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# Formation of Isomeric Dimolybdenum(II) Compounds Using the Potentially Ambidentate Ligands $[R_2PC(S)NR']^-$ (R/R′ = Ph/Ph, Ph/Me) and $[Me_2NC(S)NPh]^-$

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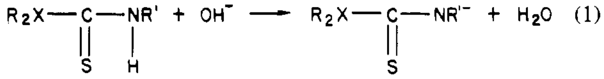
Ligands of the type $[R_2PC(S)NR']^-$ or $[R_2NC(S)NR']^-$ displace acetate ions from $Mo(O_2CCH_3)_4$ to afford products of general formula $Mo_2[R_2XC(S)NR']_4$. Four such products are reported here: **1**, $R_2X = Ph_2P$ and R′ = Ph; **2a**, $R_2X = Ph_2P$, R′ = Me, green; **2b**, $R_2X = Ph_2P$, R′ = Me, yellow; **3**, $R_2X = Me_2N$, R′ = Ph. A variety of physical data, including single-crystal X-ray structural studies of **2a** and **2b**, provide information on the structures and properties of these compounds. Compounds **1** and **2b** have all four ligands coordinated in the same manner, through the N and S atoms, and in the case of **2b** the crystal structure shows that the arrangement is such that like atoms on a given molybdenum atom are trans to each other. The Mo–Mo distance in **2b** is 2.083 (1) Å. In compound **3** the spectroscopic data suggest that coordination is through N and S for all four ligands. Compound **2a** is an isomer of **2b** in which two ligands (trans to each other) are N,S coordinated while the other two are N,P coordinated. On each Mo atom the N atoms are cis to each other, and the Mo–Mo distance in **2a** is 2.104 (2) Å. Crystallographic data are as follows: For **2a** the space group is $P2_1/c$ with unit cell dimensions of $a = 13.163$ (4) Å, $b = 14.502$ (4) Å, $c = 16.719$ (6) Å, $\beta = 105.38$ (3)°, $V = 3077$ (3) Å$^3$, and $Z = 2$. For **2b** the space group is $P\bar{1}$ with unit cell dimensions of $a = 15.513$ (3) Å, $b = 16.150$ (3) Å, $c = 14.909$ (3) Å, $\alpha = 94.68$ (2)°, $\beta = 118.53$ (2)°, $\gamma = 63.93$ (1)°, $V = 2908$ (2) Å$^3$, and $Z = 2$.

## Introduction

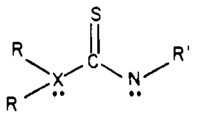
Although the number of known compounds containing quadruply bonded dimetal units, especially the $Mo_2^{4+}$ entity, is now quite large,[2] there are still many types of potential ligands that have not as yet been incorporated into such compounds. For example, the phenomenon of isomerism based on the behavior of ambidentate ligands has not previously been observed. In this report we shall describe the preparation and properties of some $Mo_2^{4+}$ compounds containing ligands of the type $R_2PC(S)NR'$, where R/R′ = Ph/Ph, Ph/Me, and $Me_2NC(S)NPh$, in which this sort of behavior can occur. In one case its occurrence has been thoroughly substantiated by a variety of measurements, including X-ray crystallographic characterization of a pair of representative isomeric compounds.

The anionic ligands we have used are derived by deprotonation of neutral thioamide molecules (eq 1). It is to be

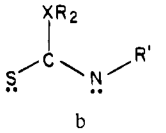


$$R_2X-\underset{\underset{S}{\|}}{C}-\underset{\underset{H}{|}}{N}R' + OH^- \longrightarrow R_2X-\underset{\underset{S}{\|}}{C}-NR'^- + H_2O \quad (1)$$

expected that these anions will have as their most basic position the deprotonated nitrogen atom. Beyond that, it is not clear a priori whether the X atom or the sulfur atom would be the more likely to function also as a donor; in either case, species a or b, a three-atom anionic ligand of the type well-known to



a



b

conform to the stereoelectronic preferences of $Mo_2^{4+}$ and other binuclear, multiply bonded cations is presented. Ligands of this type were found to react readily with $Mo_2(O_2CCH_3)_4$ to displace the acetate ions and give the complexes $(Mo_2(R_2XC(S)NR')_4$, which are the subject of this paper.

## Experimental Section

**Preparation of Compounds.** All preparations were performed under an atmosphere of dry nitrogen with use of standard Schlenk apparatus. Solvents and chemicals were of analytical quality and were dried before use.

$Mo_2(OAc)_4$,[3] $Ph_2PC(S)N(H)Ph$,[4] $Ph_2PC(S)N(H)Me$,[5] and $Me_2NC(S)N(H)Ph$[6] were prepared as described in the literature.

**$Mo_2(Ph_2PC(S)NPh)_4$ (1).** A 2.8-mmol amount of $Ph_2PC(S)N(H)Ph$ and 2.86 mmol of KOH were added to a suspension of 0.7 mmol of $Mo_2(OAc)_4$ in 40 mL of EtOH. After the mixture was stirred for 2 h, the orange solid was filtered and recrystallized from $CH_2Cl_2$/*n*-hexane; yield 80%. The compound can also be prepared with use of benzene as solvent and $Et_3N$ as base. After the mixture was refluxed a few hours, the solid was filtered and washed with ethanol to remove the ammonium acetate.

**$Mo_2(Ph_2PC(S)NMe)_4$ (2a).** Addition of 0.73 g (2.8 mmol) of $Ph_2PC(S)N(H)Me$ and 0.16 g (2.86 mmol) of KOH to a mixture of 0.30 g (0.7 mmol) of $Mo_2(OAc)_4$ and 40 mL of ethanol immediately gives a green product. After the mixture was stirred for several hours, the precipitate was filtered off. It may be recrystallized from $C_6H_6$/*n*-hexane; yield 75%. The crystals used in the X-ray study were obtained from $CH_2Cl_2$.

**$Mo_2(Ph_2PC(S)NMe)_4$ (2b).** A mixture of 50 mL of ethanol, 2.8 mmol of $Ph_2PC(S)N(H)Me$, 2.86 mmol of KOH, and 0.7 mmol of $Mo_2(OAc)_4$ is warmed to reflux temperature. The color immediately turned to green. After the mixture was refluxed for 2 days, however, a yellow solid precipitated. This solid was filtered off and recrystallized from benzene/*n*-hexane; yield 75%. This product can also be prepared from **2a** by refluxing a suspension of **2a** in ethanol for 5–7 days. The green color slowly turns to yellow, and the product separates from the solution in almost quantitative yield. Crystals were grown over a period of ca. 2 days from $CH_2Cl_2$.

**$Mo_2(Me_2NC(S)NPh)_4$ (3).** A 3-mmol amount of BuLi was added to a LiOAc of 40 mL of $C_6H_6$, 0.7 mmol of $Mo_2(OAc)_4$, and 2.8 mmol of $Me_2NC(S)N(H)Ph$. This mixture was refluxed for 6 h and the LiOAc filtered off. The orange product precipitated upon addition of *n*-hexane. The precipitate was filtered off and washed with ethanol and diethyl ether; yield 50%.

Analytical data and molecular weight determinations are given in Table II. Mo, P, and S elemental analyses were performed by Professor Dipl. Ing. H. Malissa and G. Reuter, Analytische Laboratorien, Elbach Uber Engelskirchen, West Germany.

**Spectroscopic Measurements.** Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. UV spectra were recorded on a Perkin-Elmer 555 spectrophotometer. $^1H$ NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WH-FT spectrometer at 90 and 36.43 MHz, respectively, or on a Varian XL spectrometer.

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**Table I.** Crystallographic Parameters

| | $Mo_2S_4P_4N_4C_{56}H_{52}\cdot 2CH_2Cl_2$ (**2a**) | $Mo_2S_4P_4N_4C_{56}H_{52}\cdot {}^1/_2CH_2Cl_2$ (**2b**) |
|---|---|---|
| fw | 1394.96 | 1267.56 |
| space group | $P2_1/c$ (No. 14) | $P\bar{1}$ (No. 2) |
| *a*, Å | 13.163 (4) | 15.513 (3) |
| *b*, Å | 14.502 (4) | 16.150 (3) |
| *c*, Å | 16.719 (6) | 14.909 (3) |
| α, deg | | 94.68 (2) |
| β, deg | 105.38 (3) | 118.53 (2) |
| γ, deg | | 63.93 (1) |
| *V*, Å³ | 3077 (3) | 2908 (2) |
| *Z* | 2 | 2 |
| $d_{calcd}$, g/cm³ | 1.513 | 1.447 |
| cryst size, mm | 0.2 × 0.15 × 0.07 | 0.25 × 0.20 × 0.20 |
| μ(Mo Kα), cm⁻¹ | 8.50 | 7.52 |
| data collection instrument | Enraf-Nonius CAD-4, room temp | Enraf-Nonius CAD-4, room temp |
| radiation | Mo Kα | Mo Kα |
| scan method | $\omega/2\theta$ | $\omega/2\theta$ |
| data collection range, 2θ, deg | 4–50 (2θ); $+h,+k,\pm l$ | 4–45 (2θ); $+h,\pm k,\pm l$ |
| no. of unique data, total with $F_o^2 \geqslant 3\sigma(F_o^2)$ | 5870, 2430 | 7575, 3898 |
| no. of parameters refined | 333 | 643 |
| $R^a$ | 0.077 | 0.0578 |
| $R_w{}^b$ | 0.089 | 0.0670 |
| quality-of-fit indicator$^c$ | 1.99 | 1.49 |
| largest shift/esd, final cycle | 0.01 | 0.32 |
| largest peak, e/Å³ | 1.9 | 0.68 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Solid-state $^{31}P\{^1H\}$ NMR spectra were recorded at 72.862 MHz on a home-built spectrometer. Molecular weight determinations were carried out with a Hewlett-Packard 302B vapor pressure osmometer. The field desorption (FD) mass spectra were obtained with a Varian MAT 711 double-focusing mass spectrometer with a combined EI/FI/FD ion source and coupled to an MAT 100 Spectro System data acquisition unit. Ten micrometer tungsten-wire FD emitters containing carbon microneedles with an average length of 30 μm were used. The samples were dissolved in chloroform and then loaded onto the emitters with the dipping technique. An emitter current of 15 mA was used to desorb the samples. The ion source temperature was generally 70 °C.

**Electrochemical Measurements.** These were made with a three-electrode Bruker E 310 instrument with Pt working and auxiliary electrodes. Measurements were made in the concentration range $10^{-4}$–$10^{-3}$ mol/dm³ in $CH_2Cl_2$ ($CH_2Cl_2$ was dried over molecular sieves (4 Å) before use; the inert electrolyte was 0.1 mol/dm³ $Bu_4NPF_6$). Measurements were made with a Ag/AgI (0.05 mol/dm³ $Bu_4NI$ and 0.4 mol/dm³ $Bu_4NClO_4$ in $CH_2Cl_2$) reference electrode in the potential range −1.6 to +2.0 V.[7] For convenience, in the following text potentials are referred to a SCE (*E* vs. Ag/AgI = *E* vs. SCE + 0.18 V).

Cyclic voltammograms were taken with a scan rate of 25–1000 mV s⁻¹. All values reported are measured on the first or second scan. Normal and differential pulse polarograms were obtained at a scan rate of 5 mV s⁻¹ with a pulse frequency of 2 pulses/s and with a pulse voltage of 25 mV for the differential pulse polarography.

Electrolyses were carried out on a Pt electrode in similar solutions at potentials up to 200 mV beyond the $E_{1/2}$ value of the redox couple of interest, with a Wenking LB 75 potentiostat and a Birtly electronic integrator.

**X-ray Crystallographic Studies.**[8] **Compound 2a.** Since the only crystal habit found was very thin plates, one of these relatively undesirable crystals was perforce used. It was mounted on a glass fiber in air. Unit cell dimensions, given in Table I, were determined from 25 centered reflections with 2θ ≥ 25°. The space group, $P2_1/c$, was uniquely determined by the systematic absences. The structure was solved from the Patterson function and difference Fourier maps. The molecule of $CH_2Cl_2$ found on a general position in the unit cell showed some evidence of disorder, but no satisfactory model for this was found, and it was refined as an ordered $CCl_2$ molecule with rather high thermal parameters, C–Cl distances of 1.61 (3) and 1.69 (3) Å, and a Cl–C–Cl angle of 115 (2)°. The relatively high final *R* values are due to the poor crystal quality and the nonideal behavior of the $CH_2Cl_2$ molecules. The relatively large residual peaks in the final difference map were in the region of the $CH_2Cl_2$ molecule. The atomic positional parameters for this compound are reported in Table VII.

**Compound 2b.** A crystal was mounted on a glass fiber. Preliminary measurements using 25 centered reflections with 2θ ≥ 25° provided unit cell dimensions. The structure was solved with use of direct methods and then refined, with use of iterative least-squares and Fourier methods, in space group $P\bar{1}$. One molecule of $CH_2Cl_2$ was also found in the unit cell, located with its center of mass approximately on the inversion center of the cell at $^1/_2$, $^1/_2$, $^1/_2$. There are two orientations that change from cell to cell in such a way that we were able to refine with each orientation at 50% occupancy. Crystallographic information is summarized in Table I. The positional parameters for this compound are reported in Table VIII.

## Results

**Reactions and Products.** In the reaction of $Mo_2(OAc)_4$ with $Ph_2PC(S)N(H)Ph$ and KOH in ethanol a complex is obtained with stoichiometry $Mo_2(Ph_2PC(S)NPh)_4\cdot 2H_2O$ (**1**). Elemental analysis indicates the presence of water. Attempts to coordinate small molecules like $CH_3CN$, $Me_2SO$, and THF failed. When prepared in benzene with $Et_3N$ or BuLi as base, the complex is obtained without water as can readily be seen in the elemental analyses.

From $Mo_2(OAc)_4$, $Ph_2PC(S)N(H)Me$, and KOH in ethanol a green compound is obtained with composition $[Mo(Ph_2PC(S)NMe)_2\cdot H_2O]_n$ (**2a**), which is slowly converted in refluxing ethanol into a yellow complex with the same stoichiometry (**2b**). The rate of formation of the green $[Mo(Ph_2PC(S)NMe)_2\cdot H_2O]_n$ is decreased by the use of excess ligand. This observation may be attributed to the existence of an intermediate with more than two ligands per molybdenum atom, which can give the green compound only after expelling the additional ligand(s). The yellow compound can be prepared directly in a water-free form by using benzene as solvent and BuLi as the base (see Table II).

$Mo_2(OAc)_4$ reacts with $Me_2NC(S)N(H)Ph$ in benzene with BuLi as base to form $Mo_2(Me_2NC(S)NPh)_4\cdot {}^1/_2C_6H_6$ (**3**).

**Infrared and $^1H$ and $^{31}P\{^1H\}$ NMR Spectra.** The infrared spectra (Table III) of the prepared compounds show several bands that we assign to ligand vibrations. For **1** we assigned the band at 1480 cm⁻¹ to ν(CN). The low wavenumber of this

**Table II.** Elemental Analyses and Molecular Weight Determinations (Calculated Values in Parentheses)

| no. | compd | % C | % H | % N | % Mo | % P | % S | mol wt$^a$ | mol wt$^b$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $Mo_2(Ph_2PC(S)NPh)_4\cdot 2H_2O$ | 58.9 (60.5) | 4.2 (4.2) | 3.5 (3.7) | | | | 1485 (1509) | 1472 (1473) |
| | $Mo_2(Ph_2PC(S)NPh)_4$ | 61.3 (62.0) | 3.9 (4.1) | 3.7 (3.8) | | | | | |
| 2a | $Mo_2(Ph_2PC(S)NMe)_4\cdot 2H_2O$ | 52.8 (53.3) | 4.4 (4.5) | 4.7 (4.4) | 15.9 (15.2) | 10.0 (9.8) | 10.3 (10.2) | | |
| 2b | $Mo_2(Ph_2PC(S)NMe)_4\cdot 2H_2O$ | 51.8 (53.3) | 4.3 (4.5) | 4.1 (4.4) | | | | 1075 (1262) | 1225 (1225) |
| | $Mo_2(Ph_2PC(S)NMe)_4$ | 54.7 (54.9) | 4.3 (4.3) | 4.3 (4.6) | | | | | |
| 3 | $Mo_2(Me_2NC(S)NPh)_4\cdot {}^1/_2C_6H_6{}^c$ | 49.4 (49.4) | 5.1 (5.0) | 11.6 (11.8) | | | | 886 (948) | 911 (909) |

[a] Determined osmometrically in benzene. [b] From mass spectroscopic measurements. [c] The presence of $C_6H_6$ was confirmed by $^1H$ NMR spectroscopy.

**Table III.** Infrared Spectral Data[a]

| no. | compd | ligand vibration bands | | | | | |
|---|---|---|---|---|---|---|---|
| **1** | $Mo_2(Ph_2PC(S)NPh)_4$ | 1480 s | 1401 s | | | 1000 m | 764 m |
| **2a** | $Mo_2(Ph_2PC(S)NMe)_4$ | 1458 s | 1374 s | 1363 s | 1038 s | 955 w | |
| **2b** | $Mo_2(Ph_2PC(S)NMe)_4$ | 1461 s | 1385 s | | | 954 m | |
| **3** | $Mo_2(Me_2NC(S)NPh)_4$ | 1482 s | 1329 s | 1197 s | 1107 s | 965 m | 794 m |

[a] Measured in CsI pellets, absorptions given in $cm^{-1}$.

**Table IV.** $^1H$ and $^{31}P\{^1H\}$ NMR Data

| no. | compd | $\delta(CH_3)$[a] | $\delta(P)$[b] | solvent | $^{31}P$ ref[b] |
|---|---|---|---|---|---|
| | $Ph_2PC(S)NHMe$ | ... | 16.45 | $CDCl_3$ | $H_3PO_4$ |
| **1** | $Mo_2[Ph_2PC(S)NPh]_4$ | ... | 13.95 | $C_7D_8$ | $(MeO)_3PO$ |
| **2a** | $Mo_2[Ph_2PC(S)NMe]_4$ | 2.54 (S), 2.68 (D) | 13.19,[c] 41.65[c] | $CD_2Cl_2$ | $H_3PO_4$ |
| | | | 18.49, 44.26 | $CDCl_3$ | $H_3PO_4$ |
| **2b** | $Mo_2[Ph_2PC(S)NMe]_4$ | 3.04 (D) | | $CD_2Cl_2$ | |
| | | ... | 9.97 | $C_7D_8$ | $(MeO)_3PO$ |
| | | ... | 13.97 | $CDCl_3$ | $H_3PO_4$ |
| **3** | $Mo_2[Me_2NC(S)NPh]_4$ | 3.34 | ... | $CD_2Cl_2$ | |

[a] All $^1H$ $\delta$ values relative to $SiMe_4$ (internal); S = singlet, D = doublet. [b] 85 wt % $H_3PO_4$ or $(MeO)_3PO$ references as indicated, with positive $\delta$ values downfield. The solvent was used as internal lock. All $^{31}P$ signals were singlets. [c] Solid-state $^{31}P\{^1H\}$ spectrum.

band is an indication that the nitrogen atom is coordinated to the metal. In complexes in which a $Ph_2PC(S)NPh^-$ ligand is coordinated by S and P, a $\nu(CN)$ is found at about 1550 $cm^{-1}$.[9-12] The medium band at about 1000 $cm^{-1}$ we assign to $\nu(CS)$.

In the $^{31}P\{^1H\}$ NMR spectrum of **1** only one signal at 13.95 ppm is found (Table IV), indicating that all P atoms are equivalent. The chemical shift for a P atom coordinated to a Mo(II) center is expected in the 30 to 60 ppm region. The chemical shift of 13.95 ppm is in the range for the free ligand. On this basis we assume that the P atoms are not bonded to the metal so ligand behavior of type b (S,N coordination) seems to be indicated. Water molecules present are assumed to coordinate axially.

The infrared spectra of **2a** and **2b** show some striking differences. In the spectrum of **2a**, a strong band at 1038 $cm^{-1}$ and a weak band at about 995 $cm^{-1}$ are found, while **2b** shows a medium band at 954 $cm^{-1}$ and no band at 1038 $cm^{-1}$. Furthermore, **2a** shows two bands at about 1370 $cm^{-1}$ and **2b** only one. The spectrum of **2b** shows a pattern similar to that of **1**, indicating that **2b** has the same type of structure as **1**. The $^1H$ NMR spectrum of **2b** shows one doublet with a coupling of 0.9 Hz. This is assumed to be a $^4J(^{31}P-^1H)$ coupling, in accordance with the proposed structure. The $^{31}P\{^1H\}$ NMR spectrum of **2b** shows one singlet, indicating a noncoordinated $PPh_2$ group as in **1**. The strong band at 1038 $cm^{-1}$ in the spectrum of **2a** may be attributed to a $\nu(CS)$ of a noncoordinated sulfur atom. The $\nu(CN)$ is found at 1458 $cm^{-1}$, indicating nitrogen coordination.

In the $^1H$ NMR spectrum of **2a** one singlet and one doublet for the methyl groups are found. This indicates two different coordination modes of the ligands to be present in **2a**; the doublet could be due to a $^4J(^{31}P-^1H)$ coupling in one of the two. A solid-state $^{31}P\{^1H\}$ NMR spectrum of **2a** gave two signals, one in the range for a coordinated phosphorus atom and the other in the range for a noncoordinated P atom. The data would indicate that two ligands are type a (P,N) and the other two type b (S,N) coordinated in the green compound. Although the solubility of the green compound is low, which is why a solid-state NMR spectrum was run, we eventually succeeded in recording a spectrum in $CDCl_3$ solution and it too contained two signals, indicative of coordinated and noncoordinated phosphorus atoms.

The infrared spectrum of **3** shows a very low value of $\nu(CN)$ at 1482 $cm^{-1}$. The other absorption bands (given in Table III) give rise to the assumption that the ligands are S,N coordinated. The $^1H$ NMR spectrum shows one singlet for all methyl groups, revealing free rotation around the C–$NMe_2$ bond, and is consistent with the low $\nu(CN)$ found in the infrared spectrum.

**Table V.** UV Spectral Data[a]

| no. | compd | abs max ($\epsilon$) | | |
|---|---|---|---|---|
| 1 | $Mo_2(Ph_2PC(S)NPh)_4$ | 310 sh | 436 (6100) | |
| 2a | $Mo_2(Ph_2PC(S)NMe)_4$ | 348 (25 500) | 410 (6000) | 592 (800) |
| 2b | $Mo_2(Ph_2PC(S)NMe)_4$ | 312 sh | 423 (8800) | |
| 3 | $Mo_2(Me_2NC(S)NPh)_4$ | 310 sh | 432 (1200) | 510 (800) |

[a] Measured in $CH_2Cl_2$ solutions. Absorption maxima are given in nm; sh = shoulder.

**UV Spectral Data.** The absorption maxima in $CH_2Cl_2$ solution for compounds **1**–**3** are given in Table V. The spectra of **1** and **2b** have a pattern similar to that of $Mo_2(O_2CCH_3)_4$ in solution.[13] The molar extinctions of the bands of lowest energy are higher for the newly prepared complexes than that of the acetate compound. This band is attributed to the $\delta \rightarrow \delta^*$ transition, which has been demonstrated by polarized UV spectra measured on single crystals of $K_4Mo_2(SO_4)_4 \cdot 2H_2O$,[14] $K_4Mo_2Cl_8 \cdot 2H_2O$,[15] and $Mo_2(O_2CCH_3)_4$.[16] It is striking that in the spectrum of **3** the lowest energy band is found about 100 nm higher than for **1** and **2b**.

The UV spectrum of **2a** is quite different from that of **2b**.

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Table VI. $E_{1/2}$ Values for the Oxidation of Compounds with the $Mo_2^{4+}$ Unit

| compd | solvent | $E_{1/2}$, V | ref |
|---|---|---|---|
| $Mo_2(O_2CC_3H_7)_4$ | $CH_3CN$ | +0.39 | 17 |
| | $CH_2Cl_2$ | +0.45 | 17 |
| | EtOH | +0.30 | 17 |
| $Mo_2(SO_4)_4^{4-}$ | $H_2SO_4$ | +0.22 | 18 |
| $Mo_2Cl_8^{4-}$ | HCl | +0.50[a] | 17 |
| $Mo_2Cl_4(PEt_3)_4$ | $CH_2Cl_2$ | +0.35 | 19 |
| $Mo_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ | $CH_2Cl_2$ | +0.38 | 19 |
| $Mo_2Cl_4(Ph_2PCH_2CH_2PPh_2)_2$ | $CH_2Cl_2$ | +0.52 | 19 |
| $Mo_2Br_4(Ph_2PCH_2CH_2PPh_2)_2$ | $CH_2Cl_2$ | +0.54 | 19 |
| $Mo_2(NCS)_4(PEt_3)_4$ | $CH_2Cl_2$ | +0.80 | 19 |
| $Mo_2(NCS)_4(Ph_2PCH_2CH_2PPh_2)_2$ | $CH_2Cl_2$ | +0.74[a] | 19 |
| $Mo_2(NCS)_4(Ph_2PCH_2PPh_2)_2$ | $CH_2Cl_2$ | +0.84[a] | 19 |
| $Mo_2(Ph_2PC(S)NPh)_4$ (1) | $CH_2Cl_2$ | +0.70 | this work |
| $Mo_2(Ph_2PC(S)NMe)_4$ (**2b**) | $CH_2Cl_2$ | +0.64 | this work |
| $Mo_2(Me_2NC(S)NMe)_4$ (**2a**) | $CH_2Cl_2$ | +0.67 | this work |
| $Mo_2(Me_2NC(S)NPh)_4$ (3) | $CH_2Cl_2$ | −0.18 | this work |
| | $CH_2Cl_2$ | +0.60 | this work |

[a] $E_{p,a}$ rather than $E_{1/2}$.

**Electrochemistry.** The electrochemistry of the molybdenum complexes was studied at a Pt electrode in dichloromethane solutions in the potential range −1.6 to +2.0 V vs. a Ag/AgI reference electrode[7] using normal pulse voltammetry and cyclic voltammetry. In order to facilitate comparison with the literature, all potentials are referred to a SCE ($E$ vs. Ag/AgI = $E$ vs. SCE + 0.18 V). Both $Mo_2(Ph_2PC(S)NPh)_4$ (**1**) and $Mo_2(Ph_2PC(S)NMe)_4$ (**2b**) show an oxidation wave at about 0.65 V. Controlled-potential oxidation at room temperature leads to decomposition of the solutions, 1.4 and 1.3 electrons being transferred for $Mo_2(Ph_2PC(S)NPh)_4$ (**1**) and $Mo_2(Ph_2PC(S)NMe)_4$ (**2b**), respectively. At −10 °C electrolysis leads to a 1.1-electron oxidation of the latter compound. As the current function ($i_d/c$) is rougly equal for these compounds, it is concluded that these oxidations are one-electron processes.

The $E_{1/2}$ values are summarized in Table VI, together with some known $E_{1/2}$ values for analogous compounds.[17-19] From these data it is seen that the $E_{1/2}$ values for $Mo_2(Ph_2PC(S)NPh)_4$ and $Mo_2(Ph_2PC(S)NMe)_4$ are between those of $Mo_2(NCS)_4L_x$ (coordination of the NCS ligand via the N atom) and $Mo_2X_4L_x$ (X = Cl or Br; L is a ligand that coordinates via P atoms ($x = 4$, L = $PEt_3$ or $P(n\text{-}Pr)_3$; $x = 2$, L = $Ph_2PCH_2PPh_2$ or $Ph_2PCH_2CH_2PPh_2$). Assuming an identical molecular structure for $Mo_2(Ph_2PC(S)NPh)_4$ (**1**) and yellow $Mo_2(Ph_2PC(S)NMe)_4$ (**2b**), the lower $E_{1/2}$ value for the latter can be ascribed to the electron-releasing effect of the methyl group with respect to the phenyl group. The same argument can be used to account for the decrease in ionization potential for $Mo_2(O_2CR)_4$ in which R passes through the series H, $CH_3$, and $C(CH_3)_3$.[20]

According to the diagnostic criteria of Nicholson and Shain[21] ($i_b/i_f$ increases to a value of 1 as $v$ increases; $i_p/v^{1/2}$ decreases as $v$ increases) the one-electron oxidation of $Mo_2(Ph_2PC(S)NMe)_4$ is a quasi-reversible one-electron transfer followed by an irreversible chemical reaction ($E_rC_i$ mechanism). So the one-electron oxidation of $Mo_2(Ph_2PC(S)NMe)_4$ can be represented by

$$Mo_2(Ph_2PC(S)NMe)_4 \xrightarrow{E_{1/2} = +0.64\ V} Mo_2(Ph_2PC(S)NMe)_4^+ \rightarrow \text{products}$$

Table VII. Table of Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(C_{14}H_{13}NPS)_4\cdot 2CH_2Cl_2$[a]

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Mo(1) | 0.0189 (1) | 0.01660 (8) | 0.44430 (7) | 1.95 (2) |
| S(1) | 0.1979 (3) | 0.0659 (3) | 0.5141 (2) | 2.65 (8) |
| P(2) | 0.0603 (3) | −0.1773 (3) | 0.5462 (2) | 2.48 (8) |
| P(1) | 0.3268 (3) | 0.0952 (3) | 0.6958 (3) | 3.2 (1) |
| S(2) | 0.1290 (4) | −0.2903 (3) | 0.4140 (3) | 4.3 (1) |
| N(1) | −0.1254 (9) | −0.0189 (8) | 0.3582 (6) | 2.4 (2) |
| N(2) | 0.0792 (9) | −0.1087 (8) | 0.4048 (6) | 2.7 (3) |
| C(1) | −0.134 (1) | −0.009 (1) | 0.2686 (8) | 3.3 (3) |
| C(2) | 0.203 (1) | 0.0577 (9) | 0.6158 (8) | 2.6 (3) |
| C(3) | 0.405 (1) | 0.144 (1) | 0.6311 (9) | 3.1 (4) |
| C(4) | 0.390 (1) | 0.236 (1) | 0.5995 (9) | 4.3 (4) |
| C(5) | 0.458 (1) | 0.270 (1) | 0.556 (1) | 4.7 (5) |
| C(6) | 0.538 (1) | 0.215 (1) | 0.539 (1) | 5.8 (5) |
| C(7) | 0.553 (1) | 0.127 (1) | 0.570 (1) | 5.4 (5) |
| C(8) | 0.484 (1) | 0.089 (1) | 0.615 (1) | 5.2 (5) |
| C(9) | 0.272 (1) | 0.199 (1) | 0.7362 (9) | 3.7 (4) |
| C(10) | 0.340 (1) | 0.230 (1) | 0.8115 (9) | 3.9 (4) |
| C(11) | 0.308 (2) | 0.313 (1) | 0.847 (1) | 5.3 (5) |
| C(12) | 0.210 (1) | 0.354 (1) | 0.807 (1) | 5.2 (5) |
| C(13) | 0.147 (1) | 0.320 (1) | 0.734 (1) | 4.7 (5) |
| C(14) | 0.181 (1) | 0.243 (1) | 0.696 (1) | 3.8 (4) |
| C(15) | 0.114 (1) | −0.108 (1) | 0.327 (1) | 4.2 (4)* |
| C(16) | 0.091 (1) | −0.191 (1) | 0.4443 (8) | 2.8 (3) |
| C(17) | 0.202 (1) | −0.205 (1) | 0.7011 (9) | 4.0 (4) |
| C(18) | 0.190 (1) | −0.1840 (9) | 0.6181 (8) | 3.0 (4) |
| C(19) | 0.279 (1) | −0.162 (1) | 0.5876 (9) | 3.3 (4) |
| C(20) | 0.381 (1) | −0.159 (1) | 0.648 (1) | 4.4 (4) |
| C(21) | 0.390 (1) | −0.183 (1) | 0.728 (1) | 5.1 (5) |
| C(22) | 0.302 (1) | −0.203 (1) | 0.758 (1) | 4.8 (5) |
| C(23) | −0.002 (1) | −0.2852 (9) | 0.5623 (9) | 3.9 (4) |
| C(24) | 0.061 (1) | −0.365 (1) | 0.585 (1) | 4.9 (5) |
| C(25) | 0.005 (2) | −0.449 (1) | 0.5911 (9) | 5.2 (5) |
| C(26) | −0.103 (1) | −0.453 (1) | 0.5768 (9) | 4.6 (4) |
| C(27) | −0.162 (1) | −0.372 (1) | 0.557 (1) | 5.2 (5) |
| C(28) | −0.111 (1) | −0.289 (1) | 0.550 (1) | 4.3 (4) |
| Cl(1) | 0.3162 (7) | 0.4910 (6) | 0.6765 (6) | 14.6 (3) |
| Cl(2) | 0.4138 (9) | 0.5501 (7) | 0.5561 (8) | 20.9 (4) |
| C(29) | 0.363 (2) | 0.579 (2) | 0.630 (2) | 13 (1)* |

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

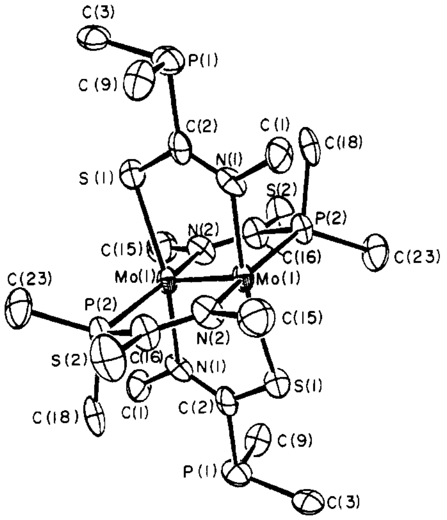

**Figure 1.** Molecular structure of compound **2a**. The atom-labeling scheme for Table VII is defined.

As for some other $Mo_2^{4+}$ compounds it has been reported that the oxidized products are not stable and decompose; it is assumed that in general the one-electron oxidation of compounds containing the $Mo_2^{4+}$ unit follows an $E_rC_i$ mechanism.

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**Table VIII.** Table of Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(C_{14}H_{13}NPS)_4 \cdot {}^1/_2CH_2Cl_2$[a]

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ | atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo(1) | 0.30345 (7) | 0.16444 (6) | 0.04719 (7) | 2.43 (2) | C(22) | −0.1896 (8) | 0.3148 (8) | 0.074 (1) | 5.3 (4) |
| Mo(2) | 0.23687 (7) | 0.30352 (6) | 0.06740 (7) | 2.47 (3) | C(23) | 0.0637 (7) | 0.1008 (8) | 0.1944 (8) | 3.6 (3) |
| Cl(1) | 0.442 (1) | 0.0344 (9) | 0.441 (1) | 14.1 (5)* | C(24) | 0.1447 (9) | 0.0468 (9) | 0.2916 (9) | 4.8 (4) |
| Cl(2) | 0.3737 (9) | 0.1266 (8) | 0.4293 (9) | 11.8 (4)* | C(25) | 0.162 (1) | −0.0464 (9) | 0.3089 (9) | 5.7 (4) |
| S(1) | 0.4039 (2) | 0.1823 (2) | −0.0332 (2) | 3.21 (8) | C(26) | 0.100 (1) | −0.0828 (9) | 0.229 (1) | 6.0 (4) |
| S(2) | 0.2121 (2) | 0.1167 (2) | 0.1151 (2) | 3.17 (8) | C(27) | 0.0185 (9) | −0.0277 (8) | 0.133 (1) | 5.6 (4) |
| S(3) | 0.0769 (2) | 0.3623 (2) | −0.1087 (2) | 3,53 (9) | C(28) | −0.0008 (9) | 0.0665 (8) | 0.1126 (9) | 4.5 (4) |
| S(4) | 0.3862 (2) | 0.2819 (2) | 0.2432 (2) | 3.18 (9) | C(29) | 0.0908 (7) | 0.2616 (7) | −0.1624 (8) | 3.1 (3) |
| P(1) | 0.4535 (2) | 0.3401 (2) | −0.0583 (2) | 3.74 (9) | C(30) | 0.1854 (9) | 0.0929 (7) | −0.1488 (9) | 4.1 (4) |
| P(2) | 0.0381 (2) | 0.2231 (2) | 0.1824 (2) | 3.88 (9) | C(31) | 0.0550 (9) | 0.2355 (8) | −0.3666 (8) | 3.7 (4) |
| P(3) | −0.0174 (2) | 0.2705 (2) | −0.2940 (3) | 3.9 (1) | C(32) | 0.004 (1) | 0.2114 (8) | −0.4624 (9) | 4.9 (4) |
| P(4) | 0.6160 (2) | 0.1214 (2) | 0.3812 (2) | 3.38 (9) | C(33) | 0.057 (1) | 0.192 (1) | −0.524 (1) | 6.4 (5) |
| N(1) | 0.1748 (6) | 0.1809 (5) | −0.1057 (6) | 2.9 (2) | C(34) | 0.158 (1) | 0.191 (1) | −0.488 (1) | 7.2 (6) |
| N(2) | 0.4528 (6) | 0.1147 (5) | 0.1918 (6) | 2.5 (2) | C(35) | 0.209 (1) | 0.211 (1) | −0.391 (1) | 6.2 (5) |
| N(3) | 0.3199 (6) | 0.3479 (6) | 0.0173 (6) | 3.0 (3) | C(36) | 0.1606 (9) | 0.2336 (9) | −0.3297 (9) | 5.3 (4) |
| N(4) | 0.1374 (6) | 0.2971 (5) | 0.1229 (6) | 2.9 (2) | C(37) | −0.1002 (9) | 0.3957 (8) | −0.3386 (9) | 4.3 (4) |
| C(1) | 0.3794 (8) | 0.2973 (7) | −0.0229 (8) | 3.0 (3) | C(38) | −0.084 (1) | 0.445 (1) | −0.399 (1) | 7.5 (6) |
| C(2) | 0.3075 (9) | 0.4429 (7) | 0.0351 (9) | 4.7 (4) | C(30) | −0.158 (1) | 0.543 (1) | −0.437 (1) | 9.6 (7) |
| C(3) | 0.3407 (9) | 0.4355 (8) | −0.1622 (9) | 4.7 (4) | C(40) | −0.243 (1) | 0.583 (1) | −0.414 (1) | 9.1 (7) |
| C(4) | 0.372 (1) | 0.4994 (9) | −0.185 (1) | 7.3 (5) | C(41) | −0.259 (1) | 0.538 (1) | −0.359 (1) | 8.3 (6) |
| C(5) | 0.291 (2) | 0.574 (1) | −0.267 (1) | 11.0 (7) | C(42) | −0.187 (1) | 0.441 (1) | −0.319 (1) | 6.7 (5) |
| C(6) | 0.185 (2) | 0.586 (1) | −0.323 (1) | 13 (1) | C(43) | 0.4797 (7) | 0.1686 (7) | 0.2605 (8) | 2.9 (3) |
| C(7) | 0.148 (2) | 0.524 (1) | −0.298 (1) | 11.1 (9) | C(44) | 0.5366 (9) | 0.0157 (7) | 0.2080 (9) | 4.5 (4) |
| C(8) | 0.231 (1) | 0.448 (1) | −0.216 (1) | 6.4 (5) | C(45) | 0.7034 (8) | 0.1143 (8) | 0.3291 (8) | 3.7 (4) |
| C(9) | 0.5083 (8) | 0.2536 (7) | −0.1290 (8) | 4.1 (3) | C(46) | 0.6672 (9) | 0.1777 (9) | 0.2446 (9) | 5.1 (4) |
| C(10) | 0.449 (1) | 0.2601 (9) | −0.2369 (9) | 5.7 (4) | C(47) | 0.7433 (9) | 0.172 (1) | 0.2149 (9) | 6.2 (5) |
| C(11) | 0.500 (1) | 0.197 (1) | −0.285 (1) | 7.3 (5) | C(48) | 0.8534 (8) | 0.1044 (9) | 0.2704 (9) | 5.8 (4) |
| C(12) | 0.6091 (9) | 0.1257 (9) | −0.230 (1) | 6.1 (4) | C(49) | 0.8913 (9) | 0.041 (1) | 0.353 (1) | 6.4 (5) |
| C(13) | 0.668 (1) | 0.1198 (8) | −0.122 (1) | 6.2 (5) | C(50) | 0.8144 (9) | 0.0457 (8) | 0.384 (1) | 4.8 (4) |
| C(14) | 0.6171 (9) | 0.1828 (8) | −0.071 (1) | 5.2 (4) | C(51) | 0.6062 (7) | 0.2234 (7) | 0.4460 (8) | 3.2 (3) |
| C(15) | 0.1309 (7) | 0.2227 (8) | 0.1370 (7) | 3.0 (3) | C(52) | 0.644 (1) | 0.2811 (9) | 0.435 (1) | 6.3 (5) |
| C(16) | 0.0636 (8) | 0.3875 (7) | 0.1389 (9) | 4.1 (4) | C(53) | 0.637 (1) | 0.358 (1) | 0.489 (1) | 7.5 (6) |
| C(17) | −0.0952 (8) | 0.2748 (7) | 0.0598 (8) | 3.5 (3) | C(54) | 0.596 (1) | 0.3735 (9) | 0.556 (1) | 6.4 (5) |
| C(18) | −0.1009 (9) | 0.2717 (8) | −0.0353 (9) | 4.8 (4) | C(55) | 0.558 (1) | 0.312 (1) | 0.567 (1) | 6.2 (5) |
| C(19) | −0.210 (1) | 0.3095 (9) | −0.124 (1) | 6.1 (5) | C(56) | 0.5650 (9) | 0.2382 (9) | 0.5123 (9) | 4.6 (4) |
| C(20) | −0.3033 (9) | 0.3450 (8) | −0.111 (1) | 5.9 (5) | C(57) | 0.437 (2) | 0.059 (2) | 0.505 (2) | 8 (1)* |
| C(21) | −0.2946 (9) | 0.3496 (8) | −0.017 (1) | 6.2 (5) | | | | | |

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

**X-ray Structural Results.** Since it was not clear from the types of evidence already described what differentiates the isomeric compounds **2a** and **2b**, this question had to be resolved by X-ray crystallography. The structures of compounds **2a** and **2b** are depicted in Figures 1 and 2, respectively. Complete lists of bond distances and bond angles are available as supplementary material. In **2a**, the molecule resides on a crystallographic inversion center so that there is only one independent ring of each type. In Figure 3 the important bond distances and angles in each of these are shown. The molecule in compound **2b** occupies a general position in the crystal, and all four rings are crystallographically independent but presumably chemically equivalent. Figure 3 shows the important distances and angles averaged over all four quadrants of this molecule.

## Discussion

We believe it is safe to conclude from the similarities in their spectral and electrochemical properties that compounds **1** and **2b** are structurally homologous. The higher value of $E_{1/2}$ for **1** as compared to that for **2b** can be attributed to the greater electron-withdrawing effect of the phenyl group.

There is still uncertainty about the structure of compound **3**. While much of its behavior is consistent with its having a structure like that of **2b**, there are aspects of its spectroscopic and especially electrochemical behavior (the appearance of an oxidation wave at −0.18 V as well as one at +0.60 V) that give rise to uncertainty. Thus far, suitable crystals of **3** have not been obtained, but further efforts in this direction are clearly desirable.

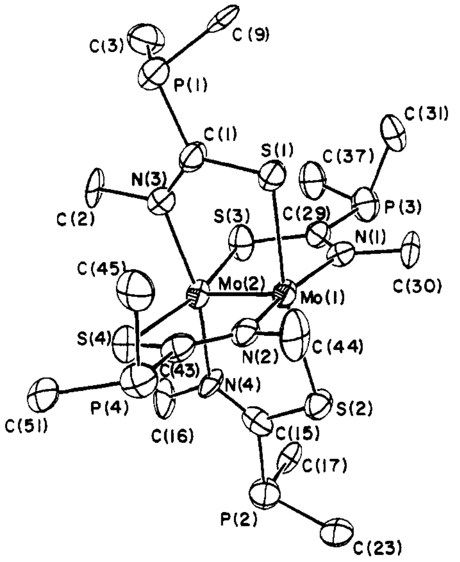


**Figure 2.** Molecular structure of compound **2b**. The atom-labeling scheme for Table VIII is defined.

For compounds **2a** and **2b** we have obtained definitive structural characterization by means of X-ray crystallography. In this way it has been shown for the first time that in complexes of binuclear, multiply bonded species such as $Mo_2^{4+}$ isomerism depending on ambidentate character of the ligands can occur.

It is convenient to discuss compond **2b** first since it has the simpler molecular structure. Each of the four ligands functions

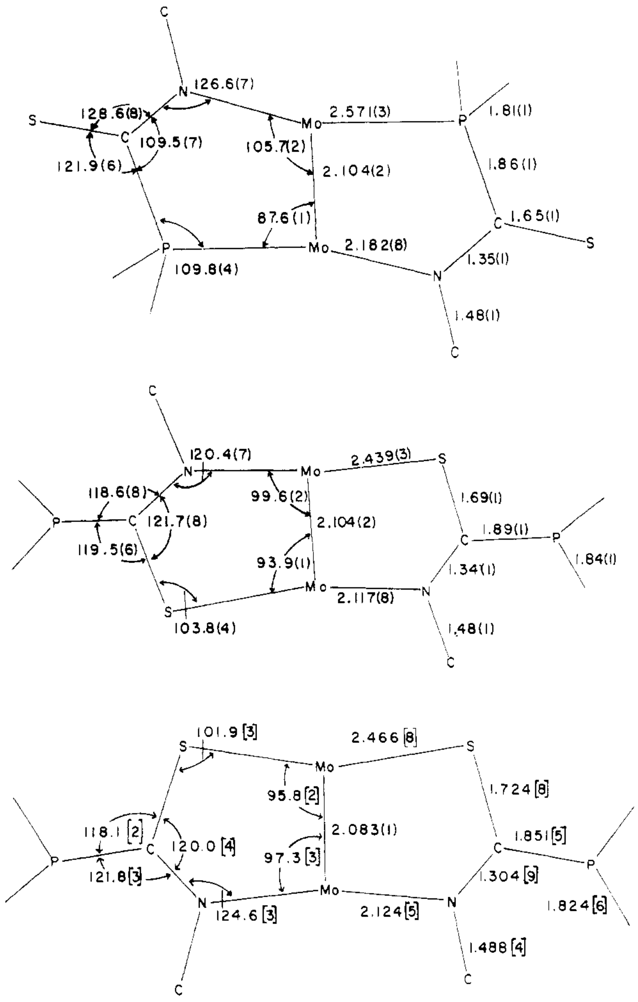
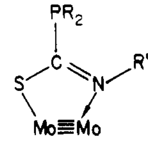


**Figure 3.** Molecular dimensions for **2a** and **2b**. The top and middle drawings are for the N,P- and N,S-bonded rings, respectively, of **2a**. The bottom drawing gives mean values for the four equivalent N,S-bonded rings of **2b**.

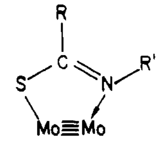
as a bidentate, bridging thioamidato unit, and the arrangement about the $Mo_2^{4+}$ core is such that, on each metal atom, like donor atoms are trans to each other. The symmetry of the $Mo_2S_4N_4$ core is thus $D_{2d}$. This arrangement has previously been found far more often than the alternative cis ($C_{2v}$) arrangement.[22] In the case of **2b**, aside from the phenyl groups, the symmetry of the molecule as a whole approaches $D_{2d}$.

The mean dimensions of the bridging ligands are shown in the lower part of Figure 3. As is evident from the small values of the deviations from the arithmetic mean values,[23] the four crystallographically independent rings are very similar to one another. The bond lengths are quite informative about the electronic structure. The ring C–N distance is indicative of considerable double-bond character, whereas the C–S bond length suggests relatively little. Thus, the best qualitative representation of the bonding in these rings would be provided by species c.

Another interesting inference that might be drawn from the dimensions is that there is no significant conjugation between the phosphorus atom and the thioamide group. The P–C distance is in the normal range for a single bond from a trivalent phosphorus atom to an $sp^2$ carbon atom. There is no significant difference between the P–C(thioamido) distance and the mean P–C(phenyl) distance. In addition the C–P–C angles (not shown) are all about 102°, which is typical for pyramidal $R_3P$ molecules.



c



d

An important implication of the simple, single-bond character of the P–C(thioamido) linkage is that the $Ph_2P$ substituent is not functioning in any special way and could be replaced by an alkyl group without any effect on the stability of the system. Thus, ordinary thioamido compounds, species d, should be obtainable, though none have yet been reported.

The structure of **2a** is more complex and even more interesting. The molecules reside on centers of inversion and contain two different ligand arrangements. Two of the ligands are arranged as in **2b**, i.e., coordinated with the N and S atoms bonded to the molybdenum atoms. The other two ligands employ their N and P atoms to form bonds to the molybdenum atoms and thus have exo C=S groups. Compound **2a**, therefore, exhibits within one molecule two of the bidentate bonding modes available to this ambidentate ligand. The dimensions of the S,N-bonded rings in **2a** are not significantly different from those of the rings in **2b**. For the P,N-bonded rings it would appear there is again considerable C=N double-bond character, possibly a bit more C=S double-bond character, but clearly only a single bond from C to P.

The Mo–Mo distances in the two molecules differ by an amount, 0.024 (3) Å, that is real in a statistical sense. The difference can be attributed to the tighter binding of the ligands in the case of **2b**. This means that more electron density is donated to the $Mo_2^{4+}$ unit, thus lowering the effective charge on the metal atoms, which in turn promotes better Mo–Mo orbital overlaps.

The Mo–S distances in **2a** and **2b**, 2.439 (3) and 2.466 [8] Å, are very similar to those few that have previously been reported for $Mo_2^{4+}$ complexes. Thus in $Mo_2(S_2CR)_4$ molecules,[24] the Mo–S distances average 2.465 [8] Å and in $Mo_2(S_2COEt)_4$ the average value was 2.478 [1] Å.[25]

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**Registry No.** **1**, 89637-07-0; **2a**, 89655-92-5; **2b**, 89637-09-2; **3**, 89655-93-6; Mo, 7439-98-7.

**Supplementary Material Available:** Tables of anisotropic thermal parameters, complete tables of bond distances and angles, and tables of observed and calculated structure factors for both structures (43 pages). Ordering information is given on any current masthead page.

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[22] See ref 2, p 90.

[23] Deviations from the mean are enclosed in brackets and are defined as $[(\sum_i \Delta_i^2)/n(n-1)]^{1/2}$, where $\Delta_i$ is the deviation of the $i$th value in a set of $n$ from the arithmetic mean of the set.

[24] Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 663.

[25] Ricard, L.; Karagiannidis, P.; Weiss, R. *Inorg. Chem.* **1973**, *12*, 2179.