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Studies on the Reactivity of Oxodihalobis(diethyldithiocarbamato) Molybdenum(VI) and Tungsten(VI) Complexes

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The complexes $OMoX_2L_2$ *(*$L = S_2CNEt_2)_2$ *react with* $Na_2S_2O_4$ *to yield* $OMoL_2$ *(*$X = Cl$*), with PhNCO to yield* $(PhN)MoX_2L_2$ *(*$X = Cl$*), with* PPh_2Et *to give* $MoX_2(PPh_2Et)L_2$ *(*$X = Cl, Br$*), and with* $OMoL_2$ *to produce* $OMoXL_2$ *(*$X = Cl, Br$*). The epr spectra of* $OMoXL_2$ *display halogen superhyperfine splitting* $[A(^{35,37}Cl) = \sim 3$ *gauss;* $A(^{79,81}Br) = 12.3$ *gauss]. Reaction of* WCl_6 *with NaL in MeOH yields the new complex* $OWCl_2L_2$ *which either does not react at all or gives no characterizable products with the above reagents. The results demonstate the lack of atom transfer ability of tungsten(VI) relative to its molybdenum analog.*

Introduction

During the past few years, a number of studies on the reactivity of the *cis*-dioxobis(dithiocarbamato)-molybdenum(VI) complexes, $MoO_2(S_2CNR_2)_2$, have been reported. For example, these complexes undergo an oxygen atom transfer reaction with tertiary phosphines (eqn. 1) [1, 2], are susceptible to oxo removal by hydrohalic acids (eqn. 2) [3], and are reduced by aqueous $Na_2S_2O_4$ (eqn. 3) [4]. In addition, $MoO_2(S_2CNR_2)_2$ reacts with $OMo(S_2CNR_2)_2$ in a reversible fashion to produce a μ-oxo dinuclear species with the Mo(VI) complex effectively sharing an oxygen atom with Mo(IV) (eqn. 4) [1, 5]. Much of this chemistry has been investigated because of its potential relevance to the mechanism of action of certain molybdoenzymes, and indeed

$$MoO_2(S_2CNR_2)_2 + PR_3 \rightarrow OMo(S_2CNR_2)_2 + OPR_2 \qquad (1)$$

$$MoO_2(S_2CNR_2)_2 + 2HX \rightarrow OMoCl_2(S_2CNR_2)_2 + H_2O \qquad (2)$$

$$MoO_2(S_2CNR_2)_2 + Na_2S_2O_4 \rightarrow OMo(S_2CNR_2)_2 \qquad (3)$$

$$MoO_2(S_2CNR_2)_2 + OMo(S_2CNR_2)_2 \rightleftarrows Mo_2O_3(S_2CNR_2)_4 \qquad (4)$$

Mo=O groups have now been shown to be present in sulfite [6] and xanthine [7] oxidases.

Although the reactivity of the *cis*-MoO_2 moiety has been fairly extensively investigated, no such studies have been reported for mono-oxo molybdenum(VI) species even though several of these compounds are known [8]. Our general interest in this area has prompted us to examine the reactivity of the complexes $OMoX_2(S_2CNEt_2)_2$ ($X = Cl, Br$) which were prepared and, for X = Cl, structurally characterized by Dirand, Ricard, and Weiss [3]. In addition, we have prepared the tungsten analog of the above chloro derivative, $OWCl_2(S_2CNEt_2)_2$, and have carried out a comparative reactivity study between this complex and $OMoCl_2(S_2CNEt_2)_2$. The results of these experiments, several of which ave resulted in the synthesis of new molybdenum dithiocarbamate complexes, are presented herein.

Experimental

Materials and Methods

All reactions were carried out under an inert atmosphere using standard Schlenk tube techniques. All solvents were dried over molecular sieves and degassed prior to use. The complexes $OMo(S_2CNEt_2)_2$ [2] and $OMoX_2(S_2CNEt_2)_2$ ($X = Cl, Br$) [3] were prepared as previously described.

Infrared spectra were recorded on a Beckman IR 20A spectrophotometer, uv-visible spectra on a Cary

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118C instrument, and EPR spectra on a Varian Associates 4502 spectrometer equipped with a Model V4560 1000KC modulation control unit, an X-band microwave bridge, and a Hewlett Packard X532 G frequency meter. Mass spectrometry was performed using a Finnegan 1015 quadrupole instrument.

Elemental analyses for CHN were determined in this laboratory using a Perkin Elmer 240 instrument equipped with a Microjector from Control Equipment Corporation. Chloride analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Reactions of $OMoCl_2(S_2CNEt_2)_2$

With $OMo(S_2CNEt_2)_2$

$OMoCl_2(S_2CNEt_2)_2$ (1.17 g; 2.44 mmol) and $OMo(S_2CNEt_2)_2$ (1.00 g; 2.44 mmol) were dissolved in CH_2Cl_2 (100 ml) and the reaction mixture stirred at room temperature for 75 min. After filtration and evaporation of the filtrate to dryness under vacuum, the residue was triturated with diethyl ether (50 ml) to yield the product as a brownish solid which was isolated by filtration, washed with ether, and dried *in vacuo*. The yield was 1.9 g, 88%. *Anal.* Calcd for $OMoCl(S_2CNEt_2)_2$ ($C_{10}H_2N_2ClMoOS_4$): C, 27.1; H, 4.51; N, 6.31; Cl, 8.00. Found: C, 27.3; H, 4.59; N, 6.16; Cl, 8.19.

A similar reaction between $OMoBr_2(S_2CNEt_2)_2$ and $OMo(S_2CNEt_2)_2$ gave $OMoBr(S_2CNEt_2)_2$ in 90% yield. *Anal.* Calcd for $C_{10}H_{20}N_2BrMoOS_4$: C, 24.5; H, 4.10; N, 5.74. Found: C, 24.3; H, 4.13; N, 5.50.

With PPh_2Et

$OMoCl_2(S_2CNEt_2)_2$ (0.50 g; 1.04 mmol) was dissolved in 1,2-dichloroethane (50 ml) and PPh_2Et (0.50 ml; 2.48 mmol) was added. After refluxing for 5 min, the reaction mixture was filtered and the filtrate evaporated under vacuum to 5 ml. Addition of methanol (50 ml) precipitated the product which was isolated by filtration, washed with methanol and ether and dried *in vacuo*. The yield was 0.46 g, 64%. *Anal.* Calcd for $MoCl_2(PPh_2Et)(S_2CNEt_2)_2$ ($C_{24}H_{25}N_2Cl_2MoPS_4$): C, 42.5; H, 5.17; N, 4.13; Cl, 10.5. Found: C, 41.8; H, 4.95; N, 4.08; Cl, 11.1.

A similar reaction between $OMoBr_2(S_2CNEt_2)_2$ and PPh_2Et gave $MoBr_2(PPh_2Et)(S_2CNEt_2)_2$ in 52% yield. *Anal.* Calcd for $C_{24}H_{25}N_2Br_2MoPS_4$: C, 37.6; H, 4.57; N, 3.66. Found: C, 37.5; H, 4.54; N, 3.58.

With PhNCO

$OMoCl_2(S_2CNEt_2)_2$ (0.50 g; 1.04 mmol) was suspended in toluene (50 ml) and PhNCO (0.56 ml; 5.15 mmol) added. After refluxing for 2.5 hr, the reaction mixture was cooled and evaporated to 10 ml under vacuum. Addition of ether (50 ml) precipitated the yellow product which was isolated by filtration, washed with ether and dried *in vacuo*. The yield was 0.52 g, 88%. The crude product was recrystallized from CH_2Cl_2/ether to obtain an analytical sample. *Anal.* Calcd. for $(PhN)MoCl_2(S_2CNEt_2)_2$-($C_{16}H_{25}N_3Cl_2MoS_4$): C, 34.7; H, 4.51; N, 7.58; Cl, 12.8. Found: C, 34.9; H, 4.53; N, 7.45; Cl, 13.2.

In a separate experiment, $^{18}OMoCl_2(S_2CNEt_2)_2$ (0.0647 g; 0.1345 mmol) and PhNCO (1.5 ml; 13.7 mmol) were suspended in xylene (10 ml) and the mixture degassed on a vacuum line by the freeze/thaw method. The suspension was then placed in an oil bath (125 °C) for 4.75 hr. After cooling to room temperature, the solution was frozen in a dry-ice/acetone bath and the evolved gas (0.1530 mmol) collected using a Toepler pump. Subsequent mass spectral analysis of the gas showed approximately equal amount of $C^{16}O^{16}$ and $C^{18}O^{16}O$. In a blank experiment, a portion of this gas mixture was condensed into a vessel containing only PhNCO (1.5 ml) in xylene (10 ml) and reheated in the oil bath at 125 °C for 4 hrs. After freezing the reaction mixture at –78 °C, the gas was again collected and its mass spectrum recorded. The spectrum now showed $C^{16}O^{16}O$ and $C^{16}O^{18}O$ in a 2:1 ratio, indicating that CO_2 exchanges its oxygen atoms with PhNCO under these conditions. The blank experiment thus showed that $C^{16}O^{16}O$ derived from reaction of $^{18}OMoCl_2(S_2CNEt_2)_2$ with PhNCO probably was formed from a $C^{16}O^{18}O$/PhCNO exchange.

With $Na_2S_2O_4$

$OMoCl_2(S_2CNEt_2)_2$ (0.20 g; 0.418 mmol) and $Na_2S_2O_4$ (2.0 g; 11.5 mmol) were suspended in H_2O (40 ml) and stirred vigorously for 5 hrs at room temperature during which time the color changed from yellow to red. The product (0.12 g) was isolated by filtration, washed with H_2O, and dried *in vacuo*. The product was identified as primarily $OMo(S_2CNEt_2)_2$ by its infrared spectrum which also showed the presence of a small amount of starting material.

Synthesis of $OWCl_2(S_2CNEt_2)$

A solution of $NaS_2CNEt_2 \cdot 2H_2O$ (1.60; 7.73 mmol) in methanol (30 ml) was added to a solution of WCl_6 (1.5 g; 3.77 mmol) in the same solvent. After 20 min at room temperature, the product, which had precipitated, was isolated by filtration, washed with methanol, and dried *in vacuo*. The yield was 0.85 g, 40%. *Anal.* Calcd for $C_{10}H_{20}N_2Cl_2OS_4W$: C, 21.2; H, 3.53; N, 4.94. Found: C, 20.8; H, 3.54; N, 4.76.

Reactions of $OWCl_2(S_2CNEt_2)_2$

With PPh_2Et

$OWCl_2(S_2CNEt_2)_2$ (0.50 g; 0.88 mmol) was dissolved in 1,2-dichloroethane (50 ml) and PPh_2Et (0.4 ml; 1.99 mmol) was added. After refluxing for 30 min, the reaction mixture was filtered, and the filtrated evaporated to dryness under vacuum. Trituration of the residue with methanol (40 ml) gave a white solid (0.20 g; 0.35 mmol) which was identified as starting material by its infrared spectrum. No product could be isolated from the methanol filtrate and the fate of the remaining tungsten-containing species is unknown.

With PhNCO

$OWCl_2(S_2CNEt_2)_2$ (0.50 g; 0.88 mmol) was dissolved in toluene (50 ml), PhNCO (0.50 ml: 4.60 mmol) was added, and the reaction mixture was refluxed for 3 hr. Filtration gave a white solid (0.44 g; 0.78 mmol) which was washed with ether, dried *in vacuo*, and shown to be unchanged starting material by its infrared spectrum.

With $OMo(S_2CNEt_2)_2$

A mixture of $OWCl_2(S_2CNEt_2)_2$ (0.50 g; 0.88 mmol) and $OMo(S_2CNEt_2)_2$ (0.36 g; 0.88 mmol) was dissolved in 1,2-dichloroethane (50 ml) and refluxed for 1 hr during which time the color changed to dark reddish-brown. After filtration, the reaction mixture was evaporated to dryness under vacuum and the residue triturated with hexane to give a brown solid which was isolated by filtration, washed with hexane and dried *in vacuo*. The yield was 0.75 g. The ir spectrum of the product was suggestive of a mixture. The epr spectrum of the product in CH_2Cl_2 contained a signal at $g = 1.980$ with $A(^{95,97}Mo) = 35$ gauss as well as a weak signal at $g = 1.963$. The former signal is probably due to the known [9] $[Mo(S_2CNEt_2)_4]^+$ as evidenced by very similar spectral parameters, while the latter signal is due to a small amount of $OMoCl(S_2CNEt_2)_2$. No signals at lower g values (the expected region for monomeric W(V) species) were observed.

With $Na_2S_2O_4$

$OWCl_2(S_2CNEt_2)_2$ (0.25 g; 0.44 mmol) was suspended in an aqueous solution (35 ml) of $Na_2S_2O_4$ (2.0 g; 11.5 mmol) and the mixture stirred at room temperature for 5 hr. The reaction mixture was filtered and the product washed with H_2O and dried *in vacuo*. The yield was 0.16 g, 64%, and the solid was identified as unreacted $OWCl_2(S_2CNEt_2)_2$ by its ir spectrum.

Results and Discussion

The overall goals of the chemistry described in this report were (1) to study the reactivity of the *mono*oxo molybdenum(VI) complexes $OMoX_2(S_2CNEt_2)$ (X = Cl, Br) with many of the same reagents known to remove an oxo group from the *di*oxo molybdenum(VI) species $MoO_2(S_2CNEt_2)_2$ and (2) to compare the reactivity of $OMoCl_2(S_2CNEt_2)_2$ with that of its tungsten analog. The capability of these complexes to transfer halogen atoms as well as oxygen atoms seemed plausible since we had previously observed an oxygen–chlorine atom exchange reaction between $MoCl_2(acac)_2$ and $MoO_2(acac)_2$ [10].

The molybdenum(VI) complexes were known [3] and could easily be prepared by reaction of $MoO_2(S_2CNEt_2)_2$ with the appropriate hydrohalic acid as in eqn. 2. The tungsten complex $OWCl_2(S_2CNEt_2)_2$ had not been reported previously but we were able to synthesize it in fair yield by reaction of WCl_6 with NaS_2CNEt_2 in methanol. The source of the oxygen atom incorporated into the complex is not known, but quite possibly it derives from water (eqn. 5) since no particular precautions were taken to dry the methanol and the ligand was in its hydrated form. The ir spectrum of the new complex was straightforward, containing a strong band at 940 cm^{-1} (assigned to the W=O stretching frequency) as well as the usual bands due to coordinated S_2CNEt_2. $OWCl_2(S_2CNEt_2)_2$ is white while its molybdenum analog is yellow, and this is not surprising since the same color difference is observed [11] between $MoO_2(S_2CNR_2)_2$ and $WO_2(S_2CNR_2)_2$.

$$WCl_6 + 2NaS_2CNEt_2 + H_2O \rightarrow OWCl_2(S_2CNEt_2)_2 + 2NaCl + 2HCl \qquad (5)$$

Reactions with PPh_2Et

This phosphine is known [1–2] to cleanly remove an oxygen atom from $MoO_2(S_2CNR_2)_2$ (eqn. 1) and it therefore seemed a logical choice for reaction with $OMoX_2(S_2CNR_2)_2$. We anticipated that PPh_2Et would either remove an oxygen atom yielding $OPPh_2Et$ and the known [12] $MoX_2(S_2CNR_2)_2$ or would abstract two halogen atoms giving X_2PPh_2Et and $OMo(S_2CNR_2)_2$. Initially, $OMoCl_2(S_2CNR_2)_2$ was heated with ~2.5 equivalents of phosphine and this reaction proceeded smoothly to give (somewhat surprisingly) a solid characterized by elemental analysis of $MoCl_2(PPh_2Et)(S_2CNEt_2)_2$ (eqn. 6). Reaction of $OMoBr_2(S_2CNEt_2)_2$ under the same conditions gave the analogous dibromo product.

$$OMoCl_2(S_2CNEt_2)_2 + 2PPh_2Et \rightarrow MoCl_2(PPh_2Et)(S_2CNEt_2)_2 + OPPh_2Et \qquad (6)$$

It seemed reasonable that the reaction involved initial abstraction of an oxygen atom by phosphine to give $MoCl_2(S_2CNEt_2)_2$, followed by this complex reacting with excess PPh_2Et to form the isolated species. To test this hypothesis, we carried out the reaction of $OMoCl_2(S_2CNEt_2)_2$ with exactly one equivalent of PPh_2Et, expecting to isolate $MoCl_2(S_2CNEt_2)_2$. No solid product could be isolated,

TABLE I. EPR Spectral Parameters for the Complexes $OMoX(S_2CNEt_2)_2$ (X = Cl, Br) in CH_2Cl_2 at Ambient Temperature.

Complex	g	$A(^{95,97}Mo)^a$	$A(^{35,37}Cl)^a$	$A(^{79,81}Br)^a$
$OMoCl(S_2CNEt_2)$	1.963	42	~3	–
$OMoBr(S_2CNEt_2)_2$	1.979	38	–	12.3

^{a}Values in gauss.

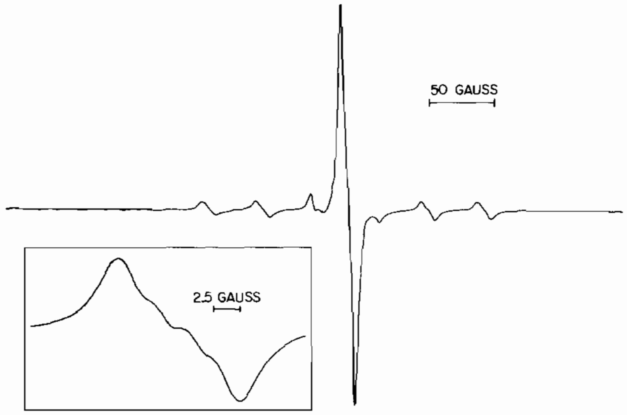

Fig. 1. EPR spectrum of $OMoCl(S_2CNEt_2)_2$ in CH_2Cl_2 at ambient temperature.

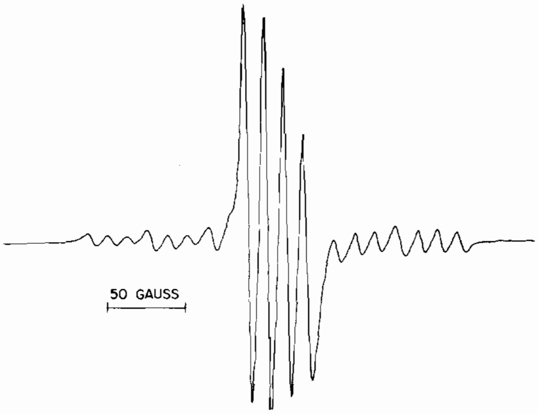

Fig. 2. EPR spectrum of $OMoBr(S_2CNEt_2)_2$ in CH_2Cl_2 at ambient temperature.

however, under experimental conditions which should have yielded the Mo(IV) species were it present. In addition we prepared $MoCl_2(S_2CNEt_2)_2$ independently [12] and reacted it with one equivalent of PPh_2Et. While some reaction took place as evidenced by color changes, the isolated solid was not $MoCl_2(PPh_2Et)(S_2CNEt_2)_2$ as might have been expected. At the present time, we have no satisfactory explanation for this apparent paradox, although perhaps a dimeric (or polymeric) structure for $MoX_2(S_2CNR_2)_2$, as isolated from reaction of $OMo(S_2CNR_2)_2$ with HX, is implicated.

The complex $OWCl_2(S_2CNEt_2)_2$ was much less reactive toward PPh_2Et than its molybdenum analog. After refluxing in 1,2-dichloroethane for 30 min [six times as long as for $OMoCl_2(S_2CNEt_2)_2$], some reaction took place as evidenced by color changes, but ~40% of the starting material could be reisolated and no other characterizable product was obtained. This lack of clean oxygen atom removal with phosphines for tungsten as opposed to molybdenum is very similar to that observed in the $MoO_2(S_2CNR_2)_2/WO_2(S_2CNR_2)_2$ systems [11].

Reactions with $OMo(S_2CNEt_2)_2$

The complexes $OMoX_2(S_2CNEt_2)_2$ (X = Cl, Br) react smoothly under mild conditions with the Mo(IV) species $OMo(S_2CNEt_2)_2$ to yield the new monomeric Mo(V) complexes $OMoX(S_2CNEt_2)_2$ (eqn. 7). The reactions

$$OMoX_2(S_2CNEt_2)_2 + OMo(S_2CNEt_2)_2 \rightarrow 2OMoX(S_2CNEt_2)_2 \qquad (7)$$

thus proceed via a halogen atom transfer pathway rather than one involving oxygen atom transfer [where the expected products would be $MoO_2(S_2CNEt_2)_2$ and $MoCl_2(S_2CNEt_2)_2$]. This chemistry provides a good example of the synthetic utility of intermolybdenum atom transfer reactions, as we have been unable to synthesize pure $OMoCl(S_2CNEt_2)_2$ by either halide substitution on $OMoCl_3(OPPh_3)_2$ [4] or by replacement of acetylacetonate from $OMoCl(acac)_2$ [10], both of which methods have previously been used to prepare monomeric Mo(V) complexes.

The ir spectra of $OMoCl(S_2CNEt_2)_2$ and $OMoBr(S_2CNEt_2)_2$ are consistent with their formulation, containing medium to strong bands at 935 cm^{-1} and 930 cm^{-1} respectively assigned to the Mo=O stretch. The complexes exhibit strong epr signals which have g values and $^{95,97}Mo$ hyperfine splitting in the range expected for $OMoXL_2$ species based on previous studies. Somewhat surprisingly, the epr spectra also exhibit $^{35,37}Cl$ and $^{79,81}Br$ superhyperfine splitting as can be seen in Figs. 1 and 2. Because both of these isotope combinations are 100% naturally abundant and have I = 3/2, a splitting of the signal into four components is predicted, and this pattern is readily observed for $OMoBr(S_2CNEt_2)_2$ where $A(^{79,81}Br)$ = 12.3 gauss. For $OMoCl(S_2CNEt_2)_2$, the magnitude of the $^{35,37}Cl$ superhyperfine splitting is much lower (less than the line width of the signal) causing the effect seen in Fig. 1 and by inspection the $A(^{35,37}Cl)$ was estimated at 3 gauss. The fact that $^{35,37}Cl$ superhyperfine splitting was observed at all is noteworthy as it was not detected in the epr spectra of any of the $OMoClL_2$ complexes previously reported [10, 13]. This lack of observation could reflect a structural difference between $OMoCl(S_2CNEt_2)_2$ and the other complexes but could also simply be due to a slightly greater line width and/or a smaller value for $A(^{35,37}Cl)$ in the other species. Synthesis and epr studies of the bromo analogs of other $OMoClL_2$ complexes should be instructive since the higher value of $A(^{79,81}Br)$ may allow the superhyperfine splitting to be observed if the proper overlap of orbitals is present. A summary of the epr parameters for $OMoX(S_2CNEt_2)_2$ (X = Cl, Br) is found in Table I.

Some reaction took place between $OWCl_2(S_2CNEt_2)_2$ and $OMo(S_2CNEt_2)_2$ as evidenced by spectral changes. However, the possible chlorine atom transfer reaction between the two species to yield $OMoCl(S_2CNEt_2)_2$ and $OWCl(S_2CNEt_2)_2$ was not realized. The epr spectrum of the isolated product showed the presence of a significant amount of the known [9] species $[Mo(S_2CNEt_2)_4]^+$ and a small amount of $OMoCl(S_2CNEt_2)_2$, but no signals were observed at lower g values where $OWCl(S_2CNEt_2)_2$ would be expected to appear. This behavior again demonstrates the inability of $OWCl_2(S_2CNEt_2)_2$ (as opposed to its molybdenum analog) to undergo clean atom transfer chemistry.

Reactions with $Na_2S_2O_4$

The original preparative method of the Mo(IV) species $OMo(S_2CNR_2)_2$ consisted of the reduction of an aqueous slurry of $Mo_2O_3(S_2CNR_2)_4$ by $Na_2S_2O_4$ [14]. We have also shown that $MoO_2(S_2CNR_2)_2$ is likewise reducible to Mo(IV) by aqueous $Na_2S_2O_4$ [4] and these results led us to test the reactivity of $OMCl_2(S_2CNEt_2)_2$ (M = Mo, W) under these effectively heterogenous conditions. In fact, $OMoCl_2(S_2CNEt_2)_2$ is reduced almost completely to $OMo(S_2CNEt_2)_2$ by a solution of excess $Na_2S_2O_4$ in H_2O over a 5 hr period at ambient temperature. It is interesting to note that $Na_2S_2O_4$ removed halogen atoms from the Mo(VI) species as opposed to PPh_2Et, which reduced the complex by Mo=O bond cleavage. The apparent specificity of these two reagents may prove useful in future synthetic efforts.

Under identical conditions, no reduction of $OWCl_2(S_2CNEt_2)_2$ by $Na_2S_2O_4$ could be detected, again exemplifying the relative inertness of the W–Cl and W=O bonds.

Reactions with PhNCO

The report by Volpin [15] that rhenium oxo linkages react with phenyl isocyanate to yield the corresponding phenylimido species and CO_2 prompted us to examine the tendency of Mo=O and W=O groups toward reactivity of this type. In fact, $OMoCl_2(S_2CNEt_2)_2$ reacts smoothly with PhNCO in refluxing toluene completely analogously to the rhenium systems (eqn. 8). The phenylimidomolybdenum product was also recently prepared by reaction of $Mo(NPh)_2(S_2CNEt)_2$ [16] with HCl and has been structurally characterized [17]. The infrared spectrum of the complex is not particularly diagnostic, but is consistent with its formulation, containing bands due to both coordinated NPh and S_2CNEt_2 moieties.

$$OMoCl_2(S_2CNEt_2)_2 + PhNCO \rightarrow (PhN)MoCl_2(S_2CNEt_2)_2 + CO_2 \qquad (8)$$

To verify that one of the oxygen atoms of the CO_2 product was derived from the oxo group of $OMoCl_2(S_2CNEt_2)_2$, the molybdenum starting material was labeled with oxygen(18) via oxidation of the known [18] $^{18}OMo(S_2CNEt_2)_2$ with Cl_2 [12]. $^{18}OMoCl_2(S_2CNEt_2)_2$ was then reacted with PhNCO *in vacuo* and the gaseous product collected using a Toepler pump and analyzed by mass spectrometry. The product gas was found to contain approximately equal amounts of $C^{16}O^{18}O$ and $C^{16}O_2$ with the total yield being slightly greater than one mol/mol of Mo(VI). The presence of such a large amount of $C^{16}O_2$ was somewhat disturbing, but a control experiment showed that under the reaction conditions, $C^{16}O^{18}O$ reacted with $PhNC^{16}O$ to form $C^{16}O_2$ suggesting that the $C^{16}O_2$ observed above was produced via this pathway. The experiment was thus fairly conclusive in demonstrating that the oxo group of $OMoCl_2(S_2CNEt_2)_2$ is the source of one of the oxygen atoms of the CO_2 product. This result in turn suggests that the mechanism of the reaction may involve attack of the carbon of PhNCO on the oxo group of $OMoCl_2(S_2CNEt_2)_2$ with subsequent cleavage of the C–N bond and coordination of the NPh fragment.

Under very similar conditions to those above for its molybdenum analog, no reaction occurred between $OWCl_2(S_2CNEt_2)_2$ and PhNCO as evidenced by reisolation of the starting material in virtually quantitative yield. This result provides another example of the inertnesss of the W=O linkage relative to Mo=O and is consistent with the lack of reactivity of $OWCl_2(S_2CNEt_2)_2$ with PPh_2Et, $OMo(S_2CNEt_2)_2$, and $Na_2S_2O_4$.

Summary and Conclusions

The most striking result of the chemistry described in this report is the large difference in reactivity between $OMoCl_2(S_2CNEt_2)_2$ and its tungsten analog. While the Mo(VI) complex was found to be capable of undergoing a variety of oxygen and halogen atom transfer reactions, $OWCl_2(S_2CNEt_2)_2$ was either completely unreactive or gave products which could not be characterized. This finding is entirely consistent with the previous comparative study [11] of the reactivities of $MO_2(S_2CNR_2)_2$ (M = Mo, W). It is now known that Mo=O linkages are present in molybdoenzymes [6–7] and it is well established that tungsten-substitution in these enzymes results in catalytically inactive species [19–21]. Although the existence of W=O groups in these enzymes has not yet been established, their presence would certainly not be inconsistent with the results of our chemical studies which indicate that their inertness could be at least a contributing factor to the lack of enzymic activity.

The reactivity studies of $OMoX_2(S_2CNEt_2)_2$ (X = Cl, Br) resulted in the synthesis of three new molybdenum dithiocarbamate complexes, *i.e.*, $MoX_2(PPh_2Et)(S_2CNEt_2)_2$, $(PhN)MoCl_2(S_2CNEt_2)_2$, and $OMoX(S_2CNEt_2)_2$. The epr spectra of the last species are consistent with their formulation as monomeric Mo(V) complexes and are particularly interesting because they exhibit halogen superhyperfine splitting. We were unable to obtain $OMoX(S_2CNEt_2)_2$ by established preparative methods for complexes of this type, and its successful synthesis via reaction of $OMoX_2(S_2CNEt_2)_2$ with $OMo(S_2CNEt_2)_2$ provides another example of the utility of atom transfer reactions in group VI B chemistry.

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