OXIDATION OF CYCLIC AMINES BY MOLYBDENUM(II) AND TUNGSTEN(II) HALOCARBONYLS, [M(CO)$_4$X$_2$]$_2$ (M = Mo, W; X = Cl, Br)

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ABSTRACT. The molybdenum(II) and tungsten(II) halocarbonyls, [M(CO)$_4$X$_2$]$_2$ (M = Mo, W; X = Cl, Br) react with a large excess of the nitrogen bases, 1-methylpyrrolidine, 1-methylpiperidine, 1-ethylpiperidine and 2-ethylpiperidine to give aminecarbonyl complexes of the type M(CO)$_3$L$_3$ (L= alkylamine). Excess piperidine reacts with the tungsten halocarbonyls, [W(CO)$_4$X$_2$]$_2$ (X = Cl, Br), to give the trans isomer of the complex, W(CO)$_3$(C$_5$H$_{11}$N)$_3$. The halogens were recovered as the amminium salts, amine, HX. The oxidized amine dimerized to form a yellow product which was recovered as an oily liquid but in very small amounts. However, in the reaction between Mo(CO)$_4$Br$_2$ and 1-ethylpiperidine, a yellow crystalline solid, with a melting point of 224 ^{o}C was recovered in sufficient amounts for elemental analysis, melting point and spectral data. Its mass spectrum showed a molecular ion peak at m$^+$/z = 222, a clear evidence that the oxidized amine dimerizes. The cyclic dibasic amine piperazine, C$_4$H$_{10}$N$_2$ is not, however, oxidized by these halocarbonyls but rather it reacts by substituting some CO groups to form products of the type, M(CO)$_3$(C$_4$H$_{10}$N$_2$)$_2$X$_2$ (M = Mo, W; X = Cl, Br). Products were characterized by elemental analysis, IR, UV, ^{1}H NMR and mass spectrometry.

KEY WORDS: Molybdenum(II), Tungsten(II), Ammines, Halocarbonyls

INTRODUCTION

All the cited references should be re-numbered and should match with the listed references ??
Previously, molybdenum aminecarbonyls have been prepared using molybdenum hexacarbonyl as the starting material following a variety of methods among them the following (i) UV-irradiation of an amine/hexacarbonyl mixture [1, 2], refluxing a carbonyl/amine mixture in a suitable solvent [3] and an indirect method whereby some of the CO groups are substituted with hydrocarbon ligands such as cyclohexatriene, norbornadiene or mesitylene and the products thus obtained are reacted with an amine [4, 5]. In a previous study, it was shown that the halocarbonyls, [Mo(CO)$_4$X$_2$]$_2$ (X = Cl, Br), react with primary amines either neat or in an alcohol such as ethanol or methanol as a solvent at ordinary conditions of temperature and pressure to form aminecarbonyls of the type, Mo(CO)$_3$L$_3$ (L = propylamine, butylamine, cyclohexylamine) which could not be obtained by refluxing an amine/hexacarbonyl mixture [3]. Piperidine, however, reacts with these halocarbonyl to give Mo(CO)$_4$(piperidine)$_2$ even when the halocarbonyl is refluxed with the neat base Where is [Ref. 6] ? [7, 8]. During these studies, piperididine was, however, the only base that gave an identifiable organic oxidation product. All the other amines gave resinous materials owing to polymerization of oxidized bases.

In this paper we wish to report the results of a study undertaken with the following objectives. First, it was of interest to find out whether, with a judicious choice of the amines, readily identifiable organic oxidation products could be obtained when the molybdenum halocarbonyls, [Mo(CO)$_4$X$_2$]$_2$ (X = Cl, Br), react with cyclic amines. The cyclic amines 1-methylpyrrolidine, 1-ethylpyrrolidine, 1-methylpiperidine, 1-ethylpiperidine and 2-ethylpiperidine were chosen for study because previous studies have shown that mercuric-oxidation of such amines gives dimeric species [9, 10].

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The second objective of our study was to find out whether the selected amines would react with the tungsten halocarbonyls, $[W(CO)_4X_2]_2$ (X = Cl, Br) the same way they react with the molybdenum analogs. The reason for this was that whereas the chemistry of molybdenum is similar to that of tungsten in many respects [11], there are also many cases where there are very distinct differences. An example of such differences is the reaction of the halocarbonyls $[M(CO)_4X_2]_2$ (M = Mo, W; X = Cl, Br) with neat benzonitrile. Thus, whereas the molybdenum halocarbonyls react with this base at ordinary conditions of temperature and pressure to give paramagnetic tervalent molybdenum complexes of the type, MoX_3L_3 [(X = Cl, Br, L = benzonitrile) [12], the tungsten analogs react with the same base to give only partially substituted products of the type, $W(CO)_xL_yX_2$ [X = Cl, Br] [13]. When the reaction mixture is heated in boiling benzene, the carbonyl groups are lost with formation of diamagnetic species of the type, WX_2L_2 [13]. Another example that shows differences in the chemistry of the two elements is observed in the reactions of both molybdenum(VI) and tungsten(VI) with hydrogen sulfide. Thus, when a solution containing both molybdenum(VI) and tungsten(VI) species is acidified with tartaric acid/formic acid mixture, the mixture heated to 60 ^{o}C and hydrogen sulfide is bubbled through the solution, molybdenum(VI) is reduced to molybdenum(IV) and precipitated as MoS_2. On the other hand, tungsten(VI) is not reduced by hydrogen sulfide and remains in solution as a tartarate complex. This property is actually made use of in separation of the two elements [14]. In comparing the similarities and differences in the way the halocarbonyls, $[M(CO)_4X_2]_2$ (M = Mo,W; X = Cl, Br) react with amines, the reaction of piperidine with $W(CO)_4Br_2$ was also attempted to find out what type of product would be formed. As noted earlier, this base reacts with the molybdenum halocarbonyls, $[Mo(CO)_4X_2]_2$ (X = Cl, Br) to form   the complex, $Mo(CO)_4(piperidine)_2$, yet the other amines formed complexes of the type $Mo(CO)_3(amine)_3$ [7, 8].

A third objective of our study was to find out how the dibasic nitrogen base, piperazine, $C_4H_{10}N_2$, (m.p. 106 ^{o}C, b.p. 146 ^{o}C), would react with the molybdenum and tungsten halocarbonyls $[M(CO)_4X_2]_2$ (M = Mo, W; X = Cl, Br). Whereas the oxidation product of this base need not form a dimer, if by any chance it is fully oxidized to pyrazine, $C_4H_4N_2$ (m.p. 54 ^{o}C, b.p. 115 ^{o}C), this is a thermally stable substance that should be easy to characterize.

EXPERIMENTAL

All preparative work was carried out in an atmosphere of dry oxygen-free nitrogen obtained by passing the White Spot Nitrogen (British Oxygen Ltd) through concentrated sulfuric acid, then over anhydrous magnesium sulfate, bubbled through a solution of sodium naphthalide and, finally, passed over phosphorus(V) oxide sprinkled on preheated pumice stone [15].

In a typical preparation, about 2-5 g of the hexacarbonyl were used to prepare the halocarbonyls $[M(CO)_4X_2]_2$ (M = Mo, W; X = Cl, Br). The molybdenum halocarbonyl, $[Mo(CO)_4Cl_2]_2$ was prepared following the original literature method [16]. The bromo complexes, $[M(CO)_4Br_2]_2$ (M = Mo, W) were prepared with a slight modification of the original literature method in that, instead of adding a few drops of bromine to either cooled $Mo(CO)_6$ [16] or cooled $W(CO)_6$ [17], a known amount of bromine was actually used. This was achieved by preparing a standard bromine solution in freshly distilled hexane and using the volume containing the exact amount of bromine needed to convert a known quantity of the hexacarbonyl $M(CO)_6$ to the halocarbonyl, $M(CO)_4Br_2$ (M = Mo, W). The halocarbonyl $M(CO)_4X_2$ (M = Mo, W; X = Cl, Br), was transferred to a Schlenk tube, 10-15 mL of the appropriate amine in about 30 mL of freshly distilled ethanol added and the mixture stirred in an atmosphere of oxygen-free nitrogen for at least twelve hours after which time, the products were recovered as outlined hereunder. It should be noted that whereas same products were obtained

by using the neat amines, use of the neat amines made isolation of the products rather cumbersome. The volume of the solvent was reduced by pumping it off and condensing the vapours in traps cooled using dry-ice/acetone slush bath to protect the pump. When the volume of the solvent had been reduced to about 10 mL, this concentrated solution was put on a basic alumina column and these products eluted using tetrahydrofuran. Three main products were recovered from different portions of the column. These were recovered in the normal way of putting portions with same product (as confirmed by spotting on thin layer plates) in same flask and evaporating the solvent under vacuum until crystals were obtained. These were separated by filtration. The product in the third portion did not, however, yield any crystals except in one case discussed later. Rather an oily residue was obtained and, unfortunately, in very small amounts which were adequate only for spectroscopic studies (IR, UV, ^{1}H NMR and mass spectra).

The IR spectra were recorded as KBr disc on an FTIR-8400 Shimadzu Spectrophotometer. The mass spectra were done on an Agilent model 7890A GCMS system. NMR spectra were recorded on either Perkin-Elmer Model-12B NMR Spectrometer or a JEOL FX-100 NMR Spectrometer using tetramethylsilane as an internal Standard and in a few cases, using dimethyl sufoxide. Molybdenum and tungsten were determined by weighing as the oxides, MO_3 after digesting the halocarbonyl $M(CO)_4X_2$ (M = Mo, W; X = Cl, Br) or the aminecarbonyl $M(CO)_3L_3$ (L= alkylamine) with nitric acid, evaporating to dryness andheating the solids left in air to convert them to the oxides. The molybdenum oxide was heated at 500 ^{o}C [18] and the tungsten oxide at 750 ^{o}C [19]. In each case, the oxide was cooled in air to a temperature such that the crucible could be touched without scolding the fingers. The crucibles were finally cooled in a desiccator kept moisture-free by use of P_2O_5 and the cooling continued for at least an hour before weighing.

The halogens in the molybdenum halocarbonyls, $Mo(CO)_4X_2$ (X = Cl, Br), were determined gravimetrically by weighing as the silver halides, AgX (X = Cl, Br) after proper digesting of the sample with concentrated nitric acid and adjusting the pH to avoid precipitation of silver molybdate [12]. Both bromine and chlorine in tungsten halocarbonyls were determined gravimetrically by weighing as the silver halides after taking the following precautions taken to avoid precipitation of either silver tungstate or tungstic acid. To a halide-containing tungstate solution, a large excess of tartaric acid was added, a few mLs of 1 M sulfuric acid added and the halide precipitated by addition of excess silver nitrate. The precipitate was washed several times with ethanoic acid. This treatment prevents precipitation of tungsten either as silver tungstate or tungstic acid [20]. Halogens in the aminium salts were determined together with carbon, hydrogen and nitrogen during microanalysis at the School of Pure and Applied Chemistry, University of KwaZulu Natal, South Africa.

RESULTS

The halocarbonyls, M(CO)$_4$X$_2$

Elemental analyses for the yellow solids obtained from the reactions of $Mo(CO)_6$ with either chlorine or bromine confirmed that the products are the halocarbonyls, $M(CO)_4X_2$, (M = Mo, W; X = Cl, Br). Thus, in a typical preparation, found (%) Cl 25.41, Mo 34.20; calculated (%) for $C_4Cl_2MoO_4$ Cl 25.47; Mo 34.38. Analysis for the bromo complex, gave (%) Br 43.28; Mo 25.98; calculated (%) for $C_4Br_2MoO_4$, Br 43.45; Mo 26.08.

Products from reactions of the halocarbonyls, M(CO)$_4$X$_2$ (M = Mo, W; X = Cl, Br) with amines (other than piperazine)

Three main products were recovered from the chromatographic separation of the products as outlined below.

(a) Product from first portion (yellow). A metal-containing but halogen-free crystalline solid was obtained from this portion. Elemental analyses and IR carbonyl stretching frequencies, νC-O), for aminecarbonyl complexes are summarized in Table 1.

Table 1. Elemental analyses and IR data of the amine carbonyl complexes of the type, $M(CO)_3(Amine)_3$.

Amine	Formula	C	H	N	Mo (W)	IR, νC-O) in cm^{-1}
1-Methylpyrrolidine	$C_{18}H_{33}MoN_3O_3$	48.86 (49.65)	7.19 (7.64)	9.28 (9.65)	22.48 (22.03)	1986.5, 1927.7, 1844.8
1-Methylpyrrolidine	$C_{18}H_{33}WN_3O_3$	40.43 (40.61)	6.89 (653)	8.05 (8.03)	34.95 (35.11)	1982.7, 1918.1, 1860.2
1-Methylpiperidine	$C_{21}H_{39}MoN_3O_3$	52.02 (52.82)	7.86 (8.23)	8.32 (8.80)	19.81 (20.09)	1981.7, 1926.8, 1864.2
1-Methylpiperidine	$C_{21}H_{39}WN_3O_3$	45.53 (44.61)	6.94 (6.95)	7.82 (7.43)	31.98 (32.51)	1981.7, 1918.1, 1860.2
Piperidine	$C_{18}H_{33}WN_3O_3$	42.68 (41.31)	5.98 (6.36)	8.14 (8.03)	36.21 (35.13)	1876.6; 1829.4,1772.5
Methylpyrrolidine	$C_{24}H_{45}WN_3O_3$	47.62 (47.45)	8.42 (7.46	7.52 (6.92)	29.13 (30.26)	1980.8, 1931.6,1861.2

(b) Product in the second portion of the column. This is a white crystalline solid. Elemental analysis showed that it is actually a salt of the amine used in the reaction with the halocarbonyl. The melting point of the salt was found to be identical to that of authentic synthetic salt of the amine. Elemental analyses data are summarized in Table 2.

Table 2. Elemental analysis of the aminium salts, amine.HX (X = Cl, Br).

Amine or base	Formula of salt and m.p. ^{o}C	C	H	X (= Br, Cl)	N
1-Methylpyrrolidine	$C_5H_{12}ClN$	50.04 (49.37)	10.11 (9.94)	29.66 (29.14)	11.32 (11.52)
1-Methylpyrrolidine	$C_5H_{12}BrN$	36.68 (36.16)	7..12 (7.28)	47.80 (48.11)	8.78 (8.43)
1-Methylpiperidine	$C_6H_{14}BrN$ (183-5°C)	39.98 (40.03)	7..36 (7.83)	45.01 (44.34)	7.48 (7.75)
1-Methylpiperidine	$C_6H_{14}BrN$ (183-5°C)	39.98 (40.03)	7..36 (7.83)	45.01 (44.34)	7.48 (7.75)
1-Ethylpiperidine	$C_7H_{16}BrN$ (197°C)	43.55 (43.34)	8.26 (8.31)	41.28 (41.14)	7.30 (7.22)
2-Ethylpiperidine	$C_7H_{16}BrN$ (176-8°C)	43.55 (43.34)	8.26 (8.31)	41.28 (41.14)	7.30 (7.22)
Piperidine	$C_5H_{12}BrN$ (233-235°C)	36.68 (36.18)	7.22 (7.27)	48.78 (48.08)	8.64 (8.44)

(c) Product in the third portion of the column. In all the preparations, the product in the third portion was, yellow coloured, oily, metal-free and contained a halogen. Unfortunately, the amount collected was very little and only adequate for spectroscopic studies (IR, UV, NMR and mass spectrometry). The ^{1}H-NMR results are as summarized in Table 3. There was, however, one exception, the reaction of 1-ethylpiperidine with $Mo(CO)_4Br_2$ gave sufficient amount of a crystalline yellow solid for both elemental analysis and melting point determination. This reaction will be discussed more fully later.

Table 3. ^{1}H-NMR peaks of the organic oxidation products of from the cyclic amines.

Base used	^{1}H-NMR (ppm)
1-Methylpyrrolidine	5.527, 10.582, 6.490
1-Methylpiperidine	6.118, 9.093
2-Ethylpiperidine	5.617, 10.853
Piperidine	5.932

Products from reactions of the halocarbonyls, $M(CO)_4X_2$ (M = Mo, W; X = Cl, Br) with piperazine. Reaction the halocarbonyls, $M(CO)_4X_2$ (M = Mo,W; X = Cl, Br), with the dibasic

amine, piperazine, $C_4H_{10}N_2$, gave halocarbonyl complexes of the type $M(CO)_3(C_4H_{10}N_2)_2X_2$. Elemental analysis results are summarized in Table 4.

Table 4. Elemental analysis of the piperazine complexes $M(CO)L_2X_2$ (M = Mo, W; X = Cl, Br; L = piperazine).

Formula	C	H	Cl(Br)	Mo(W)	N
$C_{11}H_{20}Br_2MoN_4O_3$	26.65 (25.80)	3.36 (3.94)	31.99 (31.21	19.14 (18.73	11.91 (10.94)
$C_{11}H_{20}Cl_2MoN_4O_3$	29.98 (31.22)	4.27 (4.76)	17.01 (16.75)	21.83 (22.67)	12.38 (13.24)
$C_{11}H_{20}Cl_2MoN_4O_3$	21.36 (22.02)	3.20 (3.36	25.56 (26.63)	29.80 (30.64)	29.80 (30.64)

DISCUSSION

The results from first yellow portion recovered from the chromatographic column were summarized in Table 1. The elemental analysis indicates that these were an amine carbonyl complexes of the type, $M(CO)_3L_3$ (M = Mo, W; L = an amine). The tungsten piperidine complex, $W(CO)_3(piperidine)_3$ is noteworthy because it is another example that shows some differences in the chemistries of molybdenum and tungsten. Thus, whereas this amine reacts with the molybdenum halocarbonyls, $Mo(CO)_4Cl_2$ or $Mo(CO)_4Br_2$ to give the diaminetetracarbonylmolybdenum(0) complex, $Mo(CO)_4(piperidine)_2$ [7, 8], it reacts with $W(CO)_4Br_2$ to give the tri-substituted carbonyl, $W(CO)_3(piperidine)_3$. There is no obvious reason for this difference because the two elements have very close atomic radii of 147 pm for molybdenum and 139 pm for tungsten [21]. Hence, the atomic sizes do not appear to be a factor in this difference. A possible reason for these differences may be the much larger nuclear charge of 74 protons for tungsten as compared to that of only 42 protons for molybdenum.

Each of the complexes of the type $M(CO)_3(amine)_3$ listed in Table 1 has three infrared peaks in the inorganic carbonyl region (1800-2000 cm^{-1}). For example, the molybdenum complex, $Mo(CO)_3(L_3)$ (L = 1-methylpiperidine) has three very distinct peaks at the following wave numbers: 1981.7, 1926.8 and 1864.1. The presence of three such peaks in a complex of the type, $Mo(CO)_3(L_3)$, implies that, structurally, this is the *trans* isomer of $M(CO)_3(amine)_3$ which has a C_{2v} Symmetry [22].

The second portion eluted from column was a white crystalline solid. The elemental analysis showed that it is actually a salt of the amine used in the reaction with the halocarbonyl. The melting point of the salt was found to be identical to that of authentic synthetic salt of the amine.

The products in the third portion of the column were yellow coloured, oily, metal-free and contained a halogen oxidized amines. These were studied using IR, UV, NMR and mass spectrometry. The IR spectra of the compound isolated in the third portion of the column showed infrared absorption peaks around, 1550-1660 cm^{-1} which were absent in the spectra of the parent amines. This is the region where carbon-carbon double bonds (C=C) absorb IR radiation [23]. As a specific example, consider the product in the reaction of 1-methyl-pyrrolidine with either $Mo(CO)_4Br_2$ or $W(CO)_4Br_2$. It is observed that, whereas this base has no infrared absorption band around 1600 cm^{-1}, an IR spectrum of the yellow product in the third portion from the column has a strong IR peak at 1640.3cm^{-1}. It is reasonable to assume that appearance of such a band implies formation of carbon-carbon double bond, i.e. C=C. Put differently, one can say that the amine has been oxidized. This is supported by the fact that, in the amine carbonyl complexes of the type $M(CO)_3(amine)_3$ isolated, the metal is in formal oxidation state zero, yet in the halocarbonyls $M(CO)_4X_2$ (M = Mo,W; X = Cl, Br) used, the metal is in formal oxidation state +2. Since no reduction can take place without oxidation and vice versa, we can reasonably say the reduction of Mo(II) and W(II) species is accompanied by oxidation of the amine.

At this juncture, we should point out that C=N bonds are also known to absorb IR radiation in the same spectral range as the C=C bonds [23]. However, the possibility that the IR absorption peaks observed are from C=N bonds, can be ruled out for the following reasons: first, it is not possible to have a stable species with C=N bonds in a cyclic tertiary amine such as 1-ethylpiperidine unless the alkyl group breaks off. Otherwise, if the species forms without the alkyl group breaking off, the nitrogen would be having a valence of 4 which we know is not stable. Secondly, ^{1}H NMR spectra of this yellow substance in the third portion chromatographic isolation shows presence of singlet protons otherwise called olefinic protons. Presence of C=N bonds and singlet protons in the same molecule after oxidation of a cyclic tertiary amine such 1-ethylpiperidine does not appear feasible (see proposed mechanism).

The UV data of the yellow substance in third portion indicated the presence of C=C double bonds. It is known that substances with C=C bonds such as olefins or even aromatic substances such as benzene absorb ultraviolet radiation in the range 200-380 nm [24]. The yellow product in the third portion showed such peaks, yet they were absent in the spectra of the parent amines. For example, the UV spectrum of 1-methylpyrrolidine spectrum does not show any absorption band in this spectral range. Yet, the yellow product isolated as third portion from column when this amine reacts with $Mo(CO)_4Br_2$ has two UV absorption bands 277 and 237 nm.

The ^{1}H NMR spectra of the yellow compound isolated in the third portion of the chromatographic column gave yet further support of oxidation of the cyclic amines by Mo(II) and W(II) species. The ^{1}H NMR olefinic peaks and the ^{1}H aldehydic peaks were summarized in Table 3. The ^{1}H NMR olefinic protons are expected in the range δ = 5.20-6.80 ppm [25]. When olefins are oxidized to aldehydes, aldehydic proton peaks are observed around δ = 9.5-10.95 ppm [26]. In this study, a similar behaviour was observed.

Product in third portion (yellow) in the reaction of Mo(CO)₄Br₂ with 1-ethylpiperidine

The first and second portions gave products similar to those got in reactions of other bases namely, $M(CO)_3L_3$ (L = 1-ethylpiperidine) and 1-ethylpiperidine.HBr salt. The product isolated in the third portion was a yellow crystalline solid with a melting point of 224 ^{o}C, rather than the oily material obtained in other preparations. Elemental analysis gave, (%) C 43.36, H 7.07, Br 41.37, N 7.07. There are two other salts which can give similar analyses.

(a) HBr-salt of 1-ethylpiperidine. We rule this out because this should be a white solid with a melting point of 197 ^{o}C.
(b) The other possibility is a salt of the oxidized 1-ethylpiperidine (species I).

MWt Formula $C_7H_{14}BrN$

MWt Formula $C_{14}H_{28}Br_2N_2$
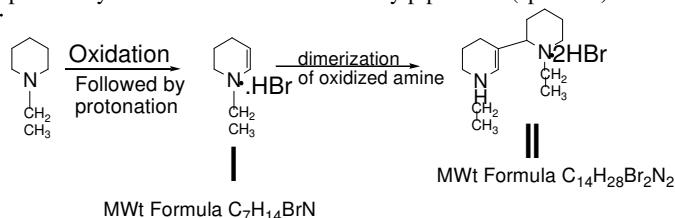
(c) The third possibility is a salt of dimerized oxidized amine, i.e. species II in above scheme. Either of these gives (%) C 43.77, H 7.35, Br 41.60, N 7.29. Whereas NMR spectra of both I and II should have singlet protons, we believe the species present is II because, whereas the commonest species in mass spectrum is one with m^+/z = 98 species, i.e. the species $C_6H_{12}N$, there is a weak molecular ion peak at m^+/z = 222. This is the mass of species II minus mass of two HBr molecules.

We note here that an identical mass spectrum is observed in the product from the reaction of 1-ethylpiperididine with $Mo(CO)_4Cl_2$, the only difference being that the reaction of the amine with the chlorocarbonyl did not give crystalline product but oily material. Reaction the halocarbonyls, $M(CO)_4X_2$ (M = Mo,W; X = Cl, Br), with the dibasic amine, piperazine, $C_4H_{10}N_2$, gave halocarbonyl complexes of the type $M(CO)_3(C_4H_{10}N_2)_2X_2$. This was the case even when the reaction mixture with a large excess of the base was heated in boiling propanol, at 95 ^{o}C. Elemental analysis results are summarized in Table 4. These are probably a polynuclear species. Further studies are required to establish their nature.

CONCLUSION

The results of our study have shown that the molybdenum(II) and tungsten(II) ions in the halocarbonyls $M(CO)_4X_2$ (M = Mo, W; X = Cl, Br) oxidize the cyclic amines studied while they are themselves reduced to oxidation state zero. Piperazine is not, however, affected.

ACKNOWLEDGEMENTS

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Ref. 24-27 should be given as one reference.

All the references should be re-numbered and should match with cited references in the text ??