A New Class of Binuclear Rhenium(II) Halide Species Containing a Strong Metal–Metal Bond: the Chemistry and Structure of Complexes of the Type $Re_2X_4(PR_3)_4$

By F. ALBERT COTTON and BERTRAM A. FRENZ

(*Department of Chemistry, Texas A&M University, College Station, Texas* 77843)

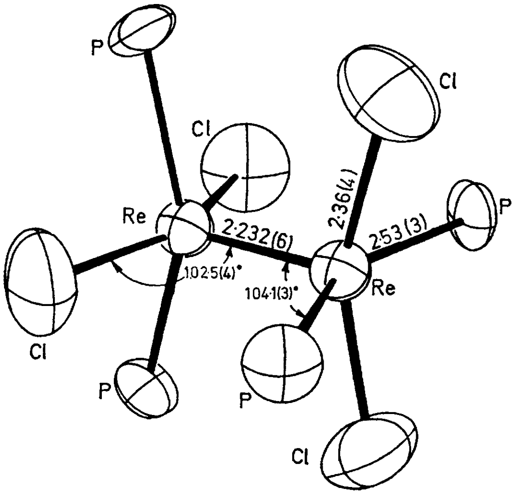
and JERRY R. EBNER and RICHARD A. WALTON*

(*Department of Chemistry, Purdue University, West Lafayette, Indiana* 47907)

Summary A new class of tertiary phosphine complexes of the type $Re_2Cl_4(PR_3)_4$ have been isolated from the reaction of Re_3Cl_9 or the $Re_2Cl_8^{2-}$ anion with the appropriate phosphine, and a single crystal *X*-ray structure analysis has shown $Re_2Cl_4(PEt_3)_4$ to possess a strong (evidently quadruple) rhenium–rhenium bond and eclipsed rotational configuration.

As a result of recent studies on the reaction of rhenium(III) chloride (Re_3Cl_9) with heterocyclic tertiary amines, a new class of polymeric rhenium(II) derivatives of the type $[Re_3Cl_6L_3]_n$ (*e.g.*, L = pyridine or benzimidazole) in which the $[Re_3Cl_3]$ cluster of the parent halide is retained, has been isolated.[1] In view of the tendency of tertiary phosphines to bring about reduction of higher oxidation state halides of the heavy transition elements [*e.g.*, the reduction of $RhCl_3$ by triphenylphosphine to afford $RhCl(PPh_3)_3$],[2] we have investigated in detail the reaction of rhenium(III) chloride with the phosphines PPh_3, PMe_2Ph, and PEt_3. Although we were able to isolate the expected red-purple crystalline adducts of the type $Re_3Cl_9(PR_3)_3$, we did not obtain any reduced species from the reactions of this halide with PPh_3 or PMe_3Ph. However, when an acetone solution of rhenium(III) chloride was refluxed for 7 days with PEt_3, black crystals of a rhenium(II) complex of stoicheiometry $[ReCl_2(PEt_3)_2]_n$ were isolated in *ca.* 50% yield. This complex was diamagnetic, and a molecular weight determination in chloroform (Found: 991) suggested it was the dimer $Re_2Cl_4(PEt_3)_4$ (Calc.: 986), implying that reduction to rhenium(II) was, in contrast to the related heterocyclic amine reactions,[1] accompanied by disruption of the $[Re_3Cl_3]$ cluster. Since we suspected that such a species should be readily formed directly from the octachlorodirhenate(III) dianion,[3] we studied the reactions of the salt $(Bu_4N)_2Re_2Cl_8$ with PEt_3, PPr^n_3, and PEt_2Ph in refluxing ethanol or acetone and found that this is indeed a general route to complexes of this type. These reactions are believed to proceed *via* the rhenium(III) intermediates $Re_2Cl_6(PR_3)_2$.[4,5] The related reaction of $(Bu_4N)_2Re_2Br_8$ with PEt_3 has also been explored and black crystals of $Re_2Br_4(PEt_3)_4$ have been isolated.

Preliminary studies on the reactivity of these new complexes indicate that they have a rich chemistry. For instance, reaction of $Re_2Cl_4(PEt_3)_4$ and its bromo-analogue with CCl_4 affords the rhenium(III) complex salts $[Et_3PCl]_2Re_2Cl_8$ and $[Et_3PCl]_2Re_2Cl_4Br_4$, respectively. The formation of the $Re_2Cl_8^{2-}$ anion by oxidation with CCl_4 suggests that $Re_2Cl_4(PEt_3)_4$ and $Re_2Cl_8^{2-}$ are structurally related and that the former complex can indeed be considered as a derivative of the elusive $Re_2Cl_8^{4-}$ anion, a species which has been generated in solution by the polarographic reduction[6] of the $Re_2Cl_8^{2-}$ anion. The reaction of $Re_2Cl_4(PEt_3)_4$ with 1,2-bis(diphenylphosphino)ethane (dppe) to afford purple-violet crystals of $[ReCl_2(dppe)]_n$ (n probably 2) suggests that these species may be useful intermediates in the synthesis of new derivatives of this rare oxidation state. Such investigations are currently in progress.†



FIGURE

These phosphine complexes clearly constitute a new structural class of rhenium(II) derivatives. Since they are apparently derivatives of the uncharacterized $Re_2Cl_8^{4-}$ anion and, in addition, are probably close structural analogues of the recently prepared[7] molybdenum(II) derivatives $Mo_2Cl_4(PR_3)_4$, we have carried out a single crystal X-ray structure analysis on $Re_2Cl_4(PEt_3)_4$.

The compound $Re_2Cl_4(PEt_3)_4$ crystallizes in the cubic system, space group $Im3m$ with $a = 12{\cdot}345(4)$ Å and $Z = 2$. The special positions 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ are occupied by disordered sets of three 'one-third molecules,' whose axes lie parallel to the x, y, and z directions, thus forming an octahedron of Re/3 atoms. The P and Cl atoms lie nearly superposed over the faces of the Re/3 octahedra. On the basis of the disorder scheme which was assumed the structure was refined anisotropically to $R_1 = 0{\cdot}041$ and $R_2 = 0{\cdot}052$, using 109 reflections for which $|F^2| > 3\sigma(F^2)$ and 22 variable parameters.

The $Re_2Cl_4P_4$ skeleton and the dimensions thereof are shown in the Figure. Its most important features are: (i) The $ReCl_2(PEt_3)_2$ halves are in a rigorously eclipsed relationship, and the point symmetry is D_{2d}; (ii) the Re–Re distance is the same as those (2·22—2·25 Å) of quadruply bonded dirhenium(III) compounds,[3,8] whereas loss of the Re–Re δ bond has been shown[9] to cause an increase of *ca.* 0·06 Å and removal of even one δ bonding electron from an Mo–Mo quadruple bond[10] causes an increase of 0·05 Å. (iii) the Re–Cl and Re–P bond lengths are about 0·04 and 0·08 Å longer than those[5] in $Re_2Cl_6(PEt_3)_2$ as expected for the lower formal oxidation number of rhenium.

It appears certain, especially from the Re–Re distance, which remains as short as that in $Re_2Cl_6(PEt_3)_2$ despite pronounced nonbonded repulsive forces tending to elongate it, that $Re_2Cl_4(PEt_3)_4$ has a quadruple Re–Re bond. Therefore, the two electrons beyond those in the $\sigma^2\pi^4\delta^2$ set constituting the quadruple bond presumably occupy the lower σ nonbonding orbital, of a_{2u} symmetry.[11] This implies that the order of orbitals is $\sigma\pi\delta \ldots \sigma(a_{2u})\delta^*(b_{1u})$-$\sigma(a_{1g})$ as previously supposed, although the order of the last three might well vary depending on whether $\sigma(a_{2u})$ is occupied or not. Interelectronic repulsion effects would seem to favour occupancy of $\sigma(a_{2u})$ even if the ordering of the virtual orbitals were $\delta^*(B_{1u}) < \sigma(a_{2u})$.

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† All complexes described in this report had satisfactory microanalyses and have been characterized by ^1H n.m.r., i.r. (4000—400 cm^{-1}), and/or electronic absorption spectroscopy.

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