Rhenium and Osmium Thionitrosyl Complexes

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Summary The rhenium(v) and osmium(vi) nitrido-complexes, $[ReNX_2(PR_3)_2]$ (X = Cl or Br; PR_3 = PMe_2Ph, $PMePh_2$, or PEt_2Ph) and $[OsNX_3L_2]$ (X = Cl, L_2 = $2PMe_2Ph$, $2AsPh_3$, or bipy; X = Br, L_2 = $2AsPh_3$ or bipy), react with disulphur dichloride to give the thionitrosyl complexes $[ReClX(NS)(PR_3)_3]$ and $[OsClX_2(NS)L_2]$ respectively, whereas an excess of disulphur dichloride with the nitrides $[ReNCl_2(PR_3)_3]$ gives the rhenium(III) derivatives $[ReCl_3(NS)(PR_3)_2]$.

WE recently reported[1] that the reaction of elemental sulphur or propylene sulphide with some molybdenum nitrido-complexes gave thionitrosyl complexes. Rhenium and osmium nitrido-complexes did not react with either of those sulphur reagents, but with S_2Cl_2 they have given a number of thionitrosyl complexes in good yields.

The nitrides $[ReNX_2(PR_3)_3]$ (X = Cl or Br; PR_3 = PMe_2Ph, $PMePh_2$, or PEt_2Ph) react with 0·5 equiv. of S_2Cl_2 in CH_2Cl_2 at room temperature to give the thionitrosyl complexes $[ReClX(NS)(PR_3)_3]$ (I) (*ca.* 90%). Under similar conditions cationic $[ReClN(dpe)_2]^+$ (dpe = $Ph_2PCH_2CH_2PPh_2$)[2] gives $[ReCl(NS)(dpe)_2]Cl$. The osmium nitrido-complexes $[OsNX_3L_2]$[3] (X = Cl, L_2 = $2PMe_2Ph$, $2AsPh_3$, or bipy; X = Br, L_2 = $2AsPh_3$ or bipy) react analogously to give $[OsClX_2(NS)L_2]$.

TABLE

Complex		Colour	M.p./°C[a]	ν(N–S)/ cm^{-1} [b]
$[ReCl_2(NS)(PMe_2Ph)_3]$	..	Pink	166—167	1180
$[ReCl_2(NS)(PMePh_2)_3]$	..	Pink	160—162	1172
$[ReCl(NS)(Ph_2PCH_2CH_2PPh_2)_2]Cl$	..	Yellow	202—204	1185
$[ReCl_3(NS)(PMe_2Ph)_2]$	..	Purple	172—174	1228
$[ReCl_3(NS)(PMePh_2)_2]$	..	Purple	176—178	1220
$[OsCl_3(NS)(PMe_2Ph)_2]$	..	Green	189—192	1285
$[OsCl_3(NS)(AsPh_3)_2]$ ..	..	Green	138—141	1282

[a] With decomposition. [b] Recorded as Nujol mulls.

The mechanism of formation of the thionitrosyls is not known, but when X = Br, the chlorine originally attached to the sulphur becomes bound to the metal, apparently displacing a bromine atom. The fate of this expelled halogen has not been determined but we found no evidence for the formation of the tertiary phosphine dihalide.

The rhenium thionitrosyl complexes (I) are all air-stable, diamagnetic, crystalline solids with strong bands at *ca.* 1180 cm^{-1} in their i.r. spectra assigned to ν(N–S). Treatment of $[ReCl_2(NS)(PMe_2Ph)_3]$ with an excess of dpe under reflux in benzene results in loss of the thionitrosyl sulphur and formation of $[ReClN(dpe)_2]Cl$ in high yield. The ^1H n.m.r. spectrum of $[ReCl_2(NS)(PMe_2Ph)_3]$ in $CDCl_3$ shows a pair of triplets and a doublet in the phosphine methyl region, confirming that the complex has the same meridional configuration as the parent nitrido-complex.

The nitrido-complexes $[ReNCl_2(PR_3)_3]$ react with an excess of S_2Cl_2 to give the trichloro-rhenium thionitrosyl complexes $[ReCl_3(NS)(PR_3)_2]$ (II) (*ca.* 70%) and $[ReNCl_2(PPh_2Pr^n)_2]$ reacts with 0·5 equiv. of S_2Cl_2 to give the analogous trichloro-rhenium thionitrosyl complex (*ca* 90%). The complexes (II) are isolated as paramagnetic (μ_{eff} 1·8—1·9 B.M.) crystalline solids with ν(N–S) in the range 1220—1230 cm^{-1} in their i.r. spectra.

The neutral rhenium thionitrosyls are analogous to the recently reported[4] nitrosyls $[ReCl_2(NO)(PR_3)_3]$ and $[ReCl_3(NO)(PR_3)_2]$. The nitrosyl analogue of $(ReCl(NS)(dpe)_2]Cl$ has not been prepared. An *X*-ray crystal structure of $[ReCl_2(NO)(PMe_2Ph)_3]$ shows that the Re–N–O system is linear[5] and doubtless the Re–N–S systems above are also linear with the thionitrosyl ligand as a three electron-donor.

Some physical properties of representative complexes of the above types are given in the Table.

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