Thionitrosyl Complexes of Molybdenum

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Summary The molybdenum nitrido-complexes $[MoN(S_2CNR_2)_3]$ (R_2 = 2Me, 2Et, or $[CH_2]_5$) react with sulphur to give the thionitrosyl complexes $[Mo(NS)(S_2CNR_2)_3]$, in high yield; the sulphur can be removed by tributylphosphine to regenerate the nitrido-complexes.

THIOCARBONYL complexes of transition metals have recently been prepared from thiocarbonyl dichloride[1] but no thionitrosyl complexes are known, although NS^+ salts were reported in 1971[2] and its complexes could doubtless be prepared from them. We now report their preparation by the novel reaction of certain nitrido-complexes with sulphur as follows.

The nitrido-complexes $[MoN(S_2CNR_2)_3]$ (R_2 = 2Me,2Et, or $[CH_2]_5$) react with sulphur or propylene sulphide[3] in refluxing methyl cyanide to give the thionitrosyl complexes $[Mo(NS)(S_2CNR_2)_3]$ in 80—90% yield. The complex $[Mo(NS)(S_2CNMe_2)_3]$ can also be prepared in *ca.* 50% yield by the reaction of $[MoO_2(S_2CNMe_2)_2]$ with trimethylsilyl azide in the presence of tetramethylthiuram disulphide. This reaction presumably proceeds by initial formation of a nitrido-complex which then reacts with sulphur originating from the sulphur ligands.

The thionitrosyls are orange-red, air-stable, crystalline solids, monomeric in 1,2-dichloroethane solution. The ^1H n.m.r. spectrum of $[Mo(NS)(S_2CNMe_2)_3]$ in nitrobenzene at room temperature shows a 1 : 2 : 3 triplet (two overlapping doublets), consistent with a pentagonal bipyramidal structure with an apical NS. This triplet pattern is also observed at *ca.* 60° in the spectrum of the related complex, $[Mo(NO)(S_2CNMe_2)_3]$ in nitrobenzene, but at room temperature further splitting into a 1 : 2 : 1 : 2 quartet occurs.[4] The mass spectrum of $[Mo(NS)(S_2CNMe_2)_3]$ shows strong peaks around *m/e* 502 due to the parent ion, and also around *m/e* 456 corresponding to the formation of $[Mo(S_2CNMe_2)_3]^+$ by loss of NS. Appropriate peaks of metastable ions are also shown. The i.r. spectra of the thionitrosyls shows a very strong band at *ca.* 1100 cm^{-1} assigned to $\nu(N{-}S)$. Reaction of the thionitrosyls with tributylphosphine regenerates the nitrido-complexes in high yield, the reaction being monitored by disappearance of the N–S band at 1100 cm^{-1} and appearance of $\nu(Mo\equiv N)$ at *ca.* 1020 cm^{-1}.

The cleavage of cyclo-octasulphur to give the thionitrosyls suggests that the nitride ligands in $[MoN(S_2CNR_2)_3]$ are highly nucleophilic. Neither of the rhenium complexes, $[ReN(S_2CNEt_2)_2]$ or $[ReCl_2N(PMe_2Ph)_3]$, reacts to give the thionitrosyl with sulphur under the above reaction conditions, but the latter is certainly sufficiently nucleophilic to form weak complexes with boron halides or the $PtCl_2(PEt_3)$ unit.[5] On the other hand, the nitride ligand in $[MCl_3N(PMe_2Ph)_2]$ (M = Os or Ru) is definitely electrophilic, acting as an electron acceptor to form phosphiniminato-complexes with tertiary phosphines, *e.g.*, $[MCl_3(-N{=}PEt_2Ph)(PEt_2Ph)_2]$.[6]

It is interesting that the nucleophilicity of the nitride ligands in the above complexes appears to fall in the sequence Mo > Re > Os. Although the complexes from each Group are not strictly comparable, the trend in nucleophilicity is so marked that it may be general.

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