Inorg. Chem. 1995, 34, 3485−3490

Synthesis, Characterization, and Reactivity of Sulfido- and Selenidomolybdenum(IV) Porphyrin Complexes. X-ray Structure of Sulfido(5,10,15,20-tetratolylporphyrinato)molybdenum(IV)

Lisa M. Berreau, Victor G. Young, Jr., and L. Keith Woo*[1]

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

Received January 20, 1995⊗

Treatment of (TTP)Mo($PhC\equiv CPh$) (TTP = *meso*-tetra-*p*-tolylporphyrinato) with S_8 or Cp_2TiS_5 in toluene results in the formation of (TTP)Mo=S. The sulfide complex may also be prepared from the treatment of (TTP)$MoCl_2$ with Li_2S in THF. Similarly, a terminal selenide complex may be prepared from treatment of (TTP)$MoCl_2$ with Na_2Se. The structure of (TTP)Mo=S has been determined by single-crystal X-ray diffraction analysis (triclinic, $P\bar{1}$, a = 12.735(2) Å, b = 13.521(2) Å, c = 13.920(2) Å, α = 74.76(1)°, β = 78.95(1)°, γ = 80.85(1)°, V = 2254.7(5) Å^3, Z = 2, R = 3.1%, R_w = 4.2%). Complete sulfur atom transfer occurs between (TTP)Mo($PhC\equiv CPh$) and (TTP)Sn=S to give (TTP)Mo=S, (TTP)Sn^{II}, and $PhC\equiv CPh$. The net result is a formal two-electron redox process that occurs irreversibly between Sn(IV) and Mo(II). Correspondingly, no reaction is observed between (TTP)Mo=S and (TTP)Sn^{II} in the presence of excess $PhC\equiv CPh$. The analogous treatment of (TTP)Mo($PhC\equiv CPh$) with (TTP)Sn=Se results in the reversible exchange of a selenium ligand to form (TTP)Mo=Se, (TTP)Sn^{II}, and $PhC\equiv CPh$. When treated with excess PPh_3, the sulfido or selenido complex is reduced to (TTP)Mo(PPh_3)$_2$ with formation of either $Ph_3P=S$ or $Ph_3P=Se$. However, when (TTP)Mo=S or (TTP)Mo=Se is reduced with PPh_3 in the presence of $PhC\equiv CPh$, (TTP)Mo($PhC\equiv CPh$) is formed. The alkyne ligand of (TTP)Mo($PhC\equiv CPh$) may be displaced by 4-picoline to give *trans*-(TTP)Mo(4-picoline)$_2$. Ligand preference for the porphyrin Mo(II) center is thus PPh_3 < $PhC\equiv CPh$ < 4-picoline.

Introduction

The chemistry of molybdenum porphyrin complexes has been dominated by high oxidation state species containing terminal oxo ligands.[2] This stems in part from the lack of suitable starting materials for the synthesis of non-oxo-containing derivatives. In general, insertion of molybdenum into a free base porphyrin results in the isolation of a very stable molybdenum(V) porphyrin complex of the formula (POR)Mo(O)X[3] where X may be halide or alkoxide.[2] It is from these molybdenum(V) precursors that virtually all molybdenum porphyrins, from oxidation states +2 to +6, have been derived. Recently, we reported a new synthetic route for the preparation of (TTP)$MoCl_2$, a useful starting material for entry into the lower-valent chemistry of molybdenum porphyrins.[4] Most examples of molybdenum(IV) metalloporphyrins contain the very robust Mo=O unit and are therefore quite unreactive. The exception is (TTP)$MoCl_2$, which has been studied by Weiss as a precursor to the formally Mo(0) species (TTP)Mo(NO)$_2$, as well as to the Mo(II) species (TTP)Mo($PhC\equiv CPh$), (TTP)Mo(CO)$_2$, (TTP)Mo(py)$_2$, and (TTP)Mo(NO)(CH_3OH).[5] (TTP)$MoCl_2$ has also been utilized as a precursor to a molybdenum(IV) porphyrin diazo compound, (TTP)Mo(−N=NPh)$_2$.[6]

As an extension of our work involving the synthesis and reactivity of early transition metal porphyrin complexes, we have initiated a study of the preparation of terminal sulfido and selenido complexes of molybdenum(IV) porphyrins. Prior to this work, only terminal sulfido and selenido complexes of titanium, vanadium, and tin porphyrins have been isolated.[7]

Experimental Section

General Procedures. Toluene, THF, benzene-d_6, and hexanes for glovebox use were distilled from purple solutions of sodium benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2. Dry solvents were subsequently degassed on a vacuum line (10^{-5} Torr) with three successive freeze−pump−thaw cycles. Neutral alumina was purchased from Fisher and was heated at 150 °C for 24 h prior to use. Li_2S and Cp_2TiS_5 were purchased from Aldrich and used without further purification. Na_2Se was purchased from Alfa and used without further purification. Elemental sulfur was purchased from J. T. Baker and was sublimed prior to use. Elemental selenium was purchased from Alfa and was used without further purification. PPh_3 was purchased from Aldrich, recrystallized from hexanes, and dried under high vacuum at 50 °C for 12 h prior to use. (TTP)Mo($PhC\equiv CPh$), (TTP)$MoCl_2$, (TTP)Sn=S, and (TTP)Sn=Se were prepared according to literature procedures.[4,5a,7c,8]

All manipulations were performed either in a Vacuum Atmospheres glovebox equipped with a Model MO40H Dri-Train gas purifier or on a vacuum line using standard Schlenk techniques. UV−visible data were obtained using a Hewlett-Packard HP 8452A diode-array spectrophotometer. ^{1}H NMR spectra were recorded on a Nicolet NT300 spectrometer or on a Varian VXR 300-MHz spectrometer. IR spectra were recorded from KBr pellets on an IBM/Bruker IR-98 or on a Bio-

---

⊗ Abstract published in *Advance ACS Abstracts*, June 1, 1995.

[1] Presidential Young Investigator, 1990−1995; Camille and Henry Dreyfus Teacher-Scholar, 1993−1998.

[2] Matsuda, Y.; Murakami, Y. *Coord. Chem. Rev.* **1988**, *92*, 157.

[3] Abbreviations: POR is a general porphyrinato dianion, TTP is *meso*-tetra-*p*-tolylporphyrinato, and OEP is octaethylporphyrinato.

[4] Berreau, L. M.; Hays, J. A.; Young, V. G.; Woo, L. K. *Inorg. Chem.* **1994**, *33*, 105.

[5] (a) De Cian, A.; Colin, J.; Schappacher, M.; Richard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850. (b) Diebold, T.; Schappacher, M.; Chevrier, B.; Weiss, R. *J. Chem. Soc., Chem. Commun.* **1979**, 693. (c) Colin, J.; Strich, A.; Schappacher, M.; Chevrier, B.; Veillard, A.; Weiss, R. *Nouv. J. Chim.* **1984**, *8*, 55.

[6] Colin, J.; Butler, G.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 3828.

[7] (a) Woo, L. K.; Hays, J. A.; Young, V. G.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4186. (b) Poncet, J. L.; Guilard, R.; Friant, P.; Goulon-Ginet, C.; Goulon, J. *Nouv. J. Chim.* **1984**, *8*, 583. (c) Guilard, R.; Ratti, C.; Barbe, J.-M.; Dubois, D.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 1537.

[8] Berreau, L. M.; Woo, L. K. *J. Am. Chem. Soc.* **1995**, *117*, 1314.

0020-1669/95/1334-3485$09.00/0

Rad Digilab FTS-7 spectrometer. Elemental analyses were obtained from Atlantic Microlabs, Norcross, GA.

Sulfido(5,10,15,20-tetratolylporphyrinato)molybdenum(IV), 1. Method 1. From (TTP)Mo(PhC≡CPh) and S$_8$. (TTP)MoCl$_2$ (109 mg, 0.131 mmol), LiAlH$_4$ (26 mg, 0.65 mmol), and PhC≡CPh (133 mg, 0.747 mmol) were stirred in a toluene/THF (25 mL/0.3 mL) solution at 40−50 °C for 45 min. The reaction mixture was then checked by UV−vis to verify the formation of (TTP)Mo(PhC≡CPh) [UV−vis (toluene, nm): 428 (Soret), 544]. After the solution was allowed to cool to room temperature, the solvent was removed *in vacuo*. The residue was dissolved in toluene (20 mL), and the mixture was filtered. The filtrate was reduced in volume to ca. 15 mL. Elemental sulfur (55 mg, 0.22 mmol) was added to the solution in ca. 10 mL of toluene. The reaction mixture was stirred at 50−60 °C for 30 min. After the reaction mixture was allowed to cool to room temperature, the solvent was removed *in vacuo*. The residue was redissolved in CH$_2$Cl$_2$ (15 mL), and the solution was filtered. The filtrate was evaporated to dryness. Recrystallization from CH$_2$Cl$_2$/hexanes (1:4), filtration, washing with hexanes, and drying *in vacuo* produced a red/purple solid (45 mg, 43% based on (TTP)MoCl$_2$). UV−vis (toluene, nm): 438 (Soret), 556. ^{1}H NMR (C$_6$D$_6$, 300 MHz, ppm): 9.27 (s, 8H, β-H), 8.06 (d, 4H, -C$_6H_4$CH$_3$), 7.99 (d, 4H, -C$_6H_4$CH$_3$), 7.28 (m, 8H, -C$_6H_4$CH$_3$), 2.41 (s, 12H, -C$_6$H$_4$CH_3). IR (KBr): $\nu_{\mathrm{Mo=S}}$ = 542 cm^{-1}. MS{EI} Calcd (found) *m/e*: 798 (798) [M]$^+$. Anal. Calcd (found) for C$_{48}$H$_{36}$N$_4$MoS: C, 72.16 (71.60); H, 4.55 (4.74); N, 7.02 (6.87).

Method 2. From (TTP)Mo(PhC≡CPh) and Cp$_2$TiS$_5$. (TTP)MoCl$_2$ (91 mg, 0.11 mmol), LiAlH$_4$ (27 mg, 0.66 mmol), and PhC≡CPh (95 mg, 0.53 mmol) were stirred in a toluene (20 mL) solution at 50−60 °C for 24 h. The reaction mixture was then checked by UV−vis to verify the formation of (TTP)Mo(PhC≡CPh) and was then filtered. Cp$_2$TiS$_5$ (68 mg, 0.20 mmol) in ca. 10 mL of toluene was added to the filtrate, and the reaction mixture was stirred at room temperature for 24 h. After the solvent was removed *in vacuo*, the residue was redissolved in a minimal amount of toluene (4 mL), and the solution was placed on a 1 cm × 12 cm basic alumina column. Using toluene as the eluent, an orange/red band was collected. The solvent was removed *in vacuo*, and the product was recrystallized from toluene/hexanes (1:3). Workup as above produced a purple microcrystalline solid (36 mg, 42% based on (TTP)MoCl$_2$). The ^{1}H NMR spectrum of the isolated product matched that obtained in method 1.

Method 3. From (TTP)MoCl$_2$ and Li$_2$S. (TTP)MoCl$_2$ (83 mg, 0.10 mmol) was stirred with Li$_2$S (12 mg, 0.26 mmol) in THF (20 mL) at 40−50 °C for 10 h. During this time, the color of the solution changed from green to orange/brown. The solution was then cooled to ambient temperature and was subsequently evaporated to dryness. The residue was redissolved in a minimal amount of toluene (ca. 3 mL), and the solution was placed on a 1 cm × 10 cm neutral alumina column. Using toluene as the eluent, the first band off the column, an orange-red fraction, was collected. Following removal of the solvent *in vacuo*, the product was redissolved in toluene (1.5 mL), the solution was layered with ca. 6 mL of hexanes, and the mixture was cooled to −20 °C for 36 h. Workup as above produced a red/purple solid (15 mg, 19%). The ^{1}H NMR spectrum of the isolated product matched that obtained in method 1.

Selenido(5,10,15,20-tetratolylporphyrinato)molybdenum(IV), 2. Method 1. From (TTP)MoCl$_2$ and Na$_2$Se. (TTP)MoCl$_2$ (81 mg, 0.10 mmol) was stirred with Na$_2$Se (20 mg, 0.16 mmol) in THF (20 mL) at 40−50 °C for 24 h. During this time, the color of the solution changed from green to orange/brown. The solution was cooled to room temperature and was subsequently evaporated to dryness. The residue was redissolved in a minimal amount of toluene (ca. 5 mL), and the solution was placed on a 1 cm × 10 cm neutral alumina column. Using toluene as the eluent, an orange/red band was collected. Following removal of the solvent *in vacuo*, the crude product was redissolved in ca. 1 mL of toluene, the solution was layered with ca. 6 mL of hexanes, and the mixture was cooled to −20 °C for 2 h. Filtration, washing with hexanes, and drying *in vacuo* produced a red/purple solid (14 mg, 17%). UV−vis (toluene, nm): 432 (Soret), 554. ^{1}H NMR (C$_6$D$_6$, 300 MHz, ppm): 9.25 (s, 8H, β-H), 8.03 (d, 4H, -C$_6H_4$CH$_3$), 7.96 (d, 4H, -C$_6H_4$CH$_3$), 7.27 (m, 8H, -C$_6H_4$CH$_3$), 2.41 (s, 12H, -C$_6$H$_4$CH_3). MS{EI} Calcd (found) *m/e*: 844 (844) [M]$^+$. Anal. Calcd (found) for C$_{48}$H$_{36}$N$_4$MoSe: C, 68.08 (68.09); H, 4.29 (4.53); N, 6.62 (6.30).

Method 2. From (TTP)Mo(PhC≡CPh) and Elemental Selenium. (TTP)MoCl$_2$ (111 mg, 0.130 mmol), LiAlH$_4$ (23 mg, 0.60 mmol), and PhC≡CPh (70.6 mg, 0.400 mmol) were stirred in a toluene/THF (15 mL/0.2 mL) solution at 40−50 °C for 45 min. The reaction mixture was then checked by UV−vis to verify the formation of (TTP)Mo(PhC≡CPh). After the solution was allowed to cool to room temperature, the solvent was removed *in vacuo*. The residue was dissolved in toluene (20 mL), and the solution was filtered. Elemental selenium (42 mg, 0.54 mmol) was added to the solution in ca. 5 mL of toluene. The reaction mixture was stirred at 50−60 °C for 48 h. After the reaction mixture was allowed to cool to room temperature, the solvent was removed *in vacuo*. The reaction mixture was redissolved in a minimal amount of toluene (5 mL), and the solution was placed on a 1 × 10 cm neutral alumina column. Using toluene as the eluent, an orange-red band was collected. The solvent was removed *in vacuo*, and the product was redissolved in ca. 1 mL of toluene. The solution was then layered with hexane (ca. 3 mL), and the mixture was stored at −20 °C for 1 h. Workup as above produced a red solid (25 mg). ^{1}H NMR indicated that a mixture of (TTP)Mo(PhC≡CPh) and (TTP)Mo=Se (8:1) had been isolated.

Treatment of (TTP)Mo(PhC≡CPh) with (TTP)Sn=S. An NMR tube containing a C$_6$D$_6$ solution of (TTP)Sn=S (3.3 mg, 4.0 × 10^{-3} mmol) and (TTP)Mo(PhC≡CPh) (1.0 mg, 1.1 × 10^{-3} mmol) and sealed under nitrogen was monitored at ambient temperature over a 2 day period. ^{1}H NMR spectra indicated that atom transfer occurred quantitatively, producing (TTP)Sn$^{\mathrm{II}}$, (TTP)Mo=S, and PhC≡CPh.

Treatment of (TTP)Mo=S with (TTP)Sn$^{\mathrm{II}}$ in the Presence of PhC≡CPh. An NMR tube containing a C$_6$D$_6$ solution of (TTP)Mo=S (1.9 mg, 2.4 × 10^{-3} mmol), (TTP)Sn$^{\mathrm{II}}$ (1.5 mg, 1.9 × 10^{-3} mmol), and excess PhC≡CPh (>10-fold) and sealed under nitrogen was monitored at ambient temperature over a 48 h period. ^{1}H NMR spectra indicated that no reaction occurred.

Treatment of (TTP)Mo(PhC≡CPh) with (TTP)Sn=Se. An NMR tube containing a C$_6$D$_6$ solution of (TTP)Sn=Se (0.7 mg, 8 × 10^{-4} mmol) and (TTP)Mo(PhC≡CPh) (0.6 mg, 6 × 10^{-4} mmol) and sealed under nitrogen was monitored at ambient temperature over a 2 day period. ^{1}H NMR spectra indicated the formation of an equilibrium mixture.

Equilibrium Measurements. Samples for equilibrium determinations were prepared in a glovebox by adding specific volumes of known-concentration stock solutions of (TTP)Mo=Se, (TTP)Sn$^{\mathrm{II}}$, PhC≡CPh and an internal standard, triphenylmethane, to a 5-mm NMR tube attached to a ground glass joint. The solvent was removed under reduced pressure. The tube was then attached to a high-vacuum stopcock and connected to a high-vacuum line. After the addition of benzene-*d*$_6$ by vacuum distillation, the tube was flame sealed. The equilibrium constants were determined using a Lorentzian curve fitting to obtain an integrated intensity for each of the pyrrole β signals associated with the porphyrin species involved in the equilibrium. An integrated intensity was also obtained for the resonance associated with the *o*-protons of free PhC≡CPh. The samples were monitored in a temperature-controlled NMR probe until no further changes in peak areas were observed.

Bis(triphenylphosphine)(5,10,15,20-tetratolylporphyrinato)molybdenum(II), 3. (TTP)Mo=S (39 mg, 0.05 mmol) was stirred with PPh$_3$ (63 mg, 0.24 mmol) in toluene (15 mL) at 50−60 °C for 18 h. The solution was then cooled to room temperature and filtered, removing a green solid (14 mg). The filtrate was collected, and the solvent volume was reduced to ca. 8 mL. The solution was then stirred for an additional 24 h at room temperature. Filtration produced an additional crop of a green solid (22 mg, overall yield 48%). UV−vis (toluene, nm): 390 (Soret), 472, 490, 558, 582, 598. ^{1}H NMR (C$_6$D$_6$, 300 MHz, ppm): 30.67 (br, 12H, *o*-H of PPh$_3$), 12.08 (br, 6H, *p*-H of PPh$_3$), 11.50 (br, 12H, *m*-H of PPh$_3$), 4.09 (br, 8H, -C$_6H_4$CH$_3$), 2.63 (br, 8H, -C$_6H_4$CH$_3$), −1.63 (br, 12H, -C$_6$H$_4$CH_3), -11.60 (br, 8H, β-H). Anal. Calcd (found) for C$_{84}$H$_{66}$N$_4$MoP$_2$: C, 78.25 (78.00); H, 5.16 (5.37); N, 4.35 (4.16).

Treatment of (TTP)Mo=X with PPh$_3$ in the Presence of PhC≡CPh. An NMR tube containing a C$_6$D$_6$ solution of (TTP)Mo=S

(1.6 mg, 2.0×10^{-3} mmol), PPh_3 (2.6 mg, 9.9×10^{-3} mmol), and $PhC{\equiv}CPh$ (5.1 mg, 2.9×10^{-2} mmol) and sealed under nitrogen was monitored at ambient temperature over a 24 day period. ^{1}H NMR spectra indicated formation of (TTP)Mo($PhC{\equiv}CPh$) and $Ph_3P{=}S$. In an analogous manner, treatment of (TTP)Mo=Se with PPh_3 in the presence of $PhC{\equiv}CPh$ resulted in the formation of (TTP)Mo($PhC{\equiv}CPh$) and $Ph_3P{=}Se$. However, in contrast to the relatively slow transfer of the sulfur atom from molybdenum to phosphorus, the transfer of a terminal selenium atom is complete within 1 h after the addition of solvent to the solid starting materials.

Treatment of (TTP)Mo(PPh_3)$_2$ with $PhC{\equiv}CPh$. (TTP)Mo(PPh_3)$_2$ (37 mg, 0.03 mmol) and $PhC{\equiv}CPh$ (11 mg, 0.06 mmol) were stirred in toluene at ambient temperature for 2 h. The solvent was then removed *in vacuo*. Recrystallization of the product from toluene/hexane (1:4) produced a red solid (18 mg, 67%). ^{1}H NMR spectroscopy indicated formation of (TTP)Mo($PhC{\equiv}CPh$). ^{1}H NMR (C_6D_6, 300 MHz, ppm): 8.99 (s, 8H, β-H), 8.04 (m, 8H, -$C_6H_4CH_3$), 7.30 (m, 8H, -$C_6H_4CH_3$), 6.54 (m, 6H, *m*-, *p*-H of $PhC{\equiv}CPh$), 4.90 (d, 4H, *o*-H of $PhC{\equiv}CPh$), 2.39 (s, 12H, -$C_6H_4CH_3$).

Treatment of (TTP)Mo($PhC{\equiv}CPh$) with 4-Picoline. (TTP)MoCl_2 (57 mg, 0.07 mmol), $LiAlH_4$ (13 mg, 0.35 mmol), and $PhC{\equiv}CPh$ (37 mg, 0.21 mmol) were stirred in a toluene/THF mixture (15 mL/0.1 mL) for 1 h at ambient temperature. The reaction mixture was then checked by UV−vis to verify the formation of (TTP)Mo($PhC{\equiv}CPh$). The solvent was then removed *in vacuo*. The residue was redissolved in toluene (15 mL), and the solution was filtered. 4-Picoline (ca. 0.2 mL) was added to the filtrate. The reaction mixture was stirred at ambient temperature for 36 h. Over this time, the solution color gradually changed from the orange/red of the π-alkyne complex to the green/brown color of the bis(picoline) derivative. Filtration of the solution resulted in the isolation of a purple solid (21.0 mg, 33% based on (TTP)MoCl_2). UV−vis (toluene, nm): 380 (Soret), 418, 470, 558, 652. ^{1}H NMR (C_6D_6, 300 MHz, ppm): 47.47 (br, 6H, *p*-CH_3 of picoline); 33.63 (br, 4H, aromatic H of picoline), 5.52 (br, 8H, -$C_6H_4CH_3$), 2.76 (br, 8H, -$C_6H_4CH_3$), −0.15 (br, 8H, β-H), −1.59 (br, 12H, -$C_6H_4CH_3$). One aromatic picoline resonance was not observed. Anal. Calcd (found) for $C_{60}H_{50}N_6Mo$: C, 75.61 (74.86); H, 5.29 (5.26); N, 8.82 (8.54).

X-ray Crystal Structure Determination of (TTP)Mo=S. Crystals of (TTP)Mo=S·1.5C_6H_6 suitable for single-crystal X-ray diffraction were grown by layering a benzene solution of (TTP)Mo=S with hexane. A purple crystal ($0.40 \times 0.25 \times 0.25$ mm) was attached to the tip of a glass fiber and mounted on a Siemens P4/RA diffractometer for data collection at 223 ± 1 K using Cu Kα radiation ($\lambda = 1.541\ 78$ Å). High-angle cell constants were determined from a subset of intense reflections in the range 35.0−50.0° 2θ. Lorentz and polarization corrections were applied. A series of azimuthal reflections was collected. A nonlinear correction based on the decay in the standard reflections and a semiempirical absorption correction based on the azimuthal scans were applied to the data.

The space group $P\bar{1}$ was chosen on the basis of the lack of systematic absences and intensity statistics. This assumption proved to be correct by a successful direct-methods solution and subsequent refinement. All non-hydrogen atoms were placed directly from the *E* map and were refined with anisotropic displacement parameters. Hydrogen atoms were refined as riding atoms with C−H distances of 0.96 Å with individual isotropic displacement parameters except in the case of the tolyl methyl groups and benzenes, which were refined with common isotropic parameters. One of the benzene solvates is located on a general site while the other (half) molecule is centered at the origin.

Data collection and structure solution were carried out at the Iowa State University Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment MicroVAX 3100 computer using the SHELXTL-PLUS programs.[9]

Results

Synthesis of Sulfido and Selenido Mo(IV) Porphyrin Complexes. A terminal sulfido Mo(IV) porphyrin complex, (TTP)Mo=S, may be prepared from either Mo(II) or Mo(IV) precursors. As illustrated in reactions 1 and 2, treatment of a

$$\text{(TTP)Mo(PhC}{\equiv}\text{CPh)} + {}^1/_8\text{S}_8 \rightarrow \text{(TTP)Mo}{=}\text{S} + \text{PhC}{\equiv}\text{CPh} \quad (1)$$

$$\text{(TTP)Mo(PhC}{\equiv}\text{CPh)} + \text{Cp}_2\text{TiS}_5 \rightarrow \text{(TTP)Mo}{=}\text{S} + \text{PhC}{\equiv}\text{CPh} \quad (2)$$

Mo(II) η^2-diphenylacetylene complex with either elemental sulfur or Cp_2TiS_5 in toluene results in the formation of (TTP)Mo=S, **1**, in 40−45% yield. The sulfido complex exhibits a ^{1}H NMR spectrum typical of a diamagnetic porphyrin complex with a pyrrole β-proton singlet at 9.27 ppm and a tolyl CH_3 singlet at 2.41 ppm in benzene-d_6. In the IR spectrum, the Mo=S stretch is observed as a medium-intensity band at 542 cm^{-1}. The electronic absorption spectrum of **1** in toluene contains an intense Soret band at 438 nm with an additional band at 556 nm. Donor ligands such as THF do not appear to bind to the empty coordination site trans to the sulfido ligand; the complex exhibits the same UV−vis spectra in pure toluene and in toluene/THF mixtures.

Treatment of (TTP)MoCl_2 with Li_2S in THF also results in formation of (TTP)Mo=S (eq 3). The yield from this reaction

$$\text{(TTP)MoCl}_2 + \text{Li}_2\text{S} \rightarrow \text{(TTP)Mo}{=}\text{S} + 2\text{LiCl} \quad (3)$$

is low due to contamination with (TTP)Mo=O. The formation of the terminal oxo complex is probably the result of the reaction of either the starting material, (TTP)MoCl_2, or the product, (TTP)Mo=S, with water which we have been unable to eliminate from the sulfide reagent, Li_2S. However, separation of the terminal oxo and sulfido complexes is easily accomplished on a neutral alumina column with toluene as the eluent. The sulfido complex moves quickly down the column whereas the terminal oxo species moves very slowly and requires a more polar solvent (e.g., THF) to be eluted.

Similar to the preparation of (TTP)Mo=S, a terminal selenido molybdenum(IV) porphyrin, (TTP)Mo=Se, **2**, may be prepared from (TTP)MoCl_2 and Na_2Se (eq 4). Again, contamination with

$$\text{(TTP)MoCl}_2 + \text{Na}_2\text{Se} \rightarrow \text{(TTP)Mo}{=}\text{Se} + 2\text{NaCl} \quad (4)$$

(TTP)Mo=O requires purification of the product by column chromatography and results in a relatively low yield. The ^{1}H NMR spectrum of **2** is typical of a diamagnetic porphyrin complex with a pyrrole β-proton singlet at 9.25 ppm. The electronic absorption spectrum in toluene of the terminal selenide complex has an intense Soret band at 432 nm with an additional band at 554 nm.

Attempts to prepare the terminal selenido complex from (TTP)Mo($PhC{\equiv}CPh$) and elemental selenium (eq 5) resulted

$$\text{(TTP)Mo(PhC}{\equiv}\text{CPh)} + \text{Se} \rightarrow \text{(TTP)Mo}{=}\text{Se} + \text{PhC}{\equiv}\text{CPh} \quad (5)$$

in the isolation of a mixture of (TTP)Mo($PhC{\equiv}CPh$) and (TTP)Mo=Se (8:1) despite excess Se, extended reaction times, and heating.

X-ray Structure of (TTP)Mo=S. The molecular structure of **1** was determined by single-crystal X-ray diffraction. The molecular structure and atom-numbering scheme are shown in Figure 1. Crystallographic data for the structure determination are listed in Table 1, atomic positional parameters are given in Table 2, and selected bond distances and angles are listed in Table 3.

Complex **1** crystallizes in the space group $P\bar{1}$ with 2 molecules per unit cell. The Mo−N distances vary from 2.093-

---

(9) SHELXTL-PLUS, Siemens Analytical X-ray, Inc., Madison, WI.

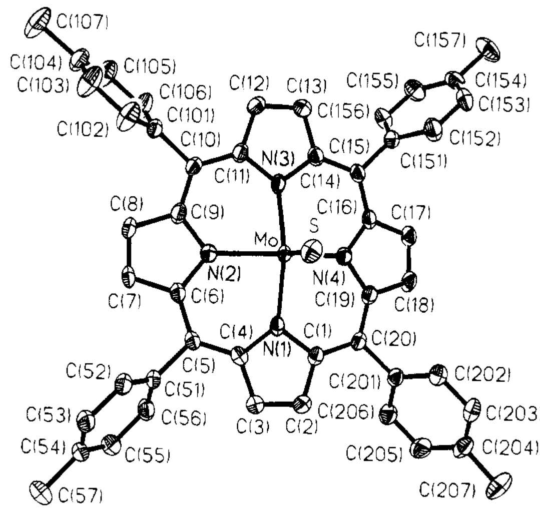

Figure 1. Molecular structure and atom-labeling scheme for (TTP)Mo=S. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Structure Determination Summary

empirical formula	$C_{57}H_{45}MoN_4S$
color; habit	purple; triclinic
crystal size	0.40 × 0.25 × 0.25
crystal system	triclinic
space group	$P\bar{1}$
a	12.735(2) Å
b	13.521(2) Å
c	13.920(2) Å
α	74.76(2)°
β	78.95(2)°
γ	80.85(2)°
V	2253.9(4) $Å^3$
Z	2
fw	914.0
density (calcd)	1.347 Mg/m^3
abs coeff	3.143 mm^{-1}
diffractometer	Siemens P4RA
radiation	Cu Kα (λ = 1.541 78 Å)
T	223 K
monochromator	highly-oriented graphite crystal
2θ range	4.0−115.0°
scan type	$2\theta-\theta$
no. of reflns collected	6376
no. of independent reflns	6047 (R_{int} = 1.13%)
no. of obsd reflns	5532 ($F \geq 6.0\sigma(F)$)
abs correction	semiempirical
min/max transmission	0.6686/0.8504
no. of parameters refined	599
final R indices (obsd data)	R^a = 2.86%, $R_w{}^b$ = 4.14%
R indices (all data)	R^a = 3.10%, $R_w{}^b$ = 4.19%
goodness-of-fit	2.02^c
largest and mean Δ/σ	0.012, 0.001
data-to-parameter ratio	9.2:1
largest difference peak	0.36 e $Å^{-3}$
largest difference hole	−0.49 e $Å^{-3}$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] $\mathrm{GoF} = [\sum w(|F_o| - |F_c|)^2/(N_{\mathrm{observns}} - N_{\mathrm{params}})]^{1/2}$.

(2) to 2.113(2) Å and are typical of those observed for other molybdenum porphyrins.[2,10] The Mo−S distance of 2.100(1) Å is similar to that reported for a number of complexes containing the Mo=S moiety.[11] The molybdenum ion is displaced from the mean porphyrin plane 0.65 Å toward the S ligand. A slight doming of the porphyrin ligand was observed.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ × 10^3) for (TTP)Mo=S

	x	y	z	U(eq)[a]
Mo	4997(1)	3005(1)	4074(1)	22(1)
S	4046(1)	2469(1)	3284(1)	37(1)
N(1)	4027(2)	3087(2)	5460(2)	26(1)
N(2)	5883(2)	1734(2)	4929(2)	28(1)
N(3)	6479(2)	3227(2)	3115(2)	27(1)
N(4)	4654(2)	4613(2)	3678(2)	26(1)
C(1)	3134(2)	3817(2)	5559(2)	26(1)
C(2)	2384(2)	3405(2)	6423(2)	30(1)
C(3)	2832(2)	2464(2)	6878(2)	30(1)
C(4)	3861(2)	2262(2)	6287(2)	28(1)
C(5)	4572(2)	1376(2)	6507(2)	27(1)
C(6)	5530(2)	1148(2)	5886(2)	30(1)
C(7)	6293(2)	258(2)	6131(2)	39(1)
C(8)	7100(2)	294(2)	5335(2)	39(1)
C(9)	6855(2)	1214(2)	4585(2)	31(1)
C(10)	7519(2)	1531(2)	3666(2)	28(1)
C(11)	7337(2)	2471(2)	2976(2)	28(1)
C(12)	7990(2)	2814(2)	2027(2)	33(1)
C(13)	7559(2)	3776(2)	1593(2)	33(1)
C(14)	6634(2)	4050(2)	2273(2)	29(1)
C(15)	6015(2)	5012(2)	2149(2)	27(1)
C(16)	5133(2)	5286(2)	2832(2)	28(1)
C(17)	4559(2)	6299(2)	2758(2)	32(1)
C(18)	3728(2)	6238(2)	3528(2)	32(1)
C(19)	3768(2)	5188(2)	4097(2)	27(1)
C(20)	3005(2)	4801(2)	4925(2)	26(1)
C(51)	4303(2)	610(2)	7501(2)	28(1)
C(52)	4156(2)	−392(2)	7525(2)	32(1)
C(53)	3908(2)	−1091(2)	8447(2)	37(1)
C(54)	3797(2)	−803(2)	9346(2)	40(1)
C(55)	3949(3)	201(2)	9310(2)	41(1)
C(56)	4199(2)	895(2)	8394(2)	34(1)
C(57)	3509(3)	−1550(3)	10350(3)	65(2)
C(101)	8522(2)	820(2)	3450(2)	30(1)
C(102)	8471(3)	−132(3)	3294(3)	49(1)
C(103)	9405(3)	−803(3)	3141(3)	55(2)
C(104)	10404(3)	−533(2)	3133(3)	41(1)
C(105)	10448(3)	411(3)	3297(3)	51(1)
C(106)	9518(3)	1080(2)	3455(3)	48(1)
C(107)	11417(3)	−1255(3)	2955(4)	70(2)
C(151)	6341(2)	5836(2)	1224(2)	30(1)
C(152)	5724(3)	6141(3)	457(2)	42(1)
C(153)	5998(3)	6929(3)	−384(2)	44(1)
C(154)	6889(3)	7426(2)	−471(2)	38(1)
C(155)	7506(3)	7110(2)	289(2)	41(1)
C(156)	7242(3)	6318(2)	1125(2)	36(1)
C(157)	7182(3)	8288(3)	−1389(3)	59(2)
C(201)	1972(2)	5467(2)	5121(2)	27(1)
C(202)	1301(2)	5771(2)	4397(2)	35(1)
C(203)	303(2)	6335(2)	4583(3)	39(1)
C(204)	−51(2)	6597(2)	5494(3)	39(1)
C(205)	621(3)	6289(2)	6218(3)	41(1)
C(206)	1625(2)	5740(2)	6033(2)	34(1)
C(207)	−1157(3)	7179(3)	5703(3)	64(2)
C(31)	434(8)	5284(8)	1175(6)	141(5)
C(32)	1315(11)	4630(5)	1413(7)	167(5)
C(33)	2148(6)	5050(8)	1624(5)	146(4)
C(34)	2040(6)	6054(7)	1571(4)	116(4)
C(35)	1182(6)	6631(5)	1317(5)	114(3)
C(36)	371(6)	6264(7)	1137(6)	135(4)
C(41)	9026(3)	−340(4)	101(4)	80(2)
C(42)	9123(4)	398(4)	560(4)	84(2)
C(43)	10106(4)	735(4)	463(4)	89(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The structure of (TTP)Mo=S is very similar to the previously reported structure of (TTP)Mo=O.[12]

Inter-Metal Atom Transfer Reactions. Treatment of (TTP)Mo(PhC≡CPh) with (TTP)Sn=S in benzene-d_6 results

---

(10) Kim, J. C.; Rees, W. S., Jr.; Goedken, V. L. *Inorg. Chem.* **1994**, *33*, 3191.

(11) (a) Huneke, J. T.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3698. (b) Young, C. G.; Roberts, S. A.; Ortega, R. B.; Enemark, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2938.

(12) Diebold, T.; Chevrier, B.; Weiss, R. *Inorg. Chem.* **1979**, *18*, 1193.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**

Mo–S	2.100(1)	Mo–N(3)	2.106(2)
Mo–N(1)	2.101(2)	Mo–N(4)	2.093(2)
Mo–N(2)	2.113(2)		
S–Mo–N(1)	105.4(1)	N(2)–Mo–N(3)	84.8(1)
S–Mo–N(2)	109.4(1)	N(1)–Mo–N(2)	85.3(1)
S–Mo–N(3)	106.2(1)	N(1)–Mo–N(4)	85.6(1)
S–Mo–N(4)	104.6(1)	N(2)–Mo–N(4)	146.0(1)
N(1)–Mo–N(3)	148.5(1)	N(3)–Mo–N(4)	86.1(1)

in spectral changes consistent with the complete transfer of a terminally bound sulfur ligand between two metal complexes as shown in eq 6. For example, new pyrrole β-proton resonances

$$\text{(TTP)Mo(PhC}\equiv\text{CPh)} + \text{(TTP)Sn}{=}\text{S} \rightarrow \text{(TTP)Mo}{=}\text{S} + \text{(TTP)Sn}^{\text{II}} + \text{PhC}\equiv\text{CPh} \quad (6)$$

$$\text{(TTP)Mo}{=}\text{S} + \text{(TTP)Sn} + \text{PhC}\equiv\text{CPh} \rightarrow \text{NR} \quad (7)$$

$$\text{(TTP)Mo(PhC}\equiv\text{CPh)} + \text{(TTP)Sn}{=}\text{Se} \rightleftharpoons \text{(TTP)Mo}{=}\text{Se} + \text{(TTP)Sn}^{\text{II}} + \text{PhC}\equiv\text{CPh} \quad (8)$$

appear, signifying the formation of (TTP)Mo=S (9.27 ppm) and (TTP)Sn$^{\text{II}}$ (9.19 ppm). The pyrrole β-proton signals for (TTP)Mo(PhC≡CPh) (8.99 ppm) and (TTP)Sn=S (9.14 ppm) quantitatively disappear, indicating that eq 6 is an irreversible process. Consequently, treatment of (TTP)Mo=S with (TTP)Sn$^{\text{II}}$ in the presence of PhC≡CPh (eq 7) results in no reaction. However, reversible selenium atom transfer occurs on treatment of (TTP)Mo(PhC≡CPh) with (TTP)Sn=Se in benzene-d_6 as shown in eq 8. For example, very small new pyrrole β-proton resonances appear for (TTP)Mo=Se (9.25 ppm) and (TTP)Sn$^{\text{II}}$ (9.19 ppm) while signals associated with the pyrrole β-protons of (TTP)Mo(PhC≡CPh) (8.99 ppm) and (TTP)Sn=Se (9.16 ppm) diminish only slightly, indicating the equilibrium distribution lies largely toward the reactants. This equilibrium can be achieved by starting with (TTP)Mo=Se, (TTP)Sn$^{\text{II}}$, and PhC≡CPh. The equilibrium constant at 25 °C for eq 8 ($K = (8 \pm 2) \times 10^{-3}$) was determined by integration of the pyrrole β-proton resonances for each of the porphyrin species and the *o*-proton resonances of PhC≡CPh.

Atom Transfer Reactions Involving PPh$_3$. Treatment of (TTP)Mo=S or (TTP)Mo=Se with an excess of PPh$_3$ (eq 9) in

$$\text{(TTP)Mo}{=}\text{X} + 3\text{PPh}_3 \rightarrow \text{(TTP)Mo(PPh}_3)_2 + \text{Ph}_3\text{P}{=}\text{X} \qquad \text{X} = \text{S, Se} \quad (9)$$

toluene results in the formation of Ph$_3$P=S or Ph$_3$P=Se and a new porphyrin complex, (TTP)Mo(PPh$_3$)$_2$. In the case of sulfur atom transfer, this reduction occurs over the course of hours with mild heating (50–60 °C) of the toluene solution. For selenium atom transfer from molybdenum to PPh$_3$, the transfer occurs in a matter of minutes at ambient temperature. Once formed, the bis(phosphine) complex precipitates from the toluene solution and is easily isolated by filtration. The ^{1}H NMR spectrum of (TTP)Mo(PPh$_3$)$_2$ indicates that the Mo(II) porphyrin complex is paramagnetic, with resonances distributed over a 40-ppm range from −11 to +31 ppm. Despite the paramagnetism of the bis(phosphine) species, sharp NMR signals are still observed and integration of the resonances indicates that two axial ligands are present. Furthermore, the appearance of a single resonance for each set of *o*- and *m*-protons of the tolyl substituents is consistent with a *trans*-geometry (D_{4h} symmetry) of the complex. Signals associated with the axially coordinated phosphine ligands are shifted dramatically downfield to 30.67 (12H), 12.08 (6H, *p*-H), and 11.50 ppm (12H). The porphyrin resonances are instead shifted strongly upfield, with the pyrrole β-proton resonance occurring at −11.60 ppm. A signal for the bound PPh$_3$ ligands was not observed in the ^{31}P NMR spectrum over a window of ±1000 ppm. The electronic absorption spectrum of (TTP)Mo(PPh$_3$)$_2$ is dramatically different from those of both the sulfido and selenido complexes with the Soret band blue-shifted more than 30 nm to 390 nm.

Ligand Displacement Reactions. Reduction of either the terminal sulfido or selenido complex by PPh$_3$ in the presence of diphenylacetylene, results in the formation of exclusively the Mo(II) π-alkyne complex (eq 10). In an independent experiment,

$$\text{(TTP)Mo}{=}\text{X} + \text{PPh}_3 + \text{PhC}\equiv\text{CPh} \rightarrow \text{(TTP)Mo(PhC}\equiv\text{CPh)} + \text{Ph}_3\text{P}{=}\text{X} \qquad \text{X} = \text{S, Se} \quad (10)$$

$$\text{(TTP)Mo(PPh}_3)_2 + \text{PhC}\equiv\text{CPh} \rightarrow \text{(TTP)Mo(PhC}\equiv\text{CPh)} + 2\text{PPh}_3 \quad (11)$$

$$\text{(TTP)Mo(PhC}\equiv\text{CPh)} + 2\ \text{4-picoline} \rightarrow \text{(TTP)Mo(4-picoline)}_2 + \text{PhC}\equiv\text{CPh} \quad (12)$$

treatment of (TTP)Mo(PPh$_3$)$_2$ with excess PhC≡CPh (eq 11) resulted in the rapid displacement of the phosphine ligands to produce (TTP)Mo(PhC≡CPh) and free PPh$_3$. For example, addition of diphenylacetylene to an NMR tube containing (TTP)Mo(PPh$_3$)$_2$ in benzene-d_6 results in a color change within seconds from the green of the bis(phosphine) species to the orange/red of the π-alkyne complex. Proton NMR spectroscopy readily confirms the formation of (TTP)Mo(PhC≡CPh) and the appearance of free phosphine. Displacement of the alkyne ligand from the molybdenum center results when (TTP)Mo(PhC≡CPh) is treated with 4-picoline (eq 12). In the ^{1}H NMR spectrum, signals associated with the alkyne complex disappear while signals for free diphenylacetylene and a new molybdenum porphyrin complex appear. This displacement reaction occurs over the course of hours at ambient temperature. The new substitution product, a bis(picoline) complex, (TTP)Mo(NC$_6$H$_4$CH$_3$)$_2$, is paramagnetic in solution as indicated by the broad chemical shift range in the ^{1}H NMR spectrum. Signals from the protons of the bound picoline ligands are shifted significantly downfield to 47.5 and 33.8 ppm in benzene-d_6. One set of picoline protons was not observed. Similar to those of the bis(phosphine) complex, resonances associated with the porphyrin ring are shifted significantly upfield, with the β-H signal appearing at −0.15 ppm.

Discussion

The first terminal sulfido and selenido molybdenum porphyrin complexes have been synthesized and characterized. The terminal chalcogenides may be prepared by a number of synthetic routes involving either Mo(II) or Mo(IV) precursors. The terminal sulfido and selenido complexes are diamagnetic, similar to the terminal oxo complex.[12] In the ^{1}H NMR spectrum, the β-H resonance for (TTP)Mo=S in benzene-d_6 is found at 9.27 ppm, shifted only slightly downfield of its position in (TTP)Mo=O (9.26 ppm). For the selenido derivative, the β-H resonance is shifter slightly upfield, appearing at 9.25 ppm. The remaining resonances in the ^{1}H NMR spectra of all three chalcogenide complexes are at virtually the same chemical shifts in benzene-d_6.

Although these molybdenum porphyrin chalcogenide complexes have very similar ^1H NMR properties, noticeable differences are exhibited for the Mo=X stretching frequencies, as expected. In the oxo complex, the Mo=O bond appears near 980 cm^{-1}. However, for the sulfido analog, a new band of medium intensity is present at 542 cm^{-1}, which has been assigned as the Mo=S stretch. This assignment compares well with those for other complexes containing the Mo=S moiety. For example, in $\{HB(Me_2pz)_3\}MoS(S_2CNEt_2)$ the Mo=S stretch is found at 512 cm^{-1} and in $[MoS(S_4)_2]^{2-}$ the same stretch is found at 525 cm^{-1}.[11,13]

Electronic absorption spectra of the terminal chalcogenides differ only slightly, with the largest difference exhibited in the position of the Soret bands in the oxo and selenido derivatives versus the sulfido complex. For the terminal oxo and selenido species, the Soret band appears at 432 nm in toluene, while for (TTP)Mo=S, the Soret band is shifted to 438 nm. Addition of THF to a toluene solution of (TTP)Mo=X (X = S, Se) produces no change in position or intensity of the absorption maxima, indicating that THF does not appear to bind to the position *trans* to the chalcogenide.

(TTP)Mo=S is the first metalloporphyrin complex to be structurally characterized that contains a heavier group 16 element as a terminal ligand. The Mo−S bond length is similar to those in other structurally characterized terminal sulfido molybdenum complexes.[11]

The molybdenum sulfido porphyrin complex may also be generated by an inter-metal atom transfer reaction involving transfer of a terminally bound sulfur ligand from a tin porphyrin, (TTP)Sn=S, to a low-valent molybdenum porphyrin, (TTP)-Mo(PhC≡CPh). In contrast to the complete transfer observed for sulfur, the analogous reaction between (TTP)Sn=Se and (TTP)Mo(PhC≡CPh) produces an equilibrium which lies largely to the side of the reactants.

In contrast to the Mo=O fragment, which is relatively inert, the heavier chalcogenide porphyrin complexes readily undergo reduction with PPh_3 to produce a paramagnetic bis(phosphine) complex, $(TTP)Mo(PPh_3)_2$, and the corresponding phosphine chalcogenide. As shown in eq 13, (TTP)Mo=O cannot be

$$\text{(TTP)Mo=O} + \text{PPh}_3 \rightarrow \text{no reaction} \qquad (13)$$

reduced by PPh_3, presumably due to the very strong Mo=O bond. The rate of atom transfer from molybdenum to phosphorus qualitatively increases on descending the chalcogenide group. For example, treatment of (TTP)Mo=S with an excess of PPh_3 in C_6D_6 in an NMR tube at ambient temperature requires hours for the reduction to go to completion, whereas the same experiment utilizing (TTP)Mo=Se requires only minutes to reach completion. A similar trend has been observed in reactions involving inter-metal sulfur and selenium atom transfer reactions between tin porphyrins.[8] In this case, the relative rate of selenium versus sulfur atom transfer at 30 °C was 218:1.

The molybdenum bis(phosphine) complex is related in general coordination geometry to $(OEP)Re(PMe_3)_2$ and $(OEP)W(PEt_3)_2$, which were prepared as precursors to the corresponding metalloporphyrin dimers.[14] The tungsten(II) complex has a magnetic moment of $\mu_{eff} = 3.0\ \mu_B$. As expected, the isoelectronic $(TTP)Mo(PPh_3)_2$ is also paramagnetic, as evidenced by its broad chemical shift range in the ^1H NMR spectrum. Despite its paramagnetic nature, sharp signals were observed in its ^1H NMR spectrum.

The phosphine ligands of $(TTP)Mo(PPh_3)_2$ are readily displaced upon addition of diphenylacetylene to give (TTP)-Mo(PhC≡CPh) and free PPh_3. The alkyne may be displaced by addition of 4-picoline to give the bis(picoline) derivative $(TTP)Mo(4\text{-picoline})_2$. The analogous *trans*-(TTP)Mo(pyridine)$_2$ has been structurally and magnetically characterized ($\mu_{eff} = 2.80\ \mu_B$, $S = 1$).[5c] From substitution studies, the order of ligand preference for Mo(II) porphyrins is PPh_3 < PhC≡CPh < 4-picoline. The lability of the phosphine ligands in (TTP)-Mo$(PPh_3)_2$ makes this an attractive complex for studying the reaction chemistry of the Mo(II) center.

Conclusions

Multiple bonding between the transition metals and the heavier main group elements has been the focus of a number of recent studies.[15] Interest in these derivatives stems from the limited number of known examples containing multiple bonds to N, P, S, Se, and Te.[16] As reported here, (TTP)Mo=S and (TTP)Mo=Se exhibit a rich chemistry unique to the metal−ligand multiple bonds of the heavier members of group 16. In particular, reduction of the terminal chalcogenides represents a new synthetic route for the preparation of low-valent molybdenum porphyrins. Further studies of the synthesis and reactivity of low-valent early transition metal porphyrins are underway.

Acknowledgment. Support of this work was provided by a Department of Education GAANN Fellowship to L.M.B., the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society. We thank Mr. Chris Hamaker for ^1H NMR assistance.

Supporting Information Available: Tables of bond distances, angles, and anisotropic displacement coefficients for (TTP)Mo=S (7 pages). Ordering information is given on any current masthead page.

IC950063W

---

(13) Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321.

(14) (a) Collman, J. P.; Garner, J. M.; Kim, K.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 4513. (b) Collman, J. P.; Garner, J. M.; Woo, L. K. *J. Am. Chem. Soc.* **1989**, *111*, 8141.

(15) (a) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448. (b) Siemeling, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 67. (c) Nelson, J. E.; Parkin, G.; Bercaw, J. E. *Organometallics* **1992**, *11*, 2181. (d) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426. (e) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761. (f) Housmekerides, C. E.; Ramage, D. L.; Kretz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 4453. (g) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 5904. (h) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 9421. (i) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240. (j) Rabinovich, D.; Parkin, G. *Inorg. Chem.* **1994**, *33*, 2313. (k) Howard, W. A.; Parkin, G. *J. Am. Chem. Soc.* **1994**, *116*, 606.

(16) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186.