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Trinuclear, tetranuclear and octanuclear chalcogenido clusters of molybdenum and tungsten supported by trimethylphosphine ligands

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Dedicated with respect and gratitude to John E. Bercaw, EQG, on the occasion of his 70th birthday. Happy birthday, John!

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ABSTRACT

A variety of trinuclear, tetranuclear and octanuclear chalcogenido compounds of molybdenum and tungsten that are supported by PMe_3 ligands has been synthesized and structurally characterized by X-ray diffraction. For example, the tetranuclear sulfido cluster, $Mo_4S_6(SH)_2(PMe_3)_6$, has been obtained by reaction of $Mo(PMe_3)_6$ with H_2S, while the trinuclear selenido and tellurido compounds, $Mo_3Se_5(PMe_3)_6$ and $Mo_3Te_5(PMe_3)_6$, may be obtained by thermolysis of $Mo(PMe_3)_4Se_2$ and $Mo(PMe_3)_4Te_2$, respectively. In contrast to the formation of a trinuclear compound analogous to $Mo_3E_5(PMe_3)_6$ (E = Se, Te), thermolysis of the tungsten complex, $W(PMe_3)_4S_2$, produces the octanuclear sulfido cluster, $W_8S_{16}(PMe_3)_{10}$. Of these compounds, $Mo_4S_6(SH)_2(PMe_3)_6$ and $W_8S_{16}(PMe_3)_{10}$ possess M:S stoichiometries of 1:2 and so may be regarded as molecular derivatives of the respective disulfides, MS_2, which are important components of hydrotreating catalysts.

1. Introduction

Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), which respectively remove sulfur- and nitrogen-containing impurities from crude petroleum feedstocks, comprise the largest volume catalytic application of transition metals [1–3]. Such processes are essential because these impurities have serious environmental impacts that result from the formation of sulfur and nitrogen oxides during combustion. Furthermore, the removal of sulfur- and nitrogen-containing impurities is important because they are catalyst poisons that prevent crude feedstocks from being used for subsequent chemical transformations. The catalysts employed for hydroprocessing are typically cobalt- or nickel-promoted MoS_2 or WS_2 supported on Al_2O_3 [1], and although general features pertaining to the mechanisms of HDS and HDN are appreciated, detailed aspects of the transformations are not known with certainty because of the heterogeneous nature of the reactions [4]. For this reason, it is of considerable benefit to investigate the reactivity of homogenous small molecule systems [5] and, in this regard, we have employed molybdenum and tungsten compounds, such as $Mo(PMe_3)_6$ [6], $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ [7] and $[Me_2Si(C_5Me_4)_2]MoH_2$ [8], to emulate transformations that pertain to HDS and HDN. Here we describe the molecular structures of molybdenum and tungsten chalcogenido compounds that bear relationships to MoS_2 and WS_2.

2. Results and discussion

We have previously reported the terminal sulfido compounds, $Mo(PMe_3)_4S_2$ [9–11] and $W(PMe_3)_4S_2$ [11–13], which are of interest because they may be viewed as soluble molecular adducts of MoS_2 and WS_2. In addition, these compounds are noteworthy because they possess rare examples of "pure" M=S double bonds, as opposed to the more commonly encountered $M^-\equiv S^+$ triply bonded form [11]. We have now examined these systems in more detail and describe here the formation of small molybdenum and tungsten chalcogenido clusters that are supported by PMe_3 ligands.

2.1. Molybdenum chalcogenido clusters supported by PMe_3 ligands

Our earlier studies demonstrated that the terminal sulfido compound, $Mo(PMe_3)_4S_2$, can be obtained from $Mo(PMe_3)_6$ [14] *via* a sequence that involves (i) conversion of $Mo(PMe_3)_6$ to $Mo(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, (ii) reaction of $Mo(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$

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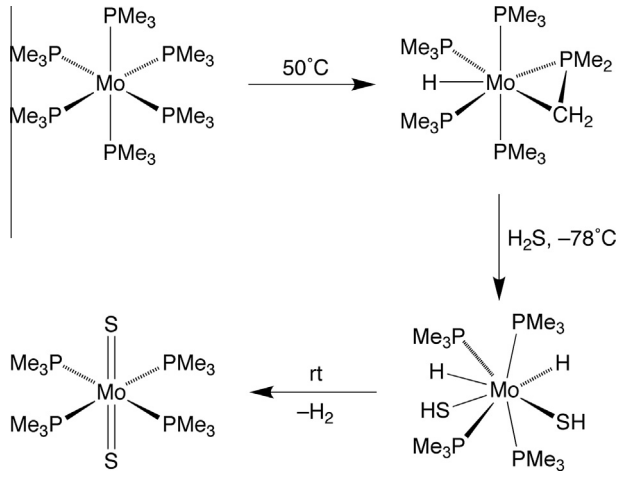


Scheme 1. Synthesis of $Mo(PMe_3)_4S_2$.

with H_2S at −78 °C to generate $Mo(PMe_3)_4H_2(SH)_2$, and (iii) elimination of H_2 from $Mo(PMe_3)_4H_2(SH)_2$ at room temperature (Scheme 1) [9]. This three-step sequence was employed because $Mo(PMe_3)_4S_2$ was not obtained cleanly by the direct reaction between $Mo(PMe_3)_6$ and H_2S [9]. It is, therefore, of note that we have re-examined the reaction between $Mo(PMe_3)_6$ and H_2S and have observed that one of the products is the tetranuclear cluster, $Mo_4S_6(SH)_2(PMe_3)_6$ (Scheme 2).

The formation of $Mo_4S_6(SH)_2(PMe_3)_6$ in this system is consistent with the observations that this cluster has previously been obtained *via* the reactions of (i) $[NH_4]_2[Mo_3S(S_2)_6]$ with PMe_3 [15] and (ii) $[NH_4]_2[MoS_4]$ with PMe_3 in the presence of H_2S [10b]. Also of relevance to the formation of $Mo_4S_6(SH)_2(PMe_3)_6$ upon reaction of $Mo(PMe_3)_6$ with H_2S, Rauchfuss has noted that treatment of $[NH_4]_2[MoS_4]$ with PMe_3 generates $Mo(PMe_3)_4S_2$ and that the latter reacts with H_2S to form $Mo_2S(SH)_3(PMe_3)_4$, which ultimately converts to $Mo_4S_6(SH)_2(PMe_3)_6$ in the presence of excess H_2S [10b]. Since $Mo_4S_6(SH)_2(PMe_3)_6$ possesses a Mo:S stoichiometry of 1:2, the cluster can be formally regarded as a derivative of partially hydrogenated MoS_2 [16].

The molecular structure of $Mo_4S_6(SH)_2(PMe_3)_6$, in the form of the benzene solvate, has been determined by X-ray diffraction (Fig. 1) and is similar to other crystalline forms that have been reported for this compound [10b,15]. Specifically, the four molybdenum atoms of $Mo_4S_6(SH)_2(PMe_3)_6$ lie in a plane and are arranged in a rhombus in which two Mo_3 triangles are bridged by μ_3-S face-capping ligands on opposite sides. Furthermore, each edge of the rhombus is bridged by a μ-S ligand, while two of the molybdenum atoms also possess terminal SH groups. The five Mo–Mo bond lengths are very similar, ranging from 2.8199(2) to 2.8303(3) Å, and are consistent with their assignment as single bonds [17], as would be predicted on the basis of it being an electron precise cluster [18,19] possessing the same number of skeletal valence

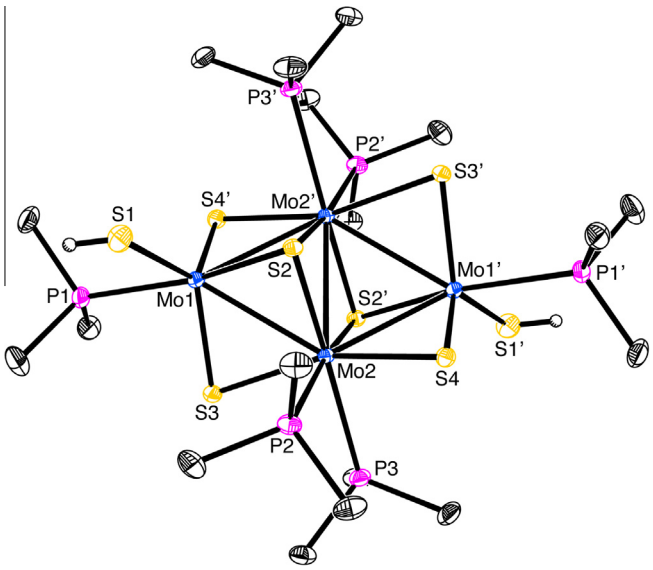


Fig. 1. Molecular structure of $Mo_4S_6(SH)_2(PMe_3)_6$.

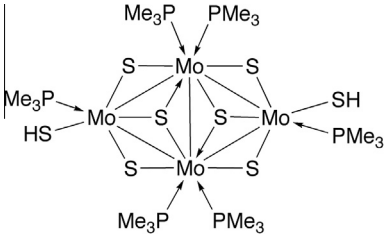
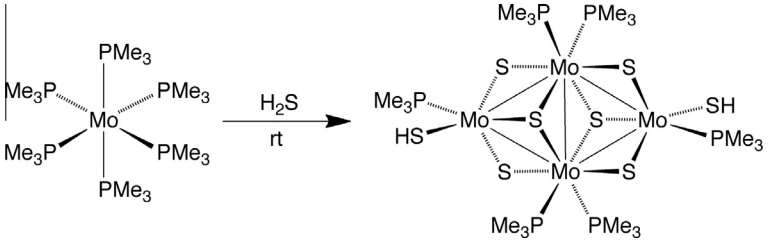


Fig. 2. A structure-bonding representation for $Mo_4S_6(SH)_2(PMe_3)_6$ that is consistent with the presence of five Mo–Mo bonds.

Table 1
Molybdenum and tungsten sulfido and hydrosulfido clusters supported by PR_3 ligands.

Compound	Mo,S,H[a] composition	Mo,S,H ratio	Reference
$Mo_6S_{10}(SH)_2(PEt_3)_6$	$Mo_6S_{12}H_2$	$MoS_2H_{0.33}$	[15]
$Mo_6S_8(PR_3)_6$	Mo_6S_8	$MoS_{1.33}$	[21,24]
$Mo_{12}S_{16}(PR_3)_{10}$	$Mo_{12}S_{16}$	$MoS_{1.33}$	[21,24]
$Mo_4S_6(SH)_2(PMe_3)_6$	$Mo_4S_8H_2$	$MoS_2H_{0.5}$	[10b,15], this work
$Mo_6S_{10}(SH)_2(PEt_3)_6$	$Mo_6S_{10}H_2$	$MoS_{1.67}H_{0.33}$	[15]
$Mo_3S_5(PMe_3)_6$	Mo_3S_5	$MoS_{1.67}$	[25]
$W_8S_{16}(PMe_3)_{10}$	W_8S_{16}	WS_2	this work
$W_4S_6(SH)_2(PMe_2Ph)_6$	$W_4S_8H_2$	$WS_2H_{0.5}$	[44]
$W_4S_6(PMe_2Ph)_4$	W_4S_6	$WS_{1.5}$	[44]

[a] Number of hydrogen atoms attached to sulfur.



Scheme 2. Formation of $Mo_4S_6(SH)_2(PMe_3)_6$.