Metal Complexes containing 'Inorganic (Carbon-free) Chelate Rings.' Reactivity of the $[Re{\equiv}O]^{3+}$ Core toward Bis(diphenylphosphino)amine Derivatives. Crystal Structures of $[ReOCl_2\{N(XPPh_2)_2\}(PPh_3)]$ (X = O or S) and $[ReO(OEt)\{N(SPPh_2)_2\}_2]$†

Roberto Rossi,*[a] Andrea Marchi,[a] Luciano Magon,*[a] Umberto Casellato,[b] Sergio Tamburini[b] and Rodolfo Graziani[c]

[a]*Laboratorio di Chimica Nucleare ed Inorganica e Centro di Fotochimica del C.N.R., Dipartimento di Chimica, Università di Ferrara, Italy*

[b]*Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Padova, Italy*

[c]*Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova, Italy*

The complexes $[ReOCl_3(PPh_3)_2]$ and $[ReOCl_2(OEt)(PPh_3)_2]$ react with an excess of $NH(OPPh_2)_2$ to give $[ReOCl_2\{N(OPPh_2)_2\}(PPh_3)]$ **1**. When the donor atoms are changed by using $NH(SPPh_2)_2$ as the ligand the mono- and di-substituted complexes $[ReOCl_2\{N(SPPh_2)_2\}(PPh_3)]$ **2** and $[ReOCl\{N(SPPh_2)_2\}_2]$ **3a** are obtained. Complex **3a** can also be prepared by using the anionic compound $[ReOCl_4]^-$ as the starting material. When complex **3a** is crystallized from CH_2Cl_2–EtOH, $[ReO(OEt)\{N(SPPh_2)_2\}_2]$ **3b** is obtained. The structures of complexes **1**, **2** and **3b** were determined by X-ray crystallography. Compound **1** is triclinic, space group $P\bar{1}$, with $a = 14.885(5)$, $b = 13.815(5)$, $c = 10.019(5)$ Å, $\alpha = 92.35(3)$, $\beta = 108.46(3)$, $\gamma = 99.10(3)°$ and $Z = 2$. The structure was refined to $R = 0.028$, based on 4204 observed reflections. Compound (**2**) is triclinic, space group $P\bar{1}$, with $a = 16.831(5)$, $b = 14.667(5)$, $c = 9.918(5)$ Å, $\alpha = 99.48(3)$, $\beta = 104.93(3)$, $\gamma = 92.57(3)°$ and $Z = 2$. The structure was refined to $R = 0.038$, based on 5955 observed reflections. Compound **3b** is trinclinic, space group $P\bar{1}$, with $a = 10.214(5)$, $b = 10.750(5)$, $c = 13.947(4)$ Å, $\alpha = 111.72(3)$, $\beta = 113.07(3)$, $\gamma = 64.06(3)°$ and $Z = 1$. The structure was refined to $R = 0.063$, based on 4062 observed reflections. All three compounds show slightly distorted octahedral geometries. The chlorine atoms are *trans* in **1** and *cis* in **2**. The Re–O(oxide) bonds show some triple bond character, and exert a strong *trans* influence.

Bidentate phosphine ligands of the type $R_2P(CH_2)_nPR_2$ (R = alkyl or aryl) have been extensively used in transition-metal chemistry. They not only chelate or bind in a monodentate fashion to a single metal centre but, in the case of $n = 1$ or 2, they can also bridge dimetal units to give quite stable five- or six-membered rings.[1] In contrast, little has been reported on the behaviour of a related class of ligands, *viz.* bis(diphenylphosphino)amine and its derivatives,[2] $NH(PPh_2)_2$ and $NH(XPPh_2)_2$ (X = O, S or Se), which contain no carbon atoms in their chelate rings. These compounds provide an ideal system for studying the effect of the variation of the ring size and of the donor group X on the co-ordination properties. The work described herein concerns the reactions of iminobis(diphenylphosphine oxide), $NH(OPPh_2)_2$, and iminobis(diphenylphosphine sulphide), $NH(SPPh_2)_2$, with the rhenium(v) complexes $[ReOCl_3(PPh_3)_2]$, $[ReOCl_2(OEt)(PPh_3)_2]$ and $[AsPh_4][ReOCl_4]$, all of which contain the $[Re{\equiv}O]^{3+}$ core.

Results and Discussion

Reaction of $[ReOCl_3(PPh_3)_2]$ with an excess of $NH(OPPh_2)_2$ or its alkali-metal salt in $CHCl_3$ under reflux for 30 min produces the complex $[ReOCl_2\{N(OPPh_2)_2\}(PPh_3)]$ **1**, in which the $N(OPPh_2)_2$ ligand behaves as a chelating monoanion. It is noteworthy that when the reaction is carried out in a C_6H_6–EtOH mixture complex **1** is not obtained, and instead the ethoxy compound $[ReOCl_2(OEt)(PPh_3)_2]$ is formed. This complex can also be prepared by refluxing a suspension of $[ReOCl_3(PPh_3)_2]$ in C_6H_6–EtOH in the absence of ligand.[3] Complex **1** can also be obtained directly from the ethoxy compound in $CHCl_3$ solution. This behaviour shows that the alcoholic medium affects the formation of complex **1** and this is reinforced by the observed decomposition of **1** upon attempts to crystallize samples from CH_2Cl_2–EtOH mixtures.

Structural studies on complex **1** show the rhenium atom in a distorted octahedral co-ordination with one apical position occupied by the oxygen atom of the $[Re{\equiv}O]^{3+}$ core and the other by an oxygen atom of the chelate ligand (Fig. 1). On this basis, the first step in complex formation is probably substitution of the charged group (Cl^- or EtO^-) *trans* to the $[Re{\equiv}O]^{3+}$ core by the negatively charged oxygen atom of the ligand. Presumably the presence of ethanol in the reaction mixture inhibits this substitution.

When the environment of the $[Re{\equiv}O]^{3+}$ core is modified, and the five-co-ordinated anion $[ReOCl_4]^-$ is used as the starting material, no reaction products are obtained and only the starting rhenium compound is recovered. This behaviour is in contrast to the observed reactivity with monoanionic chelating Schiff base ligands. In this case a comparison of rhenium(v) oxohalide compounds reveals a higher reactivity of $[ReOCl_4]^-$ over $[ReOCl_3(PPh_3)_2]$.[4]

† *trans*-[Bis(diphenylphosphinoyl)amido-*O,O'*]dichlorooxo(triphenylphosphine)rhenium(v), *cis*-[bis(diphenylthiophosphinoyl)amido-*S,S'*]dichlorooxo(triphenylphosphine)rhenium(v) and bis[bis(diphenylthiophosphinoyl)amido-*S,S'*]ethoxooxorhenium(v).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

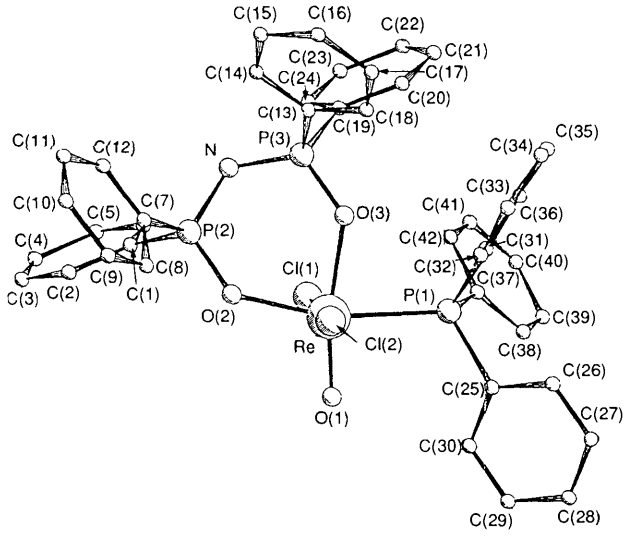

Fig. 1 Crystal structure of $[ReOCl_2\{N(OPPh_2)_2\}(PPh_3)]$ **1**

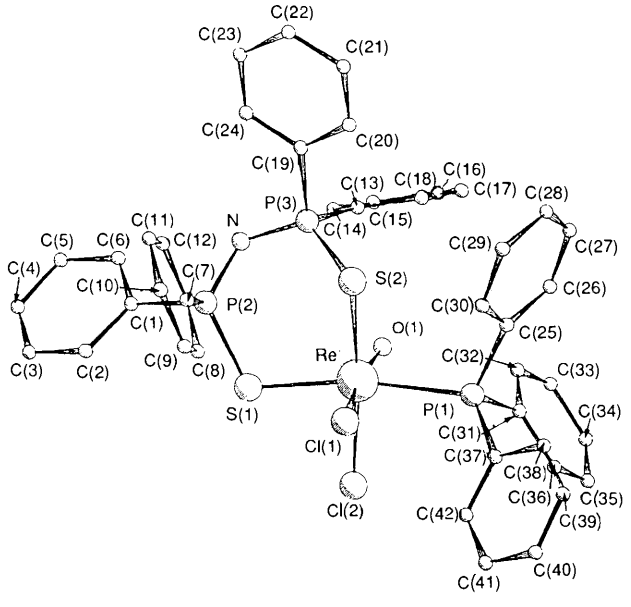

Fig. 2 Crystal structure of $[ReOCl_2\{N(SPPh_2)_2\}(PPh_3)]$ **2**

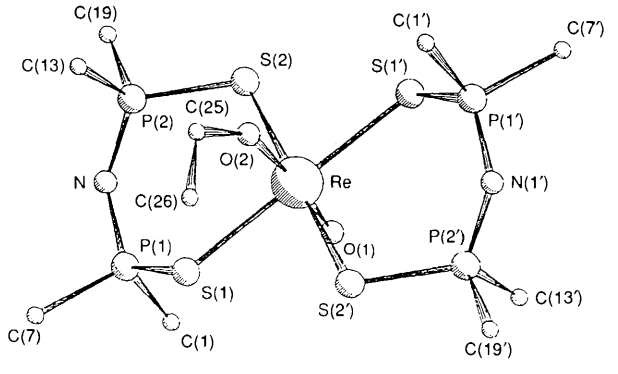

Fig. 3 Crystal structure of $[ReO(OEt)\{N(SPPh_2)_2\}_2]$ **3b**. Only the first carbon atom of each phenyl group is shown for clarity. Primed atoms are related to unprimed atoms by the inversion centre.

Upon changing the donor atoms by using iminobis(diphenylphosphine sulphide) $NH(SPPh_2)_2$, as the ligand, a different behaviour is observed with the oxorhenium(v) complexes. Treatment of $[ReOCl_3(PPh_3)_2]$ with $NH(SPPh_2)_2$ in a 1:1 molar ratio in refluxing tetrahydrofuran (thf) for 30 min gives the monosubstituted complex $[ReOCl_2\{N(SPPh_2)_2\}(PPh_3)]$ **2**, whereas when the reaction is carried out in a 1:2 molar ratio the disubstituted complex $[ReOCl\{N(SPPh_2)_2\}_2]$ **3a** is obtained. If, however, the anionic complex $[ReOCl_4]^-$ is used as the starting material only complex **3a** is obtained irrespective of the molar ratio; no evidence of the formation of the monosubstituted complex was observed even at a 1:1 molar ratio.

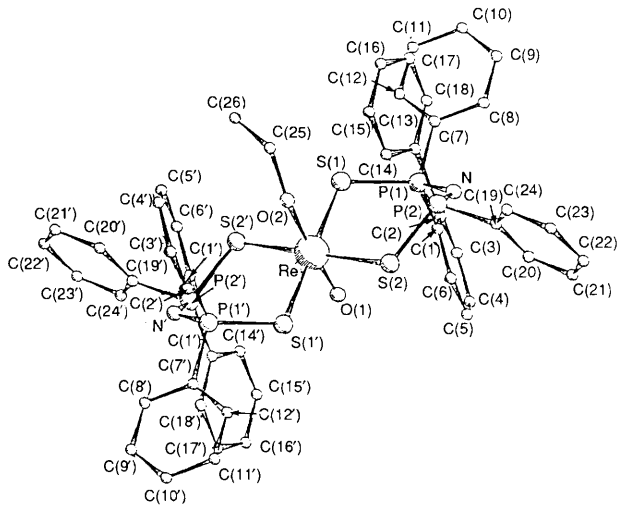

Fig. 4 Atom numbering scheme in $[ReO(OEt)\{N(SPPh_2)_2\}_2]$ **3b**

Compound **2** was crystallized from CH_2Cl_2–Et_2O, whereas for the disubstituted compound crystals suitable for a structural characterization could only be obtained using CH_2Cl_2–EtOH. In the presence of ethanol however the colour of the solution changed from blue-green to yellow-green and the first crop of crystals (**3a**) was obtained only as very small blue-green plates by slow evaporation of the solution. Removal of these by filtration and further evaporation of the resulting solution gave a second crop of yellow-green crystals (**3b**) suitable for diffraction studies.

The crystal structures of the monosubstituted (**2**) and disubstituted (**3b**) complexes show the rhenium atom in a distorted octahedral co-ordination with the chelate ligand in the equatorial plane and a Cl^- or EtO^- group in an apical position *trans* to the Re≡O(oxide) group respectively (Figs. 2 and 3). The observed differing behaviour of $NH(OPPh_2)_2$ and $NH(SPPh_2)_2$ is in accord with the hard acid character of Re^V.[5]

Surprisingly, complex **3b** was not obtained using the ethoxo compound $[ReOCl_2(OEt)(PPh_3)_2]$ as the starting material; complex **3a** was formed, even when ethanol was present in the reaction medium. This observation suggests that the reaction mechanism could be more complicated than the elementary replacement of the two ligands (Cl^- and PPh_3) in the equatorial plane.

The IR spectra of the complexes show the ν(Re≡O) band at 960, 980 and 970 cm^{-1} for **1**, **2** and **3a** respectively, whereas in the ethoxo compound **3b** this band is present at a slightly lower frequency (950 cm^{-1}) as expected for complexes containing the EtO–Re≡O group.[3] The position of the higher frequency P_2N stretching band of the chelate ligands appears at 1205 cm^{-1} in complex **1**, whereas it is centred below this value (1170 cm^{-1}) for **2** and above (1210 cm^{-1}) for **3a** and **3b**. The frequency of this band is diagnostic for complexes of $[N(XPPh_2)_2]^-$ (X = O or S); when the ligand chelates in the protonated form, $NH(XPPh_2)_2$, this band is shifted to *ca.* 900 cm^{-1}.[6] The P–S stretching frequencies for unco-ordinated $[N(SPPh_2)_2]^-$ occur in the region 550–580 cm^{-1} and fall by 60–70 cm^{-1} upon co-ordination.[6] In complex **1** the bands at 1125 and 1060 cm^{-1} could probably be assigned to the P=O groups co-ordinated to the metal through their oxygen atoms.[7]

X-Ray Crystal Structures.—The crystal and molecular structures of compounds **1**, and **2** and **3b** are shown in Figs. 1–4.

Despite the similarity in their chemical composition, the molecular conformations of compounds **1** and **2** differ. If the donor atoms of the bidentate ligands are considered to lie in the equatorial plane, then the chlorine atoms are *trans* and apical in the oxygen compound **1** but are in *cis* positions in the sulphur compound **2** where O and Cl(1) are the apical atoms. Structural details of the $N(Ph_2P)_2$ moieties are perfectly comparable in the two compounds, with the P–N and P–C bonds lying in the narrow ranges 1.58–1.59 and 1.79–1.81 Å respectively, with P–N–P angles of 124° (both), and O–P–N or S–P–N angles in the range 115–117°. It is noteworthy that the P–C bond distances in the ligands (mean 1.80 Å) are slightly, but consistently, shorter than the corresponding distances in the PPh_3 groups (mean 1.82 Å). Major structural differences in the bidentate ligands lie first in the angles at the donor atoms (both angles are 134° in **1** against a mean value of 107° in **2**) and secondly in the metal–ligand bonds in that the P–O bonds in **1** are equivalent while the P–S distances for **2** differ with the shorter P(3)–S(2) bond being associated with the longer Re–S(2) bond. The observed difference in the Re–S distances may well be a result of the differing nature of the *trans* ligands at each sulphur atom. This is surely the case in **1** where the strong *trans* influence of the Re–O(oxide) bond weakens the Re–O(3) bond with respect to Re–O(2) while the P–O bonds remain equivalent. The *trans* influence of the Re–O(oxide) bond is also evident in **2** where Re–Cl(1) (*trans* to O) is significantly longer than the other Re–Cl bond. The observed Re–O(oxide) bond lengths are very similar in the two compounds [1.660(5) in **1** and 1.677(6) Å in **2**], irrespective of the nature of the *trans* donor atoms. Using a value of 2.04 Å for an Re^V–O single bond[8] and a value of 1.765 Å for a double bond,[9] it is possible to derive bond orders of 2.6 for Re–O(oxide) in **1** and of 2.5 in **2** [calculated using the Pauling equation, bond length = $A + B$ log(bond order), where A and B are refined by fixing Re–O single and double bonds], confirming the suggestion of a considerable triple-bond character in the rhenium–oxygen interactions for terminal oxides.[10,11]

The overall configuration of $[ReO(OEt)\{N(SPPh_2\}_2]$ **3b** is shown in Figs. 3 and 4, together with the atom numbering scheme used. The Re atom is six-co-ordinate octahedral, with the two *trans* chelate ligands rigorously centrosymmetric to one another even though the molecule itself is asymmetric as a whole. Distortions from the idealized geometry are mainly due to the rather large angles (*ca.* 100°) subtended to Re in the equatorial plane by the bidentate ligands, and to the asymmetric apical Re–O bonds. The bidentate ligands bond to Re to give two non-planar six-membered metallacycles in which the Re–S bond distances (mean 2.475 Å) are longer than expected on the basis of the sum of the covalent radii, but are of the same order as those found in other rhenium complexes with bidentate S-donor ligands.[12] The P–N bonds are chemically equivalent, with observed bond distances significantly shorter than normal for a single covalent bond (1.59 instead of 1.75–1.80 Å) indicating double bond character resulting from delocalization of the π electron density. Similar P–N–P sequences with comparable bond lengths are commonly found in cyclic phosphazenes.[13,14] Also the P–N–P angle of 130° agrees with the values of *ca.* 132° found in these systems.

Other structural details of the compound, apart from the statistical distribution of the apical ligands mentioned, are normal and need no particular comment.

Experimental

Materials.—Solvents were purified and dried before use. The starting compounds $[ReOCl_3(PPh_3)_2]$, $[ReOCl_2(OEt)(PPh_3)_2]$ and $[AsPh_4][ReOCl_4]$ were prepared following the literature methods.[15,16] The ligands $NH(XPPh_2)_2$ (X = O or S) were prepared by adding H_2O_2 (X = O) or S_8 (X = S) to a solution of bis(diphenylphosphino)amine.[17] Infrared spectra were recorded on a Perkin-Elmer spectrometer. Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser.

Syntheses.—$[ReOCl_2\{N(OPPh_2)_2\}(PPh_3)]$ **1**. An excess (3:1) of $NH(OPPh_2)_2$ was added to a $CHCl_3$ solution (40 cm^3) of $[ReOCl_3(PPh_3)_2]$ or $[ReOCl_2(OEt)(PPh_3)_2]$ (0.18 mmol). After 30 min under reflux the yellow-green solution was filtered and then concentrated *in vacuo*. The resulting green precipitate was removed by filtration and washed with EtOH and Et_2O. The complex was crystallized from CH_2Cl_2–Et_2O, yield 80% (Found: C, 52.6; H, 3.6; N, 1.2. Calc. for $C_{42}H_{35}Cl_2NO_3P_3Re$: C, 53.0; H, 3.7; N, 1.5%). Infrared data (Nujol): $\nu(P_2N)$ 1205 and 830; ν(P–O) 1125 and 1060; ν(Re≡O) 960 cm^{-1}.

$[ReOCl_2\{N(SPPh_2)_2\}(PPh_3)]$ **2**. A stoichiometric amount of $NH(SPPh_2)_2$ (0.18 mmol) in thf solution was added dropwise to a stirred thf solution (40 cm^3) of $[ReOCl_3(PPh_3)_2]$ (0.18 mmol). The green solution was heated under reflux for 15 min and then evaporated to one third of its volume. The green product was obtained upon addition of Et_2O and crystallized from CH_2Cl_2–Et_2O, yield 80% (Found: C, 51.1; H, 4.0; N, 1.6; S, 5.5. Calc. for $C_{42}H_{35}Cl_2NOP_3ReS_2$: C, 51.3; H, 3.6; N, 1.4; S, 6.5%). Infrared data (Nujol): $\nu(P_2N)$ 1170 and 830; ν(Re≡O) 980; $\nu(P_2S)$ 580 and 510 cm^{-1}.

$[ReOCl\{N(SPPh_2)_2\}_2]$ **3a**. An excess (3:1) of $NH(SPPh_2)_2$ was added to a thf solution (40 cm^3) of $[ReOCl_3(PPh_3)_2]$ (0.18 mmol). The green solution was heated under reflux for 15 min and then concentrated *in vacuo*. The resulting green precipitate was recovered by filtration and washed with Me_2CO and Et_2O. The complex was crystallized from CH_2Cl_2–Et_2O, yield 85% (Found: C, 49.6; H, 3.3; N, 2.1; S, 11.2. Calc. for $C_{48}H_{40}ClN_2OP_4ReS_4$: C, 51.0; H, 3.5; N, 2.5; S, 11.3%). Infrared data (Nujol): $\nu(P_2N)$ 1210 and 815; ν(Re≡O) 970; ν(P–S) 570 and 550 cm^{-1}.

The same compound was also prepared using $[AsPh_4][ReOCl_4]$ as the starting material and carrying out the reaction under argon and anhydrous conditions.

$[ReO(OEt)\{N(SPPh_2)_2\}_2]$ **3b**. This compound was obtained from **3a** as a consequence of its crystallization from CH_2Cl_2–EtOH.

X-Ray Crystallography.—Crystals of maximum dimension 0.15 mm were used for X-ray work and examined on a Philips four-circle diffractometer. Cell dimensions for the compounds were determined by least-squares refinement of the setting angles of 25 reflections in the range $6 < \theta < 12°$.

Crystal data. $[ReOCl_2\{N(OPPh_2)_2\}(PPh_3)]$ **1**, $C_{42}H_{35}Cl_2NO_3P_3Re$, M = 951, triclinic, space group $P\bar{1}$, a = 14.885(5), b = 13.815(5), c = 10.019(5) Å, α = 92.35(3), β = 108.46(3), γ = 99.10(3)°, U = 1 920 Å^3, D_c = 1.65 g cm^{-3} for Z = 2, μ(Mo-Kα) = 36.5 cm^{-1}, Mo-Kα radiation, λ = 0.7107 Å, $F(000)$ = 944.

$[ReOCl_2\{N(SPPh_2)_2\}(PPh_3)]$ **2**. $C_{42}H_{35}Cl_2NOP_3ReS_2$, M = 983, triclinic, space group $P\bar{1}$, a = 16.831(5), b = 14.667(5), c = 9.918(5) Å, α = 99.48(3), β = 104.93(3), γ = 92.57(3)°, U = 2 324 Å^3, D_c = 1.41 g cm^{-3} for Z = 2, μ(Mo-Kα) = 31.0 cm^{-1}, Mo-Kα radiation, λ = 0.7107 Å, $F(000)$ = 976.

$[ReO(OEt)\{N(SPPh_2)_2\}_2]$ **3b**, $C_{50}H_{45}N_2O_2P_4ReS_4$, M = 1 144, triclinic, space group $P\bar{1}$, a = 10.214(5), b = 10.750(5), c = 13.947(4) Å, α = 111.72(3), β = 113.07(3), γ = 64.06(3)°, U = 1 230 Å^3, D_c = 1.54 g cm^{-3} for Z = 1, μ(Mo-Kα) = 29.4 cm^{-1}, Mo-Kα radiation, λ = 0.7107 Å, $F(000)$ = 574.

Intensities were measured with the θ–2θ scan method up to θ = 25° using monochromatized Mo-Kα radiation. The intensities were corrected for Lorentz-polarization and for absorption.[18] For **1** 5041 unique reflections were recorded, and 4204 with $I > 3\sigma(I)$ were considered as observed and used in subsequent calculations; for **2** 7245 reflections were recorded and 5955 used; for **3b** 5661 reflections were recorded and 4062 used, with the same criterion as for **1**. All crystals were stable under irradiation.

Solution of the structures was achieved by Patterson and Fourier methods alternated with cycles of least-squares refine-

Table 1 Atomic coordinates for $[ReOCl_2\{N(OPPh_2)_2\}(PPh_3)]$ **1**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Re	0.144 96(2)	0.249 91(2)	0.447 14(3)	C(18)	0.213 64(29)	0.077 46(31)	0.068 49(44)
P(1)	0.073 47(10)	0.346 17(11)	0.251 77(19)	C(13)	0.286 72(29)	0.083 72(31)	0.198 23(44)
P(2)	0.322 06(10)	0.129 54(11)	0.592 51(19)	C(20)	0.359 98(27)	0.311 46(31)	0.136 34(46)
P(3)	0.314 39(10)	0.188 70(11)	0.325 87(19)	C(21)	0.412 37(27)	0.392 84(31)	0.099 60(46)
Cl(1)	0.278 24(12)	0.376 71(12)	0.566 66(20)	C(22)	0.493 74(27)	0.448 01(31)	0.201 03(46)
Cl(2)	0.037 32(13)	0.101 72(13)	0.339 92(23)	C(23)	0.522 74(27)	0.421 80(31)	0.339 21(46)
N	0.371 92(32)	0.165 82(35)	0.479 95(56)	C(24)	0.470 35(27)	0.340 42(31)	0.375 96(46)
O(1)	0.076 49(36)	0.285 83(40)	0.535 12(54)	C(19)	0.388 98(27)	0.285 25(31)	0.274 52(46)
O(2)	0.224 59(27)	0.160 19(29)	0.575 09(47)	C(26)	−0.113 02(29)	0.374 08(36)	0.107 99(37)
O(3)	0.218 95(26)	0.223 47(27)	0.309 72(43)	C(27)	−0.198 18(29)	0.408 15(36)	0.097 20(37)
C(2)	0.414 37(27)	0.116 61(24)	0.878 56(49)	C(28)	−0.215 81(29)	0.439 77(36)	0.219 07(37)
C(3)	0.485 15(27)	0.148 23(24)	1.009 07(49)	C(29)	−0.148 29(29)	0.437 33(36)	0.351 71(37)
C(4)	0.550 23(27)	0.235 98(24)	1.025 54(49)	C(30)	−0.063 13(29)	0.403 26(36)	0.362 50(37)
C(5)	0.544 52(27)	0.292 10(24)	0.911 48(49)	C(25)	−0.045 50(29)	0.371 64(36)	0.240 63(37)
C(6)	0.473 74(27)	0.260 48(24)	0.780 96(49)	C(32)	−0.002 90(29)	0.197 88(29)	0.030 89(48)
C(1)	0.408 66(27)	0.172 73(24)	0.764 50(49)	C(33)	−0.015 14(29)	0.151 50(29)	−0.101 60(48)
C(8)	0.212 12(25)	−0.055 00(31)	0.582 46(55)	C(34)	0.033 98(29)	0.195 92(29)	−0.187 25(48)
C(9)	0.199 57(25)	−0.157 07(31)	0.584 75(55)	C(35)	0.095 34(29)	0.286 71(29)	−0.140 40(48)
C(10)	0.276 22(25)	−0.205 70(31)	0.593 19(55)	C(36)	0.107 59(29)	0.333 10(29)	−0.007 91(48)
C(11)	0.365 41(25)	−0.152 26(31)	0.599 32(55)	C(31)	0.058 47(29)	0.288 68(29)	0.077 73(48)
C(12)	0.377 95(25)	−0.050 18(31)	0.597 03(55)	C(38)	0.102 36(23)	0.553 01(28)	0.255 99(50)
C(7)	0.301 31(25)	−0.001 55(31)	0.588 59(55)	C(39)	0.158 52(23)	0.645 90(28)	0.267 59(50)
C(14)	0.342 28(29)	0.009 97(31)	0.227 99(44)	C(40)	0.256 45(23)	0.654 79(28)	0.285 91(50)
C(15)	0.324 76(29)	−0.070 04(31)	0.128 00(44)	C(41)	0.298 24(23)	0.570 79(28)	0.292 63(50)
C(16)	0.251 68(29)	−0.076 30(31)	−0.001 75(44)	C(42)	0.242 08(23)	0.477 90(28)	0.281 03(50)
C(17)	0.196 12(29)	−0.002 55(31)	−0.031 51(44)	C(37)	0.144 14(23)	0.469 01(28)	0.262 71(50)

Table 2 Atomic coordinates for $[ReOCl_2\{N(SPPh_2)_2\}(PPh_3)]$ **2**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Re	0.225 12(2)	0.228 00(2)	0.294 21(4)	C(21)	0.364 35(40)	0.589 52(39)	−0.003 58(71)
N	0.180 89(41)	0.486 34(47)	0.301 24(72)	C(22)	0.351 13(40)	0.681 04(39)	0.043 94(71)
S(1)	0.188 19(14)	0.330 14(16)	0.478 28(26)	C(23)	0.298 73(40)	0.699 72(39)	0.131 55(71)
S(2)	0.300 76(12)	0.347 97(14)	0.218 70(24)	C(24)	0.259 56(40)	0.626 88(39)	0.171 64(71)
P(2)	0.209 27(13)	0.465 74(15)	0.458 45(23)	C(25)	0.319 27(36)	0.146 88(47)	0.011 34(61)
P(3)	0.218 95(13)	0.443 42(14)	0.176 73(23)	C(26)	0.282 00(36)	0.134 73(47)	−0.134 14(61)
C(1)	0.148 50(36)	0.531 16(46)	0.555 61(54)	C(27)	0.318 64(36)	0.178 86(47)	−0.220 24(61)
C(2)	0.162 16(36)	0.531 75(46)	0.700 60(54)	C(28)	0.392 55(36)	0.235 14(47)	−0.160 86(61)
C(3)	0.113 84(36)	0.581 65(46)	0.776 21(54)	C(29)	0.429 82(36)	0.247 29(47)	−0.015 38(61)
C(4)	0.051 87(36)	0.630 96(46)	0.706 83(54)	C(30)	0.393 18(36)	0.203 16(47)	0.070 72(61)
C(5)	0.038 21(36)	0.630 37(46)	0.561 85(54)	C(31)	0.183 88(43)	0.021 43(40)	0.023 88(80)
C(6)	0.086 53(36)	0.580 47(46)	0.486 24(54)	C(32)	0.116 83(43)	0.055 09(40)	−0.062 80(80)
C(7)	0.314 19(48)	0.505 30(49)	0.546 73(84)	C(33)	0.048 46(43)	−0.005 48(40)	−0.142 37(80)
C(8)	0.367 66(48)	0.450 21(49)	0.622 65(84)	C(34)	0.047 13(43)	−0.099 71(40)	−0.135 27(80)
C(9)	0.450 27(48)	0.482 88(49)	0.685 37(84)	C(35)	0.114 17(43)	−0.133 38(40)	−0.048 59(80)
C(10)	0.479 40(48)	0.570 63(49)	0.672 19(84)	C(36)	0.182 55(43)	−0.072 81(40)	0.030 98(80)
C(11)	0.425 93(48)	0.625 72(49)	0.596 28(84)	C(37)	0.346 55(45)	0.026 24(49)	0.213 13(70)
C(12)	0.343 32(48)	0.593 06(49)	0.533 55(84)	C(38)	0.408 01(45)	−0.002 54(49)	0.148 79(70)
C(13)	0.136 93(34)	0.391 61(43)	0.023 21(60)	C(39)	0.463 28(45)	−0.062 88(49)	0.206 90(70)
C(14)	0.054 72(34)	0.400 63(43)	0.022 88(60)	C(40)	0.457 09(45)	−0.094 43(49)	0.329 36(70)
C(15)	−0.008 67(34)	0.355 65(43)	−0.092 76(60)	C(41)	0.395 63(45)	−0.065 65(49)	0.393 70(70)
C(16)	0.010 15(34)	0.301 67(43)	−0.208 06(60)	C(42)	0.340 36(45)	−0.005 32(49)	0.335 59(70)
C(17)	0.092 36(34)	0.292 65(43)	−0.207 73(60)	O	0.140 62(34)	0.222 36(39)	0.158 33(65)
C(18)	0.155 75(34)	0.337 62(43)	−0.092 09(60)	P(1)	0.271 75(14)	0.100 83(15)	0.133 90(25)
C(19)	0.272 78(40)	0.535 36(39)	0.124 12(71)	Cl(1)	0.363 26(13)	0.221 92(15)	0.445 58(23)
C(20)	0.325 18(40)	0.516 68(39)	0.036 50(71)	Cl(2)	0.173 49(17)	0.115 48(18)	0.405 37(30)

ment of the atomic parameters. Phenyl groups were refined as rigid bodies (C–C 1.395, C–H 1.08 Å) with fixed isotropic thermal parameters for the H atoms (U_{iso} = 0.08 Å^2). The quantity minimized in the refinement was $\Sigma w(\Delta F)^2$ with $w = 1$. At convergence, the residual conventional *R* factor was 0.028 for compound **1**, 0.038 for **2**, and 0.063 for **3b**. Calculations were done using the SHELX 76 programs package.[19] Scattering factors for neutral atoms were taken from ref. 20, and those of Re were corrected for anomalous dispersion.[21]

Solution of the structure of compound **3b** was troublesome. Because there is only one non-centrosymmetric molecule in the unit cell, as indicated clearly by the value of the crystal density, an attempt was made to solve the structure in the rather uncommon acentric triclinic space group. However, refinement in *P*1 resulted in unrealistic bond distances, high thermal parameters for the O atoms and C (ethanol) atoms, and inconsistent electronic density residuals which simulated unambiguously the presence of an inversion centre at the Re atom. Refinement was then carried out in the centrosymmetric space group $P\bar{1}$ assuming two asymmetric molecules being statistically present at 50% in centrosymmetric positions, with the Re atoms on the same inversion centre of the cell. Accordingly, both oxygen atoms as well as the ethanol carbon atoms were introduced with a fixed population parameter of 0.5. Several cycles of least-squares refinement led to satisfactory bond lengths and angles, reduced the thermal parameters to

Table 3 Atomic coordinates for $[ReO(OEt)\{N(SPPh_2)_2\}_2]$ **3b**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Re	0.0	0.0	0.0	C(8)	0.4407(7)	−0.3593(7)	0.3487(4)
P(1)	0.2045(3)	−0.2333(2)	0.1924(2)	C(9)	0.5798(7)	−0.4580(7)	0.3881(4)
P(2)	0.1395(3)	0.0661(2)	0.2946(2)	C(10)	0.6645(7)	−0.5604(7)	0.3181(4)
S(1)	0.2118(3)	−0.2114(2)	0.0563(2)	C(11)	0.6101(7)	−0.5642(7)	0.2087(4)
S(2)	−0.0346(3)	0.1528(2)	0.1769(2)	C(12)	0.4710(7)	−0.4656(7)	0.1693(4)
N	0.1762(9)	−0.0942(8)	0.2896(6)	C(13)	0.3051(7)	0.0999(7)	0.3110(7)
C(25)	0.3130(10)	0.0444(9)	0.0269(7)	C(14)	0.2902(7)	0.2213(7)	0.2871(7)
C(26)	0.4037(10)	−0.0751(8)	−0.0475(8)	C(15)	0.4190(7)	0.2484(7)	0.3011(7)
O(1)	−0.1243(8)	−0.0732(9)	−0.0115(7)	C(16)	0.5626(7)	0.1542(7)	0.3390(7)
O(2)	0.1565(8)	0.0641(8)	0.0192(7)	C(17)	0.5775(7)	0.0328(7)	0.3629(7)
C(1)	0.0653(7)	−0.3128(6)	0.1642(6)	C(18)	0.4487(7)	0.0057(7)	0.3489(7)
C(2)	0.1026(7)	−0.4603(6)	0.1390(6)	C(19)	0.0784(7)	0.1680(6)	0.4142(5)
C(3)	−0.0064(7)	−0.5182(6)	0.1192(6)	C(20)	−0.0198(7)	0.1301(6)	0.4356(5)
C(4)	−0.1529(7)	−0.4286(6)	0.1247(6)	C(21)	−0.0768(7)	0.2102(6)	0.5242(5)
C(5)	−0.1902(7)	−0.2811(6)	0.1500(6)	C(22)	−0.0355(7)	0.3283(6)	0.5915(5)
C(6)	−0.0811(7)	−0.2232(6)	0.1697(6)	C(23)	0.0627(7)	0.3662(6)	0.5701(5)
C(7)	0.3863(7)	−0.3632(7)	0.2393(4)	C(24)	0.1197(7)	0.2861(6)	0.4814(5)

Table 4 Bond distances (Å) and angles (°) for complex **1**

Re–P(1)	2.465(2)	Re–O(1)	1.660(5)
Re–Cl(1)	2.380(2)	Re–O(2)	2.054(4)
Re–Cl(2)	2.367(2)	Re–O(3)	2.071(4)
O(2)–P(2)	1.534(4)	P(3)–C(13)	1.798(5)
O(3)–P(3)	1.534(4)	P(3)–C(19)	1.796(5)
N–P(2)	1.591(5)	P(1)–C(25)	1.830(4)
N–P(3)	1.583(5)	P(1)–C(31)	1.818(5)
P(2)–C(1)	1.804(5)	P(1)–C(37)	1.829(4)
P(2)–C(7)	1.785(4)		
Cl(1)–Re–Cl(2)	167.7(1)	O(2)–P(2)–N	115.6(2)
O(1)–Re–O(2)	105.0(2)	O(2)–P(2)–C(1)	111.9(2)
O(1)–Re–P(1)	90.4(2)	O(2)–P(2)–C(7)	106.0(2)
O(2)–Re–O(3)	86.0(2)	O(3)–P(3)–N	115.6(3)
O(3)–Re–P(1)	78.6(1)	O(3)–P(3)–C(13)	106.4(2)
Re–O(2)–P(2)	134.4(3)	O(3)–P(3)–C(19)	106.7(2)
Re–O(3)–P(3)	134.4(3)	P(2)–N–P(3)	123.8(3)
Re–P(1)–C(25)	114.9(2)	N–P(2)–C(1)	106.5(3)
Re–P(1)–C(31)	113.9(2)	N–P(2)–C(7)	111.4(3)
Re–P(1)–C(37)	113.6(1)	N–P(3)–C(13)	112.1(2)
		N–P(3)–C(19)	108.2(2)

Table 5 Bond distances (Å) and angles (°) for complex **2**

Re–P(1)	2.534(2)	Re–O	1.677(6)
Re–Cl(1)	2.436(2)	Re–S(1)	2.394(2)
Re–Cl(2)	2.379(2)	Re–S(2)	2.450(2)
S(1)–P(2)	2.056(4)	P(3)–C(13)	1.801(6)
S(2)–P(3)	2.024(3)	P(3)–C(19)	1.810(8)
N–P(3)	1.587(7)	P(1)–C(25)	1.816(7)
N–P(2)	1.592(7)	P(1)–C(31)	1.825(7)
P(2)–C(1)	1.785(6)	P(1)–C(37)	1.815(7)
P(2)–C(7)	1.779(8)		
S(1)–Re–P(1)	169.3(1)	Re–S(1)–P(2)	110.0(1)
O–Re–Cl(1)	166.0(2)	Re–S(2)–P(3)	104.2(1)
S(2)–Re–Cl(2)	169.2(1)	Re–P(1)–C(25)	112.0(2)
O–Re–Cl(2)	96.8(2)	Re–P(1)–C(31)	110.8(3)
O–Re–S(2)	93.9(2)	Re–P(1)–C(37)	119.1(2)
O–Re–S(1)	101.5(2)	S(1)–P(2)–N	115.6(3)
O–Re–P(1)	85.7(2)	S(1)–P(2)–C(1)	105.9(3)
S(1)–Re–S(2)	96.1(1)	S(1)–P(2)–C(7)	108.9(3)
S(1)–Re–Cl(1)	91.9(1)	S(2)–P(3)–N	117.0(3)
P(1)–Re–Cl(2)	90.4(1)	S(2)–P(3)–C(13)	107.9(2)
S(1)–Re–Cl(2)	80.9(1)	S(2)–P(3)–C(19)	106.0(2)
P(1)–Re–Cl(1)	81.7(1)	P(2)–N–P(3)	124.0(4)
S(2)–Re–Cl(1)	80.2(1)	N–P(2)–C(1)	106.0(3)
S(2)–Re–P(1)	91.3(1)	N–P(2)–C(7)	113.3(4)
Cl(1)–Re–Cl(2)	89.5(1)	N–P(3)–C(13)	109.6(5)
		N–P(3)–C(19)	109.5(3)

Table 6 Selected bond distances (Å) and angles (°) for complex **3b**

Re–S(1)	2.481(2)	P(1)–N	1.609(7)
Re–S(2)	2.468(2)	P(2)–N	1.576(7)
Re–O(1)	1.70(1)	P(1)–C(1)	1.812(9)
Re–O(2)	1.90(1)	P(1)–C(7)	1.811(6)
S(1)–P(1)	2.029(5)	P(2)–C(13)	1.794(9)
S(2)–P(2)	2.030(3)	P(2)–C(19)	1.799(7)
O(2)–C(25)	1.48(1)	C(25)–C(26)	1.52(1)
S(1)–Re–S(2)	99.8(1)	S(1)–P(1)–N	118.3(3)
O(1)–Re–O(2)	173.5(1)	S(2)–P(2)–N	117.9(4)
O(1)–Re–S(1)	89.3(1)	P(1)–N–P(2)	129.7(5)
O(1)–Re–S(2)	90.1(1)	S(1)–P(1)–C(1)	111.5(3)
O(2)–Re–S(1)	84.3(1)	S(1)–P(1)–C(7)	105.2(2)
O(2)–Re–S(2)	90.4(1)	S(2)–P(2)–C(13)	110.1(2)
Re–S(1)–P(1)	110.9(1)	S(2)–P(2)–C(19)	103.6(3)
Re–S(2)–P(2)	109.5(1)	O(2)–C(25)–C(26)	122(1)
Re–O(2)–C(25)	154.2(1)		

normal values, and eliminated the residual maxima from the final electron density map, suggesting the correctness of the model. Thus, only one asymmetric molecule of the compound, statistically distributed in two centrosymmetric positions, is effectively present in the centrosymmetric cell.

Final atomic parameters are listed in Tables 1–3, bond distances and angles are reported 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.

Acknowledgements

We thank Mr. Fratta for technical assistance, and the Italian Consiglio Nazionale delle Ricerche and Ministero Pubblica Istruzione for financial support.

References

1 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99.
2 I. Haiduc and I. Silaghi-Dumitrescu, *Coord. Chem. Rev.*, 1986, **74**, 127.
3 J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 1962, 4019.
4 A. Marchi, A. Duatti, R. Rossi, L. Magon, U. Mazzi and A. Pasquetto, *Inorg. Chim. Acta*, 1984, **81**, 15.
5 R. Rossi, A. Marchi, A. Duatti, L. Magon, U. Casellato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1988, 1857.
6 G. P. Quillan and I. A. Oxton, *Inorg. Chim. Acta*, 1978, **29**, 69.
7 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.
8 F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1965, **4**, 1621.
9 C. J. L. Lock and G. Turner, *Acta Crystallogr., Sect. B*, 1978, **34**, 923.

10 J. Chatt, J. D. Garforth, N. P. Johnson and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012.
11 F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1966, **5**, 9.
12 R. Rossi, A. Marchi, A. Duatti, L. Magon, U. Casellato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1987, 2299; 1988, 899.
13 G. J. Bullen and P. A. Tucker, *Chem. Commun.*, 1970, 1185.
14 H. R. Allcock, *Science*, 1976, **193**, 1214.
15 J. Chatt, J. R. Dilworth and G. J. Leigh, *J. Chem. Soc. A*, 1970, 2239.
16 T. Lis and B. Jezowska-Trzebiatowska, *Acta Crystallogr., Sect. B*, 1977, **33**, 1248.
17 F. T. Wang, J. Najdzionek, K. L. Leneker, H. Wasserman and D. M. Braitsch, *Synth. React. Inorg. Met.-Org. Chem.*, 1978, **8**, 119.
18 A. C. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
19 G. M. Sheldrick, SHELX, Program for Crystal Structure Determination, University of Cambridge, 1976.
20 *International Tables for X-Ray Crystallography*, 2nd edn., Kynoch Press, Birmingham, 1974, vol. 4.
21 D. T. Cromer and D. Libermann, *J. Chem. Phys.*, 1970, **53**, 1891.

Received 20*th July* 1990; *Paper* 0/03277H