Nine-co-ordinate Octahydrido(tertiary phosphine)rhenate Complex Anions

By A. P. GINSBERG

(*Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey* 07974)

THIS Communication reports the preparation of salts of the nine-co-ordinate complex anions $[ReH_8(R_3M)]^-$ with M = P, R = Ph, Et, Bu^n and with M = As, R = Ph. These compounds were obtained by refluxing propan-2-ol solutions of $(Et_4N)_2ReH_9$ with the tertiary phosphine or arsine in the molar ratio $R_3M/Re = 5$. Reactions were carried out under a nitrogen atmosphere, and subsequent manipulations were in a nitrogen or argon atmosphere. All solvents were dried and degassed. Hydrogen is evolved and the reaction is complete within 5 minutes. In the case of Ph_3P, a yellow precipitate of the known compound[1] $[ReH_5(Ph_3P)_3]$ is formed. $Et_4N[ReH_8(Ph_3P)]$ was isolated from the filtrate by evaporating it to dryness, extracting the excess of phosphine with diethyl ether, and then recrystallizing the residue, first from 1:1 acetone–benzene and finally from acetonitrile by addition of ether. Ph_3As gives a yellow precipitate of the previously unreported pentahydride $ReH_5(Ph_3As)_3$ and a solution from which $Et_4N[ReH_8(Ph_3As)]$ may be isolated as described. With Et_3P and $Bu^n{}_3P$, a pentahydride does not precipitate, but the octahydride was obtained from the reaction solution in the same way as with Ph_3P.

The salts $Et_4N[ReH_8(R_3M)]$ are white, crystalline compounds all of which gave satisfactory microanalyses. Conductivity measurements, made on acetonitrile solutions as a function of concentration, support the formulation as a 1:1 electrolyte. Osmometric molecular-weight measurements on the Ph_3P and Et_3P derivatives support the formula as written. ^1H n.m.r. spectra of solutions of the phosphine derivatives in CD_3CN show a doublet on the high-field side of Me_4Si.

TABLE

Compound	τ (Re–H)[a]	J(P–H)[a] (c./sec.)	H/Re[b]	ν(Re–H)[c] (cm.$^{-1}$)	ν (Re–D)[c] cm.$^{-1}$)	δ (Re–H)[c] (cm.$^{-1}$)	δ (Re–D)[c] (cm.$^{-1}$)
$Et_4N[ReH_8(Ph_3P)]$	17·3	17·7	7·8	1860, 1940, ~1980	1350	745, 695	548, 500
$Et_4N[ReH_8(Et_3P)]$	18·2	17·3	7·8	1850, 1920, ~1980	1340	745, ~700	545, 505
$Et_4N[ReH_8(Bu^n{}_3P)]$	18·1	18·4	7·9	1850, 1920, ~1980	—	—	—
$Et_4N[ReH_8(Ph_3As)]$	17·4	—	8·0	1850, 1940, 1980	—	—	—

[a] *ca.* 5% solutions in CD_3CN.
[b] From comparison of the area of the high-field lines due to Re–H with the low-field lines due to Et_4N^+ and R_3M.
[c] KBr discs.

This is due to the Re-bonded hydridic protons coupled with the phosphorous nucleus. The high-field line of the arsine derivative is unsplit because of the quadrupole moment of the arsenic nucleus. The τ values and coupling constants are given in the Table as are the numbers of hydridic protons found by comparison of the area of the high-field line with the areas of the low-field lines due to the protons of Et_4N^+ and R_3M. Since the number of hydridic protons must be 2, 4, 6, or 8, on account of the fact that the complex is uninegative, monomeric, and diamagnetic, these results establish that there are eight Re-bonded hydrogen atoms.

The presence of eight hydridic protons in the complex is also supported by a measurement of the gas evolved in the reaction of the Ph_3P derivative with HCl in propan-2-ol. This takes place according to the following stoicheiometry; the measured amount of hydrogen is given in parentheses:

$$[ReH_8(Ph_3P)]^- + 4H^+ \rightarrow Re^{+3} + 6H_2 + PPh_3$$
$$(5{\cdot}84)$$

~70% of the rhenium is recovered as a green precipitate of $(HPPh_3)_2Re_2Cl_8$. Mass-spectrometric analysis shows the gas to be entirely hydrogen.

The i.r. spectra (KBr discs at room temperature) show three bands assignable as ν(Re–H). On account of interference by bands due to Et_4N^+ and R_3M, only a single ν(Re–D) can be discerned in the deuteriated analogues. Two bands assignable as δ (Re–H) and δ (Re–D) are observed. The deuteriation shifts of both the stretching and bending frequencies are normal. The observed frequencies are listed in the Table. The i.r. spectra also confirm that there are no Re=O or Re–OR′ groups in any of the compounds.[2]

The octahydrides are nine-co-ordinated anions and their structure is presumably similar to that of the parent ReH_9^{-2} ion.[3] The two isomers shown in the Figure are possible. Unfortunately, no structural information can be obtained from the n.m.r. spectra since only a single chemical shift due to Re-bonded hydrogen is observed. This is also true of ReH_9^{2-}, the nine-co-ordinated molecular complex $ReH_7(PEt_2Ph)_2$[1b] and $ReH_5(PPh_3)_3$. Since the hydridic protons can not be geometrically equivalent, their n.m.r. equivalence must be brought about by a dynamic process, probably a vibrational deformation of the type suggested[3] for ReH_9^{2-}. The room temperature i.r. spectra also do not provide any structural information because the number of ν(Re–H) observed is considerably fewer than predicted for either of the two possible isomers (see Figure). This is probably due to incomplete resolution of overlapping bands.

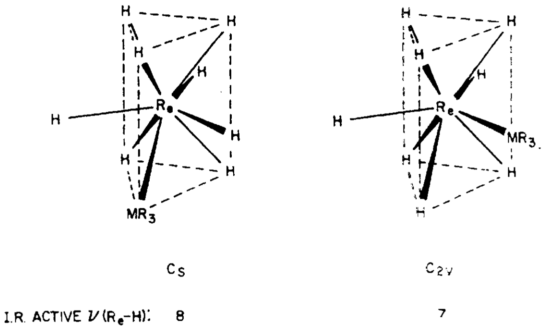

FIGURE. *Possible structures for* $[ReH_8(R_3M)]^-$.

As a final point, it is of interest to note that τ(Re–H) for $(Et_4N)_2ReH_9$ (18·5 for a 5% solution in CD_3CN) has been very little changed by substitution of a tertiary phosphine or arsine group for one of the hydrogen atoms.

(*Received, May 16th,* 1968; *Com.* 621.)

---

[1] (a) L. Malatesta, M. Freni, and V. Valenti, *Gazzetta*, 1964, **94**, 1278; (b) J. Chatt and R. S. Coffey, *Chem. Comm.*, 1966, 545.
[2] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 1962, 4019.
[3] S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, 1964, **3**, 558.