and 2.26 (4) Å, respectively. The metal coordination is octahedral with a slight tetragonal distortion. Various dimeric structures of stoichiometry $\mathrm{Co_2(acac)_4L}$ and $\mathrm{Co_2(acac)_4L_2}$ have also been characterized.[12]

Dark red crystals of Co(2,4-pentanedionate)$_2$(*N,N,N′,N′*-tetraethyl-1,2-diaminoethane) (**8**) were obtained by recrystallization from hexane at −25 °C. Data were obtained at room temperature, and an ORTEP plot of the resulting structure is shown in Figure 1. Selected structural parameters are listed in Tables IV and V.

The compound is a slightly distorted octahedron. There is some asymmetry in the coordination of the amine chelate with Co–N(1) = 2.32 (1) Å and Co–N(2) = 2.20 (1) Å. The former value is quite long, perhaps indicative of steric congestion. As previously determined spectroscopically,[12b] the Co–O bond lengths trans to the nitrogen atoms are slightly longer than those trans to oxygen atoms: 2.06 (1) and 2.08 (1) Å vs 2.03 (1) and 2.04 (1) Å. The latter two values are typical of the Co–O bond lengths in trans complexes.[11] Deviations from planarity for all atoms including the cobalt are less than 0.05 Å for the three planes of the octahedron containing ligands. The largest deviation from a 90° angle is in the amine chelate (∠N(1)–Co–N(2) = 82.2 (4)°).

In conclusion, we have prepared a wide variety of new adducts of $\mathrm{Co(acac)_2}$. Preliminary evidence suggests that the thermal dissociation of the ligands varies significantly throughout the series. We hope to utilize such control for catalysis such that the base is released from the metal center upon thermal activation. Our results in this area will appear subsequently.

Acknowledgment. The assistance of Steve Dorn and Nancy Marotta in analytical services is gratefully acknowledged.

Registry No. **1**, 116128-88-2; **2**, 116128-89-3; **3**, 116128-90-6; **4**, 116128-91-7; **5**, 73946-62-0; **6**, 116128-92-8; **7**, 116128-93-9; **8**, 116128-94-0; **9**, 116128-95-1; **10**, 116128-96-2; $\mathrm{Co(acac)_2}$, 14024-48-7.

Supplementary Material Available: Listings of complete crystallographic details on collection of data (Table SI), anisotropic temperature factors (Table SII), hydrogen coordinates (Table SIII), and elemental analyses of the new compounds (Table SIV) (5 pages). Ordering information is given on any current masthead page.

---

(12) (a) Cotton, F. A.; Elder, R. C. *Inorg. Chem.* **1966**, *5*, 423. (b) Hursthouse, M. B.; Laffey, M. A.; Moore, P. T.; New, D. B.; Raithby, P. R.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1982**, 307. (c) Bertrand, J. A.; Kalyanaran, A. R. *Inorg. Chim. Acta* **1971**, *5*, 167.

Notes

Contribution from the Department of Chemistry,
Indian Institute of Technology, Kanpur-208 016, India

Synthesis and Characterization of $[\mathrm{Mo_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$ and Rational Synthesis of $[\mathrm{M_2(L)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$ (M = Mo, W; L = O, S) Anions

Jayanthi Chandrasekaran, Mohammad A. Ansari,
and Sabyasachi Sarkar*

Received August 6, 1987

Recently the syntheses of $[\mathrm{Mo_2(O)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$ and $[\mathrm{W_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$ have been reported from the oxidation of $[\mathrm{MoO(S_4)_2}]^{2-}$ and from the acidification of $[\mathrm{WS_4}]^{2-}$ in the presence of manganous chloride, respectively.[1,2] The molybdenum complex has also been synthesized by the nitrosylation of heptamolybdate with hydroxylamine and denitrosylation of [MNO] moiety under basic conditions.[3] The nitrosylation reaction is rather curious because several poly(thiomolybdates) are synthesized by this method where invariably the oxidation state of Mo is quite low.[4] Protonation of $[\mathrm{WS_4}]^{2-}$ has long been known to yield several poly(thiotungstate) anions with the involvement of reduction of some tungsten centers.[5-7] Again, it is curious to note that manganous chloride is not involved in the reduction of tungsten center but brings about the oxidation of coordinated sulfido group to disulfido group.[2] When $[\mathrm{Mn(NCS)_4}]^{2-}$ is used instead of $\mathrm{MnCl_2}$, a mixture of $[\mathrm{W_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$ and $[\mathrm{W_2(O)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$ are isolated.[8] We decided to check the protonation reaction of the thiometalates (Mo, W) in the presence of elemental sulfur, which can serve as an oxidizing agent and contribute to the formation of a disulfido group. With this methodology the synthesis of $[\mathrm{Mo_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$ and of the reported compounds, $[\mathrm{Mo_2(O)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$, $[\mathrm{W_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$, and $[\mathrm{W_2(O)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4}]^{2-}$, have been achieved for which the details are presented herein.

Experimental Section

All manipulations were carried out in air unless mentioned otherwise. $\mathrm{(PPh_4)_2MoS_4}$, $\mathrm{(AsPh_4)_2MoS_4}$, $\mathrm{(AsPh_4)_2MoOS_3}$, $\mathrm{(PPh_4)_2WOS_3}$, $\mathrm{(AsPh_4)_2WOS_3}$, and $\mathrm{(AsPh_4)_2WS_4}$ were all made by cation exchange from a solution of the corresponding ammonium salts. $\mathrm{(NH_4)_2MoO_2S_2}$ and $\mathrm{(NH_4)_2MoS_4}$ were made by literature method.[9] $\mathrm{(Et_2NH_2)_2MoS_4}$ was prepared by our method described below. Dimethylamine and diethylamine (AR grade) were used as purchased. Acetonitrile and DMF were distilled and stored over molecular sieves (4 Å) before use.

$\mathbf{[(C_2H_5)_2NH_2]_2MoS_4}$.[10] $\mathrm{H_2MoO_4}$ (1.62 g, 0.1 mmol) was dissolved in a mixture of $\mathrm{H_2O}$ (10 mL) and $\mathrm{Et_2NH}$ (10 mL). $\mathrm{H_2S}$ gas was passed into the solution until the red crystals of $\mathrm{(Et_2NH_2)_2MoS_4}$ separated out (~30 min). The crystals were washed with cold ethanol and ether and dried under vacuum. Yield: 85%. Anal. Calcd for $\mathrm{C_8H_{24}N_2MoS_4}$: C, 25.81; H, 6.45; N, 7.53. Found: C, 25.60; H, 6.38; N, 7.45. IR: 470 ($\nu_{\mathrm{Mo{=}S}}$) cm^{-1}. UV-vis: 467, 316, 241 nm.

$\mathbf{(AsPh_4)_2Mo_2S_{11}}$.[11] To a solution of 370 mg (0.37 mmol) of $\mathrm{(Ph_4As)_2MoS_4}$ in 10 mL of $\mathrm{CH_3CN}$ was added 20 mg (0.62 mmol) of sulfur. After the solution was stirred for 2 min, 0.04 mL of glacial acetic acid in 5 mL of methanol was added into the mixture whereby the orange-red color of the solution changed to dark brown. The solution was stirred for 5 min more, filtered, and cooled in the refrigerator to produce brown crystals. The crystals were filtered, washed with ether, and dried under vacuum. Yield: 25%. Anal. Calcd for $\mathrm{C_{50}H_{43}As_2Mo_2S_{11}N}$: C, 44.41; H, 3.18; S, 26.05; N, 1.04. Found: C, 44.10; H, 3.00; S, 26.00; N, 1.01. IR (KBr pellet): 530 ($\nu_{\mathrm{S-S}}$), 520 ($\nu_{\mathrm{Mo{=}S}}$) cm^{-1}. UV-vis: 590, 485, 400, 360 nm.

$\mathbf{(AsPh_4)_2W_2O_2S_9}$.[11] A 230-mg (0.24-mmol) sample of $\mathrm{[Ph_4As]_2WOS_3}$ was dissolved in 7 mL of $\mathrm{CH_3CN}$. Into this clear solution was added 10 mg (0.31 mmol) of sulfur. A green tinge developed, which soon became dark brown. Then 0.1 mL of glacial acetic acid in 5 mL of methanol was added into the mixture whereby the solution became orange-red. After an additional stirring of 1 h, the solution was filtered and cooled (0 °C) to produce orange-red crystals, which were washed with ether and dried in vacuo. Yield: 36%. Anal. Calcd for $\mathrm{C_{50}H_{43}As_2W_2O_2S_9N}$: C, 40.13;

---

* To whom correspondence should be addressed.

(1) Coucouvanis, D.; Hadjikyriacou, A. *Inorg. Chem.* **1987**, *26*, 1.
(2) Manoli, J. M.; Potvin, C.; Sêcheresse, F. *Inorg. Chem.* **1987**, *26*, 340.
(3) Xintao, W.; Shaofeng, L.; Lianyong, Z.; Qiangjin, W.; Jiaxi, L. *Inorg. Chim. Acta* **1987**, *133*, 43.
(4) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89.
(5) Sêcheresse, F.; Lefebvre, J; Daran, J. C.; Jeannin, Y. *Inorg. Chem.* **1982**, *21*, 1311.
(6) Koniger-Ahlborn, E.; Müller, A. *Angew. Chem.* **1975**, *87*, 598.
(7) Bhaduri, S.; Ibers, J. A. *Inorg. Chem.* **1986**, *25*, 3.
(8) Manoli, J. M; Potvin, C. *Inorg. Chim. Acta* **1987**, *133*, 27.
(9) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205.
(10) $\mathrm{(Me_2NH_2)_2MoS_4}$ was synthesized similarly by using dimethylamine in the place of diethylamine.
(11) The corresponding $[\mathrm{Ph_4P}]^+$ salts of these complexes can be isolated by using similar methods.

0020-1669/88/1327-3663$01.50/0

Table I. Electronic Spectral[a] and Electrochemical[b] Data

compd	λ_{max}, nm	E_{p_c}, V	E_{p_a}, V	DPP, V
$(Me_2NH_2)_2Mo_2O_2S_9$	527, 432, 392	–1.445	+0.735	–1.425
$(PPh_4)_2Mo_2O_2S_9$	522, 432, 392	–1.445, 1.885	+0.745	–1.393, –1.745, +0.625
$(Et_2NH_2)_2Mo_2S_{11}$	590, 485, 400, 360	–0.565	+0.595	–0.505
$(AsPh_4)_2Mo_2S_{11}$	590, 485, 400, 360	–0.695, –1.705	+0.645	–0.685, –1.585, +0.585
$(PPh_4)_2W_2O_2S_9$	440, 370, 337	–1.665, –1.800	+0.745	–1.605, –1.725, +0.645
$(AsPh_4)_2W_2S_{11}$	550, 470, 370, 340	–0.775, –1.595	+0.685	–0.865, –1.545, +0.625
$(Me_2NH_2)_2MoOS_3$		–1.400		
$(Me_2NH_2)_2MoS_4$		–1.300	+0.165	
$Cs_2(MoOS_3)$			+0.254	
$Cs_2(MoS_4)$			+0.225	

[a] In CH_3CN. [b] Scan rate: 100 mV s^{-1} (CV), 20 mV s^{-1} (DPP). In 0.10 M $[(C_2H_5)_4N]ClO_4$. All values vs SCE.

H, 2.88; S, 19.26; N, 0.94. Found: C, 39.91; H, 2.68; S, 20.59; N, 1.03. IR (KBr pellet): 945 ($\nu_{W=O}$), 527 (ν_{S-S}) cm^{-1}. UV–vis: 450, 370, 337 nm.

$[(C_2H_5)_2NH_2]_2Mo_2S_{11}$. Method A. A 372-mg (1-mmol) sample of $(Et_2NH_2)_2MoS_4$ was dissolved in 5 mL of DMF, and 64 mg (2 mmol) of sulfur was added. The solution was stirred overnight under nitrogen atmosphere and filtered. 2-Propanol (150 mL) and petroleum ether (bp 40–60 °C) (60 mL) were added into the clear filtrate, and the solution was cooled at 5 °C for 20 h under inert atmosphere. The brown crystals that separated out were filtered, washed with 2-propanol and petroleum ether, and dried under vacuum. Yield: 25%.

Method B. A 260-mg (1-mmol) sample of $(NH_4)_2MoS_4$ was dissolved in 5 mL of DMF, and 3 mL of diethylamine was added into it. Then 64 mg (2 mmol) of sulfur was added into the clear solution, and the reaction mixture was purged with nitrogen and stirred overnight. It was then filtered, and 2-propanol (150 mL) and petroleum ether (bp 40–60 °C) (60 mL) were added and the mixture kept at 5 °C under nitrogen atmosphere overnight. The brown crystals thus formed were filtered, washed with 2-propanol and petroleum ether, and dried under vacuum. Yield: 25%. Anal. Calcd for $C_8H_{24}N_2Mo_2S_{11}$: C, 13.87; H, 3.47; S, 50.86; N, 4.05. Found: C, 13.79; N, 3.41; S, 50.75; N, 3.99. IR (KBr pellet): 527 (ν_{S-S}), 522 ($\nu_{Mo=S}$) cm^{-1}. UV–vis: 590, 485, 400, 360 nm.

$(AsPh_4)_2Mo_2O_2S_9$.[11] A 210-mg (0.215-mmol) sample of $(Ph_4As)_2MoOS_3$ was dissolved in 5 mL of CH_3CN, and 10 mg (0.31 mmol) of sulfur was added into it with stirring for 2 min. Then 0.04 mL of glacial acetic acid in 3 mL of methanol was added, and the reaction mixture was stirred for 5 min more. The resulting solution was filtered and kept at 5 °C. The brown crystals thus formed were filtered and washed with ether and dried in vacuo. Yield: 45%. Anal. Calcd for $C_{50}H_{43}As_2Mo_2O_2S_9N$: C, 45.98; H, 3.26; S, 21.83; N, 1.06. Found: C, 45.30; H, 3.18; S, 22.09; N, 0.99. IR (KBr pellet): 920 ($\nu_{Mo=O}$), 535 (ν_{S-S}) cm^{-1}. UV–vis: 522, 432, 392 nm.

$[(CH_3)_2NH_2]_2Mo_2O_2S_9$. A 230-mg (1-mmol) sample of $(NH_4)_2MoO_2S_2$ was dissolved in 5 mL DMF, and 3 mL of dimethylamine was added into it. Then 96 mg (3 mmol) of sulfur was added into the solution with stirring under nitrogen atmosphere. The stirring was continued overnight, and then the solution was filtered, 2-propanol (150 mL) and petroleum ether (bp 40–60 °C) (60 mL) were added, and the solution was kept at 0 °C to yield brown crystals. The crystals were washed with 2-propanol and petroleum ether. Yield: 20%. Anal. Calcd for $C_4H_{16}N_2Mo_2O_2S_9$: C, 7.95;; H, 2.65; S, 47.68; N, 4.64. Found: C, 7.87; H, 2.59;; S, 47.62; N, 4.61. IR (KBr pellet): 910 ($\nu_{Mo=O}$), 535 (ν_{S-S}) cm^{-1}. UV–vis: 527, 432, 392 nm.

$(AsPh_4)_2W_2S_{11}$.[11] To a solution of 260 mg (0.24 mmol) of $(AsPh_4)_2WS_4$ in 5 mL of CH_3CN was added 11 mg (0.34 mmol) of sulfur, and the mixture was stirred for 5 min. Then 0.1 mL of glacial acetic acid in 5 mL of methanol was added to the above solution and stirred for 1 h, after which the solution was filtered and refrigerated overnight. The resulting brown crystals were filtered, washed with ether, and dried under vacuum. Yield: 25%. Anal. Calcd for $C_{50}H_{43}As_2W_2S_{11}N$: C, 39.29; H, 2.81; S, 23.05; N, 0.92. Found: C, 39.10; H, 2.59; S, 23.41; N, 0.99 IR (KBr pellet): 525 (ν_{S-S}), 495 ($\nu_{W=S}$) cm^{-1}. UV–vis: 550, 470, 370, 340 nm.

Physical Measurements. Electronic spectra were recorded at 25 °C on a Shimadzu (UV 190) double-beam spectrophotometer. Infrared spectra as KBr pellets were recorded on a Perkin-Elmer Model 580 spectrophotometer. X-ray diffractograms were obtained on ISOBEBY-FLEX X-200 diffractometer using a Cu K_α radiation source. C, H, and N were analyzed at the microanalytical laboratory, IIT Kanpur, and sulfur was estimated gravimetrically as $BaSO_4$. Electrochemical studies were performed on a BAS 100 electrochemical analyzer unit, Houston Instruments HIPLOT DMA 40 Series digital plotter and BAS printer. All of the experiments were performed under nitrogen atmosphere in a three-electrode configuration using a glassy-carbon working electrode in the positive and negative potential region and referenced to a saturated calomel electrode (SCE) at 25 °C. $[(C_2H_5)_4N]ClO_4$ was used as the supporting electrolyte.

Results and Discussion

It is well documented that $[MoS_4]^{2-}$ reacts with S_8 to give Mo(IV) with oxidation of S^{2-} (coordinated) to S_2^{2-}.[12] For $[WS_4]^{2-}$ this reaction demands the use of protonated ammonium salts and elevated temperature to produce W(V) and coordinated S_4^{2-}.[13] The redox condensation of $[WS_4]^{2-}$ in the presence of H^+ is well-known, and several condensed species are isolated.[5–7] The reduction of the central atom is invariably an outcome of all these reactions at the expense of oxidation of other coordinated ligands. In the present study, not only has the central metal not been reduced but the presence of a proton has been found to be necessary. The general tendency regarding the sluggish nature of the formation of tungsten compounds over molybdenum analogues is observed here also in this series of reactions. The protonated cationic salt of thiotungstate does not respond to any such reaction under ambient conditions. However, external acidification leads to the desired transformation.

Electronic absorption spectra for all the complexes prepared by this synthetic route are presented in Table I. For $[Mo_2S_{11}]^{2-}$, the lowest energy band at 590 nm is assigned to a charge transfer transition from the S_2^{2-} to $Mo-S_t$ antibonding orbital. The band at 485 nm then corresponds to a charge-transfer transition from bridging sulfur to $Mo-S_t$ antibonding orbital.[14] Thus for $[Mo_2S_{11}]^{2-}$ the higher energy band at 400 nm may be assigned to $\pi_v^* \rightarrow d(Mo)$.[15] The corresponding tungsten systems, $[W_2S_{11}]^{2-}$ and $[W_2O_2S_9]^{2-}$, show electronic spectra similar in nature; thus the origin of these bands may be due to similar transitions, and as expected, all these absorption bands are shifted hypsochromically (Table I) compared to those for corresponding molybdenum analogue.

The IR spectrum of $[Mo_2S_{11}]^{2-}$ as the $[AsPh_4]^+$ salt shows a strong absorption at 530 cm^{-1} for ν_{S-S}).[15a] $[AsPh_4]_2W_2S_{11}$ shows this vibration at 525 cm^{-1}. The $\nu_{Mo=S}$ and $\nu_{W=S}$ are found at 520 and 495 cm^{-1}, respectively. $[Mo_2O_2S_9]^{2-}$ and $[W_2O_2S_9]^{2-}$ as $[AsPh_4]^+$ salt show $\nu_{Mo=O}$, ν_{S-S} at 920, 535[1] and $\nu_{W=O}$), ν_{S-S} at 945, 527 cm^{-1} respectively. The anions $[Mo_2O_2S_9]^{2-}$ and $[W_2S_{11}]^{2-}$ have been found to belong to monoclinic space group[1,3] whereas $[W_2O_2S_9]^{2-}$ belongs to orthorhombic.[8] All the quarternary salts show the presence of one CH_3CN molecule of crystallization as indicated by elemental analysis. The *d* spacings of the four anions suggest that $[Mo_2S_{11}]^{2-}$ may be isostructural to $[W_2O_2S_9]^{2-}$.

All these anions show irreversible reduction in their CV study (Table I), whereas the Cs^+ salt of $[MoS_4]^{2-}$ and $[MoOS_3]^{2-}$ ions do not show any reduction up to –2.0 V. When the protonated cations like $[(CH_3)_2NH_2]^+$ is used, MoS_4^{2-} and $MoOS_3^{2-}$ show irreversible reduction below –2.0 V. $[(CH_3)_2NH_2]_2MoOS_3$ un-

---

(12) Simhon, E. D.; Baenziger, N. C.; Kanatzidis, M.; Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *103*, 1218.

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

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

(15) (a) Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245 and references therein. (b) Müller, A.; Jaegermann, W. *Inorg. Chem.* **1979**, *18*, 2633. (c) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348.

dergoes reduction at a higher negative potential than $[(CH_3)_2NH_2]_2MoS_4$ (Table I). A similar trend is observed in the anions under study. The all-sulfur complexes $[M_2S_{11}]^{2-}$ (M = Mo, W) are easily reducible compared to their oxo analogues, $[M_2O_2S_9]^{2-}$ (M = Mo, W). In general, the molybdenum complexes are more easily reducible than their tungsten counterparts. The anodic peak potential is almost nonvariant for all the anions, presumably due to the oxidation of the disulfido group, S_2^{2-}. The reduction step involved in higher negative potentials in the case of $(Ph_4X)_2M_2O_nS_{11-n}$, (X = P or As; M = Mo, W; n = 0, 2) is due to the cation, which has been confirmed by using simple $[Ph_4X]^+$ (X = P or As) salts.

The early work on $[W_2S_{11}H]^-$ [16] and $[W_2S_{11}]^{2-}$ [2] requires some explanation. It is interesting to note that $[W_2S_{11}H]^-$ reacts with elemental sulfur to give $[W_2S_{11}]^{2-}$. Thus acidification of WS_4^{2-} in the presence of elemental sulfur (not filtering out as has been done in the earlier work)[16] produces the desired compound. In all of these acidification reactions, H_2S is one of the byproducts. So, the condensation process in acidic medium in the presence of sulfur may follow the reactions shown in eq 1 and 2. The formation of $[Mo_2S_7]^{2-}$ during the acidification of aqueous solutions of MoS_4^{2-} has been proposed previously on the basis of pH and conductometric titrations.[17]

$$MS_4^{2-} \xrightarrow{H^+} [M_2S_7]^{2-} + H_2S \qquad (1)$$

$$[M_2S_7]^{2-} + S_8 \rightarrow [M_2S_{11}]^{2-} \qquad (2)$$

In the present study, it is also of interest to stress that the stoichiometry of the thiometalate and sulfur is not the crucial factor to dictate the course of the reaction. It is the protonated cationic species that drives the reaction resulting in the condensation product (eq 3). The difference in reactivity as described in these two equations (eq 3 and 4) may be attributed to an entirely different course of reactions. In the absence of protons, induced electron transfer takes place across the Mo=S bond and the external oxidant S_8 on reduction produces S_4^{2-}, which stabilizes the generated Mo(IV)[12] under ambient conditions. A similar transformation can be brought about in a variety of ways where the oxidation state of the central atom may vary.[18] However for the reaction in the presence of protonated cation or free proton, the condensation reaction with dimerization (eq 1) may be the first stage followed by intramolecular electron transfer between the metal-sulfur bond, which happens in tungsten-sulfur chemistry.[2,5-7,13] In the presence of elemental sulfur the stability of the dimeric condensation product probably is achieved by coordination expansion under ambient conditions as shown in eq 1 and 2.

$$(Et_2NH_2)_2MoS_4 \xrightarrow{S_8} (Et_2NH_2)_2Mo_2S_{11} \qquad (3)$$

$$(Et_4N)_2MoS_4 \xrightarrow{S_8} (Et_4N)_2MoS_9{}^{12} \qquad (4)$$

Acknowledgment. We thank the Department of Science and Technology, Government of India, and The Indian National Science Academy, New Delhi, India, for financial support.

Registry No. $[(C_2H_5)_2NH_2]_2MoS_4$, 59129-76-9; H_2MoO_4, 7782-91-4; H_2S, 7783-06-4; $(AsPh_4)_2Mo_2S_{11}$, 116026-61-0; $(Ph_4As)_2MoS_4$, 14493-05-1; S, 7704-34-9; $(AsPh_4)_2W_2O_2S_9$, 116026-62-1; $[Ph_4As]_2WOS_3$, 116026-66-5; $[(C_2H_5)_2NH_2]_2Mo_2S_{11}$, 116026-64-3; $(NH_4)_2MoS_4$, 15060-55-6; $(AsPh_4)_2Mo_2O_2S_9$, 116026-65-4; $(Ph_4As)_2MoOS_3$, 116026-67-6; $[(CH_3)_2NH_2]_2Mo_2O_2S_9$, 116052-58-5; $(NH_4)_2MoO_2S_2$, 16150-60-0; $(AsPh_4)_2W_2S_{11}$, 116126-35-3; $(AsPh_4)_2WS_4$, 14348-12-0; $(PPh_4)_2Mo_2O_2S_9$, 116026-68-7; $(PPh_4)_2W_2O_2S_9$, 112469-34-8; $(Me_2NH_2)_2MoOS_3$, 116026-69-8; $(Me_2NH_2)_2MoS_4$, 116026-70-1; $Cs_2(MoOS_3)$, 86915-92-6; $Cs_2(MoS_4)$, 15060-35-2; $[(PPh_4)_2W_2S_{11}]$, 106213-35-8; $[(PPh_4)_2Mo_2S_{11}]$, 116026-71-2.

Supplementary Material Available: A table of interplanar (d) spacings of the most prominent peaks (Å) for all four complexes as tetraphenylphosphonium salts (1 page). Ordering information is given on any current masthead page.

---

(16) Sécheresse, F.; Manoli, J. M.; Potvin, C. *Inorg. Chem.* **1986**, *25*, 3967.
(17) Saxena, R. S.; Jain, M. C.; Mittal, M. L. *Aust. J. Chem.* **1968**, *21*, 91.
(18) (a) Chandrasekaran, J.; Ansari, M. A.; Sarkar, S. *J. Less-Common Met.* **1987**, *134*, L23. (b) Sarkar, S.; Ansari, M. A. *J. Chem. Soc., Chem. Commun.* **1986**, 324. (c) Ansari, M. A.; Chandrasekaran, J.; Sarkar, S. *Inorg. Chem.* **1988**, *27*, 763.

Contribution from the Departments of Chemistry,
The Pennsylvania State University,
University Park, Pennsylvania 16802,
and The University of Delaware, Newark, Delaware 19716

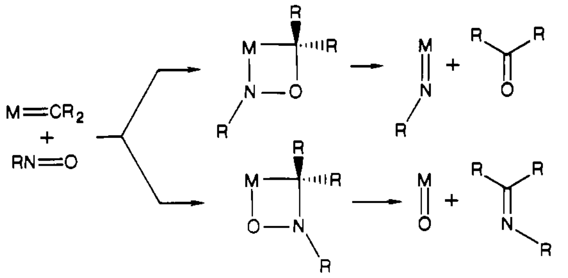
Metathesis-like Reactions between the Carbene Complex $(CO)_5W{=}C(OMe)Ph$ and Organic Nitroso Reagents

Robert S. Pilato, Gregory D. Williams, Gregory L. Geoffroy,* and Arnold L. Rheingold

Received March 14, 1988

Nitrene (NR, imido) ligands invariably assume bridging positions, typically μ_3, in low-valent, electron-rich metal complexes. Mononuclear nitrene complexes are known only for the more electron-deficient metals.[1] Carbonyl-nitrene complexes such as $(CO)_5Cr{=}NR$ have been invoked as reactive intermediates,[2] but such compounds have never been characterized, apparently because the metal-nitrogen bond is too weak and the nitrogen too poor a π-acceptor to give stability to such species. Nevertheless, if such complexes could be generated as reactive transients, it might prove possible to trap the nitrene ligand with added organic substrates and thereby accomplish useful synthetic chemistry, much like the impressive syntheses that have resulted from the corresponding metal carbene complexes.[3]

We reasoned that a possible route to such $(CO)_xM{=}NR$ species would be through metathesis-like reactions between carbene complexes and nitroso reagents, eq 1a. Metathesis could also proceed in the opposite sense as illustrated in eq 1b to generate an oxo complex and an imine. Herein we present results that indicate that the metathesis-like reaction of eq 1 does occur to generate transient nitrene complexes, although such species have proven too elusive to characterize. However, one such reaction has led to the formation of the first metal complex possessing an azoxy ligand, and this species has been structurally characterized.



(1a)

(1b)

Results and Discussion

The carbene complex $(CO)_5W{=}C(OMe)Ph$ (**1**)[4] was chosen for initial study since it was expected to yield a more stable third-row metal nitrene complex. Complex **1** reacts immediately with PhNO in toluene solution to give the products shown in eq 2, along with organometallic residues containing some $W(CO)_6$. Even at −78 °C the reaction is rapid, and the carbene complex **1** is completely consumed if a slight excess of nitrosobenzene is used. ^1H NMR analysis indicated that all of the carbene ligand was converted into methyl benzoate (**2**) and the imidate **3**, with an approximate 1.75:1 ratio of these products. The high yield

---

[*] To whom correspondence should be addressed at The Pennsylvania State University.

0020-1669/88/1327-3665$01.50/0 © 1988 American Chemical Society