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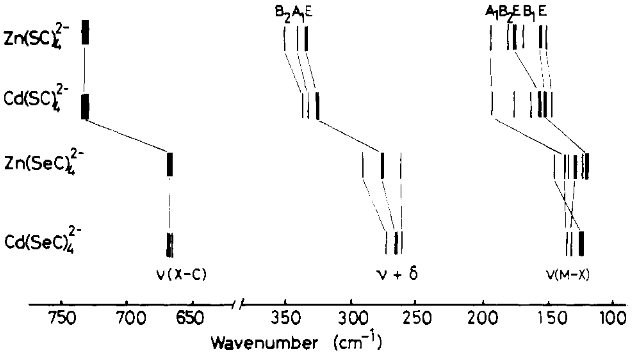

Figure 6. Calculated vibrational frequencies of ideal D_{2d} [M(X—C=)$_4$]$^{2-}$ (M = Zn(II), Cd(II), X = S, Se). The following parameters were employed for the normal-coordinate analysis. Bond lengths: Zn–S = 2.36 Å, Cd–S = 2.54 Å, Zn–Se = 2.47 Å, Cd–Se = 2.65 Å, S–C = 1.76 Å, Se–C = 1.90 Å. Bond angles: Zn–S–C = 109.35°, Cd–S–C = 107.59°, Zn–Se–C = 106.95°, Cd–Se–C = 105.03°. Force constants:[23-25] K_γ(M–X) = 0.60 mdyn/Å, K_γ(X–C) = 2.75 mdyn/Å, H_θ(X–M–X) = 0.31 mdyn Å/rad^2, H_θ(X–C) = 1.39 mdyn Å/rad^2, F_R(M–X,M–X) = 0.14 mdyn/Å, F_R(M–X,X–C) = 0.17 mdyn/Å, $F_{R\theta}$(M–X,X–M–X) = 0.128 mdyn/rad, $F_{R\theta}$(M–X,M–X–C) = 0.128 mdyn/rad, $F_{R\theta}$(X–C,M–X–C) = 0.128 mdyn/rad, T(M–X,X–C) = 0.1 mdyn Å/rad.

tively.[21] Haberkorn et al. reported the Cd–S Raman bands at 197 and 160 cm^{-1} for [Cd$_{10}$(SCH$_2$CH$_2$OH)$_{16}$][ClO$_4$] and at 190 and 168 cm^{-1} for Cd(SCH$_2$CH$_2$OH)$_2$.[22]

Normal-Coordinate Analysis. For the assignment of the vibrational frequencies of these four complexes, the normal coordinate analysis was carried out by using the lattice Vibration Program.[23] For a simple calculation of the frequencies in the region 800–100 cm^{-1}, a point carbon atom was employed, in stead of the phenyl group, as [M(XC=)$_4$]$^{2-}$ (M = Zn, Cd, X = S, Se) in the calculation because of the convenient analysis of M–S frequencies in the 800–100-cm^{-1} region. The coordinate parameters obtained by the X-ray analysis were used. The force constants were obtained by fitting the observed values in the reference with the literature values for the related compounds.[23-25] The same force constants (Figure 6) were utilized for the normal-coordinate analysis to compare the M–X bond character. A D_{2d} structure was adopted as an ideal geometry because it has the highest symmetry for the [M(XPh)$_4$]$^{2-}$ structure. Figure 6 shows the calculated vibrational frequencies if ideal D_{2d} [M(X—C=)$_4$]$^{2-}$. The Raman band in **1** and **2** (695–698 cm^{-1}) or **3** and **4** (666–667 cm^{-1}) is assigned to ν(X–S). An M–Se stretching vibration (A$_1$) of **3** and **4** also shifts to lower frequency (120-cm^{-1} shift). The vibrational frequencies for the four complexes with C_2 point symmetries were calculated by using the coordinates obtained by the X-ray analysis and compared with the above results for the D_{2d} structure. The calculated M–X stretching frequencies are in good agreement with the observed bands and support the assignment in Table VII. Thus, no significant difference in M–X stretching bands (A$_1$ and A) between D_{2d} and C_2 was found. Therefore, the M–X stretching band (A) is not suitable as a monitor for the distortion from D_{2d} to C_2. For the vibrational frequencies of phenyl ring, two bands at 750 and 618 cm^{-1} for **1**–**4** were assigned.

In the cases of native proteins, a distorted ZnS$_4$ core in pseudo-C_2 symmetry has been found for the [Zn(cys-*S*)$_4$]$^{2-}$ core of horse liver alcohol dehydrogenase.[2,26] The less distorted ZnS$_4$ core in pseudo-D_{2d} symmetry has been reported for aspartate carbamoyltransferase.[3,26] Likewise, rubredoxin has a pseudo-D_{2d} structure around the active site, [Fe(cys-*S*)$_4$]$^-$.[4] These alternative structures are probably fixed with different peptide conformations due to the characteristic amino acid fragments such as Cys-X-Y-Cys for aspartate carbamoyltransferase and rebredoxin, and Cys-X-Y-Cys-A-B-Cys for horse liver alcohol dehydrogenase.

In conclusion, distinguishable distorted-tetrahedral structures were found for the MX$_4$ cores of **1**–**3** and only a slight distortion was found for **4**. The X-ray analyses of **1**–**4** indicate C_2 geometries for [M(XPh)$_4$]$^{2-}$. M–X stretching bands (A) for **1**–**4** were assigned by the polarized Raman spectral method and the normal-coordinate analysis.

Acknowledgment. We thank Professor Masamichi Kobayashi and Dr. Kohji Tashiro for the normal-coordinate analysis.

Registry No. **1**, 76915-22-5; **2**, 82677-50-7; **3**, 112247-25-3; **4**, 112247-26-4; (trimethylsilyl)selenophenol, 33861-17-5.

Supplementary Material Available: Listings of complete atomic parameters and anisotropic thermal parameters for **1**–**4** (10 pages); listings of observed and calculated structure factors for **1**–**4** (44 pages). Ordering information is given on any current masthead page.

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Notes

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Reactions at a Dimolybdenum(V) Sulfur Bridge. Alkyne Additions

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Addition reactions of metal sulfide, hydrosulfide, disulfide, and higher polysulfide complexes with alkenes and alkynes have recently revealed a variety of product types. Some products are characterized as arising from formal S,S-addition to unsaturated substrates and contain 1,2-alkanedithiolate and 1,2-alkenedithiolate ligands.[1-16] M,S-addition (M = metal) to alkynes has been shown to give alkene disulfide complexes wherein the ligand is bound to the metal via carbon and sulfur.[15-18] Formal S,H-addition to

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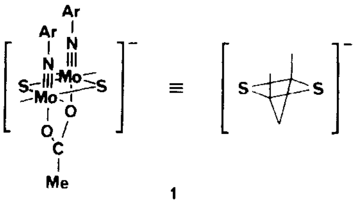
alkenes and alkynes has produced alkanethiolate and alkenethiolate ligands, the latter sometimes capable of undergoing a second S,H-addition to give alkanedithiolate products.[13,19-24] Although most of the reactions studied can be classified as one of these three types of additions, and while most also involve overall 1,2-addition, distinct permutations have also been demonstrated.[11,12,18,19,23]

Most, but not all,[24] of the S,H-addition types follow classical nucleophilic thiol addition chemistry.[25] Commonly for the metal systems, a sulfide-bridged dimer is reacted with alkene or alkyne and subsequently protonated,[13,20,22] or a hydrosulfide bridge reacts with substrate in the presence of base.[19,21,23] The nucleophilic aspect of this additivity became of interest for studies using the anion $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(O_2CMe)]^-$ (**1**),[26] which contains an imido(dithiophosphato)molybdenum(V) dimer bridged by sulfide and carboxylate ligands. This anion, generated in situ by an equilibrium between $[Mo(NAr)(S_2P(OEt)_2)S]_4$ and carboxylate anion,[27] has demonstrated its sulfur-based nucleophilicity in reactions with alkyl halides and sulfur halides, which have given S-derivatized dimers, $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SZ)]$ (**2**).[28,29] It was this nucleophilic character that prompted the present investigation into addition reactions with alkynes.



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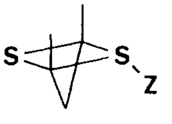


2

Experimental Section

Commercial reagents were used as received except as noted. $^{31}P\{^1H\}$ and ^1H NMR spectra were obtained in $CDCl_3$ on a Varian XL-300 spectrometer at 121 and 300 MHz and are referenced to 85% H_3PO_4 and Me_4Si, respectively. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 283 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

$[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SC(CO_2Me)CHCO_2Me)]$. To a solution of $[Mo(NAr)(S_2P(OEt)_2)S]_4$[27] (0.4022 g, 0.240 mmol), $MeCO_2H$ (0.114 mL, 2.0 mmol), and Et_3N (0.070 mL, 0.50 mmol) in CH_2Cl_2 (4 mL) was added dimethyl 2-butynedioate (0.155 mL, 1.26 mmol). After it was stirred for 4 h, the solution was rotavaporated and the resulting residue was dissolved (THF) and filtered; the filtrate (3 mL) was treated with 2/1 $MeOH/H_2O$ (10 mL). The precipitate was filtered, washed (4/1 $MeOH/H_2O$), and vacuum-dried, giving orange crystals (0.2994 g, 60%). Anal. Calcd for $C_{30}H_{44}N_2O_{10}P_2S_6Mo_2$: C, 34.7; H, 4.3; S, 18.5. Found: C, 34.6; H, 4.2; S, 18.8. NMR data are as follows (ppm).[30] ^{31}P: 115.2, (114.8). ^1H: 6.97 s, (6.87 s), SCCH; (6.73 d), 6.60 d, 6.48 d, Ar H; 4.21–3.95 m, $POCH_2$ + (OCH_3); 3.91 s, 3.69 s, OCH_3; 2.09 s, Ar CH_3; 1.31 t, 1.21 t, $POCCH_3$; 1.26 s, μ-O_2CCH_3. Selected IR bands (cm^{-1}): 1731 s, 1532 m, 1444 s, 1036 sh, 1010 vs, 962 s, 817 s, 787 m.

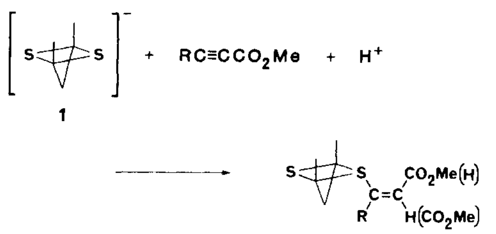
$[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCHCHCO_2Me)]$. This derivative was prepared by using reagents and quantities similar to those above, but with methyl 2-propynoate (0.057 mL, 0.64 mmol) as the alkyne. After it was stirred for 1 h, the solution was rotavaporated, and the residue was then treated with MeOH (5 mL). Filtration gave a clean but stereoisomerically mixed product (84%) with a cis/trans ratio of 4.5. Recrystallization from a THF filtrate (2 mL) using MeOH (3 mL) gave a solid (65% recovery) with a cis/trans ratio of 14. A final recrystallization from THF (2 mL) and MeOH (4 mL) gave orange crystals (71% recovery; 39% overall yield) with a cis/trans ratio of 19. Anal. Calcd for $C_{28}H_{42}N_2O_8P_2S_6Mo_2$: C, 34.3; H, 4.3; S, 19.6. Found: C, 34.4; H, 4.3; S, 19.7. NMR data are as follows (ppm).[30] ^{31}P: (115.3), 114.9. ^1H: (6.74 d), 6.69 d, (6.63 d), 6.50 d, Ar H; (6.60 d), 6.35 d, SCH; 6.37 d, (6.03 d), SCCH; 4.21–3.96 m, $POCH_2$; 3.93 s, (3.92 s), OCH_3; (2.16 s), 2.09 s, Ar CH_3; (1.32–1.15 m) $POCCH_3$ + μ-O_2CCH_3; 1.31 t, 1.20 t, $POCCH_3$; 1.28 s, μ-O_2CCH_3. Selected IR bands (cm^{-1}): 1726 m, 1543 m, 1448 s, 1048 sh, 1010 vs, 962 s, 817 s, 798 m, 790 m.

A sample enriched in the trans isomer was obtained by slurrying a mixed product (0.1006 g, cis/trans = 4.1) in EtOH (3 mL) for 4 h. After filtration, the filtrate was stripped to give a residue with a cis/trans ratio of 0.6. NMR data for the trans isomer, were clearly discernible from the cis, are as follows (ppm).[30] ^{31}P: (114.9), 114.6. ^1H: (7.43 d), 7.14 d, SCH; (6.77 d), 6.74 d, SCCH; (6.69 d), 6.59 d, (6.56 d), 6.48 d, Ar H; 4.22–3.95 m, $POCH_2$; 3.71 s, (3.60 s), OCH_3; (2.13 s), 2.09 s, Ar CH_3; 1.34–1.14 m, $POCCH_3$ + μ-O_2CCH_3.

$[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCH_2Cl)]$. On a vacuum line under N_2, a solution of $[Mo(NAr)(S_2P(OEt)_2)S]_4$ (0.4086 g, 0.244 mmol), $MeCO_2H$ (0.114 mL, 2.0 mmol), and Et_3N (0.140 mL, 1.0 mmol) in dry CH_2Cl_2 (4 mL) was stirred 24 h. Opened to air, the solution was rotavaporated, and the resulting residue was dissolved in THF and filtered. The filtrate (5 mL) was treated with 2/1 $MeOH/H_2O$ (5 mL), and the precipitate was collected. Recrystallization from THF (2 mL) and 2/1 $MeOH/H_2O$ (4 mL) gave orange-red crystals (0.3190 g, 69%). Anal. Calcd for $C_{25}H_{39}N_2O_6P_2S_6ClMo_2$: C, 31.9; H, 4.2; S, 20.4. Found: C, 31.8; H, 4.0; S, 20.7. NMR data are as follows (ppm).[30] ^{31}P: 114.9, (114.9, 8 Hz upfield of major invertomer). ^1H: (6.77 d), (6.62 d), 6.59 d, 6.48 d, Ar H; (4.81 s), 4.23 s, SCH_2Cl; 4.23–3.98 m, $POCH_2$; (2.15 s), 2.08 s, Ar CH_3; 1.33 t, 1.21 t, (1.20 t), $POCCH_3$; 1.28 s, (1.22 s), μ-O_2CCH_3. Selected IR bands (cm^{-1}): 1533 m, 1444 s, 1048 sh, 1009 vs, 963 vs, 818 s, 798 m, 728 w.

Results and Discussion

Reactions of the dimer anion **1** with dimethyl 2-butynedioate or methyl 2-propynoate in the presence of excess acid resulted in formal S,H-addition to the alkyne to give the corresponding S-bridged alkenethiolate complexes $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCRCHCO_2Me)]$ (**3**; eq 1, R = CO_2Me, H). Elemental analyses, IR spectroscopy, and ^{31}P and ^1H NMR spectroscopy were fully consistent with the formulations. Ester car-



(1)

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(30) Where the minor invertomer is clearly discernible, these values are given in parentheses. All integrations were consistent.

bonyl bands were clearly seen in IR spectra at 1731 cm^{-1} (R = CO_2Me) and 1726 cm^{-1} (R = H), in addition to the usual dimer absorptions.[28] For ^1H NMR spectra, the vinyl proton assignments were unambiguous due to the use of $MeCO_2D$ in alternate syntheses, which gave the deuterioalkene derivative. Deuteriation gave the expected loss of SCCH alkene resonances for both products and resulted in a singlet for the SCH alkene resonance in the methyl propenoate derivative. The ^1H and ^{31}P NMR spectra also showed invertomers for both products in solution arising from inversion of the pyramidal sulfur bridge, a characteristic previously documented for other derivatives (**2**).[28]

For the dimethyl butenedioate product **3** (R = CO_2Me), invertomers were observed in a ratio of 2.5 with the major isomer as depicted by **3**, based on earlier conformational studies.[28] Coalescence in the ^{31}P NMR spectrum by 50 °C supports the assignments as invertomers and contraindicates the possibility that the two resonances are due to cis/trans isomers for this derivative. Indeed, no evidence for such stereoisomers was ever observed, and the actual stereochemistry of this product cannot be assigned on the basis of spectral data alone.

For the methyl propenoate product **3** (R = H), cis/trans isomers are indeed observed, each with its own pair of invertomers. The cis/trans mixed product is obtainable in high yields from the reaction and in ratios of approximately 4/1, but separation is difficult and has never been achieved in toto for either stereoisomer. Repeated recrystallization gives the cis isomer in high purity (~95%) but low overall yield. The trans derivative was never obtained in high purity and could at best be obtained as an enriched sample through EtOH digestion of mixed products. Attempts at column chromatography also failed to provide separation. Assignment of the major product as the cis isomer was based on $^3J_{HH} = 10$ Hz for the alkene protons, compared to $^3J_{HH} = 15$ Hz for those of the minor derivative (trans isomer). Such assignments are fully consistent with established vicinal couplings for alkenes[31] and parallel recent stereochemical conclusions regarding cyclopentadienylmolybdenum S,H-additions to ethyl 2-propynoate.[20,24] The major product therefore arises from trans addition across the alkyne triple bond and reflects the common stereochemistry of thiol addition to alkynes.[25] Invertomer ratios for the stereoisomers are 3.8 (cis) and 1.9 (trans), the major invertomer again being assigned the conformation at the pyramidal sulfur as given by **3**.

While dimethyl 2-butynedioate and methyl 2-propynoate readily gave addition products as per eq 1, no alkene products were observed for attempted reactions with acetylene, 1-hexyne, 4-octyne, diphenylacetylene, ethyl 3-phenyl-2-propynoate, or methyl 2-butynoate, suggesting that reaction was facile only with the most activated and sterically uninhibited alkynes. The reactions attempted with these alternate substrates gave only $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCH_2Cl)]$ (**2**, Z = CH_2Cl), which arises from nucleophilic substitution on solvent dichloromethane. This solvent reaction is notably slow and had posed no problem with earlier work on readily substituted substrates[28] but did interfere with the slower synthesis of $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SEt)]$ (**2**, Z = Et), which therefore required a different solvent.[29] The chloromethanethiolate-bridged dimer gives an invertomer ratio of 1.5 in $CDCl_3$. A peak at 728 cm^{-1} in the IR spectrum is tentatively attributed to a C–Cl stretch.

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Registry No. **3** (R = CO_2Me), 112246-91-0; *cis*-**3** (R = H), 112295-33-7; *trans*-**3** (R = H), 112196-28-8; $[Mo(NAr)(S_2P(OEt)_2)S]_4$, 73037-71-5; $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCH_2Cl)]$, 112196-29-9; S, 7704-34-9; CH_2Cl_2, 75-09-2; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; methyl 2-propynoate, 922-67-8.

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The SMo_2SSR Unit. Cyanide Reactions and Crystal Structure

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Metal–sulfur complexes containing S–S bonds within the ligand framework have been the subject of much interest in recent years. Disulfide (S_2^{2-}), higher polysulfides (S_x^{2-}) and disubstituted organic disulfides (RSSR) have amply demonstrated ligative properties to metals and a large variety of structures and reactivities have been demonstrated.[1-5] Perthio chelates are also well-known in which a normal sulfur bidentate has one or more additional sulfurs in the chelate ring.[5-12]

Less developed are perthio derivatives of simple thiolates representable as RSS^-. Consideration of these ligands is a natural extension of the interest in M–S–S systems; furthermore, their roles as intermediates in thiolate–disulfide interconversions have been proposed for molybdenum systems[13,14] and have been more definitively established for reactions of $(C_5H_5)W(NO)R_2$ with sulfur.[15,16] A modest number of M–SSR complexes have been described.[5,15-25]

Compounds of the general formula $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR)]$ (**1**, R = Et, Bz, Ph, To;[26] dithiophosphate ligands are excluded from structure diagrams for clarity) have been previously reported and contain an imido(di-

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(26) Abbreviations used in this paper: Me, methyl; Et, ethyl; Bu, *n*-butyl; Ph, phenyl; To, *p*-tolyl; Bz, benzyl.

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