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Diphos–Dithiophosphate–Carboxylate Variations on the $Mo_2S_2^{6+}$ Core

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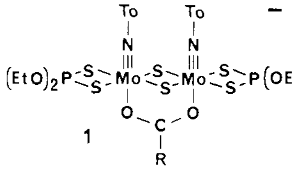
Diphos ($Ph_2PC_2H_4PPh_2$) complexes of the $Mo_2S_2^{6+}$ core with *p*-tolylimido, dithiophosphate, and carboxylate coligands were prepared and characterized. These included the neutral dimers $[Mo_2(NC_7H_7)_2(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)(Ph_2PC_2H_4PPh_2)(\mu\text{-}O_2CR)]$ (R = CH_3, C_3H_7, C_7H_{15}) and the dimer cations $[Mo_2(NC_7H_7)_2(\mu\text{-}S)_2(Ph_2PC_2H_4PPh_2)_2(\mu\text{-}S_2P(OC_2H_5)_2)]^+$ and $[Mo_2(NC_7H_7)_2(\mu\text{-}S)_2(Ph_2PC_2H_4PPh_2)_2(\mu\text{-}O_2CCH_3)]^+$. Diphos coordination was achieved by displacement of a bound dithiophosphate, although substitution was not possible in all cases. The crystal structure of $[Mo_2(NC_7H_7)_2(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)(Ph_2PC_2H_4PPh_2)(\mu\text{-}O_2CC_7H_{15})]$ was determined. The compound crystallized in space group *C*2/*c* with a = 28.664 (6) Å, b = 14.653 (4) Å, c = 32.304 (4) Å, β = 122.11 (2)°, and Z = 8, and final R and R_w of 0.056 and 0.051.

Introduction

Recent emphases in sulfidometal chemistry have included reactions at the sulfur itself, usually as a sulfide or as a di- or polysulfide unit within complexes of a variety of metals.[1-10] Specifically for molybdenum,[11-19] a great impetus in this area has been related to the presence of Mo–S systems in hydrodesulfurization and hydrodenitrogenation catalysis and in biological processes.[20-24] Various proposed mechanisms for these have invoked active roles for the chalcogen.

The (tolylimido)(dithiophosphato)molybdenum dimer anions, $[Mo_2(NTo)_2S_2(S_2P(OEt)_2)_2(O_2CR)]^-$ (1) (for abbreviations see below[25]), which contain bridging sulfide and carboxylate, and the photogenerated dimer radicals $[Mo_2(NTo)_2S_2(S_2P(OEt)_2)_2(O_2CR)]^\bullet$ have displayed nucleophilic and radical chemistries centered at the sulfur bridge positions. Reactions have been demonstrated for a range of substrates including alkyl halides, sulfur halides, alkynes, mercaptans, Ph_3P, $(EtO)_3P$, and organic disulfides.[9,26,27] In an effort to investigate sulfur–N_2 radical type interactions for possible nitrogenase modeling, reactions were conducted between $[Mo_2(NTo)_2S_2(S_2P(OEt)_2)_2(O_2CR)]^\bullet$ precursors and $Mo(N_2)_2(Ph_2PC_2H_4PPh_2)_2$, a complex well-known for N_2 radical chemistry.[28] Early results in this area indicated gross exchange of diphos and dithiophosphate chelating ligands. This prompted a study for fuller characterization of variations on the general structure $[Mo_2(NTo)_2S_2]^{2+}$ involving dithiophosphate, diphos, and carboxylate ligands. It is these results that are reported herein.



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Experimental Section

Most operations were conducted open to air. Those stated as performed under N_2, however, were done on a vacuum line with use of dried solvents.

$[Mo(NTo)(S_2P(OEt)_2)S]_4$ was prepared as previously reported;[29] $Ph_2PC_2H_4PPh_2$ was recrystallized from CH_2Cl_2/MeOH. Other reagents were used as commercially available. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra were recorded on a Varian XL300 spectrometer at 121, 75, and 300 MHz and are reported as downfield shifts from 85% H_3PO_4 (^{31}P) and Me_4Si (^{13}C, ^1H). The solvent was $CDCl_3$ except as noted. All ^1H NMR integrations were consistent with the assignments. IR spectra were obtained as KBr pellets on a Perkin-Elmer 283 spectrophotometer; only selected bands are listed. Galbraith Laboratories, Inc. (Knoxville, TN), performed the elemental analyses.

$[Mo_2(NTo)_2S_2(S_2P(OEt)_2)(Ph_2PC_2H_4PPh_2)(O_2CR)]$ (2). R = Me. $Ph_2PC_2H_4PPh_2$ (0.1421 g, 0.357 mmol) was added to a solution of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.2097 g, 0.125 mmol), $MeCO_2H$ (18 μL, 0.31 mmol), and Et_3N (43 μL, 0.31 mmol) in C_6H_6 (10 mL) under N_2. After being stirred for 3 h, the solution was opened to air and rotavapped. A CH_2Cl_2 filtrate (4 mL) of the residue was treated with MeOH (12 mL); the resulting precipitate was filtered out, washed, and partially dried. Recrystallization from CH_2Cl_2 (2.5 mL)/MeOH (5 mL) and vacuum-drying for 5 days gave orange crystals (0.2047 g, 74%). Anal. Calcd for $Mo_2C_{46}H_{51}N_2O_4P_3S_4$: C, 49.8; H, 4.6; N, 2.5; S, 11.6. Found: C, 49.5; H, 4.4; N, 2.4; S, 12.0. NMR data are as follows (ppm).[30] ^{31}P: 116.9 t, $S_2P(OEt)_2$; 40.6 d, $Ph_2PC_2H_4PPh_2$; $^4J_{P-P}$ = 7 Hz. ^1H: 8.16 m, 7.67 m, 7.28 m, PC_6H_5; 6.75 d, 6.56 d, 5.93 d, 5.16 d, To–H; 4.24 dq, 4.12 dq, $POCH_2$; 3.13 m, PCH_2; 2.07 s, 1.86 s, To–CH_3; 1.28 t, 1.25 t, $POCCH_3$; 0.60 s, O_2CCH_3. IR (cm^{-1}): 1545 m, 1492 m, 1437 sh, 1417 s, 1330 m, 1015 s, 949 m, 693 m, 651 m, 525 m.

R = Pr. The procedure followed that for R = Me, using 0.2094 g (0.125 mmol) of $[Mo(NTo)(S_2P(OEt)_2)S]_4$, 28 μL (0.30 mmol) of

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(1) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

(2) Giolando, D. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 6455.

(3) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 7800.

(4) Seyferth, D.; Henderson, R. S.; Song, L.-C.; Womack, G. B. *J. Organomet. Chem.* **1985**, *292*, 9.

(5) Coucouvanis, D.; Patil, P. R.; Kanatzidis, M. G.; Detering, B.; Baenziger, N. C. *Inorg. Chem.* **1985**, *24*, 24.

(6) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742.

(7) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89.

(8) Wachter, J. *J. Coord. Chem.* **1987**, *15*, 219.

(9) Lizano, A. C.; Noble, M. E. *Inorg. Chem.* **1988**, *27*, 747 and references therein.

(10) Ansari, M. A.; Chandrasekaran, J.; Sarkar, S. *Polyhedron* **1988**, *7*, 471.

(11) Pan, W.-H.; Leonowicz, M. E.; Stiefel, E. I. *Inorg. Chem.* **1983**, *22*, 672.

(12) Wedd, A. G. *Stud. Inorg. Chem.* **1984**, *5*, 181.

(13) Xin, X.; Morris, N. L.; Jameson, G. B.; Pope, M. T. *Inorg. Chem.* **1985**, *24*, 3482.

(14) Cohen, S. A.; Stiefel, E. I. *Inorg. Chem.* **1985**, *24*, 4657.

(15) Casewit, C. J.; Coons, D. E.; Wright, L. L.; Miller, W. K.; Rakowski DuBois, M. *Organometallics* **1986**, *5*, 951.

(16) Bernholc, J.; Stiefel, E. I. *Inorg. Chem.* **1986**, *25*, 3876.

(17) Casewit, C. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 5482.

(18) Hadjikyriacou, A. I.; Coucouvanis, D. *Inorg. Chem.* **1987**, *26*, 2400.

(19) Tanner, L. D.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Inorg. Chem.* **1988**, *27*, 1736.

(20) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128.

(21) Stiefel, E. I.; Chianelli, R. R. In *Nitrogen Fixation. The Chemical-Biochemical-Genetic Interface*; Müller, A., Newton, W. E., Eds.; Plenum: New York, 1983; p 341.

(22) Burgmayer, S. J. N.; Stiefel, E. I. *J. Chem. Educ.* **1985**, *62*, 943.

(23) Harris, S.; Chianelli, R. R. *J. Catal.* **1986**, *98*, 17.

(24) Ho, T. C. *Catal. Rev.—Sci. Eng.* **1988**, *30*, 117.

(25) Abbreviations used in this paper: Me, methyl; Et, ethyl; Pr, *n*-propyl; Hp, *n*-heptyl; Ph, phenyl; To, *p*-tolyl.

(26) Noble, M. E. *Inorg. Chem.* **1986**, *25*, 3311.

(27) Noble, M. E. *Inorg. Chem.* **1987**, *26*, 877.

(28) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197.

(29) Noble, M. E.; Wentworth, R. A. D. *Inorg. Chem.* **1983**, *22*, 1756.

(30) Multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; p, quintet; h, sextet; m, one or more multiplets.

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Table I. Crystallographic Data for $[Mo_2(NTo)_2S_2(S_2P(OEt)_2)(Ph_2PC_2H_4PPh_2)(O_2CHp)]$

$C_{52}H_{63}Mo_2N_2O_4P_3S_4 \cdot 0.12CH_2Cl_2$	fw = 1203.3
space group: $C2/c$ (No. 15)	T = 23 °C
a = 28.664 (6) Å	λ = 0.71073 Å
b = 14.653 (4) Å	ρ_{calcd} = 1.42 g cm^{-3}
c = 32.304 (4) Å	μ = 7.4 cm^{-1}
β = 122.11 (2)°	abs cor = 0.939–0.999
V = 11493.2 Å^3	R = 0.056
Z = 8	R_w = 0.051

$PrCO_2H$, 43 μL (0.31 mmol) of Et_3N, and 0.1418 g (0.356 mmol) of $Ph_2PC_2H_4PPh_2$. After rotavaporation, dissolution (CH_2Cl_2), and filtration, the filtrate (3 mL) was treated with MeOH (9 mL). The precipitate was collected, and subsequent recrystallization from CH_2Cl_2 (1.2 mL)/MeOH (2.4 mL) and vacuum-drying for 5 days gave orange crystals (0.2175 g, 65%). Anal. Calcd for $Mo_2C_{48}H_{55}N_2O_4P_3S_4$: C, 50.7; H, 4.9; N, 2.5; S, 11.3. Found: C, 50.3; H, 5.0; N, 2.1; S, 11.5. NMR data are as follows (ppm).[30] ^{31}P: 117.4 t, $S_2P(OEt)_2$; 40.2 d, $Ph_2PC_2H_4PPh_2$; $^4J_{P-P}$ = 7 Hz. ^1H: 8.13 m, 7.73 m, 7.26 m, PC_6H_5; 6.78 d, 6.58 d, 5.90 d, 5.12 d, To–H; 4.23 dq, 4.12 dq, $POCH_2$; 3.15 m, PCH_2; 2.08 s, 1.85 s, To–CH_3; 1.26 t, $POCCH_3$; 0.74 t, O_2CCH_2; 0.46 h, O_2CCH_2; 0.30 t, O_2CCCCH_3. IR (cm^{-1}): 1542 s, 1493 m, 1440 s, 1416 s, 1331 m, 1018 s, 958 m, 693 m, 651 m, 525 m.

R = Hp. The procedure followed that for R = Me, using 0.2060 g (0.123 mmol) of $[Mo(NTo)(S_2P(OEt)_2)S]_4$, 49 μL (0.31 mmol) of $HpCO_2H$, 43 μL (0.31 mmol) of Et_3N, and 0.1411 g (0.354 mmol) of $Ph_2PC_2H_4PPh_2$. After rotavaporation, dissolution (CH_2Cl_2), and filtration, the filtrate (3 mL) was treated with MeOH (6 mL) and the precipitate was collected. Recrystallization from CH_2Cl_2 (1.2 mL)/MeOH (2.4 mL) and vacuum-drying for 10 days gave orange crystals (0.2200 g, 75%). NMR data are as follows (ppm).[30] ^{31}P: 117.3 t, $S_2P(OEt)_2$; 40.1 d, $Ph_2PC_2H_4PPh_2$; $^4J_{P-P}$ = 7 Hz. ^1H: 8.13 m, 7.74 m, 7.25 m, PC_6H_5; 6.78 d, 6.58 d, 5.91 d, 5.12 d, To–H; 4.23 dq, 4.12 dq, $POCH_2$; 3.16 m, PCH_2; 2.08 s, 1.85 s, To–CH_3; 1.26 t, $POCCH_3$; 1.16 m, 1.02 m, 0.86 m, 0.81 t, 0.77 m, 0.63 m, 0.41 m, $O_2CC_7H_{15}$. IR (cm^{-1}): 1540 s, 1496 s, 1440 s, 1412 s, 1332 m, 1017 s, 958 m, 693 m, 651 m, 524 m.

$[Mo_2(NTo)_2S_2(Ph_2PC_2H_4PPh_2)_2(S_2P(OEt)_2)]^+(S_2P(OEt)_2)^-$ (3). $Ph_2PC_2H_4PPh_2$ (0.3400 g, 0.853 mmol) was added to a solution of $[Mo(NTo)(S_2P(OEt)_2)S]_4$ (0.3501 g, 0.209 mmol) in C_6H_6 (10 mL), followed by addition of MeOH (10 mL). This mixture was stirred for 5 h and then rotavapped. A CH_2Cl_2 filtrate (3 mL) of the residue was treated with Et_2O (30 mL). The resulting precipitate was filtered, washed (Et_2O), and vacuum-dried to give orange crystals (0.6342 g, 93%). Anal. Calcd for $Mo_2C_{74}H_{82}N_2O_4P_6S_6$: C, 54.4; H, 5.1; S, 11.8. Found: C, 54.5; H, 5.1; S, 12.1. NMR data are as follows (ppm).[30] ^{31}P: 115.2 s, $S_2P(OEt)_2$ (anion); 97.3 p, $S_2P(OEt)_2$ (bridge); 35.2 d, $Ph_2PC_2H_4PPh_2$; $^3J_{P-P}$ = 24 Hz. ^1H: 8.31 m, 8.22 m, 7.32 m, 7.21 m, PC_6H_5; 5.84 d, 5.09 d, To–H; 4.22 m, $POCH_2$ (anion); 3.60 m, PCH_2; 2.06 m, $POCH_2$ (bridge); 1.79 s, To–CH_3; 1.29 t, $POCCH_3$ (anion); 0.42 t, $POCCH_3$ (bridge). Peaks due to $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and $Ph_2PC_2H_4PPh_2$ are also present due to the equilibrium described in the text. IR (cm^{-1}): 1490 m, 1437 s, 1315 m, 1030 s, 932 m, 692 s, 679 s, 641 m, 521 s.

$[Mo_2(NTo)_2S_2(Ph_2PC_2H_4PPh_2)_2(O_2CMe)]^+(S_2P(OEt)_2)^-$ (4). To a solution of $MeCO_2H$ (5.4 μL, 0.094 mmol) and Et_3N (13 μL, 0.094 mmol) in CH_2Cl_2 (10 mL) was added $[Mo_2(NTo)_2S_2(Ph_2PC_2H_4PPh_2)_2(S_2P(OEt)_2)]^+(S_2P(OEt)_2)^-$ (**3**) (0.1498 g, 0.0917 mmol). The solution was stirred for 1 h and then rotavapped. The residue was slurried in 1/1 acetone/H_2O (5 mL), and the slurry was filtered; this was then repeated three times. Finally, the solid was slurried in 1/1 acetone/H_2O (10 mL), filtered out, and washed (Et_2O). The product was dissolved in CH_2Cl_2, and the solution was filtered, followed by rotavaporation of the filtrate. Recrystallization of this material from CH_2Cl_2 (0.5 mL)/Et_2O (20 mL) gave orange crystals (0.0902 g, 64%). Anal. Calcd for $Mo_2C_{72}H_{75}N_2O_4P_5S_4$: C, 57.4; H, 5.0; P, 10.3; S, 8.5. Found: C, 57.4; H, 5.3; P, 10.6; S, 8.7. NMR data are as follows (ppm).[30] ^{31}P: 115.3 s, $S_2P(OEt)_2$; 42.8 s, $Ph_2PC_2H_4PPh_2$. ^1H: 8.19 m, 7.51 m, 7.32 m, 7.16 m, PC_6H_5; 6.26 d, 5.57 d, To–H; 4.18 p, $POCH_2$; 3.32 m, PCH_2; 2.02 s, To–CH_3; 1.27 t, $POCCH_3$; −0.17 s, O_2CCH_3. IR (cm^{-1}): 1522 m, 1512 m, 1490 m, 1436 s, 1323 m, 1032 m, 923 m, 691 s, 676 sh, 522 m.

Crystallography. A red block crystal of **2** (R = Hp), from CH_2Cl_2/MeOH, measuring 0.26 × 0.33 × 0.38 mm, was used for data collection. Crystal data and experimental details are given in Table I. Cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry of 25 accurately centered reflections (13° < θ < 16°). The choice of space group was determined by the systematic absences and confirmed by using the program TRACER[31] and subsequent least-squares refinement. Data were collected at room temperature on an Enraf-Nonius CAD4 automated diffractometer by using the ω–2θ scan technique. As a check on crystal and electronic stability, three representative reflections were measured every 60 min. The intensities of these reflections remained constant within experimental error throughout data collection, so no decay correction was applied. The data were corrected for Lorentz and polarization effects,[32] and an empirical absorption correction (ψ scans) was applied.

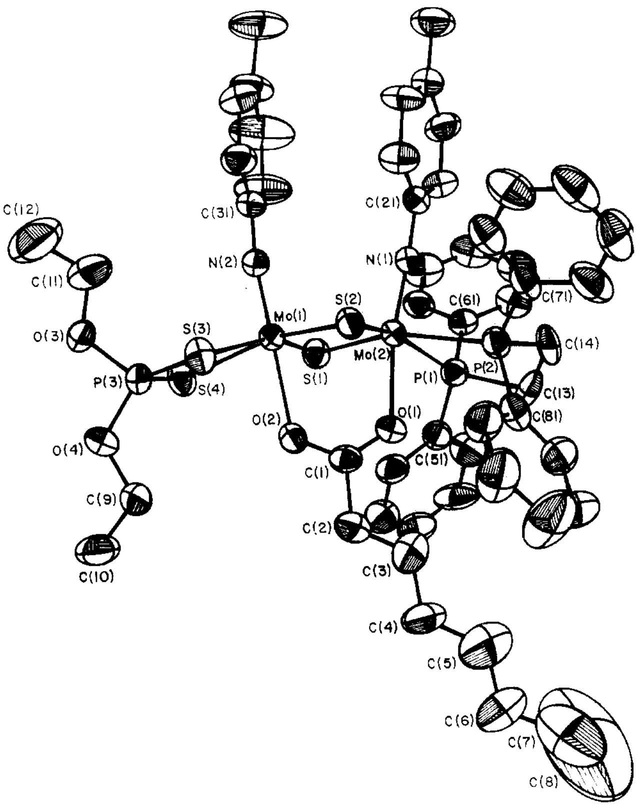

Figure 1. ORTEP view of $[Mo_2(NTo)_2S_2(S_2P(OEt)_2)(Ph_2PC_2H_4PPh_2)(O_2CHp)]$.

The structure was solved by using the Patterson method, which revealed the positions of the molybdenum atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculation in idealized positions with isotropic thermal parameters set to 1.3 × B_{iso} of the bonded atom. Hydrogen parameters were not refined. Refinement was carried out by full-matrix least squares on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where the weight w is defined as $[\sigma^2(F) + (0.04F)^2 + 2.0]^{-1}$.[33] Scattering factors were taken from Cromer and Waber,[34] and anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[35] An isotropic extinction parameter was not refined. CH_2Cl_2 solvate (clearly evident in the ^1H NMR spectrum and estimated to be 12 mol % for that crystal) was only partially located as disordered chlorine atoms lying across the crystallographic 2-fold axis. The carbon atom of the solvate was not located. Carbon atoms at the end of the octanoate ligand have very large thermal parameters, indicative of significant movement of the carbon chain, but no disorder was observed. In the final cycles of refinement the parameters for these atoms were held constant. The model converged with final agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.056$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.051$. The highest peak in the final difference Fourier map had a height of 1.25 (5) e/Å^3.

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(31) Lawson, S. L.; Jacobsen, R. A. Ames Laboratory Report IS-141; USAEC, Iowa State University: Ames, IA, 1965.

(32) All computations were performed by using the Enraf-Nonius VAX/SDP system of crystallographic programs unless otherwise stated: Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R., vanKonigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978.

(33) Killean, R. C.; Lawrence, J. L. *Acta Crystallogr.* **1969**, *B25*, 1750.

(34) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(35) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table II. Positional Parameters for Non-Hydrogen Atoms and Equivalent Isotropic Temperature Factors

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Mo(1)	0.82286 (2)	0.10061 (3)	0.41526 (1)	2.869 (7)	C(25)	0.5997 (3)	0.3876 (6)	0.3045 (3)	5.5 (1)
Mo(2)	0.79969 (2)	0.25595 (2)	0.35588 (1)	2.792 (7)	C(26)	0.6465 (2)	0.3594 (5)	0.3049 (2)	4.7 (1)
Cl(11)[a]	0.0479 (8)	0.5765 (7)	0.2470 (5)	7.5 (4)	C(27)	0.5518 (4)	0.4365 (8)	0.3468 (4)	7.6 (2)
Cl(12)[a]	−0.0128 (7)	0.693 (1)	0.2693 (7)	7.3 (4)	C(31)	0.7197 (2)	0.1189 (3)	0.4229 (2)	3.5 (1)
S(1)	0.77108 (5)	0.10334 (8)	0.32911 (4)	3.46 (2)	C(32)	0.7243 (3)	0.1481 (5)	0.4662 (3)	4.8 (1)
S(2)	0.85729 (5)	0.24877 (7)	0.44215 (4)	3.25 (2)	C(33)	0.6747 (3)	0.1696 (6)	0.4645 (3)	5.4 (2)
S(3)	0.89676 (6)	0.05053 (9)	0.50229 (5)	4.03 (3)	C(34)	0.6268 (3)	0.1616 (5)	0.4244 (3)	6.2 (2)
S(4)	0.82388 (6)	−0.07269 (8)	0.40743 (5)	4.07 (3)	C(35)	0.6218 (4)	0.1336 (9)	0.3792 (4)	9.0 (3)
P(1)	0.77007 (5)	0.28669 (8)	0.26642 (5)	3.30 (3)	C(36)	0.6696 (3)	0.1141 (8)	0.3802 (3)	7.9 (2)
P(2)	0.83971 (5)	0.41636 (8)	0.36284 (5)	3.41 (3)	C(37)	0.5717 (3)	0.192 (1)	0.4197 (4)	9.1 (2)
P(3)	0.87670 (5)	−0.07781 (8)	0.47933 (5)	3.53 (3)	C(51)	0.7879 (2)	0.2119 (4)	0.2316 (2)	3.9 (1)
O(1)	0.8755 (2)	0.2190 (2)	0.3589 (1)	3.63 (8)	C(52)	0.7689 (3)	0.2311 (6)	0.1838 (2)	5.9 (2)
O(2)	0.8955 (1)	0.0909 (2)	0.4040 (1)	3.68 (8)	C(53)	0.7839 (3)	0.174 (1)	0.1566 (3)	7.5 (2)
O(3)	0.8535 (2)	−0.1329 (3)	0.5069 (1)	5.11 (9)	C(54)	0.8160 (3)	0.1048 (6)	0.1771 (2)	5.6 (2)
O(4)	0.9281 (2)	−0.1425 (3)	0.4950 (2)	4.81 (9)	C(55)	0.8343 (3)	0.0796 (5)	0.2240 (3)	5.9 (2)
N(1)	0.7402 (2)	0.3026 (3)	0.3494 (2)	3.45 (9)	C(56)	0.8198 (3)	0.1349 (5)	0.2519 (2)	4.6 (1)
N(2)	0.7676 (2)	0.1057 (3)	0.4232 (1)	3.60 (8)	C(61)	0.6955 (2)	0.2989 (4)	0.2251 (2)	4.0 (1)
C(1)	0.9055 (2)	0.1518 (4)	0.3815 (2)	3.3 (1)	C(62)	0.6709 (3)	0.3791 (5)	0.2003 (3)	5.1 (2)
C(2)	0.9565 (3)	0.1375 (5)	0.3792 (3)	5.7 (2)	C(63)	0.6158 (3)	0.3848 (7)	0.1706 (3)	6.0 (2)
C(3)	0.9757 (4)	0.2087 (8)	0.3632 (5)	11.4 (3)	C(64)	0.5813 (3)	0.3118 (7)	0.1621 (3)	6.0 (2)
C(4)	1.0225 (4)	0.2022 (9)	0.3584 (4)	10.1 (2)	C(65)	0.6052 (3)	0.2291 (7)	0.1872 (3)	6.2 (2)
C(5)	1.0419 (6)	0.275 (1)	0.3411 (6)	24 (1)	C(66)	0.6624 (2)	0.2255 (4)	0.2192 (3)	4.4 (1)
C(6)	1.0869 (6)	0.273 (1)	0.3371 (6)	25 (1)	C(71)	0.8357 (3)	0.5012 (3)	0.4017 (3)	4.3 (1)
C(8)	1.1264 (8)	0.381 (1)	0.3324 (7)	38 (1)	C(72)	0.8503 (4)	0.5945 (5)	0.3993 (4)	6.7 (2)
C(7)	1.0931 (9)	0.340 (1)	0.3031 (8)	35 (1)	C(73)	0.8514 (4)	0.6571 (4)	0.4320 (4)	6.7 (2)
C(9)	0.9643 (2)	−0.1211 (4)	0.4775 (3)	5.1 (1)	C(74)	0.8407 (4)	0.6330 (5)	0.4675 (4)	7.2 (2)
C(10)	0.9866 (3)	−0.2084 (6)	0.4698 (3)	6.5 (2)	C(75)	0.8259 (4)	0.5455 (5)	0.4680 (3)	6.5 (2)
C(11)	0.8065 (3)	−0.0990 (8)	0.5065 (3)	7.0 (2)	C(76)	0.8218 (3)	0.4801 (4)	0.4354 (3)	5.2 (2)
C(12)	0.8118 (6)	−0.130 (2)	0.5532 (5)	21.1 (4)	C(81)	0.9118 (3)	0.4298 (3)	0.3831 (2)	4.1 (1)
C(13)	0.8008 (2)	0.3991 (4)	0.2643 (2)	4.6 (1)	C(82)	0.9305 (3)	0.4640 (5)	0.3543 (4)	6.0 (2)
C(14)	0.8020 (3)	0.4652 (3)	0.3008 (2)	4.7 (2)	C(83)	0.9878 (3)	0.4767 (8)	0.3736 (4)	7.3 (2)
C(21)	0.6938 (2)	0.3388 (3)	0.3479 (2)	3.3 (1)	C(84)	1.0242 (4)	0.458 (1)	0.4209 (6)	11.4 (4)
C(22)	0.6973 (3)	0.3528 (6)	0.3912 (3)	5.3 (2)	C(85)	1.0063 (4)	0.4180 (8)	0.4499 (5)	8.7 (3)
C(23)	0.6507 (2)	0.3823 (6)	0.3909 (3)	5.8 (2)	C(86)	0.9515 (3)	0.4060 (6)	0.4319 (3)	5.7 (2)
C(24)	0.6015 (2)	0.4037 (5)	0.3479 (2)	4.8 (1)					

[a] Atoms due to partial CH_2Cl_2.

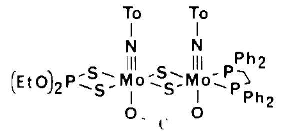
Table III. Selected Bond Distances (Å)

Mo(1)–S(1)	2.355 (1)	Mo(1)–Mo(2)	2.8161 (5)
Mo(1)–S(2)	2.350 (1)	P(1)–C(13)	1.885 (7)
Mo(1)–S(3)	2.567 (1)	P(2)–C(14)	1.839 (6)
Mo(1)–S(4)	2.552 (1)	C(13)–C(14)	1.51 (1)
Mo(1)–O(2)	2.300 (6)	P(3)–S(3)	1.989 (2)
Mo(1)–N(2)	1.732 (5)	P(3)–S(4)	1.987 (2)
Mo(2)–S(1)	2.379 (1)	N(1)–C(21)	1.408 (8)
Mo(2)–S(2)	2.366 (1)	N(2)–C(31)	1.384 (8)
Mo(2)–P(1)	2.578 (2)	C(1)–O(1)	1.254 (6)
Mo(2)–P(2)	2.571 (1)	C(1)–O(2)	1.274 (7)
Mo(2)–O(1)	2.189 (5)	C(1)–C(2)	1.52 (1)
Mo(2)–N(1)	1.743 (5)		

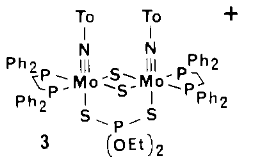
Selected results are given in Tables II–IV; Figure 1 shows the molecular structure.

Results

Ligand permutations on the $[Mo_2(NTo)_2S_2]^{2+}$ core obtained in the current work include the dithiophosphate–diphos–μ-carboxylate dimer **2**, the bis(diphos)–μ-dithiophosphate dimer cation **3**, and the bis(diphos)–μ-acetate dimer cation **4**. Both **3** and **4** are readily isolated with $(EtO)_2PS_2^-$ counterions.



2



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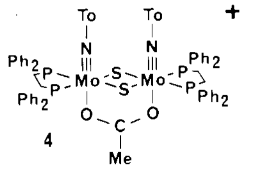
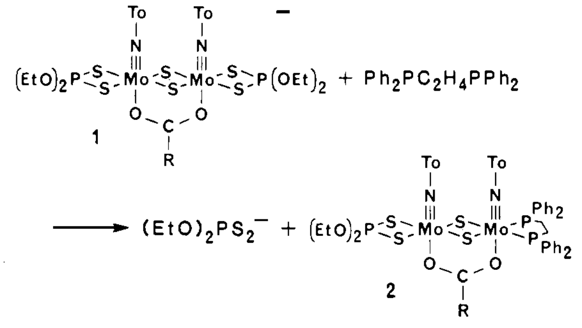


4

Table IV. Selected Bond Angles (deg)

S(1)–Mo(1)–S(2)	107.33 (4)	S(1)–Mo(2)–S(2)	106.02 (5)
S(1)–Mo(1)–S(4)	86.18 (4)	S(1)–Mo(2)–P(1)	84.99 (5)
S(2)–Mo(1)–S(3)	85.36 (4)	S(2)–Mo(2)–P(2)	86.42 (4)
S(3)–Mo(1)–S(4)	77.17 (5)	P(1)–Mo(2)–P(2)	78.75 (5)
N(2)–Mo(1)–O(2)	178.8 (2)	N(1)–Mo(2)–O(1)	170.4 (2)
Mo(2)–Mo(1)–N(2)	99.3 (1)	Mo(1)–Mo(2)–N(1)	105.1 (2)
Mo(2)–Mo(1)–O(2)	81.32 (9)	Mo(1)–Mo(2)–O(1)	84.3 (2)
Mo(1)–N(2)–C(31)	170.8 (4)	Mo(2)–N(1)–C(21)	175.8 (4)
Mo(1)–O(2)–C(1)	122.8 (3)	Mo(2)–O(1)–C(1)	125.3 (4)
O(1)–C(1)–O(2)	126.1 (6)		

The neutral dimer **2** is readily obtained by reaction of $Ph_2PC_2H_4PPh_2$ with the dimer anion **1** (eq 1). The dimer anion



(1)

1 is itself generated in situ by the favorable equilibrium of eq 2,[36] further enhanced by use of excess carboxylate in the syntheses. Compounds **2** were characterized by NMR and IR spectroscopy, and the crystal structure of the octanoate derivative (R = Hp) was obtained. A telltale feature of ^{31}P NMR spectra is the

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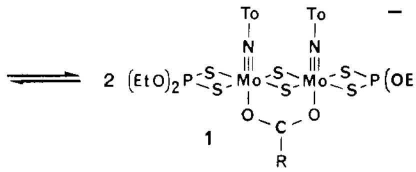
(36) Noble, M. E.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1983**, *22*, 1756.

$[Mo(NTo)(S_2P(OEt)_2)S]_4 + 2\ RCO_2^-$



1

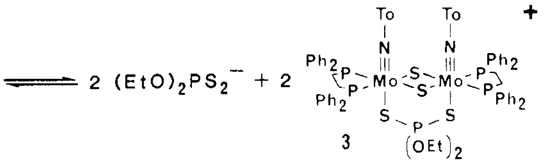
(2)

observation of ${}^4J_{P-P}$ = 7 Hz due to the different ligands. The products are extremely tenacious for a variety of lattice solvents, and long periods of vacuum-drying are needed even to totally remove CH_2Cl_2. It was this property that dictated synthesis of the three carboxylate derivatives for crystallographic purposes: only with the octanoate derivative was lattice solvent retention sufficiently stable during data collection, although some solvent was nevertheless present.

Interestingly, treatment of the dimer anion **1** or the singly exchanged product **2** with excess $Ph_2PC_2H_4PPh_2$ fails to displace the second dithiophosphate. This is unexpected, since the anticipated bis(diphos)–μ-acetate dimer **4** is obtainable by other means described below.

The bis(diphos)–μ-dithiophosphate dimer cation **3** is obtained in high yield as the $(EtO)_2PS_2^-$ salt by simple ligand exchange between $[Mo(NTo)(S_2P(OEt)_2)S]_4$ and $Ph_2PC_2H_4PPh_2$ (eq 3).

$[Mo(NTo)(S_2P(OEt)_2)S]_4 + 4\ Ph_2PC_2H_4PPh_2$



3

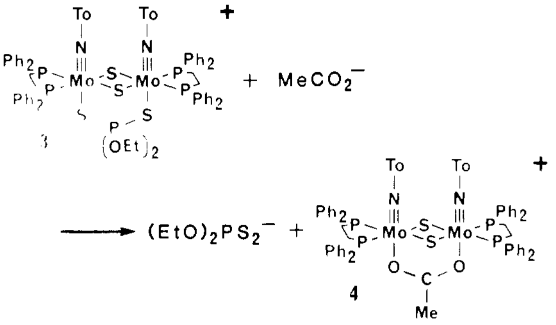
(3)

The products were characterized by NMR and IR spectroscopy. The ${}^{31}P$ NMR spectrum was most definitive: equivalent phosphines are clearly contained within one doublet, while the bridge $(EtO)_2PS_2$ appears as a quintet, ${}^3J_{P-P}$ = 24 Hz. The $(EtO)_2PS_2$ anion is clearly observed separately from its bridge counterpart, in both ${}^{31}P$ and ${}^1H$ NMR spectra. Bridge dithiophosphates are well-known as asymmetrically bridging or as symmetrically bridging, albeit puckered or twisted.[37-41] The NMR data of **3** clearly indicate a bridge of high (at least averaged) symmetry.

Equation 3 is in fact an equilibrium, and all species are clearly seen in the NMR spectra. The equilibration is rapid and displays a marked solvent dependence. Attempts to determine K values were inconsistent and indicated substantial ion pairing. The solvent dependence was demonstrable by product/reactant ratios, however, as determined by ${}^{31}P$ NMR spectroscopy. For solutions that were 0.055 F in **3**, the observed ratios were 80 (1/1 C_6D_6/MeOH), 16 (CH_2Cl_2), 9 ($CDCl_3$), 0.19 (THF), and 0.024 (C_6D_6). The equilibrium of eq 3 prevents NMR analysis of the presence of coprecipitated starting materials in the isolated products. That the high yield is indeed of clean product is discernible by other means. The presence of coprecipitated $Ph_2PC_2H_4PPh_2$ is not evident in IR spectra; this was determined by doping a sample of **3** with 2% diphos: the dopant gave a very distinct peak at 729 cm^{-1} not previously present. Further substantiation was obtained by dissolving a sample of **3** in $CDCl_3$ containing a 3-fold excess of $Et_3NH(O_2CMe)$: ${}^{31}P$ NMR analysis showed the μ-acetate dimer **4** with no peaks attributable to any coprecipitated impurities.

The equilibrium of eq 3 is also all-or-none: there is no indication whatsoever of an intermediate containing one chelating dithiophosphate and one chelating diphos, regardless of bridge.

The bis(diphos)–μ-acetate dimer cation **4** is obtained by simple bridge exchange between the bis(diphos)–μ-dithiophosphate dimer cation **3** and acetate (eq 4). The reaction is total and no equilibrium is observed, even with isolation of the dimer cation as the $(EtO)_2PS_2^-$ salt. The products were characterized by NMR and IR spectroscopy, the results of which were fully consistent with the structure shown.



3 4

(4)

In addition to the irreversibility of eq 4, anionic $(EtO)_2PS_2^-$ does not exchange with bound $Ph_2PC_2H_4PPh_2$, which would give the neutral dithiophosphate–diphos–μ-acetate dimer **2**. The neutral dimer **2**, however, is obtained as an impurity when the sequence of addition in the synthesis is reversed: dissolution first of the bis(diphos)–μ-dithiophosphate dimer cation **3** sets up the equilibrium of eq 3; treatment with acetate then gives some **2** due to the sequence of eq 2 and eq 1.

NMR Spectroscopy. Some ${}^{31}P$ NMR results have been noted above in terms of P–P couplings. ${}^1H$ NMR spectra display unusual upfield shifts due to proximity to $Ph_2PC_2H_4PPh_2$ phenyl rings. Tolylimido ring resonances in the neutral dimers **2** lie at δ 6.8 and 6.6 for those next to $(EtO)_2PS_2$ but at δ 5.9 and 5.1 for those next to $Ph_2PC_2H_4PPh_2$. The upfield shift is also seen in the bis(diphos)–μ-dithiophosphate dimer cation **3** and, albeit less dramatically, in the bis(diphos)–μ-acetate dimer cation **4**. Upfield shifts for bridge resonances are also clearly seen in both bis(diphos) dimer cations **3** and **4**. For the μ-dithiophosphate dimer **3**, the bridge $POCH_2$ resonance is at δ 2.06 versus δ 4.22 for the anion. For the μ-acetate dimer **4**, the acetate resonance is upfield of Me_4Si at δ −0.17.

Observation of interligand ${}^3J_{P-P}$ in the bis(diphos)–μ-dithiophosphate dimer cation **3** suggested ${}^3J_{P-C}$ coupling might be observable between $Ph_2PC_2H_4PPh_2$ and bridge acetate C-1 positions in the neutral dimer **2** (R = Me) and in the bis(diphos)–μ-acetate dimer cation **4**. This was considered further confirmation for the structure of the latter. The coupling was readily seen by using enriched products obtained in syntheses with $CH_3{}^{13}CO_2H$. [1-^{13}C]Acetate **2** indeed showed coupling to $Ph_2PC_2H_4PPh_2$ but not to $(EtO)_2PS_2$: the carboxylate ${}^{13}C$ resonance was a triplet at δ 174.3, and the diphos ${}^{31}P$ resonance was now a double doublet; ${}^3J_{P-C}$ = 3.5 Hz. Likewise, [1-^{13}C]acetate **4** showed the carboxylate ${}^{13}C$ resonance as a quintet at δ 175.0 and the diphos ${}^{31}P$ resonance as a doublet; ${}^3J_{P-C}$ = 3.5 Hz.

As a final note on interligand P–C coupling, this was also observed for the tolylimido ipso (N-bound) carbon (${}^{13}C$: δ 151.5 t; ${}^3J_{P-C}$ = 2 Hz) at the diphos end in the neutral dimer **2** (R = Me) but not for the dithiophosphate end (${}^{13}C$: δ 153.6 s), thereby allowing a distinction between the two. No such coupling was resolved for ipso carbons in the bis(diphos) dimer cations **3** and **4** although these peaks were noticeably broader. Nielson[42] has

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(37) Lawton, S. L.; Rohrbaugh, W. J.; Kokotailo, G. T. *Inorg. Chem.* **1972**, *11*, 2227. See also: Jiang, Y.; Alvarez, S.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 749.

(38) Wasson, J. R.; Woltermann, G. M.; Stoklosa, H. J. *Fortschr. Chem. Forsch.* **1973**, *35*, 65.

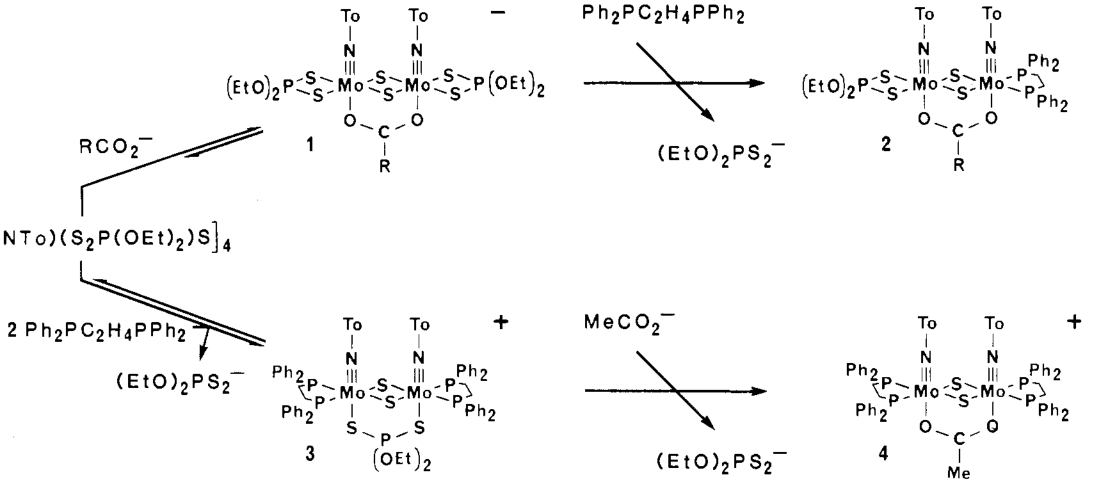
(39) Mehrotra, R. C.; Srivastava, G.; Chauhan, B. P. S. *Coord. Chem. Rev.* **1984**, *55*, 207.

(40) Chisholm, M. H.; Ho, D. M.; Huffman, J. C.; Van Der Sluys, W. G. *Polyhedron* **1987**, *6*, 1115.

(41) Drew, M. G. B.; Hobson, R. J.; Mumba, P. P. E.; Rice, D. A. *Inorg. Chim. Acta* **1988**, *142*, 301.

(42) Nielson, A. J. *Inorg. Chim. Acta* **1987**, *133*, 305.

Scheme I



related ^{13}C ipso shifts for (phenylimido)tungsten complexes to electronic influences of the metal. While the shift difference (2.1 ppm) presently observed in **2** (R = Me) is significant relative to the range reported (5.4 ppm),[42] electronic conclusions thereby regarding cis dithiophosphate ligation versus cis diphos ligation would necessarily be tempered by anisotropic contributions to the shift difference.

Crystal Structure. Many crystal structures of *syn*-$[Mo_2Z_2(\mu\text{-}S)_2L_2]$ (Z = O, S, NR; L = chelating ligand) have been reported for a variety of molybdenum(V) compounds.[1,13,43–57] Several imido–dithiophosphate–μ-carboxylate derivatives have also been reported.[36,58–60] The crystal structure results for the present dithiophosphate–diphos–μ-octanoate **2** (R = Hp) show basic similarities to the general features of these compounds, and these aspects need not be further discussed. The primary features for present consideration are the ligation by $Ph_2PC_2H_4PPh_2$ on an $Mo_2S_2^{6+}$ core and any end-to-end inequivalence in the structure that may be a result of the different bidentate ligands. While many lower valent (up to Mo(IV)) Mo–diphos complexes have been crystallographically characterized, Mo(V)–diphos crystal structures are lacking. Several end-to-end inequivalent $[Mo_2Z_2(\mu\text{-}S)_2L_2]$ complexes have also been structurally characterized; these generally involve dimers with different terminal groups, Z, or different end ligands, L.[13,46,48,52,56,57]

Mo–P bond lengths for **2** (R = Hp) are long compared to a range (2.485–2.565 Å) observed for Mo(IV)–$Ph_2PC_2H_4PPh_2$ complexes;[61–66] this range, however, extends to 2.688 Å when steric or trans influences are operative.[67,68] Steric effects are presently attributable to juxtaposition with the tolylimido ring. The edge of the imido ring is in the face of the diphos C(61) ring, with the distances between the ortho imido H and C(61) ring carbons as short as 2.8 Å, corresponding to van der Waals contacts.[69] Closest contact between the tolylimido ring and the C(71) ring, however, is only at their mutual ortho hydrogens, with a separation of 2.37 (1) Å, again of a van der Waals distance.[69] The proximity of the tolylimido and phenyl rings is consistent with the NMR anisotropic shifts discussed above.

End-to-end structural differences are evident primarily in Mo–S(bridge) bond lengths and the binding of the octanoate. The difference in Mo–N bond lengths is of questionable significance and is nevertheless observed in end-to-end equivalent structures.[36,59]

Average Mo(2)–S(bridge) bond lengths are distinctly longer than those for Mo(1) by 0.020 Å. An explanation for the disparity based on steric or electronic considerations is not obvious here, since even greater disparities have been reported for $[Mo_2S_4(S_2)(S_4)]^{2-}$,[48] $[Mo_2O_2S_2(S_2)(S_3O_2)]^{2-}$,[49] and $[Mo_2S_4(HB(C_5H_7N_2)_3)(S_2CNEt_2)]$,[57] which had average Mo–S(bridge) end-to-end differences of 0.046, 0.034, and 0.033 Å, respectively. Symmetrically ligated $[Mo_2O_2S_2(S_4)_2]^{2-}$ shows a corresponding difference of ~0.04 Å although its Mo_2S_2 core showed a substantial skew in individual Mo–S(bridge) lengths.[56]

The octanoate bridge in the present structure is greatly displaced from a symmetric position, as evidenced by Mo–O bond lengths. Actually, the entire octanoate chain appears to be elongated and pulled to one side of the molecule. C(1) through C(8) are somewhat planar, with plane deviations of 0.00–0.05 Å for C(1) through C(6), although C(7) and C(8) deviate by ±0.5 Å. The orientation is believed to be due to packing, although there are no unusually short distances to the octanoate chain. Packing diagrams show C(8) approaches the spatial region bordered by the C(51) and C(81) rings of an adjacent molecule, but there remains no obvious reason to favor this overall arrangement over

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(43) Atovmyan, L. O.; Tkachev, V. V.; Shchepinov, S. A. *Sov. J. Coord. Chem.* (*Engl. Transl.*) **1978**, *4*, 460.

(44) Bunzey, G.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 682.

(45) Huneke, J. T.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3698.

(46) Newton, W. E.; McDonald, J. W.; Yamanouchi, K.; Enemark, J. H. *Inorg. Chem.* **1979**, *18*, 1621.

(47) Clegg, W.; Mohan, N.; Müller, A.; Neumann, A.; Rittner, W.; Sheldrick, G. M. *Inorg. Chem.* **1980**, *19*, 2066.

(48) Clegg, W.; Christou, G.; Garner, C. D.; Sheldrick, G. M. *Inorg. Chem.* **1981**, *20*, 1562.

(49) Müller, A.; Reinsch-Vogell, U.; Krickemeyer, E.; Bögge, H.; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 796.

(50) Coucouvanis, D.; Draganjac, M. *J. Am. Chem. Soc.* **1982**, *104*, 6820.

(51) Wall, K. L.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1983**, *22*, 2366.

(52) Noble, M. E.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1983**, *22*, 3671.

(53) Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476.

(54) Shaofang, L.; Maoyu, S.; Wendan, C.; Meiyun, H.; Jinling, H. *Fenzi Kexue Yu Huaxue Yanjiu* **1984**, *4*, 345.

(55) Pan, W.-H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459.

(56) Müller, A.; Römer, M.; Römer, C.; Reinsch-Vogell, U.; Bögge, H.; Schimanski, U. *Monatsh. Chem.* **1985**, *116*, 711.

(57) Roberts, S. A.; Young, C. G.; Cleland, W. E., Jr.; Yamanouchi, K.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1988**, *27*, 2647.

(58) Noble, M. E.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1984**, *23*, 631.

(59) Noble, M. E.; Williams, D. E. *Inorg. Chem.* **1988**, *27*, 749.

(60) Pelati, J. E.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1988**, *27*, 2194.

(61) Day, V. W.; George, T. A.; Iske, S. D. A.; Wagner, S. D. *J. Organomet. Chem.* **1976**, *112*, C55.

(62) Hidai, M.; Kodama, T.; Sato, M.; Harakawa, M.; Uchida, Y. *Inorg. Chem.* **1976**, *15*, 2694.

(63) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1978**, *17*, 668.

(64) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Motevalli, M. *J. Chem. Soc., Dalton. Trans.* **1979**, 1603.

(65) Dilworth, J. R.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *Inorg. Chim. Acta* **1983**, *71*, 21.

(66) Nicholas, K. M.; Khan, M. A. *Inorg. Chem.* **1987**, *26*, 1633.

(67) Dilworth, J. R.; Neaves, B. D.; Pickett, C. J.; Chatt, J.; Zubieta, J. A. *Inorg. Chem.* **1983**, *22*, 3524.

(68) Starker, K.; Curtis, M. D. *Inorg. Chem.* **1985**, *24*, 3006.

(69) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

one more conducive to equal Mo–O bond lengths.

Discussion

Reactions demonstrated in the current work are summarized in Scheme I. The two branches depicted differ only in the sequence of the exchange by RCO_2^- or $Ph_2PC_2H_4PPh_2$. It remains interesting that no kinetic connection was observed beween dimers **2** and **4** in the presence of excess diphos or dithiophosphate, despite the otherwise facile displacement of the latter by the former.

The vast majority (but not all) of $[Mo_2Z_2(\mu\text{-}S)_2L_2]$ complexes in recent years have involved an L = anionic (–1 or –2) sulfur donor. Two significant consequences of replacing one or both ligands L with phosphines are reduction of the overall charge on the complex and substitution of a potential π-donor by a potential π-acceptor. The π-acceptor properties per se, however, are not expected to be of great significance for d^1 Mo(V), which is itself π-accepting, particularly with regard to the terminal Z group. Reduced overall negative charge would be expected to reduce somewhat the nucleophilic reactivity at bridge sulfur positions. Initial results for the dithiophosphate–diphos–μ-carboxylate dimer **2** indeed show sulfur-based nucleophilic reactions, but these are much slower than those of dimer anion **1**. Steric effects may also be operative.

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Supplementary Material Available: Tables of full crystallographic parameters, bond lengths and angles excluded from text, hydrogen atom parameters, displacement parameters, and least-squares planes (11 pages); a table of structure factors (24 pages). Ordering information is given on any current masthead page.

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Conformational Preferences in Six-Coordinate, Octahedral Complexes of Molybdenum(III). Synthesis and Structure of MoX_3(dppe)L [X = Cl, Br, I; dppe = Bis(diphenylphosphino)ethane; L = Tetrahydrofuran, Acetonitrile, Trimethylphosphine]

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$MoBr_3(THF)_3$ can be obtained in large scale and high yields by bromination of $Mo_2Br_4(CO)_8$ in tetrahydrofuran (THF). The ligand replacement reaction of $MoX_3(THF)_3$ with bis(diphenylphosphino)ethane (dppe) in THF as solvent affords the mononuclear MoX_3(dppe)(THF) compounds. An X-ray crystal structure investigation of the iodide derivative shows an octahedral structure with a *meridional* arrangement of the three iodo ligands. Crystal data: monoclinic, space group $P2_1/n$, $a = 24.049$ (4) Å, $b = 12.283$ (2) Å, $c = 12.985$ (2) Å, $\beta = 99.94$ (2)°, $V = 3778.1$ (2) Å^3, $Z = 4$, $d_c = 1.79$ g cm^{-3}, μ(Mo Kα) = 29.34 cm^{-1}, $R = 0.0361$, $R_w = 0.0517$ for 354 parameters and 3589 observations with $F_o^2 > 3\sigma(F_o^2)$. The remaining THF ligand in MoX_3(dppe)(THF) can be replaced with MeCN or PMe_3 but not with $P(n\text{-}Bu)_3$, PPh_3, or dppe. The X-ray crystal structure of $MoI_3(dppe)(PMe_3)$ shows an octahedral geometry with a *facial* arrangement of the three iodo ligands. Crystal data: orthorhombic, space group *Pnma*, $a = 15.413$ (4) Å, $b = 21.786$ (4) Å, $c = 9.787$ (1) Å, $V = 3286$ (2) Å^3, $Z = 4$, $d_c = 1.92$ g cm^{-3}, μ(Cu Kα) = 274.81 cm^{-1}, $R = 0.080$, $R_w = 0.080$ for 154 parameters and 1091 observations with $F_o^2 > 3\sigma(F_o^2)$. For comparison purposes, a crystallographic study of *mer*-$MoI_3(PMe_3)_3$ has also been carried out. Crystal data: tetragonal, space group $I4_1/a$, $a = 18.379$ (5) Å, $c = 26.257$ (5) Å, $V = 8896$ (4) Å^3, $Z = 16$, $d_c = 2.11$ g cm^{-3}, μ(Mo Kα) = 47.62 cm^{-1}, $R = 0.064$, $R_w = 0.074$ for 145 parameters and 1854 observations with $F_o^2 > 2.5\sigma(F_o^2)$. The conformational preference in these octahedral Mo(III) complexes is discussed in terms of the steric interactions between the neutral ligands.

Introduction

Mononuclear molybdenum(III) compounds of general formula MoX_3L_3 or MoX_3(L-L)L′ (X = halogen; L, L′ = neutral monodentate ligand; L-L = neutral bidentate ligand) have been relatively well studied.[2] The neutral monodentate or bidentate ligands can be either hard[3] [tetrahydrofuran (THF), nitriles] or soft[4] (phosphines), always giving rise to high-spin stable compounds. Most of the studies, however, have been carried out on the chloride systems, primarily because the easiest route to these products is through the $MoX_3(THF)_3$ starting material (eq 1 and 2), which can be easily prepared for X = Cl.[3g,h,5]

$$MoX_3(THF)_3 + nL \rightarrow MoX_3L_n(THF)_{3-n} \qquad (1)$$

$$MoX_3(THF)_3 + \text{L-L} \rightarrow MoX_3(\text{L-L})(THF) \qquad (2)$$

Other synthetic routes employed include interaction of MoX_3 or $[MoX_5(H_2O)]^-$ with L[3d,e,6] and, in the case of hard donor ligands, disproportionation of Mo(II) carbonyl compounds.[3b,c] $MoX_3(py)_3$ (X = Cl, Br; py = pyridine) was also prepared by interaction of the Mo(II) dimer $Mo_2X_4(py)_4$ with pyridine at high temperatures.[7] These alternative methods, however, do not offer the generality and facilitation of the THF replacement reactions described in eq 1 and 2.

The large-scale synthesis and THF replacement reactions of $MoI_3(THF)_3$ have been reported recently,[8] and we have successfully employed the same strategy in the large-scale preparation of the bromide system. The reactions described in eq 1 and 2 can now be applied to the extended series of Mo(III) halide derivatives, where X = Cl, Br, I. We report here studies on mononuclear

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(2) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 3, pp 1329–1333.

(3) (a) Allen, E. A.; Feenan, K.; Fowles, G. W. A. *J. Chem. Soc.* **1965**, 1636. (b) Westland, A. D.; Muriithi, N. *Inorg. Chem.* **1972**, *11*, 2971. (c) Westland, A. D.; Muriithi, N. *Inorg. Chem.* **1973**, *12*, 2356. (d) Brencic, J. V. *Z. Anorg. Allg. Chem.* **1974**, *403*, 218. (e) Brencic, J. V.; Leban, I. *Z. Anorg. Allg. Chem.* **1978**, *445*, 251. (f) Brencic, J. V.; Ceh, B.; Leban, I. *Z. Anorg. Allg. Chem.* **1986**, *538*, 212. (g) Dilworth, J. R.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1983**, 397. (h) Roh, S.-Y.; Bruno, J. W. *Inorg. Chem.* **1986**, *25*, 3105. (i) Völp, K.; Willing, W.; Müller, U.; Dehnicke, K. *Z. Naturforsch.* **1986**, *41B*, 1196.

(4) (a) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639. (b) Atwood, J. L.; Hunter, W. E.; Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 467. (c) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *Polyhedron* **1983**, *2*, 185. (d) Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347. (e) Dahlenburg, L.; Pietsch, B. *Z. Naturforsch.* **1986**, *41B*, 70. (f) Pietsch, B.; Dahlenburg, L. *Inorg. Chim. Acta* **1988**, *145*, 195. (g) George, T. A.; Jackson, M. A. *Inorg. Chem.* **1988**, *27*, 924. (h) Brown, P. R.; Cloke, F. G. N.; Green, M. L. H.; Tovey, R. C. *J. Chem. Soc., Chem. Commun.* **1982**, 519.

(5) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1980**, *20*, 121.

(6) Rosenheim, A.; Abel, G.; Lewy, R. *Z. Anorg. Allg. Chem.* **1931**, *197*, 189.

(7) San Filippo, J., Jr.; Schaefer King, M. A. *Inorg. Chem.* **1976**, *15*, 1228.

(8) Cotton, F. A.; Poli, R. *Inorg. Chem.* **1987**, *26*, 1514.

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