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Partial Hydrolysis of $[Mo(NR)(\mu_3\text{-}S)(S_2P(OR')_2)]_4$ and Molecular Structures of $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$ and Cubane-like $[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$

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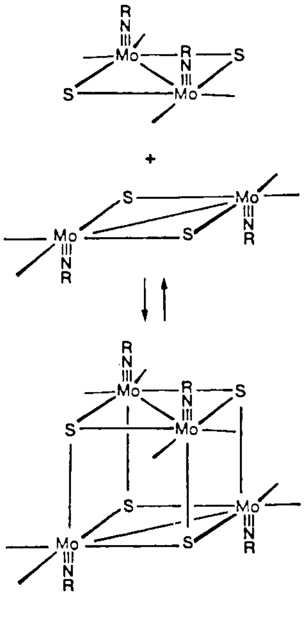
The acid-assisted hydrolysis of cubane-like $[Mo(NR)(\mu_3\text{-}S)(S_2P(OR')_2)]_4$, which ultimately yields $[MoO(\mu\text{-}S)(S_2P(OR')_2)]_2$, proceeds by way of isolable dinuclear (**D**) and tetranuclear (**T**) forms of $[Mo_2O(NR)(\mu\text{-}S)_2(S_2P(OR')_2)_2]_n$ ($R = C_6H_4CH_3$, $R' = CH_3$ or C_2H_5; $R = C_6H_5$, $R' = C_2H_5$). The dinuclear compound with $R = C_6H_4CH_3$ and $R' = CH_3$ crystallizes in the space group *Pcab* with $a = 12.514$ (1) Å, $b = 13.136$ (2) Å, $c = 28.009$ (5) Å, and $Z = 8$. Final residuals were $R(F) = 0.054$ and $R_w(F) = 0.051$. The structure consists of two square pyramids fused at the common edge containing the bridging sulfur atoms. The oxo and arylimido ligands are juxtaposed. The tetranuclear, cubane-like compound with $R = C_6H_5$ and $R' = C_2H_5$ crystallizes in the space group $P\bar{1}$ with $a = 20.026$ (6) Å, $b = 12.360$ (3) Å, $c = 12.093$ (3) Å, $\alpha = 65.46$ (1)°, $\beta = 77.46$ (1)°, $\gamma = 77.54$ (1)°, and $Z = 2$. Final values for $R(F)$ and $R_w(F)$ were 0.060 and 0.064, respectively. The average Mo–S bond length trans to an arylimido ligand is about 0.1 Å longer than those found previously for cubane-like compounds without oxo ligands while the average bond length opposite to an oxo ligand is about 0.2 Å longer than those distances. Spectroscopic evidence points to the existence of the equilibrium $2\mathbf{D} \rightleftarrows \mathbf{T}$, in solution. ^{31}P NMR studies have also indicated that exchange of the bound dithiophosphate ligands with free ligand in the acid form occurs more rapidly on the exchange sites adjacent to the oxo ligand.

Introduction

Although similarities between mononuclear arylimido and oxo compounds of molybdenum have been noted,[1] a striking difference in their polynuclear sulfur-bridged analogues has become evident. Two tetranuclear, cubane-like compounds, $[Mo(NR)(\mu_3\text{-}S)L]_4$ (NR = arylimido ligand and L = bidentate dithiophosphate and dithiocarbamate ligands) have been prepared and characterized.[2-4] Solutions of these compounds consist of equilibrium mixtures of the tetranuclear compounds and dinuclear fragments:



The strongest proof was established by the isolation of the dinuclear and tetranuclear compounds $[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$ and $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$ from the same reaction mixture, the subsequent structural characterization of each compound, and the demonstration that solutions of each compound afforded identical NMR and electronic spectra.[4] In contrast, the well-known oxo compounds $[MoO(\mu\text{-}S)L]_2$ are dinuclear in the solid state[5] and no indication for further oligomerization in solution is evident from the literature or our own work with these compounds.

This remarkable difference may stem from a weaker trans influence of the arylimido ligand or an effect in which this ligand enhances the basicity of the bridging sulfur ligands. Indeed, these effects may work in concert since CF_3CO_2H does not react with $[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$ but causes the protonation of a bridging sulfur atom in $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ and the formation of $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)]_2(\mu\text{-}S)(\mu\text{-}SH)(\mu\text{-}O_2CCF_3)$.[6]

In order to obtain another view of the relative importance of the disparate effects of the arylimido and oxo ligands, we have endeavored to prepare polynuclear sulfur-bridged compounds that contain an equal number of each of these ligands: $[Mo_2O(NR)(\mu\text{-}S)_2L_2]_n$. The HCl-assisted hydrolysis of $[Mo(NR)(\mu_3\text{-}S)(S_2P(OR')_2)]_4$ was chosen as the most probable means of reaching the desired result but the risk in this approach is the possibility of the direct addition of the acid and the formation of a product that would be similar to that formed with CF_3CO_2H. We believed, nevertheless, that the presence of water and the oxophilicity of molybdenum could tip the balance in favor of an entirely different pathway that includes the desired hydrolysis.

Experimental Section

Reagents and Procedures. The syntheses of $p\text{-}CH_3C_6H_4N_3$ and $[Mo(NR)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ ($R = C_6H_4CH_3$) were described previously.[6] Analogous procedures gave the compound with $R = C_6H_5$ without difficulty.[7] A literature method[8] provided $[(CH_3O)_2PS_2]_2$.

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[1] Haymore, B. L.; Maatta, E. A. Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063. Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409. Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Ibid.* **1980**, *19*, 1055.

[2] Edelblut, A. W.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1110.

[3] Edelblut, A. W.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1981**, *103*, 1927.

[4] Wall, K.; Folting, K.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1983**, *22*, 2366.

[5] See, for example: Atovmyan, L. O.; Tkachev, V. V.; Shchepinov, S. A. *Sov. J. Coord. Chem. (Engl. Ed.)*, **1978**, 4, 460 for $[MoO(\mu\text{-}S)(S_2P(O\text{-}i\text{-}C_3H_7)_2)]_2$.

[6] Noble, M. E.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1983**, *22*, 1756.

[7] Wall, K.; Wentworth, R. A. D., unpublished results. Anal. Calcd for $[Mo(NC_6H_5)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$: C, 29.7; H, 3.8; N, 3.5; S, 23.8. Found: C, 29.2; H, 3.8; N, 3.4; S, 24.1.

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Table I. ^{31}P and ^{1}H NMR Data for Equilibrium Mixtures of $Mo_2O(NR)(\mu\text{-}S)_2(S_2P(OR')_2)_2$ and $[Mo_2O(NR)(\mu_3\text{-}S)_2(S_2P(OR')_2)_2]_2$ in $CDCl_3$

			^{1}H[a]		
				bidentate ligand	
R	R'	^{31}P	arylimido	CH_2	CH_3
$C_6H_4CH_3$	CH_3	117.8[b] 116.3[c]	2.16 (s), 6.75 (q)		3.66 (d), 4.19 (d)[b] 3.71 (d), 4.07 (d)[c]
$C_6H_4CH_3$	CH_2CH_3	112.2[b]	2.15 (s), 6.75 (q)	3.92 (m), 4.64 (m)[b] 3.99 (m), 4.51 (m)[c]	1.29 (t), 1.53 (t)[b] 1.32 (t), 1.49 (t)[c]
C_6H_5	CH_2CH_3	112.1[b]	6.78 (m), 7.02 (m)	3.91 (m), 4.65 (m)[b] 3.99 (m), 4.53 (m)[c]	1.30 (t), 1.54 (t)[b] 1.32 (t), 1.48 (t)[c]

[a] s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. [b] Arylimido end. [c] Oxo end.

^{1}H NMR spectra were obtained on a Varian HR 220 spectrometer. ^{31}P NMR spectra were recorded on a Varian XL 100 spectrometer at 40.5 MHz as downfield shifts from external H_3PO_4. IR spectra were obtained as KBr pellets on a Perkin-Elmer 283 infrared spectrophotometer. A Perkin-Elmer 330 UV–vis–near-IR spectrophotometer provided electronic spectra. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

$[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OCH_3)_2)]_4$. A slurry of $Mo(CO)_6$ (20.3 mmol), $p\text{-}CH_3C_6H_4N_3$ (20.3 mmol), S (20.3 mmol), $[(CH_3O)_2PS_2]_2$ (14.9 mmol), and THF (~35 mL) was refluxed under N_2 for 18 h. Volatile fractions were then removed under vacuum. Benzene (30 mL) was added. The crude product was collected, washed (benzene), and dried. Recrystallization from methylene chloride/methanol afforded crystals (25%). Anal. Calcd for $[Mo(NC_6H_4CH_3)(S)(S_2P(OCH_3)_2)]_4$: C, 27.7; H, 3.4; N, 3.6; S, 24.6. Found: C, 28.2; H, 3.4; N, 3.7; S, 25.0. ^{1}H NMR ($CDCl_3$): δ 6.34 (4 H, q, aryl H), 4.20 (3 H, d, OCH_3), 3.29 (3 H, d, OCH_3), 2.00 (3 H, S, aryl CH_3). ^{31}P NMR (CH_2Cl_2): δ 115.5. Selected IR bands (cm^{-1}): 1486 (m), 1451 (m), 1320 (m), 1042 (m), 1011 (vs), 992 (sh), 803 (sh), 794 (s), 649 (sh), 638 (m), 429 (w), 390 (w).

$Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)_2$. A solution of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ (0.93 mmol), concentrated HCl (1.5 mL), and THF (75 mL) was stirred 15 min. To the orange solution were added 1 M HCl (100 mL) and diethyl ether (25 mL). The organic layer was separated, twice further extracted (1 M HCl, 50 mL), and then slowly filtered over $MgSO_4$. The filtrate was evaporated under vacuum to an orange glass. Addition of 20 mL of 1:1 diethyl ether/petroleum ether resulted in slow deposition of a yellow solid, which was collected, washed, and dried (79%). Anal. Calcd for $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)_2$: C, 24.1; H, 3.6. Found: C, 24.2; H, 3.7. Selected IR bands (cm^{-1}): 1489 (m), 1100 (m), 1047 (ms), 1002 (vs), 979 (s), 961 (s), 944 (m), 816 (s), 633 (m), 348 (w), 321 (w). NMR spectra are included in Table I.

$[Mo_2O(NC_6H_5)(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_n$ (n = 1 and 2). The procedure corresponds to that used above with $[Mo(NC_6H_5)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ (0.62 mmol), concentrated HCl (1.0 mL), and THF (50 mL) being stirred for 15 min followed by addition of diethyl ether (50 mL) and three extractions (1 M HCl, 50 mL). The glass that resulted after removal of the liquid was treated with diethyl ether (10 mL)/petroleum ether (25 mL), and crystals slowly deposited from this solution. These were collected and washed by decantation and then were dried. Recrystallization from benzene/petroleum ether gave a mixture of yellow and red crystals (59%). *Anal.* Calcd for $[Mo_2O(NC_6H_5)(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_n$: C, 22.9; H, 3.4. Found: C, 22.9; H, 3.5. Selected IR bands (cm^{-1}): yellow form 1470 (m), 1159 (m), 1050 (m), 1004 (vs), 976 (s), 965 (s), 814 (s), 796 (s), 756 (m), 631 (m), 321 (w); red form 1472 (m), 1163 (m), 1064 (sh), 1030 (sh), 1013 (vs), 969 (vs), 952 (vs), 809 (m), 791 (s), 780 (s), 760 (s), 644 (m), 630 (m), 303 (w). NMR spectra may be found in Table I.

$Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$. A slurry of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OCH_3)_2)]_4$ (0.67 mmol), concentrated HCl (1.0 mL), and THF (100 mL) was stirred 30 min. Benzene (25 mL) was added, and the resulting mixture was extracted as above. After removal of the solvent, the orange residue was treated with diethyl ether (30 mL). The product deposited slowly from this solution. Recrystallization from benzene/diethyl ether/petroleum ether afforded orange crystals (72%). Anal. Calcd for $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$: C, 19.1; H, 2.8. Found: C, 19.0; H, 2.8. Selected IR bands (cm^{-1}): 1483 (m), 1445 (m), 1327 (m), 1172 (m), 1058 (s), 1008 (vs), 960 (s), 820 (vs), 810 (vs), 638 (m), 631 (sh), 394 (m), 339 (w), 324 (m). NMR spectra are included in Table I.

X-ray Crystallography. The diffractometer, low-temperature apparatus, and computational techniques have been described previously.[9]

A suitable sample of $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$ was obtained by cleaving a larger crystal while the sample of $[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$ consisted of a small tetrahedrally shaped crystal. Details of data collection are summarized in Table II.

The structure of the dinuclear compound was solved by using standard heavy-atom methods. The metal atoms were located by direct methods, and their positions were confirmed by Patterson methods. All hydrogen atoms were located in a difference Fourier map. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The final difference Fourier map was essentially featureless with the largest peak being 0.4 e/Å^3. Additional details may be found in Table II. Final positional parameters are given in Table III.

The structure of the tetranuclear compound was solved by using a combination of direct-methods and Fourier techniques. All non-hydrogen atoms were located and refined by full-matrix least squares with anisotropic thermal parameters. The hydrogen atoms were not located but were included as fixed atoms in calculated positions in the final cycles of refinement. Due to the large number of parameters, the refinements were carried out by refining parts of the molecule cyclically. The final difference Fourier map contained several peaks of about 2 e/Å^3 in the vicinity of the heavy atoms. Additional details are given in Table II while final positional parameters are given in Table IV.

Results and Discussion

Preparation of $[Mo(NR)(\mu_3\text{-}S)(S_2P(OR')_2)]_4$. The one-pot method for the synthesis of the compound with R = $C_6H_4CH_3$ and R' = C_2H_5 has been described previously.[6] This method, which employs $Mo(CO)_6$, elemental sulfur, an aryl azide, and excess bidentate ligand in its acid form, has also been used to prepare the compound with R = C_6H_5 and R' = C_2H_5.[7] However, the reaction has now been found to fail completely when R = $C_6H_4CH_3$ and R' = CH_3. Nevertheless, the use of the disulfide $[(CH_3O)_2PS_2]_2$, along with a corresponding decrease in the quantity of the aryl azide to accommodate the additional oxidizing equivalents, provided satisfactory yields (~25%) of the desired compound. Interestingly, yields of less than 10% were obtained when the revised method was used in the preparation of the corresponding compound with R = $C_6H_4CH_3$ and R' = C_2H_5 whereas the original procedure gave yields of approximately 40%.[6]

Hydrolyses. The reactions, which were conducted in a mixture of tetrahydrofuran and aqueous HCl, proceeded more rapidly than anticipated at least in their initial stages. One of these reactions was monitored by using ^{31}P NMR spectroscopy. In that instance, the single resonance due to an equilibrium mixture of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ and its dinuclear components gave way to two

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(8) Lippman, A. E. *J. Org. Chem.* **1966**, *31*, 471.

(9) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Table II. Crystal Data

compd	$Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$	$[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$
space group	*Pcab*	$P\bar{1}$
temp, °C	−163	−163
a, Å	12.514 (1)	20.026 (6)
b, Å	13.136 (2)	12.360 (3)
c, Å	28.009 (5)	12.093 (3)
α, deg		65.46 (1)
β, deg		77.46 (1)
γ, deg		77.54 (1)
Z	8	2
V, Å^3	4604.4	2631.1
d_{calcd}, g/cm^3	1.995	1.852
cryst size, mm	0.18 × 0.17 × 0.15	0.08[a]
radiation	Mo Kα (0.71069 Å)	
linear abs coeff, cm^{-1}	17.478	15.348
detector aperture, mm	3.0 × 4.0	
detector–sample dist, cm	22.5	
sample–source dist, cm	23.5	
takeoff angle, deg	2	
scan speed, deg/min	4.0	
scan width, deg	2.0 + dispersion	1.8 + dispersion
single bkgd time at extrema, s	3	
2θ limits, deg	$6 \leq 2\theta \leq 45$	
data collected	$+h, +k, +l$	$+h, \pm k, \pm l$
unique data	2999	6912
data with $F > 2.33\sigma(F)$	2242	5708
$R(F)$	0.054	0.060
$R_w(F)$	0.051	0.064
goodness of fit	1.201	1.709
largest Δ/σ	0.05	

[a] Along each edge of a tetrahedron.

Table III. Final Positional (×10^4) Parameters for the Non-Hydrogen Atoms in $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$

atom	*x*	*y*	*z*
Mo(1)	666 (1)	2536 (1)	486.4 (3)
Mo(2)	164 (1)	2339 (1)	1460.9 (3)
S(3)	1695 (2)	3058 (2)	1131 (1)
S(4)	−482 (2)	1362 (2)	839 (1)
S(5)	517 (2)	1261 (2)	−168 (1)
S(6)	2390 (2)	2801 (2)	49 (1)
S(7)	−696 (2)	949 (2)	1953 (1)
S(8)	1306 (2)	2352 (2)	2197 (1)
P(9)	1745 (2)	1983 (2)	−485 (1)
P(10)	259 (2)	1381 (2)	2483 (1)
O(11)	−64 (6)	3534 (6)	307 (3)
N(12)	−734 (7)	3324 (6)	1528 (3)
O(13)	2575 (6)	1250 (5)	−741 (3)
C(14)	3070 (12)	436 (11)	−471 (5)
O(15)	1415 (6)	2623 (6)	−929 (2)
C(16)	636 (11)	3435 (10)	−886 (5)
O(17)	−348 (6)	1853 (6)	2925 (3)
C(18)	−965 (11)	2789 (11)	2855 (5)
O(19)	766 (6)	406 (6)	2714 (3)
C(20)	1507 (12)	455 (12)	3105 (6)
C(21)	−1496 (8)	4090 (8)	1476 (4)
C(22)	−1756 (9)	4692 (8)	1875 (4)
C(23)	−2557 (9)	5444 (9)	1825 (4)
C(24)	−3066 (8)	5571 (9)	1384 (4)
C(25)	−2793 (8)	4961 (8)	1004 (4)
C(26)	−2016 (9)	4253 (9)	1040 (4)
C(27)	−3929 (11)	6366 (11)	1336 (5)

new resonances of equal intensity, the expected pattern for $[Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_n$. A second, slower reaction then ensued with the gradual loss of these signals and the growth of a single resonance due to $[MoO(\mu\text{-}S)(S_2P(OC_2H_5)_2)]_2$.[6]

The isolation of the intermediate described above led to yellow crystals that were sometimes mixed with a few red crystals. Past experience[4] suggested that the yellow compound was dinuclear while the red compound was tetranuclear. In contrast, only an orange compound was obtained with R = $C_6H_4CH_3$ and R′ = CH_3. These were shown to be dinuclear $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$ by the X-ray studies described in subsequent paragraphs. A mixture of easily separable yellow and red crystals was always obtained with R = C_6H_5 and R′ = C_2H_5. Again, X-ray methods were used and led to the identification of $[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$ as the red compound.

Further proof of the presence of the oxo ligand in $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$ came from the infrared spectrum. An absorption at 960 cm^{-1} was readily assigned as ν(MoO). Absorptions due to $S_2P(OC_2H_5)_2$ ligands obscured this region in the spectra of the remaining compounds.

Previous studies of the reactions of mononuclear (arylimido)molybdenum compounds with acids in nonaqueous solvents have revealed three pathways. The first involves protonation of the arylimido ligand, loss of the amine, and binding of the conjugate base of the acid. Thus, the reaction of either $MoO(NC_6H_5)(S_2CN(C_2H_5)_2)_2$ or $Mo(NC_6H_5)_2(S_2CN(C_2H_5)_2)_2$ with HCl gave $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$.[1] The second pathway involves protonation and loss of an ancillary ligand along with binding of the conjugate base of the acid. This pathway has only been observed when a monodentate dithiophosphate ligand was present.[2,10] The third, which involves protonation of a bridging sulfur atom, has already been mentioned. The acid-assisted hydrolyses that were described above fall into the first category with the hydronium ion being the acid and the oxo ligand being the conjugate base.

Structural Studies. The selection of $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$ and $[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$ for structural analyses by X-ray methods was dictated by the chronology of the preparation rather than any other consideration.

The molecular structure of the dinuclear compound is shown in Figure 1 while pertinent bond distances and bond angles are given in Tables V and VI. Distances and angles within the bidentate ligands and the aryl ring are unexceptional. The

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[10] Noble, M. E.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1982**, *21*, 2101.

Table IV. Final Positional (×10^4) Parameters for Non-Hydrogen Atoms in $[\mathrm{Mo_2O(NC_6H_5)}(\mu_3\text{-S})_2(\mathrm{S_2P(OC_2H_5)_2})_2]_2$

atom	x	y	z
Mo(1)	2178.5 (4)	−110 (1)	6369 (1)
Mo(2)	1221.6 (4)	1721 (1)	6929 (1)
Mo(3)	3045.9 (4)	1812 (1)	7291 (1)
Mo(4)	2823.3 (5)	3023 (1)	4798 (1)
S(5)	2033 (1)	299 (2)	8158 (2)
S(6)	1722 (1)	1757 (2)	4963 (2)
S(7)	2126 (1)	3336 (2)	6508 (2)
S(8)	3386 (1)	1059 (2)	5729 (2)
S(9)	2847 (2)	−546 (2)	4537 (3)
S(10)	3104 (1)	−1795 (2)	7322 (3)
S(11)	796 (1)	2506 (2)	8628 (2)
S(12)	491 (1)	3684 (2)	5858 (2)
S(13)	3659 (1)	−178 (3)	8650 (3)
S(14)	2577 (2)	1828 (3)	9418 (3)
S(15)	3072 (2)	2685 (3)	2818 (3)
S(16)	1971 (2)	4666 (2)	3553 (3)
P(17)	3353 (2)	−2003 (3)	5726 (3)
O(18)	4148 (4)	−2213 (8)	5294 (10)
C(19)	4616 (9)	−1387 (15)	5159 (22)
C(20)	5015 (10)	−2017 (21)	6487 (18)
O(21)	3199 (4)	−3220 (6)	5789 (7)
C(22)	2522 (6)	−3595 (10)	6204 (12)
C(23)	2459 (8)	−4431 (14)	7505 (12)
P(24)	178 (2)	3801 (2)	7493 (3)
O(25)	−609 (4)	3721 (7)	8011 (7)
C(26)	−883 (6)	2597 (11)	8598 (12)
C(27)	−1255 (8)	2499 (12)	9832 (15)
O(28)	143 (5)	5094 (7)	7432 (7)
C(29)	623 (8)	5884 (12)	6736 (13)
C(30)	504 (7)	6897 (10)	7172 (12)
P(31)	3323 (2)	419 (3)	9990 (3)
O(32)	3080 (4)	−580 (8)	11268 (7)
C(33)	2571 (6)	−1296 (11)	11399 (11)
C(34)	2506 (9)	−2220 (13)	12667 (13)
O(35)	3959 (5)	704 (9)	10294 (9)
C(36)	3968 (10)	1268 (21)	10873 (23)
C(37)	4576 (7)	2026 (15)	10494 (16)
P(38)	2520 (2)	4318 (3)	2131 (3)
O(39)	2983 (4)	5344 (7)	1373 (7)
C(40)	3461 (8)	5344 (14)	351 (13)
C(41)	4030 (7)	6044 (13)	180 (13)
O(42)	2080 (4)	4413 (6)	1148 (6)
C(43)	1545 (6)	3655 (10)	1486 (11)
C(44)	1143 (7)	4105 (11)	463 (11)
N(45)	557 (4)	912 (7)	7207 (7)
C(46)	−14 (5)	449 (8)	7189 (8)
C(47)	−245 (5)	804 (9)	6067 (9)
C(48)	−815 (6)	371 (10)	6014 (10)
C(49)	−1157 (5)	−395 (9)	7074 (9)
C(50)	−920 (6)	−750 (9)	8170 (10)
C(51)	−347 (5)	−325 (8)	8243 (9)
O(52)	1585 (3)	−999 (6)	6671 (6)
O(53)	3473 (4)	3852 (6)	4421 (7)
N(54)	3699 (4)	2590 (8)	7061 (8)
C(55)	4302 (8)	2959 (14)	7062 (14)
C(56)	4918 (8)	2103 (18)	7388 (17)
C(57)	5516 (9)	2599 (18)	7299 (18)
C(58)	5461 (10)	3931 (16)	6773 (18)
C(59)	4913 (10)	4620 (15)	6633 (19)
C(60)	4352 (10)	4172 (14)	6619 (20)

Table V. Some Bond Distances (Å) in $\mathrm{Mo_2O(NC_6H_4CH_3)}(\mu\text{-S})_2(\mathrm{S_2P(OCH_3)_2})_2$

	Mo(1)–Mo(2)	2.812 (1)	
Mo(1)–S(3)	2.321 (3)	Mo(1)–S(6)	2.505 (3)
Mo(1)–S(4)	2.327 (3)	Mo(2)–S(7)	2.527 (3)
Mo(2)–S(3)	2.327 (3)	Mo(2)–S(8)	2.510 (3)
Mo(2)–S(4)	2.309 (3)	Mo(1)–O(11)	1.675 (7)
Mo(1)–S(5)	2.490 (3)	Mo(2)–N(12)	1.724 (9)

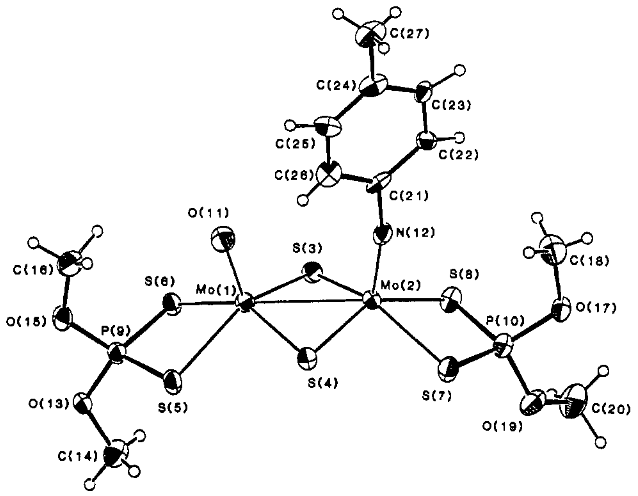

Figure 1. ORTEP drawing of $\mathrm{Mo_2O(NC_6H_4CH_3)}(\mu\text{-S})_2(\mathrm{S_2P(OCH_3)_2})_2$ with thermal ellipsoids at the 50% probability level.

Table VI. Some Bond Angles (deg) in $\mathrm{Mo_2O(NC_6H_4CH_3)}(\mu\text{-S})_2(\mathrm{S_2P(OCH_3)_2})_2$

S(3)–Mo(1)–S(4)	102.0 (1)	S(4)–Mo(1)–O(11)	108.0 (3)S
S(3)–Mo(2)–S(4)	102.4 (1)	S(3)–Mo(2)–N(12)	106.0 (3)
Mo(1)–S(3)–Mo(2)	74.5 (1)	S(4)–Mo(2)–N(12)	105.8 (3)
Mo(1)–S(4)–Mo(2)	74.7 (1)	S(5)–Mo(1)–O(11)	105.4 (3)
S(5)–Mo(1)–S(6)	78.3 (1)	S(6)–Mo(1)–O(11)	102.4 (3)
S(7)–Mo(2)–S(8)	78.4 (1)	S(7)–Mo(2)–N(12)	101.8 (3)
S(3)–Mo(1)–O(11)	107.7 (3)	S(8)–Mo(2)–N(12)	106.0 (3)
	Mo(2)–N(12)–C(21)	167.4 (8)	

aryl ring is planar within experimental error. The structure, which can be described as two square pyramids fused at the common edge containing the bridging sulfur atoms (S$_b$), is similar to those found in $[\mathrm{Mo(NC_6H_4CH_3)}(\mu\text{-S})(\mathrm{S_2CN}(i\text{-}\mathrm{C_4H_9})_2)]_2$[4] and $[\mathrm{MoO}(\mu\text{-S})(\mathrm{S_2P(O}\text{-}i\text{-}\mathrm{C_3H_7})_2)]_2$,[5] as well as other examples.[11,12]

Molecular parameters (averaged[13] where required) for $\mathrm{Mo_2O(NC_6H_4CH_3)}(\mu\text{-S})_2(\mathrm{S_2P(OCH_3)_2})_2$ are compared to parameters for $[\mathrm{Mo(NC_6H_4CH_3)}(\mu\text{-S})(\mathrm{S_2CN}(i\text{-}\mathrm{C_4H_9})_2)]_2$ and $[\mathrm{MoO}(\mu\text{-S})(\mathrm{S_2P(O}\text{-}i\text{-}\mathrm{C_3H_7})_2)]_2$ in Table VII. The results indicate that a decreasing number of oxo ligands leads to shorter Mo–Mo bonds accompanied by slight closure of the Mo–S$_b$–Mo bond angles, lengthening of the Mo–S$_b$ bonds (even though these bond lengths are virtually indistinguishable on either end of the oxo–arylimido molecule), an opening of the S$_b$–Mo–S$_b$ bond angles that vanishes after the loss of the first oxo ligand, and a slight opening of the dihedral angle in the $\mathrm{Mo}(\mu\text{-S})_2\mathrm{Mo}$ moiety. However, bonds from the metal atoms to the sulfur atoms (S$_l$) of the bidentate ligands have an identical average length for the dioxo and diarylimido compounds. The corresponding average bond lengths in the oxo–arylimido compound are slightly longer with a larger increase occurring on the arylimido end of the molecule. Scatter prevents a meaningful comparison of the lengths of these bonds in the three compounds by a χ^2 test.[14]

The decrease in the MoO bond length that appears to occur on moving from the dioxo compound to the oxo–arylimido compound may only be illusory since the positional parameters for the oxo ligands in the former were not evaluated with great precision. In fact, substantially shorter MoO bond lengths have been reported for $[\mathrm{MoO}(\mu\text{-S})(\mathrm{S_2CN}(n\text{-}\mathrm{C_4H_9}))]_2$ (1.66 (1) Å average)[11] and $[\mathrm{MoO}(\mu\text{-S})(\mathrm{S_2C_2(CN)_2})]_2^{2-}$ (1.664 (4) Å average).[12] Finally, the MoN bond distances for the arylimido

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(11) Winograd, R.; Spivack, B.; Dori, Z. *Cryst. Struct. Commun.* **1976**, *5*, 373.

(12) Gelder, J. I.; Enemark, J. H. *Inorg. Chem.* **1976**, *15*, 1839.

(13) Standard deviations for average bond lengths have been calculated from the differences between individual bond lengths and the average bond length.

(14) Stout, G. H.; Jensen, L. H. "X-ray Structure Determination"; Macmillan: New York, 1968; p 421.

Table VII. Molecular Parameters[a] for Three Dinuclear Compounds

	$[MoO(\mu\text{-}S)(S_2P(O\text{-}i\text{-}C_3H_7)_2)]_2$ [b]	$Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$	$[Mo(NC_6H_4CH_3)(\mu\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_2$ [c]
Mo-Mo, Å	2.819 (1)	2.812 (1)	2.807 (2)
Mo-S_b, Å	2.304 (9)	2.324 (4)[d] 2.32 (1)[e]	2.33 (2)
Mo-S_b-Mo, deg	75.5 (1)	74.6 (1)	74.1 (2)
S_b-Mo-S_b, deg	100.8 (3)	102.0 (1)[d] 102.4 (1)[e]	102.3 (0)
Mo-S_l, Å	2.48 (1)	2.50 (1)[d] 2.52 (1)[e]	2.48 (2)
Mo-X (X = O or N), Å	1.71 (3)	1.675 (7)[d] 1.724 (9)[e]	1.720 (1)
dihedral angles, deg			
$Mo(S_b)_2Mo$	147	148	149
$(S_l)_2(S_b)_2(S_l)_2$	157	156	158

[a] Averaged where required. [b] Reference 5. [c] Reference 4. [d] Oxo end. [e] Arylimido end.

Table VIII. Some Bond Distances (Å) in $[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$

Mo(1)-Mo(2)	2.845 (1)	Mo(4)-S(6)	2.898 (3)
Mo(3)-Mo(4)	2.842 (1)	Mo(1)-S(9)	2.527 (3)
Mo(1)-S(5)	2.365 (3)	Mo(1)-S(10)	2.523 (3)
Mo(1)-S(6)	2.358 (3)	Mo(2)-S(11)	2.535 (3)
Mo(2)-S(5)	2.363 (2)	Mo(2)-S(12)	2.527 (3)
Mo(2)-S(6)	2.358 (3)	Mo(3)-S(13)	2.544 (3)
Mo(3)-S(7)	2.370 (3)	Mo(3)-S(14)	2.545 (3)
Mo(3)-S(8)	2.351 (3)	Mo(4)-S(15)	2.526 (3)
Mo(4)-S(7)	2.356 (3)	Mo(4)-S(16)	2.527 (3)
Mo(4)-S(8)	2.351 (3)	Mo(1)-O(52)	1.671 (6)
Mo(1)-S(8)	2.881 (3)	Mo(2)-N(45)	1.727 (8)
Mo(2)-S(7)	2.800 (3)	Mo(3)-N(54)	1.695 (7)
Mo(3)-S(5)	2.792 (3)	Mo(4)-O(53)	1.697 (7)

Table IX. Some Bond Angles (deg) for $[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$

S(5)-Mo(1)-S(6)	101.3 (1)	S(15)-Mo(4)-S(16)	78.7 (1)
S(5)-Mo(2)-S(6)	101.4 (1)	S(5)-Mo(1)-O(52)	104.2 (2)
S(7)-Mo(3)-S(8)	101.0 (1)	S(6)-Mo(1)-O(52)	103.9 (2)
S(7)-Mo(4)-S(8)	101.4 (1)	S(5)-Mo(2)-N(45)	103.1 (2)
S(5)-Mo(1)-S(8)	82.9 (1)	S(6)-Mo(2)-N(45)	99.2 (3)
S(6)-Mo(1)-S(8)	82.7 (1)	S(7)-Mo(3)-N(54)	103.5 (3)
S(5)-Mo(2)-S(7)	83.9 (1)	S(8)-Mo(3)-N(54)	101.9 (3)
S(6)-Mo(2)-S(7)	85.4 (1)	S(7)-Mo(4)-O(53)	105.0 (3)
S(7)-Mo(3)-S(5)	84.0 (1)	S(8)-Mo(4)-O(53)	101.9 (3)
S(8)-Mo(3)-S(5)	85.1 (1)	S(9)-Mo(1)-O(52)	95.2 (2)
S(7)-Mo(4)-S(6)	83.2 (1)	S(10)-Mo(1)-O(52)	95.3 (2)
S(8)-Mo(4)-S(6)	82.5 (1)	S(11)-Mo(2)-N(45)	98.1 (3)
Mo(1)-S(5)-Mo(2)	74.0 (1)	S(12)-Mo(2)-N(45)	92.0 (2)
Mo(1)-S(6)-Mo(2)	74.2 (1)	S(13)-Mo(3)-N(54)	94.3 (3)
Mo(3)-S(7)-Mo(4)	73.9 (1)	S(14)-Mo(3)-N(54)	94.0 (3)
Mo(3)-S(8)-Mo(4)	74.4 (1)	S(15)-Mo(4)-O(53)	94.8 (3)
S(9)-Mo(1)-S(10)	77.9 (1)	S(16)-Mo(4)-O(53)	97.3 (2)
S(11)-Mo(2)-S(12)	78.1 (1)	Mo(2)-N(45)-C(46)	167.6 (6)
S(13)-Mo(3)-S(14)	78.7 (1)	Mo(3)-N(54)-C(55)	166.1 (9)

compounds in Table VII do not differ significantly nor do they differ significantly from the value of 1.732 (4) Å found[10] in the mononuclear Mo(V) compound $Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)_3$.

The cubane-like structure of $[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$ is shown in Figure 2. Relevant bond distances and bond angles can be found in Tables VIII and IX. No remarkable distances or angles occur within the bidentate ligands or the aryl rings while the latter are planar within experimental error.

A comparison of several average molecular parameters in this compound with those of $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$[3] and $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$[4] can be found in Table X. In contrast to the comparison of dinuclear compounds in Table VII, fewer trends can be observed. It is clear, however, that the compounds with no oxo ligands have significantly longer Mo–Mo bonds, a result that is exactly opposite the one found for the dinuclear compounds.

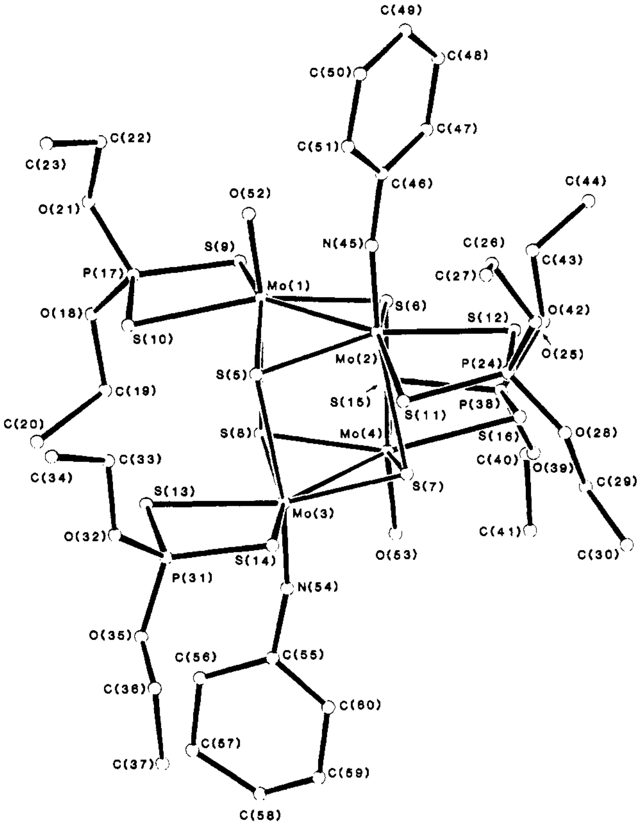

Figure 2. Ball-and-stick drawing of $[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$.

Perhaps the most striking and important comparison can be found with the lengths of the Mo–S_b bonds that bind the dinuclear units together. The average bond length trans to an arylimido ligand in $[Mo_2O(NC_6H_4CH_3)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$ is about 0.1 Å longer than those found in the two compounds without oxo ligands while the average bond length opposite an oxo ligand is about 0.2 Å longer than the distances in those compounds.

Equilibria between Oligomers. Proof of the equilibria between oligomers was established from several pieces of evidence. Separate solutions of $Mo_2O(NC_6H_5)(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)_2$ and $[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$ in $CDCl_3$ afforded identical ^1H and ^{31}P NMR spectra. Moreover, when these solutions were evaporated on CsI plates, the infrared spectra of the orange glasses that resulted were identical. Finally, deviations from the Beer–Lambert law at or near 520 nm for all of the compounds in CH_2Cl_2 are qualitatively similar to those that were previously found for the tetranuclear compounds in which oxo ligands are absent.[2,4]

Table X. Molecular Parameters[a] for Three Cubane-like Compounds

	$[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$[b]	$[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$[c]	$[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$
Mo–Mo, Å	2.862 (1)	2.881 (3)	2.844 (2)
Mo···Mo, Å	3.69 (4)	3.66 (4)	3.85 (4)
Mo–S_b, Å	2.366 (5)[d]	2.38 (2)[d]	2.361 (8)[d,f]
	2.70 (1)[e]	2.69 (3)[e]	2.358 (5)[d,g]
			2.796 (6)[e,f]
			2.89 (1)[e,g]
Mo–S_b–Mo,[h] deg	74.5 (2)	74.4 (5)	74.1 (4)
	93 (1)	92 (1)	95 (1)
S_b–Mo–S_b,[i] deg	102.0 (1)	102.4 (7)	101.2 (4)[f]
			101.4 (1)[g]
	85 (1)	86 (2)	84 (1)
			82.8 (3)[g]
Mo–S_l, Å	2.55 (1)	2.52 (2)	2.538 (8)[f]
			2.526 (3)[g]
Mo–X (X = O or N), Å	1.72 (1)	1.72 (1)	1.71 (2)[f]
			1.68 (2)[g]
dihedral angles,[j] deg	148 (0)	150 (1)	144 (0)
	90	90	90

[a] Averaged. [b] Reference 3. [c] Reference 4. [d] Adjacent to Mo–Mo bonds. [e] Trans to an arylimido or oxo ligand. [f] Arylimido end. [g] Oxo end. [h] The smaller angle is opposite an Mo–Mo bond. [i] The larger angle(s) can be segmented by a plane containing a Mo–Mo bond. [j] The larger angle is identical with the $Mo(\mu\text{-}S)_2Mo$ angle in the dinuclear compounds while the smaller angle measures the angular deviation between a plane defined by two bonded Mo atoms and the S atoms on the opposite face and a plane defined by the remainder of the atoms in the core. The smaller angle indicates a pseudodiad axis in each compound.

A comparison of the equilibrium constants for all of these systems will be presented in a subsequent paper. We anticipate, however, that the substantially larger elongation of the $[Mo(\mu_3\text{-}S)]_4$ core in $[Mo_2O(NC_6H_5)(\mu_3\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$, which is shown in Table X and which is presumably shared by the other oxo–arylimido compounds, will have a considerable impact on the stability of the tetranuclear compounds in these systems.

NMR Studies. The ^{31}P NMR spectrum of a $CDCl_3$ solution containing an equilibrium mixture of dinuclear and tetranuclear compounds with R = $C_6H_4CH_3$ and R′ = C_2H_5 consists of two resonances at δ 111.1 and 112.2, as shown in Table I. The gradual addition of the dinuclear compound having R = C_6H_5 and R′ = C_2H_5 resulted in the growth of two additional resonances while the original signals remained unshifted.[15] One of these was 4.3 Hz downfield from the original resonance at δ 112.2 while the other was 1.8 Hz from the absorption at δ 111.1. The assignments for these compounds, which are also given in Table I, are based on the presumption that the frequencies of the resonances due to the ^{31}P atoms on the arylimido ends will differ by more than those of the resonances due to the ^{31}P atoms on the oxo ends since the structure of the latter is unchanged. The assignments for the system with R = $C_6H_4CH_3$ and R′ = CH_3 are based on the additional assumption that the resonance frequencies follow the same pattern.

These assignments have allowed a study of the relative labilities of the bidentate ligands on either end of the system with R = $C_6H_4CH_3$ and R′ = CH_3. The ^{31}P NMR spectra of a $CDCl_3$ solution containing the dinuclear compound with these substituents and 1 equiv of $HS_2P(OC_2H_2)_2$ were obtained several times during a period of about 1.7 h. In the first 25 min, changes were confined to the decay of the original signals at δ 117.8 and 116.3 as well as the one due to $HS_2P(OC_2H_5)_2$, the appearance of a resonance due to $HS_2P(OCH_3)_2$, and the growth of two signals of equal intensity at δ 117.9 and 111.0. On the basis of the previous assignments, this pair is attributed to an equilibrium mixture of dinuclear and tetranuclear compounds with a $S_2P(OCH_3)_2$ ligand adjacent to an arylimido ligand, causing the signal at δ 117.9, and a $S_2P(OC_2H_5)_2$ ligand next to the oxo ligand, leading to the resonance at δ 111.0. After about 40 min, two additional pairs of signals began to appear at roughly equivalent rates. According to the chemical shifts, one of these pairs is due to the known system in which $S_2P(OC_2H_5)_2$ ligands are adjacent to both the arylimido and oxo ligands. The other pair is due to a system with a $S_2P(OC_2H_5)_2$ ligand next to the arylimido ligand, with a resonance at δ 112.2, and a $S_2P(OCH_3)_2$ ligand on the oxo end, with a signal at δ 116.4. All of these signals were still clearly evident at the completion of 1.7 h but their intensities suggested an approach to a statistical distribution.

These results clearly indicate that the initial interchange of bidentate ligands occurs only on one end, and entirely reasonable assignments indicate that this end contains the oxo ligand. The increased lability on this end cannot be predicted or rationalized from the Mo–S_l bond lengths since they appear to be slightly shorter on the oxo ends of both the dinuclear and tetranuclear molecules whose structures are reported herein.

Assignments of the signals in the ^1H NMR spectra were achieved by means of concomitant monitoring of these spectra during the exchange reaction.

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Registry No. $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OCH_3)_2)]_4$, 87393-43-9; $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)_2$, 87393-44-0; $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)_2]_4$, 73037-71-5; $Mo_2O(NC_6H_5)(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)_2$, 87393-45-1; $[Mo_2O(NC_6H_5)(\mu\text{-}S)_2(S_2P(OC_2H_5)_2)_2]_2$, 87393-46-2; $[Mo(NC_6H_5)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$, 87393-47-3; $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)_2$, 87393-48-4; $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)(S_2P(OC_2H_5)_2)$, isomer 1, 87393-49-5; $Mo_2O(NC_6H_4CH_3)(\mu\text{-}S)_2(S_2P(OCH_3)_2)(S_2P(OC_2H_5)_2)$, isomer 2, 87393-50-8; $[Mo_2O(NC_6H_4CH_3)(\mu_3\text{-}S)_2(S_2P(OCH_3)_2)(S_2P(OC_2H_5)_2)]_2$, isomer 1, 87393-51-9; $[Mo_2O(NC_6H_4CH_3)(\mu_3\text{-}S)_2(S_2P(OCH_3)_2)(S_2P(OC_2H_5)_2)]_2$, isomer 2, 87393-52-0; $Mo(CO)_6$, 13939-06-5; Mo, 7439-98-7; p-$CH_3C_6H_4N_3$, 2101-86-2; S, 7704-34-9.

Supplementary Material Available: Listings of positional parameters for the hydrogen atoms of the dinuclear compound, all thermal parameters, observed and calculated structure amplitudes, and all bond distances and angles (75 pages). Ordering information is given on any current masthead page.

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(15) Although a mixed tetranuclear compound must have been present, its formation has no impact on the chemical shifts.