Reactivity of the $[Re{\equiv}NR]^{3+}$ and $[Re{\equiv}N]^{2+}$ Cores toward Bis(diphenylphosphino)amine and its Derivatives. Synthesis and Crystal Structures†

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The complexes *fac*-$[Re(NMe)Cl_3\{NH(PPh_2)_2\text{-}P,P'\}]$ **1**, $[ReNCl\{NH(PPh_2)_2\text{-}P,P'\}_2]X$ (X = Cl **2** or BPh_4 **2a**), $[Re(NMe)Cl_2\{N(XPPh_2)_2\text{-}X,X'\}(PPh_3)]$ (X = O **3**, S **4** or Se **8**), $[Re(NMe)Cl\{N(XPPh_2)_2\text{-}X,X'\}_2]$ (X = S **5** or Se **9**), $[ReNCl\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$ **6**, $[ReN\{N(XPPh_2)_2\text{-}X,X'\}_2]$ (X = S **7** or Se **10**) and *trans*-$[ReOCl_2\{N(OPPh_2)_2\text{-}O,O'\}(AsPh_3)]$ **11** were obtained by treatment of $[Re(NMe)Cl_3(PPh_3)_2]$, $[ReNCl_2(PPh_3)_2]$ or $[ReOCl_3(AsPh_3)_2]$ with the appropriate ligand under different experimental conditions. The structures of complexes **1**, **2a** and **6** were determined by X-ray crystallography. In **1** and **2a** the Re atom is six-co-ordinate in a distorted octahedral configuration, whereas in **6** the Re atom is five-co-ordinate square pyramidal with the N atom in the apical position.

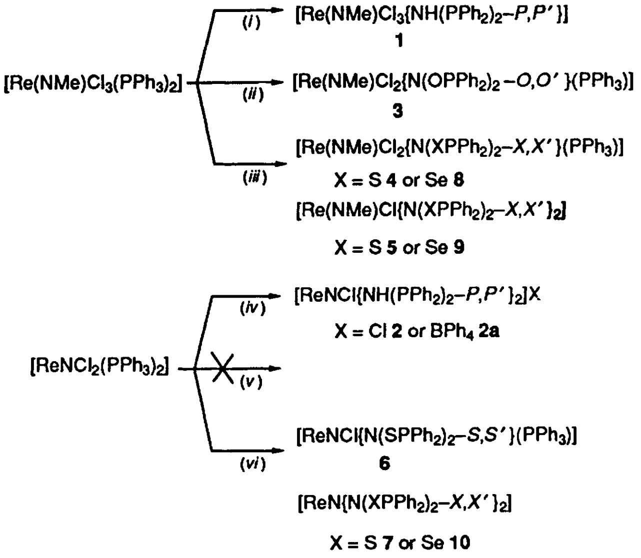
The most important class of octahedral rhenium(V) halide compounds includes the oxo, imido, and nitrido complexes $[ReOX_3L_2]$, $[Re(NR)X_3L_2]$ and $[ReNX_2L_3]$ (X = halogen, L = tertiary phosphine), in which the $[Re{\equiv}O]^{3+}$, $[Re{\equiv}NR]^{3+}$ and $[Re{\equiv}N]^{2+}$ cores constitute isoelectronic groups.

The electronic structure of the metal–ligand multiple bond not only determines its reactivity, but also affects the structure and the reactivity of the complexes as a whole. As a general rule, the oxo group seems to form the most polar bonds as a consequence of its poor electron donating capacity, while the nitrido group is considered a powerful π-donor ligand, which makes the $[Re{\equiv}N]^{2+}$ core more suitable to co-ordinate with 'soft' donors.

Little has been reported up to now on the co-ordination chemistry of diphosphines such as bis(diphenylphosphino)amine, $NH(PPh_2)_2$, and its derivatives $NH(XPPh_2)_2$ (X = O, S or Se). These compounds provide an ideal system to study as the variation of the ring size and the 'hard–soft' character of the donor group X affects their co-ordination properties.

The co-ordination chemistry of such ligands has been the subject of recent studies by us and two papers dealing with rhenium–oxo compounds have been published.[1,2]

Herein we describe the reactivity of $NH(PPh_2)_2$ and $NH(XPPh_2)_2$ ligands (X = O, S or Se) toward rhenium–imido and -nitrido complexes, and the crystal structures of some of the complexes obtained.



Scheme 1 (*i*) $NH(PPh_2)_2$, refluxing chloroform or toluene; (*ii*) $NH(OPPh_2)_2$, refluxing chloroform; (*iii*) $[N(XPPh_2)_2]^-$, refluxing toluene (X = S) or refluxing chloroform (X = Se); (*iv*) $NH(PPh_2)_2$, refluxing chloroform; (*v*) $NH(OPPh_2)_2$; (*vi*) $[N(XPPh_2)_2]^-$, refluxing toluene (X = S) or refluxing chloroform (X = Se)

Results and Discussion

The results are summarized in Scheme 1.

Reactions with $NH(PPh_2)_2$.—When $NH(PPh_2)_2$ was treated with $[Re(NMe)Cl_3(PPh_3)_2]$ or $[ReNCl_2(PPh_3)_2]$ under the same experimental conditions, only the monosubstituted complex *fac*-$[Re(NMe)Cl_3\{NH(PPh_2)_2\text{-}P,P'\}]$ **1** and the disubstituted complex $[ReNCl\{NH(PPh_2)_2\text{-}P,P'\}_2]Cl$ **2** were obtained irrespective of the stoichiometric ratio. Complex **1** is scarcely soluble in common organic solvents but suitable crystals for an X-ray crystal structure analysis were grown from dimethylformamide.

Reactions with $NH(OPPh_2)_2$.—With this ligand the rhenium–imido complex behaves in the same manner as $[ReOCl_3(PPh_3)_2]$,[1] and only the monosubstituted complex $[Re(NMe)Cl_2\{N(OPPh_2)_2\text{-}O,O'\}(PPh_3)]$ **3** was obtained even when an excess of the ligand salt $K[N(OPPh_2)_2]$ was used. No reactivity was observed with the $[Re{\equiv}N]^{2+}$ core, which could be

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

attributed to its more 'soft' character which makes it less reactive toward 'hard' donor ligands.[3]

Reactions with $NH(SPPh_2)_2$.—When reactions of $[Re(NMe)Cl_3(PPh_3)_2]$ or $[ReNCl_2(PPh_3)_2]$ with $NH(SPPh_2)_2$ were carried out in refluxing toluene, only the latter reacted, to give the monosubstituted complex $[ReNCl\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$ **6**. Use of $Li[N(SPPh_2)_2]$ was necessary to obtain the disubstituted compound $[ReN\{N(SPPh_2)_2\text{-}S,S'\}_2]$ **7** and the methylimido complexes $[Re(NMe)Cl_2\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$ **4** and $[Re(NMe)Cl\{N(SPPh_2)_2\text{-}S,S'\}_2]$ **5**. Many attempts were made to obtain the imido complexes using the protonated ligand; although the solution changed from green-blue to deep violet, suggesting the formation of the monosubstituted compound, we were unable to isolate any product. This behaviour differs from that of $[ReOCl_3(PPh_3)_2]$, for which both mono- and di-substituted compounds were obtained.[1]

Reactions with $K[N(SePPh_2)_2]$.—The complex $[Re(NMe)Cl_3(PPh_3)_2]$ reacts with $K[N(SePPh_2)_2]$ in 1:1 or 1:3 molar ratio in boiling chloroform to give the light blue-violet $[Re(NMe)Cl_2\{N(SePPh_2)_2\text{-}Se,Se'\}(PPh_3)]$ **8** and brown $[Re(NMe)Cl\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ **9** respectively. When the same reaction was carried out with $[ReNCl_2(PPh_3)_2]$, only the disubstituted compound $[ReN\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ **10** was obtained. This preference to form the disubstituted complex was also observed with the rhenium–oxo complexes $[ReOCl_3(PPh_3)_2]$ and $[AsPh_4][ReOCl_4]$, however the complex $[ReOCl\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ shows a lower stability in solution than that shown by the imido or nitrido analogues, and tends to transform into $[ReOCl\{N(SePPh_2)(PPh_2)\text{-}Se,P\}_2]$ by loss of one Se atom from each ligand.[2] This behaviour probably is due to the more 'hard' character of the $[Re{\equiv}O]^{3+}$ core, which disfavours co-ordination of the rhenium(v) atom to four 'soft' selenium donors.

All the complexes were characterized by elemental analyses, IR and NMR spectroscopy and, for some of them, X-ray analyses.

Vibrational Spectroscopy.—The solid-state (KBr pellets) IR spectra show absorptions characteristic of the presence of P–N bonds. The position of the higher-frequency P_2N stretching band of the chelate ligands[4] is observable in the region 1230–1174 cm^{-1}, whereas for the ionic complex $[ReNCl\{NH(PPh_2)_2\text{-}P,P'\}_2][BPh_4]$ **2a** this is shifted towards higher frequency (1304 cm^{-1}. Bands in the region 855–790 cm^{-1} are also assigned to P–N stretches.[4] The P–S stretching frequencies appear in the region 582–560 cm^{-1}, while the band at 1125 cm^{-1} for complex **3** is assigned to the P=O groups co-ordinated to the metal through the oxygen atoms.[4,5] For complexes **1** and **2a** the imine N–H stretching bands are present at 3220 and 3260 cm^{-1} respectively.

NMR Spectroscopy.—In order to record significant NMR spectra of **1**, dimethylsulfoxide was used as the solvent. The $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibits a sharp singlet (δ 17.18), indicating the equivalence of the two phosphorus atoms of the chelate ligand. The ^1H NMR spectrum shows the methyl group of the organoimido ligand as a triplet at δ 0.69 [^4J(HP) 5.0 Hz]. On the basis of these data we assigned a *fac* configuration to complex **1**. For **2a** the $^{31}P\text{-}\{^1H\}$ NMR spectrum (CD_2Cl_2) shows a singlet resonance at δ 39.99. Such a pattern, together with the elemental analyses, suggests the presence of two chelate ligands in the equatorial plane of the octahedron and a chlorine atom *trans* to the $[Re{\equiv}N]^{2+}$ core. The assigned geometry for the complexes **1** and **2a** were confirmed by their X-ray crystal structures.

Compounds **3**, **4** and **8** exhibit $^{31}P\text{-}\{^1H\}$ NMR spectra ($CDCl_3$) consisting of an AMX spin system in line with the presence of a single bidentate $N(XPPh_2)_2$ (X = O, S or Se) ligand and a triphenylphosphine molecule. The resonances due to this latter ligand fall invariably at higher field with respect to those assigned to the two magnetically inequivalent P donors of the $N(XPPh_2)_2$ ligands. Similar NMR patterns have been also found for the X-ray authenticated rhenium(v)–oxo complexes *trans*-$[ReOCl_2\{N(OPPh_2)_2\text{-}O,O'\}(PPh_3)]$ and *cis*-$[ReOCl_2\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$.[1] Indeed, their $^{31}P\text{-}\{^1H\}$ NMR spectra consist of three well separated resonances* whose δ values well match those found for complexes **3**, **4** and **8** (see Experimental section). We therefore assign a *trans* configuration for **3** and *cis* configuration for **4** and **8** by analogy with the rhenium(v)–oxo complexes. In order to confirm further the NMR assignment, we have synthesized the complex $[ReOCl_2\{N(OPPh_2)_2\text{-}O,O'\}(AsPh_3)]$ **11** which contains $AsPh_3$ in place of PPh_3. Complex **11** shows an AM splitting pattern in its $^{31}P\text{-}\{^1H\}$ NMR spectrum [δ_A 33.48, δ_M 31.29; $^2J(P_AP_M)$ 6.3 Hz] without any high-field signal, which can then be assigned to the PPh_3 ligand in the related complexes.

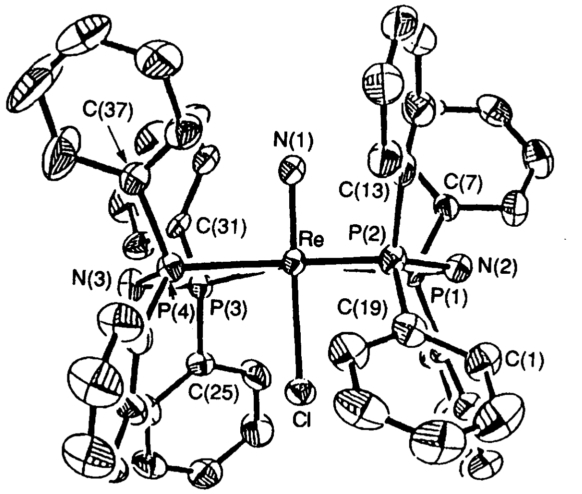

Fig. 1 ORTEP[6] drawing of the molecular structure of the $[ReNCl\{NH(PPh_2)_2\text{-}P,P'\}_2]^+$ cation of **2a**. For clarity, only the *ipso* carbon atom of each phenyl group has been labelled

The methylimido hydrogens of complexes **1**, **3**–**5**, **8** and **9** resonate in their ^1H NMR spectra ($CDCl_3$) between δ 1.78 and −0.10. The observed doublet multiplicity for **3**, **4** and **8** is in accord with coupling only to the P_X (PPh_3) nucleus. Complex **6**, which exhibits a distorted square-pyramidal geometry (see X-ray section), shows in the $^{31}P\text{-}\{^1H\}$ NMR spectrum (CD_2Cl_2) an AMX spin system. However, the PPh_3 phosphorus resonance, is shifted significantly to low field in comparison to the octahedral species **3**, **4** and **8**. This behaviour might be ascribed to the different geometry of this complex rather than to the different electronic properties of the nitrido and imido groups.

Complexes **5**, **7**, **9** and **10**, which contain two bidentate $N(XPPh_2)_2$ ligands (X = S or Se), exhibit singlet signals in their broad-band proton decoupled ^{31}P NMR spectra. The two selenium derivatives, **9** and **10**, show satellite resonances according to the presence of the NMR-active ^{77}Se nuclei. The coupling constants [^1J(PSe) 558 and 547 Hz, respectively] agree with literature data.[2] Such NMR patterns point to the equivalence of the four phosphorus atoms of the $N(XPPh_2)_2$ ligands which lie in the equatorial plane of the co-ordination polyhedra.

X-Ray Crystal Structures.—$[ReNCl\{NH(PPh_2)_2\text{-}P,P'\}_2][BPh_4]\cdot EtOH$ **2a·EtOH**. As shown in Fig. 1 the complex is a

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* *trans*-$[ReOCl_2\{N(OPPh_2)_2\text{-}O,O'\}(PPh_3)]$: δ_X −27.76 (t), δ_M 31.03 (t), δ_A 32.36 (t); $^2J(P_AP_M)$ 6.3, $^3J(P_AP_X) \approx {}^3J(P_MP_X)$ 6.4 Hz. *cis*-$[ReOCl_2\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$: δ_X −27.76, δ_M 42.49, δ_A 47.45; J(PP) not resolved. The P_A and P_M resonances are arbitrary since the NMR data do not allow unambiguous assignment.

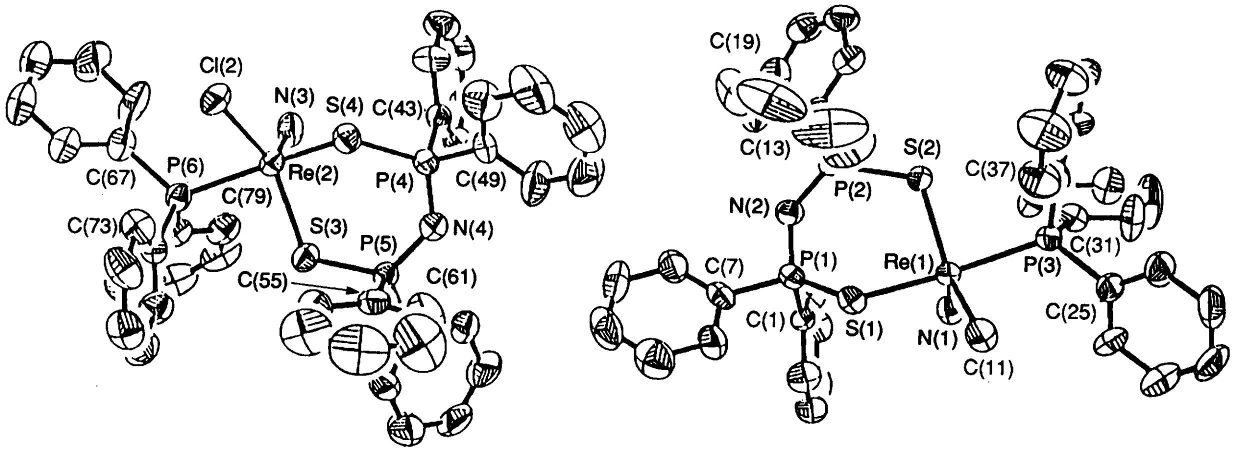

Fig. 2 An ORTEP[6] diagram of $[ReNCl\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$ **6**. For clarity, only the *ipso* carbon atom of each phenyl group has been labelled

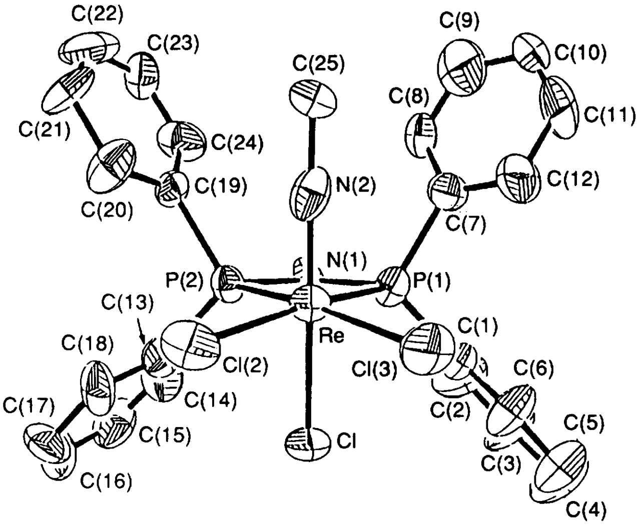

Fig. 3 An ORTEP[6] drawing of the molecular structure of $[Re(NMe)Cl_3\{NH(PPh_2)_2\text{-}P,P'\}]$ **1**

salt-like compound in which the metal ion is distorted octahedral. Major asymmetries in bond angles are due to geometrical constraints of the chelate ligands, which subtend chelation angles of only 67°. The Re–N distance of 1.711(8) Å can be compared with values of 1.709(4) and 1.690(5) Å in $[ReCl_3(NC_6H_4OMe)(PEt_2Ph)_2]$ and $[ReCl_3(NC_6H_4COMe)(PEt_2Ph)_2]$,[7] 1.685(11) Å in $[Re(NMe)Cl_3(PEtPh_2)_2]$[8] and 1.660(8) Å in $[ReNCl_2(PMe_2Ph)_3]$.[9] The metal ion is displaced by 0.195 Å from the P_4 equatorial mean plane, and the two ReP_2N chelation planes are slightly inclined (by 5.2 and 5.9°) with respect to this plane. These tetraatomic rings are almost planar, with maximum atomic deviations of 0.01 Å. The rather long Re–Cl distance of 2.496(3) Å could be ascribed to *trans* weakening or to repulsion between Cl and the two bulky adjacent bidentate ligands. The observation that the P–N distances (mean 1.70 Å) are slightly but significantly shorter than 'normal' for a single P–N bond (1.75–1.80 Å) suggests some delocalization of the ring electron pairs.

$[ReNCl\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$ **6**. As indicated by the value of the crystal density, four molecules of the compound are present in the triclinic cell, and therefore two independent molecules form the asymmetric structural unit. As shown in Fig. 2, in which both independent molecules are depicted, the structural conformation of the compound is unique. Both molecules are similar and the discussion below refers to the mean geometrical parameters of each. In each molecule the metal atom is displaced by 0.60 Å from the basal plane of the square pyramid. The Re–N bond can be considered as a triple bond and its length of 1.63 Å compares with the value of 1.602(9) Å found in $[ReNCl_2(PPh_3)_2]$.[10] The Re–S bond, *trans* to Cl (2.375 Å), is significantly shorter than the corresponding bond *trans* to PPh_3 (2.450 Å). Moreover, the P–S bond of the more strongly co-ordinated S atom, is slightly longer (by about 0.027 Å) than the other, which suggests that the bidentate ligand can be regarded as a thiolato anion in which the negatively charged S atom is more strongly co-ordinated. Both P–S bonds are shorter than expected for a single covalent bond, and the two chemically equivalent P–N bonds show partial double bond character resulting from delocalization of π-electron density, as already found in other complexes with the same or similar ligands.[1] As a consequence of the observed asymmetry in the Re–S distances, there is a difference of about 7° in the Re–S–P angles, a larger angle being associated with a shorter Re–S distance.

$[Re(NMe)Cl_3\{NH(PPh_2)_2\text{-}P,P'\}]$ **1**. As shown in Fig. 3, the complex is distorted octahedral, with a co-ordination angle of 67.5° subtended by $NH(PPh_2)_2$ (the corresponding angle is 66.5° in **2a**·EtOH). Other distortions arise due to repulsion between the strongly electronegative Cl atoms and the multiply bonded nitrogen. Thus, whereas N subtends at the metal N–Re–Cl angles of 100° with the adjacent Cl(2) and Cl(3) atoms, the Cl(1)–Re–P angles are only 81°; as a related feature the Re–P–C angles directed towards the Cl atoms (mean 122°) are significantly larger than the corresponding angles (93°) directed towards N. The Re–N bond distance of 1.67(2) Å agrees well with the value of 1.68(1) Å found in $[Re(NMe)Cl_3(PEtPh_2)_2]$[8] and is very short when compared with the remaining co-ordination distances, which are roughly equivalent, irrespective of the nature of the *trans* ligands. Structural details of the bidentate ligand are similar to those found in **2a**·EtOH.

Experimental

Materials.—Solvents were purified and dried before use. Reactions when necessary were carried out under an atmosphere of nitrogen using degassed solvents. Literature methods were used for the preparation of the ligands $NH(PPh_2)_2$ and $NH(XPPh_2)_2$ (X = O, S or Se)[11] and of the rhenium starting materials $[Re(NMe)Cl_3(PPh_3)_2]$,[12] $[ReNCl_2(PPh_3)_2]$[13] and $[ReOCl_3(AsPh_3)_2]$.[14] Infrared spectra were recorded on a Nicolet FTIR 510P spectrophotometer, NMR spectra on a Bruker AC200P spectrometer operating at 200.13 MHz (^1H) and at 81.01 MHz (^{31}P). Peak positions are relative to $SiMe_4$ as an external reference (^1H) or to external 85% H_3PO_4 (^{31}P-

Table 1 Fractional coordinates for $[ReNCl\{NH(PPh_2)_2\text{-}P,P'\}_2][BPh_4]\cdot EtOH$ **2a**·EtOH

Atom	*x*	*y*	*z*
Re	0.409 95(3)	0.069 29(3)	0.123 42(1)
N	0.381 4(5)	0.058 2(6)	0.077 6(2)
Cl	0.454 5(2)	0.089 5(2)	0.189 95(7)
P(1)	0.577 8(2)	0.118 0(2)	0.113 80(8)
P(2)	0.433 0(2)	0.253 2(2)	0.119 44(8)
P(3)	0.390 9(2)	−0.110 6(2)	0.139 02(8)
P(4)	0.247.9(2)	0.028 0(2)	0.142 12(8)
N(2)	0.551 8(5)	0.244 6(6)	0.112 8(2)
N(3)	0.273 9(5)	−0.097 0(6)	0.150 0(2)
B(1)	0.960 8(8)	0.619 0(9)	0.116 0(3)
C(1)	0.673 0(6)	0.101 6(5)	0.148 6(2)
C(2)	0.733 4(6)	0.017 1(5)	0.147 0(2)
C(3)	0.803 1(6)	−0.000 3(5)	0.174 9(2)
C(4)	0.812 3(6)	0.066 8(5)	0.204 5(2)
C(5)	0.751 9(6)	0.151 3(5)	0.206 1(2)
C(6)	0.682 2(6)	0.168 7(5)	0.178 2(2)
C(7)	0.634 7(5)	0.087 2(5)	0.071 8(2)
C(8)	0.720 9(5)	0.134 0(5)	0.063 4(2)
C(9)	0.763 9(5)	0.110 9(5)	0.030 6(2)
C(10)	0.720 7(5)	0.041 0(5)	0.006 3(2)
C(11)	0.634 5(5)	−0.005 8(5)	0.014 8(2)
C(12)	0.591 5(5)	0.017 3(5)	0.047 5(2)
C(13)	0.373 8(5)	0.311 6(6)	0.079 8(2)
C(14)	0.294 3(5)	0.374 9(6)	0.083 3(2)
C(15)	0.241 4(5)	0.407 5(6)	0.052 2(2)
C(16)	0.268 2(5)	0.376 8(6)	0.017 5(2)
C(17)	0.347 7(5)	0.313 6(6)	0.014 0(2)
C(18)	0.400 6(5)	0.281 0(6)	0.045 1(2)
C(19)	0.417 1(5)	0.341 0(6)	0.156 7(2)
C(20)	0.331 8(5)	0.338 2(6)	0.175 3(2)
C(21)	0.316 8(5)	0.407 4(6)	0.203 4(2)
C(22)	0.387 0(5)	0.479 6(6)	0.212 9(2)
C(23)	0.472 4(5)	0.482 5(6)	0.194 3(2)
C(24)	0.487 4(5)	0.413 2(6)	0.166 2(2)
C(25)	0.456 0(5)	−0.162 6(6)	0.178 1(2)
C(26)	0.555 9(5)	−0.166 4(6)	0.176 4(2)
C(27)	0.611 2(5)	−0.211 1(6)	0.204 8(2)
C(28)	0.566 7(5)	−0.252 2(6)	0.234 9(2)
C(29)	0.466 9(5)	−0.248 4(6)	0.236 7(2)
C(30)	0.411 5(5)	−0.203 7(6)	0.208 2(2)
C(31)	0.397 5(5)	−0.211 2(6)	0.104 9(2)
C(32)	0.405 3(5)	−0.312 7(6)	0.115 8(2)
C(33)	0.416 6(5)	−0.388 9(6)	0.089 7(2)
C(34)	0.420 2(5)	−0.363 4(6)	0.052 7(2)
C(35)	0.412 4(5)	−0.261 8(6)	0.041 8(2)
C(36)	0.401 1(5)	−0.185 7(6)	0.067 9(2)
C(37)	0.157 0(5)	0.039 7(5)	0.105 7(2)
C(38)	0.160 6(5)	0.123 1(5)	0.082 2(2)
C(39)	0.095 4(5)	0.130 7(5)	0.052 2(2)
C(40)	0.026 6(5)	0.054 8(5)	0.045 8(2)
C(41)	0.023 0(5)	−0.028 7(5)	0.069 3(2)
C(42)	0.088 3(5)	−0.036 2(5)	0.099 3(2)
C(43)	0.195 0(6)	0.073 2(6)	0.183 2(2)
C(44)	0.120 8(6)	0.144 7(6)	0.181 5(2)
C(45)	0.083 5(6)	0.182 0(6)	0.213 7(2)
C(46)	0.120 4(6)	0.147 7(6)	0.247 6(2)
C(47)	0.194 6(6)	0.076 2(6)	0.249 3(2)
C(48)	0.231 8(6)	0.039 0(6)	0.217 1(2)
C(49)	1.020 5(5)	0.677 3(5)	0.151 7(2)
C(50)	1.102 6(5)	0.631 3(5)	0.167 5(2)
C(51)	1.154 3(5)	0.679 6(5)	0.196 1(2)
C(52)	1.123 9(5)	0.773 9(5)	0.208 9(2)
C(53)	1.041 8(5)	0.819 8(5)	0.193 1(2)
C(54)	0.990 1(5)	0.771 5(5)	0.164 5(2)
C(55)	1.020 8(5)	0.635 4(6)	0.077 5(2)
C(56)	0.974 0(5)	0.608 4(6)	0.044 4(2)
C(57)	1.018 1(5)	0.625 9(6)	0.011 5(2)
C(58)	1.109 0(5)	0.670 5(6)	0.011 6(2)
C(59)	1.155 9(5)	0.697 6(6)	0.044 7(2)
C(60)	1.111 8(5)	0.680 0(6)	0.077 7(2)
C(61)	0.951 2(5)	0.494 6(6)	0.126 7(2)
C(62)	0.964 7(5)	0.419 5(6)	0.100 4(2)
C(63)	0.946 0(5)	0.317 8(6)	0.108 5(2)
C(64)	0.913 8(5)	0.291 1(6)	0.142 8(2)
C(65)	0.900 3(5)	0.366 2(6)	0.169 1(2)
C(66)	0.919 0(5)	0.468 0(6)	0.161 1(2)
C(67)	0.852 1(6)	0.673 5(5)	0.109 0(2)
C(68)	0.770 7(6)	0.637 1(5)	0.125 6(2)
C(69)	0.681 4(6)	0.682 2(5)	0.117 9(2)
C(70)	0.673 5(6)	0.763 8(5)	0.093 5(2)
C(71)	0.755 0(6)	0.800 2(5)	0.076 8(2)
C(72)	0.844 3(6)	0.755 1(5)	0.084 6(2)
O(1)	0.700 8(7)	0.110 7(8)	0.602 5(3)
C(73)	0.716(1)	0.069(1)	0.566 9(5)
C(74)	0.626(1)	0.058(2)	0.548 1(5)

$\{^1H\}$). Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser.

Preparations.—*fac*-$[Re(NMe)Cl_3\{NH(PPh_2)_2\text{-}P,P'\}]$ **1**. Bis(diphenylphosphino)amine (0.36 mmol) was added to a chloroform solution (40 cm^3) of $[Re(NMe)Cl_3(PPh_3)_2]$ (0.18 mmol). Within a few minutes at reflux the green-blue solution turned grey-violet and a precipitate began to form. After 30 min the violet precipitate was removed by filtration and washed with acetone and diethyl ether. Recrystallisation from dimethylformamide–ethanol gave the product as a blue-violet crystalline solid, yield 75% (Found: C, 42.3; H, 3.2; N, 3.7. $C_{25}H_{24}Cl_3N_2P_2Re$ requires C, 42.5; H, 3.4; N, 4.0%); ν(NH) 3220m, $\nu(P_2N)$ 1227s, other ligand bands 850s, 815s, 580s cm^{-1}. NMR $[(CD_3)_2SO]$: $^{31}P\text{-}\{^1H\}$, δ 17.18 (s); ^1H, δ 0.69 [t, ^4J(HP) 5.0 Hz, CH_3].

$[ReNCl\{NH(PPh_2)_2\text{-}P,P'\}_2]X$ (X = Cl **2** *or* BPh_4 **2a**). A mixture of $[ReNCl_2(PPh_3)_2]$ (0.18 mmol) and $NH(PPh_2)_2$ (0.40 mmol) in chloroform (40 cm^3) was stirred at reflux for 90 min. The red suspension dissolved to give a yellow solution and a pale yellow solid, which was filtered off. A further amount of the solid was collected when the filtrate was concentrated to a small volume. The product was obtained as pale yellow plates upon recrystallisation from methanol–ethanol, yield 80%. Yellow crystals suitable for diffraction studies were obtained by addition of $Na[BPh_4]$ to a solution of the chloride derivative in methanol. The precipitate which formed was filtered off, washed with water, ethanol and diethyl ether and recrystallised from dichloromethane–ethanol (Found: C, 64.8; H, 5.3; N, 2.6. $C_{72}H_{62}BClN_3P_4Re$ requires C, 65.3; H, 4.7; N, 3.2%); ν(NH) 3260m, $\nu(P_2N)$ 1304, 853 cm^{-1}. $^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2): δ 39.99 (s).

trans-$[Re(NMe)Cl_2\{N(OPPh_2)_2\text{-}O,O'\}(PPh_3)]$ **3**. An excess (3 : 1) of $NH(OPPh_2)_2$ was added to a hot chloroform solution (40 cm^3) of $[Re(NMe)Cl_3(PPh_3)_2]$ (0.18 mmol) and the reaction mixture stirred at reflux for 40 min, during which the colour changed from pale blue to dark green. The suspension was filtered off and the filtrate evaporated to a small volume and diethyl ether added until a green precipitate was obtained. The powder was dissolved in dichloromethane and the residual white ligand was filtered off as a solid. Slow evaporation of the solution, after addition of acetone, gave the required product as a green microcrystalline solid, yield 80% (Found: C, 53.5; H, 3.8; N, 2.7. $C_{43}H_{38}Cl_2N_2O_2P_3Re$ requires C, 53.1; H, 3.7; N, 2.9%); $\nu(P_2N)$ 1210s, ν(PO) 1125s, other ligand bands 1085s, 1060s, 725s, 586m, 540s cm^{-1}. NMR (CD_2Cl_2): $^{31}P\text{-}\{^1H\}$, AMX spin system, δ_X −5.94 (m, PPh_3), δ_M 27.21 (dd), δ_A 27.83 (dd) [$^3J(P_XP_A)$ 7.2, $^3J(P_XP_M)$ 5.1, $^2J(P_AP_M)$ 4.4 Hz]; ^1H, δ 1.78 [d, $^4J(HP_X)$ 4.8 Hz, Me].

cis-$[Re(NMe)Cl_2\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$ **4**. A suspension of $NH(SPPh_2)_2$ (0.35 mmol) and LiBu (0.25 mmol) in

Table 2 Fractional coordinates for $[ReNCl\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$ **6**

Atom	x	y	z	Atom	x	y	z
Re(1)	0.200 02(2)	0.456 30(3)	0.054 47(4)	Re(2)	−0.398 17(2)	−0.150 29(3)	0.405 56(5)
Cl(1)	0.207 3(1)	0.585 8(2)	0.137 4(3)	Cl(2)	−0.488 1(1)	−0.152 1(2)	0.291 1(3)
S(1)	0.115 1(1)	0.421 7(2)	0.186 0(3)	S(3)	−0.327 0(1)	−0.099 1(2)	0.592 5(3)
S(2)	0.153 9(1)	0.358 8(2)	−0.122 8(3)	S(4)	−0.366 4(1)	−0.031 6(2)	0.264 3(3)
P(1)	0.088 9(1)	0.299 8(2)	0.206 2(3)	P(4)	−0.279 3(1)	−0.003 0(2)	0.261 2(3)
P(2)	0.075 8(1)	0.275 2(2)	−0.076 9(3)	P(5)	−0.263 8(1)	0.007 4(2)	0.546 8(3)
P(3)	0.264 6(1)	0.526 8(2)	−0.111 0(3)	P(6)	−0.456 6(1)	−0.230 8(2)	0.572 6(3)
N(1)	0.246 8(4)	0.425 7(6)	0.144(1)	N(3)	−0.379 6(4)	−0.219 9(6)	0.335(1)
N(2)	0.071 8(4)	0.244 5(5)	0.073 3(9)	N(4)	−0.240 7(4)	0.012 6(6)	0.403 4(9)
C(1)	0.144 1(4)	0.275 1(4)	0.309 6(7)	C(43)	−0.266 4(3)	−0.080 6(5)	0.166 9(7)
C(2)	0.165 2(4)	0.313 3(4)	0.436 1(7)	C(44)	−0.224 0(3)	−0.111 4(5)	0.218 1(7)
C(3)	0.207 3(4)	0.293 4(4)	0.516 9(7)	C(45)	−0.213 3(3)	−0.171 2(5)	0.145 1(7)
C(4)	0.228 3(4)	0.235 3(4)	0.471 1(7)	C(46)	−0.245 1(3)	−0.200 3(5)	0.020 9(7)
C(5)	0.207 2(4)	0.197 1(4)	0.344 7(7)	C(47)	−0.287 5(3)	−0.169 5(5)	−0.030 3(7)
C(6)	0.165 1(4)	0.217 0(4)	0.263 9(7)	C(48)	−0.298 2(3)	−0.109 7(5)	0.042 7(7)
C(7)	0.027 1(4)	0.272 7(5)	0.304 7(8)	C(49)	−0.253 7(3)	0.086 5(6)	0.164 3(9)
C(8)	−0.013 4(4)	0.193 9(5)	0.290 3(8)	C(50)	−0.287 9(3)	0.102 6(6)	0.056 3(9)
C(9)	−0.059 9(4)	0.168 9(5)	0.370 9(8)	C(51)	−0.265 7(3)	0.173 1(6)	−0.015 8(9)
C(10)	−0.066 0(4)	0.222 8(5)	0.465 9(8)	C(52)	−0.209 3(3)	0.227 5(6)	0.020 1(9)
C(11)	−0.025 5(4)	0.301 6(5)	0.480 3(8)	C(53)	−0.175 1(3)	0.211 4(6)	0.128 1(9)
C(12)	0.021 0(4)	0.326 5(5)	0.399 7(8)	C(54)	−0.197 3(3)	0.140 9(6)	0.200 2(9)
C(13)	0.017 8(4)	0.311 8(5)	−0.130(1)	C(55)	−0.287 9(4)	0.089 8(5)	0.583(1)
C(14)	−0.039 2(4)	0.256 0(5)	−0.141(1)	C(56)	−0.250 3(4)	0.168 2(5)	0.562(1)
C(15)	−0.086 1(4)	0.282 1(5)	−0.172(1)	C(57)	−0.266 3(4)	0.234 2(5)	0.591(1)
C(16)	−0.075 9(4)	0.364 0(5)	−0.193(1)	C(58)	−0.320 0(4)	0.221 8(5)	0.641(1)
C(17)	−0.018 9(4)	0.419 7(5)	−0.181(1)	C(59)	−0.357 6(4)	0.143 4(5)	0.662(1)
C(18)	0.028 0(4)	0.393 6(5)	−0.150(1)	C(60)	−0.341 6(4)	0.077 3(5)	0.633(1)
C(19)	0.064 7(3)	0.187 6(4)	−0.183 9(7)	C(61)	−0.202 3(3)	0.019 7(5)	0.668 3(8)
C(20)	0.066 9(3)	0.195 8(4)	−0.323 2(7)	C(62)	−0.207 4(3)	0.024 5(5)	0.806 5(8)
C(21)	0.062 6(3)	0.129 6(4)	−0.405 1(7)	C(63)	−0.160 5(3)	0.028 8(5)	0.899 9(8)
C(22)	0.056 0(3)	0.055 0(4)	−0.347 7(7)	C(64)	−0.108 4(3)	0.028 3(5)	0.855 2(8)
C(23)	0.053 8(3)	0.046 8(4)	−0.208 4(7)	C(65)	−0.103 2(3)	0.023 5(5)	0.717 1(8)
C(24)	0.058 2(3)	0.113 1(4)	−0.126 5(7)	C(66)	−0.150 2(3)	0.019 2(5)	0.623 7(8)
C(25)	0.315 5(4)	0.627 7(5)	−0.064 4(7)	C(67)	−0.525 2(4)	−0.307 1(6)	0.504(1)
C(26)	0.325 5(4)	0.691 8(5)	−0.152 7(7)	C(68)	−0.521 9(4)	−0.365 0(6)	0.413(1)
C(27)	0.370 9(4)	0.765 1(5)	−0.119 8(7)	C(69)	−0.572 7(4)	−0.426 6(6)	0.361(1)
C(28)	0.406 2(4)	0.774 5(5)	0.001 4(7)	C(70)	−0.626 8(4)	−0.430 3(6)	0.399(1)
C(29)	0.396 2(4)	0.710 4(5)	0.089 7(7)	C(71)	−0.630 1(4)	−0.372 4(6)	0.490(1)
C(30)	0.350 9(4)	0.637 1(5)	0.056 8(7)	C(72)	−0.579 3(4)	−0.310 8(6)	0.543(1)
C(31)	0.313 6(4)	0.478 4(4)	−0.167(1)	C(73)	−0.472 3(4)	−0.159 2(5)	0.678 8(7)
C(32)	0.365 4(4)	0.525 0(4)	−0.220(1)	C(74)	−0.507 4(4)	−0.118 1(5)	0.621 5(7)
C(33)	0.401 8(4)	0.487 8(4)	−0.267(1)	C(75)	−0.515 4(4)	−0.056 4(5)	0.695 3(7)
C(34)	0.386 5(4)	0.404 0(4)	−0.261(1)	C(76)	−0.488 4(4)	−0.035 9(5)	0.826 3(7)
C(35)	0.334 7(4)	0.357 4(4)	−0.209(1)	C(77)	−0.453 4(4)	−0.077 0(5)	0.883 6(7)
C(36)	0.298 2(4)	0.394 6(4)	−0.161(1)	C(78)	−0.445 3(4)	−0.138 6(5)	0.809 8(7)
C(37)	0.221 9(4)	0.540 2(5)	−0.260 4(9)	C(79)	−0.426 5(3)	−0.290 9(6)	0.682 3(9)
C(38)	0.228 4(4)	0.515 9(5)	−0.389 6(9)	C(80)	−0.454 8(3)	−0.327 2(6)	0.794 0(9)
C(39)	0.193 8(4)	0.527 8(5)	−0.500 9(9)	C(81)	−0.432 4(3)	−0.375 5(6)	0.875 9(9)
C(40)	0.152 8(4)	0.564 0(5)	−0.483 0(9)	C(82)	−0.381 5(3)	−0.387 5(6)	0.846 1(9)
C(41)	0.146 3(4)	0.588 4(5)	−0.353 8(9)	C(83)	−0.353 2(3)	−0.351 2(6)	0.734 4(9)
C(42)	0.180 8(4)	0.576 5(5)	−0.242 5(9)	C(84)	−0.375 6(3)	−0.302 9(6)	0.652 5(9)

anhydrous toluene (30 cm^3) was stirred under nitrogen for 10 min at room temperature. Then a solution of $[Re(NMe)Cl_3(PPh_3)_2]$ (0.25 mmol) in the same solvent (30 cm^3) was added, and the suspension was stirred with gentle heating for 20 min and then refluxed for 40 min. During this time the solution changed from pale blue to pale violet. The solution was filtered, evaporated to a small volume and acetone–diethyl ether (1 : 3) was added until a light blue precipitate was obtained. The solid was filtered off and washed with water, ethanol and diethyl ether. Recrystallisation from dichloromethane–diethyl ether gave a blue-violet microcrystalline solid, yield 70% (Found: C, 51.4; H, 4.0; N, 2.9; S, 5.8. $C_{43}H_{38}Cl_2N_2P_3ReS_2$ requires C, 51.8; H, 3.8; N, 2.8; S, 6.4%); $\nu(P_2N)$ 1200s, 808s; $\nu(PS)$ 560s cm^{-1}. NMR (CD_2Cl_2): $^{31}P\text{-}\{^1H\}$, AMX spin system, δ_X −16.16 (dd, PPh_3), δ_M 39.48 (dd), δ_A 45.74 (dd) [$^3J(P_XP_A)$ 11.1, $^3J(P_XP_M)$ 6.8, $^2J(P_AP_M)$ 4.0 Hz]; ^1H, δ 0.97 [d, $^4J(HP_X)$ 4.6 Hz, CH_3].

$[Re(NMe)Cl\{N(SPPh_2)_2\text{-}S,S'\}_2]$ **5**. The disubstituted complex was prepared analogously to **4**, using an excess (1 : 4) of the alkali-metal salt $Li[N(SPPh_2)_2]$ of the ligand. The blue-violet solution was filtered, evaporated to a small volume and acetone was added until a brown precipitate was obtained. The solid was filtered off, and washed with water, ethanol and diethyl ether. Recrystallisation from dichloromethane–acetone gave brown-orange microcrystals, yield 85% (Found: C, 51.8; H, 3.4; N, 3.7; S, 10.8. $C_{49}H_{43}ClN_3P_4ReS_4$ requires C, 51.3; H, 3.8; N, 3.7; S, 11.2%); $\nu(P_2N)$ 1228s, 802s; $\nu(PS)$ 564s cm^{-1}. NMR ($CDCl_3$): $^{31}P\text{-}\{^1H\}$, δ 42.03 (s); ^1H, δ 0.13 (s, CH_3).

$[ReNCl\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$ **6**. A mixture of $[ReNCl_2(PPh_3)_2]$ (0.18 mmol) and $NH(SPPh_2)_2$ (0.54 mmol) in toluene (40 cm^3) was refluxed for 3 h, during which the orange suspension became a yellow solution. The solution was evaporated to a small volume and ethanol added until a yellow precipitate was obtained. The product was washed with acetone and diethyl ether and then crystallised from dichloromethane–diethyl ether, yield 85% (Found: C, 52.8; H, 3.6; N, 2.8; S, 6.2. $C_{42}H_{35}ClN_2P_3ReS_2$ requires C, 53.3; H, 3.7; N, 3.0; S, 6.8%);

Table 3 Fractional coordinates for $[Re(NMe)Cl_3\{NH(PPh_2)_2\text{-}P,P'\}]$ **1**

Atom	*x*	*y*	*z*
Re	0.205 24(4)	0.214 31(4)	0.005 67(7)
P(1)	0.271 0(3)	0.170 1(3)	0.128 5(5)
P(2)	0.218 0(3)	0.300 4(3)	0.118 5(5)
Cl(1)	0.319 8(3)	0.261 2(3)	−0.032 4(4)
Cl(2)	0.156 9(4)	0.286 4(4)	−0.110 0(5)
Cl(3)	0.221 9(4)	0.121 8(4)	−0.101 4(6)
N(1)	0.266(1)	0.246 3(9)	0.182(1)
C(25)	0.067(1)	0.159(2)	0.099(2)
N(2)	0.131(1)	0.186(1)	0.052(2)
C(1)	0.362(1)	0.141(1)	0.122(2)
C(2)	0.412(2)	0.159(3)	0.187(2)
C(3)	0.482(2)	0.134(2)	0.174(3)
C(4)	0.505(2)	0.098(2)	0.101(2)
C(5)	0.454(2)	0.084(2)	0.041(2)
C(6)	0.386(2)	0.106(2)	0.049(2)
C(7)	0.225(1)	0.102(1)	0.190(2)
C(8)	0.196(1)	0.115(1)	0.273(2)
C(9)	0.158(2)	0.063(2)	0.313(3)
C(10)	0.152(2)	−0.002(2)	0.277(3)
C(11)	0.179(2)	−0.013(2)	0.196(3)
C(12)	0.216(2)	0.036(2)	0.153(2)
C(13)	0.264(1)	0.382(1)	0.100(2)
C(14)	0.310(2)	0.410(2)	0.160(2)
C(15)	0.343(2)	0.472(2)	0.148(3)
C(16)	0.325(1)	0.510(2)	0.084(3)
C(17)	0.279(2)	0.489(1)	0.023(2)
C(18)	0.245(2)	0.425(2)	0.035(2)
C(19)	0.137(1)	0.322(1)	0.174(2)
C(20)	0.079(1)	0.345(2)	0.121(2)
C(21)	0.016(1)	0.362(2)	0.169(3)
C(22)	0.013(2)	0.353(2)	0.259(3)
C(23)	0.068(2)	0.335(2)	0.307(2)
C(24)	0.129(2)	0.317(2)	0.266(2)

Table 4 Selected bond lengths (Å) and angles (°) for $[ReNCl\{NH(PPh_2)_2\text{-}P,P'\}_2][BPh_4]\cdot EtOH$ **2a**·EtOH

Re–N(1)	1.711(8)	Re–Cl	2.496(3)
Re–P(1)	2.463(3)	Re–P(3)	2.448(3)
Re–P(2)	2.442(3)	Re–P(4)	2.447(3)
P(1)–N(2)	1.701(8)	P(3)–N(3)	1.704(8)
P(2)–N(2)	1.687(8)	P(4)–N(3)	1.703(8)
P(1)–C(1)	1.809(8)	P(3)–C(25)	1.793(7)
P(1)–C(7)	1.803(8)	P(3)–C(31)	1.821(7)
P(2)–C(13)	1.805(8)	P(4)–C(37)	1.800(8)
P(2)–C(19)	1.804(9)	P(4)–C(43)	1.802(8)
B–C(49)	1.70(1)	O–C(73)	1.44(2)
B–C(55)	1.68(1)	C(73)–C(74)	1.41(3)
B–C(61)	1.69(1)		
B–C(67)	1.68(1)		
Cl–Re–N(1)	178.5(3)	P(3)–Re–P(4)	67.0(1)
P(1)–Re–P(2)	66.8(1)	P(2)–Re–P(4)	111.2(1)
P(1)–Re–P(3)	113.4(1)	P(3)–N(3)–P(4)	105.0(5)
P(1)–N(2)–P(2)	105.7(4)	Re–P(3)–N(3)	93.9(3)
Re–P(1)–N(2)	93.2(3)	Re–P(4)–N(3)	94.4(3)
Re–P(2)–N(2)	94.3(3)	Re–P(2)–C(13)	114.3(3)
Re–P(1)–C(1)	122.6(3)	Re–P(2)–C(19)	124.5(3)
Re–P(1)–C(7)	121.2(3)	Re–P(4)–C(37)	113.7(3)
Re–P(3)–C(25)	119.8(3)	Re–P(4)–C(43)	125.1(3)
Re–P(3)–C(31)	122.1(2)	C(13)–P(2)–C(19)	105.5(4)
C(1)–P(1)–C(7)	103.6(4)	C(37)–P(4)–C(43)	106.6(4)
C(25)–P(3)–C(31)	103.3(4)	N(3)–P(3)–C(25)	107.9(4)
N(2)–P(1)–C(1)	106.3(4)	N(3)–P(3)–C(31)	108.4(4)
N(2)–P(1)–C(7)	107.6(4)	N(3)–P(4)–C(37)	110.2(4)
N(2)–P(2)–C(13)	109.2(4)	N(3)–P(4)–C(43)	105.6(4)
N(2)–P(2)–C(19)	107.8(4)		

Table 5 Selected bond lengths (Å) and angles (°) for $[ReNCl\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$ **6**

Re(1)–N(1)	1.63(1)	Re(2)–N(3)	1.63(1)
Re(1)–Cl(1)	2.376(3)	Re(2)–Cl(2)	2.384(3)
Re(1)–P(3)	2.414(3)	Re(2)–P(6)	2.409(3)
Re(1)–S(1)	2.452(3)	Re(2)–S(4)	2.449(3)
Re(1)–S(2)	2.375(3)	Re(2)–S(3)	2.375(3)
S(1)–P(1)	2.033(4)	S(4)–P(4)	2.022(4)
S(2)–P(2)	2.055(4)	S(3)–P(5)	2.054(4)
N(2)–P(1)	1.580(9)	N(4)–P(4)	1.597(9)
N(2)–P(2)	1.585(9)	N(4)–P(5)	1.57(1)
S(1)–Re(1)–S(2)	95.9(2)	S(3)–Re(2)–S(4)	97.8(2)
S(1)–Re(1)–Cl(1)	78.4(2)	S(4)–Re(2)–Cl(2)	77.7(2)
S(2)–Re(1)–P(3)	85.0(1)	S(3)–Re(2)–P(6)	84.0(1)
Cl(1)–Re(1)–P(3)	86.8(2)	Cl(2)–Re(2)–P(6)	86.1(2)
Re(1)–S(1)–P(1)	105.2(2)	Re(2)–S(4)–P(4)	105.4(2)
Re(1)–S(2)–P(2)	113.0(2)	Re(2)–S(3)–P(5)	110.9(2)
S(1)–P(1)–N(2)	118.0(4)	S(4)–P(4)–N(4)	117.4(4)
S(2)–P(2)–N(2)	117.4(4)	S(3)–P(5)–N(4)	117.4(4)
P(1)–N(2)–P(2)	126.0(6)	P(4)–N(4)–P(5)	126.4(7)

Table 6 Selected bond lengths (Å) and angles (°) for $[Re(NMe)Cl_3\{NH(PPh_2)_2\text{-}P,P'\}]$ **1**

Re–Cl(1)	2.418(6)	Re–P(1)	2.413(7)
Re–Cl(2)	2.423(8)	Re–P(2)	2.393(7)
Re–Cl(3)	2.426(8)	Re–N(2)	1.67(2)
P(1)–N(1)	1.66(2)	P(2)–N(1)	1.68(2)
P(1)–C(1)	1.82(3)	P(2)–C(13)	1.81(3)
P(1)–C(7)	1.83(3)	P(2)–C(19)	1.81(3)
N(2)–C(25)	1.49(4)		
Cl(1)–Re–N(2)	168.5(8)	N(2)–Re–P(1)	89.1(8)
Cl(1)–Re–Cl(2)	87.4(2)	N(2)–Re–P(2)	89.7(8)
Cl(1)–Re–Cl(3)	89.1(2)	Cl(2)–Re–Cl(3)	87.6(3)
Cl(1)–Re–P(1)	81.6(2)	P(1)–Re–P(2)	67.5(2)
Cl(1)–Re–P(2)	80.5(2)	Cl(2)–Re–P(2)	100.7(2)
N(2)–Re–Cl(2)	100.5(8)	Cl(3)–Re–P(1)	102.3(2)
N(2)–Re–Cl(3)	99.5(7)	Re–N(2)–C(25)	177.0(2)
Re–P(1)–N(1)	93.1(7)	C(1)–P(1)–C(7)	106.0(1)
Re–P(1)–C(1)	123.6(9)	C(1)–P(1)–N(1)	110.0(1)
Re–P(1)–C(7)	113.9(9)	C(7)–P(1)–N(1)	109.0(1)
Re–P(2)–N(1)	93.3(7)	C(13)–P(2)–C(19)	107.0(1)
Re–P(2)–C(13)	121.0(1)	C(13)–P(2)–N(1)	111.0(1)
Re–P(2)–C(19)	114.5(8)	C(19)–P(2)–N(1)	109.0(1)
		P(1)–N(1)–P(2)	106.0(1)

ν(P_2N) 1194s, 823m, ν(PS) 582s, 557s cm^{-1}. $^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2): AMX spin system, δ_X 27.78 (dd, PPh_3), δ_M 36.45 (dd), δ_A 41.43 (dd) [$^3J(P_XP_A)$ 21.0, $^3J(P_XP_M)$ 6.4, $^2J(P_AP_M)$ 4.4 Hz].

$[ReN\{N(SPPh_2)_2\text{-}S,S'\}_2]$ **7**. A suspension of $NH(SPPh_2)_2$ (0.72 mmol) and LiBu (0.54 mmol) in anhydrous toluene (40 cm^3) was stirred for 10 min at room temperature. Then $[ReNCl_2(PPh_3)_2]$ (0.18 mmol) was added. The suspension was stirred with gentle heating for 20 min and then heated under reflux for 40 min. The orange solution was filtered, evaporated to a small volume and ethanol added until a yellow-orange precipitate was obtained. This product was filtered off and washed with water, ethanol and dried with diethyl ether. Recrystallisation from dichloromethane–acetone–ethanol gave an orange microcrystalline solid, yield 80% (Found: C, 52.9; H, 3.8; N, 4.0; S, 11.9. $C_{48}H_{40}N_3P_4ReS_4$ requires C, 52.5; H, 3.7; N, 3.8; S, 11.7%); ν(P_2N) 1196s, 816m, ν(PS) 557s cm^{-1}. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 38.12 (s).

cis-$[Re(NMe)Cl_2\{N(SePPh_2)_2\text{-}Se,Se'\}(PPh_3)]$ **8**. A stoichiometric amount of $K[N(SePPh_2)_2]$ was added to a degassed chloroform solution (40 cm^3) of $[Re(NMe)Cl_3(PPh_3)_2]$ (0.18 mmol). The reaction mixture was stirred at reflux under nitrogen for 40 min, during which the solution changed from pale blue to blue-violet. The solution was filtered and concentrated to a small volume. After addition of acetone–

diethyl ether (1 : 3) the product crystallised as light blue-violet microcrystals and was recrystallised from dichloromethane–ethanol, yield 60% (Found: C, 47.5; H, 3.5; N, 2.6. $C_{43}H_{38}Cl_2N_2P_3ReSe_2$ requires C, 47.3; H, 3.5; N, 2.6%); ν(P_2N) 1192s, 798m, other ligand band 534s cm^{-1}. NMR ($CDCl_3$): ^{31}P-{^1H}, AMX spin system, δ_X −19.25 (dd, PPh_3), δ_A 31.40 (d) [$^3J(P_XP_A)$ 12.2, $^3J(P_XP_M)$ 6.9, $^1J(P_ASe)$ 532, $^1J(P_MSe)$ 540 Hz]; ^1H, δ −0.10 [d, $^4J(HP_X)$ 6.3 Hz, CH_3].

[Re(NMe)Cl{N($SePPh_2$)$_2$-*Se,Se′*}$_2$] **9**. The disubstituted complex was obtained by the same procedure as for **8** using an excess (3 : 1) of the ligand. The reaction mixture was stirred for 20 min during which it changed from pale blue to brown. The solution was filtered and concentrated to a small volume. A microcrystalline brown solid was obtained on standing after addition of acetone to the solution, yield 70% (Found: C, 44.7; H, 3.6; N, 2.9. $C_{49}H_{43}ClN_3P_4ReSe_4$ requires C, 44.1; H, 3.2; N, 3.1%); (P_2N) 1210s, 792s, other ligand band 534s cm^{-1}. NMR ($CDCl_3$): ^{31}P-{^1H}, δ 27.25 (s) [^1J(PSe) 558 Hz]; ^1H, δ −0.02 (s, CH_3).

[ReN{N($SePPh_2$)$_2$-*Se,Se′*}$_2$] **10**. To [$ReNCl_2(PPh_3)_2$] (0.18 mmol) in degassed chloroform (50 cm^3) was added K[N($SePPh_2$)$_2$] (0.45 mmol). This suspension was stirred at reflux under nitrogen for 90 min during which an orange cloudy solution was obtained. The solution was filtered and evaporated to a small volume and acetone added to obtain a yellow-orange precipitate. The product was washed with acetone and diethyl ether. Recrystallisation from dichloromethane–acetone gave an orange microcrystalline solid, yield 85% (Found: C, 45.4; H, 3.2; N, 3.3. $C_{48}H_{40}N_3P_4ReSe_4$ requires C, 44.9; H, 3.1; N, 3.2%); ν(P_2N) 1174s, 803m, other ligand band 534s cm^{-1}. ^{31}P-{^1H} NMR ($CDCl_3$): δ 21.60 (s) [^1J(PSe) 547 Hz].

trans-[$ReOCl_2${N($OPPh_2$)$_2$-*O,O′*}($AsPh_3$)] **11**. This compound was prepared as reported previously for the analogous triphenylphosphine derivative.[1] ^{31}P-{^1H} NMR ($CDCl_3$): δ_M 31.29 (d), δ_A 33.48 (d) [$^2J(P_AP_M)$ 6.3 Hz]. The P_A and P_M resonances can be reversed because of the uncertainty in their assignment.

Crystallography.—Crystal data. **2a**·EtOH. $C_{74}H_{68}BClN_3OP_4Re$, $M = 1371.2$, monoclinic, space group $P2_1/c$, $a = 13.922(4)$, $b = 13.132(4)$, $c = 36.535(7)$ Å, $\beta = 92.53(3)°$, $U = 6673(2)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.7107$ Å), $Z = 4$, $D_c = 1.36$ g cm^{-3}, $F(000) = 2796$. Maximum crystal dimensions = 0.2 mm, μ(Mo-Kα) = 20 cm^{-1}.

6. $C_{42}H_{35}ClN_2P_3ReS_2$, $M = 946.5$, triclinic, space group $P\bar{1}$, $a = 24.577(6)$, $b = 17.669(5)$, $c = 9.935(4)$ Å, $\alpha = 89.92(3)$, $\beta = 95.08(3)$, $\gamma = 110.67(3)°$, $U = 4018(2)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.7107$ Å), $Z = 4$, $D_c = 1.56$ g cm^{-3}, $F(000) = 1880$. Maximum crystal dimension 0.25 mm, μ(Mo-Kα) = 35 cm^{-1}.

1. $C_{25}H_{24}Cl_3N_2P_2Re$, $M = 706.0$, tetragonal, space group $I\bar{4}$, $a = 18.952(5)$, $b = 18.952(5)$, $c = 15.372(5)$ Å, $U = 5521(2)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.7107$ Å), $Z = 8$, $D_c = 1.70$ g cm^{-3}, $F(000) = 2744$. Maximum crystal dimension 0.2 mm, μ(Mo-Kα) = 48 cm^{-1}.

Data collection and processing. Philips PW1100 diffractometer, θ–2θ scan mode., scan speed 2° min^{-1}, graphite-monochromated Mo-Kα radiation, $\theta_{max} = 25°$; **2a**·EtOH, 11 004 reflections measured, 6057 observed [$I > 3\sigma(I)$]; **6**, 14 617 reflections measured, 6477 observed [$I > 3\sigma(I)$]; **1**, 3261 reflections measured, 2026 observed [$I > 3\sigma(I)$]. All reflections were corrected for Lorentz polarization and absorption.[15] No crystal decay was observed during irradiation.

Structure analysis and refinement. The heavy-atom procedure was used for structure determinations. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with one, overall U_{iso} [= 0.08 Å^2], The positions of the hydrogen atoms attached to N(2) and N(3) in **2a**·EtOH were well located in the Fourier difference map. These atoms were introduced but not refined. The function minimized was $\Sigma w \Delta F^2$ with $w = 1$, final R values are 0.038 for **2a**·EtOH, 0.037 for **6** and 0.056 for **1**. Programs and computers used and sources of scattering factor data are given in ref. 16. Atomic coordinates are listed in Tables 1–3, bond distances and angles in Tables 4–6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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