The Redox Nature of the Reaction of β-Rhenium(IV) Chloride with Triphenylphosphine in Acetonitrile, and the Crystal Structure of the Reduction Product Trichloro(acetonitrile)bis(triphenylphosphine)rhenium(III)

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Summary An unusual redox reaction of β-rhenium(IV) chloride with triphenylphosphine in acetonitrile is described, and the crystal structure of one of the reduction products, $ReCl_3$,$2PPh_3$,MeCN shows that this molecule contains σ-bonded acetonitrile.

Following our chance discovery of the new halide β-$ReCl_4$,[1] we studied its reactivity towards a variety of donor molecules using acidified methanol or acetone as reaction solvent. Under these conditions, the reaction products were typical of those formed by the rhenium(III) anion [$Re_2Cl_8^{2-}$];[2] in no instances did we isolate rhenium(IV) complexes of the type $ReCl_4$,2L. We now find that by using strictly anhydrous conditions, the reactions of this halide are more complex than was previously noted[1] using the above reaction conditions, and reveal several novel features. These studies are of interest in view of the structural relationship of β-$ReCl_4$[3] to other heavy transition-metal tetrahalides (*e.g.*, NbX_4, TaX_4, MoX_4, and WX_4).[4]

Whereas the latter halides invariably react to form adducts of the type $MX_4,2L$,[5] β-$ReCl_4$ forms a variety of derivatives. We find, for instance, that in its reaction with an excess of triphenylphosphine using acetonitrile as solvent,† three halide complexes can be isolated from the same reaction mixture. These are *trans*-$ReCl_4,2PPh_3$ (I), dinuclear $[ReCl_3,PPh_3]_2$ (II), and $ReCl_3,2PPh_3,MeCN$. (I) is an authentic rhenium(IV) complex and (II) is a derivative of the $[Re_2Cl_8{}^{2-}]$ anion; both have properties identical with those of the same complexes prepared by alternative routes.[6,7] (III) is apparently identical with the product of this same stoicheiometry isolated by Rouschias and Wilkinson[6] from the reaction of *trans*-$ReOCl_3,2PPh_3$ with acetonitrile. This reaction in which three different classes of metal halide complexes are produced together, is unique for the behaviour of transition-metal halides of Groups IV—VII.

A particularly interesting feature of complex (III) is that the $C{\equiv}N$ stretching mode of the co-ordinated acetonitrile molecule cannot be located in the i.r. mull spectra; a similar observation is true for other derivatives of the type.[6] Rouschias and Wilkinson[6] advanced several alternative explanations which might possibly account for this behaviour, *viz.*, (i) σ-bonded RCN but with $\nu(C{\equiv}N)$ unusually weak, (ii) bonding from the π-electrons of the $C{\equiv}N$ bond, or (iii) a tautomeric equilibrium. We have now solved this problem by a single-crystal *X*-ray analysis of the acetonitrile complex.

$ReCl_3,2PPh_3,MeCN$ crystallizes as pale orange-yellow plates in the monoclinic spacegroup $P2_1/n$, with $a = 10{\cdot}036(8)$, $b = 15{\cdot}239(12)$, $c = 23{\cdot}280(17)$ Å, $\beta = 90{\cdot}56(8)°$, $Z = 4$, $U = 3560{\cdot}28$ Å^3, $M = 857{\cdot}7$, $D_m = 1{\cdot}59$ and $D_c = 1{\cdot}600$ g/cm^3. Intensities of 3335 independent reflections with $2\theta \leqslant 40°$ were recorded with a GE XRD-5 manual diffractometer, using Zr filtering Mo-K_α radiation and the stationary crystal, stationary counter method. The structure was solved from 2221 reflections, whose intensities were significantly above background, by Patterson and Fourier methods and refined by full-matrix least-squares (Re,P,Cl anisotropic, C,N isotropic) to an *R* of 0·077.

The structure consists of discrete molecules of $ReCl_3,2PPh_3,MeCN$ with the Re atom in a distorted octahedral environment (see Figure). The estimated standard deviations range from 0·01 Å (Re–Cl,P) through 0·03 Å for Re–N to 0·05 Å for C–C,C–N. The parameters of the 36 carbon atoms in the two triphenylphosphine molecules have refined to satisfactory values. The angles subtended by mutually *cis*-atoms at the Re are all within 6° of 90°. Of the three angles subtended by mutually *trans*-atoms, only the Cl–Re–Cl angle at 171·4(3)° is appreciably distorted from 180°. The dimensions of the co-ordinated acetonitrile and the linearity of the Re–N–C linkage are characteristic of the σ-bonded ligand,[8,9] and the Re–N bond length (2·05 Å) appears normal.[10] This complex is therefore structurally related to *trans*-$ReCl_3,3PMe_2Ph$[11] and other metal halide derivatives of this type,[11] and there is good agreement between the Re–Cl (*trans* to Cl) and Re-P (*trans* to P) distances for $ReCl_3,3PMe_2Ph$ and $ReCl_3,2PPh_3,MeCN$. Acetonitrile clearly has a weaker *trans*-labilizing effect than PMe_2Ph since Re–Cl (*trans* to MeCN) is significantly shorter at 2·40 Å than the corresponding Re–Cl distance (2·45 Å) *trans* to PMe_2Ph.[11]

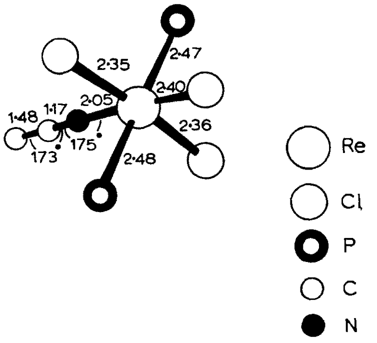

FIGURE. *The molecular structure of* $ReCl_3,2PPh_3,MeCN$ *showing the principal bond lengths.*

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† Reactions were carried out in sealed ampoules; contents of the ampoules were maintained under gentle reflux until reaction was complete.

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