An Anomaly in the Reactivity Patterns of the Octachlorodirhenate(III) Anion. The Chemistry and Crystal Structure of the μ-Dichloro-rhenium(III) Complex of 1,2-Bis(diphenylphosphino)ethane, $Re_2Cl_6(dppe)_2{\cdot}2MeCN$

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Summary The complexes $[ReCl_3(dppe)]_n$ and $[ReCl_{2\cdot5}(dppe)]_n$, formed from the reaction of the salt $[Bu_4N]_2Re_2Cl_8$ with 1,2-bis(diphenylphosphino)ethane (dppe), are not structurally related to analogous 2,5-dithiahexane complexes, a conclusion which has been confirmed by a single crystal X-ray structure analysis on the acetonitrile solvate $[ReCl_3(dppe){\cdot}MeCN]_n$.

THE chemistry of the octachlorodirhenate(III) anion $Re_2Cl_8^{2-}$ is dominated by the presence of a strong rhenium–rhenium bond, formally of bond order four.[1] Reaction of this dianion with Br^-, SCN^-, carboxylic acids, and a variety of phosphorus and sulphur donors affords derivatives in which this metal–metal bond is retained.[1] Furthermore, the Re_2 structural unit persists in the products formed from its polarographic reduction ($Re_2Cl_8^{3-}$ and $Re_2Cl_8^{4-}$)[2] and chlorine oxidation ($Re_2Cl_9^{n-}$, $n = 1$ or 2)[3]. However, evidence that the chemistry of this important model metal–metal bonded species is not as straightforward or predictable as might be supposed is provided by our recent results on its reaction with the bidentate ditertiary phosphine 1,2-bis(diphenylphosphino)ethane (dppe) preliminary details of which are presented herein.

$[Bu_4N]_2Re_2Cl_8$ reacts with an acetonitrile solution of dppe to afford a magenta complex of stoicheiometry $[ReCl_3(dppe)]_n$.[4] By analogy with the reaction of the dianion with the bidentate sulphur donor 2,5-dithiahexane (dth),[5] in which the metal–metal bonded dimers $Re_2Cl_6(dth)_2$ and $Re_2Cl_5(dth)_2$ are formed,[5,6] this complex might be expected to be the metal–metal bonded dimer $Re_2Cl_6(dppe)_2$. We have now found that a new complex of stoicheiometry close to $[ReCl_{2\cdot5}(dppe)]_n$ can be isolated as black crystals from the filtrate of the $[Bu_4N]_2Re_2Cl_8$–dppe–MeCN system upon prolonged reflux, so that the reactivity pattern with dppe formally resembles that of the related $[Bu_4N]_2Re_2Cl_8$–dth–MeCN system.[5] However, the reactivities of $[ReCl_3(dppe)]_n$ and $Re_2Cl_6(dth)_2$ suggest the absence of such a structural analogy. Whereas $Re_2Cl_6(dth)_2$ readily reacts with an acetonitrile solution of triphenylphosphine and with acetic acid–acetic anhydride under mild reflux conditions to

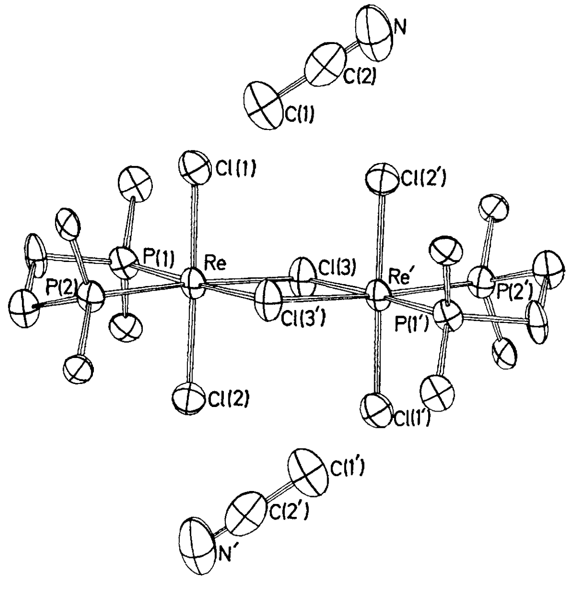

FIGURE. ORTEP diagram of the molecular structure of $[ReCl_3(dppe)]_2$ and the relative positions of the MeCN molecules of crystallization. 50% Probability envelopes for the vibrational ellipsoids of non-hydrogen atoms are shown. The phenyl rings have been omitted for clarity. Important bond distances (Å) and bond angles (°) are as follows: Re–Re′, 3·809(1); Re–Cl(1), 2·307(3); Re–Cl(2), 2·322(3); Re–Cl(3), 2·496(3); Re–Cl(3′), 2·503(3); Re–P(1), 2·370(3); Re–P(2), 2·371(3); ∠Cl(1)–Re–Cl(2), 177·97(12); Cl(1)–Re–Cl(3), 91·77(12); Cl(1)–Re–P(1), 88·63(12); Cl(1)–Re–P(2), 92·06(11); Cl(2)–Re–Cl(3), 88·75(11); Cl(2)–Re–P(1), 89·35(12); Cl(2)–Re–P(2), 87·48(12); Cl(3)–Re–P(1), 98·31(12); Cl(3)–Re–P(2), 175·80(11); P(1)–Re–P(2), 83·50(11); Cl(3)–Re–Cl(3′), 80·84(11); Re–Cl(3)–Re′, 99·48(13).

afford the known derivatives $Re_2Cl_6(PPh_3)_2$ and $Re_2(O_2CMe)_4Cl_2$, which are also readily formed directly from the $Re_2Cl_8^{2-}$ anion,[1,4] the related dppe complex does not react in this fashion. Also, in contrast to the lack of reactivity of $Re_2Cl_6(dth)_2$ towards chlorocarbons of the type CCl_3X, X = Cl, NO_2, CN, or CO_2H, the phosphine complex $[ReCl_3(dppe)]_n$ was oxidized to the new yellow-orange rhenium(IV) solvates $ReCl_4(dppe) \cdot xCCl_3X$, $x = 0{\cdot}75$ or 1.†

The above differences suggested a gross structural difference between $Re_2Cl_6(dth)_2$ and $[ReCl_3(dppe)]_n$, and in particular the absence of a strong rhenium–rhenium bond in the dppe complex, a conclusion which has been confirmed by a single-crystal *X*-ray structural analysis. Crystals of the acetonitrile solvate were grown from an acetonitrile solution by a slow diffusion procedure. *Crystal data:* $[ReCl_3(dppe) \cdot MeCN]_2$, triclinic, space group $P\bar{1}$, $a = 10{\cdot}299(1)$, $b = 11{\cdot}556(1)$, $c = 12{\cdot}991(1)$ Å, $\alpha = 104{\cdot}45(1)°$, $\beta = 104{\cdot}53(1)°$, $\gamma = 98{\cdot}54(1)°$; $D_m = 1{\cdot}729$ g cm^{-3}; $D_c = 1{\cdot}722$ g cm^{-3} for $Z = 1$ (dimeric unit). The intensities of 4507 independent reflections with $4° < 2\theta < 50°$ were measured and the structure was solved with 3250 non-zero reflections using standard Patterson and Fourier techniques. Corrections were made for Lorentz-polarization and absorption effects and the structure refined (Re,P,Cl,C,N anisotropic), to a current conventional R value of 0·06.

The structure (Figure) is a centrosymmetric chlorine-bridged dimer with the rhenium atoms in a distorted octahedral environment. Within the dimer there is no significant rhenium–rhenium interaction. The Re–Re distance of 3·809 Å may be compared with that of 3·74 Å in the chlorine-bridged rhenium(V) dimer Re_2Cl_{10}.[7] The terminal Re–Cl (2·307—2·322 Å) and Re–P (2·370—2·371 Å) distances compare well with those reported for mononuclear six-co-ordinate rhenium(III) phosphine complexes,[8,9] and the bridging Re–Cl distances (2·496—2·503 Å) are, as expected,[7] *ca.* 0·20 Å longer than the related terminal bonds. Parameters for dppe and MeCN are normal.[9,10]

The reactivity of $[ReCl_3(dppe)]_2$ is readily understood in terms of this structure. The failure to obtain metal–metal bonded dimers from reaction with triphenylphosphine and acetic acid–acetic anhydride is, as we suspected, due to the absence of this structural unit. This in turn also explains the ease with which it is oxidized to $ReCl_4(dppe) \cdot xCCl_3X$ in reactions with the chlorocarbons CCl_3X.

While we do not yet have information on the detailed structure of the complex $[ReCl_{2\cdot5}(dppe)]_n$, it is clearly not isostructural with $Re_2Cl_5(dth)_2$. Its solid-state electronic absorption spectrum and magnetic properties (μ_{eff} *ca.* 2·2 B.M. at 295 K) are quite different from those of $Re_2Cl_5(dth)_2$.[5,6] Also, a comparison of the *X*-ray photoelectron spectra of these two complexes shows a significant difference in the widths of the rhenium $4f$ binding energies. While the $4f_{7/2}$ energies are as expected[11] very similar (41·7 and 41·6 eV respectively), the F.W.H.M. value of *ca.* 2·2 eV for the $4f_{7/2}$ component of $Re_2Cl_5(dth)_2$ is consistent with the known presence of two strikingly dissimilar rhenium environments. For the complex $[ReCl_{2\cdot5}(dppe)]_n$, the corresponding F.W.H.M. value is 1·1 eV and is characteristic of systems possessing a single type of rhenium environment.[11]

We thank the National Science Foundation and the Camille and Henry Dreyfus Foundation for grants.

(*Received*, 14*th January* 1974; *Com.* 038.)

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† All new compounds gave satisfactory analyses.

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