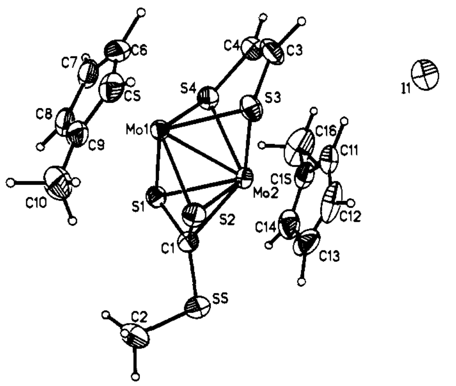

Figure 1. Perspective view and numbering scheme for $[(MeCpMo)_2(SC_2H_2S)(S_2CSMe)]I$. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å): $Mo_1–Mo_2$, 2.623 (1); $Mo_2–C_1$, 2.195 (6); $C_1–S_1$, 1.749 (7); $C_1–S_2$, 1.754 (6); $C_1–S_5$, 1.755 (6); $S_5–C_2$, 1.789 (8); $Mo_1–S_1$, 2.423 (2); $Mo_1–S_2$, 2.438 (2); $Mo_2–S_1$, 2.452 (2); $Mo_2–S_2$, 2.442 (2). Angles (deg): $S_1–C_1–S_2$, 108.4 (3); $S_1–C_1–S_5$, 124.3 (4); $S_2–C_1–S_5$, 125.7 (4); $Mo_2–C_1–S_5$, 126.5 (3).

example, the average $Mo_2–C_{Cp}$ distance of 2.327 Å is approximately 0.03 Å longer than the $Mo_1–C_{Cp}$ average distance (2.292 Å); $Mo_2–S_{3(4)}$ (2.473 (2) Å) is 0.04 Å longer than $Mo_1–S_{3(4)}$. Other structural features of the $Cp_2Mo_2S_4$ core are similar to those observed for related cations, including the Mo–Mo distance of 2.623 (1) Å.[8,17]

In a somewhat related example of unusual coordination geometries, a 1,2-alkenedithiolate ligand has been found to display an μ-η^2,η^4-bonding interaction in a neutral dinuclear ruthenium complex.[18] The dithiolene ligand bonds to one Ru ion through the two sulfur atoms and to the second Ru ion through the two sulfur and two carbon atoms. In this system, the formation of the dithiolate ligand with the unusual bonding mode was induced by phosphine abstraction of a disulfido ligand. In contrast, the formation of complex II appears to be induced by the generation of a positive charge on the dithio ligand and results in an expansion of the molybdenum coordination sphere.[19] The complex provides a rare example of verified reactivity of a molybdenum ion in these tetrasulfur-bridged complexes and suggests that the characteristic reactivity of the Mo ion in complexes of this type is that of a Lewis base. This permits the stabilization of unusual types of electron-deficient ligands. The basicity of the metal ion may also have important implications for the reactions of related molybdenum complexes which result in the heterolytic cleavage of the hydrogen molecule.[20]

Acknowledgment. Support from the National Science Foundation and, in part, from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged. M.R.D. is grateful for a Dreyfus Fellowship, 1981-1986, and a Guggenheim Fellowship, 1984-1985.

Supplementary Material Available: Crystal data and details of the structural determination and tables of bond distances, bond angles, and atomic and thermal parameters for $[(MeCpMo)_2(SC_2H_2S)(S_2CSMe)]I$ (5 pages); observed and calculated structure factor table for $[(MeCpMo)_2(SC_2H_2S)(S_2CSMe)]I$ (13 pages). Ordering information is given on any current masthead page.

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(17) Rakowski; BuBois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245.

(18) Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114.

(19) Previous examples of an expanded molybdenum coordination sphere have been reported in cluster syntheses. See, for example: Cowans, B.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1983**, *2*, 931.

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Facile Reductive Cleavage of the C=O Bond of Acyl Halides and the C≡N Bond of Nitriles by Hydrogen in the Presence of Sulfido-Bridged Molybdenum Complexes

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We have recently reported that cationic dinuclear molybdenum complexes of the type $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)]^+$ undergo unusual reactions with molecular hydrogen to form protons and types of molybdenum and organic products which vary depending on the nature of R.[1,2] We report here extensions of this reactivity which result in the reductive cleavage of the C=O and C≡N bonds in acyl halides and nitriles, respectively, under mild homogeneous conditions.

Although many organic halides react with $(CpMo\mu\text{-}S)_2S_2CH_2$ (I) to form the cationic derivatives of the type discussed above,[1,3] acyl halides do not form isolable sulfur-acylated cations. However, when a solution containing complex I and excess acyl halide is placed under an atmosphere of hydrogen at room temperature, two competing reactions are observed by ^1H NMR spectroscopy. One is the hydrogenolysis of the acyl halide to the corresponding aldehyde catalyzed by I. The second competing reaction eventually consumes all of I to form a catalytically inactive molybdenum product. The final molybdenum products have been isolated (in ca. 80% yield) from reactions with acetyl halides and benzoyl chloride and identified by NMR as derivatives of low symmetry. For example, the NMR spectrum for the product of the reaction with acetyl bromide shows two cyclopentadienyl resonances at 6.74 and 5.69 ppm. The methanedithiolate ligand is represented by an AX pattern with doublets at 7.16 and 5.31 ppm. A singlet at 2.57 ppm is assigned as the methyl resonance.

Single crystals of the bromide salt of this product were obtained by addition of pentane to an ethanol solution, and an X-ray diffraction study has been completed.[4] The product, which is pictured in Figure 1, is a salt of composition $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br\cdot{}^1/_2EtOH$ (II). The cation contains a bridging dithioacetate ligand which is coordinated to Mo(2) through the two sulfur atoms and to Mo(1) through the two sulfur atoms and the chelated carbon atom of the ligand. The ligand is approximately planar. Selected bond distances and angles are presented with Figure 1. The structural parameters are similar to those observed for a related cationic complex.[5] The structure provides another example of the ability of the molybdenum ion in these complexes to function as a Lewis base and thereby stabilize the formation of an unusual electron-deficient dithiolate ligand.[5]

A possible mechanism for the cleavage of the carbon-oxygen bond in the acyl group is shown in Scheme I. The cationic derivative A has been detected by NMR spectroscopy in the presence of excess acyl halide and in the absence of hydrogen. Intermediate A is proposed to react with hydrogen by a pathway analogous to those of related cations.[1,2] Intramolecular S-H addition to the carbonyl group would form a ethanol-1,1-dithiolate

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(1) Laurie, J. C. V.; Duncan, L.; Weberg, R. T.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234.

(2) Weberg, R. T.; Laurie, J. C. V.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6242.

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(4) $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br$ crystallized in space group $P2_1/c$ with cell dimensions a = 13.9834 (32) Å, b = 8.1974 (15) Å, c = 15.9709 (34) Å, β = 90.721 (18)°, and V = 1830.6 $Å^3$, Z = 4, ρ_{calcd} = 2.13 g/cm^3. From a crystal of dimensions 0.27 × 0.38 × 0.50 mm, 11 139 reflections were measured at values of $\pm h$, $+k$, and $\pm l$ over a 2θ range of 4.0–60.0°. These were averaged to 5379 independent reflections (R_{av} = 0.016). Full-matrix least-squares calculations on 204 variables using 3522 observed reflections ($F_o > 6.0\sigma(F_o)$) converged with residuals of R = 0.033 and R_w = 0.041.

(5) Wright, L. L.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *J. Am. Chem. Soc.*, preceding paper in this issue.

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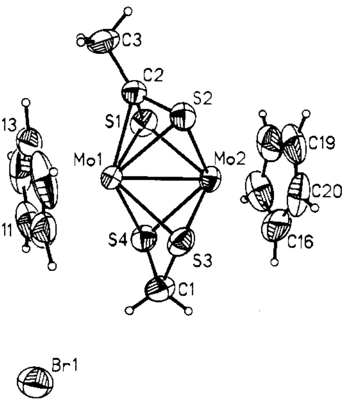
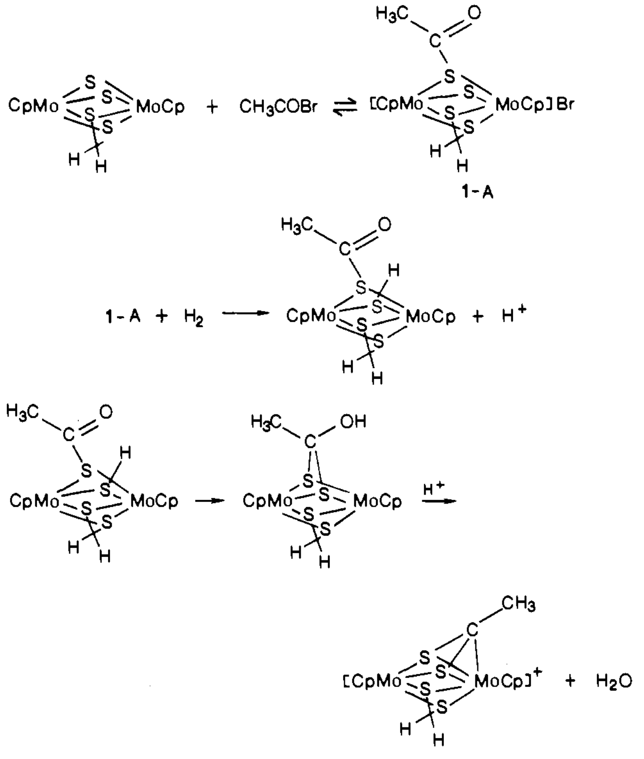


Figure 1. Perspective view and numbering scheme for [(CpMo)$_2$(S$_2$CH$_2$)(S$_2$CCH$_3$)]Br. Thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å): Mo$_1$–Mo$_2$, 2.635 (1); Mo$_1$–C$_2$, 2.224 (4); C$_2$–S$_1$ 1.735 (5); C$_2$–S$_2$, 1.733 (4); C$_2$–C$_3$, 1.502 (6); Mo$_1$–S$_1$, 2.436 (1); Mo$_1$–S$_2$, 2.442 (1); Mo$_2$–S$_1$, 2.426 (1); Mo$_2$–S$_2$, 2.429 (1). Selected angles (deg): S$_1$–C$_2$–S$_2$, 108.9 (2); S$_1$–C$_2$–C$_3$, 124.1 (3); S$_2$–C$_2$–C$_3$, 124.3 (4); Mo$_1$–C$_2$–C$_3$, 131.5 (3).

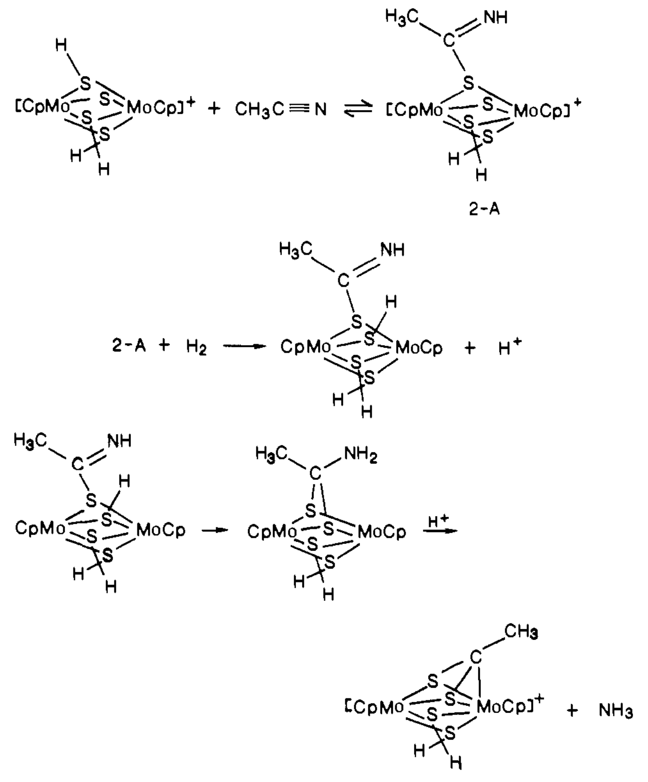
Scheme I

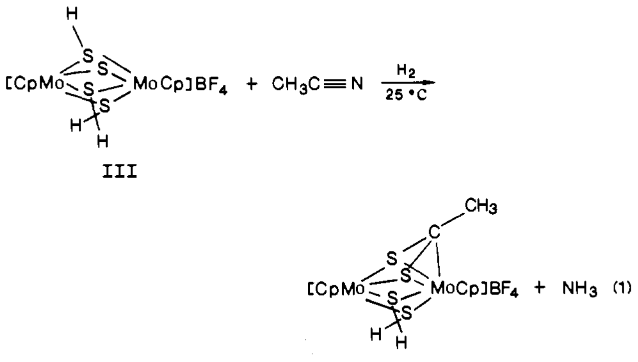


ligand which is expected to undergo facile dehydration in the presence of acid.[6]

In order to apply the hydrogen activating ability of the cationic derivatives to substrates other than organic halides, we have begun to investigate the reactivity of a related dinuclear cation where R = H. When 1-2 equiv of strong acid (HBF$_4$·Et$_2$O or HOSO$_2$CF$_3$) are added to a slurry of I in acetonitrile, a red soluble complex is formed which has been isolated and characterized as [(CpMo)$_2$(S$_2$CH$_2$)(μ-S)(μ-SH)]X (III).[7] Complex III is stable at room temperature in acetonitrile solution under nitrogen. However, when an acetonitrile solution of III is stirred under hydrogen (1 atm) at room temperature, we observe over a period of several hours the formation of complex II which has been isolated in 80% yield as the BF$_4$ salt and identified by ^{1}H NMR and mass spectroscopy (eq 1). Ammonia (0.88 equiv/equiv of complex III) has also been detected as a product of this reaction by the indophenol test.[8] Analogous reactions have been characterized with deuteroacetonitrile, propionitrile, and benzonitrile to form, in each case, ammonia and the cations with μ-η^2,η^3-CD$_3$CS$_2$, CH$_3$CH$_2$CS$_2$, and C$_6$H$_5$CS$_2$ ligands.[9]

Scheme II





III

II

By analogy to previous reactions, we propose that the cleavage of the C≡N bond involves the activation of hydrogen by a cationic derivative (e.g., III or intermediate 2-A) and stepwise S–H additions. One such sequence is shown in Scheme II.

The facile reductive cleavage of carbon–oxygen and carbon–nitrogen multiple bonds presented here represents a working model for the types of reactions which occur on sulfided molybdenum surfaces in the commercial hydrotreating catalysts.[10] The ne-

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(6) The water produced in this system reacts with excess acetyl halide to form acetic acid, which has been observed by NMR.

(7) Complex IV is precipitated as a red solid by reducing the solution volume and adding diethyl ether. The product was filtered, washed liberally with ether to remove excess acid, and dried in vacuo. Yield 90–95%; IR (Nujol) 2420 cm^{-1} (ν_{S-H}, weak); ^{1}H NMR (CF$_3$SO$_3$ salt, CD$_3$CN) δ 7.08 (s, 10, Cp), 4.14 (s, 2, S$_2$CH$_2$), the SH proton was not observed; mass spectrum (FAB), m/e 465 (P of cation); 419 (P − SCH$_2$)$^+$. Anal. Calcd for C$_{12}$H$_{13}$F$_3$Mo$_2$O$_3$S$_5$: C, 23.46; H, 2.13; S, 26.09. Found: C, 23.47; H, 2.27; S, 26.18.

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(9) The cations with the dithiopropionate and dithiobenzoate ligands have been isolated and characterized by ^{1}H NMR, mass spectral data, and (for R = Et) elemental analyses (supplementary material). The amount of ammonia detected was 0.94 equiv (from propionitrile) and 0.70 equiv (from benzonitrile).

cessity for a Brönsted acid in these model processes is particularly noteworthy since both the source and role of Brönsted acid sites on the surface catalysts have been the subject of considerable speculation.[11] The facile S-H additions in the systems presented here also suggest intriguing mechanistic possibilities for the reduction of nitriles and other substrates of nitrogenase, in which a sulfido-bridged molybdenum iron cluster is proposed as the active site.[12]

Acknowledgment. We thank the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U. S. Department of Energy, and the National Institutes of Health for support of this work. M.R.D. is grateful for a Dreyfus Fellowship, 1981-1986, and a John Simon Guggenheim Fellowship, 1984-1985.

Supplementary Material Available: Crystal data and details of the structural determination and tables of bond distances, bond angles, and atomic and thermal parameters for $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br\cdot{}^1/_2EtOH$ and characterization data for cationic molybdenum derivatives (10 page); table of observed and calculated structure factors for $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br\cdot{}^1/_2EtOH$ (32 pages). Ordering information is given on any current masthead page.

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[4 + 2] Cycloaddition of Azodicarboxylate and Glycals: A Novel and Simple Method for the Preparation of 2-Amino-2-deoxy Carbohydrates

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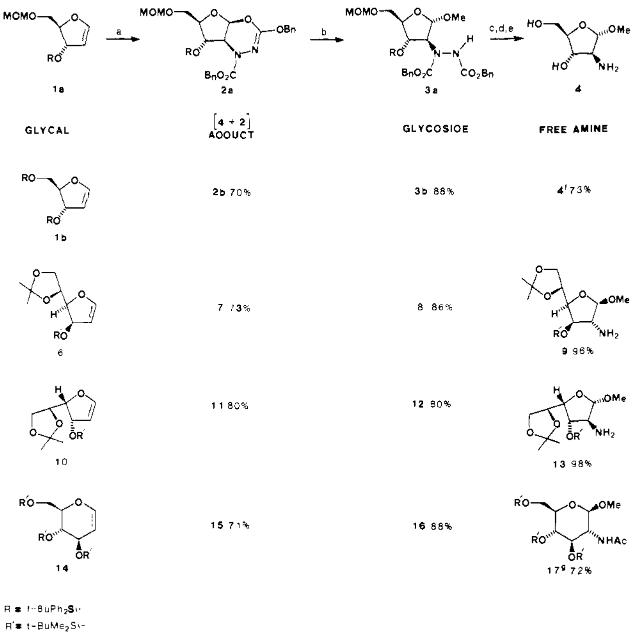
The amino sugars are an important group of natural products. These molecules are widely distributed in nature, being found in almost all living creatures, and play diverse biologically important roles. While the amino sugar is often part of a larger molecule, its presence is usually important to the biological function. Examples of important molecules containing amino sugars are aminosaccharide antibiotics,[1] antigenic determinants,[2] glycoproteins, and glycolipids.[3]

Despite their ubiquitous nature, few methods exist for the preparation of amino sugars. The most stereoselective method for the synthesis of amino sugars is a S_N2 displacement of an epoxide or sulfonate ester by azide or ammonia.[4] However, this reaction requires selective derivatization and in the sulfonate ester case is often not possible at C-2. An amino group may also be introduced by reduction of carbon-nitrogen double bond[5] or by oxy-amination of a double bond.[6-8] These methods, while being widely used, can lead to stereo- and/or regioisomers. Therefore a method which would allow the stereo- and regioselective introduction of a nitrogen to a carbohydrate derivative leading to only one amino sugar would be of considerable utility.

Scheme I[a]



[a] (a) $BnO_2C—N{=}N—CO_2Bn$, cyclohexane, CH_2Cl_2, 350 nm, 18 h (73%); (b) p-$TSOH\cdot H_2O$, MeOH (95%); (c) Raney Ni, W-2, H_2 40PSI, MeOH-AcOH (60:1) (80%); (d) n-Bu_4NF, THF (95%); (e) AcCl, MeOH (4 N HCl) (95%); (f) the hydrogenolysis was performed on the free diol obtained by desilylation of compound **3b** (n-Bu_4NF 10 equiv AcOH 3 equiv THF, 90%); (g) The free amine was converted to its N-acetate by treatment with acetic anhydride.

Herein we report a novel, simple, and mild method for the stereoselective introduction of a nitrogen functionality and the subsequent transformation of the products of this reaction into 2-amino glycosides. The cycloaddition of azodicarboxylates on simple vinyl ethers was first reported in 1969[9] to give [4 + 2] and/or [2 + 2] adducts, depending on the substrate. This reaction was thoroughly studied from a mechanistic point of view on simple substrates. For this reaction to be synthetically useful a high diastereoselectivity would be desirable. It was felt that this diastereoselectivity would be most readily attainable with a rigid substrate having an appropriately placed substituent, such as an allylically substituted cyclic vinyl ether. Carbohydrate-derived glycals meet these criteria well, since a stereoselective cycloaddition between an azodicarboxylate and a glycal would give a convenient method to introduce an amino function at C-2 of a carbohydrate. This approach was taken to explore the synthetic utility of this reaction.

The glycals **1a**, **6**, and **10** were prepared by the procedure of Ireland et al.[10] The glycal **1b** was prepared by dehydration of 3,5-di-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-D-ribofuranose (**5**)[11,12]

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(12) The lactol **5** was prepared starting from the methyl 2-deoxy-D-ribofuranoside. The diol was protected as its bis(*tert*-butyldiphenylsilyl ether). Subsequent hydrolysis of the methyl furanoside using a mixture of $ACOH/THF/H_2O$ (7:2:2) at 65 °C for 6 h gave the lactol **5**.

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