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# FIRST REPORT OF THE REDUCTIVE NITROSYLATION OF TUNGSTATE(VI) BY HYDROXYLAMINE. STEREOSPECIFIC SYNTHESIS OF $[W(NO)_2Cl_2(L)_2]$ (L = py, 3-Mepy, 4-Mepy)

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Stereospecific synthesis of cis-dichlorotrans-bis(pyridine)-cis-dinitrosyltungsten(0) and the related 3-picoline and 4-picoline derivatives have been achieved by a single pot reductive nitrosylation of sodium tungstate(VI) by hydroxylamine in the presence of excess of pyridine (or picolines) as solvent.

Since the characterization of the Heide-Hofmann cyanide1) to be a nitrosylmolybdenum(0) compound,2) the reductive nitrosylation method using hydroxylamine has been extensively used in alkaline medium3) and recently even in neutral to acidic media.4) Amongst these, the chromium group metals except tungsten give extensive chemistry of the nitrosyl derivatives. Tungstate(VI) thwarted all previous attempts to be nitrosylated by the hydroxylamine method. Molybdenum besides giving the conventional mononitrosyl derivatives can produce the dinitrosyl derivatives with the configuration $\{Mo(NO)_2\}^6$. This dinitrosyl species can be readily obtained from $Mo(CO)_6$ and NOCl. However, it is noticed that the synthesis of $[W(NO)_2Cl_2]_x$ just a kin to $[Mo(NO)_2Cl_2]_x$ is not smooth and it is difficult to isolate the tungsten analogue.5) For the corresponding hexacoordinated $[Mo(NO)_2Cl_2L_2]$ (L = monodentate N, P donors) all the different stereoisomers are formed which could be chromatographically separated.6) The use of these derivatives as olefin metathesis catalysts7) prompted us to develop an alternative easy route for the synthesis of these dinitrosyl derivatives.8) Herein we report the first case of reductive nitrosylation of tungstate(VI) using hydroxylamine to get stereospecific synthesis of cis-dichlorotrans-bis(pyridine)cis-dinitrosyltungsten(0) and the related 3-Mepy and 4-Mepy compounds.

In a typical experiment, sodium tungstate (1.0 g) and hydroxylamine hydrochloride (0.85 g) were taken in 30 ml of pyridine and the mixture was refluxed for 90 min. The initial vigorous reaction with the appearance of green colour finally changed to reddish brown. This mixture was acidified with concentrated hydrochloric acid (7 ml) and diluted with water (250 ml) and boiled for 30 min and was kept overnight. The yellow green solid separated out was filtered, washed with dilute hydrochloric acid, methanol and diethylether and dried. This crude was extracted with dichloromethane, and the extracts were taken to dryness in vacuo to give the pure green product. Yield: 0.12 g. Found: C, 25.48; H, 2.42; N, 11.80; Cl, 14.73%. Calcd. for $[W(NO)_2Cl_2(py)_2]$: C, 25.39; H, 2.11; N, 11.84; Cl, 14.99%. IR in CsI:

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$\nu$(NO)'s, 1760(vs), 1648(vs) $cm^{-1}$; $\nu$(W-Cl)'s, 310(m) and 287(m) $cm^{-1}$. The 3-Mepy and 4-Mepy derivatives were isolated by a similar procedure and the respective picoline was used instead of pyridine in these cases.

The infrared spectra of these compounds show two very strong bands in the region 1760-1640 $cm^{-1}$ suggesting the cis-attachment of the nitrosyl groups. The appearance of two $\nu$(W-Cl)'s in the range 320-280 $cm^{-1}$ proves that the chloro groups are located cis to each other. This is in accordance to the cis-chloro attachment of $[Mo(NO)_2Cl_2(PPh_3)_2]$ ($\nu$(Mo-Cl)'s at 346 and 318 $cm^{-1}$).[9] The presence of two N-donors either in cis or trans position has been tested chemically where the following reaction does not take place:

$$[W(NO)_2Cl_2(py)_2] + \text{o-phen} \not\longrightarrow [W(NO)_2Cl_2(\text{o-phen})] + py$$

All these three compounds give only one spot in TLC (in $CH_2Cl_2$/silica gel) suggesting the formation of only one isomer. Infrared spectra of these in $CH_2Cl_2$ show two sharp $\nu$(NO)'s without any splitting of the bands in each case. The $^1H$ NMR spectra of the compounds $[W(NO)_2Cl_2(4\text{-Mepy})_2]$ and $[W(NO)_2Cl_2(3\text{-Mepy})_2]$ in $D_2$-dichloromethane show only one methyl singlet at 2.68 ppm and 2.50 ppm relative to TMS, respectively. Thus the attachment of the N-donors is in trans-position to each other.

The fact that $CrO_4^{2-}$ or $MoO_4^{2-}$ reacts with $NH_2OH$ in varied pH in the presence of coligands to generate mononitrosyl moiety contrary to the $WO_4^{2-}$ system is noteworthy. However, for molybdenum the dinitrosylation step is followed after the mononitrosylation reaction.[8] The inability to isolate the corresponding mononitrosyl derivatives of tungsten depends on the specific methodology and work on this aspect is in progress.

## References

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