Substrate Uptake and Activation by Dimolybdenum and Ditungsten Hexaalkoxides—Factors Influencing the Cleavage of C–X Multiple Bonds in the Reactions Between $[Mo_2(OR)_6]$ (R = *t*Bu or CH_2tBu) and $Ar_2C{=}S$, $Et_2NC{\equiv}N$, and $P(nBu)_3$

T. A. Budzichowski, M. H. Chisholm,* and K. Folting

Dedicated to Professor R. R. Schrock at the start of his sixth decade

Abstract: The reaction between diarylthiones and $[Mo_2(OCH_2tBu)_6]$ in hydrocarbon solvents yielded $[Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CAr_2)]$ by cleavage of the C=S double bond. The Lewis base adduct $[Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CPh_2)(PMe_3)]$ (**2**) has been crystallographically characterized; it contains six- and five-coordinate Mo atoms linked through μ-S and μ-OR groups. The rate of the cleavage of the C=S bond has been studied by variable-temperature ^1H NMR in [D$_8$]toluene. A Hammett plot shows that both electron-donating and electron-releasing substituents in the aryl groups enhance the rate relative to $Ph_2C{=}S$. The activation parameters for cleavage of the C=S bonds in $Ph_2C{=}S$, $(p\text{-}MeOC_6H_4)_2C{=}S$, and $(m\text{-}CF_3C_6H_4)_2C{=}S$ exhibit essentially identical values for $\Delta S^{\neq}$, while $\Delta H^{\neq}$ is somewhat smaller for the thiones bearing electron-donating or -withdrawing substituents. We also studied the reversible binding of $Et_2NC{\equiv}N$ to $[Mo_2(OtBu)_6]$ as a model system wherein the C≡N bond is reduced but not cleaved and the $(M{\equiv}M)^{6+}$ center oxidized. Finally, the reversible binding of $P(nBu)_3$ to $[Mo_2(OCH_2tBu)_6]$, wherein the product exhibits no net oxidation of the metal centers, has been similarly studied. The activation parameters for these three classes of reactions are compared with previous studies of the reversible binding of CN^- to $[M_2(OR)_6]$ compounds and the reaction $2[W_2(OiPr)_6] \rightleftharpoons [W_4(OiPr)_{12}]$. We propose that the activation parameters associated with C=S cleavage are associated with the formation of a $\mu\text{-}\eta^1,\eta^2\text{-}S\text{-}CAr_2$ reactive complex similar to others described elsewhere,[23] and that they result from a) the bimolecular nature of the reaction and b) reorganizational energy. The greater facility of C–X multiple-bond cleavage in reactions involving $[W_2(OR)_6]$ compounds relative to $[Mo_2(OR)_6]$ compounds, the substituent effects, and the dependence on R are discussed in terms of the orbital energy match between the M–M and C–X π and π* orbitals, and an analogy is made with neutral Diels–Alder cycloaddition reactions.

Keywords
kinetics · metal–metal bonds · molybdenum complexes · multiple bonds · tungsten complexes

Introduction

The chemistry of compounds containing metal–metal multiple bonds represents an important chapter in modern coordination chemistry.[1] Aside from interest in structure and bonding, the reactivity of these dinuclear complexes often reveals features that do not occur in mononuclear chemistry.[2] These arise from two important factors: a) the M–M multiple bond provides a reservoir of electrons for substrate activation, and b) a dinuclear center affords unique modes of substrate binding. Amongst the many interesting reactions in which these complexes participate, those involving the six-electron reductive cleavage of alkynes,[3] nitriles,[3a, 4] and even carbon monoxide[5] by compounds containing $(W{\equiv}W)^{6+}$ are particularly fascinating [Eqs. (1–3), where R = Me, Et, *n*Pr and silox = tBu_3SiO].[6]

$$[W_2(OtBu)_6] + RC{\equiv}CR \xrightarrow[\text{hexane}]{22\,^\circ C} 2[(tBuO)_3W{\equiv}CR] \quad (1)$$

$$[W_2(OtBu)_6] + RC{\equiv}N \xrightarrow[\text{hexane}]{22\,^\circ C} [RC{\equiv}W(OtBu)_3] + [(tBuO)_3W{\equiv}N] \quad (2)$$

$$[W_2Cl_2(silox)_4(CO)_2] \xrightarrow[\text{toluene}]{80-100\,^\circ C} [W_2(O)(\mu\text{-}C)(silox)_4Cl_2] + CO \quad (3)$$

The reactivity of the $(W{\equiv}W)^{6+}$ center is greatly influenced by its attendant ligands, as is evidenced by the fact that $[W_2(OSiMe_2tBu)_6]$ and $[W_2(OC(CF_3)Me_2)_6]$ do not react with MeC≡N in a manner similar to that shown in Equation (2) but rather MeC≡N reversibly binds to each metal center.[7] The related $[Mo_2(OtBu)_6]$ compound fails to show any reactivity toward nitriles and dialkylacetylenes, and may even be recrystallized from anhydrous MeC≡N.[6] Similarly, whereas $[W_2(OiPr)_6(py)_2]$ and acetone react rapidly at 0 °C in

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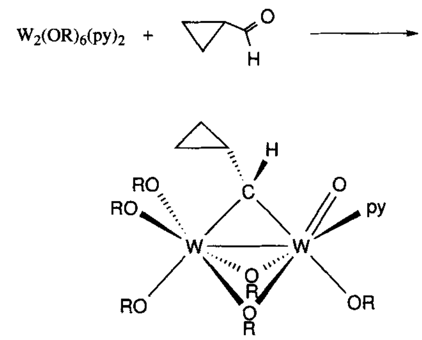
$[D_8]$toluene to yield $[W_2(\mu\text{-}CMe_2)(O\mathit{i}Pr)_6(O)(py)]$ by reductive cleavage of the ketonic C=O double bond, the corresponding molybdenum complex, $[Mo_2(O\mathit{i}Pr)_6]$, does not react with this substrate and may be dissolved in dry acetone.[8]

We were interested in establishing how and why such strong C–X multiple bonds are cleaved in some instances but not in others. From the study of the reaction between cyclopropane carboxaldehyde and $[W_2(OCH_2\mathit{t}Bu)_6(py)_2]$ we obtained the μ-CH-*c*-C_3H_5-containing ditungsten complex of Scheme 1, which implies that radical character or carbonium character was not involved.[9] If either a significant positive charge or a free radical were localized at the ketonic carbon during bond cleavage then ring-opening of the cyclopropyl group would have occurred.



Scheme 1.

In order to investigate the manner in which C–X multiple bonds are activated by these $(M{\equiv}M)^{6+}$ centers we have studied the reaction of diarylthiones with $[M_2(OR)_6]$ compounds, where the metal and the nature of the R group may be systematically varied along with the substituents on the aryl group. We have, furthermore, studied the reversible binding of *N*,*N*-diethylcyanamide to $[Mo_2(OR)_6]$ compounds that form 1:1 adducts wherein the nitrile moiety is reduced but not cleaved.[10] Finally, we have examined the reversible uptake of tri-*n*-butylphosphine ($(\mathit{n}Bu)_3P$) by $[Mo_2(OCH_2\mathit{t}Bu)_6]$ in $[D_8]$toluene as an example in which substrate reduction is not important. These studies are reported herein. They provide the first mechanistic insight into the factors influencing the reductive cleavage of C–X multiple bonds at dinuclear metal centers. The cleavage of C=S double bonds represents a four-electron oxidative addition and the quantitative data obtained may be compared with the now well-studied two-electron oxidative addition of C–X bonds to mononuclear metal centers.[11]

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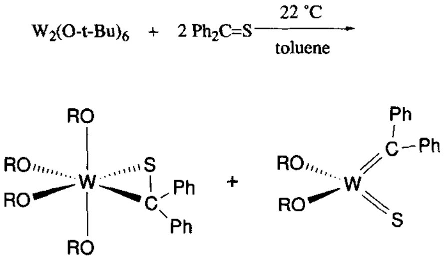
Results and Discussion

Reactions involving diarylthiones: The reaction between diarylthiones and $[W_2(O\mathit{t}Bu)_6]$ in hydrocarbon solvents rapidly affords a 1:1 mixture of two products (Scheme 2), as evidenced by NMR spectroscopic studies employing the labeled thione $Ph_2{}^{13}C{=}S$.[12a] The uptake of *two* equivalents of $Ph_2C{=}S$ parallels the reactivity of benzophenone with $[W_2(O\mathit{i}Pr)_6]$, which has previously been investigated.[12b] By contrast, $[Mo_2(O\mathit{t}Bu)_6]$ and $Ph_2C{=}S$ failed to react in hydrocarbon solvents at room temperature, whereas the less sterically demanding $[Mo_2(OCH_2\mathit{t}Bu)_6]$ reacted with just *one* equivalent of the thione [Eq. (4)]. Reaction (4) is readily monitored by the eye, as bright blue $Ph_2C{=}S$ and yellow $[Mo_2(OCH_2\mathit{t}Bu)_6]$ give red **1** within minutes of mixing. The reaction is also readily followed by NMR spectroscopy, and reactions employing $Ph_2{}^{13}C{=}S$ al-



Scheme 2.

$$[Mo_2(OCH_2\mathit{t}Bu)_6] + Ph_2C{=}S \xrightarrow[\text{hydrocarbons}]{22\,^{\circ}C} \underset{\mathbf{1}}{[Mo_2(OCH_2\mathit{t}Bu)_6(\mu\text{-}S)(CPh_2)]} \tag{4}$$

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[*] Members of the Editorial Board will be introduced to the readers with their first manuscript.

low easy identification of the $Mo{=}^{13}CPh_2$ moiety by the ^{13}C-labeled alkylidene resonance at $\delta = 279.2$ relative to Me_4Si in the $^{13}C\{^1H\}$ NMR spectrum. At room temperature the NMR data indicate a fluxional molecule, shown by a single set of resonances for the OCH_2tBu ligand. However, at low temperatures (− 80 °C and below, $[D_8]$toluene) the ^1H NMR spectrum contains five broad resonances in the methylene region ($\delta = 3.5-5.5$) in a 1:1:1:2:1 ratio and four resonances in the *t*Bu region ($\delta = 0.4-1.6$) in the integral ratio 2:2:1:1 (Fig. 1).

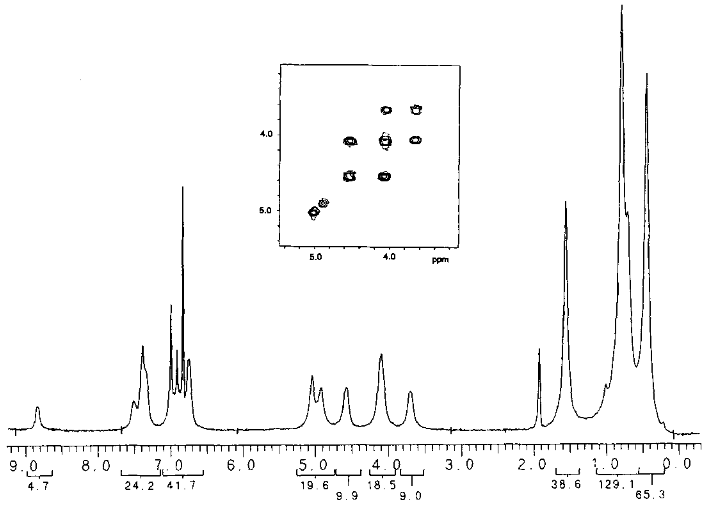
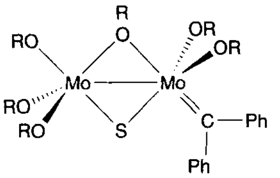


Fig. 1. ^1H NMR spectrum for $[Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CPh_2)]$, **1**, at −80 °C in $[D_8]$toluene. Inset: $^1H-^1H$ correlation spectrum (COSY) showing the $-CH_2$ region at −80 °C in $[D_8]$toluene.

We have not been able to obtain compound **1** in a crystalline form suitable for an X-ray study, but we are confident in formulating its low-temperature structure as **A**. For structure **A** the alkoxides clearly fall into four groups (2:2:1:1 ratio) but, based on the C_s symmetry of the molecule, there should be six resonances in the methylene region: two singlets due to the alkoxides that lie on the mirror plane and four doublets due to the diastereotopic methylenes of the remaining alkoxides. A COSY spectrum (− 80 °C, $[D_8]$toluene) clearly indicates that two resonances (of 1:1 relative intensity) are both coupled to a third resonance (of relative integral intensity 2). This is consistent with the assigned structure if the latter resonance is actually composed of two doublets that appear as a broad singlet because of coincidental overlap and poor lineshape. Finally, while the fluxional process could not be completely frozen out, the aryl-CH resonances are indicative of two different phenyl group environments. This is consistent with the proposed structure **A**, since of the two Mo d orbitals available for Mo−C π bonding, one is involved in formation of the Mo−Mo bond. As a result the alkylidene fragment is constrained to a conformation parallel to the Mo−Mo bond with the phenyl groups proximal and distal as shown in **A**.



A

Compound **1** reacts reversibly with donor ligands such as phosphines and pyridine [Eq. (5), where L = PMe_3, $P(nBu)_3$, py], and the trimethylphosphine adduct $[Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CPh_2)(PMe_3)]$ (**2**) has been fully characterized by a single-crystal X-ray diffraction study as well as by ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectroscopy (vide infra). Thus, there really is no question that the C=S double bond is cleaved in Reaction (4).

$$\underset{\mathbf{1}}{[Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CPh_2)]} + L \rightleftharpoons [Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CPh_2)L] \qquad (5)$$

While this reversible adduct formation is observed when donor ligands are added after the cleavage reaction is complete, their presence during the course of the reaction [Eq. (4)] causes a dramatic deceleration, presumably because they compete for binding sites at the metal centers. An example of this effect is seen in the following. Whereas a 1:1 mixture of $[Mo_2(OCH_2tBu)_6]$ and $Ph_2C{=}S$ react completely (>95%) within approximately 30 min at room temperature in C_6D_6, only 15% of the starting materials are consumed after 1 day if the reaction is carried out in $[D_5]$pyridine solution. It should be noted that Lewis bases such as pyridine bind rather tightly to $[Mo_2(OCH_2tBu)_6]$ to form $[Mo_2(OCH_2tBu)_6L_2]$,[13] and in the reaction between $[W_2(OiPr)_6(py)_2]$ and acetone in $[D_8]$toluene, the rate-determining step for C=O bond cleavage is the loss of pyridine from the starting material.[14]

The reaction shown in Equation (4) was conveniently monitored by ^1H NMR spectroscopy under pseudo-first-order reaction conditions (excess $Ph_2C{=}S$), and the observed rate constants were found to be linearly dependent on $[Ph_2C{=}S]$ with $k_{obs} = k[Ph_2C{=}S]$ (see Table 1a, ref. [32]). The activation parameters ($\Delta H^{\neq} = 10.2(2)\,kcal\,mol^{-1}$, $\Delta S^{\neq} = -29.5(9)$ eu) were determined from the temperature dependence (− 36.7 to − 5.3 °C) of the rate constant, *k*, by means of an Eyring plot. In this temperature range the fluxionality of **1** was quite helpful in monitoring the reaction (Fig. 2). At lower temperatures (≤ −40°) decoalescence of the alkoxide resonances for **1** occurs and this prevented accurate measurement of the signal intensities.

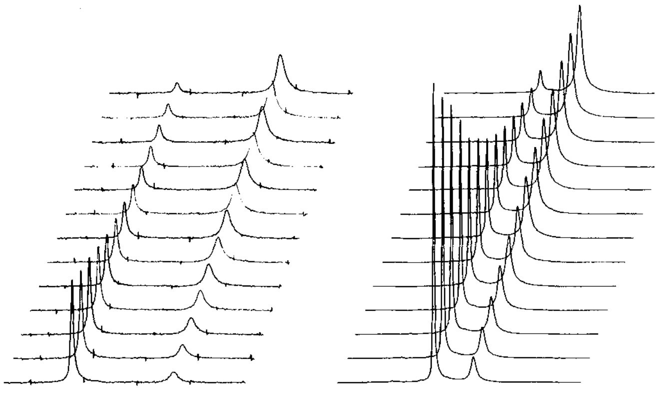


Fig. 2. ^1H NMR stacked plot for Reaction (4) showing the spectral changes which occur as the reaction proceeds at −5.3 °C in $[D_8]$toluene. The timescale for the first to the last spectrum is 4000 s.

The electronic characteristics of the cleavage reaction [Eq. (4)] were investigated by measuring the rate constants of the cleavage of a variety of substituted thiobenzophenones $(X-C_6H_4)_2C{=}S$. Interestingly, the reaction was shown to be facilitated by both electron-withdrawing and electron-donating substituents on the aromatic rings. A Hammett plot [$\ln(k/k_H)$ vs. σ] is shown in Figure 3. No correlation was observed for plots against other Hammett constants[15] such as σ^+, σ^-, or σ_p^+; this suggests that charge is not developed in the transition state for

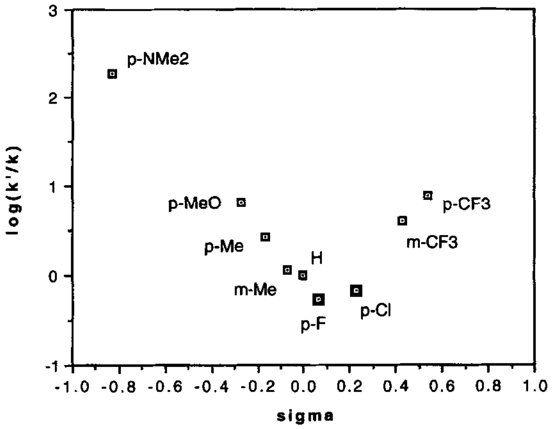


Fig. 3. Hammett plot for the reaction between $(X\text{-}C_6H_4)_2C{=}S$ and $[Mo_2(OCH_2tBu)_6]$ at −5.3 °C.

the reaction. This is consistent with our earlier observations concerning the reaction between cyclopropane carboxaldehyde and $[W_2(OCH_2tBu)_6(py)_2]$, which produced a bridging alkylidene complex that retained the strained three-membered cyclopropane ring as mentioned previously in discussion of Scheme 2. A generalized reaction sequence is shown in Equation (6). The reaction proceeds without detectable intermediates

$$[Mo_2(OCH_2tBu)_6] + Ar_2C{=}S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{“}Mo_2(OCH_2tBu)_6(Ar_2C{=}S)\text{”} \xrightarrow{k_2} \mathbf{1} \quad (6)$$

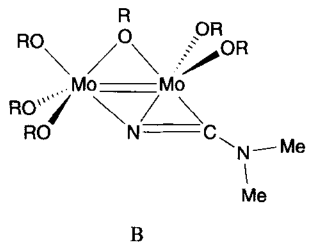
in the temperature ranges investigated, so that a steady-state approximation is applicable to the overall rate expression with $k = k_1k_2/(k_{-1} + k_2)$.

Three scenarios exist. In one, cleavage of the C=S bond is fast relative to substrate uptake ($k_2 \gg k_{-1}$) and the calculated rate constant reflects k_1 for adduct formation: $k = k_1$. In a second scenario, the intermediate adduct dissociates much more rapidly than cleavage occurs ($k_{-1} \gg k_2$) and the observed rate constant consists of the product of the equilibrium constant for adduct formation and the rate constant for cleavage: $k = k_1k_2/k_{-1}$. In the final scenario a balance exists between the rate constants for cleavage and dissociation ($k_{-1} \approx k_2$) and the expression for k does not simplify.

Based on the current experimental evidence, we can only say that adduct formation is not rate-limiting, since this is inconsistent with the observed rate acceleration by electron-withdrawing substituents. Furthermore, when 30 equiv of $Ph_2C{=}S$ were added to a $[D_8]$toluene solution of $[Mo_2(OCH_2tBu)_6]$ there was no evidence by ^1H NMR spectroscopy for formation of an adduct even at −100 °C. The 1:1 adduct must have a very small negative or even modest positive enthalpy of binding.

A Hammett plot is constructed with rate data obtained at one temperature. We therefore determined the activation parameters for the cleavage of the C=S bond in a diarylthione with an electron-releasing substituent and one with an electron-withdrawing substituent by measurement of the influence of temperature on the rate and use of an Eyring plot. For $(p\text{-}MeOC_6H_4)_2C{=}S$, $\Delta H^{\ddagger} = 9.1(3)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -30(2)$ eu; for $(m\text{-}CF_3C_6H_4)_2C{=}S$, $\Delta H^{\ddagger} = 9.1(3)$ and $\Delta S^{\ddagger} = -31(2)$ eu. The activation parameters are identical within experimental error, and the only reason that both react faster than $Ph_2C{=}S$ [Eq. (4)] is because of a modest decrease in $\Delta H^{\ddagger}$ brought about by the substitution of H on the phenyl ring by either a p-OMe or a m-CF_3 group.

Reversible binding of *N,N*-dialkylcyanamides to $[Mo_2(OR)_6]$ compounds: In an attempt to place these activation parameters into perspective, we decided to examine the reversible binding of a *N,N*-dialkylcyanamide and $P(nBu)_3$ to a $[Mo_2(OR)_6]$ center. *N,N*-dialkylcyanamides are known to form μ-$NCNR_2$ complexes of type **B**, wherein the C≡N moiety is partially reduced and the $(Mo{\equiv}Mo)^{6+}$ center oxidized.[10] It should be emphasized that there is no cleavage of the C≡N bond in reactions with $[Mo_2(OR)_6]$ compounds, whereas with $[W_2(OtBu)_6]$ cleavage to give $[(tBuO)_3W{\equiv}N]$ and $[(tBuO)_3W{\equiv}CNR_2]$ is rapid even at low temperatures.[4] In the case of the reversible binding of $P(nBu)_3$ there is no reduction of the substrate or oxidation of the $(Mo{\equiv}Mo)^{6+}$ center.[13]



B

The crystal and molecular structure of $[Mo_2(OCH_2tBu)_6(\mu\text{-}NCNMe_2)]$ had been previously reported, and it was known that reversible adduct formation according to Equation (7),

$$[Mo_2(OR)_6] + R'_2NC{\equiv}N \rightleftharpoons [Mo_2(OR)_6(\mu\text{-}NCNR'_2)] \quad (7)$$

where R = tBu, iPr, CH_2tBu and R′ = Me, Et, is greatly influenced by the steric properties of R and R′.[10] When the cyanide bound to the Mo_2^{6+} center, the C≡N triple bond was stretched from 1.160 Å (typical for a C≡N bond) to 1.334(4) Å, and the Mo≡Mo triple bond in $[Mo_2(OCH_2tBu)_6]$ (2.222(2) Å) was lengthened to 2.449(1) Å in **B** (R = CH_2tBu). While it is hard to say quantitatively how far advanced the oxidation–reduction reaction is, it is at least worth noting that the C–N distance of 1.33 Å and Mo–Mo distance of 2.45 Å are in the range expected for C=N and Mo=Mo double bonds.[16] This is most consistent with a 2-electron reduction of the diethylcyanamide substrate by the Mo_2^{6+} center.

The most suitable combination of R and R′ for NMR studies of the equilibrium shown in Equation (7) was found to be R = tBu and R′ = Et. As shown in Figure 4, the approach to equilibrium when R = tBu was easily followed by ^1H NMR spectroscopy at low temperature ($[D_8]$toluene, −88.2 to −56.4 °C) in the presence of a large excess of Et_2NCN. The observed rate constants were found to be linearly dependent on $[Et_2NCN]$, with $k_{obs} = k_1[Et_2NCN] + k_{-1}$. The forward ($k_1$)

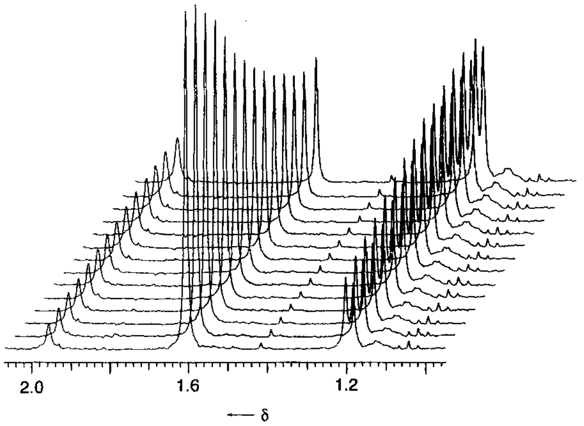


Fig. 4. ^1H NMR stacked plot for the approach to Equilibrium (7) at −60 °C showing some of the key spectral changes which occur as the reaction proceeds. Resonances for $(CH_3CH_2)_2NCN$ used in large excess occur at δ = 2.35 and 0.78; these have been omitted for clarity.

and reverse (k_{-1}) rate constants were calculated utilizing the thermodynamic data in Table 1 and the relationship $K_{eq} = k_1/k_{-1}$.[17] The temperature dependence of these rate constants allowed determination of the activation barrier: for k_1, $\Delta H^{\ddagger} = 8.6(5)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -30(2)$ eu, while for k_{-1}, $\Delta H^{\ddagger} = 17.0(5)$ kcal mol^{-1} and $\Delta S^{\ddagger} = +6(2)$ eu.

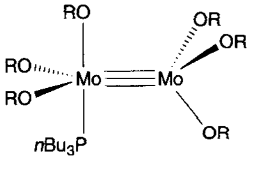
Table 1. Thermodynamic parameters for Equilibrium (7).

$[Mo_2(OR)_6]$	ΔH° (kcal mol^{-1})	ΔS° (eu)
R = *t*Bu	− 8.4(1)	− 36.8(3)
R = CH_2*t*Bu	−15.5(8)	− 34.5(13)
R = *i*Pr	−13.2(3)	− 33.4(8)

Reversible binding of P(*n*Bu)$_3$ to [Mo$_2$(OCH$_2$*t*Bu)$_6$]: The $[M_2(OR)_6]$ (M≡M) compounds are coordinatively unsaturated and π-buffered by the presence of the six OR ligands. With nucleophiles such as $HNMe_2$, py, and PMe_3, a number of $[M_2(OR)_6L_2]$ structures are known wherein two four-coordinate M atoms are united by a M≡M bond.[13] In solution there exist dynamic equilibria of the type shown in Equation (8). The

$$[M_2(OR)_6] + 2L \rightleftharpoons [M_2(OR)_6L_2] \qquad (8)$$

relative values of K_{eq} depend upon M, R, and L. The monoligated adducts $[M_2(OR)_6L]$ are intermediates in Reaction (8), and are favored relative to the formation of $[Mo_2(OR)_6L_2]$ by the use of a more bulky tertiary phosphine such as P(*n*Bu)$_3$. A $(M{\equiv}M)^{6+}$ center ligated by seven ligands has been seen before, as in the structurally characterized compounds [K$^+$(18-crown-6)Mo$_2$(OCH$_2$*t*Bu)$_7$], [W$_2$(*p*-tolyl)$_2$(O*i*Pr)$_4$(HNMe$_2$)], and [Mo$_2$(CH$_2$Ph)$_2$(O*i*Pr)$_4$(PMe$_3$)].[18] In this work we studied the equilibrium shown in Equation (9) by both ^{1}H and ^{31}P NMR spectroscopy and found no evidence for the formation of a [Mo$_2$(OCH$_2$*t*Bu)$_6$(P(*n*Bu)$_3$)$_2$] complex. The ^{1}H NMR data at low temperature are consistent with the adoption of structure **C**, where one Mo atom is four-coordinate and the other three-coordinate.



C

From the determination of K_{eq} as a function of temperature for the equilibrium expressed in Equation (9) we determined

$$[Mo_2(OCH_2tBu)_6] + P(nBu)_3 \rightleftharpoons [Mo_2(OCH_2tBu)_6P(nBu)_3] \qquad (9)$$

that $\Delta H^\circ = -7.1(2)$ kcal mol^{-1} and $\Delta S^\circ = -25(1)$ eu for P(*n*-Bu)$_3$ binding. A stacked plot showing the methylene proton signals of the CH$_2$*t*Bu ligands as a function of temperature is given in Figure 5, emphasizing the dynamic nature of this equilibrium in the temperature range −75 to + 0 °C, and also supporting our structural assignment **C**. At the low-temperature limit, four resonances are observed consistent with a nonfluxional (relative to the NMR timescale) phosphine complex that exhibits rapid Mo≡Mo bond rotation.

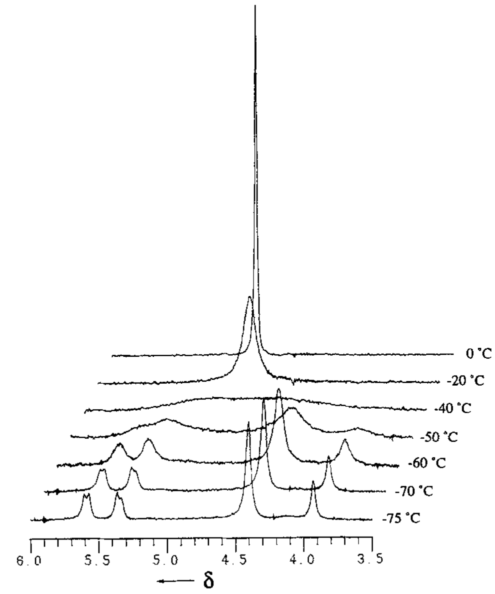


Fig. 5. ^{1}H NMR stacked plot (−75 °C to 0 °C) of the -CH$_2$ region illustrating the dynamic behavior of Equilibrium (9). The timescale for the first to the last spectrum is 7800 s.

The dynamic behavior of the Equilibrium (9) was studied by ^{13}P{^{1}H} NMR spectroscopy using the line-shape analysis program DNMR 5.[19] This allowed the determination of the activation parameters: $\Delta H^{\ddagger} = +10.4(5)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0(1)$ eu for the dissociative reaction, and for P(*n*Bu)$_3$ association, the forward reaction of Equation (9), $\Delta H^{\ddagger} = 3(\pm 1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -25(1)$ eu. The simple formation of a Mo–P σ bond is thus seen to have a very low enthalpy of activation, as might have been expected, since no bonds are being broken and relatively little reorganizational energy is necessary to accommodate the new metal–ligand bond, other than that required by steric considerations. The entropy of activation for the associative process, −25(1) eu, is rather typical of a bimolecular reaction and certainly is not in any way particularly large, which implies that the transition state is not highly ordered. Likewise the minimal entropy of activation for dissociation $\Delta S^{\ddagger} \approx 0$ implies an early transition state with no significant gain in degrees of freedom.

Before proceeding to speculate about the mechanism of C–X bond cleavage, it is worth mentioning briefly our earlier study of the reversible binding of CN$^-$ to $[M_2(OR)_6]$ compounds [Eq. (10)].[20] Equilibrium (10) was studied in

$$[M_2(OR)_6] + Q^+CN^- \rightleftharpoons Q^+[M_2(CN)(OR)_6]^- \qquad (10)$$

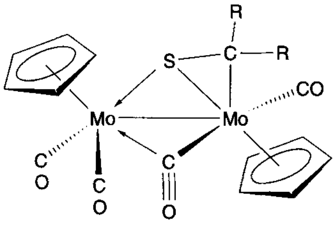
[D$_8$]toluene and [D$_6$]benzene with $Q^+ = N(nBu)_4^+$. In this solvent system ion-pairing and solvation factors will clearly be important for the position of the equilibrium and thus will influence the values of ΔH° and ΔS°. However, the trends seen for variation in R and M = Mo versus W are cosidered to be significant. Thus, for M = Mo and R = *t*Bu, *i*Pr, and CH$_2$*t*Bu, $\Delta H^\circ = -8.8(1)$, $-10.5(1)$, and $-13.5(1)$ kcal mol^{-1}, respectively, whereas for M = W and R = *t*Bu and CH$_2$*t*Bu, $\Delta H^\circ = -11.2(1)$ and $-16.9(1)$ kcal mol^{-1}. In each instance, $\Delta S^\circ = -18$ eu.[20] Thus we see that while steric factors are important, the relative binding for a given R group is favored by tungsten over molybdenum by about 2 or 3 kcal mol^{-1}. The thermodynamic parameters for the uptake of Et$_2$NC≡N by $[Mo_2(OR)_6]$ compounds given in Table 1 reveal a similar trend in the enthalpy of binding of the cyanamide ligand as a function of R, but a comparison with uptake by $[W_2(OR)_6]$ compounds is not possible owing to facile cleavage of the C≡N bond, as shown in Equation (2).

Mechanistic speculation concerning the cleavage of C–X multiple bonds: It has been said "kinetics is to mechanism as science is to fiction".[21] Nevertheless, a chemist performs kinetics and related studies in order to gain the privilege of insightful speculation.

Table 2 summarizes the activation parameters for substrate uptake and activation by various $[M_2(OR)_6]$ complexes. It is immediately obvious that the $[M_2(OR)_6]$ compounds are kinetically labile and show relatively small values of $\Delta H^{\neq}$ for substrate uptake. Moreover, the magnitudes of $\Delta S^{\neq}$ for the associative reactions fall within the range $-25(1)$ to $-39(3)$ eu in going from the simple binding of $P(nBu)_3$ to $[W_2(OiPr)_6]$ in the formation of the cluster $[W_4(OiPr)_{12}]$.[22] The activation parameters for the binding of $Et_2NC{\equiv}N$ to $[Mo_2(OtBu)_6]$ are essentially identical to those involved in the reaction leading to cleavage of the C=S double bond in diarylthiones. We are particularly attracted to this similarity because it is known that $Ph_2C{=}S$ adds to the M≡M triple bonds in $Cp_2Mo_2(CO)_4$ to give an adduct of structure **D** that bears remarkable resemblance to the cyanamide adduct shown in **B**.[23]

Table 2. Activation parameters for reactions of $[M_2(OR)_6]$ complexes with various substrates.

metal alkoxide	substrate	k_1 $\Delta H^{\neq}$	k_1 $\Delta S^{\neq}$	k_{-1} $\Delta H^{\neq}$	k_{-1} $\Delta S^{\neq}$
$[Mo_2(OtBu)_6]$	CN^-	13.2(5)	− 5.3(8)	22.0(5)	13.5(8)
$[Mo_2(OCH_2tBu)_6]$	CN^-	10.6(5)	− 4.6(8)	22.2(5)	13.9(8)
$[Mo_2(OCH_2tBu)_6]$	$P(nBu)_3$	3.0(5)	− 25(1)	10.4(5)	0(1)
$[Mo_2(OtBu)_6]$	Et_2NCN	8.6(5)	− 30(2)	17.0(5)	6(2)
$[Mo_2(OCH_2tBu)_6]$	$Ph_2C{=}S$	10.2(2)	− 29.5(9)		
$[W_2(OiPr)_6]$	$[W_2(OiPr)_6]$	10(1)	− 39(3)	30(2)	18(6)



D

We conclude that the entropies of activation for C–X bond cleavage are largely the determinants in accessing a structure of type **B** or **D**, and that these are associated with a) the fact that this is a bimolecular reaction and b) bond reorganizations. However, the actual C–X bond rupture, with or without M–M bond cleavage, adds little if any further entropic barrier.

Why do these C–X multiple bond cleavages occur so much more readily for tungsten than molybdenum, and why do electron-donating and electron-withdrawing substituents accelerate the C=S bond cleavage of diarylthiones? Based on the differences in the enthalpy of binding of CN^- and related σ-donor ligands, the greater reactivity of tungsten relative to molybdenum cannot be attributed alone to thermodynamic factors, which differ only by 2 to 3 kcal mol^{-1} in favor of tungsten. We propose that electronic factors are responsible and that the enthalpies of activation are significantly influenced by the orbital energetics of the M≡M and substrate π and π* orbitals. For related $[M_2(OR)_6]$ compounds, the photoionization from the M–M π orbital is approx. 0.5 eV lower in energy for M = W relative to M = Mo.[24] The ionization energy is, however, significantly influenced by the nature of R, as is shown in Table 3, where M = Mo and R = tBu, $(CF_3)Me_2C$, or $(CF_3)_2MeC$.[25] On the substrate, electron-donating groups will favor association [k_1 in Eq. (6)] and overlap with the vacant M–M π* orbitals, while electron-withdrawing substituents will lower the substrate π* orbitals, favor overlap with the filled M–M π-orbitals, and facilitate reduction [k_2 in Eq. (6)]. This type of analysis has been previously applied to 1,3-dipolar cycloadditions and Diels–Alder reactions.[26] Indeed, an analogy may be drawn with the type B or "neutral" Diels–Alder cycloaddition reactions in organic chemistry, which are accelerated by both electron-donating and -withdrawing substituents on the dienophile.[26]

Table 3. Ionization potentials (eV) of metal alkoxides from PES [25].

	IP (M–Mσ)	IP (M–Mπ)
$[Mo_2(OCMe_3)_6]$	7.80	6.79
$[Mo_2(OCMe_2(CF_3))_6]$	9.00	7.92
$[Mo_2(OCMe(CF_3)_2)_6]$	9.89	8.78
$[W_2(OCMe_3)_6]$	7.79	6.27
$[W_2(OCMe_2(CF_3))_6]$	8.98	7.31

The reduction in the W–W π orbital energy in going from $[W_2(OtBu)_6]$ to $[W_2(OCMe_2(CF_3))_6]$ causes a substrate such as $MeC{\equiv}N$ to change its mode of reaction from cleavage [Eq. (2), R = tBu] to simple Lewis base adduct formation [Eq. (8), R = $CMe_2(CF_3)$]. However, for arylnitriles which are better π acceptors, having lower energy C–N π* orbitals, cleavage of the C≡N bond still occurs, albeit more slowly, to give $[((CF_3)Me_2CO)_3WN]_3$.[27]

Crystal and molecular structure of $[Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CPh_2)(PMe_3)]$ (2): A view of the molecule is given in Figure 6 and selected bond lengths and bond angles are given in Table 4. The molecule has no element of symmetry and involves one six-coordinate Mo atom and one that is five-coordinate joined through μ-S and μ-OR groups. The Mo–Mo distance of 2.77 Å is quite long but can still be viewed as consistent with the presence of a Mo–Mo single bond.[16b] The terminal $Mo{=}CPh_2$ and $Mo{-}PMe_3$ bonds are adjacent to one another. The Mo(1)–S distance is nearly 0.2 Å less than the Mo(2)–S distance, a fact that may reflect internal redox compensation within the molecule.

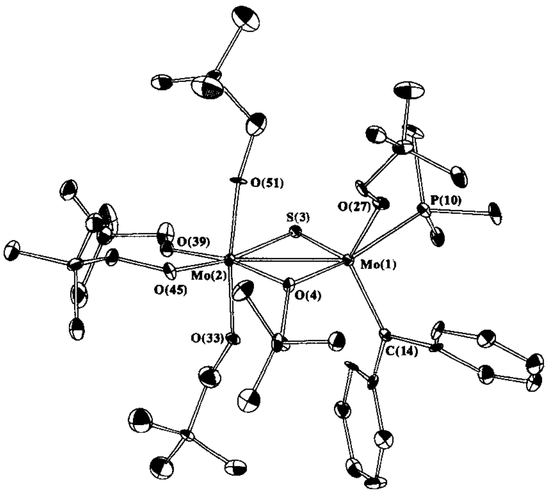


Fig. 6. ORTEP drawing of $[Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CPh_2)(PMe_3)]$, **2**, with the core atoms labeled. Ellipsoids are at the 30% probability level and hydrogen atoms have been omitted for clarity.

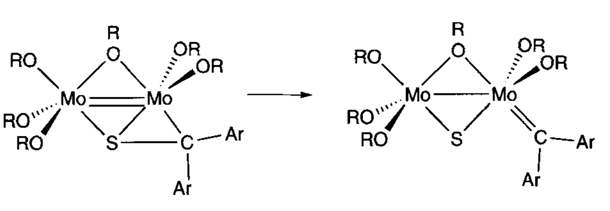
The ^1H NMR spectrum is consistent with the structure observed in the solid-state. Most significantly there are six different methylene groups each having diastereotopic protons, with one methylene proton exhibiting a small coupling to ^{31}P. NMR data are given in the Experimental Section.

Table 4. Selected bond lengths (Å) and angles (°) (esd in parentheses) for $[Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CPh_2)(PMe_3)]$ (**2**).

Mo(1)–Mo(2)	2.7722(11)	Mo(2)–O(4)	2.119(6)
Mo(1)–P(10)	2.5058(25)	Mo(2)–O(39)	1.927(7)
Mo(1)–O(27)	1.942(6)	Mo(2)–O(51)	1.890(6)
Mo(1)–S(3)	2.2548(24)	Mo(2)–S(3)	2.4266(23)
Mo(1)–O(4)	2.116(6)	Mo(2)–O(33)	1.861(7)
Mo(1)–C(14)	1.951(10)	Mo(2)–O(45)	1.945(6)
Mo(1)-S(3)-Mo(2)	75.52(7)	S(3)-Mo(2)-O(39)	89.25(20)
Mo(1)-O(4)-Mo(2)	81.79(20)	S(3)-Mo(2)-O(45)	170.32(21)
S(3)-Mo(1)-P(10)	80.66(8)	S(3)-Mo(2)-O(51)	84.59(21)
S(3)-Mo(1)-O(4)	105.76(17)	O(4)-Mo(2)-O(33)	85.06(26)
S(3)-Mo(1)-O(27)	122.18(21)	O(4)-Mo(2)-O(39)	169.02(26)
S(3)-Mo(1)-C(14)	108.7(3)	O(4)-Mo(2)-O(45)	87.47(26)
P(10)-Mo(1)-O(4)	165.64(18)	O(4)-Mo(2)-O(51)	88.12(26)
P(10)-Mo(1)-O(27)	75.59(20)	O(33)-Mo(2)-O(39)	88.8(3)
P(10)-Mo(1)-C(14)	87.3(3)	O(33)-Mo(2)-O(45)	96.03(28)
O(4)-Mo(1)-O(27)	89.20(25)	O(33)-Mo(2)-O(51)	171.0(3)
O(4)-Mo(1)-C(14)	102.4(3)	O(39)-Mo(2)-O(45)	84.12(27)
O(27)-Mo(1)-C(14)	122.2(3)	O(39)-Mo(2)-O(51)	98.8(3)
S(3)-Mo(2)-O(4)	99.93(17)	O(45)-Mo(2)-O(51)	89.45(28)
S(3)-Mo(2)-O(33)	90.87(20)		

Concluding Remarks

In this work we have examined the reversible binding of $P(nBu)_3$ and $Et_2NC{\equiv}N$ to $[Mo_2(OCH_2tBu)_6]$ to determine the activation parameters associated with substrate uptake at the $(M{\equiv}M)^{6+}$ center. In one case the substrate was reduced ($Et_2NC{\equiv}N$), and in the other the substrate acted as a simple Lewis base. We have also studied the cleavage of the C=S bond of diarylthiones in reactions involving $[Mo_2(OCH_2tBu)_6]$, and shown that this reaction is accelerated by both electron-releasing and electron-withdrawing substituents on the aryl group in the *para* and *meta* positions. The activation parameters for the cleavage of the C=S double bond in the reaction with $Ph_2C{=}S$ closely resemble those for uptake of $Et_2NC{\equiv}N$. We propose that the transition state for cleavage of the C=S bond has a geometry resembling that shown in **B** and **D**, wherein the substrate is bound to both metal centers. The activation parameters are determined largely in attaining this geometry and there is little in the way of an additional kinetic barrier to the actual C=S bond cleavage. Indeed, it may be thought of as an intramolecular reorganization of electron density involving little nuclear motion (Scheme 3).



Scheme 3.

Finally it is worth noting that this represents the first comprehensive study of a four-electron oxidative addition reaction wherein the activation parameters reveal insight into the nature of the process. This contrasts, for example, with the reductive cleavage of ketones by $[WCl_2(PMePh_2)_4]$ and $[W_2(OiPr)_6(py)_2]$, where Lewis base dissociation is rate-determining.[14, 28] With the insight gained from this work we expect that further synthetic strategies employing $[M_2(OR)_6]$ compounds will become accessible.

Experimental Section

All preparations were carried out in an inert atmosphere by using standard Schlenk techniques in conjunction with a Vacuum Atmospheres Company Dri-Lab System. Hydrocarbon solvents were distilled from sodium/benzophenone and stored over 4 Å molecular sieves. $[D_8]$toluene was degassed with dry nitrogen and stored over 4 Å molecular sieves. PMe_3 was used as received from Aldrich. Et_2NCN and Me_2NCN were purchased from Aldrich but were purified by vacuum distillation through a column of $CaCl_2$, degassed with N_2, and stored over 4 Å molecular sieves prior to use. NMR spectra were recorded on Varian XL-300, Nicolet NT-360 or Bruker AM500 spectrometers. Thermodynamic and kinetic measurements were performed with temperatures calibrated using a sample of neat methanol and Van Geet's equations [29]. The data were analyzed according to standard procedures [17]. The thioketones were prepared from the corresponding commercially available ketones with Lawesson's reagent [30] and were purified by sublimation or distillation (60–100 °C, 0.01 Torr). Analysis of $^{13}C\{^1H\}$ NMR spectra was assisted by utilizing ^{13}C enriched $Ph_2{}^{13}C{=}S$. The latter was prepared from $Ph_2{}^{13}C{=}O$, which was in turn prepared from $^{13}CO_2$ and 2 equiv of PhLi according to Gilman [31].

Preparation of $[Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CPh_2)]$ (1): $[Mo_2(OCH_2tBu)_6]$ (50 mg, 70 mmol) was dissolved in benzene (2 mL) and a solution of $Ph_2C{=}S$ (14 mg, 71 mmol) in benzene (2 mL) was added through a cannula. The reaction mixture turned from green to brown and finally to red as the starting materials, which are yellow and blue respectively, were consumed. After 30 min the solvent was removed in vacuo (23 °C, 0.01 Torr) and the residue analyzed by NMR spectroscopy. For **1**: ^1H NMR (300 MHz, $[D_8]$toluene, −80 °C): $\delta = 8.9$ (brs, 1H), 7.6 (brs, 1H), 7.45 (brm, 5H), 6.8 (brm, 3H), 5.15 (brs, 2H), 5.0 (brs, 2H), 465 (brs, 2H), 4.2 (brs, 4H), 3.8 (brs, 2H), 1.65 (brs, 9H), 0.9 (brs, 18H), 0.85 (brs, 9H), 0.55 (brs, 18H); $^{13}C\{^1H\}$ NMR (125 MHz, $[D_8]$toluene, 23 °C): $\delta = 279.2$ ($=CPh_2$), 93.1 ($-OCH_2tBu$), 35.0 ($-OCH_2CMe_3$), 27.1 ($-OCH_2C(CH_3)_3$), aryl region not resolved. To date crystalline material has not been obtained for **1** or any other related derivative with substituents on the aryl rings. These complexes slowly and irreversibly decomposed ($t_{1/2} = 24$ h at 23 °C for **1**) to produce a nearly quantitative yield of $Ph_2CHCHPh_2$. The molybdenum-containing product(s) have thus far eluded characterization. This decomposition does not complicate the kinetics of the cleavage reaction [Eq. (4)], which is several orders of magnitude faster at low temperature (− 40 to 0 °C).

Preparation of $[Mo_2(OCH_2tBu)_6(\mu\text{-}S)(=CPh_2)(PMe_3)]$ (2): One equiv PMe_3 (7 µL, 72 mmol) was added to freshly prepared **1** in $[D_8]$toluene. For **2**: ^1H NMR (500 MHz, $[D_8]$toluene, 23 °C): $\delta = 7.24$ (brm, 2H), 7.15 (t, $J = 7.5$ Hz, 2H), 7.1 (brm, 2H), 6.93 (t, $J = 7.5$ Hz, 1H), 6.92 (t, $J = 7.5$ Hz, 2H), 6.77 (t, $J = 7.5$ Hz, 1H), 5.56, 5.53, 5.40, 5.27, 5.15, 4.99, 4.15, 3.88, 3.65, 3.42, 3.21, 3.03 (all d, $J = 10$–12.5 Hz, 1H each for $-CH_2C(CH_3)_3$), 1.36, 1.34, 1.23, 1.06, 0.72, 0.70 (s, 9H each for $-CH_2C(CH_3)_3$), 1.20 (d, $J = 8.6$ Hz, $P(CH_3)_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $[D_8]$toluene, 23 °C): $\delta = 302.87$ (d, $J = 25$ Hz, $=CPh_2$), 98.1, 87.8, 86.7, 84.8, 82.3 (s, 1:1:1:1:1 for $-OCH_2tBu$), 84.4 (d, $J_{CP} = 7.5$ Hz, $-OCH_2tBu$), 36.1, 35.3, 35.0, 34.5, 33.9 (s, 1:1:1:2:1 for $-OCH_2CMe_3$), 28.5, 28.3, 28.1, 27.8, 27.5, 27.2 (s, 1:1:1:1:1:1 for $-OCH_2C(CH_3)_3$), 16.8 (d, $J_{CP} = 25$ Hz, $P(CH_3)_3$), aryl region not resolved. Recrystallization could be performed for preparative scale reactions in hexanes/PMe_3 (1:1) or neat PMe_3 at −34 °C. The latter solvent provided crystalline material suitable for analysis by single-crystal X-ray diffraction. Calcd. for $C_{46}H_{85}Mo_2O_6PS$: C = 55.68, H = 8.66, found: C = 55.56, H = 8.52. While this phosphine adduct appears to be indefinitely stable in the solid state it decomposed slowly at room temperature in solution ($t_{1/2} \approx 1$ week) to afford $Ph_2CHCHPh_2$ as the predominant (>90%) organic by-product by NMR spectroscopy. The fate of the molybdenum-containing products has yet to be determined.

Studies in kinetics: $(X\text{-}Ph)_2C{=}S + [Mo_2(OCH_2tBu)_6]$: Measurements of the kinetics were performed in $[D_8]$toluene under pseudo-first-order reaction conditions: $[Mo_2(OCH_2tBu)_6]$ ca. 5×10^{-3} M, $[Ph_2C{=}S]$ ca. 5×10^{-2}–1×10^{-1} M. For complete experimental details along with rate constants and Eyring plots for X = H, *p*-MeO, and *m*-CF_3, see ref. [32].

Equilibrium measurements for $Et_2NCN + [Mo_2(OR)_6]$: The spectral properties associated with these equilibria have been previously reported [10]. Quantitative measurements were performed over a 50 °C range for each sample. For tables of K_{eq} and plots of $\ln(K_{eq})$ versus $1/T$, see ref. [32].

Studies in kinetics: $Et_2NCN + [Mo_2(OtBu)_6]$: The approach to equilibrium was monitored for 1–5 half-lives where time permitted. ($[Mo_2(OtBu)_6] = 2.46 \times 10^{-2}$–$3.87 \times 10^{-2}$ M; $[Et_2NCN] = 2.48 \times 10^{-1}$–$5.80 \times 10^{-1}$ M). At the lowest temperature (− 80 °C) the approach to equilibrium was exceedingly slow ($k_{obs} \approx 2.5 \times 10^{-5}$) and was followed for only 1 $t_{1/2}$ (for observed rate constants, calculated k_1 and k_{-1}, and Eyring plots for the latter two, see ref. [32]).

Equilibrium measurements for $P(nBu)_3 + [Mo_2(OCH_2tBu)_6]$: The addition of $P(nBu)_3$ to a yellow toluene solution of $[Mo_2(OCH_2tBu)_6]$ resulted in a chemically labile equilibrium as shown in Equation (9). At room temperature, the equilibrium was far to the left and no appreciable color change was noted. Upon cooling to

$-78\,°C$, however, the solution turned deep red, consistent with the formation of a phosphine adduct. The equilibrium was conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy, which clearly indicated that only one equivalent of phosphine was associated at the lowest temperature. ^1H NMR spectroscopy substantiated this fact and provided evidence for the structural assignment. For $[Mo_2(OCH_2tBu)_6(P(nBu)_3)]$: ^1H NMR (300 MHz, $[D_8]$toluene, $-75\,°C$): -CH_2- region; $\delta = 5.6$ (d, $J = 7$ Hz, 2H), 5.35 (d, $J = 7$ Hz, 2H), 4.42 (s, 6H), 3.93 (s, 2H). The -CH_3 resonances are not well resolved and overlap with those due to $P(nBu)_3$. However, from titration experiments involving spectroscopic detection of the -CH_2 region it is clear that binding of only one equivalent of phosphine occurs. $^{31}P\{^1H\}$ NMR (146 MHz, $[D_8]$toluene, $-75\,°C$): $\delta = 8.40$ (s, 1P). Quantitative measurements for the equilibrium were obtained from the $^{31}P\{^1H\}$ data (free $P(nBu)_3$ resonates at $\delta = -32.9$) which allowed calculation of K_{eq} over a 50 °C range (-75 to $-25\,°C$) (for a table of K_{eq} versus T and a plot of $\ln(K_{eq})$ versus $1/T$, see ref. [32]).

Studies in kinetics: $P(nBu)_3 + [Mo_2(OCH_2tBu)_6]$: The dissociation of $P(nBu)_3$ from $[Mo_2(OCH_2tBu)_6(P(nBu)_3)]$ is the slow step in the interconversion of bound and free $P(nBu)_3$ in solution. The rate of interconversion was estimated by simulating the lineshapes of the respective signals for $P(nBu)_3$ and $[Mo_2(OCH_2tBu)_6(P(nBu)_3)]$ with the program DNMR 5 [19] over the temperature range -75 to $-25\,°C$ (for a table of k_{diss} versus T and a plot of $\ln(k/T)$ versus $1/T$, see ref. [32]).

Crystallography for $[Mo_2(OCH_2tBu)_6(\mu\text{-}S)({=}CPh_2)(PMe_3)]$ (2) [33]: Single crystals suitable for study by X-ray diffraction were grown from neat PMe_3 at $-34\,°C$. A crystal was selected under an inert atmosphere, attached to a glass fiber with silicone grease, and transferred to the goniostat where it was cooled to $-170\,°C$ for characterization and data collection. For **2** ($C_{46}H_{85}Mo_2O_6PS$, FW = 989.09): monoclinic $P2_1$, $a = 10.913(2)$ Å, $b = 19.752(4)$ Å, $c = 12.871(2)$ Å, $\beta = 111.95(1)°$; $V = 2573.27$ Å^3; $\rho_{calc} = 1.277\,g\,cm^{-3}$ ($Z = 2$). A total of 3500 independent reflections were collected on a Picker four-circle diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. The final residuals were $R_F = 0.0454$, $R_{wF} = 0.0442$ for 3208 reflections observed with $F_0 > 3\sigma(F_0)$.

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[32] Supplementary material, including complete experimental details not given in the manuscript and VERSORT drawings showing the atom numbering scheme, may be obtained from the authors.

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