Inorganica Chimica Acta, 22 (1977) L10
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Complex Halides of the Transition Metals. XXIII.[†] A Four-Electron Reduction of the Dinuclear Nonachlorodirhenate(IV) Anion by Tertiary Phosphines

C. A. HERTZER and R. A. WALTON*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.

Received January 26, 1977

In investigating the redox reactions of metal halides containing pairs or clusters of metal atoms, we recently discovered [1, 2] that the octahalodirhenate (III) anions $Re_2X_8^{2-}$, X = Cl or Br, could be converted to reduced phases of stoichiometry $Re_2X_5(PR_3)_3$ or $Re_2X_4(PR_3)_4$. The extent to which reduction occurred was dependent upon the choice of phosphine, the more basic phosphines (PMe_3, PEt_3, PPr_3^n, PMe_2Ph and PEt_2Ph) favoring the formation of the two-electron reduced products. However, no reduction was observed upon reaction of these haloanions with triphenylphosphine, and only the substitution products $Re_2X_6(PPh_3)_2$ were isolated [1,3]. In view of the ease with which halogen oxidation of $Re_2X_8^{2-}$ affords a route to nonahalodirhenate species [4] of the type $Re_2X_9^-$, we became interested in the possibility that the reaction of salts of these latter anions with tertiary phosphines might lead to an unprecedented four-electron reduction of a metal–metal bonded dimer. Such a reduction has now been accomplished and leads to a product in which the strong metal–metal bond is retained.

Whereas the reaction of the salt $[Bu_4N]Re_2Cl_9$ with PPh_3 in MeOH–HCl affords the green rhenium (III) dimer $Re_2Cl_6(PPh_3)_2$, the same species which is formed upon reacting this phosphine with $(Bu_4N)_2Re_2Cl_8$ [3], further reduction is encountered with more basic phosphines. Thus, reaction of an acetone solution of $(Bu_4N)Re_2Cl_9$ with $PEtPh_2$ affords the dark green dimer $Re_2Cl_5(PEtPh_2)_3$ whereas with PEt_3, black crystals of the rhenium(II) dimer $Re_2Cl_4(PEt_3)_4$ were obtained. In each instance, the reaction solutions turned from deep green to purple within a few minutes of the phosphine being added. This suggests that the purple $Re_2Cl_9^{2-}$ anion [4], or a derivative thereof, is a reaction intermediate. The tertiary phosphine complexes made from $Re_2Cl_9^-$ were identified by means of IR and electronic absorption spectroscopy. These spectra were identical with those exhibited by the complexes of these same stoichiometries which were obtained from the reaction $Re_2Cl_8^{2-}$ with tertiary phosphines under similar reaction conditions [1, 3].

To our knowledge, the reduction of $Re_2Cl_9^-$ to $Re_2Cl_4(PEt_3)_4$ is the first example of a 4-electron reduction of a metal–metal dimer which is not accompanied by the disruption of the strong metal–metal bond.

Experimental

Starting Materials

$(Bu_4N)Re_2Cl_9$ was prepared by the method described by Bonati and Cotton [4]. The phosphines and solvents used were supplied by commercial sources. The solvents were dried and then deoxygenated with N_2 before use and all reactions were carried out in a nitrogen atmosphere.

Triphenylphosphine

A quantity of PPh_3 (0.14 g) was added to a mixture of $(Bu_4N)Re_2Cl_9$ (0.10 g), 10 ml of methanol, and 1 ml of conc. HCl. The reaction mixture was refluxed under N_2 for 1 day and the resulting green precipitate was filtered off, washed with methanol, and dried *in vacuo*. The spectral properties of this product showed [1, 3] it to be $Re_2Cl_6(PPh_3)_2$. Yield: 45%.

Ethyldiphenylphosphine

$PEtPh_2$ (0.8 ml) was added to a mixture of $(Bu_4N)Re_2Cl_9$ (0.10 g) and 10 ml acetone and the resulting solution was refluxed under N_2 for 10 days. The green solid which formed was filtered off, washed with ethanol and dried *in vacuo*. The microanalytical data agreed with the stoichiometry $[ReCl_{2.5}(PEtPh_2)_{1.5}]$ and its spectral properties showed [1] it to be the dimer $Re_2Cl_5(PEtPh_2)_3$. *Anal.* Calcd. for $[ReCl_{2.5}(PEtPh_2)_{1.5}]_n$: C, 42.3; H, 3.8. Found: C, 42.5; H, 3.9. Yield: 61%.

Triethylphosphine

The reaction mixture which resulted upon adding PEt_3 (1.0 ml) to $(Bu_4N)Re_2Cl_9$ (0.20 g) and 10 ml of acetone was refluxed under N_2 for 4 days and the insoluble product filtered off and dried *in vacuo*. The black crystals had spectral properties which were consistent [1] with their formulation as the rhenium(II) dimer $Re_2Cl_4(PEt_3)_4$. Yield: 47%.

Support from the National Science Foundation (Grant CHE74-12788A02) is gratefully acknowledged.

1 J. R. Ebner and R. A. Walton, *Inorg. Chem.*, *14*, 1987 (1975).
2 F. A. Cotton, B. A. Frenz, J. R. Ebner and R. A. Walton, *Inorg. Chem.*, *15*, 1630 (1976).
3 F. A. Cotton, N. F. Curtis and W. R. Robinson, *Inorg. Chem.*, *4*, 1696 (1965).
4 F. Bonati and F. A. Cotton, *Inorg. Chem.*, *6*, 1353 (1967).

[†] Part XXII: C. A. Hertzer and R. A. Walton, *J. Organomet. Chem.*, in press.

*Address any correspondence to this author.