795. *Bis*cyclo*pentadienylrhenium Hydride.*

By M. L. H. GREEN, L. PRATT, and G. WILKINSON.

The preparation and properties of bis*cyclo*pentadienylrhenium hydride, $(C_5H_5)_2ReH$, are described. In contrast to other known metal-complex hydrides of transition metals the compound behaves as a base somewhat weaker than ammonia and with acids it forms the cation $[(C_5H_5)_2ReH_2]^+$. High-resolution nuclear magnetic resonance and infrared spectra of the compound and its salts are given.

FOR the metals of the first transitional series from titanium to nickel, inclusive, the *cyclo*pentadienyl compounds of the formula $(C_5H_5)_2M$ have now been characterized.[1] With the exception of the manganese compound, these have metal-to-ring bonds of the " sandwich bond " type as in ferrocene.[2] The manganese compound is unique in that it is ionic and must be regarded as a *cyclo*pentadienide; [3] this view has been recently confirmed by paramagnetic resonance absorption studies.[4] In view of the marked difference between the chemistry of manganese and of rhenium it seemed unlikely that a rhenium compound of similar type would exist and it was expected that bis*cyclo*pentadienylrhenium compounds of the type formed by molybdenum and tungsten [5] would be obtained. A bis*cyclo*pentadienylrhenium compound has been prepared, but of an unexpected and unusual type.

When the general method for the preparation of *cyclo*pentadienyl compounds was used, involving the reaction of the metal halide with sodium *cyclo*pentadienide in tetrahydrofuran solution,[3] direct vacuum-sublimation of the product from rhenium pentachloride at 120—200° gave a yellow crystalline substance. Elemental analysis and molecular-weight determinations suggested that this was the neutral compound $(C_5H_5)_2Re$; it was insoluble in and unaffected by water, soluble in light petroleum, and, unlike $(C_5H_5)_2Mn$, it did not react with ferrous chloride in tetrahydrofuran solution to give ferrocene. The infrared spectrum was also consistent with the formulation as a sandwich-bonded bis*cyclo*pentadienyl compound, and further, the compound dissolved in dilute mineral acids to give solutions which contained a cation. This cation formed insoluble precipitates with silicotungstic acid, sodium tetraphenylborate, and Reinecke's salt similar to those obtained with other bis*cyclo*pentadienyl-metal cations in aqueous solution.

Measurement of the magnetic susceptibility of the compound both as the solid and in solution in benzene showed, however, that it was diamagnetic. The only acceptable explanation of this fact was that the compound was not $(C_5H_5)_2Re$, which would be paramagnetic, but was a hydride, $(C_5H_5)_2ReH$.

Proof of the presence of a hydrogen atom bound directly to the metal was first obtained

---

[1] For references see Fischer and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **2**, 149.

[2] For references to electronic structures see Liehr and Ballhausen, *Acta Chem. Scand.*, 1957, **11**, 207.

[3] Wilkinson, Birmingham, and Cotton, *J. Inorg. Nuclear Chem.*, 1956, **2**, 95.

[4] Voitländer and Schimitschek, *Z. Elektrochem.*, 1957, **61**, 941.

[5] Cotton and Wilkinson, *Z. Naturforsch.*, 1954, **9b**, 417.

by high-resolution nuclear magnetic resonance studies, as was reported in a preliminary note.[6] The present evidence available for the formulation of the compound as $(C_5H_5)_2ReH$ and of the cation as $[(C_5H_5)_2ReH_2]^+$ is as follows.

Nuclear Magnetic Resonance Studies.—A typical spectrum of the compound in saturated solution in benzene or carbon disulphide shows two main peaks, the first at 45 ± 2 cycles per second (at 40 Mc./sec.) and the second at 733 ± 2 cycles per second, both on the high-field side relative to water at 21°. The relative areas of these two peaks are 10 : 1 respectively. The first resonance peak lies in the region where the protons of ferrocene and other π-*cyclo*pentadienyl derivatives show resonances,[7] and is obviously attributable to the protons of the two equivalent π-*cyclo*pentadienyl groups in $(C_5H_5)_2ReH$. The low-intensity absorption at the high field can be attributed only to a proton which is diamagnetically very well shielded. At the time of the first measurements on this compound, no other proton resonances with such an unusual displacement were known. Shortly afterwards it became known [8] that cobalt hydrocarbonyl $HCo(CO)_4$ showed a similar, although somewhat smaller, proton chemical shift. Since then, however, numerous other compounds in which a hydrogen atom is probably bound directly to a transition-metal atom have been examined, *e.g.*, $H_2Fe(CO)_4$,[9] $HM(CO)_3C_5H_5$ (M = Cr, Mo, W),[7] $HPtCl(PR_3)_2$,[10] $HMn(CO)_5$, $H_2Mo(C_5H_5)_2$, and $H_2W(C_5H_5)_2$,[11] and it can now be assumed that large chemical shifts, of the order 450—800 c./sec. at 40 Mc./sec., are characteristic of hydrogen atoms directly bound to a transition-metal atom.

Infrared Spectra.—The infrared spectrum of $(C_5H_5)_2ReH$ and the corresponding deuteride $(C_5H_5)_2ReD$ have been measured over the range 625—3400 cm.$^{-1}$ in carbon disulphide solution, in Nujol mulls and on single crystals, a microscope attachment being used. The data are presented in Table 1.

TABLE 1. *Infrared spectra of bis*cyclo*pentadienylrhenium hydrogen and deuterium compounds.*

Compound	C–H	Re–H	Re–D	*cyclo*Pentadienyl
$(C_5H_5)_2ReH$ in CS_2	3100w	2030w	—	1391s, 1341w, 1260vw, 1182w, 1096s, 1053w, 1004s, 990s, 892m, 885m, 809s, 785s
$(C_5H_5)_2ReH$ crystal	3073w	2037w, 2000w	—	—
$(C_5H_5)_2ReD$ crystal	3040	—	1458, 1432	
$[(C_5H_5)_2ReH_2]Cl$ in Nujol mull	~3100w	2330vw?, 2360vw?, 2070vw?, 2250vw?		1413s, 1365w, 1100s, 1010s, 800s

Whilst the spectrum is generally similar to that of ferrocene, a band at 2000 cm.$^{-1}$ in the solution spectrum of intensity comparable with that of the C–H stretching band does not occur in ferrocene. This band is not present in solution spectra of $(C_5H_5)_2ReD$. In the single-crystal and mull spectra of $(C_5H_5)_2ReH$, splitting of the peak at ~2000 cm.$^{-1}$ occurs, presumably owing to crystalline interactions; the deuteride shows similar bands but displaced to ~1460 cm.$^{-1}$. The allocation of the sharp band at 2000 cm.$^{-1}$ in the solution spectrum to an Re–H stretching mode is therefore certain. From the solid-state spectra $\nu_{Re-H}/\nu_{Re-D} = 1{\cdot}396$ and $1{\cdot}397$ for the two peaks, respectively. This very high frequency, which is in the same region as the stretching frequencies in gaseous diatomic transition-metal hydrides, indicates a very strong metal-to-hydrogen bond consistent with the high thermal stability of the rhenium compound.

Mass Spectra.—In the study of the mass spectra of neutral bis*cyclo*pentadienyl-metal compounds,[12] examination of the spectra from $(C_5H_5)_2ReH$ unequivocally showed the presence of the ion $C_{10}H_{11}Re^+$.

---

[6] Birmingham and Wilkinson, *J. Amer. Chem. Soc.*, 1955, **77**, 3421.

[7] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[8] Friedel, Wender, Shufler, and Sternberg, *J. Amer. Chem. Soc.*, 1955, **77**, 3951.

[9] Cotton and Wilkinson, *Chem. and Ind.*, 1956, 1305.

[10] Chatt, Duncanson, and Shaw, *Proc. Chem. Soc.*, 1957, 343.

[11] Down, Green, and Wilkinson, unpublished work.

[12] Friedman, Irsa, and Wilkinson, *J. Amer. Chem. Soc.*, 1955, **77**, 3689.

Chemical Properties of $(C_5H_5)_2ReH$.—Bis*cyclo*pentadienylrhenium hydride forms lemon-yellow acicular crystals, m. p. 161—162°, from benzene, ether, or light petroleum. The compound is thermally stable to at least 250° and sublimes readily in a vacuum above 80°. It is soluble in carbon disulphide and hydrocarbon solvents, giving yellow solutions. In carbon tetrachloride the compound decomposes rather rapidly to give insoluble material which does not give a test for bis*cyclo*pentadienyl cations on dissolution in acids, together with chloroform; the formation of chloroform from carbon tetrachloride appears to be a characteristic reaction of compounds with transition-metal–hydrogen bonds (cf. ref. 7).

Whilst the solid compound reacts only slowly with air, and is decomposed, it may be handled for periods of a few minutes in air, but solutions of the compound are rapidly attacked, purple-brown decomposition products being obtained. The compound is insoluble in liquid ammonia, and no colour change occurs, unlike the cases of $(C_5H_5)_2V$ and $(C_5H_5)_2Cr$, which form ammoniates.[3]

The compound does not react with diazomethane in cold or refluxing ether, or with nitric oxide or carbon dioxide at ordinary pressures. Carbon monoxide at 100°/200 atm. converts it[13] into a compound of stoicheiometry $C_{10}H_{11}Re(CO)_2$, the structure of which we will discuss in a later paper. Although the hydride is unaffected by concentrated (8N) sodium hydroxide, it dissolves without effervescence in dilute hydrochloric or sulphuric acid. The solid hydride rapidly absorbs gaseous hydrogen chloride or bromide, and salts are formed quantitatively as white amorphous powders:

$$(C_5H_5)_2ReH + HCl \longrightarrow [(C_5H_5)_2ReH_2]Cl$$

It is interesting that the white solid in presence of excess of hydrogen chloride has a strong pink colour, which disappears on removal of the excess of gas; the pink colour may be due to the presence of an easily dissociated salt $[(C_5H_5)_2ReH_2]^+HCl_2^-$ similar to those formed by cæsium and other large cations.[14]

These salts are exceedingly deliquescent and must be handled in a vacuum or in an inert dry atmosphere. The colourless aqueous solutions give the usual precipitation reactions characteristic of bis*cyclo*pentadienyl-metal cations; the reineckate has been analysed. The solutions are fairly rapidly decomposed by air, and oxidation by chemical agents completely disrupts the cation.

Addition of ammonia or alkali to the aqueous solutions liberates the free base $(C_5H_5)_2ReH$, which can be quantitatively recovered by solvent extraction:

$$[(C_5H_5)_2ReH_2]^+ + OH^- \longrightarrow (C_5H_5)_2ReH + H_2O$$

The $(C_5H_5)_2ReH$–$[(C_5H_5)_2ReH_2]^+$ system is thus analogous to the NH_3–NH_4^+ system, except that the base is insoluble in water. Determining the base constant by pH measurement and titrations of $(C_5H_5)_2ReH$ at 25° with acid and of $[(C_5H_5)_2ReH_2]Cl$ with base, in 60% dioxan solution, gave a value of p*K* 8·5. The value for ammonia in 60% dioxan interpolated from published data[15] is p*K* 8·85.

The nuclear magnetic resonance spectrum of the cation, which is discussed below, confirms the stoicheiometry $[(C_5H_5)_2ReH_2]^+$.

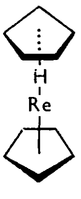
Discussion.—The bis*cyclo*pentadienylrhenium hydride is the only bis*cyclo*pentadienylrhenium compound that we have been able to isolate. Attempts to obtain species that might have been expected to exist, such as $(C_5H_5)_2ReCl_n$, failed. No products of this type were obtained either by reaction of stoicheiometric amounts of rhenium pentachloride with *cyclo*pentadiene in piperidine and diethylamine[3] or with sodium *cyclo*pentadienide. In the former reaction extractions of the dry product even with aqueous acid gave no evidence for bis*cyclo*pentadienyl-metal ions; and in the latter only the hydride could be extracted with light petroleum or chloroform or the $[(C_5H_5)_2ReH_2]^+$ ion with dilute acid.

[13] Fischer and Wirtzmuller, *Z. Naturforsch.*, 1957, **12**b, 737.

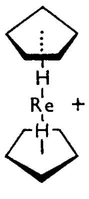
[14] See, *e.g.*, West, *J. Amer. Chem. Soc.*, 1957, **79**, 4568; Waddington, *J.*, 1958, 1708; Sharp, *J.*, 1958, 2558.

[15] Rumpf, Gerault-Vexlearschi, and Schoal, *Bull. Soc. chim. France*, 1955, 554.

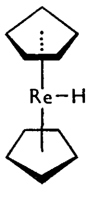
There are several possible structures for the hydride and its cation. Liehr[16] has suggested that the hydrogen atom in the hydride and two hydrogen atoms in the cation can be located between the *cyclo*pentadienyl rings and the metal atom (IA, IB). The hydrogen atoms are considered to be in the $d(a_{1g})$ orbital, which, according to a molecular-orbital view of the bonding in neutral bis*cyclo*pentadienyl-metal compounds, is non-bonding as far as the primary metal–ring bonding is concerned. Of other possible structures for the hydride, (IIA) and (IIC) are the most likely; in (IIA), the *cyclo*pentadienyl rings are aligned as in ferrocene, in (IIC) the metal–ring axes are at an angle. Corresponding structures for the cation are (IIB and D, respectively). Either of the structures (I, II) could equally well account for the large chemical shift of the hydridic hydrogen atom and for the basic character of the hydride.



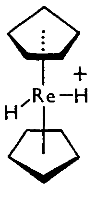
(IA)



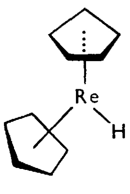
(IB)



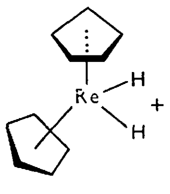
(IIA)



(IIB)



(IIC)



(IID)

The infrared spectrum of the cation $[(C_5H_5)_2ReH_2]^+$ might have been expected to provide useful information, since, if the hydrogen atoms were symmetrically located between the rings (IB) or symmetrically on either side of the metal atom (IIB), only one Re–H stretching frequency would be expected. For structures with the hydrogen atoms at an angle (IIB, IID), both symmetric and asymmetric vibrations should be observed. Unfortunately, however, the Re–H stretching bands are so weak that even by using very concentrated aqueous solutions of the salt we have been unable to identify the Re–H bands reliably. In the solid-state spectra of the hydride, the Re–H bands are split. The solid-state splitting of the hydride is rather difficult to reconcile with formula (IA), since with the hydrogen atoms buried between the metal atoms and the ring it is not easy to see how intermolecular interaction in the crystal lattice could affect such hydrogen atoms.

TABLE 2. *Nuclear magnetic resonance data at* 40 *Mc./sec.*

The high field side is designated –; shifts are referred to water at 21° ± 1·0°.

Compound	Proton resonance (cycles)	Relative intensity	Assignment	Fine structure	Multiplet width (cycles)	Splitting (cycles)
$C_5H_5)_2ReH$ in C_6H_6 and CS_2	−46	10	π-C_5H_5	Doublet	1·9	$1{\cdot}0_5$
	−732	1	hydridic	Not detected	18	
$(C_5H_5)_2ReD$ in C_6H_6	−46	—	π-C_5H_5	Singlet	$\leqslant$0·5	—
	No hydride peak	—	—			
$[(C_5H_5)_2ReH_2]^+Cl^-$ in H_2O	+33	10	π-C_5H_5	Triplet	1·45	0·56 *
	−734·5	2	hydridic	Not detected	$\gtrsim$8	
$[(C_5H_5)_2ReD_2]^+Cl^-$ in D_2O	+32·5	—	π-C_5H_5	Singlet	$\leqslant$0·5	—
	No hydride peak	—	—			

* Confirmed also by the ringing-beat procedure (Reilly, *J. Chem. Phys.*, 1956, **25**, 604).

The nuclear magnetic resonance data are presented in Table 2. Whilst all four compounds show the resonances due to the *cyclo*pentadienyl ring hydrogen atoms, and the hydrides show the shielded-proton resonances, the fine structure on these resonances is more consistent with structure (II) than with Liehr's model, and we consider first the consequences of (II). The absence of fine structure on the *cyclo*pentadienyl peaks in the deuterides, and its appearance in the hydrides, suggests that this structure is produced by

---

[16] Liehr, *Naturwiss.*, 1957, **44**, 61.

the indirect spin–spin coupling interaction[17] between the hydridic proton(s) and the ring protons, and is not attributable to chemical shifts of non-equivalent *cyclo*pentadienyl rings. The single proton in $(C_5H_5)_2ReH$ should split the *cyclo*pentadienyl peak into a symmetrical doublet, and two equivalent protons in $[(C_5H_5)_2ReH_2]^+$ should split the *cyclo*pentadienyl peak into a triplet with intensity ratios 1 : 2 : 1. The replacement of hydrogen by deuterium which has spin 1 would be expected to split the *cyclo*pentadienyl peak into a triplet in $(C_5H_5)_2ReD$ and a quintuplet in $[(C_5H_5)_2ReD_2]^+$, but the smaller magnetic moment of the deuteron (about one-third of that of the proton) would mean that these splittings would be only about one-third as great, so that they would not be resolved under the conditions of the measurements. It is also possible that these splittings would be removed by quadrupole relaxation[18] of the deuterium nucleus. In fact, a single peak is observed of width 0·5 cycle/sec. in both deutero-compounds, any fine structure being obscured.

The hydridic-proton peaks in both hydride compounds should also show a splitting by the ten *cyclo*pentadienyl ring protons into eleven components, the splitting being $1{\cdot}0_5$ cycles/sec. in $(C_5H_5)_2ReH$ and 0·56 cycle/sec. in the cation. Although the overall line-width of the hydride peak of the cation is about twice that in the neutral compound, no splitting was observed on these peaks: this is not surprising, since both were weak and could not be measured under conditions required for good resolution. No splitting of either the hydridic- or the *cyclo*pentadienyl-proton peaks was found which could be attributed to spin–spin coupling of the protons with the magnetic moments of the two rhenium nuclei, but this splitting would probably be destroyed since both these nuclei have large electric quadrupole moments.[18]

As noted above, the observed data are consistent with formulation (II). Now in structure (IA) the two *cyclo*pentadienyl rings are not equivalent in that a proton is inserted between one of them and the metal atom, and they would be expected to give rise to a double peak in both $(C_5H_5)_2ReH$ and $(C_2H_5)_2ReD$; also in the former each of these two peaks would be split by unequal amounts by the hydridic proton. For the cations, $[(C_5H_5)_2ReD_2]^+$ should give one peak, but the *cyclo*pentadienyl peaks in $[(C_5H_5)_2ReH_2]^+$ would be split into a doublet by the nearest proton and each further split into a doublet by the more distant proton, although the ratios of these two doublet splittings could conceivably overlap to give the appearance of the triplet.

The nuclear magnetic resonance data do not allow a distinction to be made between the two main structural types (IIA,B) and (IIC,D). There is nothing in the spectra of the hydride or the deuteride to indicate that the *cyclo*pentadienyl rings are not freely rotating in the free molecule, and such free rotation is known to occur for ferrocene and some of its substitution products. The relative dispositions of the rings shown in (IIA—D) are merely symbolic. The large displacement (79 cycles/sec.) of the *cyclo*pentadienyl peaks to lower applied fields in the cations relatively to the neutral molecules may be significant, but the present state of knowledge on chemical shifts in *cyclo*pentadienyl-metal compounds is not yet adequate to provide an explanation.

It is to be noted that the protons in the cation undergo only very slow exchange with protons in aqueous solution. In aqueous solutions which are slightly acid, the appearance of the hydridic peak shows[19] that the average chemical lifetime of the proton on the cation must be $>1/(2\pi \times 730)$ sec.$^{-1}$. If, as discussed above, the triplet on the *cyclo*pentadienyl-proton resonance is attributed to splitting by the hydridic protons, then the minimum lifetime must be even greater than this or of the order of $1/(2\pi \times 0{\cdot}56)$, *i.e.*, 0·3 sec. It may be also noted that in one preparation of $(C_5H_5)_2ReD$, the $[(C_5H_5)_2ReH_2]Cl$ salt was dissolved in a large excess of D_2O and after 20 min. NaOD in D_2O was added: the resulting neutral product showed a pronounced hydridic-proton resonance. After equilibration

---

[17] Gutowsky, McCall, and Slichter, *J. Chem. Phys.*, 1953, **21**, 279.
[18] Pople, *Mol. Phys.*, 1958, **1**, 168.
[19] Gutowsky and Saika, *J. Chem. Phys.*, 1953, **21**, 1688.

of the hydrogen chloride salt for 12 hr. under the same conditions, the recovered product had no detectable hydridic-proton resonance.

EXPERIMENTAL

Preparations and operations with the rhenium compounds were carried out in oxygen-free nitrogen in a glove-box or in a vacuum. Solvents and reagent solutions were thoroughly degassed before use. Infrared spectra were measured with a Perkin-Elmer Model 21 spectrophotometer with both sodium chloride and calcium fluoride optics. Single-crystal measurements were made with the assistance of Dr. Orr at the Chester Beatty Research Institute, using a microscope attachment to a single-beam Perkin-Elmer instrument. High-resolution nuclear magnetic resonance spectra were measured at 40 Mc./sec. on a Varian Associates Model 4300 B spectrometer with super-stabiliser. Microanalyses of $(C_5H_5)_2ReH$ were obtained through the courtesy of Dr. E. O. Brimm of Linde Air Products, Tonawanda, N.Y.; other analyses were by the Microanalytical Laboratory, Imperial College.

*Bis*cyclo*pentadienylrhenium Hydride*.—Rhenium pentachloride was prepared by direct chlorination of the metal at 600°; the product was sublimed in nitrogen to remove oxychlorides. To a cold solution (0°) of sodium *cyclo*pentadienide (0·2 mole) in tetrahydrofuran (150 ml.) was added solid rhenium pentachloride (0·03 mole). The purple mixture was stirred for ~5 hr. with heating to 50°. Originally the solvent was removed at this point and the hydride was sublimed in a vacuum from the residue at 120—200°. The product always contained some oil and subsequent purification was difficult; the light petroleum solution was extracted with 2N-hydrochloric acid and after washing of the aqueous layer with light petroleum the hydride was liberated by alkali and extracted into light petroleum. It was then crystallized from light petroleum and sublimed in a vacuum. These steps were repeated several times. A better procedure, which gives a purer product and higher yields, is to add sodium borohydride (0·08 mole) to the reaction mixture in tetrahydrofuran; after a further hour's refluxing, the solvent was removed and the product sublimed as pale yellow crystals free from oil and sticky material in yields of 35—40% based on $ReCl_5$. This product was purified by crystallisation from light petroleum and by sublimation. The molecular weight was determined by Clark's modification of the Signer isothermal method,[20] ether and benzene being used as solvents and ferrocene as a reference. From two measurements in each solvent, $M = 310 \pm 5$ [Calc. for $(C_5H_5)_2ReH$: M, 317·5].

The magnetic susceptibility was measured on the solid and the melt over the range 77—510° K, by the Gouy method. $\chi^{273}_{\text{mol}} = -135 \pm 5 \times 10^{-6}$ c.g.s. unit. The compound was also diamagnetic in benzene solution (16 mg./ml.).

*Bis*cyclo*pentadienylrhenium Deuteride*.—The sublimed hydride (~0·5 g.) was dissolved in 2N-deuterium chloride in D_2O (~10 ml.); the base was liberated by addition of 6N-sodium deuteroxide in D_2O and was extracted with light petroleum. The procedure was then repeated; the deuteride, finally purified by sublimation, had m. p. 168—169°. The yield was ~90%.

*Bis*cyclo*pentadienylrhenium Dihydrogen Chloride* (*Bromide*).—The hydride was treated with hydrogen chloride at room temperature. A rapid reaction gave the *chloride* as a white powder, from which excess of the gas was removed by pumping {Found: Re, 52·0; Cl, 8·5. $[(C_5H_5)_2ReH_2]Cl$ requires Re, 52·65; Cl, 8·6%}. The compound sublimes slightly at ~140° in a vacuum with extensive decomposition; no hydride is formed.

A bromide was similarly obtained.

Addition of Reinecke's salt to aqueous solutions of the salt gives a rose pink precipitate of the *derivative* {Found: C, 26·1; H, 2·4; Re, 29·5; Cr, 8·2. $[(C_5H_5)_2ReH_2][Cr(NH_3)_2(CNS)_4]$ requires C, 26·5; H, 2·5; Re, 29·4; Cr, 8·2%}.

Physical Measurements.—Nuclear magnetic resonance measurements on the hydride were made by using both benzene and carbon disulphide saturated solutions with a water capillary reference; the cation was studied in concentrated aqueous solution with a *cyclo*hexane capillary reference. The measurements were made at 21° ± 1·0°. The solutions were contained in spinning 5 mm. (outer diameter) sealed Pyrex tubes, with sealed capillary internal reference tubes. The base constant of the hydride was determined in 60% dioxan solution by titration

---

[20] Weissberger (Editor), "Technique of Organic Chemistry," Interscience Publ. Inc., New York, 1954, Vol. VI.

with standard acid; the titration curve was repeated by titrating the chloride with standard base. The pH of the solutions was measured with a Cambridge Instrument Co. pH meter and a glass electrode. The neutralisation curves were typical of those for a weak base. The pH of the hydride in the dioxan solution (0·0224 mole/l.) was 10·13.

We are indebted to the European Research Associates for financial support (to M. L. H. G.), and to Johnson, Matthey and Co. Ltd. for the loan of rhenium metal. Part of this work was done in the Mallinckrodt Laboratory, Harvard University, and thanks are offered to Dr. J. M. Birmingham for his assistance. The senior author is indebted to the John Simon Guggenheim Foundation for a Fellowship, and to Professor J. Bjerrum for the hospitality in his laboratories.

INORGANIC CHEMISTRY LABORATORIES,
IMPERIAL COLLEGE, LONDON, S.W.7.

[*Received, June* 17*th*, 1958.]