Reactivity of the $[Re{\equiv}O]^{3+}$ Core toward $Ph_2P(Se)NH(Se)PPh_2$ †

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The salt $K[N(PPh_2Se)_2]$ reacts with $[ReOCl_3(PPh_3)_2]$ or $[AsPh_4][ReOCl_4]$ to give $[ReO(Cl)\{N(PPh_2Se)_2\}_2]$. In solution this compound tends to transform into $[ReO(Cl)(Ph_2PNPPh_2Se)_2]$, by loss of one Se atom from each ligand. Recrystallization from CH_2Cl_2–EtOH yielded $[ReO(OEt)(Ph_2PNPPh_2Se)_2]$ the crystal structure of which has been determined.

We have recently described the co-ordination chemistry of the ligands $Ph_2P(X)NH(X)PPh_2$ (X = O or S) toward rhenium compounds having the $[Re{\equiv}O]^{3+}$ core.[1] In this paper we report the reactivity of $K[Ph_2P(Se)N(Se)PPh_2]$ to determine how further variation of the donor group X modifies the co-ordination properties.

Results and Discussion

The green complex $[ReO(Cl)\{N(PPh_2Se)_2\}_2]$ **1** can be obtained by the reaction of $[ReOCl_3(PPh_3)_2]$ or $[AsPh_4][ReOCl_4]$ with $K[N(PPh_2Se)_2]$ in low-boiling solvents ($CHCl_3$ or CH_2Cl_2, 40–45 min), or in a shorter time (15–30 min) using a higher-boiling solvent such as toluene. This disubstituted compound is obtained irrespective of the molar ratio used and the monosubstituted complex was never observed even when the reaction was carried out at room temperature in a 1:1 molar ratio. This behaviour is similar to that of the iminobis(diphenylphosphine sulfide), $NH(PPh_2S)_2$, the disubstituted derivative of which was observed to form in preference to the monosubstituted one.[1] The IR spectrum of complex **1** shows a $\nu(Re{\equiv}O)$ band at 970 cm^{-1}, while a large strong band characteristic of P–N bonds is observed as a triplet at 1220, 1200 and 1180 cm^{-1}.

Attempts to crystallize the green product **1** failed completely. It is not stable in solution and tends to transform into a brown-orange compound. The latter was also formed in some reactions performed in $CHCl_3$ or CH_2Cl_2, under conditions suitable for obtaining **1**. In these reactions the green solution became brown during reflux and a brown powder was collected after concentration. It was recrystallized from CH_2Cl_2–Me_2CO to give brown-orange crystals of compound **2**. Elemental analysis showed a higher amount of carbon than that in compound **1**. In the IR spectrum the $\nu(Re{\equiv}O)$ band at 970 cm^{-1} is still present, but now the P_2N stretching of the chelate ligand appears as a large strong band at lower wavenumber (1135 cm^{-1}).

The ^{31}P-$\{^1H\}$ NMR spectrum of complex **1** consists of a singlet at δ 34.36 with ^{77}Se satellites [$^1J(PSe)$ 524.6 Hz] whereas the ^{31}P NMR spectrum of compound **2** shows a complex pattern centred at δ 73.0, characteristic of an AA′BB′ spin system and deshielded with respect to **1**. This low-field shift indicates that the P atoms of the ligand are in a shielding six-membered ring in **1**, and in a highly deshielding five-membered ring in **2**.[2] Both elemental analyses and the ^{31}P NMR spectra suggest that two selenium atoms are lost from **1** to give $[ReO(Cl)(Ph_2PNPPh_2Se)_2]$ **2**. When this compound was recrystallized from CH_2Cl_2–EtOH the ethoxo-derivative $[ReO(OEt)(Ph_2PNPPh_2Se)_2]$ **3** was obtained as brown-orange crystals suitable for diffraction studies. The IR spectrum of **3** shows a Re≡O absorption band at 950 cm^{-1} as expected for complexes containing the EtO–Re≡O group.[3] The proton signals expected for the ethoxo ligand are observed in the ^1H NMR spectrum while the ^{31}P NMR spectrum is similar to that of **2**. Our formulation of **3** was confirmed by an X-ray structure analysis.

Crystal Structure of Complex **3**.—The structure of $[ReO(OEt)(Ph_2PNPPh_2Se)_2]$ **3** is shown in Fig. 1 together with the atom numbering scheme. The geometry of the Re is six-co-ordinate octahedral and, as described in detail in the Experimental section, the two *trans* chelated ligands are rigorously centrosymmetric even though the molecule itself is asymmetric as a whole. The bidentate ligand forms an approximately planar pentaatomic metallacycle with Re where the Re–Se bond distance of 2.562(1) Å is about 0.1 Å longer than expected on the basis of the sum of covalent radii. The P–N bonds are chemically equivalent with lengths (mean 1.61 Å) significantly shorter than normal for a single covalent bond (1.75–1.80 Å) showing double-bond character and delocalization of the electron density. Similar P–N–P sequences, with comparable bond lengths, are commonly found in cyclic phosphazenes[4,5] and were also observed in other rhenium complexes.[1] Other structural details of the compound are normal and need no particular comment.

Experimental

Materials.—Solvents were purified and dried before use. All reactions were performed under an argon atmosphere. The starting compounds $[ReOCl_3(PPh_3)_2]$ and $[AsPh_4][ReOCl_4]$ were prepared following the literature methods.[6,7] The salt $K[N(PPh_2Se)_2]$ was prepared by adding KSeCN to a MeCN

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

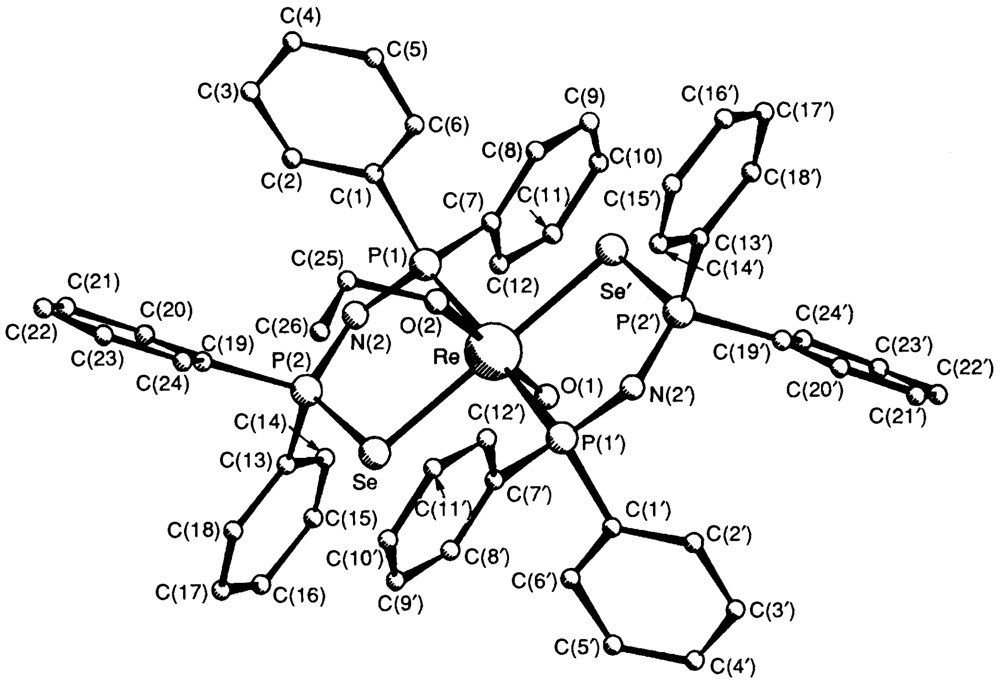

Fig. 1 Crystal structure of complex **3**

Table 1 Atomic coordinates for $[ReO(OEt)(Ph_2PNPPh_2Se)_2]$ **3**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Re	0.0	0.0	0.0
O(1)	−0.0361(10)	0.1476(11)	0.0273(4)
O(2)	0.0407(10)	−0.1607(11)	−0.0302(4)
Se	−0.2339(1)	−0.0934(1)	0.0435(1)
P(1)	0.1305(2)	−0.0559(2)	0.0853(1)
P(2)	−0.1452(2)	−0.1401(2)	0.1247(1)
N	0.0156(8)	−0.0860(8)	0.1351(3)
C(1)	0.2499(7)	−0.1969(7)	0.0776(2)
C(2)	0.2386(7)	−0.2963(7)	0.1156(2)
C(3)	0.3265(7)	−0.4065(7)	0.1105(2)
C(4)	0.4258(7)	−0.4172(7)	0.0675(2)
C(5)	0.4371(7)	−0.3177(7)	0.0295(2)
C(6)	0.3491(7)	−0.2076(7)	0.0345(2)
C(7)	0.2528(6)	0.0686(5)	0.1117(2)
C(8)	0.3961(6)	0.0832(6)	0.0917(2)
C(9)	0.4862(6)	0.1823(6)	0.1113(2)
C(10)	0.4330(6)	0.2668(6)	0.1508(2)
C(11)	0.2897(6)	0.2522(6)	0.1708(2)
C(12)	0.1996(6)	0.1531(6)	0.1513(2)
C(13)	−0.2694(6)	−0.0742(7)	0.1742(3)
C(14)	−0.2244(6)	0.0291(7)	0.2066(3)
C(15)	−0.3232(6)	0.0848(7)	0.2432(3)
C(16)	−0.4670(6)	0.0369(7)	0.2475(3)
C(17)	−0.5120(6)	−0.0664(7)	0.2151(3)
C(18)	−0.4132(6)	−0.1220(7)	0.1784(3)
C(19)	−0.1553(10)	−0.3135(10)	0.1360(4)
C(20)	−0.1291(10)	−0.3599(10)	0.1883(4)
C(21)	−0.1284(10)	−0.4928(10)	0.1981(4)
C(22)	−0.1540(10)	−0.5791(10)	0.1557(4)
C(23)	−0.1801(10)	−0.5327(10)	0.1034(4)
C(24)	−0.1808(10)	−0.3998(10)	0.0936(4)
C(25)	0.0250(29)	−0.3025(28)	−0.0146(10)
C(26)	−0.0884(37)	−0.3629(33)	−0.0489(13)

Table 2 Selected bond distances (Å) and angles (°) for complex **3**

Re–O(1)	1.70(2)	N–P(1)	1.639(8)
Re–O(2)	1.86(2)	N–P(2)	1.579(8)
Re–Se	2.562(1)	P(2)–Se	2.208(3)
Re–P(1)	2.479(3)	P(1)–C(1)	1.824(7)
O(2)–C(25)	1.52(3)	P(1)–C(7)	1.818(6)
C(25)–C(26)	1.47(4)	P(2)–C(13)	1.794(8)
		P(2)–C(19)	1.817(11)
P(1)–Re–Se	87.1(1)	C(1)–P(1)–C(7)	104.2(3)
Re–Se–P(2)	99.4(1)	Se–P(2)–C(13)	107.8(3)
Re–P(1)–N	112.2(3)	Se–P(2)–C(19)	109.7(4)
Se–P(2)–N	113.8(3)	C(13)–P(2)–C(19)	113.8(4)
P(1)–N–P(2)	122.0(5)	Re–O(2)–C(25)	138.0(1)
Re–P(1)–C(1)	112.3(3)	O(2)–C(25)–C(26)	109.0(2)
Re–P(1)–C(7)	115.3(3)		

solution of bis(diphenylphosphino)amine.[8] Infrared spectra were recorded on a Perkin-Elmer spectrometer, $^{31}P-\{^1H\}$ NMR spectra on a Bruker AC 200 spectrometer operating at 81.01 MHz using an internal deuterium lock and 85% H_3PO_4 as external standard, and ^1H NMR spectra on a Bruker AC 200 instrument with $SiMe_4$ as internal reference. Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser.

Syntheses.—$[ReO(Cl)\{N(PPh_2Se)_2\}_2]$ **1**. A stoichiometric amount of $K[N(PPh_2Se)_2]$ (0.36 mmol) was added to a toluene solution (40 cm^3) of $[ReOCl_3(PPh_3)_2]$ or $[AsPh_4][ReOCl_4]$ (0.18 mmol). The green solution was heated under reflux for 15–30 min and then concentrated *in vacuo*. A green solid precipitated upon addition of Et_2O. The crude product was dissolved in CH_2Cl_2 and a green powder obtained by adding Me_2CO, yield 80%. When the reaction was performed in $CHCl_3$ or CH_2Cl_2, sometimes the green solution turned brown in a few minutes and the brown-orange product $[ReO(Cl)(Ph_2PNPPh_2Se)_2]$ **2** was collected under the same conditions used to obtain the product **1**, yield 80%. Complex **1** (Found: C, 43.1; H, 2.8; N, 1.9. $C_{48}H_{40}ClN_2OP_4ReSe_4$ requires C, 43.6; H, 3.0; N, 2.1%); ν(P_2N) 1220, 1200, 1180 and 800; ν(Re≡O) 970 cm^{-1} (Nujol). $^{31}P-\{^1H\}$ NMR (CD_2Cl_2): δ 34.36 [s, ^1J(PSe) 524.6 Hz]. Complex **2** (Found: C, 50.1; H, 3.3; N, 2.1. $C_{48}H_{40}ClN_2OP_4ReSe_2$ requires C, 49.5; H, 3.5; N, 2.4%); ν(P_2N) 1135 and 800; ν(Re≡O) 970 cm^{-1} (Nujol). $^{31}P-\{^1H\}$ NMR (CD_2Cl_2): δ 73.0 (m).

$[ReO(OEt)(Ph_2PNPh_2Se)_2]$ **3**. This compound was obtained from **2** upon crystallization of the latter from CH_2Cl_2–EtOH. ν(Re≡O) 950 cm^{-1} (Nujol). NMR (CD_2Cl_2): $^{31}P-\{^1H\}$, δ 72.6 (m); ^1H, δ 1.74 (2 H, m, OCH_2CH_3) and −0.50 (3 H, t, 7.0 Hz, OCH_2CH_3).

X-Ray Crystallography.—A crystal of complex **3** of maximum dimension 0.2 mm was used for the X-ray measurements. Data were collected on a Philips diffractometer with Mo-K radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle reflections.

Crystal data. $C_{50}H_{45}N_2O_2P_4ReSe_2$, $M = 1174$, monoclinic, space group $P2_1/c$, $a = 9.042(5)$, $b = 10.343(5)$, $c = 24.642(5)$ Å, $\beta = 90.07(3)°$, $U = 2304.6$ Å^3, $D_c = 1.69$ g cm^{-3} for $Z = 2$, μ(Mo-Kα) = 46.7 cm^{-1}, $F(000) = 1156$.

The crystal was stable under irradiation. Of a total of 4271 reflections obtained, whose intensities were corrected for Lorentz polarization and for absorption,[9] 2608 with $I > 3\sigma(I)$ were considered observed and used in subsequent calculations. Solution of the structure was achieved by Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. As clearly indicated by the crystal density, only two molecules are present in the centrosymmetric cell. This requires the Re atoms to be located on a set of special positions at inversion centres, which is only possible if the bidentate ligands are rigorously centrosymmetric and if the oxide O atom and the co-ordinated EtO group are statistically distributed at 50% in centrosymmetric positions $0, \frac{1}{2}, \frac{1}{2}$. Electron-density maps were calculated on this basis. The positions of all remaining atoms were successfully determined in this way and in the final least-squares cycle the maximum shift/error was less than 0.1. The phenyl groups, including H atoms in calculated positions, were refined as rigid bodies, and the O atom and the EtO group introduced with a fixed population parameter of 0.5 and refined isotropically because of possible interactions of the anisotropic components of the thermal parameters (these atoms being statistically distributed in close proximity). Several cycles of least-squares refinement led to satisfactory bond lengths and angles and to normal values for the thermal factors, suggesting that the assumed model was correct.

At convergence, the residual conventional R factor was 0.052, based on the observed reflections. No significant residuals of electronic density were observed in the final Fourier difference map. The function minimized was $\Sigma w(\Delta F)^2$ with $w = 1$. Calculations were done using the SHELX 76 program package.[10] Scattering factors for neutral atoms were taken from ref. 11, and those of Re were corrected for anomalous dispersion.[12] Final atomic parameters are listed in Table 1, selected bond lengths and angles in Table 2.

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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