Reactivity of the Rhenium(v)–Oxo Complex $[AsPh_4][ReOCl_4]$ toward Bis(diphenylphosphino)amine $NH(PPh_2)_2$. Synthesis and Crystal Structures†

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The complexes $[ReCl_3(H_2O)\{NH(OPPh_2)PPh_2\text{-}P,O\}]$ **1**, $[ReCl_4\{NH(OPPh_2)PPh_2\text{-}P,O\}]$ **3** and $[AsPh_4][ReCl_4\{N(OPPh_2)PPh_2\text{-}P,O\}]$ **4** were obtained by treatment of $[AsPh_4][ReOCl_4]$ with $NH(PPh_2)_2$ under different experimental conditions. Their structures were determined by X-ray crystallography. In all complexes the co-ordination is nearly octahedral where a molecule of the ligand binds to rhenium through a phosphorus and oxygen. The Re–O distances, which range from 2.054(3) to 2.071(6) Å indicate the presence of neutral or partially negatively charged oxygens. The Re–Cl bond distances *trans* to oxygen are strongly related to the oxygen charge and hybridization.

In recent years, work in this laboratory has centred on the reactivity of rhenium and technetium complexes with different phosphines. We have studied the co-ordination chemistry of rhenium(v)–oxo, –imido and –nitrido complexes with bidentate phosphines such as $NH(XPPh_2)_2$ (X = O, S or Se),[1–3] in order to determine how the variation of the donor group X of the ligand and the nature of the groups multiply bonded to the metal centre (O, NMe or N) modify the co-ordination properties. We have observed how the reactivity of these ligands is affected by the nature of the oxo-complex used: $[AsPh_4][ReOCl_4]$, $[ReOCl_3(PPh_3)_2]$ or $[ReO(OEt)Cl_2(PPh_3)_2]$. We have now undertaken a systematic study on the reactivity of bis(diphenylphosphino)amine $NH(PPh_2)_2$ with the oxo-complexes mentioned above, and here report the first results regarding the ionic square-pyramidal complex $[AsPh_4][ReOCl_4]$.

Results and Discussion

When $[AsPh_4][ReOCl_4]$ reacted with the potentially chelating ligand $NH(PPh_2)_2$ in a 1:1 molar ratio, in boiling degassed chloroform, the green rhenium(III) complex $[ReCl_3(H_2O)\{NH(OPPh_2)PPh_2\text{-}P,O\}]$ **1** was obtained as a solid in good yield (80%). In this complex the diphosphine behaves as a diphosphine monoxide ligand, bound to the metal through a phosphorus and an oxygen atom. The complex is paramagnetic in the solid state and exhibits a magnetic moment of 2.80 μ_B at 27 °C. This value is within the expected range for other octahedral rhenium(III) complexes for which there is no spin–orbit coupling.[4] No significant NMR spectrum could be obtained owing to the paramagnetic properties of the complex. The solid-state (KBr pellet) IR spectrum shows two bands at 3520 and 2617 cm^{-1}. The former has been assigned to the water molecule co-ordinated to the metal, the latter to the imine N–H stretching affected by intermolecular hydrogen bonding. The band at 1130 cm^{-1} has been assigned to the P=O group co-ordinated to the metal.[5,6]

We carried out the same reaction in anhydrous degassed chloroform in an attempt to obtain the complex $[AsPh_4][ReCl_4\{NH(OPPh_2)PPh_2\text{-}P,O\}]$ **2**. Under these conditions, a yellow-green precipitate was formed. Its IR spectrum does not show bands for co-ordinated water while the N–H stretching is significantly shifted to lower wavenumber (2546 cm^{-1}) compared to complex **1**. This compound was crystallized from dried and degassed solvents (CH_2Cl_2–CCl_4), as yellow crystals of good quality for an X-ray analysis. The structure shows (see below) that this compound is not the expected ionic rhenium(III) complex **2** but the neutral rhenium(IV) complex $[ReCl_4\{NH(OPPh_2)PPh_2\text{-}P,O\}]$ **3**. In the solid the crystal packing also consists of Cl^- and $[AsPh_4]^+$ ions, where the Cl^- ion links a pair of molecules by means of $NH\cdots Cl^-\cdots HN$ hydrogen bonds (the IR N–H stretching band at 2546 cm^{-1} can therefore be ascribed to this interaction[7]). Complex **3** is paramagnetic in the solid state and exhibits a magnetic moment of 3.2 μ_B at 27 °C that is within the values expected for d^3 rhenium complexes.[8] The formation of **3** is not surprising since we have already obtained the rhenium(IV) diphosphine monoxide complex $[ReCl_4\{CH_2(OPPh_2)PPh_2\text{-}P,O\}]$ by reaction of $[ReOCl_3(PPh_3)_2]$ with bis(diphenylphosphino)methane.[9]

When complex **3** reacts further with an excess of the ligand in anhydrous chloroform the ionic complex $[AsPh_4][ReCl_4\{N(OPPh_2)PPh_2\text{-}P,O\}]$ **4** is produced in low yield. In **4** the ligand is present in its deprotonated form (see below). This deprotonation is probably promoted by the excess of the ligand which may form its hydrochloride salt. We have also observed that, when the reaction is carried out starting from the oxo-complex $[ReOCl_4]^-$ with an excess of ligand, complex **4** does not form and instead a yellow product **5** is precipitated. We could not identify **5** owing to its poor solubility in most organic solvents, and attempts to obtain crystals suitable for a diffraction study were unsuccessful. Its IR spectrum exhibits strong bands at 1408, 1180 and 830 cm^{-1} and differs from the spectra of the complexes **1**, **3** and **4**. This compound is paramagnetic in the solid state and elemental analyses suggest the presence of two molecules of ligand. In view of this we carried out the reaction starting from $[ReCl_3(MeCN)(PPh_3)_2]$ in order to verify if it would lead to the same product, but the new ionic compound $[ReCl_2\{NH(PPh_2)_2\text{-}P,P'\}_2]Cl$ **6** was obtained instead.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Fractional coordinates for $[ReCl_3(H_2O)\{NH(OPPh_2)PPh_2\}]\cdot EtOH$ **1**

Atom	*x*	*y*	*z*
Re	0.312 57(2)	0.044 23(6)	0
Cl(1)	0.194 8(2)	−0.017 9(4)	0.008 0(6)
Cl(2)	0.317 5(2)	0.051 4(5)	0.152 7(3)
Cl(3)	0.433 0(2)	0.077 6(4)	−0.009 8(4)
P(1)	0.309 3(2)	−0.006 2(4)	−0.157 7(2)
P(2)	0.328 4(2)	−0.254 8(4)	−0.069 2(2)
O(1)	0.334 1(4)	−0.155 4(9)	0.005 3(10)
O(2)	0.285 8(3)	0.249 0(5)	−0.015 8(4)
N	0.325 0(5)	−0.168 0(11)	−0.161 9(6)
C(1)	0.375 4(7)	0.070 6(14)	−0.225 6(10)
C(2)	0.439 1(8)	0.004 5(18)	−0.237 2(10)
C(3)	0.490 1(8)	0.051 7(21)	−0.295 8(12)
C(4)	0.477 2(9)	0.166 6(20)	−0.339 1(13)
C(5)	0.416 1(11)	0.234 2(20)	−0.326 6(14)
C(6)	0.363 9(10)	0.186 5(21)	−0.268 9(13)
C(7)	0.228 3(7)	0.022 8(14)	−0.215 5(10)
C(8)	0.192 9(8)	0.140 1(17)	−0.208 3(11)
C(9)	0.134 1(8)	0.168 0(19)	−0.257 9(13)
C(10)	0.110 1(9)	0.073 1(21)	−0.314 1(13)
C(11)	0.144 4(9)	−0.046 3(21)	−0.323 0(12)
C(12)	0.205 4(8)	−0.072 2(16)	−0.274 2(11)
C(13)	0.402 9(7)	−0.355 8(15)	−0.074 0(9)
C(14)	0.399 4(8)	−0.490 1(17)	−0.090 7(12)
C(15)	0.459 8(9)	−0.563 0(16)	−0.098 2(15)
C(16)	0.523 2(8)	−0.504 5(19)	−0.090 8(13)
C(17)	0.527 7(8)	−0.368 3(21)	−0.073 4(13)
C(18)	0.469 3(7)	−0.298 2(17)	−0.065 0(11)
C(19)	0.253 8(7)	−0.351 2(14)	−0.058 2(10)
C(20)	0.229 7(7)	−0.398 1(18)	0.023 0(9)
C(21)	0.170 3(8)	−0.465 2(25)	0.027 2(14)
C(22)	0.134 2(8)	−0.507 9(20)	−0.040 2(13)
C(23)	0.155 4(11)	−0.468 4(26)	−0.120 2(13)
C(24)	0.213 9(9)	−0.389 5(22)	−0.128 2(11)
O(1′)	0.655 0(6)	0.310 5(15)	0.186 6(8)
C(1′)*	0.586 2(18)	0.365 3(38)	0.178 6(25)
C(1″)*	0.599 4(20)	0.267 5(40)	0.116 4(27)
C(2′)	0.551 7(16)	0.319 7(38)	0.126 7(25)

* Occupancy 0.5.

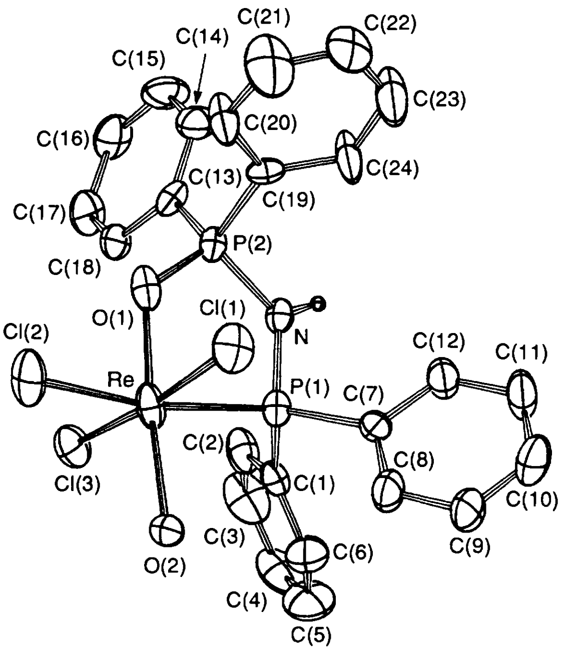

Fig. 1 An ORTEP view of complex **1** showing thermal ellipsoids at 30% probability

Crystal Structures.—Final positional parameters for the three compounds are given in Tables 1–3, ORTEP[10] views in Figs. 1–4 and bond distances and angles in Tables 4–6. In all complexes the co-ordination is nearly octahedral. The Re–O distances, which range from 2.054(3) to 2.071(6) Å, indicate the presence of neutral or partially negative charged oxygens. These bond lengths are significantly longer than the Re–O⁻ distances observed in complexes of rhenium with Schiff bases, which fall in the range 1.95–1.99 Å[11–14] if not affected by strong *trans*-influence ligands. In compound **1** the crystals are built up of molecules of $[ReCl_3(H_2O)\{NH(OPPh_2)PPh_2\text{-}P,O\}]$ and of EtOH, in the ratio 1:1, linked by hydrogen bonds [N • • • O 2.76(2) Å]. The water molecule is situated *trans* to the oxygen atom of the P=O group; the Re–O(water) bond distance of

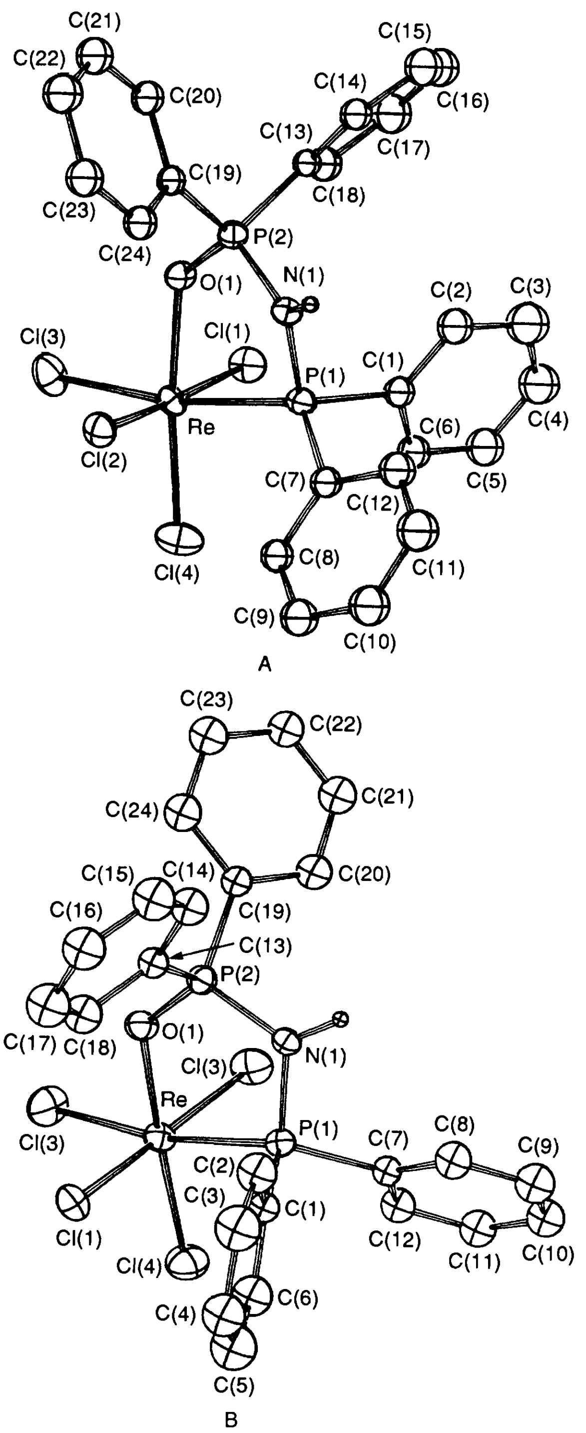

Fig. 2 The ORTEP views of the two independent molecules A and B of complex **3** showing the thermal ellipsoids at 30% probability

Table 2 Fractional coordinates for $2[ReCl_4\{NH(OPPh_2)PPh_2\}]\cdot Cl^-\cdot[AsPh_4]^+\cdot CH_2Cl_2$ **3**

Atom	*x*	*y*	*z*
Re(1)	0.226 11(2)	0.525 14(2)	0.143 95(4)
Cl(1A)	0.115 2(1)	0.488 8(1)	0.097 1(3)
Cl(2A)	0.339 2(1)	0.557 3(1)	0.205 2(3)
Cl(3A)	0.139 7(2)	0.622 1(1)	0.177 5(3)
Cl(4A)	0.245 3(2)	0.532 3(1)	−0.081 8(3)
P(1A)	0.308 4(1)	0.417 0(1)	0.154 2(2)
P(2A)	0.244 0(1)	0.452 6(1)	0.418 3(2)
O(1A)	0.222 0(4)	0.511 3(3)	0.348 5(6)
N(1A)	0.274 7(4)	0.399 3(3)	0.298 7(7)
C(1A)	0.416 7(5)	0.404 4(4)	0.173 5(9)
C(2A)	0.462 1(6)	0.376 8(5)	0.283 3(11)
C(3A)	0.546 6(7)	0.369 9(6)	0.291 6(13)
C(4A)	0.580 5(7)	0.391 9(5)	0.192 8(12)
C(5A)	0.536 6(7)	0.419 1(5)	0.085 9(12)
C(6A)	0.453 2(6)	0.426 0(4)	0.075 1(10)
C(7A)	0.299 2(5)	0.359 2(4)	0.029 4(9)
C(8A)	0.254 8(6)	0.373 5(4)	−0.090 4(10)
C(9A)	0.250 9(6)	0.327 4(5)	−0.182 8(11)
C(10A)	0.291 1(7)	0.270 1(5)	−0.155 5(12)
C(11A)	0.334 3(7)	0.255 2(5)	−0.035 1(12)
C(12A)	0.340 6(6)	0.299 7(5)	0.056 2(11)
C(13A)	0.325 8(5)	0.446 9(4)	0.538 9(9)
C(14A)	0.347 5(5)	0.398 7(4)	0.620 0(10)
C(15A)	0.417 9(7)	0.386 2(5)	0.701 1(12)
C(16A)	0.465 1(7)	0.423 5(5)	0.704 5(12)
C(17A)	0.444 4(7)	0.472 7(5)	0.628 1(12)
C(18A)	0.373 2(6)	0.485 3(5)	0.540 6(10)
C(19A)	0.160 3(5)	0.442 5(4)	0.500 8(9)
C(20A)	0.144 3(6)	0.467 3(4)	0.632 1(10)
C(21A)	0.076 7(6)	0.462 7(5)	0.693 7(11)
C(22A)	0.024 1(7)	0.436 1(5)	0.629 6(12)
C(23A)	0.038 2(6)	0.413 3(5)	0.498 2(11)
C(24A)	0.107 3(6)	0.416 4(4)	0.431 6(10)
Re(2)	0.196 45(2)	0.061 61(2)	0.166 08(4)
Cl(1B)	0.188 8(2)	0.013 4(1)	0.363 9(3)
Cl(2B)	0.204 7(2)	0.118 1(1)	−0.016 3(3)
Cl(3B)	0.084 7(2)	0.037 4(1)	0.067 4(3)
Cl(4B)	0.291 6(2)	−0.021 5(1)	0.081 7(3)
P(1B)	0.296 2(1)	0.106 4(1)	0.284 5(2)
P(2B)	0.138 1(1)	0.191 9(1)	0.315 7(3)
O(1B)	0.117 5(4)	0.138 0(3)	0.252 0(7)
N(1B)	0.238 0(4)	0.177 2(3)	0.315 6(8)
C(1B)	0.336 0(5)	0.077 1(4)	0.447 2(9)
C(2B)	0.316 7(7)	0.109 2(5)	0.567 4(12)
C(3B)	0.345 1(8)	0.081 7(6)	0.691 2(14)
C(4B)	0.389 3(7)	0.022 8(6)	0.691 4(13)
C(5B)	0.409 5(8)	−0.007 9(6)	0.575 1(14)
C(6B)	0.383 0(7)	0.016 7(5)	0.448 8(12)
C(7B)	0.385 9(5)	0.111 2(4)	0.200 5(9)
C(8B)	0.431 2(6)	0.144 3(5)	0.261 8(11)
C(9B)	0.501 6(7)	0.147 9(5)	0.204 4(12)
C(10B)	0.525 5(7)	0.116 7(5)	0.083 4(12)
C(11B)	0.480 4(6)	0.083 4(5)	0.022 1(12)
C(12B)	0.408 9(6)	0.079 9(5)	0.079 6(11)
C(13B)	0.105 3(5)	0.204 6(4)	0.486 3(9)
C(14B)	0.102 2(6)	0.257 4(5)	0.556 6(11)
C(15B)	0.083 2(7)	0.264 1(6)	0.691 9(13)
C(16B)	0.069 7(7)	0.218 5(6)	0.757 4(13)
C(17B)	0.073 6(7)	0.166 4(6)	0.689 4(13)
C(18B)	0.092 2(7)	0.157 1(5)	0.551 7(12)
C(19B)	0.092 6(5)	0.257 9(4)	0.226 1(9)
C(20B)	0.136 0(6)	0.279 1(5)	0.137 3(11)
C(21B)	0.098 1(6)	0.330 3(5)	0.069 5(12)
C(22B)	0.018 9(6)	0.359 2(5)	0.083 4(11)
C(23B)	−0.026 0(7)	0.338 9(5)	0.167 6(12)
C(24B)	0.011 0(6)	0.288 0(5)	0.240 6(11)
Cl	0.303 6(2)	0.277 6(1)	0.434 7(3)
As	0.223 99(7)	0.820 75(6)	0.428 1(1)
C(1)	0.165 7(7)	0.825 9(5)	0.255 8(12)
C(2)	0.140 7(8)	0.777 5(6)	0.198 8(15)
C(3)	0.101 1(8)	0.781 7(6)	0.075 3(15)
C(4)	0.087 1(9)	0.834 2(7)	0.007 4(16)
C(5)	0.108 8(9)	0.880 6(7)	0.059 3(17)
C(6)	0.149 4(9)	0.877 2(7)	0.186 5(15)
C(7)	0.172 5(7)	0.888 5(6)	0.540 5(13)
C(8)	0.089 6(9)	0.906 4(7)	0.547 4(16)
C(9)	0.049 3(9)	0.952 6(7)	0.638 3(17)
C(10)	0.094 5(9)	0.979 1(7)	0.720 4(17)
C(11)	0.175 4(10)	0.963 2(8)	0.716 8(17)
C(12)	0.216 1(8)	0.915 4(6)	0.626 4(14)
C(13)	0.222 6(7)	0.750 6(6)	0.517 9(13)
C(14)	0.247 3(8)	0.695 3(6)	0.450 1(15)
C(15)	0.240 9(9)	0.645 8(7)	0.512 5(16)
C(16)	0.216 9(8)	0.649 0(6)	0.643 5(14)
C(17)	0.195 6(8)	0.705 5(7)	0.713 4(15)
C(18)	0.195 9(8)	0.757 3(6)	0.647 8(15)
C(19)	0.335 8(7)	0.817 1(5)	0.408 4(12)
C(20)	0.396 0(8)	0.774 4(6)	0.471 0(15)
C(21)	0.477 0(9)	0.771 2(7)	0.454 2(16)
C(22)	0.496 5(9)	0,809 5(7)	0.378 6(16)
C(23)	0.435 5(9)	0.853 4(7)	0.315 6(16)
C(24)	0.352 8(8)	0.859 0(6)	0.330 1(15)
C(1′)	0.560 6(12)	0.260 9(6)	0.958 2(17)
Cl(1′)	0.674 0(4)	0.203 7(3)	1.080 0(9)
Cl(2′)	0.639 9(6)	0.292 2(4)	0.891 5(9)

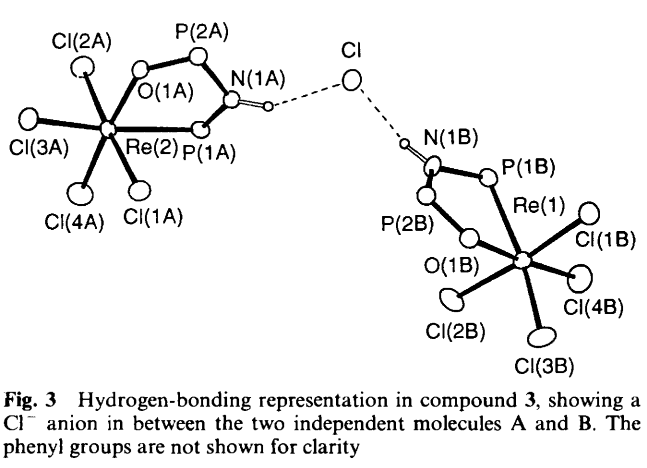

Fig. 3 Hydrogen-bonding representation in compound **3**, showing a Cl^- anion in between the two independent molecules A and B. The phenyl groups are not shown for clarity

2.141(5) Å can be compared with those of 2.23(1), 2.29(2) and 2.20(1) Å [15–17] observed in octahedral Re–O(oxo) complexes. The lengthening of these Re–O(water) bond distances can be accounted for by the greater *trans* influence exerted by oxo-oxygen (O^{2-}) with respect to the neutral oxygen in the present compound. The P–N distances of 1.660(12) and 1.670(11) Å are representative of single-bond distances.[3,18–20] The co-ordination of the ligand to the Re gives rise to a slight polarization of the P=O bond manifested by its lengthening from that of a pure double bond [1.470(1) and 1.485(7) Å [21,22]] to 1.522(13) Å.

The crystals of compound **4** consist of a packing of $[ReCl_4\{N(OPPh_2)PPh_2\text{-}P,O\}]^-$ anions and $[AsPh_4]^+$ cations. The complex differs from **1** by the ligand *trans* to the oxygen of P=O group, which is now a chlorine atom, and by the presence of a negative charge produced by deprotonation of the nitrogen of the ligand. This situation gives rise to a remarkable change in bond distances and angles of the ligand, showing a π-electron delocalization along the P–N–P–O fragment. Accordingly the P–N bond lengths are shorter, at 1.594(4) and 1.621(4), and P–O is longer, at 1.543(3) Å, at the same time the angles P–N–P and P–O–Re change from 119.3(6) in **1** to 116.4(2) in **4** and from 126.9(8) to 121.1(2)° respectively, in agreement with data for other octahedral rhenium complexes with similar negatively charged ligands.[1–3]

Table 3 Fractional coordinates for $[AsPh_4][ReCl_4\{N(OPPh_2)PPh_2\}]$ **4**

Atom	*x*	*y*	*z*
Re	0.762 17(1)	0.226 82(1)	0.168 93(1)
Cl(1)	0.785 34(8)	0.140 52(9)	0.069 88(6)
Cl(2)	0.733 49(8)	0.326 40(9)	0.258 79(6)
Cl(3)	0.719 01(9)	0.096 04(9)	0.231 24(7)
Cl(4)	0.902 98(8)	0.217 0(1)	0.207 57(7)
P(1)	0.774 40(7)	0.364 29(8)	0.093 88(6)
P(2)	0.611 15(7)	0.308 48(8)	0.074 91(6)
O	0.638 5(2)	0.239 7(2)	0.133 1(2)
N	0.679 2(2)	0.385 8(3)	0.063 3(2)
C(1)	0.817 8(3)	0.468 2(4)	0.133 8(3)
C(2)	0.793 0(4)	0.552 7(4)	0.107 0(3)
C(3)	0.828 4(4)	0.633 6(4)	0.133 0(3)
C(4)	0.890 6(4)	0.628 5(4)	0.187 7(3)
C(5)	0.917 1(4)	0.546 0(5)	0.214 5(3)
C(6)	0.880 4(3)	0.465 3(4)	0.188 1(3)
C(7)	0.838 5(3)	0.353 0(4)	0.020 1(2)
C(8)	0.924 2(4)	0.354 7(6)	0.027 8(3)
C(9)	0.970 2(4)	0.347 8(7)	−0.030 6(4)
C(10)	0.929 8(4)	0.336 3(5)	−0.095 5(3)
C(11)	0.846 2(3)	0.334 2(4)	−0.103 1(2)
C(12)	0.800 0(3)	0.342 6(4)	−0.046 0(3)
C(13)	0.515 2(3)	0.360 8(3)	0.098 4(2)
C(14)	0.465 9(3)	0.411 1(3)	0.049 4(3)
C(15)	0.392 9(3)	0.453 8(4)	0.068 3(3)
C(16)	0.369 1(3)	0.445 4(4)	0.134 8(3)
C(17)	0.416 8(4)	0.394 0(4)	0.182 5(3)
C(18)	0.490 2(4)	0.352 5(4)	0.165 5(3)
C(19)	0.586 0(3)	0.241 5(3)	−0.002 4(2)
C(20)	0.575 5(4)	0.147 1(4)	0.003 5(3)
C(21)	0.562 7(4)	0.093 2(4)	−0.056 3(3)
C(22)	0.561 7(4)	0.132 1(4)	−0.121 2(3)
C(23)	0.272 7(4)	0.225 0(4)	−0.127 6(3)
C(24)	0.584 0(3)	0.280 0(4)	−0.068 8(3)
As	0.761 17(3)	0.652 25(3)	0.395 10(2)
C(25)	0.799 3(3)	0.769 1(3)	0.367 7(2)
C(26)	0.833 5(3)	0.830 8(4)	0.417 1(3)
C(27)	0.864 4(4)	0.914 5(4)	0.395 1(3)
C(28)	0.862 9(4)	0.935 1(4)	0.325 8(3)
C(29)	0.828 3(4)	0.874 0(4)	0.277 4(3)
C(30)	0.796 2(3)	0.791 1(4)	0.297 7(3)
C(31)	0.670 6(3)	0.614 5(3)	0.330 7(2)
C(32)	0.589 5(3)	0.634 4(4)	0.344 5(3)
C(33)	0.524 7(4)	0.615 4(4)	0.295 3(3)
C(34)	0.541 7(4)	0.576 7(4)	0.233 3(3)
C(35)	0.622 5(4)	0.553 5(4)	0.219 7(3)
C(36)	0.688 3(3)	0.572 4(4)	0.268 9(3)
C(37)	0.851 6(3)	0.567 8(3)	0.395 7(2)
C(38)	0.933 0(3)	0.599 2(4)	0.401 8(3)
C(39)	0.999 1(4)	0.536 7(4)	0.404 4(3)
C(40)	0.981 3(4)	0.444 5(5)	0.401 9(4)
C(41)	0.900 1(4)	0.413 5(5)	0.396 8(4)
C(42)	0.834 3(4)	0.474 3(4)	0.392 8(3)
C(43)	0.721 8(3)	0.661 4(3)	0.486 3(2)
C(44)	0.674 7(4)	0.736 2(4)	0.503 1(3)
C(45)	0.642 0(4)	0.740 9(4)	0.568 1(3)
C(46)	0.657 2(4)	0.670 3(5)	0.613 9(3)
C(47)	0.702 8(4)	0.595 0(5)	0.597 2(3)
C(48)	0.736 9(4)	0.589 9(4)	0.532 1(3)

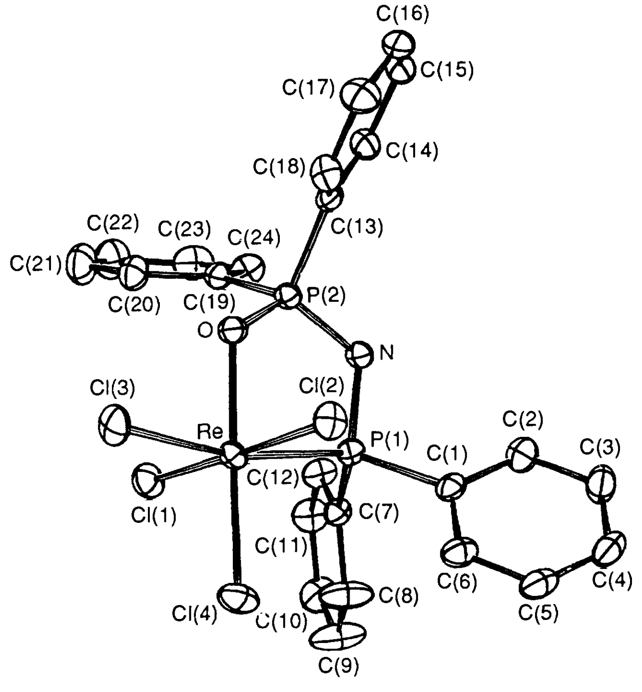

Fig. 4 An ORTEP view of the anion complex **4** showing the thermal ellipsoids at 30% probability

Table 4 Selected bond distances (Å) and angles (°) for $[ReCl_3(H_2O)\{NH(OPPh_2)PPh_2\}]\cdot EtOH$ **1**

Re–Cl(1)	2.341(3)	Re–O(2)	2.141(5)
Re–Cl(2)	2.341(4)	P(1)–N	1.660(12)
Re–Cl(3)	2.332(3)	P(2)–N	1.670(11)
Re–P(1)	2.468(4)	P(2)–O(1)	1.522(13)
Re–O(1)	2.055(9)		
Cl(1)–Re–Cl(2)	89.7(3)	Cl(3)–Re–O(1)	86.9(2)
Cl(1)–Re–Cl(3)	172.8(1)	Cl(3)–Re–O(2)	95.2(2)
Cl(1)–Re–P(1)	88.4(2)	P(1)–Re–O(1)	80.9(4)
Cl(1)–Re–O(1)	85.9(2)	P(1)–Re–O(2)	94.7(2)
Cl(1)–Re–O(2)	91.9(2)	O(1)–Re–O(2)	175.1(4)
Cl(2)–Re–Cl(3)	91.2(2)	Re–P(1)–N	103.6(4)
Cl(2)–Re–P(1)	169.9(2)	O(1)–P(2)–N	107.1(6)
Cl(2)–Re–O(1)	89.0(4)	Re–O(1)–P(2)	126.9(8)
Cl(2)–Re–O(2)	95.3(2)	P(1)–N–P(2)	119.3(6)
Cl(3)–Re–P(1)	89.6(2)		

Compound **3** presents a more complex crystal packing which consists of a pattern of neutral molecules of $[ReCl_4\{NH(OPPh_2)PPh_2\text{-}P,O\}]$, Cl^- and $[AsPh_4]^+$ ions, and solvent molecules of CH_2Cl_2 in the ratio 2:1:1:1. The Cl^- ions link pairs of molecules by means of NH $\cdots$ Cl $\cdots$ HN hydrogen bonds (Fig. 3) [N(1A) $\cdots$ Cl 3.12(1), N(1B) $\cdots$ Cl 3.07(1) Å]. With respect to compound **1** these molecules present a chlorine atom *trans* to the oxygen of P=O group and are characterized by short Re–Cl distances of 2.292(3) and 2.284(3) Å. In general, Re–Cl bond distances in octahedral rhenium complexes display a wide range of values, from 2.28 to 2.63 Å, which can be rationalized only in terms of *trans* effects. Table 7 reports a selection of these Re–Cl bond distances. Although Re–Cl bond lengths *trans* to another Cl or P atoms are statistically distributed around the average values of 2.35(3) and 2.37(3) Å respectively, those *trans* to oxygen are strongly related to the oxygen charge and hybridization. The correlation between Re–Cl and Re–O(*trans*) distances given in Fig. 5 shows that the maximum lengthening arises from the presence of an oxo group *trans*, and that the Re–Cl bond distances decrease regularly from 2.452(3) to 2.284(3) Å when Re–Cl is placed *trans* to a neutral oxygen. In order to stress the importance of the *trans* effect, it can be noted that the longest Re–Cl bond distances have been found in octahedral co-ordination compounds when Re–Cl is *trans* to a Re≡N(nitrido) group [Re–Cl 2.563(4)[25] and 2.633(2)[26] Å] or to a Re=Re multiple metal bond [Re–Cl = 2.54 Å (on average)[18]] which are well known to be the groups which exert the maximum *trans* effect.[27]

Table 5 Selected bond distances (Å) and angles (°) for $2[ReCl_4\{NH(OPPh_2)PPh_2\}]\cdot Cl^-\cdot[AsPh_4]^+\cdot CH_2Cl_2$ **3**

	Molecule A	Molecule B
Re–Cl(1)	2.337(3)	2.339(4)
Re–Cl(2)	2.336(3)	2.329(3)
Re–Cl(3)	2.329(2)	2.323(3)
Re–Cl(4)	2.292(3)	2.284(3)
Re–P(1)	2.510(2)	2.488(3)
Re–O(1)	2.071(6)	2.064(6)
P(1)–N(1)	1.685(8)	1.681(7)
P(2)–N(1)	1.655(7)	1.650(7)
P(2)–O(1)	1.510(6)	1.514(7)
Cl(1)–Re–Cl(2)	175.7(1)	174.0(1)
Cl(1)–Re–Cl(3)	91.2(1)	91.4(1)
Cl(1)–Re–Cl(4)	92.6(1)	91.4(1)
Cl(1)–Re–P(1)	85.1(1)	89.7(1)
Cl(1)–Re–O(1)	90.3(2)	87.6(2)
Cl(2)–Re–Cl(3)	90.6(1)	92.5(1)
Cl(2)–Re–Cl(4)	91.1(1)	92.8(1)
Cl(2)–Re–P(1)	92.4(1)	85.6(1)
Cl(2)–Re–O(1)	85.8(2)	87.9(2)
Cl(3)–Re–Cl(4)	96.4(1)	95.5(1)
Cl(3)–Re–P(1)	168.0(1)	168.8(1)
Cl(3)–Re–O(3)	89.5(2)	88.8(2)
Cl(4)–Re–P(1)	95.1(1)	95.6(1)
Cl(4)–Re–O(1)	173.3(2)	175.6(2)
P(1)–Re–O(1)	79.1(2)	80.1(2)
Re–O(1)–P(2)	128.2(3)	127.5(4)
Re–P(1)–N	100.1(2)	101.5(3)
O(1)–P(2)–N	106.5(4)	107.6(4)
P(1)–N–P(2)	118.3(5)	119.2(5)

Table 6 Selected bond distances (Å) and angles (°) for $[AsPh_4][ReCl_4\{N(OPPh_2)PPh_2\}]$ **4**

Re–Cl(1)	2.339(1)	Re–O	2.054(3)
Re–Cl(2)	2.332(1)	P(1)–N	1.621(4)
Re–Cl(3)	2.385(1)	P(2)–N	1.594(4)
Re–Cl(4)	2.322(1)	P(2)–O	1.543(3)
Re–P(1)	2.490(1)		
Cl(1)–Re–Cl(2)	173.31(4)	Cl(3)–Re–P(1)	167.42(4)
Cl(1)–Re–Cl(3)	92.82(5)	Cl(3)–Re–O	86.3(1)
Cl(1)–Re–Cl(4)	91.08(5)	Cl(4)–Re–P(1)	96.85(5)
Cl(1)–Re–P(1)	86.34(4)	Cl(4)–Re–O	178.0(1)
Cl(1)–Re–O	89.0(1)	P(1)–Re–O	81.2(1)
Cl(2)–Re–Cl(3)	92.56(5)	Re–P(1)–N	104.7(1)
Cl(2)–Re–Cl(4)	92.33(5)	O–P(2)–N	113.8(2)
Cl(2)–Re–P(1)	87.54(4)	Re–O–P(2)	121.1(2)
Cl(2)–Re–O	87.36(9)	P(1)–N–P(2)	116.4(2)
Cl(3)–Re–Cl(4)	95.71(5)		

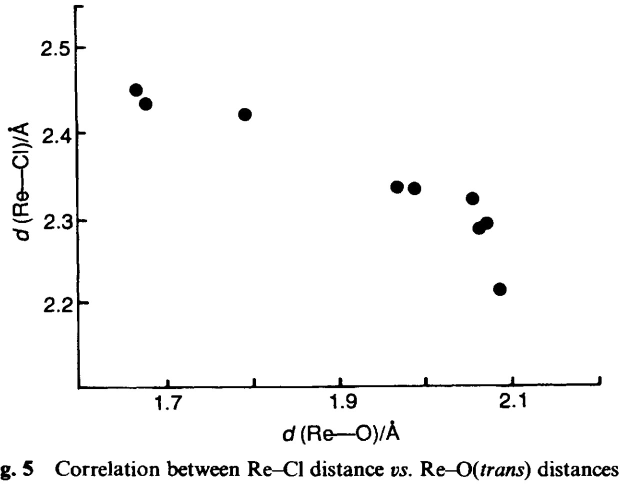

Fig. 5 Correlation between Re–Cl distance *vs.* Re–O(*trans*) distances in octahedral complexes of rhenium

Experimental

Materials.—All preparations were carried out under nitrogen using freshly distilled, dried and degassed solvents unless stated otherwise. Infrared spectra (KBr pellets) were recorded on a Nicolet FTIR 510P spectrophotometer. Elemental analyses were performed on a Carlo Erba model 1106 elemental analyser. Magnetic susceptibilities of solid samples were measured on a Faraday balance as previously described.[28] Literature methods were used for the preparation of $NH(PPh_2)_2$[29] and of the rhenium starting materials $[AsPh_4][ReOCl_4]$[30] and $[ReCl_3(MeCN)(PPh_3)_2]$.[31]

Preparations.—$[ReCl_3(H_2O)\{NH(OPPh_2)PPh_2\text{-}P,O\}]$ **1**. Bis(diphenylphosphino)amine (0.4 mmol) was added to a non-dried chloroform solution (50 cm^3) of $[AsPh_4][ReOCl_4]$ (0.4 mmol) under nitrogen. Within a few minutes at reflux the emerald-green suspension changed to a yellow solution. After 30 min the solution was filtered, evaporated to a small volume and diethyl ether added until a yellow-green precipitate was obtained. The solid was filtered off and washed with water, ethanol and diethyl ether. Recrystallization from acetone–ethanol gave a green-yellow crystalline solid, yield 80% (Found: C, 41.1; H, 3.5; N, 1.8. $C_{24}H_{23}Cl_3NO_2P_2Re$ requires C, 40.5; H, 3.2; N, 2.0%); ν(H_2O) 3520, ν(NH) 2617, ν(PO) 1130; other ligand bands at 1338, 1050, 937 and 563 cm^{-1}.

$2[ReCl_4\{NH(OPPh_2)PPh_2\text{-}P,O\}]\cdot Cl^-\cdot[AsPh_4]^+$ **3**. When the above reaction was carried out in anhydrous chloroform the emerald-green suspension changed to a yellow solution and a yellow-green precipitate slowly formed. Recrystallization from an anhydrous CH_2Cl_2–CCl_4 mixture under nitrogen gave the product **3** as a yellow-green crystalline solid, yield 70% (Found: C, 45.3; H, 3.0; N, 1.4. $C_{72}H_{62}AsCl_9N_2O_2P_4Re_2$ requires C, 46.1; H, 3.3; N, 1.5%); ν(NH) 2546, ν(PO) 1128; other ligand bands at 1327, 1051, 933 and 563 cm^{-1}.

$[AsPh_4][ReCl_4\{N(OPPh_2)PPh_2\text{-}P,O\}]$ **4**. Complex **3** (0.4 mmol) was treated with an excess of $NH(PPh_2)_2$ (1 : 4) in boiling chloroform (30 cm^3) for 30 min. During this time the solution turned from yellow to orange. After filtration the solution was evaporated to a small volume and dichloromethane, acetone and ethanol were added. Slow evaporation gave a small amount of the product **4** as yellow microcrystals, yield 40% (Found: C, 52.1; H, 3.3; N, 1.2. $C_{48}H_{40}AsCl_4NOP_2Re$ requires C, 51.8; H, 3.7; N, 1.3%); ν(PO) 1128; other ligand bands at 991, 819 and 574 cm^{-1}.

$[ReCl_2\{NH(PPh_2)_2\text{-}P,P'\}_2][BPh_4]$ **6**. The complex $[ReCl_3(MeCN)(PPh_3)_2]$ (0.4 mmol) and $NH(PPh_2)_2$ (0.8 mmol) were heated under reflux in tetrahydrofuran (50 cm^3) for 40 min. During this period an orange precipitate formed, which was filtered off and washed with tetrahydrofuran and ethanol. The tetraphenylborate derivative was obtained by adding $Na[BPh_4]$ to a solution of the chloride derivative in methanol. The precipitate which formed was filtered off, washed with water, methanol and diethyl ether and recrystallized from dichloromethane–ethanol, yield 70% (Found: C, 61.7; H, 4.4; N, 2.1. $C_{72}H_{62}BCl_2N_2P_4Re$ requires C, 62.6; H, 4.5; N, 2.0%); ν(NH) 3250, ν(P_2N) 840 cm^{-1}.

Crystallography.—Crystals of complexes **1**·EtOH, **3**·CH_2Cl_2 and **4** were obtained as described in the corresponding syntheses.

Crystal data. $C_{26}H_{29}Cl_3NO_3P_2Re$ **1**, $M = 758.0$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 19.125(3)$, $b = 10.079(2)$, $c = 15.315(2)$ Å, $U = 2952.1(6)$ $Å^3$ (by least-squares analysis of diffractometer angles for 25 automatically centred reflections in the range $9 \leqslant \theta \leqslant 13$), $\lambda = 0.710\,69$ Å, $Z = 4$, $D_c = 1.70$ g cm^{-3}, μ(Mo-Kα) = 45.8 cm^{-1}, $F(000) = 1488$, crystal dimensions 0.10 × 0.12 × 0.28 mm.

$C_{73}H_{64}AsCl_{11}N_2O_2P_4Re_2$, $M = 1962.4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 17.249(2)$, $b = 23.486(2)$, $c = 9.870(1)$ Å, $\alpha = 93.14(1)$, $\beta = 92.91(1)$, $\gamma = 72.32(1)°$, $U = 3801.2(4)$ $Å^3$ (by least-squares analysis of diffractometer angles for 25 automatically centred reflections in the range $9 \leqslant \theta \leqslant 14$), $\lambda =$

Table 7 Comparison of selected Re–Cl and Re–O bond distance (Å) in octahedral complexes of rhenium, with estimated standard deviations (e.s.d.s) in parentheses

Complex[a]	Re–Cl			Re–O	Ref.
	trans to Cl	*trans* to P	*trans* to O	*trans* to Cl	
$[ReCl_3(H_2O)\{NH(OPPh_2)PPh_2\text{-}P,O\}]$	2.341(3) 2.332(3)	2.341(3)			*b*
$[ReCl_4\{N(OPPh_2)PPh_2\text{-}P,O\}]^-$	2.339(1) 2.332(1)	2.385(1)	2.322(1)	2.054(3)	*b*
$[ReCl_4\{NH(OPPh_2)PPh_2\text{-}P,O\}]$	2.337(3) 2.336(3) 2.339(4) 2.329(3)	2.329(2) 2.323(3)	2.292(3) 2.284(3)	2.071(6) 2.064(6)	*b*
trans-$[ReOCl_2(PPh_3)(msal)]$	2.430(2) 2.375(2)				12
cis-$[ReOCl_2(PPh_3)(msal)]$		2.397(3)			12
$[ReCl_2(PMe_2Ph)_2(psal)]$			2.383(3)	1.990(7)	13
$[ReCl_3(PMe_2Ph)(psal)]$	2.345(1) 2.337(1)		2.334(1)	1.970(2)	14
$[ReOCl_2(PPh_3)\{N(OPPh_2)_2\}]$	2.380(2) 2.367(2)				1
$[ReOCl_2(PPh_3)\{N(SPPh_2)_2\}]$			2.436(2)	1.677(6)	1
$[ReOCl_3(dppm\text{-}P,P')]$		2.365(4) 2.373(3)	2.452(3)	1.671(6)	9
$[ReCl_4(dppom\text{-}P,O)]$	2.361(3) 2.340(3)	2.353(3)	2.215(5)	2.087(7)	9
$[ReCl_3(OH)(PEt_2Ph)_2]$	2.364(2) 2.389(2)		2.428(2)	1.795(4)	23
$[Re_2O_2Cl_4(PPh_3)(salen)]$		2.416(4) 2.409(4)			24
Average	2.35[3]	2.37[3]			

[a] msal = *N*-Methylsalicylideneiminate, psal = *N*-phenylsalicylideneiminate, dppm = $Ph_2PCH_2PPh_2$; salen = *N,N'*-ethylenebis(salicylideneiminate). [b] Present work.

0.710 69 Å, $Z = 2$, $D_c = 1.72$ g cm^{-3}, μ(Mo-Kα) = 41.5 cm^{-1}, $F(000) = 1924$, crystal dimensions 0.07 × 0.12 × 0.28 mm.

$C_{48}H_{40}AsCl_4NOP_2Re$, $M = 1111.7$, monoclinic, space group $P2_1/c$ (no. 14), $a = 15.992(2)$, $b = 14.595(3)$, $c = 19.265(3)$ Å, $\beta = 94.34(1)°$, $U = 4483.6(5)$ Å^3 (by least-squares analysis of diffractometer angles for 25 automatically centred reflections in the range $8 \leqslant \theta \leqslant 13°$), $\lambda = 0.710\,69$ Å, $Z = 4$, $D_c = 1.65$ g cm^{-3}, μ(Mo-Kα) = 38.2 cm^{-1}, $F(000) = 2196$, crystal dimensions 0.14 × 0.19 × 0.33 mm.

Data collection and processing. CAD4 diffractometer, ω–2θ scan mode, graphite-monochromated Mo-Kα radiation. For complex **1** 3334 unique reflections measured ($2 \leqslant \theta \leqslant 27°$) giving 1751 with $I \geqslant 3\sigma(I)$; for **3**, 16 538 unique reflections measured giving 7970 observed; for **4**, 9777 unique reflections giving 7098 observed. All data were corrected for Lorentz, polarization and absorption (minimum transmission factor = 0.92, 0.78 and 0.63 for **1**, **3** and **4** respectively).

Structure analysis and refinement. Solution by Patterson and Fourier methods. For complex **1**, full-matrix least-squares refinement, with all non-hydrogen atoms anisotropic and hydrogen in calculated positions [the ethanol molecule of crystallization is partially disordered and the oxygen O(1') was refined anisotropically, C(2') isotropically and C(1') bonded to O(1') isotropically in two different positions with occupancies of 0.5]. Final R and R' values 0.038 and 0.040. For **3**, full-matrix least-squares refinement (in three blocks for final cycles) with the carbon atoms isotropic, the remaining non-hydrogen atoms anisotropic, and the hydrogen atoms in calculated positions (the carbon and chlorine atoms of the solvent molecule CH_2Cl_2 were refined isotropically) gave R and R' 0.044 and 0.052. For **4**, refinement as for **3** with all non-hydrogen atoms anistropic, except the carbon atoms of $[AsPh_4]^+$ cation which were refined isotropically, and hydrogen atoms in calculated positions gave R and R' 0.032 and 0.044.

The weighting scheme $w = 4F_o^2/[\sigma^2(F_o^2) + (pF_o^2)^2]$ gave satisfactory agreement analyses, where $p = 0.04, 0.06, 0.06$ for compounds **1**, **3** and **4** respectively. Programs used and sources of scattering factors are given in ref. 32.

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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