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μ-Sulfido and μ-Oxo Dimers $M_2(\mu\text{-}E)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ Obtained by Conproportionation of $MCl_2(PMe_3)_4$ and $M(E)Cl_2(PMe_3)_3$ (M = Mo, W; E = O, S): Complete vs Incomplete Intermetal Atom Transfer

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Reactions of $MoCl_2(PMe_3)_4$ with the sulfur atom donors $SPMe_3$, $SPPh_3$, ^tBuSH, and ethylene sulfide give the μ-sulfido dimer $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$. These reactions proceed by initial formation of the tetravalent terminal sulfido complex $Mo(S)Cl_2(PMe_3)_3$ and its conproportionation with the divalent starting material. The X-ray crystal structure of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5\cdot{}^1/_6C_7H_8$ shows an edge-shared bioctahedral dimer in which three phosphines are bound to one molybdenum and two to the other. The central $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)$ core is symmetrical, indicating a Mo(III)–Mo(III) oxidation state assignment, and contains an Mo–Mo bond of 2.6956(6) Å and short Mo–S distances of 2.274(1) and 2.285(1) Å. Crystal data: $R\bar{3}$, $Z = 18$, $a = 18.840(6)$ Å, $b = 48.989(5)$ Å, $V = 15058.8(11)$ Å^3, refined to $R = 3.5\%$, $R_w = 4.7\%$, and GOF = 1.047. The conproportionation of $MCl_2(PMe_3)_4$ and terminal oxo and sulfido complexes $M(E)Cl_2(PMe_3)_3$ is a general route to the molybdenum and tungsten μ-sulfido and μ-oxo dimers $M_2(\mu\text{-}E)(\mu\text{-}Cl)Cl_3(PMe_3)_5$, which are isostructural on the basis of their very similar ^1H and $^{31}P\{^1H\}$ NMR spectra. Two isomeric mixed-metal dimers, $MoW(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$, differing only in the occupation of the two different metal sites, are formed on reactions of $Mo(S)Cl_2(PMe_3)_3$ with $WCl_2(PMe_3)_4$ or $W(S)Cl_2(PMe_3)_3$ with $MoCl_2(PMe_3)_4$. The two combinations of sulfur atom donor and acceptor yield different isomers as their kinetic product, although equilibrium is quickly established ($K_{eq} = 0.62$ at 24 °C). These conproportionation reactions are examples of incomplete sulfur or oxygen atom transfer. In contrast, the reaction of $Mo(O)Cl_2(PMe_3)_3$ with $WCl_2(PMe_3)_4$ results in complete oxygen atom transfer to give $W(O)Cl_2(PMe_3)_3$ and $MoCl_2(PMe_3)_4$. Conproportionation of the W(V) oxo complex $W(O)Cl_3(PMe_3)_2$ with $WCl_3(PMe_3)_3$ occurs by chlorine atom transfer to give the W(IV) monomers $W(O)Cl_2(PMe_3)_3$ and $WCl_4(PMe_3)_2$. The mechanisms of these reactions and the preferences for complete vs incomplete atom transfer and monomeric vs dimeric products are discussed.

Transfer of an oxygen or sulfur atom to or from a metal center is a topic of long-standing interest because such reactions are involved in a variety of organic and biological transformations and also are examples of multielectron inner-sphere electron transfer.[3–5] In previous studies, we have shown that the Mo(II) and W(II) complexes MCl_2L_4 (L = PMe_3, $PMePh_2$) are avid oxygen atom and sulfur atom acceptors, reacting with a variety of species ranging from epoxides and episulfides to phosphine sulfides and CO_2.[6] Though the transfer of a univalent atom or group such as $Cl^\bullet$ or $HO^\bullet$ between two metal centers has been extensively studied,[4] the transfer of a multivalent atom (O, S, N) or group (NR) has become a focus of attention only in recent years.[3,5] Holm has distinguished two classes of such intermetal redox processes, according to whether the transfer of the atom or group is either *complete* from one metal center to another (eq 1) or *partial* or *incomplete*, where dinuclear bridging species are formed (eq 2).[3a] Both processes have been documented for systems

$$L_nM(E) + L_mM' \rightarrow L_nM + L_mM'(E) \qquad (1)$$

$$L_nM(E) + L_mM' \rightarrow L_nM\text{–}E\text{–}M'L_m \qquad (2)$$

involving oxygen atom, nitrogen atom, and nitrene (NR) group transfer,[5] but there are far fewer examples involving sulfur atoms. It has been suggested[5a] that this is partly due to the scarcity of suitable monomeric terminal metal sulfido species, $L_nM{=}S$.

We have observed[7] complete intermetal oxygen atom transfer from molybdenum and rhenium oxo complexes to $WCl_2(PMePh_2)_4$ and $MoCl_2(PMePh_2)_4$. While these reactions are often complicated by competing chlorine atom transfer and other pathways, the major products typically result from the transfer of an oxygen atom with a two electron redox change at each metal, for instance in eq 3.[8] We report here that, with PMe_3

$$\begin{aligned} &Mo(O)Cl_2(PMePh_2)_3 + WCl_2(PMePh_2)_4 \xrightarrow[C_6D_6]{25\,°C} \\ &\quad W(O)Cl_2(PMePh_2)_3 + MoCl_2(PMePh_2)_4 + \\ &\quad\quad W(O)Cl_3(PMePh_2)_2 + WCl_3(PMePh_2)_3 + \ldots \end{aligned} \qquad (3)$$

instead of $PMePh_2$ as the ancillary ligand, these and related

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Table 1. Crystallographic Data for $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5\cdot{}^1/_6C_7H_8$ (**IIa**)

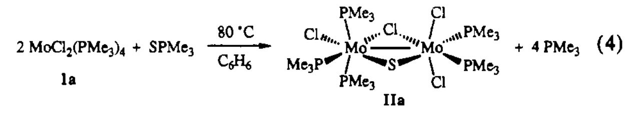
$Mo_2Cl_4SP_5C_{15}H_{45}\cdot{}^1/_6C_7H_8$	fw = 761.50
a = 18.840(6) Å	space group: $R\bar{3}$ (No. 148)
b = 18.840(6) Å	T = 24 °C
c = 48.989(5) Å	λ = 0.710 73 Å (Mo Kα)
V = 15058.8(11) Å^3	ρ_{calc} = 1.511 g cm^{-3}
Z = 18	μ = 13.52 cm^{-1} ^{a}
R = 0.035^b	transm coeff = 0.999–0.963
R_w = 0.047^b	

[a] An empirical absorption correction was applied; see ref 39. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, where $w^{-1} = [\sigma^2_{count} = (0.06F^2)^2]/4F^2$: Stout, G. H.; Jensen, L. H. *X-Ray Structure Determination*; Wiley: New York, 1989; Chapter 9, p 229, and Chapter 17, p 388.

reactions can form dimeric complexes by incomplete atom transfer.[9] This provides a rational synthesis of μ-sulfido and μ-oxo dimers $M_2(\mu\text{-}E)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (M = Mo, W; E = O, S), including mixed-metal derivatives. A discussion of the formation of these dimers and their relationship with the complete atom transfer reactions is presented, which provides insight into the preference for incomplete versus complete atom transfer as a function of the phosphine ligands, the metals, and their oxidation states. The unusually diverse coordination chemistry of the molybdenum μ-sulfido dimer will be described in a forthcoming paper.[10]

Results

Synthesis and Characterization of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (IIa). The molybdenum(II) complex $MoCl_2(PMe_3)_4$ (**Ia**) reacts with half an equivalent of $SPMe_3$ at 80 °C in benzene or toluene to cleanly form the dimer $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**IIa**) along with 4 equiv of free PMe_3 (eq 4). (In this paper, species labeled



$$2\,MoCl_2(PMe_3)_4 + SPMe_3 \xrightarrow[C_6H_6]{80\ °C} Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5 + 4\,PMe_3 \quad (4)$$

Ia **IIa**

a are molybdenum compounds while **b** refers to tungsten analogues.) The formation of **IIa** as monitored by NMR slows substantially as the concentration of free PMe_3 increases so that periodic removal of the phosphine is required in order for the reaction to go to completion. This suggests that formation of **IIa** is inhibited by the buildup of free PMe_3, a feature which is typically observed in reactions involving complex **Ia**.[6f] Complex **IIa** is isolated as an air sensitive dark blue-green solid by removal of the volatiles from the reaction mixture. The dimer is not stable towards repeated solvent evaporation, losing one PMe_3 ligand to form $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4$.[9,10] Phosphine loss is reversible so recrystallization is best accomplished by diffusion of petroleum ether into a toluene solution of the complex containing a small amount of PMe_3.

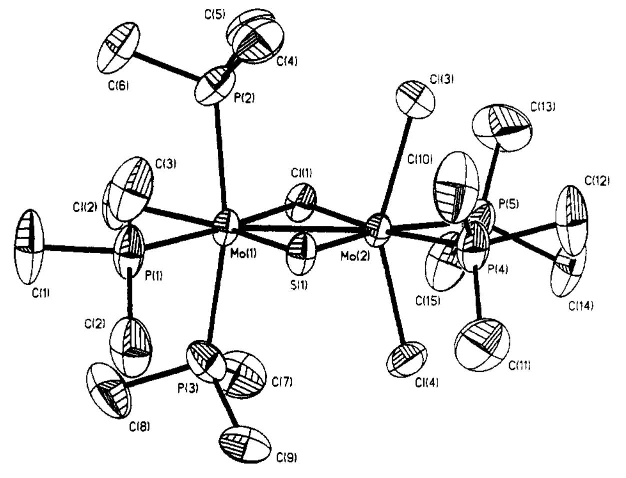


Figure 1. ORTEP drawing of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5\cdot{}^1/_6C_7H_8$ (**IIa**) showing 40% probability ellipsoids. The hydrogen atoms and toluene solvent molecule have been omitted for clarity.

Table 2. Selected Bond Distances (Å) for $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5\cdot{}^1/_6C_7H_8$ (**IIa**)

Mo(1)–Mo(2)	2.6956(6)	Mo(2)–Cl(1)	2.4427(12)
Mo(1)–Cl(1)	2.4360(12)	Mo(2)–Cl(3)	2.4096(15)
Mo(1)–Cl(2)	2.5139(14)	Mo(2)–Cl(4)	2.4286(15)
Mo(1)–S(1)	2.2740(13)	Mo(2)–S(1)	2.2852(13)
Mo(1)–P(1)	2.5238(14)	Mo(2)–P(4)	2.5242(16)
Mo(1)–P(2)	2.5375(16)	Mo(2)–P(5)	2.6866(15)
Mo(1)–P(3)	2.5414(18)		

Table 3. Selected Angles (deg) for $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5\cdot{}^1/_6C_7H_8$ (**IIa**)

Mo(1)–S(1)–Mo(2)	72.49(4)	Mo(1)–Cl(1)–Mo(2)	67.08(3)
Cl(1)–Mo(1)–Cl(2)	84.87(5)	Cl(1)–Mo(2)–Cl(3)	93.31(5)
Cl(1)–Mo(1)–S(1)	110.52(4)	Cl(1)–Mo(2)–Cl(4)	96.51(5)
Cl(1)–Mo(1)–P(1)	171.83(5)	Cl(1)–Mo(2)–S(1)	109.90(4)
Cl(1)–Mo(1)–P(2)	88.98(5)	Cl(1)–Mo(2)–P(4)	171.95(5)
Cl(1)–Mo(1)–P(3)	89.17(5)	Cl(1)–Mo(2)–P(5)	78.06(5)
Cl(2)–Mo(1)–S(1)	164.56(5)	Cl(3)–Mo(2)–Cl(4)	150.42(6)
Cl(2)–Mo(1)–P(1)	86.96(5)	Cl(3)–Mo(2)–S(1)	103.82(6)
Cl(2)–Mo(1)–P(2)	81.83(6)	Cl(3)–Mo(2)–P(4)	80.65(6)
Cl(2)–Mo(1)–P(3)	82.26(6)	Cl(3)–Mo(2)–P(5)	80.43(6)
S(1)–Mo(1)–P(1)	77.65(5)	Cl(4)–Mo(2)–S(1)	98.92(5)
S(1)–Mo(1)–P(2)	96.76(5)	Cl(4)–Mo(2)–P(4)	86.42(6)
S(1)–Mo(1)–P(3)	98.70(6)	Cl(4)–Mo(2)–P(5)	74.46(5)
P(1)–Mo(1)–P(2)	90.17(6)	S(1)–Mo(2)–P(4)	76.90(5)
P(1)–Mo(1)–P(3)	89.42(6)	S(1)–Mo(2)–P(5)	170.45(5)
P(2)–Mo(1)–P(3)	164.08(6)	P(4)–Mo(2)–P(5)	95.59(6)

$Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**IIa**) crystallizes with $^1/_6$ equiv of toluene in the trigonal space group $R\bar{3}$ (Table 1). Solution of the structure from single crystal X-ray data revealed isolated dimeric molecules (Figure 1); selected bond distances and angles are given in Tables 2 and 3, and positional parameters are given in Table 4. The dimers adopt an edge-shared bioctahedral structure, typical of M_2L_{10} dimers,[11] with the sulfide and a chloride (S(1) and Cl(1)) as the bridging ligands. Unlike most dimers of this type, however, the two metal centers are inequivalent in terms of the number of chloride and phosphine ligands. The coordination sphere about Mo(1) consists of a chloride and three phosphine ligands (Cl(2), P(1), P(2), P(3)) while Mo(2) has two chloride and two phosphine ligands (Cl(3), Cl(4), P(4), P(5)).

In spite of the asymmetry in the ligand sets of the two metals, the central $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)$ core of the dimer is symmetrical. The Mo–S(1) distances (2.274(1), 2.285(1) Å), Mo–Cl(1) distances (2.436(1), 2.443(1) Å) and the Cl(1)–Mo–S(1) angles (110.52(4), 109.90(4)°) are all essentially the same. This suggests that each metal has the same +3 oxidation state. The Mo(1)–Mo(2) distance of 2.6956(6) Å is in the range reported for Mo(III)–Mo(III) bonds (2.5–2.8 Å), suggesting the presence of a metal–metal bond in the complex.[11a] This is reflected in the small angles at the bridging ligands, Mo(1)–S(1)–Mo(2) = 72.49(4)° and Mo(1)–Cl(1)–Mo(2) = 67.08(3)°. The sum of the interior angles around Mo(1)–S(1)–Mo(2)–Cl(1) is 360.0° which indicates that the atoms of the core comprise a planar unit. The Mo–S distances are at the short end of the reported range for bridging sulfido ligands[12] but longer than terminal sulfido distances[13] which suggests partial multiple bond character. Very similar Mo–S distances (2.282(1) and 2.264(2) Å) have been

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(8) In reaction 3, $MoCl_2(PMePh_2)_4$ can not be conclusively identified because of its very broad ^1H NMR spectrum.[7]

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Table 4. Positional and Equivalent Isotropic Thermal Parameters for $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5\cdot{}^1/_6C_7H_8$ (**IIa**)[a]

atom	x	y	z	B, Å^2
Mo(1)	0.29852(2)	0.28317(2)	0.08912(1)	3.090(9)
Mo(2)	0.43329(2)	0.42744(2)	0.07734(1)	3.077(9)
Cl(1)	0.43622(6)	0.30216(6)	0.08779(3)	3.65(3)
Cl(2)	0.25424(7)	0.13643(7)	0.10004(4)	5.52(4)
Cl(3)	0.45685(9)	0.42040(9)	0.02932(3)	5.67(4)
Cl(4)	0.48035(8)	0.49147(8)	0.12171(3)	5.40(4)
S(1)	0.30160(7)	0.40260(6)	0.07921(3)	3.85(3)
P(1)	0.14924(8)	0.24263(8)	0.09234(4)	5.34(4)
P(2)	0.27638(8)	0.22876(8)	0.04063(3)	4.79(4)
P(3)	0.30943(10)	0.29687(10)	0.14077(4)	5.78(5)
P(4)	0.44697(9)	0.56174(8)	0.06212(4)	5.48(4)
P(5)	0.59499(8)	0.48148(9)	0.07835(4)	5.11(4)
C(1)	0.0770(3)	0.1372(4)	0.10196(19)	8.8(2)
C(2)	0.1214(4)	0.2984(4)	0.11684(17)	7.9(2)
C(3)	0.1010(3)	0.2554(4)	0.06202(17)	7.5(2)
C(4)	0.2619(4)	0.2861(4)	0.01303(14)	6.9(2)
C(5)	0.3572(4)	0.2109(4)	0.02759(14)	6.6(2)
C(6)	0.1859(4)	0.1266(4)	0.03526(16)	7.4(2)
C(7)	0.3981(4)	0.2969(5)	0.15459(14)	8.2(2)
C(8)	0.2276(5)	0.2144(5)	0.15954(16)	9.7(3)
C(9)	0.3115(4)	0.3843(4)	0.15810(15)	8.7(2)
C(10)	0.3787(4)	0.5534(4)	0.03494(18)	9.1(2)
C(11)	0.4294(5)	0.6193(4)	0.08846(18)	9.4(2)
C(12)	0.5442(4)	0.6390(4)	0.04735(19)	9.1(3)
C(13)	0.6396(4)	0.4571(6)	0.04905(17)	10.6(3)
C(14)	0.6678(4)	0.5896(4)	0.08460(19)	8.2(2)
C(15)	0.6237(4)	0.4353(4)	0.10533(17)	7.8(2)
C(16)	0.2484(7)	0.628(3)	0.1679(5)	20.1(7)

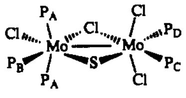
[a] Atom C(16) is the ring carbon of the toluene solvent molecule, the center of which sits on a $\bar{3}$ special position such that C(16) has a multiplicity of 1. This carbon was located on a difference map and refined with isotropic thermal parameters; the benzylic carbon atom of the toluene was not found in the difference map and so is not included. B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

reported for the related Mo(III) edge-shared bioctahedral dimer $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(S_2CNMe_2)_3(SCNMe_2)$.[12a]

The molybdenum centers in **IIa** each have a distorted octahedral coordination geometry, with cis angles that deviate from 90° by as much as ±10° for Mo(1) and ±15° for Mo(2). The largest distortion in the complex is the bending apart of the axial ligands that lie above and below the central Mo(1)–S(1)–Mo(2)–Cl(1) plane. This is revealed in the small trans angles: Cl(3)–Mo(2)–Cl(4) = 150.42(6)° and P(2)–Mo(1)–P(3) = 164.08(6)°. Despite this bending, the nonbonded Cl···CH_3 distances between the axial ligands are 3.4–3.6 Å and are still shorter than the sum of the van der Waals radii of ca. 3.8 Å.[14] Such a steric interaction between ligands that are cis across the metal–metal bond is a common feature of edge-shared bioctahedral dimers and prevents two phosphine ligands from occupying neighboring axial sites.[11] There is little twist about the central core of the dimers, as revealed in the P(2)–Mo(1)–Mo(2)–Cl(3) and P(3)–Mo(1)–Mo(2)–Cl(4) torsion angles of 1.6 and 4.5°. The plane defined by Cl(2), Mo(1), and P(1) makes a dihedral angle of only 1.3° with the plane of the core (Mo(1)–S(1)–Mo(2)–Cl(1)), and the Mo(2)–P(4)–P(5) plane makes an angle of 6.6° in the opposite direction. The net twist across the Mo(1)–Mo(2) axis of the dimer of 7.9° is typical of edge-shared bioctahedral structures (generally <10°).[11]

The Mo–P bond lengths, except for Mo(2)–P(5), range from 2.524(2) to 2.541(2) Å and are consistent with values reported for other Mo(III) compounds.[15] The Mo(2)–P(5) bond of 2.687(2) Å is ~0.15 Å longer than the others, indicating a large trans influence of the μ-sulfido ligand. Similarly, the Mo(2)–Cl(3) and Mo(2)–Cl(4) distances of 2.410(2) and 2.429(2) Å are typical,[15] while the chloride trans to the sulfido ligand (Cl(2)) has a ~0.1-Å longer bond, 2.514(1) Å. The bonds to the bridging chloride are only slightly longer (~0.02 Å) than the Mo(2)–Cl(3) and Mo(2)–Cl(4) bonds.[16]

The ^1H and ^{31}P NMR spectra of isolated $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**IIa**) are very informative because of the low symmetry (Figure 2, Table 5). Both spectra show four resonances in a 1:1:1:2 ratio,[17] consistent with the C_s structure in the solid state. The intensity 2 signal in the proton spectrum is a (poorly resolved) virtual triplet, indicating trans equivalent phosphine ligands[18] (P_A in the drawing). The other three resonances (doublets in the proton spectrum, Figure 2A) correspond to the three unique phosphine ligands in the equatorial plane of the dimer.



IIa

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(12) Mo–$S_{bridging}$ distances range from 2.20 to 2.54 Å (average = 2.32 Å), but most fall within the tighter range 2.3–2.4 Å. Most of the structures in these papers (and papers referenced therein) are d^0 or d^1 at the metal centers. (a) Herrick, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 2599–2605. (b) Dahl, L. F.; de Gil, E. R.; Feltman, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 1653. (c) Drew, D. G. B.; Kay, A. *J. Chem. Soc. A* **1971**, 1851. (d) Ricard, L.; Estienne, J.; Weiss, R. *Inorg. Chem.* **1973**, *12*, 2182–2186. (e) Weiss, R. *Inorg. Chem.* 1974, *13*, 2745. (f) Newton, W. E.; McDonald, J. W.; Yamanouchi, K.; Enemark, J. H. *Inorg. Chem.* **1979**, *18*, 1621–1626. (g) Noble, M. E.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1983**, *22*, 3671–3676. (h) Cotton, F. A.; Dori, Z.; Lusar, R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 3654–3658. (i) Harmer, M. A.; Halbert, T. R.; Pan, W.-H.; Coyle, C. L.; Cohen, S. A.; Stiefel, E. I. *Polyhedron* **1986**, *5*, 341–347. (j) Coucouvanis, D.; Hadjikyriacoo, M.; Draganjac, M.; Kanetzidis, M. G.; Ileperume, D. *Polyhedron* **1986**, *5*, 349–356. (k) Coucouvanis, D.; Hadjikyriacoo, A. J. *Inorg. Chem.* **1987**, *26*, 2400–2408. (l) Tanner, L. D.; Haltiwanger, R. C.; Rakowski-DuBois, M. *Inorg. Chem.* **1988**, *27*, 1741–1746. (m) Coucouvanis, D.; Koo, S.-M. *Inorg. Chem.* **1989**, *28*, 2–5.

(13) Terminal Mo–S distances fall in the range 2.09–2.16 Å: (a) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322. (b) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831–1838. (c) Müller, A. *Polyhedron* **1986**, *5*, 323. (d) Young, C. G.; Roberts, S. A.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1987**, *109*, 2938–2946. (e) Müller, A.; Diemann, E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987; Vol. 2, pp 515–550. (f) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 5094 and references therein.

(14) *Handbook of Chemistry and Physics*, 54th ed.; 1973–74, Weast, R. C., Ed; CRC: Boca Raton, FL, 1973–1974; p D-157. Van der Waals radii for Cl, 1.8 Å, for a methyl group, 2.0 Å.

(15) Reported bond length ranges for Mo(III): Mo–P, 2.51–2.60 Å; Mo–$Cl_{terminal}$, 2.36–2.49 Å; Mo–$Cl_{bridging}$, 2.38–2.52 Å. *Monomers:* (a) Brencic, J. V. *Z. Anorg. Allg. Chem.* **1974**, *403*, 218–224. (b) Brencic, J. V.; Leban, I. *Z. Anorg. Allg. Chem.* **1980**, *465*, 173–178. (c) Millar, M.; Lincoln, S. S. H. C. J.; Koch, S. A. *J. Am. Chem. Soc.* **1982**, *104*, 288–289. (d) Hofacker, P.; Friebel, C.; Dehnicke, K.; Bauml, P.; Hiller, W.; Strahle, J. *Z. Naturforsch.* **1989**, *44B*, 1161–1166. (e) Fernandez-Trujillo, M. J.; Basallote, M. G.; Valerga, P.; Puerta, M. C.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1991**, 3149–3151. (f) Dawson, D. M.; Henderson, R. A.; Hills, A.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1992**, *6*, 973–976. *Dimers:* (g) Boorman, P. M.; Moynihan, K. J.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1982**, 899. (h) Wieghardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 94–99. (i) Hey, E.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *568*, 86–92. (j) Cotton, F. A.; Diebold, M. P.; O'Connor, C. J.; Powell, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7438–7445. (k) Canich, J. A. M.; Cotton, F. A.; Daniels, L. M.; Lewis, D. E. *Inorg. Chem.* **1987**, *26*, 4046–4050. (l) Agaskar, P. A.; Cotton, F. A.; Dunbar, K. R.; Favello, L. R.; O'Connor, J. A. *Inorg. Chem.* **1987**, *26*, 4051–4057. (m) Bates, P. A.; Nielson, A. J.; Waters, J. M. *Polyhedron* **1987**, *6*, 2111–2118 and references therein. (n) Luck, R. L.; Cotton, F. A. *Inorg. Chem.* **1989**, *28*, 182–187. (o) Mui, H. D.; Poli, R. *Inorg. Chem.* **1989**, *28*, 3609–3612. (p) Poli, R.; Mui, H. *Inorg. Chem.* **1991**, *30*, 65–77.

(16) Mo–Cl_t distances are on average 0.09 Å shorter than Mo–Cl_b distances within the same molecule for the compounds reported in ref 15g,i,k–p. That this difference is only 0.02 Å in **IIa** suggests strong Mo–Cl bonding within the $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)$ core.

(17) Integration of the $^{31}P\{^1H\}$ spectra reported here show that the resonances occur in close to integral ratios. The integrals are therefore not compromised by differential NOE or other effects.

(18) (a) Crabtree, R. *The Organometallic Chemistry of the Transition Metals*; Wiley-Interscience: New York, 1988; Chapter 10, pp 213–214. (b) Drago, R. S. *Physical Methods in Chemistry*; Saunders College Publishing: Chicago, IL, 1977; Chapter 7, p 223.

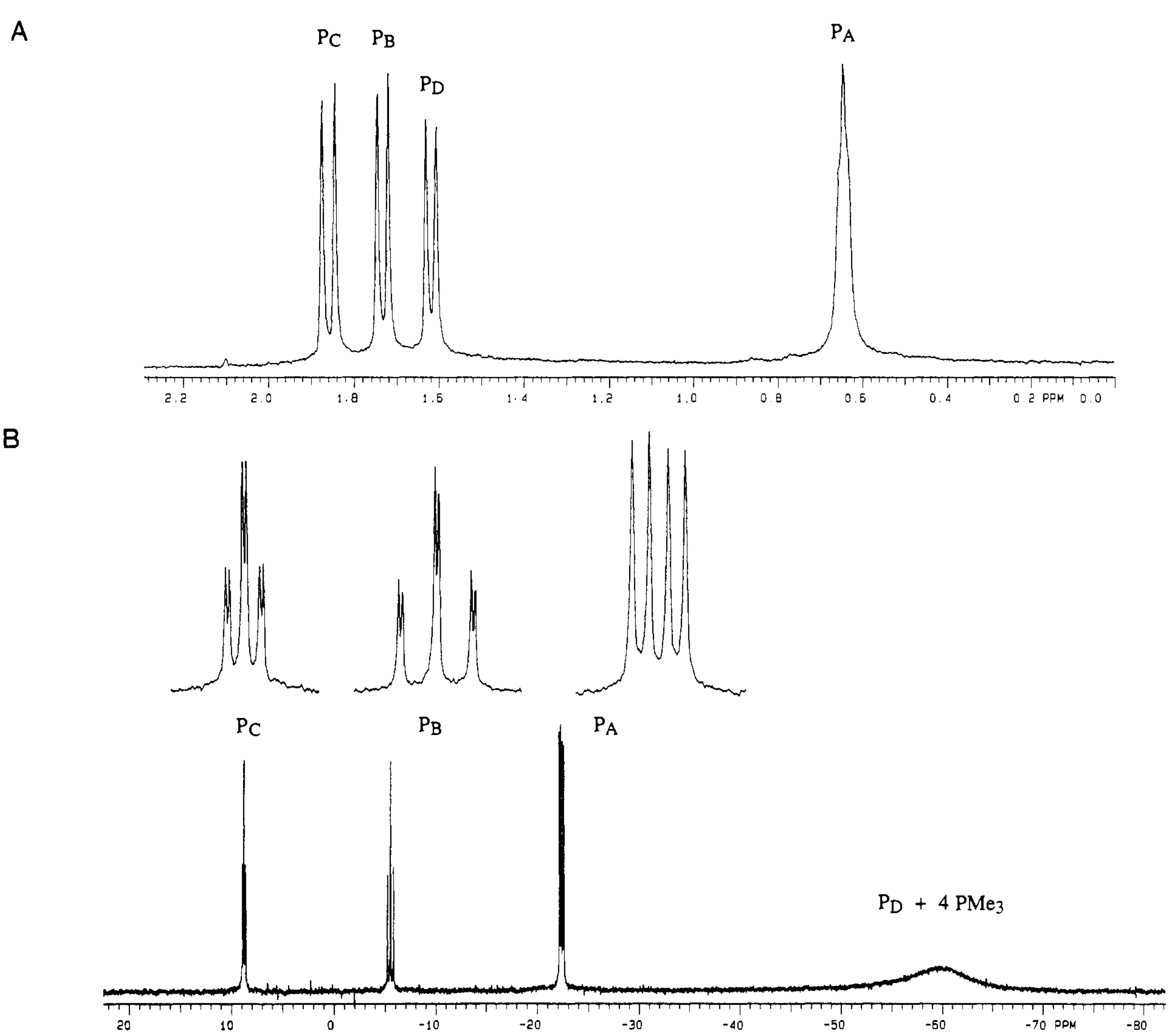


Figure 2. NMR spectra of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**IIa**) in C_6D_6. The assignments correspond to the drawing in Table 5: (A) ^1H NMR; (B) $^{31}P\{^1H\}$ NMR in the presence of 4 equiv of PMe_3 (averaged with P_D).

In the presence of free PMe_3, one of the resonances in the NMR spectra of **IIa** is missing and no peak is observed for free PMe_3. Instead, a broad peak is observed intermediate between these two positions (Figure 2B), indicating that one of the unique phosphine ligands in **IIa** rapidly exchanges with free PMe_3. The labile phosphine is the ligand *trans* to the μ-sulfido (P_D), the ligand with the unusually long bond length in the solid state structure of **IIa** (P(5)). We have isolated the compound formed on loss of a phosphine from **IIa**, $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4$, and its structure is very similar to that of **IIa** except that this phosphine is missing.[9,10] The *trans* influence of the sulfur on P_D in the X-ray structure thus manifests itself as a *trans* effect in solution.

The P_B and P_C resonances in the $^{31}P\{^1H\}$ NMR are both triplets of doublets (Figure 2B), due to a 4-Hz coupling between them and larger couplings to P_A of 37 and 17 Hz, respectively (coupling to P_D is washed out by the exchange process). The smaller coupling to P_A is attributed to the more distant ligand, P_C.

For some isolated samples of **IIa** (and the related dimers described below), the multiplet resonances of the phosphorus spectrum of **IIa** are not completely resolved. Generally, this is observed for samples that are isolated as powders rather than larger crystals. The broadening is most likely due to contamination of isolated **IIa** by a small amount of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_4$ (see above), which is in equilibrium with **IIa** on the NMR time scale.[9,10] For most samples the best resolution of these peaks is observed in the presence of free PMe_3 (Table 5).

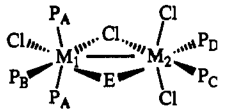
Compound **IIa** is also formed on reaction of $MoCl_2(PMe_3)_4$ (**Ia**) with 0.5 equiv of $SPPh_3$, analogous to $SPMe_3$ (eq 4); the PPh_3 byproduct does not appear to bind to molybdenum (by NMR). Complex **Ia** desulfurizes *tert*-butyl thiol in high yield (>90% by NMR) producing **IIa** and isobutane along with $SPMe_3$ and PMe_3 (eq 5). The reaction proceeds very slowly at ambient

$$\underset{\textbf{Ia}}{2MoCl_2(PMe_3)_4} + 2(CH_3)_3CSH \xrightarrow[C_6H_6]{80\ ^\circ C} \underset{\textbf{IIa}}{Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5} + SPMe_3 + 2PMe_3 + 2(CH_3)_3CH \quad (5)$$

temperatures but is essentially complete after heating for 90 min at 80 °C. The isobutane was identified by comparison of its NMR spectra with that of an authentic sample. PMe_3 and *tert*-butyl thiol are unreactive in the absence of **Ia**, so the $SPMe_3$ and an equivalent amount of isobutane produced in the reaction come from some other metal-mediated pathway. Reactions of **Ia** with EtSH, H_2S, and *p*-TolN=C=S produce uncharacterized mixtures of products and/or materials which do not give proton or phosphorus NMR spectra.

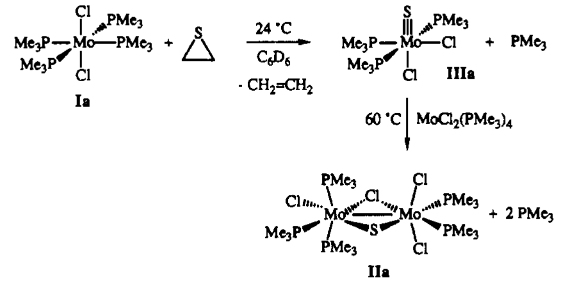
The reaction of $MoCl_2(PMe_3)_4$ (**Ia**) with ethylene sulfide yields ethylene and the terminal sulfido complex $Mo(S)Cl_2(PMe_3)_3$ (**IIIa**) at ambient temperatures.[6f] This reaction is quite sensitive to conditions and **IIIa** is not very stable in solution; it has only been successfully made on a small scale (~15 mg), contaminated with small amounts of **IIa** (see Experimental Section). When 0.5 equiv of ethylene sulfide is reacted with **Ia**, an equimolar mixture

Table 5. ^{1}H and ^{31}P{^{1}H} NMR Data for $M_2(\mu\text{-E})(\mu\text{-Cl})Cl_3(PMe_3)_5$ (II and V)[a]

		^{1}H NMR δ (m; J_{PH}, Hz; no of H)	^{31}P{^{1}H} NMR δ (m; J_{PP}, Hz; no. of P); $^nJ_{WP}$, Hz[b]
$Mo_2(\mu\text{-S})(\mu\text{-Cl})Cl_3(PMe_3)_5$ (**IIa**)	P_A	0.65 (t; 4; 18 H)	−22.2 (d of d; 36, 17; 2 P)
	P_B	1.74 (d; 8; 9 H)	−5.1 (t of d; 37, 4; 1 P)
	P_C	1.86 (d; 9; 9 H)	9.3 (t of d; 17, 4; 1 P)
	P_D	1.58 (d; 7; 9 H)	−25.6 (s; br; 1 P)
$W_2(\mu\text{-S})(\mu\text{-Cl})Cl_3(PMe_3)_5$ (**IIb**)[c]	P_A	0.76 (s; br; 18 H)	−53.1 (d of d; 16, 14; 2 P); J_{WP} = 251, 46[c]
	P_B	2.00 (d; 9; 9 H)	−11.5 (t of d; 14, 4; 1 P); J_{WP} = 218, 22[c]
	P_C	1.88 (d; 8; 9 H)	−42.5 (t of d; 16, 4; 1 P); J_{WP} = 242, 23[c]
	P_D	1.59 (d; 7; 9 H)	−40.1 (s; br; 1 P)
$Mo_2(\mu\text{-O})(\mu\text{-Cl})Cl_3(PMe_3)_5$ (**Va**)[c,d]	P_A	0.78 (t; 3; 18 H)	−20.3 (d of d; 32, 13; 2 P)[c]
	P_B	1.54 (d; 6; 9 H)	1.4 (t of d; 32, 9; 1 P)[c]
	P_C	1.56 (d; 7; 9 H)	7.8 (t of d; 13, 9; 1 P)[c]
	P_D	1.54 (d; 6; 9 H)	−28.7 (s; br; 1 P)
$W_2(\mu\text{-O})(\mu\text{-Cl})Cl_3(PMe_3)_5$ (**Vb**)[d,e]	P_A	0.94 (t; 3; 18 H)	−49.2 (t; br, 11; 2 P); J_{WP} = 280
	P_B	1.64 (d; 9; 9 H)	−27.5 (t; br, 7; 1 P)
	P_C	1.66 (d; 8; 9 H)	−7.5 (s; br; 1 P)
	P_D + PMe_3[e]	0.87 (s; br)[e]	−63 (s; vbr)[e]
$MoW(\mu\text{-S})(\mu\text{-Cl})Cl_3(PMe_3)_5$ (**IIab**)[e]	P_A	0.67 (s; br; 18 H)	−42.7 (d of d; 31, 13; 2 P); J_{WP} = 47
	P_B	1.71 (d; 7; 9 H)	−20.3 (t; 31; 1 P); J_{WP} = 31
	P_C	2.03 (d; 9; 9 H)	0.88 (t; 13; 1 P); J_{WP} = 203
	P_D + PMe_3[e]	1.06 (s; br)[e]	−55 (s; vbr)[e]
$WMo(\mu\text{-S})(\mu\text{-Cl})Cl_3(PMe_3)_5$ (**IIba**)[e]	P_A	0.77 (s; br; 18 H)	−27.6 (d of d; 22, 17; 2 P); J_{WP} = 240
	P_B	1.92 (d; 8; 9 H)	−23.3 (t; 22; 1 P); J_{WP} = 218
	P_C	1.85 (d; 9; 9 H)	−3.3 (t; 17; 1 P); J_{WP} = 17
	P_D + PMe_3[e]	1.06 (s; br)[e]	−55 (s; vbr)[e]

[a] Spectra taken in C_6D_6. The ^{1}H and ^{31}P{^{1}H} NMR data have been correlated by ^{1}H{^{31}P} NMR experiments and are reported such that the ^{1}H and ^{31}P NMR entries on the same line correspond to the same phosphine ligand. [b] J_{WP} values >200 Hz are one-bond coupling constants ($^1J_{WP}$) while those <50 are $^2J_{WP}$. [c] ^{31}P{^{1}H} spectra of isolated samples are broad, probably due to exchange with a small amount of $M_2(\mu\text{-E})(\mu\text{-Cl})Cl_3(PMe_3)_4$ impurity (see text), and most of the P–P coupling is obscured. Addition of free PMe_3 sharpens the multiplets without other apparent changes, except for small movements of the chemical shifts (<1 ppm) and averaging of the resonance for P_D with free PMe_3. The ^{31}P spectrum listed here gives the chemical shifts for an isolated sample in the absence of PMe_3, but the coupling patterns are taken from spectra with added PMe_3. [d] NMR spectra obtained on a reaction mixture containing other complexes. [e] NMR spectra obtained on a reaction mixture containing free PMe_3; a single coalesced resonance is observed for P_D and free PMe_3 in both the ^{1}H and ^{31}P{^{1}H} spectra.

of **Ia** and **IIIa** is produced. Heating this mixture at 60 °C for ≤10 min results in the clean formation of **IIa** (eq 6).



(6)

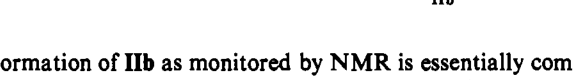
The consumption of both **Ia** and **IIIa** in the second half of reaction 6 indicates that **IIa** is formed by incomplete sulfur atom transfer from the tetravalent **IIIa** to the divalent **Ia**. Formally, this represents a conproportionation of Mo(II) and Mo(IV) because **IIa** is trivalent at each metal center. This result also implicates the terminal sulfido $Mo(S)Cl_2(PMe_3)_3$ as the kinetic product in the reactions between $MoCl_2(PMe_3)_4$ and $SPMe_3$, $SPPh_3$, and *tert*-butyl thiol.

The sulfido $Mo(S)Cl_2(PMe_3)_3$ (**IIIa**) is thermally unstable and decomposes cleanly in the absence of $MoCl_2(PMe_3)_4$ to form **IIa** and $SPMe_3$ (eq 7). Decomposition is slow at ambient temperatures but is essentially complete after heating at 60 °C for several hours. Similar clean conversion of **IIIa** to **IIa** + $SPMe_3$ is observed in the presence of 4.6 equiv of ethylene oxide, an excellent trap for Mo(II) species to give $Mo(O)Cl_2(PMe_3)_3$ (**IVa**).[6f] The absence of molybdenum oxo complexes in this reaction suggests that the decomposition of **IIIa** does not involve the *in situ* formation of Mo(II).

$$\underset{\textbf{IIIa}}{2Mo(S)Cl_2(PMe_3)_3} \xrightarrow[C_6D_6]{60\ ^\circ C} \underset{\textbf{IIa}}{Mo_2(\mu\text{-S})(\mu\text{-Cl})Cl_3(PMe_3)_5} + SPMe_3 \quad (7)$$

Synthesis of Molybdenum and Tungsten μ-Sulfido and μ-Oxo Dimers by Conproportionation. The conproportionation reaction between $MoCl_2(PMe_3)_4$ (**Ia**) and $Mo(S)Cl_2(PMe_3)_3$ (**IIIa**) (eq 6) prompted us to explore this chemistry more broadly, even though dimers had not been observed in a wide range of oxygen or sulfur atom transfer reactions involving **Ia** or $WCl_2(PMe_3)_4$ (**Ib**).[6] For instance, ≥1 equiv of $SPMe_3$ or ^{t}BuSH oxidizes **Ib** at 80 °C solely to the terminal sulfido complex $W(S)Cl_2(PMe_3)_3$ (**IIIb**) and 2 equiv of PMe_3 (eq 8).[6f] However, reaction of an isolated sample of **IIIb** with **Ib** does afford a tungsten sulfido bridged dimer, $W_2(\mu\text{-S})(\mu\text{-Cl})Cl_3(PMe_3)_5$ (**IIb**; eq 9; Scheme 1).

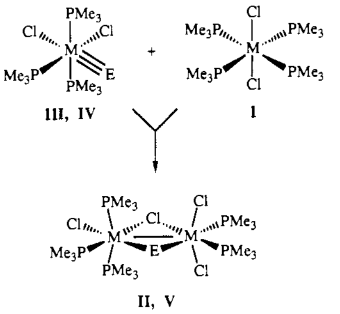
$$\underset{\textbf{Ib}}{WCl_2(PMe_3)_4} + SPMe_3 \xrightarrow[C_6H_6]{80\ ^\circ C} \underset{\textbf{IIIb}}{W(S)Cl_2(PMe_3)_3} + 2PMe_3 \quad (8)$$



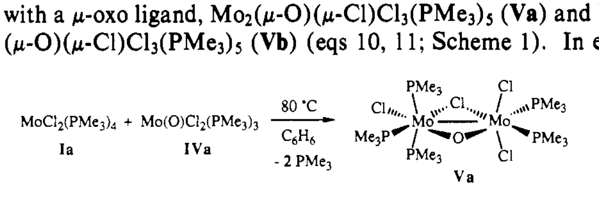
(9)

Formation of **IIb** as monitored by NMR is essentially complete after 24 h at 80 °C. Complex **IIb** is also observed when less than 1 equiv of $SPMe_3$ is reacted with $WCl_2(PMe_3)_4$. The sulfido complex **IIIb** is formed first and then undergoes further reaction with the remaining **Ib** to produce **IIb**.

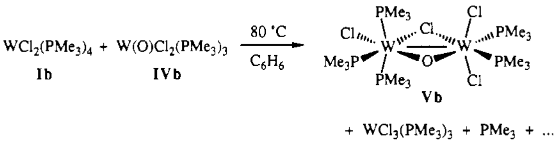
Scheme 1. Formation of μ-Sulfido and μ-Oxo Dimers (E = S, O)



The tungsten and molybdenum oxo complexes, $Mo(O)Cl_2(PMe_3)_3$ (**IVa**)[19] and $W(O)Cl_2(PMe_3)_3$ (**IVb**)[20] also react with the corresponding divalent complexes **Ia** and **Ib** to form dimers with a μ-oxo ligand, $Mo_2(\mu\text{-}O)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**Va**) and $W_2(\mu\text{-}O)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**Vb**) (eqs 10, 11; Scheme 1). In each of these conproportionation reactions, formation of dimers as monitored by NMR slows substantially as the concentration of free PMe_3 increases, consistent with phosphine inhibition. The μ-oxo complexes **Va** and **Vb** are considerably slower to form ($t_{1/2}$ ~ days at 80 °C) than the analogous μ-sulfido dimers ($t_{1/2}$ ~ minutes at 60 °C for **IIa**, hours at 80 °C for **IIb**). The formation of **Va** is accompanied by small amounts (5%) of the Mo(II) quadruply bonded dimer $Mo_2Cl_4(PMe_3)_4$, the result of thermal decomposition of **Ia**.[6f] **Vb** is formed in low yield in eq 11 and has not been isolated; the major product is $WCl_3(PMe_3)_3$, which was identified by comparison of its ^1H NMR spectra with an authentic sample.[21] Though not unusual in the redox chemistry of **Ib**,[6f] the formation of $WCl_3(PMe_3)_3$ is not easily explained and obscures the reaction mass balance, indicating that other, unobserved products are also formed.



(10)



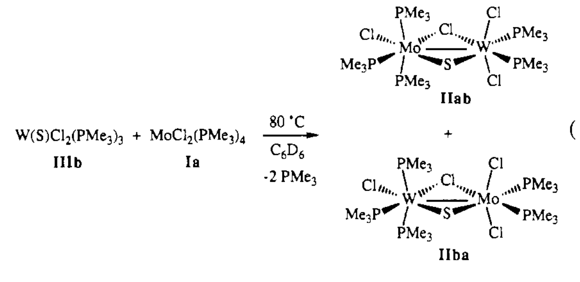
(11)

The dimeric complexes **IIb**, **Va**, and **Vb** have been identified in the respective reactions on the basis of the remarkable similarity of their proton and phosphorus NMR spectra with the NMR spectra of **IIa** (Table 5). Rapid exchange of a single phosphine ligand with free PMe_3 is observed for all four dimers, and in all cases except **Vb** the multiplets in the ^{31}P NMR are better resolved in the presence of excess PMe_3. In the tungsten–sulfido dimer **IIb**, tungsten satellites in the ^{31}P NMR spectrum reveal both one-bond ($^1J_{WP}$ = 218–251 Hz) and two-bond ($^2J_{WP}$ = 22–46 Hz) W–P couplings for all the multiplet resonances. For **Vb**, the low yield of formation and consequent low signal to noise has precluded seeing all but one of the tungsten satellites. All of this data indicate that complexes **IIb**, **Va**, and **Vb** have the same stereochemistry, structure, and ligand exchange behavior (of P_D with free PMe_3) as **IIa**.

$W_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**IIb**) is isolated as a dark purple solid by removing the volatiles from the reaction mixture. As with the molybdenum analogue, **IIb** readily loses a bound phosphine ligand on repeated trituration with solvent and is thus best recrystallized in the presence of PMe_3. Large scale preparations of the molybdenum μ-oxo dimer **Va** are plagued by formation of the Mo(II) dimer $Mo_2Cl_4(PMe_3)_4$ and by an inability to obtain $Mo(O)Cl_2(PMe_3)_3$ (**IVa**) free from $MoCl_3(PMe_3)_3$.[19] Unlike the molybdenum terminal sulfido complex **IIIa**, $W(S)Cl_2(PMe_3)_3$ (**IIIb**), $Mo(O)Cl_2(PMe_3)_3$ (**IVa**), and $W(O)Cl_2(PMe_3)_3$ (**IVb**) are stable at 80 °C, showing no decomposition to dimers. This indicates that complexes **IIb** and **Va** are formed solely from conproportionation of the divalent and tetravalent components and not by some other pathway.

Synthesis of an analogous μ-imido dimer from $W(N\text{-}p\text{-}Tol)Cl_2(PMe_3)_3$ and $WCl_2(PMe_3)_4$ (**Ib**) is not successful, as no reaction is observed at 80 °C. Similarly, there is no reaction between **Ib** and the tungsten alkylidyne complex $W(\equiv CCH_3)Cl(PMe_3)_4$.[22] The nature of the phosphine ligand also appears to be critical to the formation of dimers, as no reactions are observed between $MoCl_2(PMePh_2)_4$ and $Mo(O)Cl_2(PMePh_2)_3$, or between $WCl_2(PMePh_2)_4$ and $W(S)Cl_2(PMePh_2)_3$ or $W(O)Cl_2(PMePh_2)_3$ [$Mo(S)Cl_2(PMePh_2)_3$ is not known]. Because of the thermal instability of the divalent $PMePh_2$ complexes,[6f] the study of these reactions is limited to ambient temperatures.

The conproportionation approach allows the preparation of mixed metal dimers. The reaction of $MoCl_2(PMe_3)_4$ (**Ia**) with $W(S)Cl_2(PMe_3)_3$ (**IIIb**) produces a deep navy-blue solution accompanied by the formation of both isomers of the heterobimetallic bridged sulfido species, $MoW(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**IIab**, **IIba**) along with 2 equiv of PMe_3 (eq 12). The two isomers are possible because of the asymmetry in the ligand sets of the dimers; **IIab** refers to the isomer with the trans axial phosphines bound to the molybdenum. Heating the reaction at 80 °C for 20 h cleanly produces complexes **IIab** and **IIba** in a ratio of 1.3:1 by NMR. As observed in the reactions which produce **IIa**–**Vb**, formation of **IIab** and **IIba** is inhibited by the buildup of free PMe_3. At no point during the formation of **IIab** and **IIba** are the homobimetallic dimers **IIa** and **IIb** observed.



(12)

The mixed-metal dimers **IIab** and **IIba** are also formed on reaction of $Mo(S)Cl_2(PMe_3)_3$ (**IIIa**) and $WCl_2(PMe_3)_4$ (**Ib**) at 60 °C (eq 13), the opposite combination of oxidant and reductant from eq 12. A number of other products are also formed in this reaction, with the dominant species being $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**IIa**) and $SPMe_3$ as expected from thermal decomposition of **IIIa** (eq 7). Formation of $W(S)Cl_2(PMe_3)_3$ (**IIIb**) may be due to reaction of $SPMe_3$ with **Ib** (eq 8).[6f] The presence of significant amounts of $WCl_3(PMe_3)_3$ suggests that other paramagnetic product(s) are also formed. **IIab** and **IIba** appear to be produced exclusively by conproportionation of **IIIa** and **Ib**, rather than from

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(19) (a) Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347–352. (b) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 2848–2852; Butcher, A. V.; Chatt, J. *J. Chem. Soc. A* **1970**, 2652. (c) Yoon, K.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 1437–1438; **1992**, *114*, 2210–2218. Parkin, G. *Chem. Rev.* **1993**, *93*, 887–911. Desrochers, P. J.; Nebesny, K. W.; LaBarre, M. J.; Lincoln, S. E.; Loehr, T. M.; Enemark, J. *J. Am. Chem. Soc.* **1991**, *113*, 9193. These papers include and reference preparations of $Mo(O)Cl_2(PR_3)_3$ and discuss the difficulty of separating them from $MoCl_3(PR_3)_3$.

(20) Carmona, E.; Sanchez, L.; Poveda, M. L.; Jones, R. A.; Hefner, J. G. *Polyhedron* **1983**, *2*, 797.

(21) (a) Sharp, P. R. *Organometallics* **1984**, *3*, 1217–1223. (b) Atwood, J. L.; Hunter, W. E.; Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1991**, 4550–4. (c) Reference 30f.

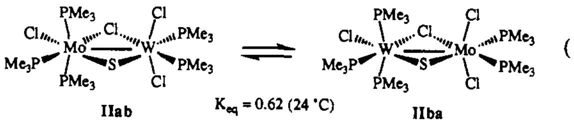
(22) Atagi, L. M; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 1483–1484.

$$\underset{\textbf{IIIa}}{\mathrm{Mo(S)Cl_2(PMe_3)_3}} + \underset{\textbf{Ib}}{\mathrm{WCl_2(PMe_3)_4}} \xrightarrow[\mathrm{C_6D_6}]{60\ ^\circ\mathrm{C}} \underset{\textbf{IIab}}{\mathrm{MoW(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5}} + \underset{\textbf{IIba}}{\mathrm{WMo(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5}} + \underset{\textbf{IIIb}}{\mathrm{W(S)Cl_2(PMe_3)_3}} + \mathrm{WCl_3(PMe_3)_3} + \mathrm{PMe_3} + \underset{\textbf{IIa}}{\mathrm{Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5}} + \mathrm{SPMe_3} + \ldots \quad (13)$$

other products of the reaction. For example, there is no reaction at 60 °C between $WCl_2(PMe_3)_4$ (**Ib**) and $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (**IIa**) or between **IIIa** and **IIIb** (only decomposition of **IIIa** to **IIa** + $SPMe_3$ is observed).

Complexes **IIab** and **IIba** have been identified during the reaction by the close similarity of their ^1H and ^{31}P NMR spectra with the spectra of the homobimetallic dimers (Table 5). The presence of a broad peak at 1.06 ppm in the proton spectrum and a very broad lump at −55 ppm in the phosphorus spectrum again indicates that one phosphine ligand in both isomers is exchanging with free PMe_3 on the NMR time scale. Most informative are the tungsten satellites observed in the phosphorus NMR spectrum of the mixture of **IIab** and **IIba**, which demonstrate the mixed-metal nature of **IIab** and **IIba** and allow each group of phosphorus resonances to be assigned to the correct isomer. (The ^1H and ^{31}P spectra have been correlated by selective phosphorus-decoupled proton spectra.) Complex **IIba** has three phosphine ligands bound to the tungsten, a trans equivalent pair (P_A) and a single meridional one (P_B), which give ^{31}P signals with large, one-bond W–P coupling constants of 240 and 218 Hz respectively. The other equatorial phosphine of this complex (P_C, which is not undergoing rapid exchange with free PMe_3) is bound to molybdenum and therefore only displays a smaller $^2J_{WP}$ coupling of 17 Hz. For the other isomer, **IIab**, the opposite pattern is observed, with only one phosphine giving a large $^1J_{WP}$ (203 Hz) and the other two resonances showing only two-bond W–P couplings ($^2J_{WP}$ = 31 and 47 Hz).

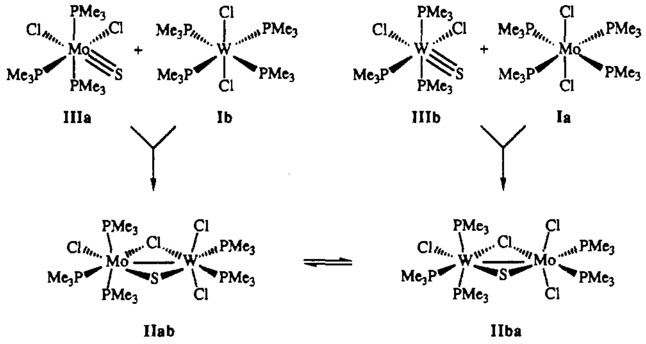
Dissolving a 1.3:1 mixture of **IIab** and **IIba** in toluene-d_8 and allowing the solution to stand at ambient temperatures results in an increase in the **IIab**/**IIba** ratio to 1.6:1. The increase in the amount of **IIab** is accompanied by a simultaneous decrease the amount of **IIba**. Heating the mixture at 85–90 °C for 5 days causes the ratio to revert back to its original value of 1.3:1 while the total amount of **IIab** and **IIba** is constant. On standing at ambient temperatures, the ratio returns to 1.6:1. This establishes an equilibrium between complexes **IIab** and **IIba**, with $K_{eq} = 0.62$ at 24 °C (eq 14). The equilibrium ratio of **IIab** to **IIba** changes very little with temperature, ranging from 1.6:1 at 24 °C to 1.2:1 at 105 °C. Thus, the two isomers are essentially thermoneutral over the temperature range studied: $\Delta H = 0.8 \pm 0.1$ kcal/mol and $\Delta S = 1.7 \pm 0.2$ eu. This emphasizes that both metal centers in these dimers should be considered to be in the +3 oxidation state, rather than a mixed-valence form in which the tungsten center would prefer the more oxidized site. The equilibration of **IIab** and **IIba** is slow on the NMR time scale at 105 °C.



(14)

When **Ia** and **IIIb** are allowed to react (eq 12) at more moderate temperatures, a nonequilibrium mixture of **IIab** and **IIba** is observed at short reaction times. At 60 °C, the **IIab**:**IIba** ratio is 1:3 after 10 min and 1:1 after 90 min before reaching the equilibrium value of 1.4:1 at this temperature. These observations are consistent with initial formation of **IIba** followed by isomerization to **IIab**. Reaction of **Ib** and **IIIa** (eq 13) at 60 °C shows the opposite behavior: the ratio of **IIab** to **IIba** is highest early on, with essentially only **IIab** observed after 5 min. After 35 min at 60 °C, when all of the sulfido complex **IIIa** is consumed, the **IIab**:**IIba** ratio is 1.7:1 and by 75 min of heating has reached its 1.4:1 equilibrium value. Thus **IIab** is the kinetic product starting from the molybdenum sulfido complex **IIIa** + **Ib**, while **IIba** is formed first starting from $W(S)Cl_2(PMe_3)_3$ (**IIIb**) + **Ia** (Scheme 2).

Scheme 2. Formation of the Mixed-Metal Dimers from $MCl_2(PMe_3)_4$ (**I**) and $M(S)Cl_2(PMe_3)_3$ (**III**)



In contrast to reactions 12 and 13, the analogous μ-oxo mixed-metal dimers have not been observed. Reaction of **Ib** with the Mo(IV) oxo complex **IVa** at 60–80 °C results in complete 2e⁻ oxygen atom transfer from Mo to W to give $W(O)Cl_2(PMe_3)_3$ (**IVb**) and $MoCl_2(PMe_3)_4$ (**Ia**), in addition to other monomeric and dimeric products (eq 15). The **Ia** that is formed decomposes to $Mo_2Cl_4(PMe_3)_4$ or reacts with **IVa** to give μ-oxo dimer **Va**. Similar observations have been reported for reaction of the analogous complexes with $PMePh_2$ ligands.[7] No reaction is observed on heating **Ia** and **IVb** at 80 °C (other than the decomposition of **Ia**). Thus oxygen atom transfer from **IVa** to **Ib** to form **Ia** and **IVb** is irreversible.

$$\underset{\textbf{IVa}}{\mathrm{Mo(O)Cl_2L_3}} + \underset{\textbf{Ib}}{\mathrm{WCl_2L_4}} \xrightarrow[\mathrm{C_6D_6}]{80\ ^\circ\mathrm{C}} \underset{\textbf{IVb}}{\mathrm{W(O)Cl_2L_3}} + \underset{\textbf{Ia}}{\mathrm{MoCl_2L_4}} + \mathrm{Mo_2Cl_4L_4} + \underset{\textbf{Va}}{\mathrm{Mo_2(\mu\text{-}O)(\mu\text{-}Cl)Cl_3L_5}} + \mathrm{WCl_3L_3} + \ldots \quad (15)$$

$$\mathrm{L = PMe_3}$$

While conproportionation of M(IV) sulfido and oxo complexes with M(II) compounds yields dimers, the W(V) oxo complex $W(O)Cl_3(PMe_3)_2$ conproportionates with W(III) $WCl_3(PMe_3)_3$ to give exclusively the W(IV) monomers $W(O)Cl_2(PMe_3)_3$ (**IVb**) and $WCl_4(PMe_3)_2$ (eq 16). The products have been identified

$$\mathrm{WCl_3(PMe_3)_3} + \mathrm{W(O)Cl_3(PMe_3)_2} \xrightarrow[\mathrm{C_6D_6}]{80\ ^\circ\mathrm{C}} \underset{\textbf{IVb}}{\mathrm{W(O)Cl_2(PMe_3)_3}} + \mathrm{WCl_4(PMe_3)_2} \quad (16)$$

by the comparison of their ^1H and ^{31}P (of **IVb**) spectra with authentic samples. This reaction represents a net transfer of a chlorine atom from $W(O)Cl_3(PMe_3)_2$ to $WCl_3(PMe_3)_3$. The analogous reaction of molybdenum complexes has not been explored because $Mo(O)Cl_3(PMe_3)_2$ is not accessible.[23] Reaction of $MoCl_3(PMe_3)_3$ with $W(O)Cl_3(PMe_3)_2$ gives only small amounts

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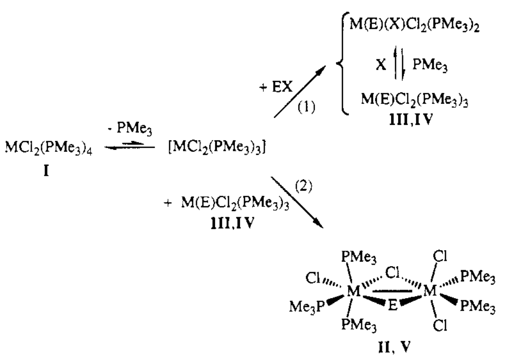
(23) $Mo(O)Cl_3(PMe_3)_2$ has to our knowledge not been reported. Attempts to prepare it from treatment of $Mo(O)Cl_3(THF)_2$ with PMe_3 result predominantly in formation of $OPMe_3$, $Mo(O)Cl_2(PMe_3)_3$, and other species.

Scheme 3. Mechanisms of Oxidation of $MCl_2(PMe_3)_4$



of unidentified paramagnetic products when heated, as observed by ^{1}H NMR.

Discussion

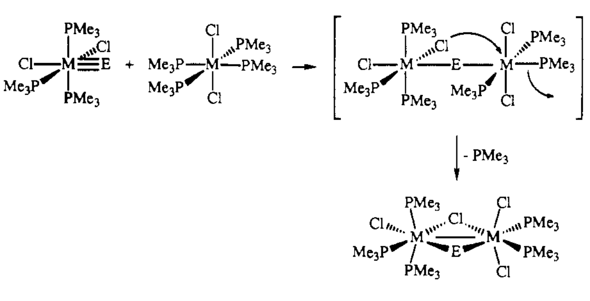
The dimers **II** and **V** are formed by conproportionation of divalent $MCl_2(PMe_3)_4$ and tetravalent terminal sulfido or oxo complexes $M(E)Cl_2(PMe_3)_3$ (Scheme 1). Conproportionation is a rational synthetic strategy to such dimers, as shown by the preparations of the mixed-metal dimers **IIab** and **IIba**.[24,25] These are unusual examples of incomplete atom transfer reactions because the products are metal–metal bonded dimers and because clear examples of intermetal sulfur atom transfer are rare.[3a,5,26] To our knowledge, dimers containing a single bridging sulfur or oxygen and a bridging halide have only previously been reported for rhenium complexes.[11,27]

Formation of μ-Sulfido and μ-Oxo Dimers. In all of the syntheses of **II** and **V**, the buildup of free phosphine markedly slows the rate of reaction. Such phosphine inhibition indicates initial preequilibrium loss of PMe_3 from one of the reactants. Alternative pathways involving electron transfer or charged species are unlikely in the nonpolar media used (benzene or toluene). Preequilibrium phosphine loss is a characteristic of essentially all of the reactions of MCl_2L_4 compounds (M = Mo, W; L = PMe_3 (**I**), $PMePh_2$).[6,28]

Initial dissociation of a phosphine ligand from $MCl_2(PMe_3)_4$ produces the intermediate species $[MCl_2(PMe_3)_3]$ which can react in two different ways (Scheme 3).[29] It can be trapped by a sulfur or oxygen atom donor EX, such as $SPMe_3$ or ethylene oxide, to give products with a terminal sulfido or oxo ligand (path 1).[6] Alternatively, $[MCl_2(PMe_3)_3]$ can be trapped by a terminal sulfido or oxo complex (**III** or **IV**) to give the dimers **II** or **V** (path 2). The relative rates of these two trapping reactions determine whether dimers or monomers are formed on oxidation of **I** by sulfur or oxygen atom donors EX. In most cases, EX is a much better trap for $[MCl_2L_3]$ than is $M(E)Cl_2L_3$. This is true for all of the reactions of the tungsten complex **Ib**, as dimers are never formed when a full equivalent of EX is present.[6] The molybdenum complex **Ia** gives dimers only with the least reactive EX oxidants: $SPMe_3$, ^{t}BuSH, and CO_2 (the last gives small amounts of **Va** together with **IVa** after weeks at 80 °C[6f]). With more reactive oxidants such as ethylene sulfide, ethylene oxide, and DMSO, **Ia** is converted to the terminal sulfido or oxo complexes **IIIa** and **IVa**. This preference for oxidation by EX is the reason dimers are not generally observed in reactions of MCl_2L_4, despite the presence of both MCl_2L_4 and $M(E)Cl_2L_3$ in the reaction mixture.[6]

In general, the ease of formation of dimers is molybdenum > tungsten, and sulfido > oxo, a pattern that can be understood based on the ability of the terminal sulfido and oxo complexes to oxidize or bind to the $MCl_2(PMe_3)_3$ intermediate. The molybdenum compounds are better oxidants than the tungsten species (though neither are good oxidants).[6,7] The sulfido compounds are better oxidants than the oxo complexes—only $Mo(S)Cl_2(PMe_3)_3$ (**IIIa**) will oxidize PMe_3 (eq 7 and ref 6f)—and are likely to be better ligands given the greater tendency of sulfur to bridge.[13e] The slower formation of the μ-oxo dimers **V** vs the μ-sulfido dimers **II** indicates poorer trapping. The lack of trapping by the imido and carbyne complexes W(N-*p*-Tol)$Cl_2(PMe_3)_3$ and $W(\equiv CCH_3)Cl_2(PMe_3)_3$ is likely due both to steric congestion around the metal–ligand multiple bond and the lack of a lone pair of electrons on the nitrogen or carbon atom.

Comparing the stereochemistry of the M(II) and M(IV) reactants with that of the dimers (Scheme 1) offers insight into how $[MCl_2(PMe_3)_3]$ may be trapped by $M(E)Cl_2(PMe_3)_3$. The metal center on the left half of the dimers has the same stereochemistry as the terminal sulfido and oxo complexes **III** and **IV**, while the stereochemistry of the metal on the right side of the dimers is that of the divalent complexes **I**, missing a pair of cis phosphine ligands. This is especially evident in the formation of the the mixed-metal complexes **IIab** and **IIba** (Scheme 2), for instance that **IIab** is the kinetic product from $Mo(S)Cl_2(PMe_3)_3$ and $WCl_2(PMe_3)_4$. A possible pathway to explain the retention of this regiochemistry is the formation of a singly bridged intermediate, followed by collapse to the products (eq 17). Similar schemes have been proposed for the formation and cleavage of edge-shared bioctahedral dimers.[11,30]



(17)

Complete vs Incomplete Atom Transfer Reactions. Conproportionation is in general a favored process for M(IV) and M(II) chlorophosphine complexes of Mo and W, even in the absence of a metal–ligand multiple bond. For example, MCl_2L_4 and MCl_4L_2 conproportionate to give monomeric MCl_3L_3 by chlorine atom transfer (eq 18).[7,31] Similar chlorine atom transfer reactions

$$MCl_4L_2 + MCl_2L_4 \rightarrow 2MCl_3L_3 \qquad (18)$$

$$L = PMe_3, PMe_2Ph, PMePh_2; M = Mo, W$$

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(24) There are, to our knowledge, seven previous examples of heteronuclear edge-shared bioctahedral dimers, all of which contain chelating phosphine ligands (L-L): (a) $MoW(\mu\text{-}H)(\mu\text{-}Cl)Cl_4(dppm)_2$: Cotton, F. A.; Jones, C. A.; Luck, R. L. *Inorg. Chem.* **1991**, *30*, 4370. (b) $MoW(\mu\text{-}Cl)_2Cl_4(L\text{-}L)_2$: Cotton, F. A.; Eglin, J. L.; James, C. A. *Inorg. Chem.* **1993**, *32*, 687–694; Cotton, F. A.; Hong, B.; Shang, M.; Stanley, G. G. *Inorg. Chem.* **1993**, *32*, 3620–3627, and references therein.

(25) A conproportionation route has been used to prepare quadruply bonded MoW compounds: Luck, R. L.; Morris, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 7978–7979. Luck, R. L.; Morris, R. H.; Sawyer, J. F. *Inorg. Chem.* **1987**, *26*, 2422–2429. Cotton, F. A.; Falvello, L. R.; James, C. A.; Luck R. L. *Inorg. Chem.* **1990**, *29*, 4759–4763.

(26) (a) Conproportionation of $M^{n+2}(O)$ with M^n compounds typically leads to singly bridged M–O–M complexes;[3,5] for recent examples, see: Nichols, P. J.; Fallon, G. D.; Moubaraki, B.; Murray, K. S.; West, B. O. *Polyhedron* **1993**, *12*, 2205–2213 and references therein. (b) The formation of dimers and clusters from reduction of terminal sulfido species such as MoS_4^{2-} is well precedented and likely involves incomplete sulfur atom transfer reactions. Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89. Müller, A.; Diemann, E.; Jostes, R.; Bogge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934. Holm, R. H. *Chem. Soc. Rev.* **1981**, 456. Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201. Reference 13e.

(27) (a) Cotton, F. A.; Foxman, B. M. *Inorg. Chem.* **1968**, *7*, 1784–1792. (b) Cotton, F. A.; Eiss, R.; Foxman, B. M. *Inorg. Chem.* **1969**, *8*, 950–957. (c) Laing, M.; Bregeault, J.-M.; Griffith, W. P. *Inorg. Chim. Acta* **1978**, *26*, L7. Ju-Sheng, Q.; Schrier, P. W.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 258–262.

(28) It is also possible that initial ligand loss occurs from $M(E)Cl_2(PMe_3)_3$ to give an intermediate that is trapped by $MCl_2(PMe_3)_4$, but this is less likely given the greater lability of the tetrakis(phosphine) compounds.[6]

(29) For $MoCl_2(PMe_3)_4$ (**Ia**), dimerization to $Mo_2Cl_4(PMe_3)_4$ represents a third, non-redox pathway which is competitive for less reactive substrates.

are observed on conproportionation of the d^1 $W(O)Cl_3L_2$ with d^3 WCl_3L_3 to give stable d^2 products $W(O)Cl_2L_3$ and WCl_4L_2 (L = PMe_3, eq 16; L = $PMePh_2$[7]). Such a 1e⁻ chlorine atom transfer reaction of $M(E)Cl_2(PMe_3)_3$ and $MCl_2(PMe_3)_4$ would, however, form $MCl_3(PMe_3)_3$ and "$M(E)Cl(PMe_3)_4$". The latter d^3-terminal sulfido or oxo complex is expected to be highly unstable because of population of metal–sulfur or metal–oxygen π-antibonding orbitals.[32] Thus, the preference for formation of the dimers **II** and **V** over monomeric M(III) species on conproportionation is driven by the instability of a possible d^3 oxo or sulfido monomer. A related (and more detailed) explanation for complete vs incomplete atom transfer has been presented by Woo.[33]

The formation of the dimers **II** and **V** is perhaps surprising given the strength of the metal–sulfido and metal–oxo multiple bonds in complexes **III** and **IV**. The W≡S bonds in $W(S)Cl_2L_3$ (L = PMe_3 **IIIb**, $PMePh_2$) have been estimated to be at least 105 kcal/mol based on the reaction of **IIb** with SPR_3[6f] and the W≡O bond in $W(O)Cl_2(PMePh_2)_3$ has been similarly estimated at ≥138 kcal/mol.[6c] However, the observation of short Mo–S bonds in the crystal structure of **IIa** suggests that some metal–sulfur or metal–oxygen π-bonding is retained in the dimers. Apparently the loss of M–E π-bonding in the terminal oxo and sulfido reactants is balanced by metal–metal and metal–ligand π-bonding within the central core of the dimers. The lack of formation of dimers with $PMePh_2$ ligands is most likely due to their destabilization due to steric crowding.

The reaction coordinate diagram in Figure 3A shows the lower energy of the dimers vs monomers for the homobimetallic case, $M(E)Cl_2(PMe_3)_3 + MCl_2(PMe_3)_4$. Because the two metals are the same, complete atom transfer is a degenerate reaction and the left and right sides of the drawing are identical. When two different metals are involved, as in parts B and C of Figure 3, the two sides of the reaction coordinate diagrams are no longer degenerate and reactions can occur by incomplete or complete atom transfer. For the sulfido compounds, the mixed-metal dimers **IIab** and **IIba** are more stable than either combination of monomers, $Mo(S)Cl_2(PMe_3)_3 + WCl_2(PMe_3)_4$ or $W(S)Cl_2(PMe_3)_3 + MoCl_2(PMe_3)_4$ (Figure 3B and eqs 12 and 13). The W(IV) + Mo(II) combination on the right-hand side is presumed to be more stable than the alternative W(II) + Mo(IV) because tungsten compounds are more easily oxidized than molybdenum ones[6,7] and by analogy with the reactions of oxo complexes: $Mo(O)Cl_2L_3$ reacts with WCl_2L_4 (L = PMe_3, $PMePh_2$) by complete oxygen atom transfer and heterobimetallic μ-oxo dimers are not been observed (eq 15, Figure 3C). Dimeric intermediates must be involved in these reactions, however, to allow transfer of the oxygen. It seems likely that these intermediates resemble the sulfido compounds **IIab** and **IIba**.[7]

All of the atom transfer reactions described here can thus be understood using the same manifold of compounds (Figure 3). The only differences are due to the relative thermodynamic stabilities of the monomers and dimers. In the homometallic case, dimers are thermodynamically favored for both sulfido and oxo ligands. Mixed-metal dimers are favored for sulfur while monomers are favored for oxygen, leading to complete oxygen atom transfer.

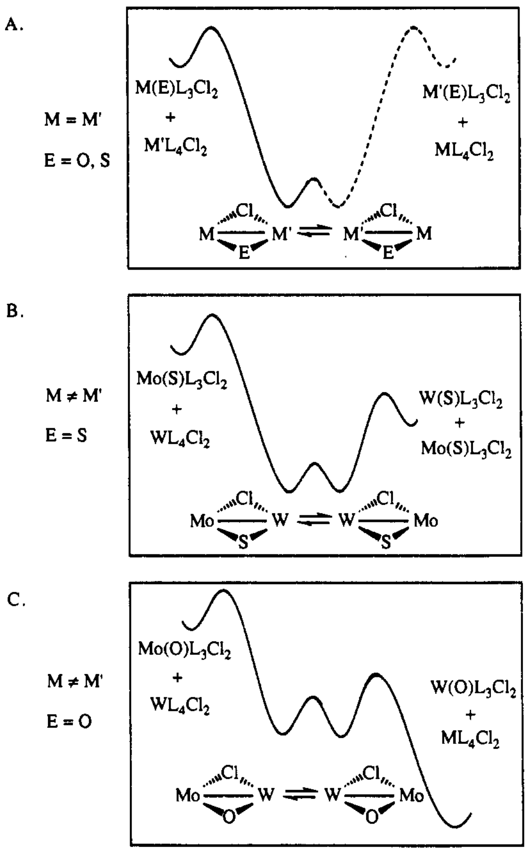

Figure 3. Reaction coordinate/energy diagrams for reactions between $M(E)Cl_2L_3$ (**III**) and $M'Cl_2L_4$ (**I**). L = PMe_3.

Experimental Section

General Considerations. All experiments were performed under a nitrogen or argon atmosphere or under vacuum employing high vacuum line or Schlenk techniques and a glovebox. Solvents were dried according to standard procedures.[34] All reagents were degassed on a vacuum line, checked for purity by NMR, and if necessary dried by standard means, except gases which were used directly from the cylinder without further purification. Ethylene sulfide (Aldrich) was freshly dried over sieves and vacuum transferred prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories. All gases were purchased from Matheson. PMe_3, $PMePh_2$, $SPMe_3$, and $SPPh_3$ were purchased from Aldrich, Strem, or Alfa. $W(O)Cl_4$ (Aldrich) was used without further purification. The following compounds have been previously reported: $MoCl_2(PMe_3)_4$ (**Ia**),[35] $Mo(O)Cl_2(PMe_3)_3$ (**IVa**),[19] $Mo(O)Cl_2(PMePh_2)_3$,[19] $WCl_2(PMe_3)_4$ (**Ib**),[36] $WCl_2(PMePh_2)_4$,[36] $MoCl_2(PMePh_2)_4$,[6f] $W(S)Cl_2(PMe_3)_3$ (**IIIb**),[6f] $W(O)Cl_2(PMe_3)_3$ (**IVb**),[20] $W(O)Cl_2(PMePh_2)_3$,[20] $W(S)Cl_2(PMePh_2)_3$,[6b,f] $W(N\text{-}p\text{-}Tol)Cl_2(PMe_3)_3$,[37] $W(\equiv CCH_3)Cl(PMe_3)_4$,[22] $MoCl_3(PMe_3)_3$,[21b] $WCl_3(PMe_3)_3$,[21a] $WCl_4(PMe_3)_n$ (n = 2, 3),[36] $MoCl_4(PMe_3)_3$.[19a]

NMR spectra were acquired at ambient temperatures (24 ± 2 °C) using Bruker WM-500, AF-300, and AC-200 and Varian VXR-300 Fourier transform spectrometers. ^1H NMR were referenced to TMS or to the residual protons of the solvent. $^{31}P\{^1H\}$ NMR spectra were recorded at 202.5, 121.4, or 80.0 MHz and were referenced to external 85% H_3PO_4. Spectra are reported in Table 5 except for the spectra of **IIIa**. Phosphorus-decoupled proton NMR ($^1H\{^{31}P\}$) spectra were obtained for **II** and **V** at 500 MHz by selectively decoupling each phosphorus resonance and observing the ^1H NMR spectrum. Infrared spectra were recorded

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on a Perkin-Elmer 1604 FTIR as Nujol mulls using NaCl plates, and are reported in cm^{-1}. Intensities of IR bands are given as (s) = strong, (m) = medium, (w) = weak, or (sh) = shoulder.

Many of the reactions studied were performed in sealed NMR tubes. In a typical procedure, an NMR tube sealed to a ground glass joint was charged with reagents and solvent in the drybox and then fitted with a Teflon needle valve. The contents of the tube were degassed on the vacuum line, and additional reagents were added if required. The contents of the tube were then frozen at −196 °C, and the tube was sealed with a torch. The tube was thawed by rinsing it with acetone, and any reactions were followed by NMR.

$Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (IIa). $MoCl_2(PMe_3)_4$ (**Ia**; 1.00 g, 2.12 mmol) and $SPMe_3$ (115 mg, 1.06 mmol, 0.5 equiv) were placed in a 25-mL glass reaction bomb, and 50 mL of benzene was vacuum transferred in. The vessel was heated to 80 °C for 3 h and the solution turned deep blue-green. The volatiles were removed under vacuum, 50 mL of fresh benzene was transferred in, and the solution was heated for another 3 h (this step removes the free PMe_3 that inhibits the reaction). The reaction mixture was stripped of volatiles under vacuum to give 0.744 g of **IIa** as a dark blue-green solid (95%). The solid loses a phosphine ligand upon continued contact with solvent but can be regenerated by addition of PMe_3. Recrystallization is best achieved by slow diffusion of petroleum ether into a saturated toluene solution containing a small amount of free PMe_3. IR (Nujol): 1419 (sh), 1296 (m), 1278 (m), 1170 (sh), 1155 (w), 1020 (w), 951 (s), 849 (w), 668 (sh). Anal. Calcd for $Mo_2SCl_4P_5C_{15}H_{45}\cdot{}^1/_6C_7H_8$: C, 25.40; H, 6.12. Found C, 25.03; H, 5.93.

$W_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (IIb). Method A. $WCl_2(PMe_3)_4$ (**Ib**; 200 mg, 0.358 mmol) and $W(S)Cl_2(PMe_3)_3$ (**IIIb**; 184 mg, 0.358 mmol) were placed in a glass-walled reaction bomb, and 10 mL of benzene was added by vacuum transfer. The solution was heated at 80 °C for 4 h, and the volatiles were removed under vacuum. The residue was taken up in 10 mL of benzene, and the solution was heated for another 4 h. The volatiles were removed under vacuum to give 297 mg (90%) deep purple solids (**IIb**). The solids were recrystallized by slow diffusion of petroleum ether into a toluene solution containing a small amount of PMe_3.

Method B. $WCl_2(PMe_3)_4$ (200 mg, 0.358 mmol) and $SPMe_3$ (19.4 mg, 0.179 mmol) were placed in a glass-walled reaction bomb, and 10 mL of benzene was added by vacuum transfer. The solution was heated at 80 °C for 3 h and stripped of volatiles under vacuum. The residue was redissolved in 10 mL of fresh benzene and heated another 3 h. This cycle of heating, removing volatiles, and redissolving was repeated for a total of four times or until the reaction was complete as determined by NMR to give 150 mg (90%) of **IIb**. IR (Nujol): 1414 (sh), 1296 (m), 1276 (m), 1168 (sh), 1154 (w), 1023 (w), 951 (s), 845 (w), 734 (sh), 710 (sh), 662 (sh). Anal. Calcd for $W_2SCl_4P_5C_{15}H_{45}$: C, 19.54; H, 4.92. Found C, 19.87; H, 4.83.

$MoW(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (IIab and IIba). Complexes **IIab** and **IIba** were detected in high yield by ^1H and ^{31}P NMR when a benzene solution (0.5 mL) of $MoCl_2(PMe_3)_4$ (**Ia**; 10 mg, 2.1×10^{-2} mmol) and $W(S)Cl_2(PMe_3)_3$ (**IIIb**; 11 mg, 2.1×10^{-2} mmol) was heated at 80 °C for 1 day.

$Mo(S)Cl_2(PMe_3)_3$ (IIIa). An NMR tube was charged with 15 mg of **Ia** (3.2×10^{-5} mol) and 0.5 mL of benzene-*d_6*. The solution was frozen at −196 °C and degassed, and in the dark, ethylene sulfide (20 Torr in 28 mL, 2.9×10^{-5} mol; 0.9 equiv) was added along with 10 Torr of TMS as an internal standard. The tube was sealed with a torch and the reaction monitored by NMR. After 2 h, when 10–20% **Ia** remained, the tube was opened in a drybox in the dark and the dark green solution was transferred into a flask and the volatiles were removed under vacuum. Under these conditions, **Ia** reacts with **IIIa** to give **IIa** so the product has an 8:1 ratio of **IIIa**:**IIa**. Solutions of the mixture were kept frozen to prevent further production of **IIa** by decomposition of **IIIa**. Attempts to scale up this procedure were not successful. ^1H NMR (C_6D_6): δ 1.51 (t, 4 Hz, 18H, *trans*-$P(CH_3)_3$); 1.46 (d, 8 Hz, 9H, *cis*-$P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −11.4 (d, 20 Hz, *trans*-PMe_3); −6.1 (t, 20 Hz, *cis*-PMe_3).

Thermal Decomposition of $Mo(S)Cl_2(PMe_3)_3$ (IIIa). A C_6D_6 solution of an 8:1 mixture of **IIIa** and **IIa** was sealed in an NMR tube and heated at 60 °C for several hours. The solution became deep blue-green and **IIa** and $SPMe_3$ were observed in a 1:1 ratio by ^1H and ^{31}P NMR.

$Mo_2(\mu\text{-}O)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (Va). Complex **Va** was detected by ^1H and ^{31}P NMR when a solution of $MoCl_2(PMe_3)_4$ (**Ia**; 10 mg, 2.1×10^{-2} mmol) and $Mo(O)Cl_2(PMe_3)_3$ (**IVa**; 9 mg, 2.1×10^{-2} mmol) in 0.5 mL of C_6D_6 was heated at 80 °C overnight. A small amount of $Mo_2Cl_4(PMe_3)_4$ (≤5%) was also observed, primarily later in the reaction. Attempts at large-scale preparations of the complex resulted in formation of significant amounts of $Mo_2Cl_4(PMe_3)_4$ and were hampered by the slowness of the reaction.

$W_2(\mu\text{-}O)(\mu\text{-}Cl)Cl_3(PMe_3)_5$ (Vb). Complex **Vb** was detected in ca. 30% yield by ^1H and ^{31}P NMR when a solution of $WCl_2(PMe_3)_4$ (**Ib**; 10 mg, 1.8×10^{-2} mmol) and $W(O)Cl_2(PMe_3)_3$ (**IVb**; 10 mg, 1.8×10^{-2} mmol) in 0.5 mL of C_6D_6 was heated at 80 °C for a week. Significant amounts of the $WCl_3(PMe_3)_3$ (and presumably other paramagnetic product(s), see text) accompany formation of **Vb**, so a large scale preparation was not attempted.

$W(O)Cl_3(PMe_3)_2$. Following the reported preparation of $W(O)Cl_3(PEt_3)_2$,[38] PMe_3 (0.59 mL, 5.84 mmol) was condensed into a 25-mL flask containing $W(O)Cl_4$ (500 mg, 1.46 mmol) and 10 mL of benzene. Stirring at 24 °C for 12 h resulted in a cloudy yellow-green solution. Filtration and removal of the volatiles from the solution gave 570 mg (85%) of the complex as a yellow-green solid. The complex was recrystallized at −10 °C by slow diffusion of diethyl ether into a saturated CH_2Cl_2 solution. IR (Nujol): 1415 (sh), 1312 (sh), 1292 (w), 1108 (m), 959 (s), 860 (w), 752 (w). Anal. Calcd for $WCl_3P_2OC_6H_{18}$: C, 15.72; H, 3.96. Found C, 15.90; H, 3.71.

X-ray Crystal Structure of $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5\cdot{}^1/_6C_7H_8$ (IIa). Large dark blue hexagonal-shaped crystals of **IIa**$\cdot{}^1/_6C_7H_8$ were grown by slow diffusion of petroleum ether into a saturated solution of **IIa** in toluene/PMe_3. A suitable crystal was mounted in a glass capillary in air and sealed under nitrogen. Data collection (24 °C) employed an Enraf-Nonius CAD4 diffractometer operating in the θ–2θ scan mode with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.710 69 Å), as previously described (Table 1).[39] The structure of **IIa** was solved in the trigonal space group $R\bar{3}$ using the SHELX direct methods structure package and refined with full-matrix least-squares methods. Other space groups in this crystal class having the same extinction conditions (e.g., $R3$, $R3m$, and $R\bar{3}m$) were eliminated on the basis that the structure did not solve in them. All non-hydrogen atoms were refined anisotropically and the positions of the hydrogen atoms were calculated (C–H = 0.95 Å). The ring carbon of the toluene solvent molecule was located on a difference map and refined isotropically; the benzylic carbon (6-fold disordered) was not observed. The assignments of the chloride and sulfide bridge were verified at an intermediate stage in the refinement by allowing the bridging ligands to be (1) both sulfides, (2) both chlorides, and (3, 4) a chloride and a sulfide in both possible permutations. Refinement of the structures for each of the cases showed one assignment to be clearly preferred, as shown below. The differences in the thermal parameters in the three cases were small and uninformative.

	case 1	case 2	case 3	case 4 (final assignt)
R_w	6.5	6.5	6.7	6.4
R	4.2	4.2	4.3	4.1
GOF	1.495	1.501	1.528	1.472

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Supplementary Material Available: Crystallographic tables, including crystal data, anisotropic thermal parameters, hydrogen atom parameters, bond distances, ligand–ligand nonbonding distances, bond angles, torsion angles, and least-squares planes, and an alternative ORTEP view for $Mo_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5\cdot{}^1/_6C_7H_8$ (**IIa**) (11 pages). Ordering information is given on any current masthead page.

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