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Reactions at a Dimolybdenum(V) Sulfur Bridge. Formation of Disulfide (S_2^{2-}), Monosubstituted Organic Disulfide (RSS^-), and Tetrasulfide (S_4^{2-}) Bridges

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Compounds of the general form $[Mo_2(NAr)_2(S_2P(OC_2H_5)_2)_2S(O_2CR)]_2(S_2)$ (Ar = C_6H_5, p-$C_6H_4CH_3$; R = alkyl, aryl) were prepared by the reaction of $[Mo(NAr)(S_2P(OC_2H_5)_2)S]_4$ with H_2O_2 in the presence of a carboxylic acid. The compounds contain a disulfide linkage bridging in inter- and intradimer fashion, formed by the oxidation of two $Mo_2S_2^{6+}$ cores to give SMo_2SSMo_2S, formally equivalent to $SMo_2S^\bullet$ thiyl radical coupling. Mixed dimer–organic disulfides were prepared by the reaction of $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2S_2(O_2CCH_3)]^-$ with sulfenyl chlorides, R′SCl (R′ = alkyl, aryl). The products, $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2S(O_2CCH_3)(SSR')]$, contain an unusual $R'SS^-$ linkage to the two Mo(V) sites within the dimer, representable by SMo_2SSR', wherein the monosubstituted organic disulfide ion bridges by its β-sulfur. A bridge tetrasulfide, $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2S(O_2CCH_3)]_2(S_4)$, was prepared by the reaction of $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2S_2(O_2CCH_3)]^-$ with S_2Cl_2 and contains the $SMo_2SSSSMo_2S$ unit, in which the tetrasulfide bridges also in inter- and intradimer fashion via its terminal sulfur atoms. Most of the compounds show stereoisomers related by bridge sulfur inversion. Reactions with triphenylphosphine gave either desulfurization or reduction.

Introduction

While biological nitrogenase and industrial hydrodesulfurization have spurred interest in molybdenum–sulfur chemistry in recent years,[1-5] so also has the variety of structural types and diverse reactivities observed thus far for sulfidomolybdenum[6-9] contributed to attention in this area. Particularly noteworthy is the noninnocence of bound sulfide in reactions that have thus far shown binding of substrate at sulfur and electronic interconversions of sulfido/disulfido configurations.[9-13]

The current work was initiated to investigate oxidative chemistry of an imido sulfido dithiophosphate oligomer of molybdenum(V). The previously structurally characterized[14] Mo_4S_4 cubane $[Mo(NTo)(S_2P(OEt)_2)S]_4$[15] was shown to dissociate into identical Mo_2S_2 dimers in an equilibrium (eq 1) displaced greatly to the

$$[Mo(NTo)(S_2P(OEt)_2)S]_4 \rightleftharpoons 2[Mo(NTo)(S_2P(OEt)_2)S]_2 \quad (1)$$

left as written, in ClC_2H_4Cl[16] and CH_2Cl_2.[17] Equilibria with a carboxylic acid to give a hydrosulfide-bridged dimer (eq 2) and

$$[Mo(NTo)(S_2P(OEt)_2)S]_4 + 2RCO_2H \rightleftharpoons 2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CR)(SH)] \quad (2)$$

a carboxylate salt to give a dimer anion (eq 3) have also been

$$[Mo(NTo)(S_2P(OEt)_2)S]_4 + 2RCO_2^- \rightleftharpoons 2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CR)]^- \quad (3)$$

established.[18] Location of the acid proton in eq 2 on the bridge sulfur[18] and S-alkylation reactions of the dimer anion with alkyl halides[19] suggested an appreciable electron availability at the bridge chalcogen. The present investigation was directed at formal one-electron, chemical oxidation of the dimer anion species $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(O_2CR)]^-$, as such or as $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CR)(SH)]$. The interest here was an attempt to generate the neutral dimer radical $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(O_2CR)]^\bullet$ and to investigate its properties. Formally, the dimer radical would contain Mo(V)–Mo(VI), but what was instead realized was a series of diamagnetic compounds characterized by the formation of bridge disulfide linkages. Subsequent to this observation, several other complexes were prepared containing monosubstituted organic disulfide bridges and a tetrasulfide bridge. The results are described herein.

Experimental Section

The majority of operations involved no significant measure of air exclusion. Those stated as performed under N_2, however, were conducted on a vacuum line, using dried and vacuum-transferred solvents subsequently stored under N_2.

$[Mo(NTo)(S_2P(OEt)_2)S]_4$ was prepared as previously described;[18] $[Mo(NPh)(S_2P(OEt)_2)S]_4$ was prepared analogously.[17,20] *N*-Chlorosuccinimide (NCS) was recrystallized from chloroform/ethanol/petroleum ether. Other reagents were used as commercially available. Aqueous H_2O_2 concentrations were measured and varied from 9% to 13%. S_2Cl_2 was dispensed in a glovebag under N_2.

$^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Varian XL300 spectrometer at 121 and 300 MHz, respectively, and are reported as downfield shifts from external 85% H_3PO_4 and internal Me_4Si, respectively. Solvent was $CDCl_3$ except where noted. Results are shown in Table I. IR spectra were obtained as KBr pellets on a Perkin-Elmer 283 spectrophotometer over the 4000–200-cm^{-1} range. Representative absorptions are listed in Table II. Galbraith Laboratories, Inc. (Knoxville, TN) performed the elemental analyses and the molecular weight determination.

Red light conditions, where indicated below, involved the lack of any white room lights and the shading of doors and windows. The shading was not rigorously total, and some low-level, very diffuse white light was acceptable. Illumination was provided by several clear red-coated 25-W incandescent bulbs (General Electric "Party Bulbs") in the immediate vicinity of the work area. Where not specifically stated as being under

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[15] Abbreviations used in this paper: Me, methyl; Et, ethyl; Pr, *n*-propyl; Hp, *n*-heptyl; Ph, phenyl; To, *p*-tolyl; Bz, benzyl; Tr, trityl (CPh_3); Ar, aryl group.

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Table I. ^{31}P and ^{1}H NMR Data[a]

		$\delta(^1H)$						
		arylimido		diethyl dithiophosphate				
	$\delta(^{31}P)$	H	CH_3	CH_2	CH_3	carboxylate	μ-S substituent	stereoisomer ratio[b]
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CR)]_2(S_2)$								
R = Me	(115.8)	6.93 (6.63), d	2.04, s	4.0–4.4, m	(1.40) 1.30, t	(1.56) 1.14, s		0.13
	115.3	(6.35) 6.30, s	(2.02)		1.25, t			
R = Pr	(116.4)	6.92 (6.60), d	2.05, s	4.0–4.4, m	1.28, t	1.34, t; 0.99, q		0.03
	115.8	6.31, d	(2.03)		1.26, t	0.58, t		
R = Hp	(116.4)	6.91, d	2.04, s	4.0–4.4, m	1.27, t	0.9–1.4, m		0.04
	115.7	6.31, d	(2.02)		1.26, t	0.83, t		
R = Ph	(116.6)	6.79, d	1.82, s	4.0–4.4, m	1.35, t	7.30, m		0.03
	115.9	5.94, d			1.25, t	7.14, t		
R = To	(116.7)	6.78, d	1.83, s	4.0–4.4, m	1.35, t	7.20, d; 6.94, d		0.02
	116.0	5.93, d			1.25, t	2.30, s		
R = Tr	115.4	6.97, d	2.00, s	3.1–3.5, m	1.15, t	7.1, m		none
		6.37, d		4.0, m; 4.3, m	0.92, t	6.95, t		
$[Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2)$								
	(115.7)	7.05, d; 6.70, t		4.0–4.4, m	(1.38) 1.29, t	(1.52) 1.12, s		0.17
	115.2	6.55, t			1.24, t			
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')]$								
R′ = Et	(115.1)	(6.79) 6.58, d	(2.14)	4.0–4.3, m	1.32, t	1.30, s	3.31, q	4
	114.8	6.48, d	2.09, s		1.20, t		1.70, t	
R′ = Bz	(115.2)	(6.73) 6.50, d	(2.12)	4.0–4.3, m	1.32, t	1.29, s	6.74, d; 6.52, m	6
	114.9	6.45, d	2.09, s		1.20, t		(4.59) 4.53, s	
R′ = Ph	(115.1)	(6.83) 6.55, d	(2.13)	4.0–4.3, m	1.34, t	1.37, s	7.96, d	4
	114.7	6.45, d	2.07, s		1.20, t		7.45, m	
R′ = To	(115.2)	(6.86) 6.53, d	(2.13)	4.0–4.3, m	1.35, t	1.37, s	7.85, d; 7.28, d	4
	114.8	6.44, d	2.07, s		1.20, t		2.44 (2.42), s	
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_4)$								
	(115.6)	(6.90) 6.77, d	2.08, s	3.9–4.3, m	1.34, t	1.38, s		17
	114.9	(6.56) 6.48, d			1.20, t			
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SBz)]$								
	(115.2)	(6.73) 6.52, d	(2.15)	4.0–4.3, m	1.35, t	1.32 (1.15), s	7.63, d; 7.47, t	5
	115.1	(6.59) 6.41, d	2.04, s		1.22, t		7.38, q; (4.39) 3.46, s	
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)]$[c]								
	114.7	6.70, d	2.13, s	4.0–4.3, m	1.31, t	1.25, s	2.96, s	none
		6.57, d			1.22, t			

[a] $CDCl_3$ solutions. Key: s, singlet; d, doublet; t, triplet; q, quartet; m, one or more multiplets. Where peaks attributable to the minor isomer were clearly discernible, these are enclosed in parentheses. All integrations were consistent with the formulations. [b] Defined as the ratio of distal to proximal configurations as described in the text. [c] Peaks due to $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and acetic anhydride are also clearly observed due to the equilibrium described in the text.

Table II. Representative IR Absorptions (cm^{-1}, KBr Pellets)

	$\nu(CO_2)$		diethyl dithiophosphate					
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CR)]_2(S_2)$								
R = Me	1533, m	1444, s	1047, m	1006, vs	951, vs	818, s	812, s	791, s
R = Pr	1529, m	1438, m	1038, sh	1010, vs	954, vs	814, s	789, m	
R = Hp	1527, m	1436, s	1054, m	1008, vs	954, vs	816, s	790, s	
R = Ph	1518, m	1411, vs	1034, sh	1011, vs	955, vs	815, s	774, m	
R = To	1519, m	1411, vs	1036, sh	1012, vs	957, vs	814, s	785, m	
R = Tr	1540, m	1376, s	1034, m	1013, vs	961, vs	815, s	797, m	
$[Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2)$	1534, m	1440, s	1045, sh	1008, vs	955, vs	816, m	788, s	
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')]$								
R′ = Et	1538, m	1447, s	1052, m	1005, vs	954, vs	818, s	790, s	
R′ = Bz	1535, m	1444, s	1053, m	1009, vs	965, vs	815, s	796, m	
R′ = Ph	1534, m	1442, vs	1040, sh	1006, vs	962, vs	814, s	784, m	
R′ = To	1538, m	1445, vs	1051, m	1007, vs	961, vs	813, vs	793, s	
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_4)$	1534, m	1444, s	1034, sh	1009, vs	958, vs	815, s	788, m	
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SBz)]$	1541, m	1444, s	1040, sh	1009, vs	962, vs	815, s	791, m	
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)]$	1535, m	1443, vs	1046, m	1005, vs	964, vs	815, s	795, m	784, m

red light, operations were conducted under normal laboratory fluorescent lighting.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CR)]_2(S_2)$. R = Me. Methanolic H_2O_2 was freshly prepared by diluting 50 μL of H_2O_2 (~13%, 0.20 mmol) to 1.0 mL with MeOH. To a slurry of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.2224 g, 0.133 mmol), $MeCO_2H$ (30 μL, 0.52 mmol), CH_2Cl_2 (2 mL), and MeOH (2 mL) was added a portion (0.5 mL) of the H_2O_2/MeOH solution. After 10 min of stirring, a second H_2O_2/MeOH aliquot (0.25 mL) was added, followed then successively by 5 min of stirring, addition of the remaining H_2O_2/MeOH solution (0.25 mL), and again 5 min of stirring. Through the sequential additions, the slurry turned orange, with precipitation of the orange product. Volatiles were then removed on a rotary evaporator. The solid was dissolved in CH_2Cl_2 and filtered. The filtrate (21 mL) was treated with MeOH (42 mL) to precipitate the product, which was collected, washed (MeOH), and vacuum-dried, giving orange-red crystals (0.1825 g, 77%). Anal. Calcd for $C_{48}H_{74}N_4O_{12}P_4S_{12}Mo_4$: C, 32.2; H, 4.2; N, 3.1; S, 21.5. Found: C, 32.2; H, 4.1; N, 3.0; S, 21.9.

R = Pr. The preparation was performed exactly as for R = Me, using 0.2225 g (0.133 mmol) of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and 50 μL (0.54 mmol) of $PrCO_2H$. After rotary evaporation, dissolution (CH_2Cl_2), and filtration, the filtrate (3 mL) was treated with MeOH (12 mL). Filtration, washing (MeOH), and vacuum-drying gave orange-brown crystals (0.1800 g, 73%). Anal. Calcd for $C_{52}H_{82}N_4O_{12}P_4S_{12}Mo_4$: C, 33.8; H, 4.5; N, 3.0. Found: C, 33.8; H, 4.4; N, 3.0.

R = Hp. This preparation was similar to the above but used 0.4447 g (0.266 mmol) of $[Mo(NTo)(S_2P(OEt)_2)S]_4$, 0.17 mL (1.1 mmol) of $HpCO_2H$, and double all other quantities as for R = Me and retained the 10–5–5 min time intervals during incremental peroxide addition. After rotary evaporation, the solid was dissolved in THF and filtered; the filtrate (20 mL) was treated with MeOH (80 mL). Filtration, washing (MeOH), and vacuum-drying gave red-orange crystals (0.3721 g, 71%). Anal. Calcd for $C_{60}H_{98}N_4O_{12}P_4S_{12}Mo_4$: C, 36.8; H, 5.0; N, 2.9; M_r, 1960. Found: C, 36.9; H, 4.8; N, 3.0; M_r, 1913 (CH_2Cl_2).

R = Ph. Via H_2O_2. This preparation was performed exactly as for R = Me, using 0.2225 g (0.133 mmol) of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and 0.0653 g (0.535 mmol) of $PhCO_2H$. Final stirring time was 15 min. MeOH (50 mL) was added to the CH_2Cl_2 filtrate (25 mL) following rotary evaporation and redissolving. Red-orange crystals (0.2042 g, 80%) were realized after filtration, washing (MeOH), and vacuum-drying. Anal. Calcd for $C_{58}H_{78}N_4O_{12}P_4S_{12}Mo_4$: C, 36.4; H, 4.1; N, 2.9. Found: C, 36.4; H, 4.2; N, 2.9.

R = Ph. Via Benzoyl Peroxide. A solution of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.2221 g, 0.133 mol), $(PhCO_2)_2$ (0.0479 g, 0.198 mmol), and ClC_2H_4Cl (2 mL) in a closed vessel was heated at 70 °C for 40 min. Volatiles were then removed by rotary evaporation. Product isolation as for the H_2O_2 route (30 mL of CH_2Cl_2, 60 mL of MeOH), gave dull orange crystals (0.2112 g, 83%). The ^{31}P NMR indicated ~4% impurities by this method.

R = To. This preparation was performed exactly as for R = Me, using 0.2223 g (0.133 mmol) of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and 0.0722 g (0.530 mmol) of $ToCO_2H$. The CH_2Cl_2 filtrate (11 mL) of the evaporated residue was treated with MeOH (22 mL). Product filtration, washing (MeOH), and vacuum-drying gave orange-brown crystals (0.1948 g, 75%). Anal. Calcd for $C_{60}H_{82}N_4O_{12}P_4S_{12}Mo_4$: C, 37.1; H, 4.3; N, 2.9. Found: C, 37.0; H, 4.2; N, 2.9.

R = Tr. This compound was prepared exactly as for R = Me by using 0.2225 g (0.133 mmol) of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and 0.1539 g (0.534 mmol) of $TrCO_2H$. MeOH (20 mL) precipitation of the CH_2Cl_2 filtrate (20 mL), followed by collection, washing (MeOH), and vacuum-drying, gave a dull orange powder (0.1968 g, 66%). Anal. Calcd for $C_{84}H_{98}N_4O_{12}P_4S_{12}Mo_4$: C, 44.9; H, 4.4; N, 2.5. Found: C, 44.9; H, 4.5; N, 2.5.

$[Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2)$. Via H_2O_2. This preparation was performed exactly as for the tolylimido analogue above, using 0.2226 g (0.138 mmol) of $[Mo(NPh)(S_2P(OEt)_2)S]_4$. After evaporation, redissolving, and filtering, the CH_2Cl_2 filtrate (2.5 mL) was treated with MeOH (10 mL). Red-orange crystals (0.1778 g, 77%) were obtained after filtration, washing (MeOH), and vacuum-drying. Anal. Calcd for $C_{44}H_{66}N_4O_{12}P_4S_{12}Mo_4$: C, 30.5; H, 3.8; N, 3.2. Found: C, 30.5; H, 3.8; N, 3.1.

Via Iodosobenzene. A slurry of $[Mo(NPh)(S_2P(OEt)_2)S]_4$ (0.2029 g, 0.125 mmol), PhIO (0.0420 g, 0.191 mmol), $MeCO_2H$ (57 μL, 1.0 mmol), and CH_2Cl_2 (1 mL) was stirred for 10 min. The deep orange solution was filtered, the solid material was rinsed (CH_2Cl_2, 1 mL), and product was precipitated from the combined filtrates with MeOH (8 mL). Filtration, washing (MeOH), and vacuum-drying gave dark red-orange crystals (0.1530 g, 71%).

Regardless of preparation and of any subsequent recrystallization schemes (CH_2Cl_2/MeOH, THF/MeOH, or CH_2Cl_2/Et_2O), this product always showed trace extraneous ^{31}P NMR peaks at δ 114.2 and δ 113.8, totaling ~2%.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')]$. R' = Et. EtSH (46 μL, 0.62 mmol) was added to a solution of NCS (0.0838 g, 0.628 mmol) in CH_2Cl_2 (2 mL). (The exothermicity of this reaction can cause solvent to boil for any of the thiols herein utilized, especially on a larger scale.) After standing in a stoppered vessel for 5 min, the yellow solution was added to a solution of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.4185 g, 0.250 mmol), $MeCO_2H$ (36 μL, 0.63 mmol), and Et_3N (87 μL, 0.63 mmol) in CH_2Cl_2 (4 mL). After the mixture was stirred for 10 min, volatiles were removed from the orange solution by rotary evaporation. The residue was taken into THF and filtered; the filtrate (4 mL) was slowly treated with 2/1 $EtOH/H_2O$ (8 mL). The resulting precipitate was filtered, washed (4/1 $EtOH/H_2O$), and vacuum-dried, giving red-orange crystals (0.3449 g, 72%). Anal. Calcd for $C_{26}H_{42}N_2O_6P_2S_7Mo_2$: C, 32.6; H, 4.4; S, 23.5. Found: C, 32.7; H, 4.4; S, 23.4.

R' = Bz. The compound was prepared as for R' = Et by using 73 μL of BzSH (0.63 mmol), 0.0833 g of NCS (0.624 mmol), and 0.4182 g of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.250 mmol). After rotary evaporation, the residue was taken into acetone and filtered; the filtrate (4.5 mL) was treated slowly with 2/1 $EtOH/H_2O$ (9 mL). The product was collected, washed (4/1 $EtOH/H_2O$) and vacuum-dried, giving orange crystals (0.3935 g, 77%). Anal. Calcd for $C_{31}H_{44}N_2O_6P_2S_7Mo_2$: C, 36.5; H, 4.4; S, 22.0. Found: C, 36.5; H, 4.4; S, 22.2.

R' = Ph. The compound was prepared as for R' = Et by using 64 μL of PhSH (0.62 mmol), 0.0836 g of NCS (0.626 mmol), and 0.4187 g of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.250 mmol) but, most notably, by working under red light conditions at all points involving product workup. The residue from rotary evaporation was taken into acetone (3 mL), and the crude product was precipitated with 2/1 $EtOH/H_2O$ (12 mL) by stirring for some time until the precipitate settled. Filtration, washing (2/1 $EtOH/H_2O$), and vacuum-drying gave a red-orange solid (0.3936 g, 78%). Recrystallization from an acetone filtrate (6 mL) with 2/1 $EtOH/H_2O$ (24 mL, added slowly), followed by collecting, washing (4/1 $EtOH/H_2O$), and vacuum-drying gave red-orange crystals (0.3427 g, 68% overall). Anal. Calcd for $C_{30}H_{42}N_2O_6P_2S_7Mo_2$: C, 35.9; H, 4.2; S, 22.3. Found: C, 35.8; H, 4.3; S, 22.5.

R' = To. This preparation, performed like that for R' = Et, used 0.0798 g of ToSH (0.643 mmol), 0.0861 g of NCS (0.645 mmol), 0.4316 g of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.258 mmol), 37 μL of $MeCO_2H$ (0.65 mmol) and 89 μL of Et_3N (0.64 mmol), working under red light conditions at all points following ToSCl addition. The evaporated residue was treated with acetone (3 mL), giving a slurry. A 2/1 mixture of $EtOH/H_2O$ (9 mL) was added and, after settling, the crude product was collected, washed (2/1 $EtOH/H_2O$), and vacuum-dried. The red-orange powder (0.4856 g, 98%) was recrystallized from a CH_2Cl_2 filtrate (2 mL) with MeOH (8 mL), allowing time for the slow crystallization. The product was filtered, washed (MeOH) and vacuum-dried, giving dark red crystals (0.3022 g, 58% overall). Anal. Calcd for $C_{31}H_{44}N_2O_6P_2S_7Mo_2$: C, 36.5; H, 4.4; S, 22.0. Found: C, 36.3; H, 4.4; S, 22.2.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_4)$. On the vacuum line under N_2, a solution of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.4184 g, 0.250 mmol), $MeCO_2H$ (36 μL, 0.63 mmol), and Et_3N (87 μL, 0.63 mmol) in CH_2Cl_2 (4 mL) was treated with S_2Cl_2 (25 μL, 0.31 mmol). After the mixture was stirred for 15 min, volatiles were stripped under vacuum. The reaction was opened to air, and CH_2Cl_2 was added to the residue and then filtered; the filtrate (4 mL) was treated with MeOH (16 mL). The resulting precipitate was filtered, washed (MeOH), and vacuum-dried, giving an orange powder (0.3739 g, 81%). Anal. Calcd for $C_{48}H_{74}N_4O_{12}P_4S_{14}Mo_4$: C, 31.1; H, 4.0; S, 24.2. Found: C, 31.0; H, 3.9; S, 24.7.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SBz)]$. The preparation was similar to that for $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CCF_3)(SBz)]$.[19] To a solution of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.2091 g, 0.125 mmol), $MeCO_2H$ (18 μL, 0.31 mmol), and Et_3N (43 μL, 0.31 mmol) in CH_2Cl_2 (2 mL) was added benzyl bromide (37 μL, 0.31 mmol). The orange solution was stirred for 10 min, followed by rotary evaporation. A THF filtrate (2.5 mL) of the residue was slowly treated with 2/1 $EtOH/H_2O$ (7.5 mL). After filtering, washing (4/1 $EtOH/H_2O$), and vacuum-drying, bright orange crystals (0.1636 g, 66%) were realized. Anal. Calcd for $C_{31}H_{44}N_2O_6P_2S_6Mo_2$: C, 37.7; H, 4.5; S, 19.5. Found: C, 37.7; H, 4.3; S, 19.8.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)]$. A solution of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.2095 g, 0.125 mmol) and acetic anhydride (0.47 mL, 5.0 mmol) in CH_2Cl_2 (1 mL) was stirred for 90 min. The orange solution was treated with petroleum ether (25 mL) and stirred for 30 min. The slurry was filtered, washed (20/1/1 petroleum ether/$Et_2O/(MeCO)_2O$), and vacuum-dried, giving bright orange crystals (0.2029 g, 86%). Anal. Calcd for $C_{26}H_{40}N_2O_7P_2S_6Mo_2$: C, 33.3; H, 4.3; S, 20.5. Found: C, 33.4; H, 4.6; S, 20.9.

Triphenylphosphine Reactions. In THF/H_2O. $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')]$ (0.025 mmol; R' = Bz or To) and Ph_3P (0.050 mmol) were taken into 10/1 THF/H_2O (0.50 mL) and stirred for 15 min. Volatiles were then removed by vacuum. The residue was dissolved in $CDCl_3$ and analyzed by ^{31}P and ^1H NMR. $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_4)$ (0.025 mmol) was treated similarly, but the reaction used 0.100 mmol of Ph_3P and 1.0 mL of 10/1 THF/H_2O.

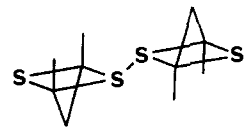
In $CDCl_3$. $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')]$ (0.025 mmol; R' = Bz, Ph or To) and Ph_3P (0.050 mmol) in a NMR tube with a septum cap under N_2 were dissolved in dry $CDCl_3$ (0.50 mL). After a minimum of 15 min, the contents were analyzed by ^{31}P and ^1H NMR. $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_4)$ (0.025 mmol) was treated similarly, but 0.100 mmol of Ph_3P and 1.0 mL of $CDCl_3$ were used.

Results and Discussion

Disulfide-Bridged Bis-Dimer Compounds. The preparative reaction (eq 4) gives reasonable yields (66–80%) of products characterized by a disulfide linkage bridging two pentavalent

$$[Mo(NAr)(S_2P(OEt)_2)S]_4 + 2RCO_2H + H_2O_2 \rightarrow \underset{\mathbf{1}}{[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CR)]_2(S_2)} + 2H_2O \quad (4)$$

molybdenum dimers (**1**). Several alkane- and arenecarboxylate



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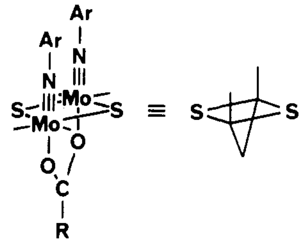


functionalities were examined for the tolylimido derivative, and acetate was also utilized with the phenylimido analogue. The various products exhibit a range of solubilities, albeit generally poor, even in CH_2Cl_2. Longer alkane carboxylates were prepared to enhance solubility, and the octanoate is indeed of good solubility in CH_2Cl_2, $CHCl_3$, and THF, although poor in benzene. Interestingly, the phenylimido/acetate derivative, $[Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2)$, greatly exceeds the solubility of the tolylimido/acetate analogue and, in fact, resembles $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CHp)]_2(S_2)$ in solubility.

Alternate synthetic reactions were also developed for two of the derivatives. Use of benzoyl peroxide as both oxidant and carboxylate source (eq 5) gave product in good yield, but was

$$[Mo(NTo)(S_2P(OEt)_2)S]_4 + (PhCO_2)_2 \rightarrow [Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CPh)]_2(S_2) \quad (5)$$

notably slower, requiring heating, and the product thus obtained contained small quantities of impurities evident only in the ^{31}P NMR spectrum. Iodosobenzene as oxidant was also used for $[Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2)$ synthesis (eq 6) giving

$$[Mo(NPh)(S_2P(OEt)_2)S]_4 + 2MeCO_2H + PhIO \rightarrow [Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2) + PhI + H_2O \quad (6)$$

a product of comparable yield and purity. This preparation was developed as part of the investigation of two "extraneous peaks" in the ^{31}P NMR of $[Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2)$ at δ 114.2 and 113.8, totaling only $\sim$2% in all samples regardless of preparation or recrystallization. While not totally clarified, the peaks may be due to persistent and consistent impurities or due to conformational isomers (see below) beyond what is observed for the tolylimido derivatives. Regardless of their nature, the general properties of the $[Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2)$ samples are not apparently affected.

The present oxidative studies were intended to determine the product of the formal one-electron, chemical oxidation of the dimer anion $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(O_2CR)]^-$. While initial efforts did indeed utilize the anion, the synthetically convenient eq 4 was developed as a preferred route. Inherent to eq 4 are eq 1 and 2, although eq 2 is greatly displaced to the left for weaker carboxylic acids.[18] Presumably even in the current CH_2Cl_2/MeOH solvent system, the concentration of $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CR)(SH)]$ is very low. Nevertheless, it is a curiosity of the system that discoloration occurs within minutes of combining $[Mo(NAr)(S_2P(OEt)_2)S]_4$, the carboxylic acid, and H_2O_2, but no significant, irreversible reaction apparently occurs in a short time period in the absence of the carboxylic acid, suggesting that the oxidation requires the presence of carboxylic acid and that $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CR)(SH)]$ may indeed be the actual reductant.

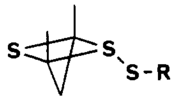
Additional observations are the requirement in the syntheses of adequate excess ($\sim$50%) H_2O_2 and the notable improvement in yield seen by utilizing incremental peroxide addition as described in the Experimental Section. Use of 50% excess H_2O_2 added initially in its entirety reduces the yield by 10–20% as observed in trials with the octanoate derivative. There appears to be a second consumption pathway of H_2O_2, which may be a molybdenum-catalyzed disproportionation.

All properties of the products are consistent with the disulfide-bridged bis-dimer structure **1**. NMR and IR spectra clearly support the presence of the dimer fragment $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(O_2CR)]$, and that these radicals per se are indeed not the isolated products is evident by the sharp ^{31}P and ^1H NMR spectra, and the observed molecular weight in CH_2Cl_2 of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CHp)]_2(S_2)$, fully consistent with the indicated molecularity. Thus the isolated compounds can be formulated as the product of the coupling of $SMo_2S^{\bullet}$ thiyl radicals to give disulfide compounds, wherein the disulfide linkage can be described as a 1-μ, 2-μ'[21] bridge or a type IId linkage according to a prior classification scheme.[22] This suggests that radicals of the form $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S_2(O_2CR)]^{\bullet}$ would not be exclusively represented as a mixed Mo(V)–Mo(VI) dimer but must include substantial contributions from location of the radical electron on a bridge sulfur. An attempt to sterically preclude radical coupling by use of triphenylmethanecarboxylate failed, and this product is also consistent with the bridge-disulfide formulation.

Infrared spectra of the current disulfide-bridged bis-dimer compounds are dominated by the usual $(EtO)_2PS_2^-$ ligand bands and by carboxylate–CO_2 stretches (Table II). No clearly discernible ν(S–S) band can be reliably assigned nor is such expected due to the symmetry about the S–S bond.

Intermetal disulfide formation from sulfidometal precursor reagents has been demonstrated previously for other systems.[22] The disulfide-bridge bis-dimer fragment has also been obtained for the $Fe_2S_2(CO)_6$ system.[23,24]

Monosubstituted Organic Disulfide-Bridged Dimers. The formation of a disulfide linkage from a bridge-sulfur position prompted investigations into syntheses of mixed dimer–organic disulfides $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')]$ (**2**). The



2

selected preparative route (eq 7) is based on a known synthetic

$$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)]^- + R'SCl \rightarrow \underset{\mathbf{2}}{[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')]} + Cl^- \quad (7)$$

pathway for unsymmetrical organic disulfides.[25] Previous work with reactions of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CCF_3)]^-$ and alkyl bromides gave S-alkylation at the bridge,[19] suggesting some feasibility to the proposed scheme.

The reaction (eq 7) proceeds readily and is complete virtually upon mixing, giving reasonable yields of the desired R'SS-bridge dimers $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')]$ (**2**). Actual yields are primarily a reflection of the high solubilities, and the low aryl yields (R′ = Ph, To), compared to those of the alkyls (R′ = Et, Bz), are attributable to the additional recrystallization step.

For convenience, the organic sulfenyl chlorides are freshly prepared via NCS chlorination of the corresponding thiol[25,26] and

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(21) This notation is adopted to indicate which sulfur atoms of the polysulfur bridge are involved, while the μ,μ' designation is given to indicate that different metal centers are bridged by the given sulfur atoms.

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are used directly in solution without isolation. This has proven very facile and does not require prior solvent drying, although an amount in excess of stoichiometry (~25%) is indeed used.

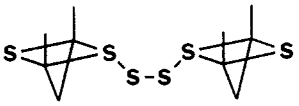
All properties of the products are consistent with formulation **2**. Thus, ^{31}P and ^{1}H NMR show equivalent halves within the dimer, and the tolylimido and dithiophosphate resonances integrate properly with the R′ group. Conformational isomers (see below) support the structural assignment of a tricoordinate sulfur bridge. Sulfur anlayses and phosphine reactions (see below) support the presence of a disulfide linkage. The IR spectra show the appropriate characteristic absorptions; no ν(S–S) can be unambiguously assigned. Initial X-ray crystallographic results for $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSEt)}]$ confirm structure **2** in the solid for this derivative.[27] These compounds therefore contain the unusual bridging group represented formally by a monosubstituted organic disulfide ion, R′SS$^-$, bound to two molybdenum sites via its β-sulfur. This ligand contrasts with well established structures and chemistries of thiol, thiolate, thioether, and 1,2-disubstituted organic disulfide (RSSR) ligands.[28,29]

Tetrasulfide-Bridged Bis-Dimer Complex. The presence of a disulfide bridge acting in 1-μ,2-μ' fashion linking two molybdenum dimers suggested other polysulfur linkages should be possible. Such was realized by reaction of the dimer anion $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)}]^-$ with $\mathrm{S_2Cl_2}$ (eq 8). This reaction

$$2[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)}]^- + \mathrm{S_2Cl_2} \rightarrow \underset{\mathbf{3}}{[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)}]_2(\mathrm{S_4})} + 2\mathrm{Cl^-} \quad (8)$$

proceeds readily and is virtually complete upon mixing, giving product in high yield. The synthesis is best done under carefully anhydrous conditions due to the moisture sensitivity of $\mathrm{S_2Cl_2}$. This contrasts with above reactions (eq 7) utilizing sulfenyl chlorides, which are also moisture sensitive but for which anhydrous rigor was not necessary. The tetrasulfide product, however, is quite stable to air, and its solution, once formed, does not require air-free manipulations.

The product is formulated as composed of two molybdenum dimers linked by a 1-μ,4-μ'-$\mathrm{S_4}$[21] bridge (**3**). The ^{31}P and ^{1}H NMR spectra are consistent with this formulation, showing equivalent dithiophosphate groups and equivalent tolylimido groups. Supportive evidence is also given by the observed sulfur analysis, conformational isomers suggesting tricoordinate bridge sulfur, and phosphine reactions (see below). The IR spectrum is quite similar to that of $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)}]_2(\mathrm{S_2})$ except for some differences associated with the dithiophosphate absorbances; below 600 cm^{-1}, the spectra only show subtle differences and no S–S bands can be uniquely identified.



3

The current tetrasulfide product is unusual in that the tetrasulfide linkage is bridging in a 1-μ,4-μ' manner. Several other molybdenum tetrasulfide complexes have been reported, along with crystallographic structural information. These include the tetravalent molybdenum monomers $(\mathrm{C_5H_5})_2\mathrm{Mo(S_4)}$,[30] $\mathrm{MoS(S_4)_2}^{2-}$, and $\mathrm{MoO(S_4)_2}^{2-}$ [6,31] and pentavalent dimers $\mathrm{Mo_2S_2(\mu\text{-}S)_2(S_2)(S_4)}^{2-}$,[32] $\mathrm{Mo_2S_2(\mu\text{-}S)_2(S_4)_2}^{2-}$,[6] $\mathrm{Mo_2O_2(\mu\text{-}S)_2(S_2)(S_4)}^{2-}$,[33] and $\mathrm{Mo_2O_2(\mu\text{-}S)_2(S_4)_2}^{2-}$.[34] All the tetravalent and pentavalent complexes thus cited contain chelating $\mathrm{S_4}^{2-}$ bidentates. The 1-μ,4-μ' tetrasulfide bridge in the current study is then another example of the structural versatility of the sulfido and polysulfido ligands in molybdenum chemistry.

$[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SBz)}]$ and $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)}]$. These were both prepared and characterized solely for clarification as products of the phosphine reactions described further below. Both are proposed to have the structure shown by **4**, Z = benzyl or acetyl.

4

The *S*-benzyl derivative is quite similar to the previously reported trifluoroacetate analogue $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CCF_3)(SBz)}]$[19] and was prepared by a similar route (eq 9)

$$[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)}]^- + \mathrm{BzBr} \rightarrow [\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SBz)}] + \mathrm{Br^-} \quad (9)$$

by simple alkylation of the bridge sulfur position in the dimer anion with benzyl bromide. Analyses and IR and NMR spectra are fully consistent with the thiolate-bridged dimer structure as demonstrated for the prior trifluoroacetate analogues.

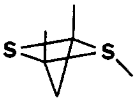
The *S*-acetyl derivative, however, displays a curious phenomenon by its solution equilibrium involving tetramer and acetic anhydride (eq 10). Thus, while the same product was first

$$[\mathrm{Mo(NTo)(S_2P(OEt)_2)S}]_4 + 2(\mathrm{MeCO})_2\mathrm{O} \rightleftharpoons 2[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)}] \quad (10)$$

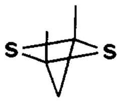
prepared by reaction of $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)}]^-$ and acetyl bromide analogous to eq 9, subsequent realization of the equilibrium (eq 10) provided a synthetically more convenient route, albeit requiring a large excess of acetic anhydride. The equilibration is slow, contrasting sharply with equilibria involving bridge sulfhydryl species (eq 2), which are synthetically instantaneous.[18]

The dissociation of $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)}]$ in $\mathrm{CDCl_3}$ solution was studied by ^{31}P and ^{1}H NMR. A 0.0504 F solution of $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)}]$ required 8–12 h to achieve equilibration. The ^{31}P NMR spectrum clearly showed both $[\mathrm{Mo(NTo)(S_2P(OEt)_2)S}]_4$ and $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)}]$. The ^{1}H NMR spectrum clearly showed both molybdenum complexes and acetic anhydride. Although rigorously anhydrous conditions were not employed, no acetic acid was seen resulting from hydrolysis. All ^{1}H NMR integrations were consistent with the equilibration. ^{31}P and ^{1}H NMR integrations after 24 h gave an equilibrium constant of 32 (~21 °C) as written to the right for eq 10.

The infrared spectrum of $[\mathrm{Mo_2(NTo)_2(S_2(P(OEt)_2)_2S(O_2CMe)(SCOMe)}]$ shows, in addition to the characteristic absorbances of the $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)}]$ unit, a second carbonyl stretch at 1731 cm^{-1} (m) attributed to the *S*-acetyl group. The IR is thus consistent with structural formulation **4**, Z = COMe.



5a



5b

Conformational Isomerism. The presence of a tricoordinate bridge sulfur allows for the presence of isomers formally related by inversion at that position. These can be diagrammatically illustrated by **5a** and **5b** for the current series of compounds, wherein the group attached to the sulfur bridge is distal or proximal, respectively, as referenced to the arylimido groups. Previously both $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CCF_3)(SH)}]$[18] and $[\mathrm{Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CCF_3)(SMe)}]$[19] were shown to exhibit the distal configuration, **5a**, in their solid structures, while

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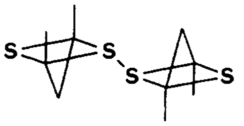
NMR indicated both invertomers for these and similar derivatives in solution.

All the disulfide-bridged bis-dimer complexes of the present study exhibit evidence in ^{1}H and ^{31}P NMR spectra of two isomers, except for the triphenylmethanecarboxylate derivative wherein only one is observed. The ratio of the two isomers is variable for the different derivatives (see Table I) and is greatest for the two acetate derivatives, $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2)$ (Ar = To, Ph). Thus, bulk at the carboxylate disfavors the minor isomer even further, so that, at the extreme with a trityl group, no second isomer is observed. This is interpreted as supportive evidence that the proximal configuration for both dimers, as represented by **1**, is the major solution isomer. The steric considerations arise from juxtaposition of the carboxylate functionality with the arylimido rings, a situation that is presumably worsened by adoption of the distal configuration for both dimers as shown by **1′**. Additional evidence is provided by ^{1}H NMR shift patterns, particularly those of the arylimido ring and CH_3 protons and the acetate CH_3 groups. Perhaps the most obvious is the great disparity in the shifts of the ortho and meta arylimido protons, expanded even more in the arenecarboxylate derivatives. The multiplicity pattern for $[Mo_2(NPh)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2)$ establishes the downfield resonance as the ortho protons and the upfield resonance as the meta. Where the minor isomers are discernible, their meta resonances coincide closely with those of the major isomer, while the ortho protons are notably upfield compared to those of the major isomer. By simultaneous consideration of the shift patterns observed for all compounds described in this report and for the previous alkanethiolate-bridged complexes, $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CCF_3)(SR')]$ (R′ = Me, Et, Bz),[19] it is proposed that the downfield shift of the arylimido ortho protons is associated with the proximal configuration, **5b**. This is then consistent with the assignment of conformation **1** as the major solution isomer of the disulfide-bridged bis-dimer complexes. It is also consistent with assignment of the distal configuration, **5a**, as the major $CDCl_3$ solution isomer in the prior $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CCF_3)(SR')]$ complexes. Not surprisingly, the current $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SBz)]$ displays a ^{1}H NMR spectrum very similar to that of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CCF_3)(SBz)]$, and its major $CDCl_3$ solution isomer is accordingly proposed to be the distal configuration, **5a**, as shown in **4** (Z = Bz).



1′

Application of this argument to the R′SS-bridged dimers $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')]$ and the tetrasulfide-bridged bis-dimer complex $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_4)$ suggests their major solution isomers are also the distal configuration, **5a**, as represented earlier by **2** and **3**. No stereoisomers are observed for $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)]$, but this process is complicated by the dissociative equilibrium in eq 10.

A slight solvent dependence is observed for the ratio of the major to minor isomers. Representative data are shown in Table III. Variable-temperature studies by ^{31}P NMR showed coalescence for $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSBz)]$ at 52 °C in $CDCl_3$. No coalescence was seen for $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CHp)]_2(S_2)$ even at 110 °C in chlorobenzene. This is not surprising, as the isomerization represented by **1** → **1′** involves simultaneous inversion at two sulfur sites.

Table III. Stereoisomer Ratios via ^{31}P NMR[a]

	$CDCl_3$	C_6D_6	$(CD_3)_2CO$	THF
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CHp)]_2(S_2)$	0.04	0.04		0.08
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSBz)]$	6	6	6	5
$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_4)$	17	11	9	14

[a] Defined as the ratio of the distal to proximal configurations as described in the text.

Triphenylphosphine Reactions. The tetrasulfide-bridged product and several R′SS-bridged compounds were examined for their reactivities with triphenylphosphine. A wealth of material has been reported for mechanisms and limitations of reactions of organic di- and polysulfides with triphenylphosphine.[25,35-39] For the present purposes, these can be summarized as desulfurization reactions (eq 11 and 12) or reductions (eq 13), with the first step being formation of a phosphonium intermediate (eq 14) whose ultimate degradation dictates the nature of the products.

$$R''SSSSR'' + 2Ph_3P \rightarrow R''SSR'' + 2Ph_3PS \qquad (11)$$

$$R''SSR'' + Ph_3P \rightarrow R''SR'' + Ph_3PS \qquad (12)$$

$$R''SSR'' + Ph_3P + HOZ' \rightarrow R''SH + R''SZ' + Ph_3PO \qquad (13)$$

$$R''SSR'' + Ph_3P \rightleftharpoons (Ph_3PSR'')^+ + R''S^- \qquad (14)$$

Equation 12 is very limited in generality and many disulfides, including dialkyl and diaryl derivatives, are resistant to this reaction.[39] Equation 13 is very general in wet solvents (Z′ = H)[37,38] or when other protic reagents are present.[39]

Reaction of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSBz)]$ with 2 equiv of Ph_3P in 10/1 THF/H_2O occurred immediately upon dissolving to give 93% $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SBz)]$ and 7% $[Mo(NTo)(S_2P(OEt)_2)S]_4$. The ^{31}P NMR showed Ph_3PS, unreacted Ph_3P, and a small amount of Ph_3PO, fully consistent with the desulfurization reaction (eq 15, R′ = Bz) as the dominant pathway with a minor contribution from reduction (eq 16, R′ = Bz). Benzyl mercaptan was also evident in the ^{1}H NMR spectrum in small quantity, consistent with the reduction.

$$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')] + Ph_3P \rightarrow [Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SR')] + Ph_3PS \qquad (15)$$

$$2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR')] + 2Ph_3P + 2H_2O \rightarrow [Mo(NTo)(S_2P(OEt)_2)S]_4 + 2MeCO_2H + 2R'SH + 2Ph_3PO \qquad (16)$$

These results contrast sharply with the reaction of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSTo)]$ under the same conditions. This reaction, also immediate, gives 97% $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and 3% unidentified product (^{31}P NMR: δ 113.0), with absolutely no evidence of Ph_3PS but with Ph_3PO and unreacted Ph_3P. Thiocresol is evident in the ^{1}H NMR spectrum, and the results show reduction (eq 16, R′ = To) as the nearly exclusive reaction under these conditions.

The same reactions were also conducted in anhydrous $CDCl_3$ under N_2, and all were again immediate upon dissolving. $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSBz)]$ gave 96% $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SBz)]$ and 4% $[Mo(NTo)(S_2P(OEt)_2)S]_4$, similar to the THF/H_2O reaction but now complicated by an inability to account for the minor product in the absence of water, although a trace of Ph_3PO was evident in the ^{31}P NMR spectrum. The reaction with $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSAr)]$ was more complex, and Ar = To and Ph were both investigated. For Ar = To, 86% $[Mo(NTo)(S_2P(OEt)_2)S]_4$, 14% $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)]$, and a trace of an unidentified compound (^{31}P NMR: δ 115.2) were realized; for Ar = Ph, these values were 80%, 18% and 2%. The first two are, of course, interrelated by the equilibrium of eq 10. Only Ph_3PO and unreacted Ph_3P are seen by ^{31}P NMR, with no evi-

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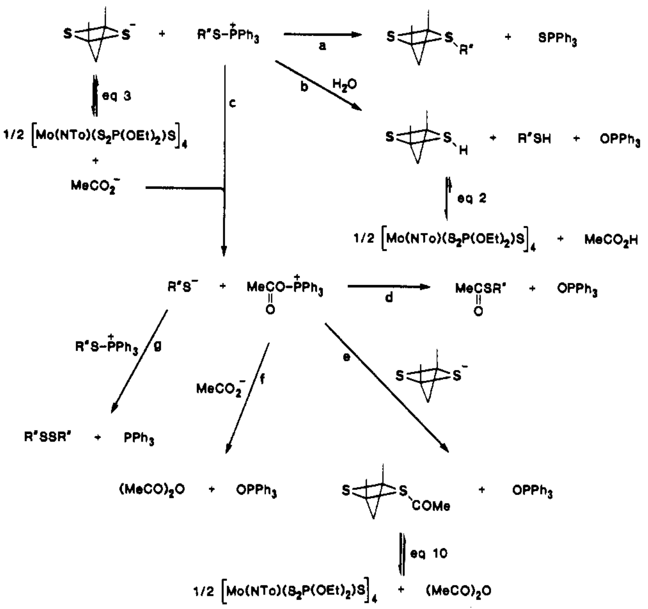
Scheme I



dence of Ph_3PS. The ^1H NMR spectrum shows all the listed products, along with acetic anhydride and *S*-aryl thioacetate esters, verified for certain in the case of Ar = Ph by comparison with a commercial sample of PhSCOMe. Production of thioacetate esters is explained by eq 17. While thioacetate ester production

$$2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSAr)] + 2Ph_3P \rightarrow [Mo(NTo)(S_2P(OEt)_2)S]_4 + 2Ph_3PO + 2ArSCOMe \quad (17)$$

was indeed unexpected, this pathway is established for reactions of organic disulfides with Ph_3P in the presence of carboxylic acids[40] and the overall process therein is reduction, eq 13, with Z' = acyl. An analogous reaction for the benzyl disulfide-bridged dimer might account for the small quantity of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and Ph_3PO therein observed, but definitive evidence of the resultant BzSCOMe was not obtained by the ^1H NMR spectrum, and such would have been expected only in small quantity.

Production of acetic anhydride for reactions of the aryl disulfide-bridged dimers is not readily explained. A proposed reaction is given by eq 18 and is substantiated by peaks attributable

$$2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSAr)] + Ph_3P \rightarrow [Mo(NTo)(S_2P(OEt)_2)S]_4 + ArSSAr + Ph_3PO + (MeCO)_2O \quad (18)$$

to ToSSTo for the tolyl derivative and by somewhat low yields of Ph_3PO for both Ar = To and Ph. The complexity of the spectra and the possibility of additional pathways precludes a definitive assessment of the fate of organic byproducts. Clearly, however, the reaction is nearly quantitative for $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and its acetic anhydride adduct.

All of the indicated products are consistent with established reactions of triphenylphosphine and organic disulfides. For the current study, proposed pathways are shown in Scheme I for the degradation of the phosphonium intermediate (eq 14) from the triphenylphosphine reaction with the dimer–organic disulfide compounds. Nucleophilic substitution by the dimer anion on a R″ α-carbon (path a) displaces triphenylphosphine sulfide and gives the thiolate-bridged dimer. This is tantamount to overall desulfurization (eq 12), which is of limited scope for many organic disulfides but very general when $(Et_2N)_3P$ is instead utilized.[41] Attack by H_2O on phosphorus[37,38] gives triphenylphosphine oxide, thiol, and the hydrosulfide-bridged dimer (path b); the latter gives $[Mo(NTo)(S_2P(OEt)_2)S]_4$ by eq 2. The carboxylate dissociation equilibrium, eq 3, yields acetate, which can attack phosphorus to generate a second phosphonium intermediate, $(MeCO_2PPh_3)^+$ (path c). Thiolate reacts at the carbonyl carbon to generate thioacetate ester[40] (path d). The dimer anion can react similarly to give the *S*-acetyl derivative (path e). Attack by acetate on the carbonyl carbon would generate acetic anhydride directly (path f). Actually, paths e and f are indistinguishable in the current study due to eq 10, and only one may be operative. Diaryl disulfide production as proposed in eq 18 can occur by path g, simply equivalent to the reverse of eq 14. Thus, while not all organic products have been identified in all the reactions, those that have, along with the identifiable molybdenum compounds, can be rationalized by known mechanisms.

$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)](S_4)$ reacts in the presence of 4 equiv of Ph_3P in 10/1 THF/H_2O to immediately give 94% $[Mo(NTo)(S_2P(OEt)_2)S]_4$. Ph_3PS, Ph_3PO, and unreacted Ph_3P are also observed, as are several other peaks accounting for the dithiophosphate–molybdenum balance but which are of individually too small a quantity to identify. The reaction overall is desulfurization and reduction (eq 19).

$$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_4) + 3Ph_3P + H_2O \rightarrow [Mo(NTo)(S_2P(OEt)_2)S]_4 + 2Ph_3PS + Ph_3PO + 2MeCO_2H \quad (19)$$

The anhydrous reaction of $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)](S_4)$ in $CDCl_3$ gave 57% $[Mo(NTo)(S_2P(OEt)_2)S]_4$, 32% $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SCOMe)]$, and 10% of an unidentified product (^{31}P NMR: δ 115.3). Ph_3PS, Ph_3PO, and unreacted Ph_3P were again observed in the ^{31}P NMR spectrum, and acetic anhydride was present in the ^1H NMR spectrum. The overall main reaction is again desulfurization and reduction (eq 20) and is further flavored by the equilibrium of eq 10.

$$[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_4) + 3Ph_3P \rightarrow [Mo(NTo)(S_2P(OEt)_2)S]_4 + 2Ph_3PS + Ph_3PO + (MeCO)_2O \quad (20)$$

Nature of the Photosensitivity. Neither of the aryl disulfide bridge dimers $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSAr)]$ (Ar = Ph, To) can be obtained pure if recrystallized under normal labortory fluorescent lighting, and instead solutions of these two derivtives were handled under red light conditions. Work yet in progress has demonstrated the photohomolytic scramble reaction represented by eq 21, which necessitates the manipulation of the

$$2[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSAr)] \underset{}{\overset{h\nu}{\rightleftharpoons}} [Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)]_2(S_2) + ArSSAr \quad (21)$$

solutions under restricted lighting. Interestingly, the dimer radicals $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S_2(O_2CMe)]^\bullet$, originally sought as the product of the oxidation of the dimer anions, are involved.

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