854 *Inorg. Chem.* **2000,** *39,* 854−856

Reactivity of the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]^{2-}$ Anion toward the Imidodiphosphinochalcogenido Ligands $[N(QPPh_2)_2]^-$ (Q = S, Se): Synthesis and Characterization of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(QPPh_2)_2\}_3]Br$

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Introduction

The trinuclear complex $[NH_4]_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(\eta^2\text{-}S_2)_3]$ was first synthesized and characterized by Müller and coworkers.[1,2] The structure of the anion can be described as a trinuclear core of Mo(IV) atoms tricapped by an S atom; each Mo atom has a terminal S_2^{2-} ligand and is bridged to another Mo atom by an S_2^{2-} ligand. Reaction of this compound with HX or X_2 (X = Cl, Br)[3,4] affords the triangular thiohalide anions $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3X_6]^{2-}$ (Figure 1) in which the X ligands are labile.[5,6] In the present work we have used the lability of the Br^- ligands in $[NEt_4]_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]$ (**1**) to afford new complexes of the imidodiphosphinochalcogenido ligands $[N(QPPh_2)_2]^-$ (Q = S, Se), namely $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SPPh_2)_2\}_3]Br$ (**2**) and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SePPh_2)_2\}_3]Br$ (**3**). Although the coordination chemistry of the $[N(SPPh_2)_2]^-$ ligand is well developed[7−14] and that of $[N(SePPh_2)_2]^-$ has been explored increasingly since Bhattacharyya et al.[15] reported a convenient synthesis of the ligand,[16−21] compounds **2** and **3** are the first examples involving Mo.

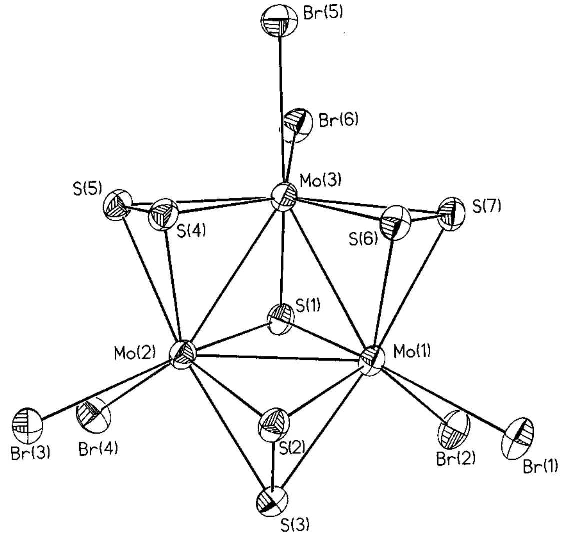

Figure 1. Drawing of the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]^{2-}$ anion in **1**. Here and in Figure 2, 50% anisotropic displacement ellipsoids are shown.

Experimental Section

Materials and Syntheses. All manipulations were performed under an inert atmosphere of N_2 with the use of standard Schlenk-line techniques. $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]^{2-}$ was synthesized from $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(\eta^2\text{-}S_2)_3]^{2-}$ and concentrated hydrobromic acid.[3,4] Addition of NEt_4Br led to the precipitation of $[NEt_4]_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]$ (**1**);[22] $K[N(SPPh_2)_2]$ and $K[N(SePPh_2)_2]$ were prepared by reported methods.[23,24] Solvents were dried, distilled, and degassed under N_2 before use. Diethyl ether and tetrahydrofuran (THF) were distilled from Na and benzophenone. Toluene was distilled from Na. Methylene chloride was distilled from P_2O_5. Dimethylformamide (DMF) was dried over molecular sieves. All other reagents were obtained commercially and were used without further purification.

Physical Measurements. ^{31}P NMR spectra were recorded on samples in 5 mm tubes on a 300 MHz Gemini Routine apparatus operating at 121.47 MHz in the Fourier transform mode. Chemical shifts are referenced to an external 85% H_3PO_4 solution. IR spectra were recorded on a BIO-RAD FTS 60 spectrometer from CsI pressed pellets. UV−vis spectra were recorded on a Varian Cary 1E spectrometer. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. Melting point determinations were performed with a Mel-Temp device on samples in glass capillaries.

Synthesis of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SPPh_2)_2\}_3]Br$, 2. $[NEt_4]_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]$ (**1**) (100 mg; 0.08 mmol) and $K[N(SPPh_2)_2]$ (120 mg; 0.25 mmol) were loaded into the same flask, and 10 mL of DMF was added. The resulting orange solution was maintained at 80 °C for

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(1) Müller, A.; Sarkar, S.; Bhattacharyya, R. G.; Pohl, S.; Dartmann, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 535.

(2) Müller, A.; Bhattacharyya, R. G.; Pfefferkorn, B. *Chem. Ber.* **1979**, *112*, 778−780.

(3) Fedin, V. P.; Sokolov, M. N.; Mironov, Y. V.; Kolesov, B. A.; Tkachev, S. V.; Fedorov, V. Y. *Inorg. Chim. Acta* **1990**, *167*, 39−45.

(4) Hegetschweiler, K.; Keller, T.; Zimmermann, H.; Schneider, W.; Schmalle, H.; Dubler, E. *Inorg. Chim. Acta* **1990**, *169*, 235−243.

(5) Fedin, V. P.; Müller, A.; Bögge, H.; Armatage, A.; Sokolov, M. N.; Yarovoi, S. S.; Fedorov, V. E. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1993**, *38*, 1563−1568.

(6) Meienberger, M. D.; Hegetschweiler, K.; Rüegger, H.; Gramlich, V. *Inorg. Chim. Acta* **1993**, *213*, 157−169.

(7) Churchill, M. R.; Cooke, J.; Fennessey, J. P.; Wormald, J. *Inorg. Chem.* **1971**, *10*, 1031−1035.

(8) Rossi, R.; Marchi, A.; Marvelli, L.; Magon, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1993**, 723−729.

(9) Haiduc, I.; Silvestru, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Polyhedron* **1993**, *12*, 69−75.

(10) Casas, J. S.; Castiñeiras, A.; Haiduc, I.; Sánchez, A.; Sordo, J.; Vázquez-López, E. M. *Polyhedron* **1994**, *13*, 2873−2879.

(11) Bhattacharyya, P.; Novosad, J.; Phillips, J.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 1607−1613.

(12) Silvestru, C.; Rösler, R.; Haiduc, I.; Cea-Olivares, R.; Espinosa-Pérez, G. *Inorg. Chem.* **1995**, *34*, 3352−3354.

(13) Cupertino, D.; Keyte, R.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Inorg. Chem.* **1996**, *35*, 2695−2697.

(14) Bhattacharyya, P.; Slawin, A. M. Z.; Smith, M. B. *J. Chem. Soc., Dalton Trans.* **1998**, 2467−2475.

(15) Bhattacharyya, P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 3189−3193.

(16) Cea-Olivares, R.; Novosad, J.; Woollins, J. D.; Slawin, A. M. Z.; García-Montalvo, V.; Espinosa-Pérez, G.; García y García, P. *Chem. Commun.* **1996**, 519−520.

(17) Cea-Olivares, R.; García-Montalvo, V.; Novosad, J.; Woollins, J. D.; Toscano, R. A.; Espinosa-Pérez, G. *Chem. Ber.* **1996**, *129*, 919−923.

(18) García-Montalvo, V.; Novosad, J.; Kilian, P.; Woollins, J. D.; Slawin, A. M. Z.; García y García, P.; López-Cardoso, M.; Espinosa-Pérez, G.; Cea-Olivares, R. *J. Chem. Soc., Dalton Trans.* **1997**, 1025−1029.

(19) Papadimitriou, C.; Veltsistas, P.; Novosad, J.; Cea-Olivares, R.; Toscano, A.; Garcia y Garcia, P.; Lopez-Cardosa, M.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **1997**, *16*, 2727−2729.

(20) Muñoz-Hernández, M.-A.; Singer, A.; Atwood, D. A.; Cea-Olivares, R. *J. Organomet. Chem.* **1998**, *571*, 15−19.

(21) Cea-Olivares, R.; Canseco-Melchor, G.; García-Montalvo, V.; Hernández-Ortega, S.; Novosad, J. *Eur. J. Inorg. Chem.* **1998**, 1573−1576.

(22) Evans, W. J.; Ansari, M. A.; Ziller, J. W. *Organometallics* **1995**, *14*, 3−4.

(23) Bhattacharyya, P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2489−2495.

(24) Haiduc, I. In *Inorganic Experiments*; Woollins, J. D., Ed.; VCH: New York, 1995; pp 145−148.

10.1021/ic9907056 CCC: $19.00

Table 1. Crystallographic Data for $[NEt_4]_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]$ (**1**), $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SPPh_2)_2\}_3]Br\cdot 2CH_2Cl_2$ (**2**), $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SePPh_2)_2\}_3]Br$ (**3**)

	1	**2**	**3**
formula	$C_{16}H_{40}Br_6Mo_3N_2S_7$	$C_{72}H_{60}BrMo_3N_3P_6S_{13}\cdot 2CH_2Cl_2$	$C_{72}H_{60}BrMo_3N_3P_6S_7Se_6$
fw	1252.20	2107.41	2218.96
space group	Pbca	$P2_1/n$	$R3c$
a (Å)	18.928(13)	13.309(4)	21.076(3)
b (Å)	12.769(9)	24.971(8)	21.076(3)
c (Å)	29.503(21)	26.206(8)	75.848(15)
α (deg)	90	90	90
β (deg)	90	93.570(6)	90
γ (deg)	90	90	120
V (Å^3)	7131(9)	8692(5)	29179(8)
T (°C)	−120	−120	−120
d_{calc} (g/cm^3)	2.333	1.610	1.515
Z	8	4	12
$\mu_{Mo\ K\alpha}$ (cm^{-1})	81.87	14.74	33.22
$R_1(F)$[a]	0.034	0.055	0.093
$R_w(F^2)$[b]	0.071	0.123	0.155

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum wF_o^4]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 > 0$ for **1** and **2**, $w^{-1} = \sigma^2(F_o^2) + (0.1F_o^2)^2$ for $F_o^2 > 0$ for **3**. $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

3 h, next concentrated to 5 mL and then cooled to 20 °C to precipitate a bright yellow solid. This solid was washed with 30 mL of diethyl ether and dried under vacuum. Yellow crystals suitable for X-ray diffraction were obtained from a solution of **2** in CH_2Cl_2 kept at 20 °C. $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SPPh_2)_2\}_3]Br$: yellow crystals, yield 55%, mp 315−317 °C. Anal. Calcd for $C_{72}H_{60}BrMo_3N_3P_6S_{13}\cdot 2CH_2Cl_2$: C, 42.25; H, 3.07; N, 2.00. Found: C, 42.61; H, 3.07; N, 2.01. $^{31}P\{^1H\}$ NMR (ppm, CH_2Cl_2/CD_2Cl_2, 295 K): δ 40.73 (s, 1), 38.80 (s, 1). UV−vis (nm, CH_2Cl_2): 417 (ϵ = 1500 M^{-1} cm^{-1}), 363 (ϵ = 2610 M^{-1} cm^{-1}). IR (cm^{-1}): 511 (s, ν_{P-S}), 565 (vs, ν_{P-S}), 697 (vs), 716 (s), 747 (s, ν_{P-N}), 800 (s, ν_{P-N}), 820 (m, ν_{P-N}), 998 (m), 1027 (m), 1108 (s), 1176 (s, ν_{P-N}), 1233 (s, ν_{P-N}), 1386 (m), 1437 (s), 1479 (m), 3055 (m).

Synthesis of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SePPh_2)_2\}_3]Br$, 3. A mixture of $[NEt_4]_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]$ (**1**) (100 mg; 0.08 mmol) and $K[N(SePPh_2)_2]$ (150 mg; 0.25 mmol) was dissolved in 10 mL of DMF, and the resultant solution was maintained at 120 °C for 3 h, next concentrated to 5 mL, and then cooled to 25 °C. The addition of 10 mL of absolute ethanol resulted in the precipitation of an orange solid that was washed with 30 mL of diethyl ether and dried under vacuum. Orange crystals suitable for X-ray diffraction were grown overnight at 4 °C from a solution of **3** in CH_2Cl_2 layered with THF. $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SePPh_2)_2\}_3]Br$: orange crystals, yield 60%, mp 314−316 °C. Anal. Calcd for $C_{72}H_{60}BrMo_3N_3P_6S_7Se_6$: C, 38.97; H, 2.73; N,1.89. Found: C, 38.29; H, 2.89; N, 1.62 (solvent molecules are apparently lost in preparation for chemical analyses.) $^{31}P\text{-}\{^1H\}$ NMR (ppm, CH_2Cl_2/CD_2Cl_2, 295 K): δ 31.10 (s, 1), 30.24 (s, 1). UV−vis (nm, CH_2Cl_2): 419 (ϵ = 1420 M^{-1} cm^{-1}), 367 (ϵ = 2480 M^{-1} cm^{-1}). IR (cm^{-1}): 508 (s, ν_{P-Se}), 538 (vs, ν_{P-Se}), 693 (vs), 716 (s), 747 (s, ν_{P-N}), 787 (s, ν_{P-N}), 808 (m, ν_{P-N}), 998 (m), 1027 (m), 1105 (s), 1174 (s, ν_{P-N}), 1232 (s, ν_{P-N}), 1387 (m), 1437 (s), 1480 (m), 3057 (m).

Crystallographic Studies. Crystals of **1**−**3** are unstable out of their mother liquors and were rapidly mounted in oil on a Nylon loop and placed under the N_2 cold stream of a diffractometer. Crystal data for **1**−**3** are listed in Table 1. Intensity data were collected at −120 °C on a Bruker SMART 1000 CCD diffractometer with Mo Kα radiation (λ = 0.710 73 Å). Final unit cell dimensions were obtained from 8192 reflections for **1**−**3**. Data were collected in the ω scan mode with the program SMART.[25] Cell refinement and data reduction were carried out with the use of the program SAINT.[25] The program SADABS in the SAINT suite[25] was used not only to apply incident beam and decay corrections but also to apply a semiempirical absorption correction based on the high redundancy of the data as face indexing of the crystals was not feasible. The structures were determined by direct methods and refined by full-matrix least-squares methods on F^2 for all data.[26]

Table 2. Selected Bond Distances (Mean Distances and Range, Å) for $[NEt_4]_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]$ (**1**), $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SPPh_2)_2\}_3]Br\cdot 2CH_2Cl_2$ (**2**), and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SePPh_2)_2\}_3]Br$ (**3**)

	1	**2**	**3**
Mo−Mo	2.746(1)	2.734(3)	2.746(2)
	2.741(2)−2.755(2)	2.727(1)−2.736(1)	
Mo−μ_3-S	2.341(1)	2.374(1)	2.405(18)
	2.337(2)−2.344(2)	2.370(2)−2.382(2)	
Mo−S_{eq}[a]	2.475(1)	2.486(1)	2.526(3)
	2.466(2)−2.484(2)	2.481(2)−2.489(2)	2.523(4)−2.529(4)
Mo−S_{ax}[a]	2.389(1)	2.404(1)	2.419(3)
	2.378(2)−2.400(2)	2.395(2)−2.410(2)	2.411(4)−2.427(4)
S_{eq}−S_{ax}	2.027(9)	2.059(2)	2.155(5)
	2.025(3)−2.030(3)	2.059(3)−2.060(2)	
S_{ax}−Br		2.988(1)	3.218(5)
		2.977(2)−3.000(2)	
Mo−S_{cis}[b]		2.540(1)	
		2.527(2)−2.552(2)	
Mo−S_{trans}[b]		2.559(1)	
		2.555(2)−2.562(2)	
Mo−Se_{cis}			2.687(2)
Mo−Se_{trans}			2.694(2)

[a] In the bridging S_2^{2-} group atom S_{eq} lies nearly in the Mo_3 equatorial plane whereas atom S_{ax} lies out of this plane away from the μ_3-S atom. [b] The Q_{cis} atom of the $[N(QPPh_2)_2]^-$ ligand (Q = S, Se) lies on the μ_3-S side of the equatorial plane; the Q_{trans} atom lies on the other side.

Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The isotropic displacement parameter of each hydrogen atom was 20% larger than the atom to which it is attached. Compound **2** crystallizes with two CH_2Cl_2 solvent molecules that were successfully refined. For compound **3**, considerable electron density remained that could not be modeled satisfactorily. Accordingly, the program SQUEEZE[27] in the PLATON[28] suite of programs was used. Residual electron density amounts to 140 e$^-$ per trinuclear cluster or about three CH_2Cl_2 molecules. Of course, other formulations of this density are possible, since other solvent molecules, for example THF, were involved in the crystallization of **3**. The final models involved anisotropic displacement parameters for all non-hydrogen atoms and converged to final R_1(F) values of 0.034 (**1**), 0.055 (**2**), and 0.093 (**3**) for those data having $F_o^2 > 2\sigma(F_o^2)$. As a result of the presence of disordered solvent molecules, crystals of compound **3** scatter poorly at

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(25) *SMART Version 5.054 and SAINT-Plus Version 6.0 Data Collection and Processing Software for the SMART System*; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 1997.

(26) Sheldrick, G. M. *SHELXTL PC Version 5.0 An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.

(27) van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 194−201.

(28) Spek, A. L. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, C34.

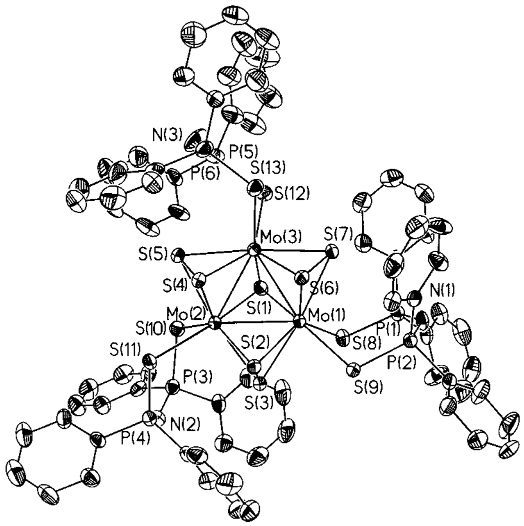

Figure 2. Drawing of the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SPPh_2)_2\}_3]^+$ cation in **2**. H atoms have been omitted for clarity.

high Bragg angles. The data set is weak, and the model is not ideal. Hence, the $R_1(F)$ value for compound **3** is large. Of course, the poor quality of this structure determination is reflected in larger standard deviations in the metrical parameters. Nevertheless, this structure determination allows useful comparisons to be made with the two other compounds. Table 2 presents a summary of selected bond distances for **1**−**3**. Further details are available as Supporting Information.

Results and Discussion

Structural Description. A drawing of the anion of **1** is shown in Figure 1, and a drawing of the cation of **2** is shown in Figure 2.

The anion $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]^{2-}$ in compound **1** and the cation $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(QPPh_2)_2\}_3]^+$ in compounds **2** and **3** contain a Mo_3 triangle capped by a μ_3-S atom that lies above the Mo_3 plane (1.722 Å for **1**, 1.772 Å for **2**, and 1.807 Å for **3**). Each Mo atom is coordinated to two bridging $\mu_2\text{-}S_2^{2-}$ ligands, to one $\mu_3\text{-}S^{2-}$ ligand tricapping the Mo_3 triangle, and to two other Mo atoms. In **1** each Mo atom is further coordinated to two Br^- ligands whereas in **2** and **3** each Mo atom is coordinated symmetrically to two *Q* atoms from the $[N(QPPh_2)_2]^-$ ligand. Bond distances (Table 2) and angles in these compounds are unexceptional. The mean Mo−Mo distances (Table 2) are in agreement with those in other Mo_3 clusters (range 2.719(2) Å−2.757(1) Å)[29−31] and are consistent with Mo−Mo single-bond lengths.[32,33] Each S_{eq} atom of the $\mu_2\text{-}S_2^{2-}$ ligand is essentially in the Mo_3 plane, deviating by less than 0.2 Å. The unsymmetrical bonding mode of the $\mu_2\text{-}S_2^{2-}$ ligand is characteristic of the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3]^{4+}$ core.[29,30,33−35]

Table 3. $^{31}P\{^1H\}$ Chemical Shifts and Coupling Constants of $K[N(SPPh_2)_2]$, $K[N(SePPh_2)_2]$, $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SPPh_2)_2\}_3]Br$ (**2**), and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SePPh_2)_2\}_3]Br$ (**3**)

	δ (ppm)	$^1J_{P-Se}$ (Hz)	$^2J_{P-P}$ (Hz)
$K[N(SPPh_2)_2]^a$	37.10		
$K[N(SePPh_2)_2]^a$	28.52	693	8
$\mathbf{2}^b$	40.73, 38.80		
$\mathbf{3}^b$	31.10, 30.24	550	not detectable

[a] Solutions prepared in DMF/CD_2Cl_2 [b] Solutions prepared in CH_2Cl_2/CD_2Cl_2

The Br^- anion lies 4.003 Å above the Mo_3 plane in **2** and 4.304 Å in **3**. The $S_{ax}\cdots Br$ distances range from 2.977(2) to 3.000(2) Å for **2**; this distance is 3.218(5) Å for **3**. These distances are shorter than the sums of the van der Waals radii[36] and are possibly indicative of weak $S_{ax}\cdots Br$ interactions.

^{31}P NMR Measurements. Table 3 displays the different ^{31}P NMR chemical shifts for $K[N(SPPh_2)_2]$, $K[N(SePPh_2)_2]$, $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SPPh_2)_2\}_3]Br$ (**2**), and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SePPh_2)_2\}_3]Br$ (**3**). The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** show two resonances each with an intensity ratio of 1:1, indicative of two chemically different P atoms in cis and trans positions relative to the μ_3-S ligand and consistent with the solid-state structures. The decrease of the $^1J_{P-Se}$ value from the K^+ salt of the ligand $[N(SePPh_2)_2]^-$ to compound **3** indicates a reduction of the P−Se bond order.

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Supporting Information Available: CIF format crystallographic files for $[NEt_4]_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Br_6]$ (**1**), $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SPPh_2)_2\}_3]Br{\cdot}2CH_2Cl_2$ (**2**), and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3\{N(SePPh_2)_2\}_3]Br$ (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Fedin, V. P.; Sokolov, M. N.; Myakishev, K. G.; Geras'ko, O. A.; Fedorov, V. Y. *Polyhedron* **1991**, *10*, 1311−1317.

(30) Fedin, V. P.; Sokolov, M. N.; Geras'ko, O. A.; Virovets, A. V.; Podberezskaya, N. V.; Fedorov, V. Y. *Inorg. Chim. Acta* **1992**, *192*, 153−156.

(31) Zhu, H.-P.; Chen, C.-N.; Liu, Q.-T.; Chen, J.-T. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1998**, *54*, 1273−1275.

(32) Xia, J.-B.; Yao, Y.-G.; Wu, L.; Huang, X.-Y.; Lu, J.-X. *Acta Crystallogr.* **1998**, *54*, 1612−1615.

(33) Zimmermann, H.; Hegetschweiler, K.; Keller, T.; Gramlich, V.; Schmalle, H. W.; Petter, W.; Schneider, W. *Inorg. Chem.* **1991**, *30*, 4336−4341.

(34) Klingelhöfer, P.; Müller, U.; Friebel, C.; Pebler, J. *Z. Anorg. Allg. Chem.* **1986**, *513*, 22−34.

(35) Müller, A.; Pohl, S.; Dartmann, M.; Cohen, J. P.; Bennett, J. M.; Kirchner, R. M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34*, 434−436.

(36) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751−767.