monoclinic, *P2<sub>1</sub>/n* (No. 13), *a* = 15.947(6) Å, *b* = 9.704(2) Å, *c* = 15.980(3) Å, β = 112.24(2)°, *V* = 2289(1) Å<sup>3</sup>, *Z* = 4. Mo(PMe<sub>3</sub>)<sub>4</sub>(Se)<sub>2</sub> is monoclinic, *P2<sub>1</sub>/n* (No. 13), *a* = 16.105(3) Å, *b* = 9.777(3) Å, *c* = 16.136(4) Å, β = 113.34(2)°, *V* = 2332(1) Å<sup>3</sup>, *Z* = 4. Mo(PMe<sub>3</sub>)<sub>4</sub>(Te)<sub>2</sub> is tetragonal, *I4<sub>2</sub>m* (No. 121), *a* = *b* = 9.738(1) Å, *c* = 12.373(2) Å, *V* = 1171.2(6) Å<sup>3</sup>, *Z* = 2.

## Introduction

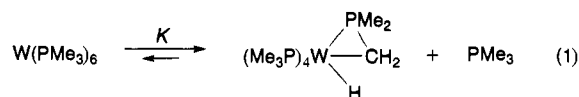
W(PMe<sub>3</sub>)<sub>6</sub><sup>1</sup> and Mo(PMe<sub>3</sub>)<sub>6</sub><sup>2</sup> represent notable examples of electron-rich transition metal complexes, a consequence of the strong σ-donor and weak π-acceptor properties of the trimethylphosphine ligand.<sup>3</sup> The electron-rich nature of the metal centers in W(PMe<sub>3</sub>)<sub>6</sub> and Mo(PMe<sub>3</sub>)<sub>6</sub> is manifested by their high reactivity, which has been utilized to prepare a variety of other tungsten and molybdenum trimethylphosphine complexes.<sup>1,2</sup> However, although W(PMe<sub>3</sub>)<sub>6</sub> may be prepared by a convenient chemical synthesis involving the reduction of WCl<sub>6</sub> with Na(K) alloy using PMe<sub>3</sub> as a reactive solvent,<sup>1</sup> the molybdenum analogue Mo(PMe<sub>3</sub>)<sub>6</sub> has to date only been synthesized by Green using metal vapor synthesis techniques, in which Mo atoms are co-condensed with PMe<sub>3</sub> at -196 °C.<sup>2</sup> The utility of Mo(PMe<sub>3</sub>)<sub>6</sub> as a synthetic precursor would, therefore, be greatly enhanced if a conventional chemical synthesis were available. Hence, in this paper, we report a convenient synthesis of Mo(PMe<sub>3</sub>)<sub>6</sub> and also describe thermodynamic details of the equilibrium of Mo(PMe<sub>3</sub>)<sub>6</sub> with its cyclometalated derivative Mo(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H and PMe<sub>3</sub>. Furthermore, in conjunction with our interest in metal-chalcogen multiple-bonding,<sup>4–7</sup> we also describe here the use of the trimethylphosphine complexes

Mo(PMe<sub>3</sub>)<sub>6</sub> and Mo(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H in the syntheses of *trans*-Mo(PMe<sub>3</sub>)<sub>4</sub>(E)<sub>2</sub> (E = S, Se, Te), the first series of terminal sulfido, selenido, and tellurido complexes of molybdenum.

## Results and Discussion

**Synthesis of Mo(PMe<sub>3</sub>)<sub>6</sub>.** Although a logical approach in the search for a conventional synthesis of Mo(PMe<sub>3</sub>)<sub>6</sub> would be to draw analogies from the corresponding tungsten system, it is apparent from the prior literature that such an extension would not necessarily be successful. Thus, whereas the tungsten complex W(PMe<sub>3</sub>)<sub>6</sub> may be synthesized by the reduction of WCl<sub>6</sub> with Na(K) alloy using PMe<sub>3</sub> as a reactive solvent,<sup>1</sup> the related reaction of MoCl<sub>5</sub> with sodium sand in PMe<sub>3</sub> has actually been reported to give the dihydride Mo(PMe<sub>3</sub>)<sub>5</sub>H<sub>2</sub>,<sup>8</sup> rather than Mo(PMe<sub>3</sub>)<sub>6</sub>. An alternative procedure for the synthesis of Mo(PMe<sub>3</sub>)<sub>6</sub> was therefore sought.

Our previous studies have demonstrated that the tungsten complex W(PMe<sub>3</sub>)<sub>6</sub> exists in facile equilibrium with its cyclometalated derivative W(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H and PMe<sub>3</sub> (eq 1).<sup>1</sup> Significantly, although the equilibrium lies heavily in favor



of W(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H, W(PMe<sub>3</sub>)<sub>6</sub> may be isolated from solutions of W(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H in PMe<sub>3</sub> by virtue of its lower solubility. The ability to isolate W(PMe<sub>3</sub>)<sub>6</sub> by using such a method suggested that the molybdenum analogue Mo(PMe<sub>3</sub>)<sub>6</sub> could also be synthesized by a related approach. However, since the synthesis of Mo(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H has not been reported (other than *via* its equilibrium with Mo-

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, March 15, 1995.

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(6) (a) Shin, J. H.; Parkin, G. *Organometallics* **1994**, *13*, 2147–2149. (b) Shin, J. H.; Parkin, G. *Organometallics* In press.

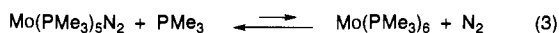
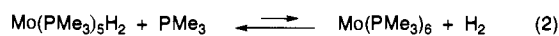
(7) (a) Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1351–1352. (b) Kuchta, M. C.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 8372–8373.

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**Table 1.** Equilibrium Data for PMe<sub>3</sub> Dissociation from Mo(PMe<sub>3</sub>)<sub>6</sub>

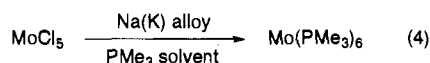
T/°C	K/M
30	8.6(4) × 10 <sup>-3</sup>
40	2.0(2) × 10 <sup>-2</sup>
50	4.3(4) × 10 <sup>-2</sup>
55	6.3(6) × 10 <sup>-2</sup>

(PMe<sub>3</sub>)<sub>6</sub>, the use of alternative starting materials was investigated. Specifically, the complexes Mo(PMe<sub>3</sub>)<sub>5</sub>N<sub>2</sub><sup>9</sup> and Mo(PMe<sub>3</sub>)<sub>5</sub>H<sub>2</sub><sup>8,10</sup> were examined since removal of the gaseous byproduct (H<sub>2</sub> or N<sub>2</sub>) would be expected to favor the formation of Mo(PMe<sub>3</sub>)<sub>6</sub> in the equilibrium mixture (eqs 2 and 3). Indeed,

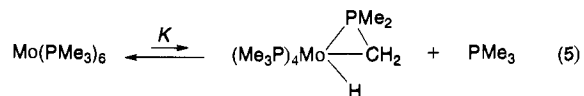


over a period of several days at room temperature, solutions of both Mo(PMe<sub>3</sub>)<sub>5</sub>N<sub>2</sub> and Mo(PMe<sub>3</sub>)<sub>5</sub>H<sub>2</sub> in PMe<sub>3</sub> are smoothly converted to Mo(PMe<sub>3</sub>)<sub>6</sub>, which may be isolated in ca. 50% yield after removal of the PMe<sub>3</sub> solvent and washing with benzene. The importance of using PMe<sub>3</sub> as a solvent in the synthesis of Mo(PMe<sub>3</sub>)<sub>6</sub> is highlighted by the fact that Carmona has prepared Mo(PMe<sub>3</sub>)<sub>5</sub>N<sub>2</sub> by reaction of the bis-dinitrogen complex *cis*-Mo(PMe<sub>3</sub>)<sub>4</sub>(N<sub>2</sub>)<sub>2</sub> with excess PMe<sub>3</sub> in petroleum ether solution under argon or helium,<sup>9</sup> and under these conditions, there was no evidence for the formation of Mo(PMe<sub>3</sub>)<sub>6</sub> from Mo(PMe<sub>3</sub>)<sub>5</sub>N<sub>2</sub>.

Since one of the literature syntheses of Mo(PMe<sub>3</sub>)<sub>5</sub>H<sub>2</sub> actually involves the use of PMe<sub>3</sub> as a reactive solvent in the reduction of MoCl<sub>5</sub> by Na sand,<sup>8</sup> we considered that modification of this procedure would provide a direct synthesis of Mo(PMe<sub>3</sub>)<sub>6</sub>, without requiring the prior isolation of Mo(PMe<sub>3</sub>)<sub>5</sub>H<sub>2</sub>. Indeed, Mo(PMe<sub>3</sub>)<sub>6</sub> may be conveniently synthesized in ca. 35% yield in a single step by reduction of MoCl<sub>5</sub> with Na(K) alloy in PMe<sub>3</sub> over a period of ca. 10 days (eq 4), rather than the 2 days used for the preparation of Mo(PMe<sub>3</sub>)<sub>5</sub>H<sub>2</sub>.



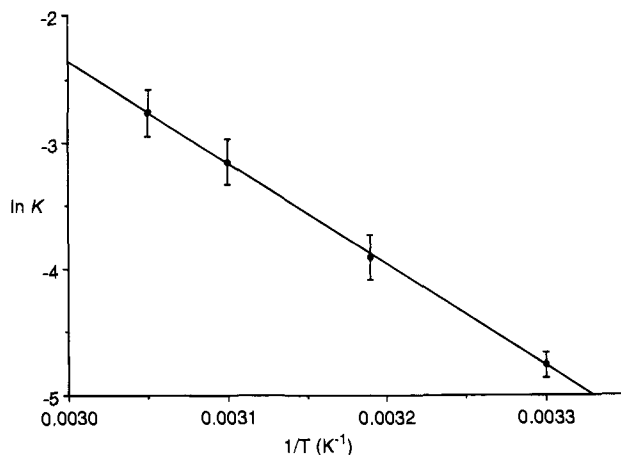
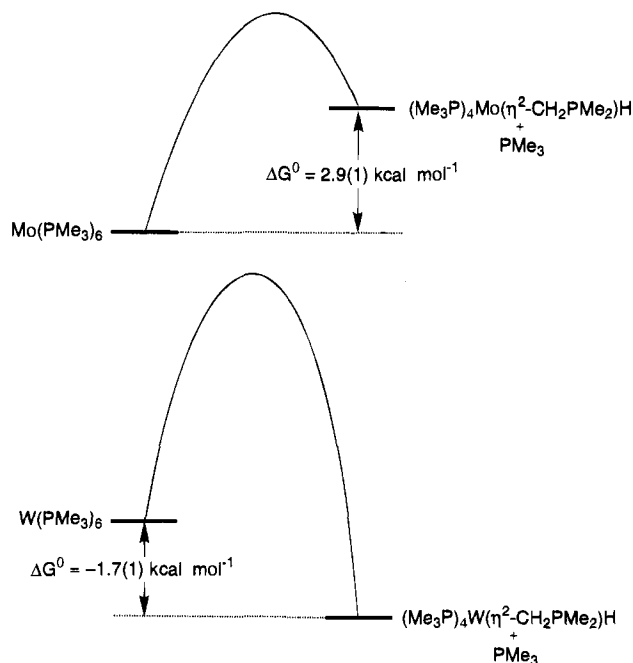
**Thermodynamics of the Equilibration of Mo(PMe<sub>3</sub>)<sub>6</sub> with Mo(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H and PMe<sub>3</sub>.** As noted previously,<sup>2</sup> Mo(PMe<sub>3</sub>)<sub>6</sub> exists in equilibrium with low concentrations of the cyclometalated complex Mo(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H and PMe<sub>3</sub> (eq 5). The equilibrium constant (*K*) has been measured by



using <sup>1</sup>H NMR spectroscopy, and its temperature dependence over the range 30–55 °C (Table 1 and Figure 1) has allowed determination of Δ*H*<sup>o</sup> and Δ*S*<sup>o</sup>, as shown in Table 2. For comparison, the thermodynamic data for the corresponding tungsten system are also included in Table 2. At 30 °C, the equilibrium constants [*K*<sub>Mo</sub> = 8.6(4) × 10<sup>-3</sup> M, *K*<sub>W</sub> = 17.8(2) M] differ by a substantial factor of ca. 2 × 10<sup>3</sup>, a difference that is largely due to enthalpic factors, consistent with stronger M–C and M–H bonds for the tungsten system.<sup>11</sup> The difference in equilibrium constants is such that solutions prepared

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**Figure 1.** van't Hoff plot for PMe<sub>3</sub> dissociation from Mo(PMe<sub>3</sub>)<sub>6</sub>.**Figure 2.** A semiquantitative comparison of the energy surfaces connecting M(PMe<sub>3</sub>)<sub>6</sub> to M(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H and PMe<sub>3</sub> at 30 °C (M = Mo, W).**Table 2.** Thermodynamic Data for PMe<sub>3</sub> Dissociation from Mo(PMe<sub>3</sub>)<sub>6</sub> and W(PMe<sub>3</sub>)<sub>6</sub>

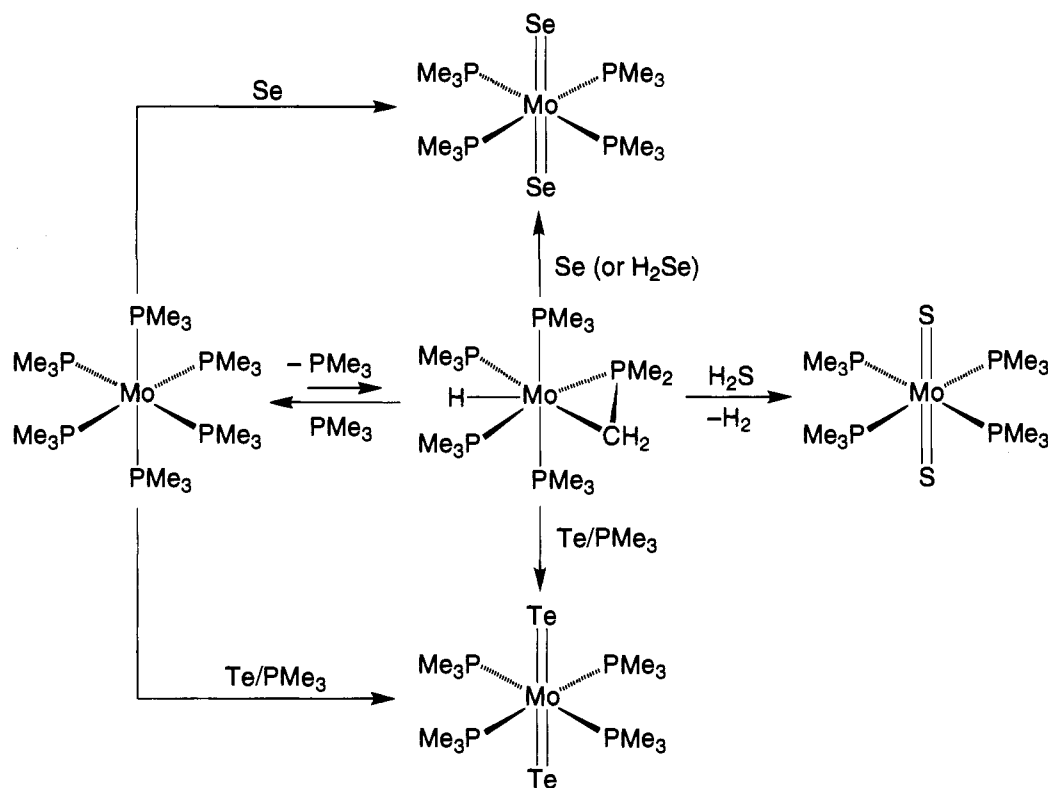
	<i>K</i> (30 °C)/M	Δ <i>H</i> <sup>o</sup> /kcal mol <sup>-1</sup>	Δ <i>S</i> <sup>o</sup> /eu
Mo	8.6(4) × 10 <sup>-3</sup>	15.9(1.7)	43(5)
W <sup>a</sup>	17.8(2)	9.3(8)	37(2)

<sup>a</sup> Data taken from ref 1.

from W(PMe<sub>3</sub>)<sub>6</sub> comprise W(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H as the major component, whereas for the molybdenum system Mo(PMe<sub>3</sub>)<sub>6</sub> is a major component. A semiquantitative comparison of the energy surfaces connecting M(PMe<sub>3</sub>)<sub>6</sub> to M(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H and PMe<sub>3</sub> for the molybdenum and tungsten systems is illustrated in Figure 2. Even though Mo(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H is initially obtained as only a minor component upon dissolution of Mo(PMe<sub>3</sub>)<sub>6</sub>, after several cycles of equilibration at ca. 50 °C and removal of the volatile components, the equilibrium for the molybdenum system is shifted so that Mo(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H may be obtained as the major component.<sup>12</sup>

(11) Preliminary kinetics studies indicate that the barrier for dissociation of PMe<sub>3</sub> from Mo(PMe<sub>3</sub>)<sub>6</sub> is substantially less than that for W(PMe<sub>3</sub>)<sub>6</sub>, consistent with a weaker Mo–P versus W–P bond.

Scheme 1



**Syntheses and Structures of the Terminal Chalcogenido Complexes  $\text{trans-Mo}(\text{PMe}_3)_4(\text{E})_2$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ).** We have previously reported the syntheses of a series of terminal chalcogenido complexes of tungsten, namely  $\text{trans-W}(\text{PMe}_3)_4(\text{E})_2$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ), from the reactions of  $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{-PMe}_2)\text{H}$  with  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ , and  $\text{Te}$ , respectively.<sup>4</sup> In a similar fashion, both  $\text{Mo}(\text{PMe}_3)_6$  and  $\text{Mo}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{-PMe}_2)\text{H}$  are useful synthetic precursors to the terminal chalcogenido derivatives of molybdenum,  $\text{trans-Mo}(\text{PMe}_3)_4(\text{E})_2$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ). For example, the selenido and tellurido complexes  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$  ( $\text{E} = \text{Se}, \text{Te}$ ) are readily prepared by the reactions of  $\text{Mo}(\text{PMe}_3)_6$  with the elemental chalcogens (Scheme 1).<sup>13</sup> In contrast, the sulfido derivative  $\text{Mo}(\text{PMe}_3)_4(\text{S})_2$  is not readily prepared by such a method, but is conveniently synthesized by the reaction of the cyclometalated derivative  $\text{Mo}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{-PMe}_2)\text{H}$  with  $\text{H}_2\text{S}$  (Scheme 1).<sup>14</sup> Similarly, the selenido derivative  $\text{Mo}(\text{PMe}_3)_4(\text{Se})_2$  is also obtained by the reaction of  $\text{Mo}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{-PMe}_2)\text{H}$  with  $\text{H}_2\text{Se}$ . Interestingly,  $\text{Mo}(\text{PMe}_3)_6$  itself does not react cleanly with excess  $\text{H}_2\text{E}$  ( $\text{E} = \text{S}, \text{Se}$ ) to give  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$ .

The structures of  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$  ( $\text{E} = \text{S}, \text{Se}, \text{Te}$ ) have been determined by X-ray diffraction (Figures 3–5), and selected bond lengths and angles are listed in Tables 3–5. Together with their tungsten analogues,<sup>4</sup>  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$  constitute a rare series of structurally-characterized terminal sulfido, selenido, and tellurido derivatives.<sup>15,16</sup> Furthermore, to our knowledge,  $\text{Mo}(\text{PMe}_3)_4(\text{Te})_2$  is the first structurally characterized terminal

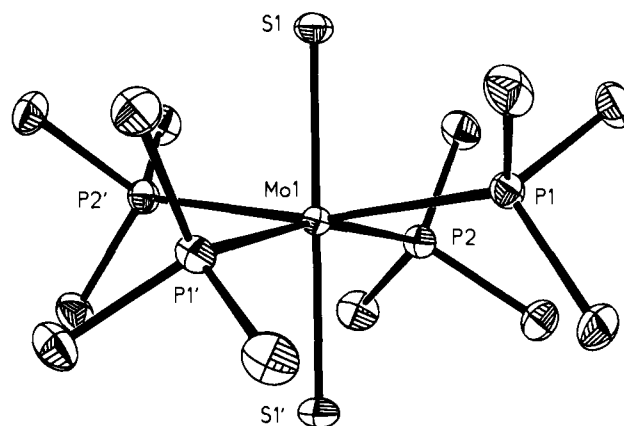


Figure 3. Molecular structure of  $\text{Mo}(\text{PMe}_3)_4(\text{S})_2$  (only one of the independent molecules is shown).

tellurido complex of molybdenum. Indeed, even though terminal chalcogenido derivatives such as  $[\text{Mo}(\text{O})_4]^{2-}$ ,  $[\text{Mo}(\text{S})_4]^{2-}$ , and  $[\text{Mo}(\text{Se})_4]^{2-}$  are well-known,<sup>17–19</sup> the synthesis of the tellurido analogue has yet to be achieved. For example, whereas derivatives of  $[\text{Mo}(\text{Se})_4]^{2-}$  have been prepared by the reactions

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(12) Small quantities of  $\text{Mo}(\text{PMe}_3)_5\text{H}_2$  are also obtained during this procedure.

(13)  $\text{Mo}(\text{PMe}_3)_5\text{N}_2$  may also be used to prepare  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$  ( $\text{E} = \text{Se}, \text{Te}$ ) by an analogous procedure. The reaction with elemental Te is also catalyzed by addition of  $\text{PMe}_3$ .

(14) The reaction between  $\text{Mo}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{-PMe}_2)\text{H}$  and  $\text{H}_2\text{S}$  proceeds via an intermediate that is tentatively characterized as  $\text{Mo}(\text{PMe}_3)_4\text{H}_2(\text{SH})_2$  by analogy with the tungsten system.

(15) Other structurally characterized series of terminal sulfido, selenido, and tellurido complexes include  $(\eta^5\text{-C}_5\text{Me}_4\text{Et})_2\text{M}(\text{E})(\text{NC}_5\text{H}_5)$  ( $\text{M} = \text{Zr}, \text{Hf}$ ;  $\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$ ). See ref 5.

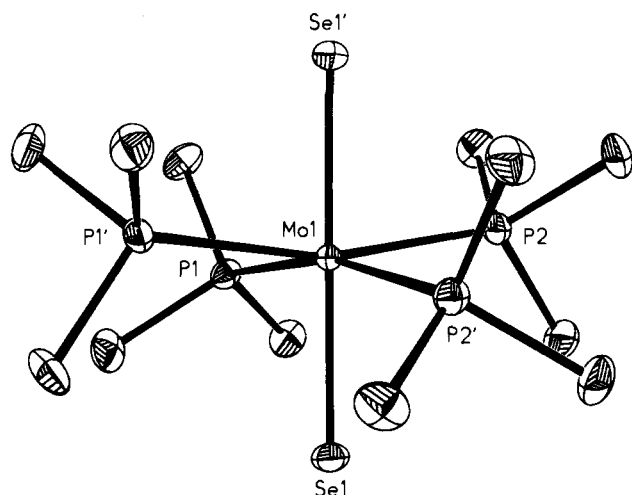


Figure 4. Molecular structure of  $\text{Mo}(\text{PMe}_3)_4(\text{Se})_2$  (only one of the independent molecules is shown).

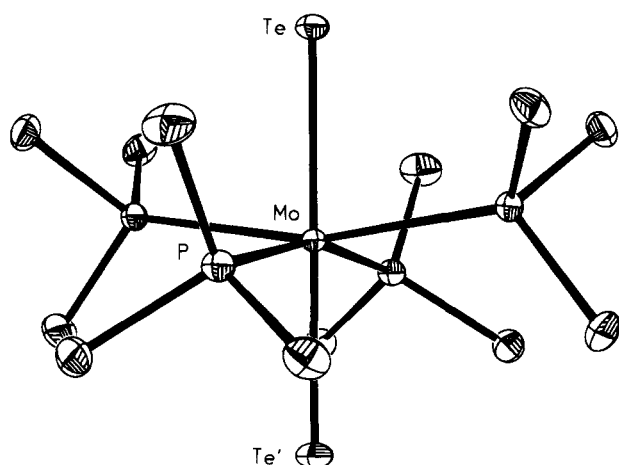


Figure 5. Molecular structure of  $\text{Mo}(\text{PMe}_3)_4(\text{Te})_2$ .

Table 3. Selected Bond Lengths (Å) and Angles (deg) for  $\text{Mo}(\text{PMe}_3)_4(\text{S})_2$

Mo(1)–S(1)	2.254(1)	Mo(2)–S(2)	2.253(1)
Mo(1)–P(1)	2.511(1)	Mo(2)–P(3)	2.523(1)
Mo(1)–P(2)	2.519(1)	Mo(2)–P(4)	2.515(1)
S(1)–Mo(1)–S(1')	179.2(1)	S(2)–Mo(2)–S(2')	179.6(1)
S(1)–Mo(1)–P(1)	82.9(1)	S(2)–Mo(2)–P(3)	82.5(1)
S(1)–Mo(1)–P(2)	96.8(1)	S(2)–Mo(2)–P(4)	97.5(1)
S(1)–Mo(1)–P(1')	97.7(1)	S(2)–Mo(2)–P(3')	97.8(1)
S(1)–Mo(1)–P(2')	82.7(1)	S(2)–Mo(2)–P(4')	82.2(1)
P(1)–Mo(1)–P(2)	90.6(1)	P(3)–Mo(2)–P(4)	89.9(1)
P(1)–Mo(1)–P(1')	90.5(1)	P(3)–Mo(2)–P(3')	92.5(1)
P(2)–Mo(1)–P(2')	91.9(1)	P(4)–Mo(2)–P(4')	91.8(1)
P(1)–Mo(1)–P(2')	165.6(1)	P(3)–Mo(2)–P(4')	164.7(1)

of  $\text{Mo}(\text{CO})_6$  with polyselenides, the corresponding reaction of  $\text{Mo}(\text{CO})_6$  with  $[\text{Te}_4]^{2-}$  gives only  $(\text{CO})_4\text{Mo}(\eta^2\text{-Te}_4)$ .<sup>20</sup>

The  $\text{Mo}=\text{E}$  bond lengths in  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$  are summarized in Table 6, which also includes for comparison the corresponding values for the tungsten analogues. The 18-electron nature of the molybdenum centers in  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$  dictates that the

Table 4. Selected Bond Lengths (Å) and Angles (deg) for  $\text{Mo}(\text{PMe}_3)_4(\text{Se})_2$

Mo(1)–Se(1)	2.381(1)	Mo(2)–Se(2)	2.385(1)
Mo(1)–P(1)	2.516(2)	Mo(2)–P(3)	2.520(2)
Mo(1)–P(2)	2.524(2)	Mo(2)–P(4)	2.516(2)
Se(1)–Mo(1)–Se(1')	179.3(1)	Se(2)–Mo(2)–Se(2')	179.3(1)
Se(1)–Mo(1)–P(1)	82.8(1)	Se(2)–Mo(2)–P(3)	82.4(1)
Se(1)–Mo(1)–P(2)	96.6(1)	Se(2)–Mo(2)–P(4)	97.1(1)
Se(1)–Mo(1)–P(1')	97.7(1)	Se(2)–Mo(2)–P(3')	98.0(1)
Se(1)–Mo(1)–P(2')	82.9(1)	Se(2)–Mo(2)–P(4')	82.5(1)
P(1)–Mo(1)–P(2)	90.6(1)	P(3)–Mo(2)–P(4)	90.0(1)
P(1)–Mo(1)–P(1')	90.5(1)	P(3)–Mo(2)–P(3')	92.1(1)
P(2)–Mo(1)–P(2')	91.9(1)	P(4)–Mo(2)–P(4')	91.8(1)
P(1)–Mo(1)–P(2')	165.7(1)	P(3)–Mo(2)–P(4')	164.9(1)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for  $\text{Mo}(\text{PMe}_3)_4(\text{Te})_2$

Mo–Te	2.597(1)	Mo–P	2.522(1)
Te–Mo–Te'	180.0	P–Mo–P'	163.9(1)
Te–Mo–P	98.0(1)	P–Mo–P''	91.1(1)
Te–Mo–P'	98.0(1)	P'–Mo–P''	91.1(1)
Te–Mo–P''	82.0(1)		

Table 6.  $\text{M}=\text{E}$  Bond Lengths for  $\text{M}(\text{PMe}_3)_4(\text{E})_2$

	$d(\text{Mo}=\text{E})/\text{Å}$	$d(\text{W}=\text{E})/\text{Å}^a$
S	2.254(2)	2.252(3)
Se	2.383(2)	2.380(1)
Te	2.597(1)	2.596(1)

<sup>a</sup> Data taken from ref 4.

molybdenum–chalcogenido interactions are best represented as  $\text{Mo}=\text{E}$  double bonds, with little contribution from the triply bonded resonance structure  $\text{Mo}^-\equiv\text{E}^+$ .<sup>21</sup> As is evident from Table 6, the  $\text{Mo}=\text{E}$  bond lengths are effectively identical to the corresponding values for the tungsten system.<sup>22</sup>

In contrast to terminal selenido and tellurido complexes of molybdenum, terminal sulfido complexes are common. However, of the known terminal molybdenum sulfido complexes, examples with “pure”  $\text{Mo}=\text{S}$  double bonds are rare. Thus, the only other structurally characterized examples of which we are aware are *trans*- $\{\text{syn-Me}_8[16]\text{janeS}_4\}\text{Mo}(\text{S})_2$  [ $d(\text{Mo}=\text{S}) = 2.239(7) \text{ Å}$ ]<sup>23</sup> and  $\text{Mo}(\text{dppe})_2(\text{O})(\text{S})$  [ $d(\text{Mo}=\text{S}) = 2.415(7) \text{ Å}$ ].<sup>24</sup> As expected, the  $\text{Mo}=\text{S}$  bond lengths in these complexes with formal  $\text{Mo}=\text{S}$  double bonds are longer (by *ca.* 0.1 Å) than the corresponding values in complexes in which there is  $\text{Mo}^-\equiv\text{S}^+$  triple bond character, as illustrated for the representative mononuclear molybdenum complexes listed in Table 7.<sup>25,26</sup> Similarly, the  $\text{Mo}=\text{Se}$  bond length in  $\text{Mo}(\text{PMe}_3)_4(\text{Se})_2$  [2.383(2) Å] is longer than the terminal selenido complexes listed in Table 8 [2.24–2.30 Å].<sup>27</sup>

However, in comparison to both  $\text{Mo}(\text{PMe}_3)_4(\text{S})_2$  and  $\{\text{syn-Me}_8[16]\text{janeS}_4\}\text{Mo}(\text{S})_2$ , the  $\text{Mo}=\text{S}$  bond length in  $\text{Mo}(\text{dppe})_2(\text{O})(\text{S})$  is abnormally long [2.415(7) Å]. Such an observation is possibly a consequence of the fact that the X-ray structure was actually performed on a crystal of composition  $(\text{dppe})_2\text{Mo}(\text{O})(\text{S})\cdot\text{SO}_2\cdot\text{H}_2\text{SO}_4\cdot\text{PhCH}_3\cdot\text{EtOH}$ . Thus, in view of the presence of  $\text{H}_2\text{SO}_4$ , a possible alternative formulation is one in which the sulfido ligand is protonated, *i.e.*  $[(\text{dppe})_2\text{Mo}(\text{O})(\text{SH})]^+$ , so

(19) (a) Berry, F. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, Chapter 17, pp 661–674. (b) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993**, *93*, 1037–1080. (c) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223–266.

(20) Roof, L. C.; Pennington, W. T.; Kolis, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 8172–8174.

(21) For theoretical studies on the model complexes  $\text{W}(\text{PH}_3)_4(\text{E})_2$ , see: Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1994**, 1391–1400.

(22) However, the average  $\text{Mo}-\text{PMe}_3$  bond lengths are *ca.* 0.015 Å longer than the corresponding  $\text{W}-\text{PMe}_3$  bond lengths. A similar observation has also been made for the  $\text{M}-\text{PMe}_3$  bond lengths in  $\text{M}(\text{PMe}_3)_6$  ( $\text{M} = \text{Mo}, \text{W}$ ). See ref 1.

(23) Yoshida, T.; Adachi, T.; Matsumura, K.; Kawazu, K.; Baba, K. *Chem. Lett.* **1991**, 1067–1070.

(24) Lorenz, I.-P.; Walter, G.; Hiller, W. *Chem. Ber.* **1990**, *123*, 979–982.

**Table 7.** Representative Terminal Mo≈S Bond Lengths in Mononuclear Complexes

	$d(\text{Mo}\approx\text{S})/\text{\AA}$	ref
Mo(PMe <sub>3</sub> ) <sub>4</sub> (S) <sub>2</sub>	2.254(2)	this work
{ <i>syn</i> -Me <sub>8</sub> [16]aneS <sub>4</sub> }Mo(S) <sub>2</sub>	2.239(7)	<i>a</i>
[{ <i>syn</i> -Me <sub>8</sub> [16]aneS <sub>4</sub> }Mo(S)(SMe)] <sup>+</sup> [I] <sup>-</sup>	2.140(5)	<i>b</i>
[{ <i>syn</i> -Me <sub>8</sub> [16]aneS <sub>4</sub> }Mo(S)(F)] <sup>+</sup> [BF <sub>4</sub> ] <sup>-</sup>	2.118(3)	<i>c</i>
<i>cis</i> -Mo( $\eta^2$ -Et <sub>2</sub> NO) <sub>2</sub> (S) <sub>2</sub>	2.154(1)	<i>d</i>
<i>cis</i> -Mo( $\eta^2$ -C <sub>5</sub> H <sub>10</sub> NO) <sub>2</sub> (S) <sub>2</sub>	2.145(2)	<i>e</i>
<i>cis</i> -Mo( $\eta^2$ -C <sub>5</sub> H <sub>10</sub> NO) <sub>2</sub> (S)(O)	2.106(5)	<i>f</i>
[NH <sub>4</sub> ] <sub>2</sub> [Mo(O) <sub>2</sub> (S) <sub>2</sub> ]	2.188(1)	<i>g</i>
[(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> ][MoS <sub>4</sub> ]	2.18	<i>h</i>
[NEt <sub>4</sub> ] <sub>2</sub> [(S <sub>4</sub> ) <sub>2</sub> Mo(S)]	2.128(1)	<i>i</i>
[Tp <sup>Me2</sup> ][Mo( $\eta^2$ -S <sub>2</sub> CNEt <sub>2</sub> )(S)]	2.129(2)	<i>j</i>
[ $\eta^3$ -{(PPh <sub>3</sub> P)AgS <sub>3</sub> }Cl]Mo(S)	2.103(3)	<i>k</i>
[PPh <sub>4</sub> ][(S <sub>2</sub> CS <sub>2</sub> ) <sub>2</sub> Mo(S)]	2.126(3)	<i>l</i>
[NEt <sub>4</sub> ][PPh <sub>4</sub> ][(S <sub>2</sub> CS <sub>2</sub> ) <sub>2</sub> Mo(S)]	2.127(4)	<i>l</i>

<sup>a</sup> Yoshida, T.; Adachi, T.; Matsumura, K.; Kawazu, K.; Baba, K. *Chem. Lett.* **1991**, 1067–1070. <sup>b</sup> Yoshida, T.; Adachi, T.; Matsumura, K.; Baba, K. *Chem. Lett.* **1992**, 2447–2450. <sup>c</sup> Yoshida, T.; Adachi, T.; Matsumura, K.; Baba, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1621–1623. <sup>d</sup> Gheller, S. F.; Hambley, T. W.; Traill, P. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1982**, *35*, 2183–2191. <sup>e</sup> Wiegardt, K.; Hahn, M.; Weiss, J.; Swiridoff, W. *Z. Anorg. Allg. Chem.* **1982**, *492*, 164–174. <sup>f</sup> Bristow, S.; Collison, D.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 2495–2499. <sup>g</sup> Kutzler, F. W.; Scott, R. A.; Berg, J. M.; Hodgson, K. O.; Doniach, S.; Cramer, S. P.; Chang, C. H. *J. Am. Chem. Soc.* **1981**, *103*, 6083–6088. <sup>h</sup> Koz'min, P. A.; Popova, Z. V. *Zh. Strukt. Khim.* **1971**, *12*, 99–101. <sup>i</sup> Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321–3332. <sup>j</sup> Young, C. G.; Roberts, S. A.; Ortega, R. B.; Enemark, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2938–2946. <sup>k</sup> Nianyong, Z.; Jianhui, W.; Shaowu, D.; Xintao, W.; Jiayi, L. *Inorg. Chim. Acta* **1992**, *191*, 65–68. <sup>l</sup> Coucouvanis, D.; Draganjac, M. E.; Koo, S. M.; Toupadakis, A.; Hadjikyriacou, A. I. *Inorg. Chem.* **1992**, *31*, 1186–1196.

that the derived Mo–S bond length is closer to that of a single bond and not a Mo=S double bond.<sup>28</sup>

The terminal chalcogenido complexes Mo(PMe<sub>3</sub>)<sub>4</sub>(E)<sub>2</sub> (E = S, Se, Te) have also been characterized by NMR spectroscopy as summarized in Table 9. Thus, the selenido and tellurido derivatives are characterized by signals in the <sup>77</sup>Se and <sup>125</sup>Te NMR spectra at  $\delta$  1133 and 1507 ppm, respectively. For comparison, the <sup>77</sup>Se and <sup>125</sup>Te NMR signals of the tungsten

(25) Although the mean terminal Mo≈S bond length for complexes listed in the Cambridge Structural Database (updated March 1994) is 2.150(7) Å, some particularly long and short values have been reported. For example, an average terminal Mo≈S bond length of 2.481 Å has been observed for [Mo<sub>3</sub>( $\mu_3$ -S)( $\mu_2$ -S<sub>2</sub>)<sub>3</sub>(S)]<sup>2-</sup>, a value that has been proposed to be indicative of a single bond.<sup>25a</sup> A Mo≈S bond length of 2.249(7) Å has been reported for (Ph<sub>3</sub>PO)<sub>2</sub>Cl<sub>2</sub>Mo(S)(O).<sup>25b</sup> However, the analysis was performed on a crystal with the apparent composition [(Ph<sub>3</sub>PO)<sub>2</sub>Cl<sub>2</sub>Mo(S)(O)][(Ph<sub>3</sub>PO)<sub>2</sub>Cl<sub>2</sub>Mo(S)(O)]. Since (Ph<sub>3</sub>PO)<sub>2</sub>Cl<sub>2</sub>Mo(S) is also a plausible contaminant, the derived Mo≈S bond length may be artificially lengthened.<sup>25c,d</sup> The complex [Tp<sup>Me2</sup>][Mo(SP(S)Pr<sub>2</sub>)(O)(S)] possesses a relatively long Mo≈S bond length of 2.227(2) Å, and a weak S···S association between the sulfido and {SP(S)Pr<sub>2</sub>} ligands has been proposed to account for this lengthening.<sup>25e</sup> Some particularly short Mo≈S bond lengths have been reported for complexes with the [Mo(O)( $\mu$ -S)<sub>2</sub>Mo(S)] core,<sup>25f,g</sup> but it is plausible that these values may have been artificially shortened due to disorder with the adjacent oxo ligand. (a) Sellmann, D.; Hannakam, M.; Knoch, F.; Moll, M. *Inorg. Chim. Acta* **1993**, *205*, 105–112. (b) Romanenko, G. V.; Podbereskaya, N. V.; Fedin, V. P.; Geras'ko, O. A.; Fedorov, V. E.; Batakin, V. V. *Zh. Strukt. Khim.* **1988**, *29*, 93–103; *J. Struct. Chem. (USSR)* **1988**, *29*, 79–89. (c) Parkin, G. *Acc. Chem. Res.* **1992**, *25*, 455–460. (d) Parkin, G. *Chem. Rev.* **1993**, *93*, 887–911. (e) Eagle, A. A.; Laughlin, L. J.; Young, C. G.; Tiekink, E. R. T. *J. Am. Chem. Soc.* **1992**, *114*, 9195–9197. (f) Coucouvanis, D.; Koo, S.-M. *Inorg. Chem.* **1989**, *28*, 2–5. (g) Dulebohn, J. L.; Stamatakis, T. C.; Ward, D. L.; Nocera, D. G. *Polyhedron* **1991**, *10*, 2813–2820.

(26) For further recent data on Mo≈S bond lengths, see: Hall, K. A.; Mayer, J. M. *Inorg. Chem.* **1994**, *33*, 3289–3298 and references therein.

(27) The mean terminal Mo≈Se bond length for complexes listed in the Cambridge Structural Database (updated March 1994) is 2.28(1) Å.

(28) The same viewpoint regarding the structure of (dppe)<sub>2</sub>Mo(O)(S) is also maintained by Professor F. A. Cotton (personal communication).

**Table 8.** Representative Terminal Mo≈Se Bond Lengths

	$d(\text{Mo}\approx\text{Se})/\text{\AA}$	ref
Mo(PMe <sub>3</sub> ) <sub>4</sub> (Se) <sub>2</sub>	2.383(2)	this work
<i>cis</i> -Mo( $\eta^2$ -C <sub>5</sub> H <sub>10</sub> NO) <sub>2</sub> (Se)(O)	2.299(1)	<i>a</i>
[Ph <sub>4</sub> P] <sub>2</sub> [Mo(Se) <sub>4</sub> ]	2.293(1)	<i>b</i>
[Ph <sub>4</sub> P] <sub>2</sub> [Mo(Se)(Se <sub>4</sub> ) <sub>2</sub> ]	2.270(4)	<i>b</i>
[Ph <sub>4</sub> P] <sub>2</sub> [Mo <sub>2</sub> (Se) <sub>2</sub> ( $\mu$ -Se) <sub>2</sub> ( $\eta^2$ -Se <sub>2</sub> ) <sub>2</sub> ]	2.237(9)	<i>c</i>

<sup>a</sup> Traill, P. R.; Tiekink, E. R. T.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Aust. J. Chem.* **1986**, *39*, 1287–1295. <sup>b</sup> O'Neal, S. C.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 1971–1973. <sup>c</sup> Eichorn, B. W.; Gardner, D. R.; Nichols-Ziebarth, A.; Ahmed, K. J.; Bott, S. G. *Inorg. Chem.* **1993**, *32*, 5412–5414.

selenido and tellurido derivatives W(PMe<sub>3</sub>)<sub>4</sub>(E)<sub>2</sub> are observed at  $\delta$  803 and 958 ppm, respectively.<sup>4b,d</sup> The sulfido and selenido complexes also exhibit <sup>1</sup>J<sub>95.97Mo-31P</sub> coupling constants of 150 and 140 Hz, respectively.<sup>29</sup> For reference, <sup>1</sup>J<sub>95.97Mo-31P</sub> coupling constants are known to span at least the range 117–290 Hz,<sup>30</sup> with values of ca. 130–160 Hz typical for [Mo–PR<sub>3</sub>] moieties.<sup>30c</sup>

As expected, the electronic spectra of Mo(PMe<sub>3</sub>)<sub>4</sub>(E)<sub>2</sub> (E = S, Se, Te) are qualitatively similar to those reported for the tungsten system,<sup>31</sup> for which Thorp has assigned the dominant features as ligand-to-metal  $\pi$ - $\pi^*$  transitions. The  $\pi$ - $\pi^*$  transitions in W(PMe<sub>3</sub>)<sub>4</sub>(E)<sub>2</sub> were observed to shift to higher energy in the order Te < Se < S (as expected on the basis of the changes in ionization potentials of the chalcogens). A similar trend is also observed for the molybdenum analogues, but these absorptions are red-shifted with respect to the corresponding values for the tungsten complexes.<sup>32</sup>

## Experimental Section

**General Considerations.** All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques.<sup>33</sup> Solvents were purified and degassed by standard procedures. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on Varian VXR 200, 300, and 400 spectrometers. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1420 spectrophotometer and are reported in cm<sup>-1</sup>. Elemental analyses were measured using a Perkin-Elmer 2400 CHN elemental analyzer. Electronic spectra were recorded on a Perkin Elmer Lambda 6 spectrometer. NMR data are listed in Table 9.

**Synthesis of Mo(PMe<sub>3</sub>)<sub>6</sub>.** (a) PMe<sub>3</sub> (ca. 30 mL) was condensed onto Na(K) alloy (1:3 w/w, 5.0 g) at –78 °C in a glass ampule, equipped with a large-bore teflon valve and a glass-covered stir bar.<sup>34</sup> The ampule was maintained at –78 °C and MoCl<sub>5</sub> (5.0 g, 18 mmol) was added to the ampule via a tygon tube under an argon atmosphere. The ampule was evacuated at –78 °C and then allowed to warm to room temperature. The mixture was stirred at room temperature for 10 days, after which period the PMe<sub>3</sub> was removed *in vacuo* and the product was extracted into pentane (4 × 300 mL) at room temperature. After each extraction the filtrate was concentrated to ca. 30 mL to give Mo-

(29) The similar magnetogyric ratios for <sup>95</sup>Mo ( $\gamma = -1.7514 \times 10^7$  rad s<sup>-1</sup> T<sup>-1</sup>,  $I = 5/2$ , 15.72%) and <sup>97</sup>Mo ( $\gamma = -1.7884 \times 10^7$  rad s<sup>-1</sup> T<sup>-1</sup>,  $I = 5/2$ , 9.46%) generally preclude the resolution of the two satellite sets that might be expected from these systems. See: Milbrath, D. S.; Verkade, J. G.; Clark, R. J. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 921–4.

(30) (a) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169–278. (b) Alyea, E. C.; Lenkinski, R. E.; Somogyvari, A. *Polyhedron* **1982**, *1*, 130–132. (c) Alyea, E. C.; Somogyvari, A. *Can. J. Chem.* **1988**, *66*, 397–400.

(31) Paradis, J. A.; Wertz, D. W.; Thorp, H. H. *J. Am. Chem. Soc.* **1993**, *115*, 5308–5309.

(32) For the dominant feature in C<sub>6</sub>H<sub>6</sub>: Mo(PMe<sub>3</sub>)<sub>4</sub>(Te)<sub>2</sub> ( $\lambda = 488$  nm,  $\epsilon \approx 7000$  M<sup>-1</sup> cm<sup>-1</sup>), Mo(PMe<sub>3</sub>)<sub>4</sub>(Se)<sub>2</sub> ( $\lambda = 424$  nm,  $\epsilon \approx 6500$  M<sup>-1</sup> cm<sup>-1</sup>), Mo(PMe<sub>3</sub>)<sub>4</sub>(S)<sub>2</sub> (not known with certainty). For comparison, the  $\pi$ - $\pi^*$  transitions for the tungsten system are the following (ref 31): W(PMe<sub>3</sub>)<sub>4</sub>(Te)<sub>2</sub> ( $\lambda = 442$  nm,  $\epsilon \approx 12000$  M<sup>-1</sup> cm<sup>-1</sup>), W(PMe<sub>3</sub>)<sub>4</sub>(Se)<sub>2</sub> ( $\lambda = 375$  nm,  $\epsilon \approx 12000$  M<sup>-1</sup> cm<sup>-1</sup>), W(PMe<sub>3</sub>)<sub>4</sub>(S)<sub>2</sub> ( $\lambda = 341$  nm,  $\epsilon \approx 12000$  M<sup>-1</sup> cm<sup>-1</sup>).

(33) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. *ACS Symp. Ser.* **1987**, *357*, 6–23. (b) Burger, B. J.; Bercaw, J. E. *ACS Symp. Ser.* **1987**, *357*, 79–97.

(34) Teflon-covered stir bars may react violently with Na(K) alloy and so glass-covered stir bars are strongly recommended.

**Table 9.** NMR Data for  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$  (E = S, Se, Te)

nucleus	$\text{Mo}(\text{PMe}_3)_4(\text{S})_2$	$\text{Mo}(\text{PMe}_3)_4(\text{Se})_2$	$\text{Mo}(\text{PMe}_3)_4(\text{Te})_2$
$^1\text{H}$	1.52 [s]	1.60 [s]	1.74 [vm, "J" = 1.3 Hz]
$^{13}\text{C}$	22.4 [br s]	24.8 [br s]	29.9 [br s]
$^{31}\text{P}$	-14.0 [s, $^1J_{\text{Mo-P}} = 150$ ]	-16.0 [s, $^1J_{\text{Mo-P}} = 140$ ]	-16.2 [s]
$^{77}\text{Se}$		1133 [s]	
$^{125}\text{Te}$			1507 [s]

$(\text{PMe}_3)_6$  as a yellow microcrystalline solid that was isolated pure by filtration, free from  $\text{Mo}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ . Combined yield of  $\text{Mo}(\text{PMe}_3)_6$  (3.4 g, 34%).  $^1\text{H}$  NMR data ( $\text{C}_6\text{D}_6$ ): 1.37 [s, 6  $\text{PMe}_3$ ]. **CAUTION:** Mixtures of metal halides, alkali metal reducing agents, and  $\text{PMe}_3$  have been reported to explode violently.<sup>35</sup> However, we have never observed such an incident following the above procedure exactly.

(b)  $\text{PMe}_3$  (ca. 20 mL) was added to  $\text{Mo}(\text{PMe}_3)_5\text{H}_2$  (400 mg, 0.84 mmol) in a glass ampule. The contents were evacuated at  $-196^\circ\text{C}$  and allowed to warm to room temperature. The mixture was stirred at room temperature for 5 days over which period the gaseous byproduct was occasionally removed. After this period, the volatile components were removed and the residue was washed with benzene (ca. 5 mL) giving  $\text{Mo}(\text{PMe}_3)_6$  as a yellow solid (220 mg, 48%).

(c)  $\text{PMe}_3$  (ca. 25 mL) was added to  $\text{Mo}(\text{PMe}_3)_5(\text{N}_2)$  (600 mg, 1.19 mmol) in a glass ampule. The contents were evacuated at  $-196^\circ\text{C}$  and allowed to warm to room temperature. The mixture was stirred at room temperature for 5 days over which period the gaseous byproduct was occasionally removed. After this period, the volatile components were removed and the residue was washed with benzene (ca. 5 mL) giving  $\text{Mo}(\text{PMe}_3)_6$  as a yellow solid (360 mg, 55%).

**Conversion of  $\text{Mo}(\text{PMe}_3)_6$  to  $\text{Mo}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ .** A solution of  $\text{Mo}(\text{PMe}_3)_6$  (0.25 g, 0.45 mmol) in cyclohexane (ca. 300 mL) was heated at  $50^\circ\text{C}$  for 10 min in a thick glass ampule (CARE!). After this period the volatile components were removed *in vacuo*. The entire procedure was repeated twice, to give  $\text{Mo}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$  as a light brown solid which was sufficiently pure for use in other reactions (0.15 g, 60%).  $^1\text{H}$  NMR data ( $\text{C}_6\text{D}_6$ ): 1.32 [s, 4  $\text{PMe}_3$ ], 1.30 [shoulder,  $\text{PMe}_2$ ], 0.08 [sextet,  $J_{\text{P-H}} = 3$  Hz,  $\text{Mo-CH}_2$ ],  $-3.95$  [quintet,  $J_{\text{P-H}} = 34$  Hz,  $\text{Mo-H}$ ].

**Equilibrium Studies.** In a typical experiment, a gas-tight NMR tube was loaded with  $\text{Mo}(\text{PMe}_3)_6$  (ca. 5 mg) and dissolved in  $\text{C}_6\text{D}_6$  containing mesitylene as an internal standard (0.018 M). The sample was placed in a constant-temperature oil bath ( $\pm 1^\circ\text{C}$ ) and removed periodically to monitor (by  $^1\text{H}$  NMR spectroscopy) the formation of the equilibrium mixture with  $\text{Mo}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$  and  $\text{PMe}_3$ . The concentrations of all species were determined directly by  $^1\text{H}$  NMR spectroscopy, being placed on an absolute scale relative to the concentration of the mesitylene internal standard (0.018 M). The equilibrium constant was measured over the temperature range  $30\text{--}55^\circ\text{C}$  (Table 1) and a plot of  $\ln K$  vs  $1/T$  (Figure 1) yielded the values  $\Delta H^\circ = 15.9(1.7)$  kcal mol $^{-1}$  and  $\Delta S^\circ = 43(5)$  eu.

**Synthesis of  $\text{Mo}(\text{PMe}_3)_4(\text{S})_2$ .**  $\text{Mo}(\text{PMe}_3)_6$  (0.10 g, 0.18 mmol) was converted to  $\text{Mo}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$  by the procedure described above. A solution of  $\text{Mo}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$  in pentane (ca. 25 mL) was treated with  $\text{H}_2\text{S}$  at  $-78^\circ\text{C}$ , resulting in the immediate formation of a brown precipitate. The precipitate was isolated by filtration and washed with pentane to produce a light brown solid, tentatively characterized as  $\text{Mo}(\text{PMe}_3)_4\text{H}_2(\text{SH})_2$  by analogy with the tungsten system. The brown solid was dissolved in benzene (ca. 20 mL) at room temperature, resulting in the evolution of  $\text{H}_2$  and the formation of a green-brown solution. The volatile components were removed *in vacuo* giving  $\text{Mo}(\text{PMe}_3)_4(\text{S})_2$  as an olive green/brown solid (0.05 g, 60% yield). Anal. Calcd for  $\text{Mo}(\text{PMe}_3)_4(\text{S})_2$ : C, 31.0; H, 7.8. Found: C, 30.2; H, 7.3. IR data: 2968 (m), 2903 (m), 1418 (m), 1293 (sh), 1279 (m), 939 (s), 851 (w), 711 (m), 662 (m), 413 (s) [ $\nu(\text{Mo}=\text{S})$ ].

**Synthesis of  $\text{Mo}(\text{PMe}_3)_4(\text{Se})_2$ .** (a) A solution of  $\text{Mo}(\text{PMe}_3)_6$  (0.10 g, 0.18 mmol) in benzene (ca. 15 mL) was treated with selenium powder (0.029 g, 0.36 mmol) and the resultant mixture was stirred for 20 min at room temperature, producing a dark brown solution. The mixture was filtered and the volatile components removed by lyophilization to

**Table 10.** Crystal and Intensity Collection Data for  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$  (E = S, Se, Te)

	$\text{Mo}(\text{PMe}_3)_4(\text{S})_2$	$\text{Mo}(\text{PMe}_3)_4(\text{Se})_2$	$\text{Mo}(\text{PMe}_3)_4(\text{Te})_2$
formula	$\text{C}_{12}\text{H}_{36}\text{P}_4\text{S}_2\text{Mo}$	$\text{C}_{12}\text{H}_{36}\text{P}_4\text{Se}_2\text{Mo}$	$\text{C}_{12}\text{H}_{36}\text{P}_4\text{Te}_2\text{Mo}$
formula wt	464.3	558.2	655.4
lattice	monoclinic	monoclinic	tetragonal
cell constants			
<i>a</i> , Å	15.947(6)	16.105(3)	9.738(1)
<i>b</i> , Å	9.704(2)	9.777(3)	9.738(1)
<i>c</i> , Å	15.980(3)	16.136(4)	12.373(2)
$\alpha$ , deg	90.0	90.0	90.0
$\beta$ , deg	112.24(2)	113.34(2)	90.0
$\gamma$ , deg	90.0	90.0	90.0
<i>V</i> , Å $^3$	2289(1)	2332(1)	1171(1)
<i>Z</i>	4	4	2
radiation ( $\lambda$ , Å)	$\text{Mo K}\alpha$ (0.71073)	$\text{Mo K}\alpha$ (0.71073)	$\text{Mo K}\alpha$ (0.71073)
space group	$P2_1/n$ (No. 13)	$P2_1/n$ (No. 13)	$I4_2m$ (No. 121)
$\rho$ (calcd), g cm $^{-3}$	1.35	1.60	1.86
$\mu$ ( $\text{Mo K}\alpha$ ), cm $^{-1}$	10.25	39.80	32.65
$2\theta$ range, deg	3–50	3–50	3–60
no. of data	3522	3142	513
[ $F > 4\sigma(F)$ ]			
no. of parameters	174	174	30
goodness of fit	1.20	1.23	1.23
<i>R</i>	0.0306	0.0404	0.0223
<i>R</i> <sub>w</sub>	0.0442	0.0524	0.0413

give  $\text{Mo}(\text{PMe}_3)_4(\text{Se})_2$  as a dark brown solid (0.075 g, 74% yield). The product is sufficiently pure for further reactions, but an analytically pure sample may be obtained by recrystallization from benzene in the presence of a small quantity of  $\text{PMe}_3$ . Anal. Calcd for  $\text{Mo}(\text{PMe}_3)_4(\text{Se})_2$ : C, 25.8; H, 6.5. Found: C, 26.3; H, 6.5. IR data: 2967 (m), 2903 (m), 1417 (m), 1292 (sh), 1276 (m), 936 (s), 852 (w), 710 (m), 661 (m).

(b) A solution of  $\text{Mo}(\text{PMe}_3)_5\text{N}_2$  (0.50 g, 1.00 mmol) in benzene (ca. 25 mL) was stirred with selenium powder (0.16 g, 2.03 mmol) for 20 h at room temperature, producing a dark brown solution. The volatile components were removed *in vacuo* giving a dark brown solid. The product was extracted into benzene (ca. 20 mL) and filtered, and the benzene was removed *in vacuo* to give  $\text{Mo}(\text{PMe}_3)_4(\text{Se})_2$  as a dark brown solid (0.40 g, 72% yield).

**Synthesis of  $\text{Mo}(\text{PMe}_3)_4(\text{Te})_2$ .** (a) A solution of  $\text{Mo}(\text{PMe}_3)_6$  (0.1 g, 0.18 mmol) in benzene (ca. 15 mL) was treated with tellurium powder (0.046 g, 0.36 mmol), and  $\text{PMe}_3$  was added to the resultant mixture at  $-78^\circ\text{C}$ . The mixture was allowed to warm to room temperature and was stirred for 45 min, producing a dark solution. The mixture was filtered and the volatile components removed by lyophilization to give  $\text{Mo}(\text{PMe}_3)_4(\text{Te})_2$  as a dark purple solid (0.060 g, 51%). Anal. Calcd for  $\text{Mo}(\text{PMe}_3)_4(\text{Te})_2$ : C, 22.0; H, 5.5. Found: C, 22.2; H, 5.4. IR data: 2961 (m), 2893 (m), 1414 (m), 1291 (sh), 1274 (m), 932 (s), 848 (w), 702 (m), 657 (m).

(b) A solution of  $\text{Mo}(\text{PMe}_3)_5(\text{N}_2)$  (0.50 g, 1.00 mmol) in benzene (ca. 25 mL) was treated with tellurium powder (0.26 g, 2.04 mmol) and  $\text{PMe}_3$  (ca. 0.1 mL). The mixture was stirred for 48 h at room temperature, producing a dark purple solution. The volatile components were removed *in vacuo* giving a dark purple solid. The product was extracted into benzene (ca. 20 mL) and filtered, and the benzene was removed *in vacuo* to give  $\text{Mo}(\text{PMe}_3)_4(\text{Te})_2$  as a dark purple solid (0.40 g, 62%).

**X-ray Structure Determinations of  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$  (E = S, Se, Te).** Crystal data, data collection, and refinement parameters for  $\text{Mo}(\text{PMe}_3)_4(\text{E})_2$  (E = S, Se, Te) are summarized in Table 10, and a typical procedure is illustrated for  $\text{Mo}(\text{PMe}_3)_4(\text{Te})_2$ . A single crystal of  $\text{Mo}$ -

(PMe<sub>3</sub>)<sub>4</sub>(Te)<sub>2</sub>, 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 using graphite monochromated Mo K $\alpha$  X-radiation ( $\lambda = 0.71073 \text{ \AA}$ ). 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 W(PMe<sub>3</sub>)<sub>4</sub>(Te)<sub>2</sub>,<sup>4b</sup> and that this also produced a successful solution. Hydrogen atoms were refined in calculated positions. Least-squares refinement converged to  $R = 0.0223$  ( $R_w = 0.0413$ ). Inversion of configuration established the correct absolute structure.

### Summary

In summary, we have developed a convenient single-step synthesis for Mo(PMe<sub>3</sub>)<sub>6</sub> by reduction of MoCl<sub>5</sub> with Na(K) alloy in PMe<sub>3</sub> solvent. Mo(PMe<sub>3</sub>)<sub>6</sub> exists in equilibrium with Mo(PMe<sub>3</sub>)<sub>4</sub>( $\eta^2$ -CH<sub>2</sub>PMe<sub>2</sub>)H and PMe<sub>3</sub>. At 30 °C, the equilibrium constant is a factor of *ca.*  $2 \times 10^3$  less than that for the tungsten system, an observation consistent with weaker M–H and M–C bonds for the molybdenum system. Finally, the reactions of Mo(PMe<sub>3</sub>)<sub>6</sub> and Mo(PMe<sub>3</sub>)<sub>4</sub>( $\eta^2$ -CH<sub>2</sub>PMe<sub>2</sub>)H with

H<sub>2</sub>S, Se, and Te have provided the syntheses of the first series of terminal sulfido, selenido, and tellurido derivatives of molybdenum, namely Mo(PMe<sub>3</sub>)<sub>4</sub>(E)<sub>2</sub> (E = S, Se, Te).

**Acknowledgment.** We thank the U. S. Department of Energy, Office of Basic Energy Sciences (No. DE-FG02-93ER14339), and the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research. We acknowledge the contribution of Daniel Rabinovich and Shannon Halkyard for preliminary experiments on the tellurium system. G.P. is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Award (1991–1996) and a Presidential Faculty Fellowship Award (1992–1997).

**Supplementary Material Available:** Tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, anisotropic displacement parameters for Mo(PMe<sub>3</sub>)<sub>4</sub>(E)<sub>2</sub> (E = S, Se, Te) (21 pages); listing of structure factors (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA943402D