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Thionitrosyl Complexes of Molybdenum, Rhenium, and Osmium

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The molybdenum nitrido-complexes $[MoN(S_2CNR_2)_3]$ react with elemental sulphur or propylene sulphide to give the thionitrosyl complexes $[Mo(NS)(S_2CNR_2)_3]$ in high yield. The rhenium nitrido-complexes $[ReX_2N(PR_3)_3]$ (PR_3 = PMe_2Ph, PEt_2Ph, or $PMePh_2$; X = Cl or Br) react with half an equivalent of S_2Cl_2 to give the pink thionitrosyl complexes $[ReCl(X)(NS)(PR_3)_3]$ in yields of 60—70%. Use of an excess of S_2Cl_2 gives the purple complexes $[ReCl_2X(NS)(PR_3)_2]$ in good yields. The five-co-ordinate nitrido-complexes $[ReCl_2N(PRPh_2)_2]$ (R = Ph or Pr^n) also give $[ReCl_3(NS)(PRPh_2)_2]$ on reaction with half an equivalent of S_2Cl_2. The osmium nitrido-complexes $[OsX_3NL_2]$ [L = $AsPh_3$, PMe_2Ph, $\frac{1}{2}$ bipy (2,2′-bipyridyl), or py (pyridine); X = Cl or Br] react analogously with S_2Cl_2 to give $[OsClX_2(NS)L_2]$. ν(N–S) appears in the i.r. spectra in the range 1 120—1 280 cm^{-1}, and the ^1H n.m.r. spectra of the diamagnetic complexes show the phosphines to be *mer* in $[ReCl_2(NS)(PR_3)_3]$ and *trans* in $[OsCl_3(NS)(PMe_2Ph)_2]$. Treatment of the thionitrosyls with tertiary phosphines regenerates the parent nitrido-complexes in high yields.

ALTHOUGH there is an extensive chemistry of nitrosyl complexes, this is the first detailed account of any thionitrosyl complexes. Whereas nitrosyl complexes are readily preparable from NO gas, nitrosyl chloride, NOCl, or nitrosonium salts, no analogous sulphur precursors are available. Nitrogen sulphide is unknown as a monomer, and thionitrosyl fluoride NSF is extremely unstable, trimerizing at −80 °C to $(NSF)_3$.[1] Other thionitrosyl halides are even less stable as monomers.[2] Salts of the thionitrosyl cation $[NS]^+$ have been prepared by reaction of NSF with AsF_5,[3] but have not been utilized to prepare thionitrosyl complexes. We now give full details of the preparation of series of thionitrosyl complexes of molybdenum, rhenium, and osmium by reaction of nitrido-complexes with elemental sulphur or with sulphur halides, as briefly reported elsewhere.[4,5]

RESULTS AND DISCUSSION

Preparation of Thionitrosyl Complexes.—Molybdenum. While trying to find an alternative route for the preparation of dithiocarbamato-nitrido-complexes, the dioxo-complex $[MoO_2(S_2CNMe_2)_2]$ was treated with trimethylsilyl azide, $SiMe_3(N_3)$, in acetonitrile under reflux. Unexpectedly, the thionitrosyl complex $[Mo(NS)(S_2CNMe_2)_3]$ was obtained in low yield, although this could be increased to *ca.* 50% by addition of half an equivalent of tetramethylthiuram disulphide. It seemed likely that this reaction proceeded *via* intermediate formation of a nitrido-complex, and in substantiation the nitrido-complexes $[MoN(S_2CNR_2)_3]$ [R_2 = Me_2, Et_2, or $(CH_2)_5$] were found to react with elemental sulphur in refluxing acetonitrile to give the same thionitrosyl complexes. It was subsequently found that improved yields (70—80%) could be obtained using propylene sulphide. The thionitrosyls prepared in this way are listed in Table 1. Although, as indicated below, some rhenium and osmium nitrido-complexes react with disulphur dichloride to give thionitrosyl complexes, the molybdenum complexes $[MoN(S_2CNR_2)_3]$ do not give thionitrosyls under analogous conditions, but uncharacterized oily products.

Rhenium and osmium. Attempts to prepare thionitrosyl complexes of rhenium and osmium by reactions of nitrido-complexes with sulphur or propylene sulphide were unsuccessful. However, the complexes, $[ReX_2N(PR_3)_3]$ (PR_3 = PMe_2Ph, PEt_2Ph, or $PMePh_2$; X = Cl or Br) reacted with half an equivalent of S_2Cl_2 to give the thionitrosyls $[ReCl(X)(NS)(PR_3)_3]$ in yields of 85—95%. Reaction of the nitrido-complexes $[ReCl_2N(PR_3)_3]$ with an excess of S_2Cl_2 or SCl_2 gave the derivatives $[ReCl_3(NS)(PR_3)_2]$ in *ca.* 60% yield. The rhenium thionitrosyl complexes $[ReCl_3(NS)(PRPh_2)_2]$ (R = Ph or Pr^n) could also be obtained in high yield by reaction of the five-co-ordinate $[ReCl_2N(PRPh_2)_2]$ with half an equivalent of S_2Cl_2.

Osmium thionitrosyl complexes were prepared analogously by reaction of $[OsX_3NL_2]$ [L = $AsPh_3$, PMe_2Ph, or $\frac{1}{2}$ bipy (2,2′-bipyridyl)] with half an equivalent of S_2Cl_2. The salt $[NBu_4][OsCl_4N]$ also reacts with S_2Cl_2 to give a pink product which, although showing i.r. bands assignable to ν(N–S), could not be fully characterized. However, addition of pyridine (py) to a methylene chloride solution of the pink product gave green [$OsCl_3(NS)(py)_2$] in *ca.* 50% yield.

Table 1

Thionitrosyl complexes of molybdenum, rhenium, and osmium

	Complex	Colour	Analysis[a] (%) C	H	N	Halogen	S	$\mu_{eff.}$[b]/ B.M.	M[a]	ν(N–S)/ cm^{-1}
(1)	[$Mo(NS)(S_2CNMe_2)_3$]	Yellow	21.5 (21.5)	3.6 (3.6)	11.2 (11.2)		44.6 (44.7)	D	521 (502)	
(2)	[$Mo(NS)(S_2CNEt_2)_3$]	Yellow	31.1 (30.7)	5.6 (5.1)	9.6 (9.5)			D		
(3)	[$Mo(NS)\{S_2CN(CH_2)_4\}_3$]	Yellow	31.3 (31.0)	4.2 (4.1)	9.8 (9.7)			D	568 (580)	
(4)	[$ReCl_2(NS)(PMe_2Ph)_3$]	Pink	40.5 (40.2)	4.7 (4.6)	2.1 (2.0)			D		1 180
(5)	[$ReCl_2(NS)(PEt_2Ph)_3$]	Pink	45.5 (45.0)	5.8 (5.6)	1.8 (1.8)	10.5 (8.9)		D	787 (801)	1 167
(6)	[$ReCl_2(NS)(PMePh_2)_3$]	Pink	51.7 (51.8)	4.3 (4.3)	1.8 (1.6)			D	840 (903)	1 172
(7)	[$ReBr(Cl)(NS)(PEt_2Ph)_3$]	Pink	42.2 (42.6)	5.1 (5.3)	1.7 (1.7)	9.5 (Br) (9.5)		D		1 168
(8)	[$ReCl(SCN)(NS)(PMe_2Ph)_3$]	Red-pink	40.7 (40.6)	4.5 (4.5)	4.0 (3.8)	5.3 (4.8)		D		1 177
(9)	[$ReCl(NS)(S_2CNMe_2)(PMe_2Ph)_2$]	Yellow-brown	33.9 (34.4)	4.1 (4.2)	4.4 (4.2)	5.8 (5.4)		D	628 (664)	1 150
(10)	[$ReCl(NS)(dppe)_2$]Cl	Yellow	56.1 (56.7)	4.6 (4.4)	1.3 (1.3)			D		1 185
(11)	[$ReCl(NS)(dppe)_2$][PF_6]	Yellow	52.1 (51.7)	4.1 (4.0)	1.3 (1.2)	3.3 (2.9)		D		1 177
(12)	[$ReCl(NS)(dppe)_2$][$FeCl_4$]	Yellow	49.6 (49.5)	4.0 (3.8)	1.3 (1.1)	14.4 (14.1)		D		1 173
(13)	[$ReCl(NS)(dppe)_2$][S_2CNEt_2]	Yellow	55.8 (56.4)	5.0 (4.8)	2.5 (2.3)			D		1 183
(14)	[$ReCl_3(NS)(PMe_2Ph)_2$]	Purple	31.7 (31.2)	3.7 (3.6)	2.5 (2.3)	17.5 (17.3)	5.5 (5.2)	1.84		1 228
(15)	[$ReCl_3(NS)(PEt_2Ph)_2$]	Purple	35.9 (35.9)	4.4 (4.5)	2.1 (2.1)	16.8 (15.9)		1.86	705 (670)	1 230
(16)	[$ReCl_3(NS)(PMePh_2)_2$]	Purple	42.2 (42.3)	3.5 (3.5)	1.8 (1.9)	14.8 (14.4)	5.4 (4.3)	2.01	754 (739)	1 220
(17)	[$ReCl_3(NS)(PPh_3)_2$]	Purple	50.6 (50.1)	5.2 (3.5)	1.5 (1.6)			1.84	826 (795)	1 214
(18)	[$ReCl_3(NS)(PPr^nPh_2)_2$]	Purple	45.2 (45.3)	4.5 (4.3)	1.9 (1.8)	14.4 (13.5)		1.81		1 226
(19)	[$OsCl_3(NS)(AsPh_3)_2$]	Green	44.9 (45.3)	3.1 (3.1)	1.6 (1.5)		2.8 (3.4)	D	800 (954)	1 282
(20)	[$OsCl_3(NS)(PMe_2Ph)_2$]	Green	31.9 (31.1)	3.8 (3.6)	2.3 (2.3)			D	686 (619)	1 285
(21)	[$OsCl_3(NS)(bipy)$)]	Green	24.1 (24.4)	1.6 (1.6)	7.9 (8.4)	20.0 (21.4)	6.2 (6.4)	D		1 282
(22)	[$OsCl_3(NS)(py)_2$]	Yellow-green	23.4 (24.0)	2.2 (2.0)	8.2 (8.4)			D		1 284
(23)	[$OsBr_2Cl(NS)(AsPh_3)_2$]	Green	41.2 (41.4)	3.3 (2.9)	1.4 (1.3)			D		1 270
(24)	[$OsBr_2Cl(NS)(bipy)$)]	Green	19.8 (20.3)	1.4 (1.4)	6.4 (7.1)			D		1 280

[a] Calculated values are given in parentheses. [b] D = Diamagnetic.

The mechanism of formation of the thionitrosyl from nitride and S_2Cl_2 is at present unknown, and a puzzling feature is the overall loss of a halogen atom as illustrated in equation (1). Observed yields (80—90%) suggest

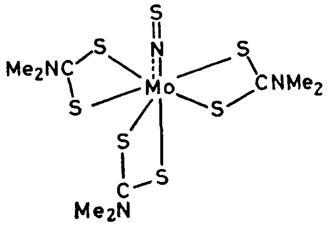
$$[ReCl_2N(PR_3)_3] + 0.5\ S_2Cl_2 \longrightarrow [ReCl_2(NS)(PR_3)_3] + \text{' Cl '} \quad (1)$$

that halogen is not removed at the expense of co-ordinated phosphine, and, indeed, attempts to identify phosphine halides in the reaction mixtures by ^{31}P n.m.r. spectroscopy failed. The preparation of [$ReBr(Cl)(NS)(PEt_2Ph)_3$] from [$ReBr_2N(PEt_2Ph)_3$] shows that in this instance the halogen originally bound to sulphur becomes attached to the metal. Reaction of the five-co-ordinate complexes [$ReCl_2N(PRPh_2)_2$] with S_2Cl_2 to give [$ReCl_3(NS)(PRPh_2)_2$] does not present the same problem since all the halogen atoms are accounted for. This suggests that the S_2Cl_2 is subject to nucleophilic attack at the sulphur atom by the nitride ligand leading to the group M=N–S–Cl which rearranges to ClM–N=S, but the detailed course of the reaction is still unknown.

Metathetical reactions were used to prepare [$ReCl(NCS)(NS)(PMe_2Ph)_3$] and [$ReCl(NS)(PMe_2Ph)_2(S_2CNMe_2)$] from [$ReCl_2(NS)(PMe_2Ph)_3$] and K[CNS] or Na[$S_2CNMe_2$] respectively. The complex [$ReCl(NS)(dppe)_2$]Cl {prepared from [$ReCl(N)(dppe)_2$]Cl (dppe = $Ph_2PCH_2CH_2PPh_2$) and S_2Cl_2} could be readily converted into the [$FeCl_4$]$^-$ or [PF_6]$^-$ salts by reaction with $FeCl_3$ or [NH_4][PF_6] respectively. But attempts to induce seven-co-ordination at Re and hence bending of the NS ligand by reaction with Na[S_2CNEt_2] gave only the salt [$ReCl(NS)(dppe)_2$][S_2CNEt_2].

The rhenium and osmium complexes prepared as above are listed in Table 1.

Properties of Thionitrosyl Complexes.—Molybdenum. The complexes $[Mo(NS)(S_2CNR_2)_3]$ are yellow, stable in air, diamagnetic, and crystalline, being monomeric and non-conducting in 1,2-dichloroethane solution. The structure of $[Mo(NS)(S_2CNMe_2)_3]$ has been determined by *X*-ray crystallography [6] and is shown schematically in (I). Full details of the structure will be published elsewhere. The molybdenum has essentially pentagonal-bipyramidal co-ordination with the NS ligand in an apical position. The Mo–N–S angle is 172° suggesting that the NS ligand is functioning as a three-electron donor.



(I)

TABLE 2

Hydrogen-1 n.m.r. spectra of thionitrosyl complexes

Complex	Tertiary phosphine protons		Dithiocarbamate alkyl groups
	alkyl [a]	phenyl	
(1)			3.16 (t, 1 : 2 : 3) [b]
(2)			1.32 (t, 18), 3.82 (q, 12) [c]
(4)	2.00 [t, 6, $\|^4J(PH) + {}^2J(PH)\|$ 4.3] 1.84 [t, 6, $\|^4J(PH) + {}^2J(PH)\|$ 4.3] 1.36 [d, 6, $\|^2J(PH)\|$ 9.5]	7.0—7.5 (m, 15)	
(5)	0.5—3.0 (m, 15)	6.95—7.5 (m, 15)	
(6)	2.16 [t, 6, $\|^4J(PH) + {}^2J(PH)\|$ 4.2] 1.81 [d, 3, $\|^2J(PH)\|$ 9.0]	7.0—7.6 (m, 30)	
(9)	1.82 [d, 6, $\|^2J(PH)\|$ 9] 1.80 [d, 6, $\|^2J(PH)\|$ 9]	7.3—7.7 (m, 10)	3.28 (s, 6)
(11)	2.6—3.2 (m, 8)	6.9—7.5 (m, 40)	
(13)	2.6—3.2 (m, 8)	6.9—7.5 (m, 40)	4.18 (q, 4), 1.17 (t, 6)
(20)	2.08 [t, 12, $\|^4J(PH) + {}^2J(PH)\|$ 4.5]	7.3—7.7 (m, 10)	

[a] Values in p.p.m. (*J* in Hz) relative to tetramethylsilane, in deuteriochloroform unless otherwise stated; integrated values and multiplicities are in parentheses. t = Triplet, q = quartet, s = singlet, and m = multiplet. [b] In nitrobenzene solution. [c] In dideuteriodichloromethane solution.

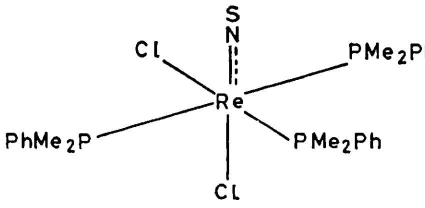
The ^1H n.m.r. spectrum of $[Mo(NS)(S_2CNMe_2)_3]$ in nitrobenzene at room temperature shows a 1 : 2 : 3 triplet (two overlapping doublets) due to the dithiocarbamate methyl groups. The collapse of the triplet into a broad singlet on warming indicates that the molecule becomes fluxional. This behaviour is typical of a series of complexes of the type $[MoY(S_2CNR_2)_3]$ (Y = Cl, N, N_2Ph, N_2COPh, NS, or NO), and the degree of fluxionality is a complex function of the nature of the ligand in the apical site.[7] The full results of a detailed study of this will be reported elsewhere.

The mass spectra of complexes (1)—(3) all show peaks attributable to the parent ions, together with ones assigned to $[Mo(S_2CNR_2)_3]^+$ and $[MoS(S_2CNR_2)_2]^+$.

Rhenium. The complexes $[ReCl(X)(NS)(PR_3)_3]$ are pink, diamagnetic, and stable in air, being monomeric and non-electrolytes in 1,2-dichloroethane. The salts $[ReCl(NS)(dppe)_2]A$ (A = Cl, $FeCl_4$, or PF_6) are yellow and have conductivities in nitrobenzene typical of 1 : 1 electrolytes. The i.r. spectra show strong sharp bands in the 1 167—1 185 cm^{-1} region assigned to ν(N–S). Medium-intensity i.r. bands in the 200—400 cm^{-1} region are tentatively assigned to ν(Re–Cl) (see Table 1).

The ^1H n.m.r. spectra of the pink rhenium thionitrosyls are summarized in Table 2. The spectrum of $[ReCl_2(NS)(PEt_2Ph)_3]$ in the tertiary-phosphine alkyl-group region is too complex to interpret, but $[ReCl_2(NS)(PMe_2Ph)_3]$ shows two triplets and a doublet in this region, indicating a ***meridional*** configuration (II) for the phosphine ligands with the NS group *trans* to Cl. An *X*-ray crystal-structure analysis of the analogous nitrosyl complex $[ReCl_2(NO)(PMe_2Ph)_3]$ shows the M–N–O system to be essentially linear with Re–N–O 178.8 (1.4)°.[8] It is therefore extremely likely that the thionitrosyl analogues are isostructural with linear NS groups.

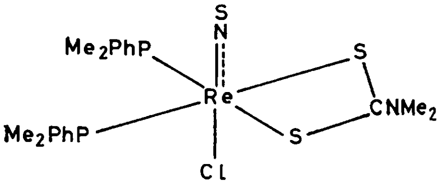
The dithiocarbamate methyl groups of $[ReCl(NS)(S_2CNMe_2)(PMe_2Ph)_2]$ appear as a singlet in the ^1H n.m.r. spectrum. This persists even at low temperatures. The tertiary-phosphine alkyl protons appear as a pair of doublets. Assuming that exchange processes are not responsible for the equivalence of the dithiocarbamate alkyl groups, this indicates the configuration (III). The ^{31}P n.m.r. spectra of $[ReCl(N)(dppe)_2]Cl$ and $[ReCl(NS)(dppe)_2]Cl$ both show a singlet at *ca.* 120 p.p.m. (relative to H_3PO_4) confirming that the four phosphorus atoms lie in the plane with the NS and Cl in *trans* positions.



(II)

The rhenium thionitrosyl complexes $[ReCl_3(NS)(PR_3)_2]$ are purple air-stable crystalline products and those investigated were found to be both monomeric and non-conducting in 1,2-dichloroethane solution.

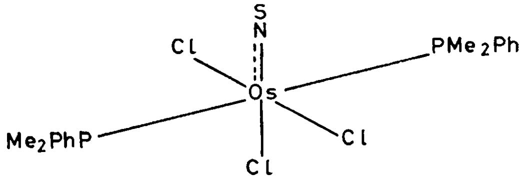
The complexes are paramagnetic with magnetic moments in the range 1.84—2.01 B.M.,* the values being very close to that found for the analogous complex $[ReCl_3(NO)(PMe_2Ph)_2]$.



(III)

Osmium. The osmium thionitrosyl complexes are isolated as green, diamagnetic, air-stable crystalline solids, which where solubility permitted were found to be monomeric and non-conducting in 1,2-dichloroethane solution. ν(N–S) was observed in the i.r. in the range 1 270—1 282 cm^{-1} and one, two, or three medium-intensity i.r. bands in the 200—300 cm^{-1} region were tentatively assigned to ν(Os–Cl).

The insolubility of the complexes generally precludes ^{1}H n.m.r., but the spectrum of $[OsCl_3(NS)(PMe_2Ph)_2]$ (Table 2) shows a triplet due to the tertiary-phosphine methyl groups. This is consistent with the configuration (IV) with *trans* virtually-coupled phosphorus ligands.



(IV)

Reactions of the Thionitrosyl Ligand.—The thionitrosyl complexes were desulphurized by PBu^n_3 in refluxing toluene or acetonitrile to give nearly quantitative yields of the parent nitrido-complex. The thionitrosyl sulphur in the complexes $[Mo(NS)(S_2CNR_2)_3]$ can also be alkylated with triphenylmethyl tetrafluoroborate to give $[Mo(NSCPh_3)(S_2CNR_2)_3][BF_4]$. Analogous products can be prepared by reaction of the complexes $[MoN(S_2CNR_2)_3]$ with sulphenyl halides.[9]

EXPERIMENTAL

The following complexes were prepared by published methods: $[MoN(S_2CNR_2)_3]$ [R_2 = Me$_2$, Et$_2$, or $(CH_2)_4$],[10] $[ReCl_2N(PRPh_2)_2]$ (R = Ph or Pr^n),[11] $[ReCl_2N(PR_3)_3]$ (PR_3 = PMe_2Ph or $PMePh_2$),[11] $[ReCl(N)(dppe)_2]Cl$,[12] $[OsCl_3N(AsPh_3)_2]$,[13] $[OsCl_3N(bipy)]$,[13] $[NBu^n_4][OsCl_4N]$,[13] and $[OsCl_3N(PMe_2Ph)_2]$.[13]

Elemental analyses were performed by Mr. and Mrs. A. G. Olney (C, H, and N) at the University of Sussex and the Dr. A. Bernhardt Microanalytical Laboratories, West Germany (S). Molecular weights were determined in 1,2-dichloroethane solution using a Hitachi–Perkin-Elmer model 115 osmometer, and conductivities in 1,2-dichloroethane or nitrobenzene solution with a Portland Electronics conductivity bridge. Magnetic moments were measured at room temperature using a Faraday balance calibrated against mercury cobalt thiocyanate. Infrared spectra were recorded on a Pye-Unicam SP 2000 spectrometer as Nujol mulls with KBr plates in the range 500—4 000 cm^{-1} and Polythene plates for the range 200—500 cm^{-1}. Hydrogen-1 n.m.r. spectra were obtained on a JEOL PS100 spectrometer at 100 MHz using tetramethylsilane as internal standard.

All the reactions were carried out under dinitrogen using dry solvents. Recrystallizations, unless otherwise indicated, were performed with reagent-grade solvents in the air.

Tris(dimethyldithiocarbamato)(thionitrosyl)molybdenum, $[Mo(NS)(S_2CNMe_2)_3]$ (1).—(*a*) Tris(dimethyldithiocarbamato)nitridomolybdenum (0.5 g) and elemental sulphur (0.5 g) were heated under reflux in acetonitrile (35 cm^3) for 0.5 h. The resulting yellow-brown solution was filtered while hot to remove residual sulphur and evaporated to near dryness at 10^{-2} Torr. The residue was triturated with methanol (30 cm) and recrystallized from dichloromethane–methanol to give the complex as orange-yellow prisms (0.35 g, 74%). Use of propylene sulphide (1—2 equivalents) in place of elemental sulphur in the above reaction improves the yield to *ca*. 80%, and the intermediate filtration is not necessary.

(*b*) Bis(dimethyldithiocarbamato)dioxomolybdenum(VI) (0.60 g, 1.6 mmol), tetramethylthiuram disulphide (0.19 g, 0.8 mmol), and trimethylsilyl azide (0.20 g, 1.7 mmol) were heated under reflux in dry acetonitrile (35 cm^3) for 0.5 h. The resulting yellow-brown solution was evaporated to *ca*. 10 cm^3 *in vacuo* at 10^{-2} Torr and the *complex* precipitated as a brown-yellow solid, recrystallized as above in *ca*. 50% yield.

Tris(diethyldithiocarbamato)(thionitrosyl)molybdenum, $[Mo(NS)(S_2CNEt_2)_3]$ (2), and *tris(tetramethylenedithiocarbamato)(thionitrosyl)molybdenum*, $[Mo(NS)\{S_2CN(CH_2)_4\}_3]$ (3), were prepared analogously to (1) above using method (a) from $[MoN(S_2CNEt_2)_3]$ and $[MoN\{S_2CN(CH_2)_4\}_3]$, respectively.

Dichlorotris(dimethylphenylphosphine)(thionitrosyl)rhenium, $[ReCl_2(NS)(PMe_2Ph)_3]$ (4).—Disulphur dichloride (0.033 cm^3, 0.43 mmol) was added to a solution of dichloronitridotris(dimethylphenylphosphine)rhenium(V) (0.50 g, 0.84 mmol) in dichloromethane (30 cm^3) and the solution stirred at room temperature for 0.5 h. The resulting pink solution was evaporated *in vacuo* at 10^{-2} Torr and the residue recrystallized as pink needles from 1,2-dichloroethane–pentane (0.45 g, 84%).

The following complexes were prepared analogously to (4) using the appropriate nitrido-complex: *dichlorotris(diethylphenylphosphine)(thionitrosyl)rhenium*, $[ReCl_2(NS)(PEt_2Ph)_3]$ (5), from $[ReCl_2N(PEt_2Ph)_3]$ (0.58 g) and S_2Cl_2 (0.033 cm^3) in dichloromethane as pink needles (0.52 g, 86%); *dichlorotris(methyldiphenylphosphine)(thionitrosyl)rhenium*, $[ReCl_2(NS)(PMePh_2)_3]$ (6), from $[ReCl_2N(PMePh_2)_3]$ and S_2Cl_2 as pink needles (76%); and *bromochlorotris(diethylphenylphosphine)(thionitrosyl)rhenium*, $[ReBr(Cl)(NS)(PEt_2Ph)_3]$ (7), from $[ReBr_2N(PEt_2Ph)_3]$ and S_2Cl_2 as pink needles (87%).

Chlorotris(dimethylphenylphosphine)isothiocyanato(thionitrosyl)rhenium, $[ReCl(NCS)(NS)(PMe_2Ph)_3]$ (8).—Complex (4) (0.3 g) and Na[NCS] (0.3 g) were heated under reflux in methanol (40 cm^3) for 1 h. The resulting reddish pink solution was evaporated at 10^{-2} Torr and the resulting

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* Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^2; 1 Torr = (101 325/760) Pa.

residue recrystallized from 1,2-dichloroethane–diethyl ether as pink-red plates (0.26 g, 84%).

Chloro(diethyldithiocarbamato)bis(dimethylphenylphosphine)(thionitrosyl)rhenium, [ReCl(NS)(S$_2$CNMe$_2$)(PMe$_2$Ph)$_2$] (9).—Complex (4) (0.4 g) and Na[S$_2$CNMe$_2$]·3H$_2$O (0.5 g) were heated under reflux in acetone (30 cm^3) for 1.5 h. The hot solution was filtered and evaporated at 10^{-2} Torr. The resulting residue was recrystallized from 1,2-dichloroethane–hexane as yellow-brown plates (0.20 g, 61%).

Bis[1,2-bis(diphenylphosphino)ethane]chloro(thionitrosyl)rhenium Chloride, [ReCl(NS)(dppe)$_2$]Cl (10).—Disulphur dichloride (0.1 cm^3) was added to a solution of [ReCl(N)(dppe)$_2$]Cl (0.4 g) in dichloromethane (20 cm^3) and stirred for 2 h at room temperature. The solvent was evaporated at 10^{-2} Torr and the residue recrystallized from 1,2-dichloroethane–diethyl ether as small yellow needles (0.33 g, 80%).

Bis[1,2-bis(diphenylphosphino)ethane]chloro(thionitrosyl)rhenium Hexafluorophosphate, [ReCl(NS)(dppe)$_2$][PF$_6$] (11).—Complex (10) (0.35 g) in methanol (60 cm^3) was added with stirring to a solution of [NH$_4$][PF$_6$] (0.5 g) in water (10 cm^3). The complex precipitated from solution as yellow needles (0.31 g, 81%).

Bis[1,2-bis(diphenylphosphino)ethane]chloro(thionitrosyl)rhenium Tetrachloroferrate(III), [ReCl(NS)(dppe)$_2$][FeCl$_4$] (12).—Complex (10) (0.2 g) in warm ethanol (15 cm^3) was added with stirring to a solution of iron(III) chloride (0.2 g) in water (10 cm^3), precipitating the complex as yellow needles (0.22 g, 95%).

Bis[1,2-bis(diphenylphosphino)ethane]chloro(thionitrosyl)rhenium Diethyldithiocarbamate, [ReCl(NS)(dppe)$_2$][S$_2$CNEt$_2$] (13).—Complex (10) (0.3 g) and Na[S$_2$CNEt$_2$] (0.3 g) were heated under reflux in acetone (30 cm^3) for 1.5 h. The solvent was evaporated at 10^{-2} Torr, and the residue recrystallized from 1,2-dichloroethane–diethyl ether as yellow-orange plates (0.24 g, 72%).

Trichlorobis(dimethylphenylphosphine)(thionitrosyl)rhenium, [ReCl$_3$(NS)(PMe$_2$Ph)$_2$] (14).—Disulphur dichloride (0.1 cm^3) was added to a solution of [ReCl$_2$N(PMe$_2$Ph)$_3$] in dichloromethane (40 cm^3) and the resulting pink-purple solution stirred for 1 h. The solvent was evaporated at 10^{-2} Torr to 5 cm^3 and the complex precipitated by the addition of pentane (60 cm^3). The product was recrystallized from 1,2-dichloroethane–diethyl ether as purple needles (0.10 g, 53%).

Trichlorobis(diethylphenylphosphine)(thionitrosyl)rhenium, [ReCl$_3$(NS)(PEt$_2$Ph)$_2$] (15), and *trichlorobis(methyldiphenylphosphine)(thionitrosyl)rhenium*, [ReCl$_3$(NS)(PMePh$_2$)$_2$] (16), were prepared analogously from S$_2$Cl$_2$ and [ReCl$_2$N(PEt$_2$Ph)$_3$] and [ReCl$_2$N(PMePh$_2$)$_3$], respectively.

Trichloro(thionitrosyl)bis(triphenylphosphine)rhenium, [ReCl$_3$(NS)(PPh$_3$)$_2$] (17).—Disulphur dichloride (0.033 cm^3) was added to a suspension of [ReCl$_2$N(PPh$_3$)$_2$] (0.6 g) in dichloromethane (40 cm^3) and the resulting red-black solution stirred for 1.5 h. The solvent was evaporated at 10^{-2} Torr and the residue crystallized from acetone by slow evaporation of the solvent as purple-black plates (0.36 g, 55%).

Trichlorobis(n-propyldiphenylphosphine)(thionitrosyl)rhenium, [ReCl$_3$(NS)(PPr^{n}Ph$_2$)$_2$] (18).—This was prepared analogously to (17) from [ReCl$_2$N(PPr^{n}Ph$_2$)$_2$] and S$_2$Cl$_2$ as green-purple needles (89%).

Trichloro(thionitrosyl)bis(triphenylarsine)osmium, [OsCl$_3$(NS)(AsPh$_3$)$_2$] (19).—Disulphur dichloride (0.2 cm^3) was added slowly to a suspension of [OsCl$_3$N(AsPh$_3$)$_2$] (0.3 g) in dry dichloromethane (30 cm^3). The yellow-brown solution was stirred at room temperature for 3 h, the solvent evaporated at 10^{-2} Torr, and the residue recrystallized from 1,2-dichloroethane–hexane as fine green needles (0.22 g, 71%).

Trichlorobis(dimethylphenylphosphine)(thionitrosyl)osmium, [OsCl$_3$(NS)(PMe$_2$Ph)$_2$] (20), was prepared analogously to (19) from S$_2$Cl$_2$ and [OsCl$_3$N(PMe$_2$Ph)$_2$], and recrystallized from 1,2-dichloroethane–pentane as green plates (0.14 g, 63%).

2,2′-Bipyridyltrichloro(thionitrosyl)osmium, [OsCl$_3$(NS)(bipy)] (21).—Disulphur dichloride (0.2 cm^3) was added to [OsCl$_3$N(bipy)] (0.3 g) in dichloromethane (30 cm^3) and the suspension stirred at room temperature for 10 h. The complex was obtained as a green precipitate which was washed successively with methanol, acetone, and diethyl ether (0.27 g, 85%).

Trichlorobis(pyridine)(thionitrosyl)osmium, [OsCl$_3$(NS)(py)$_2$] (22).—Disulphur dichloride (0.2 cm^3) was added to a solution of [NBu$^n{}_4$][OsCl$_4$N] (0.2 g) in dichloromethane (25 cm^3) and the pink solution was stirred at room temperature for 4 h. Pyridine (2 cm^3) was added to give a green solution which was evaporated to dryness at 10^{-2} Torr, and the residue recrystallized as yellow-green needles from 1,2-dichloroethane–pentane (0.09 g, 53%).

Dibromochloro(thionitrosyl)bis(triphenylarsine)osmium, [OsBr$_2$Cl(NS)(AsPh$_3$)$_2$] (23), and *(2,2′-bipyridyl)dibromochloro(thionitrosyl)osmium*, [OsBr$_2$Cl(NS)(bipy)] (24), were prepared analogously to (20), from S$_2$Cl$_2$ and [OsBr$_3$N(AsPh$_3$)$_2$] and [OsBr$_3$N(bipy)] respectively.

Reaction of Trichlorotris(diethylphenylphosphine)(thionitrosyl)rhenium with Diethylphenylphosphine.—The complex [ReCl$_3$(NS)(PEt$_2$Ph)$_3$] (0.2 g) and PEt$_2$Ph (0.5 g) were heated under reflux in benzene (40 cm^3) for 1.5 h. The solvent was removed at 10^{-2} Torr and the residue recrystallized from dichloromethane–pentane as yellow needles. These were identified as [ReCl$_2$N(PEt$_2$Ph)$_3$] by comparison of its i.r. spectrum with that of an authentic sample.

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REFERENCES

[1] O. Glemser, H. Meyer, and A. Haas, *Ber.*, 1964, **97**, 1704.

[2] W. Muthmann and E. Seither, *Ber.*, 1897, **30**, 627; O. Glemser and H. Richert, *Z. anorg. Chem.*, 1961, **307**, 313.

[3] O. Glemser and W. Koch, *Angew. Chem. Internat. Edn.*, 1971, **10**, 127.

[4] J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1974, 508.

[5] M. W. Bishop, J. Chatt, and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1975, 780.

[6] M. B. Hursthouse and M. Motevalli, unpublished work.

[7] M. W. Bishop, G. Butler, J. R. Dilworth, and G. J. Leigh, unpublished work.

[8] K. W. Muir, L. Manojlovic-Muir, and R. Herak, unpublished work.

[9] M. W. Bishop, J. Chatt, and J. R. Dilworth, unpublished work.

[10] J. Chatt and J. R. Dilworth, *J. Indian Chem. Soc.*, 1977, **54**, 13.

[11] J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc. (A)*, 1969, 2288.

[12] H. P. Gunz, D.Phil. Thesis, University of Sussex, 1969.

[13] W. P. Griffith and D. Pawson, *J.C.S. Dalton*, 1975, 417.