the six-membered rings in **1′–4′** and cis in **1″–4″** (*cf.* Scheme I).

$$\mathbf{1}\,(\mathbf{1}{:}\mathbf{1}'' = 19) \xrightarrow[\text{sens}]{h\nu} 7\%\ \mathbf{4}\,(\mathbf{4}'{:}\mathbf{4}'' = 9) + 1\%\ \mathbf{3}\,(\mathbf{3}'{:}\mathbf{3}'' \simeq 3) + \mathbf{1}\,(\mathbf{1}{:}\mathbf{1}'' = 19)$$

$$\mathbf{2}\,(\mathbf{2}''{:}\mathbf{2}' = 24) \xrightarrow[\text{sens}]{h\nu} 12\%\ \mathbf{4}\,(\mathbf{4}''{:}\mathbf{4}' = 10) + 2\%\ \mathbf{3}\,(\mathbf{3}'' > \mathbf{3}') + \mathbf{2}\,(\mathbf{2}''{:}\mathbf{2}' = 24)$$

The high retention of stereochemical relationships between H and OR in **1** (or **2**) → **4** and the unchanged stereopurity of **1** and **2** at C-6 indicate that rupture of the 1,5 bond in **1** or **2**, yielding planar **8**, occurs exclusively, or almost so; occurrence of some **4** → **3** probably accounts for the lower retention in **3**. Epimerization of **4b**-d_6 is similarly summarized

$$\mathbf{4}\,(83\%\ \mathbf{4}') \xrightarrow[\text{sens}]{h\nu} 25\%\ \mathbf{3}\,(67\%\ \mathbf{3}'') + \mathbf{4}\,(75\%\ \mathbf{4}')$$

The predominance of exo H in **3** indicates that **4b** → **3b**, like related epimerizations,[16,17] occurs largely by 1,6 bond rupture; increased endo H implies that **4b** ⇄ **3b** also occurs by 1,5 bond rupture.

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Reactions of Oxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(IV) with Unsaturated Organic Molecules and Their Biochemical Implications

Sir:

The similarity in patterns of reactivity of certain transition metals in particular oxidation states and very reactive organic species has recently been recognized.[1,2] This analogy, together with the suggestion that d^2 metal systems may act like carbenes[3–5] and the possible role of molybdenum in redox-active enzymes, has led us to examine the reactivity of pentacoordinate oxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(IV), $MoO(S_2CNR_2)_2$.

On mixing equimolar *dry* benzene solutions of oxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(IV),[6,7] **1**, and diethyl azodicarboxylate, **2**, under argon, an intense purple color[8–10] developed immediately which changed to yellow (first-order reaction, half-life at 25° *ca.* 50 sec). A yellow compound, **3**, was precipitated with ether from concentrated mixtures and recrystallized from dichloromethane–hexane (mp 105–108° dec). Identical electronic spectra were obtained for pure **3** (λ_{max} 390 nm, ϵ 4 × 10^3 cm^2/mol; λ_{min} 348 nm, ϵ 3.25 × 10^3 cm^2/mol) and the reaction mixture after the color change was complete, signifying a quantitative reaction.

Analysis of **3** indicates a 1:1 adduct of **1** and **2**. It is diamagnetic (nmr). The ir spectrum of **3** shows both an oxomolybdenum(VI) moiety[11] and a coordinated azo group (ν(C=O) at 1705 cm^{-1}).[12] Similar 1:1 adducts have been prepared previously[13] with chlorocarbonylbis(triphenylphosphine)iridium(I) and tetrakis(triphenylphosphine)platinum(0). These latter reactions were postulated as oxidative additions to the metal complexes yielding adducts containing symmetrically bound substrates. Our similar spectral data suggest **3** is formally seven-coordinate molybdenum(VI) produced by oxidative addition of the azo linkage to molybdenum(IV).

Similar reactions of oxobis(*N*,*N*-dimethyldithiocarbamato)molybdenum(IV), **4**, gave crystalline products with: diethyl azodicarboxylate, **5**; dimethyl acetylenedicarboxylate, **6**; and tetracyanoethylene, **7**. The tetracyanoethylene adduct, **8**, of **1** was also prepared. Analysis and ir spectra (Table I) are consistent with **5**, **6**, **7**, and **8** being 1:1 adducts containing the substrate bound to molybdenum(VI).

Table I. Infrared Spectral Data (KBr disks, cm^{-1})

Compound no.	ν(Mo=O)	ν(C=O)	ν(C≡C)	ν(C≡N)
3	935 (s)[a]	1705 (s)[a]		
4	975 (s)[b]			
5	933 (s)	1710, 1725 (vs)[c]		
6	938 (s)	1710, 1720 (vs)[d]	1875 (s)	
7	935 (s)			2240 (m)
8	940 (s)			2240 (m)

[a] Chloroform solution. [b] Dichloromethane solution. [c] Broad single band at 1715 cm^{-1} (vs) in chloroform. [d] Broad single band at 1720 cm^{-1} (vs) in chloroform.

Solutions of **3** and **5** are stable when water is excluded. In *moist* chloroform, however, 10^{-2} *M* solutions are completely hydrolyzed in 1–3 hr to form 1,2-bis(ethoxycarbonyl)hydrazine, **9**, and the appropriate[9,10] *cis*-dioxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(VI), **10** and **11**. The reactions were monitored by ir, nmr, and visible spectroscopy. The stoichiometries were established by quantitative chromatography on alumina (chloroform elution) for **9** and by comparing electronic spectra with authentic samples[9,10] for **10** and **11**. The isolation of **9**, the two-electron reduction product of **2**, from the hydrolysis further supports the oxidative addition of **2** across **1** and **4**.

The low hydrolytic stability of the molybdenum ad-

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[7] Contrary to ref 6, **1** was readily recrystallized from benzene and found to be diamagnetic (nmr).

[8] The purple color is not due to $Mo_2O_3(S_2CNEt_2)_4$[9,10] (by comparing visible spectra).

[9] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 1702 (1970).

[10] F. W. Moore and M. L. Larson, *Inorg. Chem.*, **6**, 998 (1967).

[11] The decrease in ν(Mo=O) from 962 cm^{-1} in **1** to 935 cm^{-1} in **3** agrees with the previously observed sequence[9] Mo(IV) > Mo(VI), and supports the proposed increase in formal oxidation state of molybdenum.

[12] **9** has ν(C=O) at 1740 cm^{-1} and **2** ν(C=O) at 1780 cm^{-1} (benzene solution).

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ducts is in striking contrast to that of the adducts with Vaska's compound and bis(triphenylphosphine)platinum(0). We find that even in boiling chloroform–water mixtures, these latter adducts are recovered unchanged.[14] The driving force for hydrolysis may be the formation of stable products. For molybdenum the *cis*-dioxomolybdenum(VI) species fits this criterion perfectly, while for iridium or platinum the appropriate oxo species is unknown and its production probably unfavorable.

Oxidative addition of the nitrogen–nitrogen multiple bond and hydrolysis of the resultant complex, occurring only for molybdenum, has an obvious analogy with the interaction of dinitrogen with nitrogenase. Further, this system may elucidate the possible role of molybdenum in other redox-active molybdoenzymes. The results detailed above suggest that the mode of reaction proposed herein for dinitrogen and its other substrates[15] with nitrogenase may be common to all redox-active molybdoenzymes, *e.g.*, nitrate reductase,[16] sulfite,[17] aldehyde,[18] and xanthine[19] oxidases. The interactions of all these enzyme systems may be interrelated through similar electronic and structural requirements for the active metal atom, *viz.*, molybdenum. For the oxidases, the "reverse" process of transfer of an oxo ligand from molybdenum(VI) to the substrate occurs causing a two-electron reduction to molybdenum(IV). This mode of action for the oxidases finds support in the reaction[20] of triphenylphosphine with *cis*-dioxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(VI) to produce triphenylphosphine oxide and oxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(IV). These reactions may all be related to the recently proposed principle of metal ion promoted atom-transfer redox reactions.[21]

Although these oxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(IV) complexes react only with highly activated multiple bonds, they do resemble the suggested structures of the active sites of molybdoenzymes,[22] *i.e.*, the involvement of sulfur ligands at the metal, more closely than previous models (*e.g.*, a platinum(II)–phosphine complex[23] for the nitrogenase active site). Therefore, we suggest that these coordinatively unsaturated molybdenum(IV) complexes and the related oxomolybdenum(VI) complexes constitute valuable probes for investigating the mode(s) of reaction of the various molybdoenzymes.

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(14) The isolation of 9 from mixtures of 2 and tetrakis(methyldiphenylphosphine)platinum(0) has been ascribed to hydrogen abstraction from the methyl group of the phosphine coordinated to platinum.[13] However, we find that 9 is not produced when water is excluded and that 2 interacts with methyldiphenylphosphine alone, the adduct so formed hydrolyzing on addition of water to produce 9 and methyldiphenylphosphine oxide. Therefore it appears that liberated methyldiphenylphosphine, not the platinum(0) complex, is responsible for the formation of 9.

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Convenient Synthesis of 1,4-Diketones. Application to the Synthesis of Dihydrojasmone

Sir:

A variety of synthetic routes for the preparation of 1,4-diketones, valuable intermediates for syntheses of cyclopentenones and furans, have been developed;[1] however, there remains room for improvement. We wish to report a convenient route for synthesis of 1,4-diketones from diphenylthioacetals and conjugated enones and to illustrate its utility in a synthesis of dihydrojasmone.

Alkylcopper reagents react with conjugated enones to give 1,4-addition products,[2] but the reaction of conjugated enones with metalated ($Mg-Cu^I$) 1,3-dithiane, which is synthetically equivalent to carbonyl function, leads only to 1,2 addition to conjugated enones.[3]

We found that lithium di[bis(phenylthio)methyl]copper (I, $R^1 = H$), which is prepared from bis(phenylthio)methyllithium and 0.5 equiv of CuI, reacts with methyl vinyl ketone (MVK) at −78° to afford the 1,4-addition product IIIa (50%) along with the 1,2-addition product IVa (23%). On the other hand, when the reaction of lithium bis[tris(phenylthio)methyl]copper (I, $R^1 = C_6H_5S$) with MVK was carried out under the same condition, the 1,4-addition product, 1-tris(phenylthio)pentan-4-one (IIIb), was selectively obtained in 70% yield.

From these results, it was expected that substituted diphenylthioacetals (I, R^1 = alkyl) would react with conjugated enones to yield 1,4-addition products exclusively. In fact, the treatment of lithium [α,α-bis(phenylthio)benzyl]copper (I, $R^1 = C_6H_5$) with MVK afforded 1-phenyl-1-bis(phenylthio)pentan-4-one (IIIc) in 94% yield according to the following procedure. To 70 ml of a dry tetrahydrofuran (THF) solution of benzaldehyde diphenylthioacetal (10 mmol) was added 6.45 ml of an *n*-hexane solution of *n*-BuLi (10 mmol) at −78° under an argon atmosphere, and the mixture was stirred for 1 hr. Cuprous iodide (5 mmol) was then added at once and the mixture was kept stirring for 1 hr at −78°. Fifteen milliliters of a THF solution of MVK (5 mmol) was added slowly at −78° and the mixture, after being stirred for 2 hr at −78°, was quenched at −78° by the addition of water, and allowed to warm to

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